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GEOPHYSICAL RESEARCH PAPERS
No. 41

# THE SHIFT AND SHAPE OF SPECTRAL LINES

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R. G. BREENE JR.
CAPT., USAF

SEPTEMBER 1955

GEOPHYSICS RESEARCH DIRECTORATE
AIR FORCE CAMBRIDGE RESEARCH CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND

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# INTRODUCTION

The importance of spectral lines to the physical sciences need hardly be stressed, and anyone having had any reason for dealing either theoretically or experimentally with spectral lines will be aware of the importance of the shift and shape of these lines. In studying an experimental spectrum or constructing a theoretical one, for example, it is imperative that the experimenter or theoretician have some idea as to the shape and shift from unperturbed location of the lines which he is studying. On the other hand, the experimentally determined shapes of spectral lines afford a method of determining, by the utilization of the proper theory, the intermolecular forces which resulted in the observed shape and shift.

Although it is to be hoped that the reader has answered the question himself as a reason for consulting this work, it appears requisite that the author begin by answering the inquiry as to why he wrote the pages which follow this one.

If one should be asked what works to consult on the question of the shift and shape of gaseous spectral lines the proper answer would be, it would appear, ample justification for the present paper, since one, two or twenty references would hardly be sufficient to cover the field in any real detail. Rather, it would be necessary to search through a great number of references, if, indeed, one had already expended the effort necessary to gather together the references for the searching. One would find even the authors of these works in some cases ignorant of certain of the other works in the field and discover a maze through which one would have to thread one's way before arriving at any information, useful in the application which our searcher originally had in mind. The idea of the present work is to eliminate this maze by gathering together, organizing, and presenting all the major theoretical work which has been done on the problem of spectral line shift and shape through the year 1953. It is to be hoped that the presentation has attained a measure of the completeness and clarity which has been sought. The final verdict as to completeness and clearness must, of course, be rendered by the reader, the user.

A word as to the general presentation would appear to be in order. Two independent methods of theory presentation have been utilized throughout, one might say, simultaneously. (1) The theory has been presented in the chronological order of its development insofar as this is practicable. (2) At the same time the theory has been separated into the various individual theories which it comprises. Thus, we divide broadening by other molecules into self-broadening and foreign gas broadening, which latter we further break down for consideration. This delineation cannot be expected to hold for every theory as, for example, the inclusion of the Jablonski theory in the chapter on Statistical Broadening would tend to indicate, but it does provide a needed sub-division and furnish, in addition, a basis for time consuming semantic arguments.

On these bases then the material has been divided among the various chapters.

Chapter 1 begins with the early work of Michelson (1895) on the broadening problem in general and Rayleigh (1889) on Doppler velocity broadening. This chapter carries broadening theory in general up through the rather well known but generally misinterpreted work of Lorentz (1906) and concludes with a paper of Rayleigh (1915). This appears to be a reasonable time to conclude the early work for it is in the subsequent years that large amounts of effort were expended on the development of specific theories.

Chapters 2 and 3 are simply sketchy treatments of some of the facets of spectral line positions and electrodynamics which will be of some use in subsequent chapters.

Chapter 4 is a study of the Stark theory of Broadening. In this chapter we first consider Holtsmark's work on classical Stark Broadening. The objection which could be raised to separating this theoretical work from other Statistical Broadening (Chapter 5) considerations is certainly a valid one. Holtsmark's theory is without doubt a statistical one, and no real objection to the lengthening of Chapter 5 by the amount required for the inclusion of this theory can be raised. It is concerned, however, with a very specifically treated phase of the general Statistical Broadening so that, if we keep our semantics straight, there appears to be no reason for our not treating it separately. Chapter 4 also includes Spitzer's quantum treatment of the Stark broadening phenomenon.

Chapter 5 concerns itself with the Statistical Theory of broadening and shift. It begins with Jablonski's qualitative utilization of the Franck-Condon principle for the construction of a broadening theory. The remainder of the chapter is principally concerned with the manner in which the giant of the field, Margenau, initiated, developed, and carried to its present level the quantitative Statistical Theory. As the author has already mentioned the inclusion of Jablonski's work in this chapter can be disputed on quite valid ground. Suffice it to say that it has been included in the Statistical chapter by virtue of its intimate association — through the approximations which enter it — with the Franck-Condon principle, one of the bases for the Statistical Theory.

Chapter 6 encompasses the development of the Interruption Theory, otherwise known as "Impact" broadening, "Velocity" broadening, or what have you. This theory is the continuation of the early utilization by Michelson of the Fourier transform in broadening theory and by Lorentz of the damping of the absorbing electronic vibrations of a molecule by collision. In either of these two approaches the interruption of the molecular emission (absorption) by collision forms the basis for the theory. The chapter begins with Lenz's "appeal to correspondences" and carries the work of the various authors up to the present.

Chapter 7 is devoted to a study of self- or Resonance Broadening. The first subject for consideration here is Holtsmark's study of coupled oscillators as a basis for the occurrence of the Resonance Broadening phenomenon. The theory is then developed chronologically as it was developed by the various workers in this field. As we have anticipated, the delineation question again raises its head here, although not to such a height as to be cause for much alarm. This chapter does not contain all that is presented on Resonance Broadening for this phenomenon represents a special case of the general Jablonski theory (Chapter 5), the refined Statistical Theory (Chapter 5), and the general Foley theory (Chapter 6) to mention a few. Sufficient research does seem to have been devoted specifically to the resonance broadening phenomenon to justify its inclusion in a separate chapter, however.

Chapter 8 represents an attempt to present the various work which has been aimed toward the specific problem of the broadening of polyatomic molecular spectral lines.

Although the disparity in number of pages and number of authors presented might tend to indicate that Chapter 9 was added as an afterthought, this is truly not the case. The broadening of the high series members presents such a unique pair of phenomena that it would tend to make its attempted inclusion in any of the other chapters rather farcical. On this basis then this phenomenon has been treated in a separate chapter.

The author wishes to express his appreciation to Professors E. Lindholm, H. Margenau, and L. Spitzer, Jr., for clarifying points in certain of their very valuable contributions to the field. Mr. James Gough of the American Meteorological Society has contributed immensely to the present work by providing translations of the preponderant majority of German articles consulted. This "preponderant majority" consists of more articles than somewhat, and the author's thanks are in the same measure.

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# THE SHIFT AND SHAPE OF SPECTRAL LINES

## CHAPTER 1

## EARLY LINE BROADENING THEORY

The year 1895 may well be chosen as the starting point for our study of the development of spectral intensity although some work had, of course, been done previous to this time. In November of that year Michelson published an article in the Astrophysical Journal in which he made the first attempt to bring together and consider all those factors which " . . . account for the finite width of the spectral lines of a substance emitting approximately homogeneous radiation. . ."[127]

### 1.1. THE CAUSES OF LINE BROADENING (1895)

Michelson began his consideration of line broadening effects by a summarization of the hypotheses which had been advanced previous to that time to account for these phenomena, and a verbatim restatement may be of interest here.

"1. As a consequence of Kirchoff's law 'the ratio of brightness of two immediately contiguous portions of a discontinuous bright-line spectrum constantly decreases, if the number of luminous strata is multiplied or if the coefficient of absorption of the single stratum is increased, until the value is reached which, for the same wavelength and the same temperature, corresponds to the ratio in the continuous spectrum of a body completely opaque for a given thickness.'[212]

"2. The direct modification of the period of the vibrating atoms in consequence of presence (sic) of neighboring molecules.

"3. The exponential diminution in amplitude of the vibrations due to communication of energy to the surrounding medium or to other causes.

"4. The change in wavelength due to the Doppler effect of the component of the velocity of the vibrating atom in the line of sight."

To these causes of line broadening Michelson added the following:

"5. The limitation of the number of regular vibrations by more or less abrupt changes of phase amplitude or plane of vibration caused by collisions.

"6. The possible variations in the properties of the atoms within such narrow limits as to escape detection by other than spectroscopic observations."

Of these six possible contributing factors, Michelson considered only the fourth and fifth as of any real importance in line broadening, although he looked on the other factors as of minor import rather than nonexistent.

As will be apparent at a later stage in the development, we can still agree with Michelson today that the fourth and fifth factors are of great import in the broadening of spectral lines.

Thus, Michelson concluded that the Doppler effect — which will be shown to be dependent on the temperature — and the effect of collisions — which will prove primarily dependent on the pressure* — are chiefly responsible for the finite width of spectrum lines.

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* This is not strictly true, since the effects of collisions will be connected with the *density* of particles. Thus, for example, from the perfect gas law ($pv = NkT$) the effects of collisions are also somewhat dependent on temperature.

Before considering the first development of the effect of pressure on the broadening of a spectral line as given by Michelson, it will perhaps be well to go back to the year 1889 and the first comprehensive consideration of the effect of temperature on the broadening of a spectral line. In that year Lord Rayleigh published an article [146] which dealt with the effect of molecular motion — the velocity being dependent on the gas temperature — on the radiation emitted by the moving molecule.

## 1.2. THE DOPPLER EFFECT IN LINE BROADENING

Let us preface the detailed consideration of this first step in the development of the theory of line broadening and line shape by a qualitative and premature — insofar as the evolution of the theory is concerned — consideration of this spectral line which we have so far glibly taken for granted.

We are not interested at this particular time in the mechanics of the occurrence of this line, but only roughly in what it is. A collection of molecules* in the gaseous state will absorb or emit approximately homogeneous electromagnetic radiation of a number of frequencies depending on the nature of the molecule. Consider one of these frequencies. One might intuitively expect this radiation to be truly homogeneous, that is, of one unique frequency, but, as Michelson noted, this is not the case.

First, let us define the word intensity of emission (absorption) as the energy emitted (absorbed) per unit area per unit time. Then if one makes a plot of frequency vs. intensity for this "almost homogeneous" radiation, one obtains a distribution of intensities over a small frequency range giving rise to a spectral line of definite shape.

We are desirous of eventually obtaining this intensity distribution, but Lord Rayleigh, in considering this problem, was primarily interested in an expression for the brightness in the fringes which are produced by an interferometer. Thus, the expression at which we shall arrive will differ slightly from that of Lord Rayleigh.

First, let us consider the effect which the motion of a molecule will have on the radiation emitted by it.

In Fig. 1.1 a molecule whose velocity vector, $v$, makes an angle $\vartheta$ with the line of sight of an observer at 0 has been depicted. The molecule is emitting radiation of frequency $\nu$ and it is with the effect of the molecular motion on this frequency, that the Doppler effect is concerned. Since the velocity of the emitted radiation is $c$ and the wavelength $\lambda$, $\frac{c}{\lambda}$ waves would reach the observer each second were the molecule at rest, but since it possesses the velocity component $\xi$ in the line of sight an additional $\frac{\xi}{\lambda}$ waves will reach the observer each second. Thus, the frequency of the radiation at 0 has been perturbed by the molecular velocity from a value $\frac{c}{\lambda}$ to:

$$\nu' = \frac{c}{\lambda} + \frac{\xi}{\lambda} = \nu\left(\frac{c+\xi}{c}\right)$$

or:

$$\lambda' = \frac{c}{\nu'} = \lambda\left(\frac{c}{c+\xi}\right) = \lambda\left(\frac{1}{1+\xi/c}\right)$$

$$= \lambda\left(1 - \frac{\xi}{c} + \left(\frac{\xi}{c}\right)^2 - \ldots\right) \doteq \lambda\left(1 - \frac{\xi}{c}\right) \tag{1.1}$$

---

* A molecule may be monatomic and the possessor of one atom or polyatomic and the possessor of many.

in which the binomial expansion and the reasonable assumption $\xi \ll c$ have been utilized. In these expressions $\nu'$ and $\lambda'$ have been used for the perturbed frequency and wavelength respectively. Thus, a moving emitter would have its radiation effected in a manner as given by Eq. (1.1).

Ebert[31] had investigated this effect on the emitted radiation under the assumption that all the molecules of the gas moved with the same velocity and had found the predicted line widths much greater than experiment showed them to be. This discrepancy which, if explained, would have dealt "... the dynamical theory of gases ... a heavy blow, from which it could only with difficulty recover"[146] was corrected by Rayleigh who substituted Maxwell's velocity distribution for Ebert's constant velocity.

The distribution of the velocities in the line of sight is given by the Maxwellian distribution as $e^{-\beta\xi^2}$. Utilizing this distribution in conjunction with the Doppler effect, Rayleigh arrived at the following expression for the intensity in the fringes of an interferometer:

$$I'd\nu = 4\sin^2 \frac{z\pi\Delta}{\lambda}\left(1 + \frac{\xi}{c}\right) I d\nu \tag{1.2}$$

*I* gives the distribution of intensity in the incident radiation (the true spectral line) while the multiplicative factor alters this to give the intensity distribution, *I'*, in the interferometer fringe. It is with *I* that we are concerned, and this is given by the Maxwellian distribution where

$$\beta = \frac{m}{2kT} \tag{1.3}$$

In Eq. (1.3) $m$ is the molecular mass, $k$ is the Boltzmann constant, and $T$ is the temperature in degrees Kelvin.

Now rewrite Eq. (1.1) as:

$$\xi = \frac{c}{\lambda}(\lambda - \lambda')$$

or:

$$\xi^2 = \frac{c^2}{\lambda^2}(\lambda' - \lambda)^2 = \lambda^2 c^2\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)^2 = \lambda^2(\Delta\nu)^2 \tag{1.4}$$

In Eq. (1.4) $\lambda$ may now be considered as the wavelength corresponding to the maximum intensity of the line (line center), and $\Delta\nu$ as the frequency increment between the line center and the frequency whose displacement corresponds to the line of sight velocity $\xi$.

Thus, if one arbitrarily equates the line center intensity to one, the Doppler effect alone produces a distribution of intensities over the spectral line which may be represented by the expression:

$$I = e^{\frac{m\lambda^2(\Delta\nu)^2}{kT}} \tag{1.5}$$

Eq. (1.5) illustrates the dependence as determined by Rayleigh of the intensity on the emitter mass, line frequency, frequency separation from line center, and, perhaps most important, temperature.

This equation then is Lord Rayleigh's solution to Michelson's Point 4. Michelson himself provided the mathematics of the fifth contributing factor, which we shall designate Interruption Broadening.

### 1.3. AN APPLICATION OF THE FOURIER ANALYSIS TO LINE BROADENING

"A group of perfectly homogeneous trains of waves . . . incident on a prism"[127] may be represented by the Fourier integral:*

$$\varphi(x) = \frac{1}{\pi}\int_0^\infty du \int_{-\infty}^{+\infty} \varphi(y) \cos u\,(x-y)\,dy$$

Since: $\cos ux \cos uv + \sin ux \sin uv = \cos u\,(x - v)$ this may be rewritten in the form which was utilized by Michelson:

$$\varphi\,(x) = \frac{1}{\pi}\int_0^\infty du\,(C \cos ux + S \sin ux) \tag{1.6a}$$

where:

$$C = \int_{-\infty}^{+\infty} \varphi\,(y) \cos uy\,dy \qquad S = \int_{-\infty}^{+\infty} \varphi(y) \sin uy\,dy \tag{1.6b}$$

At this point Michelson made the assumption which was perhaps the most important in his development. He assumed that emission terminated abruptly at an intermolecular collision, thus limiting the wave train to that length which could be emitted between successive collisions. If the mean free path of the molecule is $l$ and its velocity is $v$, then the time between molecular collisions will be $\frac{l}{v}$. This means that the length of the wave train which is emitted between collisions is:

$$r = \frac{l}{v}c \tag{1.7}$$

The uniform wave train may now be represented by:

$$\varphi\,(x) = a \cos mx + b \sin mx \tag{1.8}$$

where $a$ and $b$ are arbitrary constants and $m = \frac{2\pi}{\lambda}$. $\lambda$ is the wavelength of the incident radiation. The limits of the wave train may be taken as $-\frac{r}{2}$ and $+\frac{r}{2}$, and (1.6b) may be evaluated.

$$C = a\int_{-r/2}^{+r/2} \cos my \cos uy\,dy = a\,\frac{\sin \frac{1}{2}\,(m-u)r}{m-u} + a\,\frac{\sin \frac{1}{2}\,(m+u)r}{m+u} \tag{1.9a}$$

$$S = b\int_{-r/2}^{r/2} \sin my \sin uy\,dy = b\,\frac{\sin \frac{1}{2}\,(m-u)r}{m-u} - b\,\frac{\sin \frac{1}{2}\,(m+u)r}{m+u} \tag{1.9b}$$

It should be remembered here that:

$$\int_{-r/2}^{r/2} \cos my \sin uy\,dy = \int_{-r/2}^{r/2} \sin my \cos uy\,dy = 0$$

The terms on the right side of Eqs. (1.9a) and (1.9b) are all small except when $m$ is in the neighborhood of $u$ in which case the first term on the right side of each equation is much larger than the second. For this

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[*] See Appendix I.

reason the second term on the right of Eqs. (1.9a) and (1.9b) will be neglected. Further, in the neighborhood of $m = u$, $C$ and $S$ as given by (1.9a) and (1.9b) will control the amplitude so that, since the intensity in this case is simply the square of the amplitude:

$$I = C^2 + S^2$$

$$= \frac{a^2 + b^2}{4} \, \frac{\sin^2 \pi n r}{\pi^2 n^2} \tag{1.10}$$

where
$$m - u = 2\pi n = 2\pi\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)$$

or:
$$n = \frac{1}{\lambda} - \frac{1}{\lambda'} = \frac{\Delta\nu}{c} \tag{1.11}$$

where $\lambda$ is now the line center wavelength. If Eqs. (1.7) and (1.11) are substituted into Eq. (1.10), this equation may be expressed in a more meaningful form:

$$I = d \, \frac{\sin^2\left(\dfrac{\pi(\Delta\nu)l}{v}\right)}{\pi^2(\Delta\nu)^2} \tag{1.12}$$

where $d = \dfrac{(a^2 + b^2)c^2}{4}$. Eq. (1.12) illustrates the dependence upon pressure through the free path, $l$. Gas kinetic theory yields the mean free path:

$$l = \frac{1}{\sqrt{2}\,\pi N\sigma^2} \tag{1.13}$$

In Eq. (1.13) $\sigma$ is the gas kinetic molecular diameter, a quantity which must needs arise when impenetrable spheres are chosen as molecular models. $N$ is the number of molecules per unit of volume, and it is apparent that this is the factor through which the pressure most directly enters Eq. (1.12).

Fig. 1.2 is the curve which results from Eq. (1.12). The secondary maxima* which occur are of no import since they do not actually occur in the spectral line. It was with the central maximum that Michelson was concerned.

It is obvious that the first minimum will occur when, in Eq. (1.10), $\pi n r = \pi$, or when:

$$n = \frac{1}{r} = \frac{1}{l}\,\frac{v}{c} = \frac{\lambda^2}{l}\,\frac{v}{c} \text{ wavelengths} \tag{1.14}$$

This then would give a line width of:

$$\delta = 2\,\frac{\lambda^2}{l}\,\frac{v}{c} \tag{1.15}$$

Michelson found that Eq. (1.15) gave an order of magnitude agreement with experimental data. Somewhat better agreement was achieved by him when he took the "half-width"† as given by Eq. (1.10) — or, perhaps more correctly, as obtainable from Eq. (1.10) — and added it to the half-width which may be obtained from Eq. (1.5). As Michelson noted the problem is not herewith solved, but it will be of interest

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* For disappearance of sine see *infra*, Chap. 6.

† We now define this quantity — "half-width" — as the frequency separation between the two points on the spectral line corresponding to intensities of one-half the maximum intensity in the line.

to see if " . . . such able contributions . . . recently . . . justify the prediction that a complete and satisfactory theory will be forthcoming in the near future."[127]

Let us pause briefly to consider the remaining four contributing causes as advanced by Michelson.*

To begin with Point 3 is Michelson's manner of stating that a natural line width exists, that is, if a molecule is completely isolated from all other molecules and possesses zero velocity with respect to an observer, it will emit a spectral line having a finite width. In the classical case this is due to precisely the cause stated by Michelson as his Point 3. In the quantum mechanical case the cause may be found in a phenomenon of the type treated by Furrsow and Wlassow.† We shall not treat natural line shape.**

Point 2 is quite interesting, for it is essentially the basis for the Statistical theory of line broadening†† with which we shall deal rather extensively. This point combines with Point 5 in the Interruption theory.***

Point 1 is of no particular interest to us, and Point 6, although it shrewdly predicts isotopic spectra, is related to a "pseudo-broadening" with which we shall not concern ourselves.

It seems particularly interesting to note the correctness of the factors which Michelson listed as causing line broadening, correctness at least from the contemporary viewpoint.

The next logical step in the development would immediately appear to be the synthesis of the Doppler and Interruption broadening to arrive at some unified theory of the phenomena. This is precisely what C. Godfrey[80] attempted to do, and it is unfortunate that his results were not of too great value, since his endeavors were such a logical outgrowth of the work which has already been discussed.

## 1.4. THE MEAN FREE PATH AMONG EQUAL SPHERES

Godfrey first carried out a "Fourier Analysis of $m$ Complete Sine Waves" to arrive at Eq. (1.10) which had been given by Michelson. He then proceeded to carry out a "summation" for all molecules having definite velocities both athwart and in the line of sight. Before carrying through this procedure, it may be well to carry through the derivation for the "Mean Free Path Among Equal Spheres" which was developed by Tait.[179]

This author assumes a layer of thickness $\Delta x$ ". . . in which quiescent spheres of diameter $s$ . . . "[179] are distributed with a density $N$ per unit of volume. Now if spheres of diameter $s$ are impinging on this layer in a normal direction, the fraction:

$$1 - n_1 \pi s^2 (\Delta x) \tag{1.16}$$

of the incident particles will pass through the layer without collision, since it is apparent that when the particle center separation is less than a diameter a collision will result. Tait makes the à priori assumption that " . . . the spheres in the very thin layer are so scattered that no one prevents another from doing its full duty††† in arresting those which attempt to pass."[179]

Next the particles in the layer are considered as in a state of motion which may be described by velocity vectors of equal length, $v_1$ but of uniformly distributed orientation. Also, let the incident particles have a common velocity vector, $v$. Then the number of layer particles whose velocity vectors make an angle between $\vartheta$ and $\vartheta + d\vartheta$ with the velocity vectors of the incident particles will be given by:

$$n_1 \sin \vartheta \frac{d\vartheta}{2} \tag{1.17}$$

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* See *supra*, p. 1.

† See *infra*, Chap. 7.

** For a complete treatment see Heitler.[208]

†† See *infra*, Chap. 5.

*** See *infra*, Chaps. 1 and 6.

††† "The Royal Society expects every sphere to do its duty." J. I. F. King.

since this is merely the polar portion of the volume element and one-half the particles may be expected to proceed "north."

If the law of cosines is applied to the vector triangle which results from the addition of $v_1$ and $v$, a quantity which Tait calls the "relative speed" is obtained:

$$v_0 = \sqrt{v^2 + v_1^2 - 2v_1v_2 \cos \vartheta} \tag{1.18}$$

From this a quantity, the "virtual thickness" of the layer, may be defined:

$$\frac{v_0 \, \Delta x}{v} \tag{1.19}$$

The substitution of Eqs. (1.17) and (1.19) into Eq. (1.16) gives an expression for the number of incident particles which will penetrate the layer containing other particlcs whose velocity vectors have an orientation as given by Eq. (1.17):

$$1 - n_1\pi s^2 \, (\Delta x) \, v_0 \sin \vartheta \frac{d\vartheta}{2v} \tag{1.20}$$

Now to find the overall fraction of particles which pass through the layer without collision, the expressions as given by Eq. (1.20) for all possible orientations of $\vartheta$ between 0 and $\pi$ must be multiplied together. Each of these expressions is assumed " . . . infinitely nearly equal to unity. . . ."[179] Under this assumption the logarithm of the expression is given by:

$$ln \, (1 - x) = -x$$

Thus, when we take the logarithm of this product, we arrive at the limit of the sum of these factors:

$$- \frac{n_1\pi s^2(\Delta x)}{2v} \int_0^\pi \sqrt{v^2 + v_1^2 - 2vv_1 \cos \vartheta} \sin \vartheta \, d\vartheta \tag{1.21}$$

The variable of integration may be changed from $\vartheta$ to $v_0$ by utilizing Eq. (1.18) to yield:

$$- \frac{n_1\pi s^2}{2v^2v_1} \int v_0^2 dv_0 \tag{1.21a}$$

A straightforward application of Maxwell's law of velocity distribution, which Tait had made in a previous section of his paper, yields the number of particles in the layer whose velocity magnitudes lie between $v_1$ and $v_1 + dv_1$ :

$$n_1 = 4 \, Nv_1^2dv_1 \sqrt{\frac{\beta^3}{\pi}} \, e^{-\beta v_1^2} \tag{1.22}$$

In Eq. (1.22) $N$ is the particle density, and the other symbols have the meaning previously ascribed to them.

In Eq. (1.21a) the limits of integration depend on the relative magnitude of $v$ and $v_1$. If $v > v_1$ the limits are $v - v_1$ and $v + v_1$. If, on the other hand, $v < v_1$ the limits become $v_1 - v$ and $v_1 + v$. Hence:

$$\frac{1}{2v^2v_1} \int v_0^2dv_0 = \frac{1}{2v^2v_1} \left[ \int_{v-v_1}^{v+v_1} v_0^2dv_0 + \int_{v_1-v}^{v_1+v} v_0^2dv_0 \right] = \left(1 + \frac{v_1^2}{3v^2}\right) + \left(\frac{v}{3v_1} + \frac{v_1}{v}\right) \tag{1.23}$$

Eqs. (1.22) and (1.23) may be substituted into Eq. (1.21), and the result integrated over all $v_1$ to obtain the logarithm of the fraction of the number of incident particles of velocity $v$ which penetrate the layer without collision.

$$- 4\pi Ns^2 \sqrt{\frac{\beta^3}{\pi}} \left[ \int_0^v e^{-\beta v_1^2} \left(v_1^2 + \frac{v_1}{3v^2}\right) dv_1 + \int_v^\infty e^{-\beta v_1^2} \left(\frac{vv_1}{3} + \frac{v_1^3}{v}\right) dv_1 \right] dx \tag{1.24}$$

It should be noted that the integral in Eq. (1.24) whose limits are 0 and $v$ logically contains the results of integrating Eq. (1.21) in the case $v > v_1$. The second integral in Eq. (1.24) contains the results of the integration of Eq. (1.21) under the condition $v < v_1$.

### 1.5. A FIRST SYNTHESIS OF DOPPLER AND INTERRUPTION EFFECTS

If the bracketed expression in Eq. (1.24) is integrated by parts, the $f$ which was utilized by Godfrey is obtained:

$$-f(\Delta x) = -4\pi N s^2 \sqrt{\frac{\beta^3}{\pi}} \left[ \frac{1}{4\beta^2 v} e^{-\beta v^2} + \left( \frac{1}{4\beta^2 v^2} + \frac{1}{2\beta} \right) \int_0^\infty e^{-\beta v_1^2}\, dv_1 \right] \Delta x \tag{1.25}$$

Recalling that this is a logarithm, the expression for the number of molecules which penetrate a distance $l$ without collision becomes:

$$n_2 = e^{-fl} \tag{1.26}$$

From this equation it is apparent that the fraction of molecules which have free paths — distances of unimpeded penetration — between $l$ and $l + dl$ is:

$$f\, e^{-fl} dl \tag{1.27}$$

These molecules will then emit wave trains of length $r$ to $r + dr$ where $r$ is given by Eq. (1.7) so that Eq. (1.27) may be rewritten as:

$$\frac{vf}{c}\, e^{-\frac{vfr}{c}}\, dr \tag{1.28}$$

It is at this point that Godfrey returns to Eq. (1.10) and proceeds to carry the Michelson solution a step further. Eq. (1.10) gives the intensity distribution in an Interruption broadened spectral line under the assumption that all the molecules in the emitting gas traverse free paths of the same length. Godfrey's next step was the imposition of the distribution of free paths which is given by Eq. (1.28) under the temporary restriction of definite thwart and line of sight velocities. If the constants of Eq. (1.10) are ignored, Godfrey's result is obtained:

$$\frac{fv}{n^2 c} \int_0^\infty e^{-\frac{vfr}{c}} \sin^2 \pi n r\, dr \tag{1.29}$$

It is with Eq. (1.29) that the objection of Lord Rayleigh[147] deals. Rayleigh felt that this integral favored unduly long free paths. His solution was the division of the integrand by $r$.* Godfrey's development will be followed, however.

If $(1 - \cos 2\pi\, Nr)$ is substituted for $\sin {}^2\pi Nr$ in Eq. (1.29) any integral table may be consulted to obtain:†

$$\frac{2\pi^2}{4\pi^2 n + v^2 f^2/c^2} \tag{1.30}$$

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* A consideration of Rayleigh's objection might be tempered by the fact that in voicing it he was attempting to resolve a disparity between his own and Godfrey's results. At any rate, the author feels, for reasons which will be apparent, that it is of no great moment which viewpoint is taken.

† Godfrey gives $\frac{1}{2}\dfrac{1}{n^2 + \left(\frac{vf}{c}\right)^2}$ but his work preceding and following this expression indicates that Eq. (1.30) is the correct one.

Up to this point the thwart and line of sight velocities have been definite or fixed at various values. Now Godfrey wishes to add his final refinement to the theory by a consideration of these velocities.

Maxwell's velocity distribution yields $qe^{-\beta q^2}\,dq$ as the proportion of molecules having thwart velocities between $q$ and $q + dq$.

Next Eq. (1.30) is integrated for a definite velocity $p$ in the line of sight and all velocities $q$ thwart:

$$\int_0^\infty qe^{-\beta q^2}dq\,\frac{1}{4\pi^2 n + \frac{v^2f^2}{c^2}} \tag{1.31}$$

where $v^2 = p^2 + q^2$.

The final step is the multiplication by a distribution factor for velocities in the line of sight, $p$, and an integration over all $p$. It should be apparent from previous considerations that this will bring the Doppler effect into the picture. From Eq. (1.1) it can be seen that if the Doppler perturbation is expressed in wave numbers, $\tilde{\nu}$, the result is $\frac{p}{c\lambda}$. $n$ in Eq. (1.31) is the Interruption perturbation in wave numbers. Let $x$ be the total — Doppler plus Interruption — perturbation or the distance from line center to the point on the line under consideration. Then:

$$x = n + \frac{p}{c\lambda} \tag{1.32}$$

An expression for $n$ may be obtained from this equation and substituted into Eq. (1.31). Multiplication by the line of sight velocity distribution factor and integration over all $p$ gives:

$$\frac{1}{4\pi^2}\int_{-\infty}^{+\infty} e^{-\beta p^2}\int_0^\infty qe^{-\beta q^2}\,\frac{1}{\left(x - \frac{p}{\lambda c}\right)^2 + \left(\frac{vf}{2\pi c}\right)^2}\,dpdq \tag{1.33}$$

Eq. (1.33) then gives the distribution of intensity over the spectral line as a function of $x$, the frequency separation of a point on the spectral line from the line center.

The variables of integration may now be changed from $p$ and $q$ to $p$ and $v$ where, of course, $v^2 = p^2 + q^2$. Eq. (1.33) may be rewritten as follows:

$$\begin{aligned}
\int_{-\infty}^{+\infty} dp \int_0^\infty f(p,q;\,v)dq &= \int_0^\infty dp \int_0^\infty f(p,q;\,v)dq + \int_{-\infty}^{0} dp \int_0^\infty f(p,q;\,v)dq \\
&= \int_0^\infty dp \int_0^\infty f(p,q;\,v)dq - \int_0^{-\infty} dp \int_0^\infty f(p,q;\,v)dq = \int_0^\infty dp \int_0^\infty dq\,[f(p,q;\,v) + f(-p,q;\,v)] \\
&= \frac{1}{4\pi^2}\int_0^\infty e^{-\beta p^2}\,dp \int_0^\infty qe^{-\beta q^2}\,dq \left\{ \frac{1}{\left(x - \frac{p}{\lambda c}\right)^2 + \left(\frac{vf}{2\pi c}\right)^2} + \frac{1}{\left(x + \frac{p}{\lambda c}\right)^2 + \left(\frac{vf}{2\pi c}\right)^2} \right\}
\end{aligned} \tag{1.34}$$

$f(p,q;v)$ is an even function so that the change from an integration over $p$ from zero to minus infinity may be replaced by the integration over negative $p$ from zero to infinity as is shown in Eq. (1.34).

During the integration over $q$,$p$ is, of course, constant so that $vdv = qdq$. This leads to the result which Godfrey obtained by a slightly different integral juggle. The factor $\frac{1}{4\pi^2}$ has been dropped.

This then will lead to the polarization:

$$P_x = Nex; \qquad P_y = Ney; \qquad P_z = Nez \tag{1.38}$$

since each vibrating electron has charge $e$.

Now consider the forces on one of these vibrating electrons. First there will be a force due to the electric field of the incident radiation. A related force will arise due to the polarization of the surrounding medium by virtue of the electronic vibrations. The components of these forces will be:

$$e(E_x + \alpha P_x); \qquad e(E_y + \alpha P_y); \qquad e(E_z + \alpha P_z) \tag{1.39}$$

Since our medium is homogeneous and isotropic $\alpha$ is a constant.*

Next assume a linear central force to act upon the electron. The components of this force will be:

$$-fx; \qquad -fy; \qquad -fz \tag{1.40}$$

In Eq. (1.40) $f$ is a constant which is dependent on the nature of the molecule. No real attempt need be made to attach further physical significance to this constant. If this were the only force acting on the electron the frequency of vibration would, of course, be related to $f$ and the electron mass as follows:

$$\omega_0^2 = 4\pi^2\nu_0^2 = \frac{f}{m} \tag{1.41}$$

A dissipative force which is proportional to the velocity is now introduced. The components of this force are:

$$-g\frac{dx}{dt}; \qquad -g\frac{dy}{dt}; \qquad -g\frac{dz}{dt} \tag{1.42}$$

The force whose components are given by this equation was intended to account for the absorption of the incident radiation.

If Eqs. (1.39), (1.40), and (1.42) are substituted into Newton's equation of motion, $\mathbf{F} = m\mathbf{a}$, one obtains the component equations of motion for the electron:

$$m\ddot{x} = e(E_x + \alpha\, P_x) - fx - g\dot{x} \tag{1.43a}$$

$$m\ddot{y} = e(E_y + \alpha\, P_y) - fy - g\dot{y} \tag{1.43b}$$

$$m\dot{z} = e(E_z + \alpha\, P_z) - fz - g\dot{z} \tag{1.43c}$$

Now let:

$$m' = \frac{m}{Ne^2}; \; f' = \frac{f}{Ne^2}; \; g' = \frac{g}{Ne^2} \tag{1.44}$$

The substitution of Eq. (1.38) into Eqs. (1.43a) through (1.43c) and the utilization of Eq. (1.44) in the resulting expressions yields:

$$m'\ddot{P}_x = E_x + \alpha\, P_x - f'P_x - g'\dot{P}_x \tag{1.45a}$$

$$m'\ddot{P}_y = E_y + \alpha\, P_y - f'P_y - g'\dot{P}_y \tag{1.45b}$$

$$m'\ddot{P}_z = E_z + \alpha\, P_z - f'P_z - g'\dot{P}_z \tag{1.45c}$$

There is surely a sinusoidal time dependence associated with $E$ and $P$ so that the substitution of:

$$E_x = E_{0x}\, e^{i\omega t}; \;\; P_x = P_{0x}\, e^{i\omega t}; \;\; \text{etc.} \tag{1.46}$$

into Eqs. (1.45) is not an unreasonable one.

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* We recall that in the most extreme case of non-isotropy the polarizability tensor $\alpha$ of nine components replaces this constant.

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$$m\ddot{y} = e(E_y + \alpha P_y) - fy - g\dot{y} \tag{1.43b}$$

$$m\dot{z} = e(E_z + \alpha P_z) - fz - g\dot{z} \tag{1.43c}$$

Now let:

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The substitution of Eq. (1.38) into Eqs. (1.43a) through (1.43c) and the utilization of Eq. (1.44) in the resulting expressions yields:

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$$m'\ddot{P}_y = E_y + \alpha P_y - f'P_y - g'\dot{P}_y \tag{1.45b}$$

$$m'\ddot{P}_z = E_z + \alpha P_z - f'P_z - g'\dot{P}_z \tag{1.45c}$$

There is surely a sinusoidal time dependence associated with $E$ and $P$ so that the substitution of:

$$E_x = E_{0x}\, e^{i\omega t\phi}; \; P_x = P_{0x}\, e^{i\omega t}; \; \text{etc.} \tag{1.46}$$

into Eqs. (1.45) is not an unreasonable one.

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* We recall that in the most extreme case of non-isotropy the polarizability tensor $\alpha$ of nine components replaces this constant.

The collision of the molecule with another will serve to limit this amplitude increase, for Lorentz supposes that " . . . by this encounter the regular vibration set up in the molecule will be changed into a motion of a wholly different kind."[107]

The electron will carry out this new vibration until another collision essentially stops this vibration and starts still another one, and so on. Thus, " . . . in this way, as well as by a resistance proportional to the velocity, the amplitude of the vibrations will be prevented from passing a certain limit."[107]

In the absorbing gas then " . . . we shall suppose each molecule to remain in its place, the state of vibration being disturbed over and over again by a large number of blows, distributed in the system according to the laws of chance."[107]

Let $A$ blows be distributed among $N$ molecules per unit of time. The mean length of time between blows, that is, the mean time that the electronic vibration in the molecule proceeds undisturbed is:

$$\tau = N/A$$

Let $f(\vartheta)$ be the probability that a molecule will not be struck during a time interval $\vartheta$. The chance that it will be struck in the next interval $d\vartheta$ is $\frac{d\vartheta}{\tau}$ where $\tau$ has been defined by the last equation. Thus, the chance that the molecule will not be struck for a time $\vartheta + d\vartheta$ is:

$$f(\vartheta)\left(1 - \frac{d\vartheta}{\tau}\right) \tag{1.53}$$

This should, of course, be the same as $f(\vartheta + d\vartheta)$ or:

$$f(\vartheta) + \frac{\partial f(\vartheta)}{\partial \vartheta}\, d\vartheta \tag{1.54}$$

If Eqs. (1.53) and (1.54) are equated, the result is:

$$\frac{\partial}{\partial \vartheta} f(\vartheta) = -\frac{f(\vartheta)}{\tau} \tag{1.55}$$

Eq. (1.55) has the solution:

$$f(\vartheta) = Be^{-\vartheta/\tau}$$

where $B$ is a constant. This constant may be evaluated as follows:

$$\int_0^\infty f(\vartheta)d\vartheta = B\int_0^\infty e^{-\vartheta/\tau}d\vartheta = 1$$

$$\tau B = 1 \longleftrightarrow B = 1/\tau$$

So that:

$$f(\vartheta) = \frac{1}{\tau}e^{-\vartheta/\tau} \tag{1.56}$$

From Eq. (1.56) it is apparent that the number of molecules for which the time since the last collision is between $\vartheta$ and $\vartheta + d\vartheta$ is given by $\frac{N}{\tau}e^{-\vartheta/\tau}\, d\vartheta$.

Now reconsider Eq. (1.52), the equation of displacement for the vibrating electron. It is now possible to evaluate $C_1$ and $C_2$ for each molecule by finding $x$ and $\dot{x}$ for time $t - \vartheta$, that is, the time immediately subsequent to the last blow. In order to do this, suppose that immediately after a collision all orientations of the displacement and velocity vectors are equally probable.* This follows from the assumptions which have been made earlier with regard to the collisions, that is, the termination of one vibration and the inception of a different one by the collision. Further, when this condition holds:

$$x = \dot{x} = 0 \tag{1.57}$$

and Eq. (1.57) provides the two needed conditions for the evaluation of $C_1$ and $C_2$:

$$\frac{ae}{m(\omega_0^2 - \omega^2)} e^{i\omega(t-\vartheta)} + C_1 e^{i\omega_0(t-\vartheta)} + C_2 e^{-i\omega_0(t-\vartheta)} = 0 \tag{1.58a}$$

$$\frac{aei\omega}{m(\omega_0^2 - \omega^2)} e^{i\omega(t-\vartheta)} + C_1 i\omega_0 e^{i\omega_0(t-\vartheta)} - C_2 i\omega_0 e^{-i\omega_0(t-\vartheta)} = 0 \tag{1.58b}$$

whose solution is:

$$C_1 = -\frac{ae}{2m(\omega_0^2 - \omega^2)}\left(1 + \frac{\omega}{\omega_0}\right) e^{i\omega(t-\vartheta) - i\omega_0(t-\vartheta)} \tag{1.59a}$$

$$C_2 = -\frac{ae}{2m(\omega_0^2 - \omega^2)}\left(1 - \frac{\omega}{\omega_0}\right) e^{i\omega(t-\vartheta) + i\omega_0(t-\vartheta)} \tag{1.59b}$$

When Eqs. (1.59a) and (1.59b) are substituted into Eq. (1.52) there results:

$$x = \frac{ae}{m(\omega_0^2 - \omega^2)} e^{i\omega t}\left\{1 - \tfrac{1}{2}\left(1 + \frac{\omega}{\omega_0}\right) e^{i(\omega_0 - \omega)\vartheta} - \tfrac{1}{2}\left(1 - \frac{\omega}{\omega_0}\right) e^{-i(\omega_0 + \omega)\vartheta}\right\} \tag{1.60}$$

We may now find the average value of $x$ over all collision times $<x>$, as follows:

$$<x> = \frac{1}{\tau}\int_0^\infty x e^{-\vartheta/\tau}\, d\vartheta \tag{1.61}$$

The integrals which occur in Eq. (1.61) are of the form:

$$\frac{1}{\tau}\int_0^\infty e^{u\vartheta - \vartheta/\tau}\, d\vartheta = \frac{1}{1 - u\tau} \tag{1.62}$$

if $u$ is a pure imaginary. If Eq. (1.62) is utilized, the integration in Eq. (1.61) may be carried out quite easily to obtain:

$$<x> = \frac{ae}{m\left(\omega_0^2 + \dfrac{1}{\tau^2} - \omega^2\right) + 2\,\dfrac{im\omega}{\tau}} e^{i\omega t} \tag{1.63}$$

Compare this to Eq. (1.50). It can be seen that collisions have an effect on the electronic motion which is the same as a resistance to motion of $g = \dfrac{2m}{\tau}$ and an elastic force of $f_c = f + \dfrac{m}{\tau^2}$. This fact may be noted by comparing the terms in the denominators on the right sides of Eqs. (1.50) and (1.63).

We return to a consideration of the radiation which is to be absorbed by this vibrating electron.

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* Some forty years later Van Vleck and Weisskopf disagreed with this statement to which they attributed responsibility for certain discrepancies in the Lorentz results. We shall consider these discrepancies in Chapter 6. These two authors felt that in the case of thermal equilibrium all $x$ and $\dot{x}$ orientations should not be equally probable, but rather should be governed by a Maxwell-Boltzmann distribution.

## 1.8. EFFECT OF COLLISIONS ON THE RADIATION ABSORPTION COEFFICIENT

For simplicity, it can be assumed that propagation takes place in the $z$-direction. This would mean that the field vectors would contain a term $e^{i\omega(t-qz)}$ instead of simply $e^{i\omega t}$. Lorentz further assumes that only the $x$-components of E and D are different from zero. Since this is the case, Eq. (1.37a) reduces to:

$$-\frac{\partial}{\partial z}[H_{0y}e^{i\omega(t-qz)}] = \frac{1}{c}\frac{\partial}{\partial t}[D_{0x}e^{i\omega(t-qz)}]$$

or:

$$qH_y = \frac{1}{c}D_x \tag{1.64a}$$

Eq. (1.37b) becomes:

$$\frac{\partial}{\partial z}[E_{0x}e^{i\omega(t-qz)}] = -\frac{1}{c}\frac{\partial}{\partial t}[H_{0y}e^{i\omega(t-qz)}]$$

or:

$$qE_x = \frac{1}{c}H_y \tag{1.64b}$$

Combining Eqs. (1.64a) and (1.64b) gives:

$$D_x = c^2q^2E_x \tag{1.65a}$$

$$P_x = (c^2q^2 - 1)E_x \tag{1.65b}$$

When Eqs. (1.48a) and (1.65b) are compared, it becomes apparent that:

$$c^2q^2 - 1 = \frac{1}{\xi + i\eta} \tag{1.66}$$

According to Eq. (1.66) $q$ may be arbitrarily broken down into a real and an imaginary part. Let $q$ be given by:

$$q = \frac{1 - i\chi}{\omega'} \tag{1.67}$$

Now the exponential factor contained in the field vectors becomes:

$$e^{i\omega\left(t - z\frac{1-i\chi}{\omega'}\right)} \tag{1.68a}$$

so that the factor producing attenuation of the beam is:

$$e^{-\frac{\omega\chi}{\omega'}z} \tag{1.68b}$$

It is apparent from Eq. (1.68b) that $\frac{\omega\chi}{\omega'}$ determines the absorption; specifically it is a linear absorption coefficient or in Lorentz terminology "index of absorption."

Eq. (1.67) may now be substituted into Eq. (1.66) and the real and imaginary portions on each side of the resulting equation may be equated to obtain the two equations below.

$$\frac{2c^2}{\omega'^2} = \sqrt{\frac{(\xi+1)^2+\eta^2}{\xi^2+\eta^2}} + \frac{\xi}{\xi^2+\eta^2} + 1 \tag{1.69a}$$

$$2\frac{c^2\chi^2}{\omega'^2} = \sqrt{\frac{(\xi+1)^2+\eta^2}{\xi^2+\eta^2}} - \frac{\xi}{\xi^2+\eta^2} - 1 \tag{1.69b}$$

From these two equations $\omega'$ and $\chi$ may be obtained.

If $\xi = 0$, that is, if the frequency of the incident radiation differs only slightly from the natural frequency of the electron, Eq. (1.69b) becomes:

$$2\frac{c^2\chi^2}{\omega'^2} = \sqrt{1 + \frac{1}{\eta^2}} - 1 \tag{1.69c}$$

Over a distance $z = \lambda = \frac{2\pi c}{\omega}$ in air the amplitude decreases in the ratio $1/\exp\left(-\frac{\chi}{\omega'}2\pi c\right)$ according to Eq. (1.68b). Since this distance is so small, the absorption, and hence the factor $\frac{2\pi c\chi}{\omega'}$ can be expected to be very small. It follows that $\frac{c^2\chi^2}{w'^2}$ will be even smaller. This in turn means that $\eta \gg 1$ which allows the application of the binomial expansion to the radical in Eq. (1.69b). We rewrite this radical slightly before applying the binomial expansion as follows:

$$\left[1 + \left(\frac{2\xi + 1}{\xi^2 + \eta^2}\right)\right]^{1/2} \doteq 1 + \frac{1}{2}\frac{2\xi + 1}{\xi^2 + \eta^2} - \frac{1}{8}\frac{(2\xi + 1)^2}{(\xi^2 + \eta^2)^2} \tag{1.70}$$

Higher terms in the binomial expansion are dropped as small. The result of substituting Eq. (1.70) into Eq. (1.69b) is:

$$2\frac{c^2\chi^2}{\omega'^2} = \frac{4\eta^2 - 4\xi - 1}{8\,(\xi^2 + \eta^2)^2} \tag{1.71}$$

As long as $\xi$ is small compared with $\eta^2$, the numerator in Eq. (1.71) can be replaced by $\eta^2$. On the other hand, as soon as $\xi$ attains the order of magnitude of $\eta$, the denominator becomes so large that the right side of Eq. (1.71) is small enough to be neglected. Thus, the numerator may be taken as $4\eta^2$ to a good approximation in all cases. Hence:

$$\frac{c\chi}{\omega'} = \frac{\eta}{2(\xi^2 + \eta^2)}$$

This equation yields the linear absorption coefficient:

$$k = \frac{\omega\chi}{\omega'} = \frac{\omega}{c}\left(\frac{c\chi}{\omega'}\right) = \frac{\omega}{2c}\,\frac{\eta}{\xi^2 + \eta^2} \tag{1.72}$$

This is the line shape which we have been seeking. This may be placed in a more meaningful form. First, assume the polarization of the gas to be small so that $\alpha = 0$. Then Eq. (1.47) may be rewritten as:

$$\xi = \frac{2\pi}{Ne^2}(\nu_0 - \nu) \tag{1.73a}$$

$$\eta = \frac{\omega g}{Ne^2} = \frac{4\pi m}{N\tau e^2}\nu \tag{1.73b}$$

Eq. (1.72) may then be rewritten as:

$$k = \frac{Nme^2}{c\tau}\,\frac{\nu^2}{(\nu_0 - \nu)^2 + \frac{4m^2}{\tau^2}\nu^2} \tag{1.74}$$

By equating the right side of Eq. (1.74) to one-half $k_{\max}$, the half-width of the line is found to be:

$$\delta_L = \frac{4m}{\tau}\nu \tag{1.75}$$

where $\nu$ is the frequency of the line center.

Also the integrated absorption coefficient may be evaluated as follows:

$$S = \int_{-\infty}^{+\infty} k(\nu_0)d\nu_0 = \frac{Nme^2}{c\tau}\nu^2 \int_{-\infty}^{+\infty} \frac{d\nu_0}{(\nu_0 - \nu)^2 + \frac{4m^2}{\tau^2}\nu^2}$$

$$= \frac{2\pi}{\delta_I}\frac{Nme^2}{c\tau}\nu^2 \tag{1.76}$$

So that:

$$\frac{Nme^2}{c\tau} = \frac{S\delta_I}{2\pi\nu^2} \tag{1.77}$$

The substitution of Eqs. (1.75) and (1.76) into Eq. (1.74) yields the more familiar form of the equation for the Lorentz line:

$$k(\nu_0) = \frac{S}{\pi}\frac{(\delta_I/2)}{(\nu_0 - \nu)^2 + (\delta_I/2)^2} \tag{1.78}$$

Before considering various facets of this equation and its immediate predecessor, it will be well for us to retrace our steps by a few. The $k(\nu_0)$ which has been attained attenuates, according to Eq. (1.68b), not the intensity but the field vectors, and, in the final analysis, it is not with the field vectors that we are concerned. Although we will find that an equation identical with Eq. (1.77) results for the absorption coefficient which is responsible for the intensity attenuation, the difference should be clearly understood.

Poynting's vector* may be written as:

$$\mathbf{P} = \mathbf{E} \times \mathbf{H} \tag{1.79}$$

$P$ has the units energy per unit of surface area per unit of time and is indeed associated with the quantity which we desire, intensity of incident radiation. Thus, since the factor as given by Eq. (1.68b) occurs in both the electric and magnetic vectors, it will occur to the square in Eq. (1.78). Hence, the intensity of the incident radiation will be attenuated by the factor:

$$e^{-2ks} = e^{-\kappa s} \tag{1.80}$$

As a result, Eq. (1.76) may be rewritten as:

$$S_2 = \int_{-\infty}^{+\infty} \kappa(\nu_0)d\nu_0 = 2\int_{-\infty}^{+\infty} k(\nu_0)d\nu_0 = 2S \tag{1.81}$$

It is apparent then that the equation for $k(\nu_0)$ will be the same as Eq. (1.78) with $S_2$ substituted for $S$. Let us now reinterpret $k(\nu_0)$ in Eq. (1.78) and consider this symbol as denoting the intensity absorption coefficient.

## 1.9. AN ALTERNATE MANNER OF OBTAINING THE LORENTZ RESULT

We have obtained Lorentz's results after the fashion in which Lorentz obtained them, but now let us go back and obtain them in a slightly different form which we shall consider again at a later point.

Let us again carry out the integration of Eq. (1.61) according to Eq. (1.62) in a straightforward manner to obtain:

$$x = \mathfrak{R}\left\{\frac{eae^{i\omega t}}{m(\omega_0^2 - \omega^2)}\left[1 - \frac{1 + (\omega/\omega_0)}{2\tau\,[-\,i(\omega_0 - \omega) + 1/\tau]} - \frac{1 - (\omega/\omega_0)}{2\tau\,[i(\omega + \omega_0) + 1/\tau]}\right]\right\} \tag{1.82a}$$

$$= \mathfrak{R}\left\{ae^{i\omega t}\,(x' - ix'')\right\} \tag{1.82b}$$

---

* We may recall this vector as the measure of energy flow in the field and as having the direction of this flow.

In order to write down the desired result from Eq. (1.82b), it is necessary to digress for a moment.

We begin by considering a molecule of electric dipole moment $\mu$ which makes an angle $\psi$ with an external electric field a cos $\omega t$. In this case now, we assume that after collision a Maxwell-Boltzmann distribution governs the dipole orientation (and hence, the orientation of $x$). If the last collision occurred at time $t_0$, and the energy due to the dipole-field interaction is $\mu$ . a, we may obtain the mean polarization as:

$$<m> = \frac{\mu \int_0^\pi \cos\psi \exp\left[\mu a \cos\psi \cos(\omega t_0)/kT\right] \sin\psi \, d\psi}{\int_0^\pi \exp\left[\mu a \cos(\omega t_0)/kT\right] \sin\psi \, d\psi}$$

$$\doteq \frac{\mu^2 a \cos(\omega t_0) \int_0^\pi \cos^2\psi \sin\psi \, d\psi}{kT \int_0^\pi \sin\psi d\psi} = \frac{\mu^2 a}{3kT} \mathfrak{R}\left\{e^{i\omega t}\right\} \tag{1.83}$$

when we have expanded the exponential in a MacLaurin series and only retained the term containing $a$. The polarization per cubic centimeter may be obtained by substituting Eq. (1.83) for $x$ in Eq. (1.61) and multiplying by $N$, the number of molecules per cubic centimeter. The result is:

$$P = \frac{Na\mu^2}{3kT} \mathfrak{R}\left\{\frac{e^{i\omega t}}{1 + i\omega\tau}\right\} = a\mathfrak{R}\left\{(c - ib)e^{i\omega t}\right\} \tag{1.84}$$

The work done on the molecule by the radiation field will surely be given by the average value of a cos $\omega t \frac{dp}{dt}$. Finally, if we divide this work by the energy flow in the field, $\frac{ca^2}{8\pi}$, we should determine the energy taken out of the field by the molecule, or, simply, the absorption coefficient.

Now

$$a \cos(\omega t) \frac{dP}{dt} = E \cos\omega t \left[\frac{Na\mu^2}{3kT} \frac{\omega^2\tau \cos(\omega t) - \omega \sin\omega t}{1 + \omega^2\tau^2}\right]$$

where:

$$\frac{dP}{dt} = \frac{Na\mu^2}{3kT} \frac{\omega^2\tau \cos(\omega t) - \omega \sin\omega t}{1 + \omega^2\tau^2} \tag{1.85a}$$

and the average value is:

$$< E \cos(\omega t) \frac{dP}{dt} > = \frac{Na^2\mu^2}{6kT} \frac{\omega^2\tau}{1 + \omega^2\tau^2} \tag{1.85b}$$

As a result we obtain:

$$k = \frac{\omega}{c} \frac{4\pi N\mu^2}{3kT} \frac{\omega\tau}{1 + \omega^2\tau^2} \tag{1.86}$$

Now we note that the same result could have been obtained if we had set:

$$k = \frac{4\pi b\omega}{c} \tag{1.87}$$

from Eq. (1.84). This tells us then that, from Eq. (1.82b)

$$k = \frac{4\pi N\omega e x''}{c} = \frac{2\pi Ne^2}{mc}\left(\frac{\omega}{\omega_0}\right)\left[\frac{1/\tau}{(\omega - \omega_0)^2 + (1/\tau)^2} - \frac{1/\tau}{(\omega + \omega_0)^2 + (1/\tau)^2}\right] \tag{1.88}$$

One is not compelled to arrive at Eq. (1.88) in this manner, but it is slightly more simple than other possible methods. Let us return to a consideration of Eq. (1.78).

In Eq. (1.78) the dependence on the physical parameters which, according to this theory, govern the broadening is lost. Even so, it is perhaps of more value than Eq. (1.74) for several reasons.

Firstly, Lorentz himself found and reported in the same article that the mean time which one would suppose available from kinetic theory showed no very reasonable relation to the mean time called for by Eq. (1.75) to explain the observed half-widths of the spectral lines which he investigated.*

Next, the constants which occur in Eq. (1.74) leave little latitude for interpretation, but the question must needs arise as to whether they should be there. $N$, $c$, and $\tau$ seem reasonable of occurrence under almost any formalism, but $e$ and $m$ should perhaps not occur in the manner in which they do. If the radiation is absorbed by virtue of the classical motion of an electron of charge $e$ and mass $m$ in exactly the stipulated manner or if this classical electronic motion provides a reasonable model for the interpretation of this phenomenon, then Eq. (1.74) might be of great value. As we shall see, this is not the generally accepted view however, so that from contemporary viewpoint, the failure of Eq. (1.74) is not overly surprising.

Eq. (1.76) has withstood the ravages of time with a slightly higher degree of success. At first glance, this would appear rather paradoxical since this equation is nothing more nor less than an evolutionary descendant of Eq. (1.72) and has its roots in the vibrating electron. On the other hand, it is apparent that it relates rather different factors than does its predecessor, these factors being half-width, integrated absorption coefficient, frequency separation from line center, and absorption coefficient. Perhaps another development based on a different model would relate these same factors in a similar manner. Further, in order to utilize it one would have to use an empirically determined $S$ and $\delta$.

Few further remarks need be made with reference to this development. A somewhat interesting comparison may be in order, however.

A comparison of Eqs. (1.12) and (1.77) demonstrates the interesting tendency of $1/(\Delta\nu)^2$ to pop out of line shape theories. Although Michelson ignored the mechanics of emission and performed a Fourier transform on the wave train itself, he arrived at the same dependence on $\Delta\nu$ that Lorentz obtained by a pure consideration of the mechanics of absorption. Of course, Michelson considered emission, and Lorentz considered absorption, but the comparison is nonetheless interesting.

## 1.10. THE END OF THE EARLY PERIOD

We turn for a moment from the consideration of the Interruption Broadening effects of pressure to the Doppler broadening effects of temperature.

Schonrock[155] attacked the Doppler broadening question using the Rayleigh theory because Godfrey[60] had detected an error in the calculations which Michelson [128] had carried out on this type of broadening. "Wahrend Lord Rayleigh die benutzten Buchstaben genau definiert, ist dies bei Michelson leider nicht der Fall . . . das er (Michelson) . . . vergisst, einen Faktor 2 anzubringen."[155]† Schonrock attempted to explain the lack of agreement between theory and experiment which resulted from the introduction of this factor. His solution to the problem was the assumption that in certain diatomic molecules the atoms were the "carriers of the emission centers" so that the mass which enters the Doppler formula is halved.

Schonrock[156] later considered the pressure broadening of spectral lines and made an observation which

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* Let us note here that $\tau$ will depend on the molecular diameters. We shall see that, in general, Interruption theories are repeatedly required to predict diameters much greater than kinetic theory diameters in order to yield broadening results comparable with experiment.

† The author hastens to point out that, regardless of what factor Michelson had forgotten to bring in, his work would retain its position of eminence in the field of line broadening.

is perhaps worthy of note in the light of subsequent events. He began by utilizing Michelson's pressure broadening results with a line shape as given by Eq. (1.12). He then showed that a good approximation to the Michelson intensity curve could be obtained by using an exponential dependence on the square of the frequency distance from the line center. Fig. 1.3 illustrates this approximation. He thus purported to show a relationship between Doppler and Interruption Broadening.

This phase of the development of spectral line shape began with a list of broadening factors, and we shall end it with a similar list, this one contributed by Lord Rayleigh. Before doing so, however, let us mention another contribution which Rayleigh tucked away in the text of the same article.

" . . . Is there no distinction between encounters first of two sodium atoms and secondly of an atom say or nitrogen?"[148] Or one might simply ask if self-broadening — the broadening of the spectral line being caused by the same type of molecule as the emitter — is the same as foreign broadening — the broadening molecule is not the same type as the emitter. We shall see that this is a very pregnant question.

Rayleigh decided that the causes which underlie the broadening of spectral lines in emission " . . . may be considered under five heads, and it appears probable that the list is exhaustive:

"(1) The translatory motion of the radiating particles in the line of sight, operating in accordance with Doppler's principle.

"(2) A possible effect of the rotation of the particles.

"(3) Disturbance depending on collision with other particles either of the same or another kind.

"(4) Gradual dying down of the luminous vibrations as energy is radiated away.

"(5) Complications arising from the multiplicity of sources in the line of sight. Thus if the light from a flame be observed through a similar one, the increase of illumination near the edge of the spectrum line is not so great as towards the edge, in accordance with the principles laid down by Stewart and Kirchhoff, and the line is effectively widened."[148]

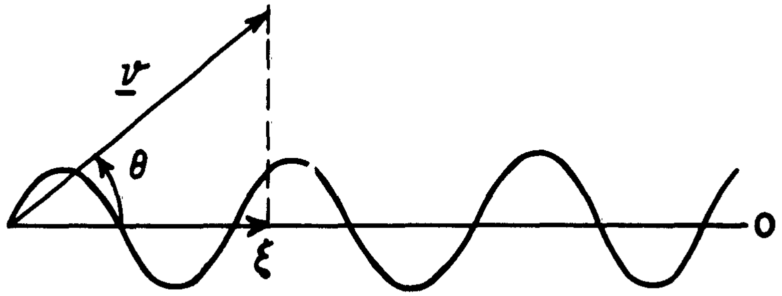

Fig. (1.1). The physical conditions requisite for the Doppler Effect. The observer is at 0. The emitter velocity vector makes the angle $\theta$ with the line of sight at this observer.

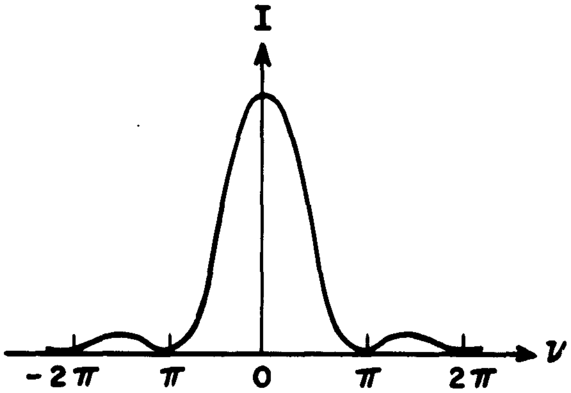

Fig. (1.2). The intensity distribution resulting from the simple application of the Fourier transform. (After Michelson[127]).

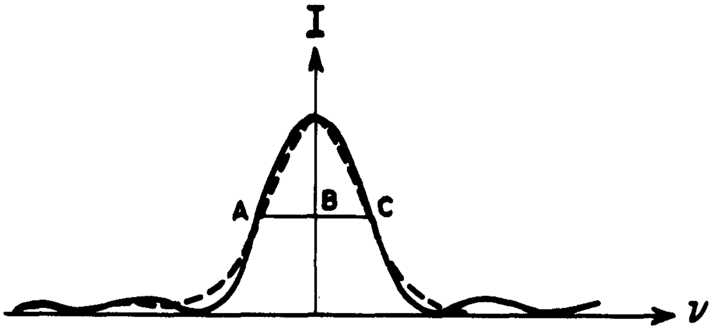

Fig. (1.3). Schonrock's attempt at the empirical fitting of an exponential to the Michelson intensity distribution. (After Schonrock[156]).

# CHAPTER 2

# SPECTRAL LINE POSITIONS

The chapter title infers an early deviation from the subject matter of this paper, and indeed such a temporary departure becomes almost unavoidable. Spectral line positions imply energy levels, and, in turn, energy levels imply level weight, probability of transition between levels and other factors which can certainly never be divorced from considerations of line shift and shape.

Let us consider only the molecular (polyatomic) energy levels which give rise to rotation-vibration spectra.*

## 2.1. THE MOLECULAR KINETIC AND POTENTIAL ENERGY EXPRESSIONS

Fig. (2.1) purports to represent a collection of atomic nuclei superposed upon which are an inertial or space fixed reference frame XYZ and a moving frame xyz. A vector triangle made up of the position vector of the moving frame origin, $\rho$,† the position vector of the $i$-th particle with respect to the moving reference frame, $\mathbf{r}_i$, and the position vector of the $i$-th particle with respect to the inertial frame, $\mathbf{R}_i$. The relation among these vectors may be written out as:

$$\mathbf{R}_i = \rho + \mathbf{r}_i \tag{2.1}$$

The absolute velocity of the $i$-th particle follows immediately from this:

$$\mathbf{V}_i = \dot{\mathbf{R}}_i = \dot{\rho} + \mathbf{v}_i + \omega \times \mathbf{r}_i \tag{2.2}$$

when the expression for the time derivative of a quantity with respect to a moving reference frame is recalled. $\omega$ is the angular velocity of the system.

Eq. (2.2) may be utilized to obtain the kinetic energy of the system.

$$\begin{aligned} 2T = \sum_i m_i \mathbf{V}_i \cdot \mathbf{V}_i &= \sum_i m_i \dot{\rho}^2 + \sum_i m_i v_i^2 + \sum_i m_i (\omega \times \mathbf{r}_i) \times (\omega \times \mathbf{r}_i) \\ &+ 2\sum_i m_i \dot{\rho} \cdot \mathbf{v}_i + 2\sum_i m_i \dot{\rho} \cdot (\omega \times \mathbf{r}_i) + 2\sum_i m_i \mathbf{v}_i \cdot (\omega \times \mathbf{r}_i) \end{aligned} \tag{2.3}$$

We may assume that the center-of-mass of the system remains at the origin of the moving frame by the substitution into Eq. (2.3) of:

$$\sum_i m_i \mathbf{r}_i = 0 \tag{2.4}$$

When Eq. (2.4) is substituted into Eq. (2.3); when the terms are internally rearranged, and when the substitutions,

$$\sum_i m_i (\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i) = \sum_{\alpha\beta}\sum I_{\alpha\beta}\omega_\alpha\omega_\beta \tag{2.5a}$$

$$\sum_i m_i = M \tag{2.5b}$$

---

* We shall only have use for hydrogen-like monatomic models. Since the treatment leading to the required results is very standard indeed, we shall neglect any monatomic energy considerations.

† Greek letters designating vectors will be written as $\rho$. Other characters representing vectors will appear in boldface, as **R**.

are made, the result is:

$$2T = M\dot{\rho}^2 + \sum_i m_i v_i^2 + \sum_{\alpha\beta}\sum I_{\alpha\beta}\omega_\alpha\omega_\beta + 2\omega \cdot \sum_i m_i \mathbf{r}_i \times \mathbf{v}_i \tag{2.6}$$

In Eq. (2.6) the first term on the right side is the translational kinetic energy of the system as a whole; the second term is kinetic energy of internal vibration; the third term is kinetic energy of overall rotation, and the last term is kinetic energy of Coriolis interaction between rotational and internal angular momenta.

Let us now consider Eq. (2.5a) briefly. The indices $\alpha$ and $\beta$ run over $x$, $y$, and $z$. If the vector multiplications indicated by the various dots and crosses on the left side of the equation are carried out, one finds the moments of rotary inertia to be given by:

$$I_{xx} = \sum_i m_i\,(y_i^2 + z_i^2) \tag{2.7a}$$

$$I_{yy} = \sum_i m_i\,(x_i^2 + z_i^2) \tag{2.7b}$$

$$I_{zz} = \sum_i m_i\,(x_i^2 + y_i^2) \tag{2.7c}$$

and the products of rotary inertia to be given by:

$$I_{xy} = I_{yx} = -\sum_i m_i x_i y_i \tag{2.7d}$$

$$I_{xz} = I_{zx} = -\sum_i m_i x_i z_i \tag{2.7e}$$

$$I_{yz} = I_{zy} = -\sum_i m_i y_i z_i \tag{2.7f}$$

The nine quantities given by Eqs. (2.7) go to make up the rotary inertia tensor:*

$$I_{\alpha\beta} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \tag{2.8}$$

Let us for a moment assume that no particle motion takes place with respect to the center-of-mass of the system, that is, let us fix the particles at their equilibrium positions. We may then rotate our coordinate system ir such a manner that the matrix which occurs in Eq. (2.8) is diagonalized. When this has been done the products of rotary inertia, of course, disappear, and we are left with the equilibrium principal moments of rotary inertia which we shall designate as $I_{0x}$, $I_{0y}$, and $I_{0z}$.

The relationship existing among these equilibrium principal moments forms the basis for rotator classification. Three possible relationships immediately appear:

$$I_{0x} = I_{0y} = I_{0z} \tag{2.9a}$$

$$I_{0x} = I_{0y} \neq I_{0z} \tag{2.9b}$$

$$I_{0x} \neq I_{0y} \neq I_{0z} \neq I_{0x} \tag{2.9c}$$

Eq. (2.9a) defines a spherical rotator; Eq. (2.9b) defines a symmetrical rotator, and Eq. (2.9c) defines an asymmetrical rotator. In cases such as Eq. (2.9b) where a symmetry axis for the mass distribution exists, this symmetry axis is normally taken as the $z$-axis.

In the event a linear mass distribution exists, a fourth type of rotator, the linear rotator, appears. It is obvious from Eq. (2.7c) that $I_{0z} = 0$ in this case.

Having obtained a kinetic energy expression, we now desire a potential energy expression. The following expression may be utilized:

$$2V = \sum_{i\,j}\sum k_{ij}q_iq_j + \sum_{i\,j\,l}\sum\sum k_{ijl}q_iq_jq_l + \sum_{i\,j\,l\,m}\sum\sum\sum k_{ijlm}q_iq_jq_lq_m \;\ldots \tag{2.10}$$

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* See *infra*, Chap. 3.

In Eq. (2.10) the $q_i$ are the coordinates which may be in use. To answer the questions as to the neglect of inverse powers of the coordinates and linear terms in the coordinates, it may be remembered that the force in related to the potential energy as follows:

$$\mathbf{F} = -\nabla V \tag{2.11}$$

If one makes the assumption, with respect to the nuclear system, that the atomic nuclei are always acted upon by forces whose magnitude increases with increasing displacement of these nuclei from their equilibrium positions—restoring forces —, then Eq. (2.11) tells us that no inverse powers of the coordinates are desired in the potential energy expression. Also Eq. (2.11) indicates that if a term linear in the coordinates occurs, a constant force independent of the nuclear displacement results. This force will surely have no effect on the internal motions of the system, so it may be neglected.

## 2.2. THE NORMAL VIBRATIONAL COORDINATES

Having obtained the kinetic and potential energy expressions, we proceed quite naturally to Lagrange's[110] equations and the Lagrangian, ". . . . the beauty of the method so suiting the dignity of the results, as to make of his great work a kind of scientific poem."[56]

Specifically, the Lagrangian for our system may be written down as:

$$L = T - V \tag{2.12}$$

where Eqs. (2.6) and (2.10) supply the expressions for $T$ and $V$.

Lagrange's equations,

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_k} = \frac{\partial L}{\partial q_k} \tag{2.13}$$

are here utilized for the solution of the harmonic vibrational problem. The atomic nuclei may vibrate, in this approximation, in such a manner that each particle carries out an oscillation of the same frequency but "not necessarily the same amplitude." Such a motion is called a normal mode of vibration of which a molecule may possess several, the number being dependent on the number of atoms going to make up the molecule. The Lagrangian for this problem is:

$$L = T - V_0 = \tfrac{1}{2}\sum_i m_i v_i^2 - \sum_i\sum_j k_{ij} q_i q_j \tag{2.14}$$

The solution of Lagrange's equations requires that the vibrational secular determinant be zero.

$$|\Lambda T_{vib} - V_0| = 0 \tag{2.15}$$

Let us suppose that there are $n$ atomic nuclei in the molecule. Since each nuclei has three Cartesian coordinates, there will be $3n$ equations of the form Eq. (2.13), and hence the determinant in Eq. (2.15) will be of order $3n$. This situation can be somewhat improved.

Since the molecule possesses $n$ particles, it has $3n$ degrees of freedom. As a whole, the molecule has three degrees of translational freedom, and, if it is a non-linear mass distribution, it has three degrees of rotational freedom. Thus, there remain $3n - 6$ degrees of vibrational freedom ($3n - 5$ for a linear mass distribution). Since we are dealing here with only the vibrational portion of the problem, it would seem reasonable to assume that we desire the number of coordinates reduced from $3n$ to $3n - 6$. This can be accomplished by the application of the Eckart conditions:[32]

$$\sum_i m_i \mathbf{r}_i^0 \times \mathbf{v}_i = 0 \tag{2.16a}$$

$$\sum_i m_i \mathbf{r}_i = 0 \tag{2.16b}$$

In these equations the convention,

$$(x_i y_i z_i) = (x_i^0 + x_i', y_i^0 + y_i', z_i^0 + z_i') \tag{2.17}$$

has been applied where $(x_i^0 y_i^0 z_i^0)$ are the equilibrium coordinates of the *i-th* particle, and $(x_i' y_i' z_i')$ are the displacements of the *i-th* particle from equilibrium.

Eq. (2.16a) removes molecular rotation from the problem, and Eq. (2.16b) removes molecular translation from the problem. Thus, Eqs. (2.16) serve the dual purpose of restricting the problem to one of internal vibration and reducing the number of coordinates to the desired number. Intermediate symmetry coordinates — coordinates which are more or less associated with the normal modes — may now be utilized to replace the Cartesian coordinates. These may be intuitively selected, utilizing Eq. (2.16) and the covering operations [195] of group theory, or we may apply the cookbook method of Nielsen and Berryman.[136]

At this point, group theory may be used to break up the determinant into steps. A lengthy discussion of group theory here would simply tend to divert us from the main stream of our development.*

After the performance of these simplifying operations, the determinant is diagonalized. A grand supposition — namely, that this can be accomplished — is here implied. In carrying out this diagonalization the laborer in the vineyard obtains the normal coordinates (describing the normal modes of vibration of the molecule) and the roots of the determinant, $\Lambda_i$. A word about these roots.

$$\Lambda_i = \omega_i^2 = 4\pi^2\nu_i^2 \tag{2.18}$$

In Eq. (2.18) $\nu_i$ is the frequency of the *i-th* vibrational mode.

A single root, $\Lambda_i$ unique, indicates that the molecule is carrying out a non-degenerate vibration. A double root indicates that the molecule is carrying out a twofold degenerate vibration. In this case, two perpendicular vibrations of the same frequency may be carried out simultaneously by some or all of the constitutent nuclei. The resultant particle motion will be elliptical, but in the case of twofold degeneracy the plane of the motion is fixed. The triple roots results in threefold degenerate vibration. Elliptical motion also results in this case, but here the plane of motion is determined by the "initial conditions."

It is apparent that an angular momentum which may be called vibrational angular momentum arises from these degenerate vibrations. We note this for future reference.

The normal coordinates which have been designated $q_i$ have now been derived, and it is generally conceded that they are the best coordinates to use in the continuation of the problem. Accordingly, Eq. (2.12) is transformed from an expression in terms of the Cartesian to an expression in terms of the normal coordinates.

## 2.3. THE COMPLETION OF THE CLASSICAL PROBLEM

It has been found that for most cases the potential energy expression need not be carried any further than quartic terms. It may be noted that the matrix of the quadratic potential energy expression where

$$V_0 = \|\tilde{q}\| \; \|V_0\| \; \|q\|$$

is now diagonal. In this equation $\|q\|$ is a column vector, and $\|V_0\|$ is a diagonal matrix containing the harmonic force constants as diagonal elements. $\|\tilde{q}\|$ is the transpose of $\|q\|$. Group theory may be

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* For a short discussion of this facet of group theory see Appendix II.

applied to the cubic and quartic portions of the potential energy expression to eliminate, on the basis of symmetry considerations, certain of the terms in these expressions.*

The internal angular momenta may be expressed as:

$$p_x = \sum_i m_i(y_i \dot{z}_i - z_i \dot{y}_i) \tag{2.19a}$$

$$p_y = \sum_i m_i(z_i \dot{x}_i - x_i \dot{z}_i) \tag{2.19b}$$

$$p_z = \sum_i m_i(x_i \dot{y}_i - y_i \dot{x}_i) \tag{2.19c}$$

We may transform Eqs. (2.19) from expressions in terms of the Cartesian coordinates and their time derivatives to expressions involving the normal coordinates and their time derivates.

The momentum conjugate to the coordinate $q_i$ may be defined as:

$$p_i = \frac{\partial T}{\partial \dot{q}_i} \tag{2.20}$$

Utilizing Eq. (2.20), Eqs. (2.19) may be further transformed into expressions involving the normal coordinates and their conjugate momenta. We now have expressions for the components of the internal angular moments in terms of the normal coordinates and their conjugate momenta. We speak here of the internal angular momentum as opposed to the total angular momentum which includes the angular momentum of overall molecular rotation.

After diagonalization of Eq. (2.15) we turn from the Lagrangian to the Hamiltonian [56,57] formulation of mechanics in order to utilize the Hamiltonian of this formalism. If we express Eqs. (2.13) and (2.10) in terms of the normal coordinates and their conjugate momenta, and if, as is the case, the system is conservative, the Hamiltonian may be written as:

$$H(q,p) = T(q,p) + V(q) \tag{2.21}$$

Wilson and Howard[196] have carried through this transformation† and have obtained the following:

$$H = \tfrac{1}{2}\sum_{\alpha,\beta} \chi_{\alpha\beta} P_\alpha P_\beta - \sum_\alpha \Upsilon_\alpha P_\alpha + \tfrac{1}{2}\sum_{\alpha,\beta} \sqrt{\chi}\, p_\alpha \chi_{\alpha\beta} \frac{1}{\sqrt{\chi}} p_\beta + \tfrac{1}{2}\sum_i \sqrt{\chi}\, p_i \frac{1}{\sqrt{\chi}} p_i + V(q_i) \tag{2.22}$$

In Eq. (2.22) $\alpha$ and $\beta$ run over $x$, $y$, and $z$. The quantities $\chi_{\alpha\beta}$ are functions of the normal coordinates and are also related to the instantaneous moments and products of rotary inertia. $\chi$ is the determinant of the matrix $||\chi_{\alpha\beta}||$. $P_\alpha$ are the components of the total angular momentum, and $p_\alpha$ are the components of the internal angular momentum. The $p_i$ are the momenta conjugate to the normal coordinates $q_i$. $V$ is the potential energy expression, a function of the normal coordinates. Finally, $\Upsilon_\alpha$ is given by:

$$\Upsilon_\alpha = \tfrac{1}{2}\sum_\beta \left\{ 2\chi_{\alpha\beta} p_\beta + (p_\beta \chi_{\alpha\beta}) + \chi_{\alpha\beta}\sqrt{\chi}\left(p_\beta \frac{1}{\sqrt{\chi}}\right)\right\} \tag{2.23}^{**}$$

The classical theory has carried us about as far as it can, and it now becomes necessary to turn to the quantum mechanics of Heisenberg,[59] Born-Jordan,[13] and Schrodinger,[157] most specifically, the latter.

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* With regard to operations of this kind, the author feels that the fact that they may be carried out is of much greater import at present than the method for so doing. In addition, the reader may consult Refs. (132) through (134) and (162) through (170) for examples of this and other detailed calculations.

† See Appendix III.

** For an explanation of the parentheses within the curly braces see Appendix III.

## 2.4. THE QUANTUM MECHANICAL PROBLEM

We may write the time independent Schrodinger equation as:

$$H\psi_n(q) = E_n\psi_n(q) \tag{2.24}$$

In Eq. (2.24) $H$ is the Hamiltonian operator which corresponds to the classical Hamiltonian for the problem in which physically observable quantities have been replaced by operators. $\psi_n(q)$ is an eigenfunction of the operator $H$ and is a function of some set of coordinates $q$. $n$ here represents the aggregate of all quantum numbers specifying the state described by the eigenfunction. $E_n$ is the energy of the state represented by $\psi_n(q)$.

The Hamiltonian operator for the molecular problem is given by Eq. (2.22) in which the angular momentum components have not as yet been replaced by their differential operator equivalents. To defer confusion (not necessarily to eliminate it) the fact that Wilson and Howard[196] had carried through the transition from classical to quantum mechanics before obtaining Eq. (2.22) was not mentioned with the presentation of this equation. This, however, was the case as might have been inferred from the classically curious method of displaying it.

The substitution of differential operators into Eq. (2.22) and the substitution of the resulting expression for $H$ into Eq. (2.24) leads to a differential equation whose difficulty of solution increases at least exponentially as the number of constituent atoms in the molecule. Concisely stated, the differential equation is not exactly solvable. This leads us to call upon perturbation theory for assistance.

Perturbation theory essentially amounts to breaking a large, unsolvable problem down into smaller problems each of which is more amenable to solution, and each successive one of which yields a closer approximation to the correct solution.

The Hamiltonian, eigenfunctions, and eigenvalues are first broken up as follows:

$$H = H^{(0)} + \epsilon H^{(1)} + \epsilon^2 H^{(2)} + \dots \tag{2.25a}$$

$$\psi_n = \psi_n^{(0)} + \epsilon\psi_n^{(1)} + \epsilon^2\psi_n^{(2)} + \dots \tag{2.25b}$$

$$E_n = E_n^{(0)} + \epsilon E_n^{(1)} + \epsilon^2 E_n^{(2)} + \dots \tag{2.25c}$$

In these equations $\epsilon$ is simply a parameter of smallness and may be equated to unity when the calculation is completed. If Eqs. (2.25) are substituted into Eq. (2.24) and the coefficients of like powers of $\epsilon$ are equated, one obtains the zeroth-, first-, and second-order problems.

$$H_1^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \tag{2.26a}$$

$$H^{(0)}\psi_n^{(1)} + H^{(1)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \tag{2.26b}$$

$$H^{(0)}\psi_n^{(2)} + H^{(1)}\psi_n^{(1)} + H^{(2)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)} \tag{2.26c}$$

It has been generally found that in molecular problems the solution through second-order contains the desired results.

## 2.5. THE ZEROTH-ORDER PROBLEM

It is apparent that the selection of the terms from Eq. (2.22) for the zeroth-order Hamiltonian comprises the first step in the continuation of the problem. Two criteria for this selection present themselves. (1) The differential equation which results from the selection should be exactly solvable. (2) The zeroth-order problem resulting from the selection should describe the phenomena which make the most important contribution to the molecular energies. Let us write down the zeroth-order Hamiltonian for the general case.

$$H^{(0)} = \left\{ \frac{P_x^2}{2I_{0x}} + \frac{P_y^2}{2I_{0y}} + \frac{P_z^2}{2I_{0z}} \right\} + \tfrac{1}{2} \sum_{i=1}^{L} (p_i^2 + \Lambda q_i^2) + \tfrac{1}{2} \sum_{i=L+1}^{\frac{1}{2}M} [p_{i1}^2 + p_{i2}^2 + \Lambda_i (q_{i1}^2 + q_{i2}^2)]$$

$$+ \tfrac{1}{2} \sum_{i=M+1}^{M+n-1} [p_{i1}^2 + p_{i2}^2 + p_{i3}^2 + \Lambda_i(q_{i1}^2 + q_{i2}^2 + q_{i3}^2)] \qquad (2.27)$$

The term in braces is the Hamiltonian for a rigid rotator, and it may be noted that the equilibrium principal moments of inertia are utilized therein. The first summation term is the Hamiltonian for a non-degenerate harmonic oscillator; the second is the Hamiltonian for a twofold degenerate harmonic oscillator, and the last summation provides us with the Hamiltonian of a threefold degenerate oscillator. It may be noted that if our molecule has, say, $L$ non-degenerate vibrations, $M - L$ twofold degenerate vibrations, and $3n - M - 6$ threefold degenerate vibrations, then, although the molecule possesses $3n - 6$ degrees of vibrational freedom, it carries out only $\frac{1}{2}L + \frac{1}{6}M + n - 2$ distinct vibrations. This fact is indicated by the method of summation which has been utilized in Eq. (2.27). The terms quadratic in the normal coordinates have, of course, been taken from the potential energy expression which, we may recall, was diagonalized as a means of ascertaining these normal coordinates.

It is generally conceded that the discovery of a problem involving angular motion which has been set up in rectangular coordinates is unfortunate. This situation presents itself, however, with regard to the first term on the right of Eq. (2.27). The Eulerian angles* are generally the best coordinates to use for this rotational portion of the problem. The indicated transformations may be made.

Finally, Eq. (2.27) is transformed to a differential operator by the substitutions:

$$P_\alpha^2 \rightarrow -\hbar^2 \frac{\partial^2}{\partial \alpha^2}; \quad p_i \rightarrow -\hbar \frac{\partial^2 h}{\partial q_i^2}; \quad q_i^2 \rightarrow q_i^2 \qquad (2.28)$$

where $\alpha$ may be $x$, $y$, or $z$. The transformation to Eulerian angles may be made prior or subsequent to this transformation[163] of Eq. (2.27).

The operator form of Eq. (2.27) is substituted into Eq. (2.26a) to arrive at a rather formidable but nonetheless solvable differential equation.

One first makes the standard assumption that:

$$\psi = \psi(\vartheta,\varphi,\chi) \prod_{i=1}^{L} \psi(q_i) \prod_{i=L+1}^{\frac{1}{2}(M)} \psi(q_{i1}\, q_{i2}) \prod_{i=M+1}^{N+n-1} \psi(q_{i1}\, q_{i2}\, q_{i3}) \qquad (2.29)$$

In Eq. (2.29) $\Pi$ is the multiplication symbol. $\psi(\vartheta,\varphi,\chi)$ is a function of the rotational coordinates; $\psi(q_i)$ is a function of the $i$-th non-degenerate vibrational coordinate, and so on.

Eq. (2.29) is substituted into Eq. (2.26a), and the resulting expression is divided by Eq. (2.29). The "constant argument"† is then utilized to break up the equation into components which are subsequently solved.

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* See Appendix IV.

† The "constant argument" is vaguely reminiscent of one of the receipts for "fixing" the "Philosopher's Mercury" of the alchemist. "To fix quicksilver. Of several things take 2, 3, and 3,1; 1 to 3 is 4; 3, 2, and 1. Between 4 and 3 there is 1, between 3 and 2 there is 1. 1, 1, 1, and 1, 2, 2, and 1, 1 and 1 to 2. Then 1 is 1. I have told you all."[214] (Copyright C. A. Watts and Co., Ltd. Reproduction permission obtained.) A thorough search of the literature has failed to yield any contemporary experimental verification of this theory.

Let us consider the solution of the vibrational problems first.

$$\psi_{v_i}(q_i) = N_{v_i} \exp\left(-\frac{q_i^2}{2}\right) H_{v_i}(q_i) \tag{2.30a}$$

$$\psi_{v_i l_i}(\rho_i, \varphi_i) = N_{v_i l_i} \exp\,(\pm\, i l_i \varphi_i) \exp\left(-\frac{\rho_i}{2}\right) \rho_i^{l_i/2} L^{l_i}_{\frac{1}{2}(v_i+l_i)}(\rho_i) \tag{2.30b}$$

$$\psi_{v_i l_i m_i}(\rho_i, \vartheta_i, \varphi_i) = N_{v_i l_i m_i} \exp\,(\pm i m_i \varphi_i) \exp\left(-\frac{\rho_i}{2}\right) \rho_i^{l_i/2} L^{l_i}_{\frac{1}{2}(v_i+l_i)}(\rho_i)$$

$$\cdot\ \sin^{-m}\vartheta \,\frac{d^{l-m}}{d(\cos\vartheta)^{l-m}}\,(\sin^{2l}\vartheta) \tag{2.30c}$$

Eq. (2.30a) is the eigenfunction of the non-degenerate harmonic oscillator; Eq. (2.30b) is the eigenfunction of the twofold degenerate oscillator; and Eq. (2.30c) is the eigenfunction of the threefold degenerate oscillator.[202]

It is apparent that we have transformed the coordinates in Eqs. (2.30b) and (2.30c). In Eq. (2.30b) plane polar coordinates have been substituted for normal coordinates, since they are generally more suitable for the description of the elliptical motions involved. This transformation is given by:

$$\begin{aligned} \rho_i &= r_i^2 \\ q_{i1} &= r_i \cos \varphi_i \\ q_{i2} &= r_i \sin \varphi_i \end{aligned}$$

In like manner, spherical polar coordinates have been utilized in Eq. (2.30c).

$$\begin{aligned} q_{i1} &= r_i \sin \vartheta_i \cos \varphi_i \\ q_{i2} &= r_i \sin \vartheta_i \sin \varphi_i \\ q_{i3} &= r_i \cos \vartheta_i \end{aligned}$$

Several symbols still require clarification. $N_v$ is, in all cases, the normalization factor which is obtained from the general relation:

$$\int_{\substack{\text{all} \\ \text{space}}} \bar{\psi}_n \psi_n d\tau = 1 \tag{2.31}$$

$H_{v_i}$ is the $v$-th Hermite polynomial.* $L^{i}_{\frac{1}{2}(v_i+l_i)}(\rho_i)$ is an associated Laguerre polynomial. $v_i$, $l_i$, and $m_i$ are quantum numbers, and it may be noted that the number of quantum numbers possessed by an oscillator corresponds to the number of degrees of freedom — or one might say the classical degeneracy — of the oscillator. $v_i$ is the vibrational quantum number for the $i$-th vibrational mode, and it may be considered as a measure of the excitation of this mode. $l_i$ specifies the vibrational angular momentum due to degeneracy of the mode, and $m_i$ specifies the projection of this angular momentum vector on the body-fixed $z$ or figure axis. All quantum numbers are restricted to integral values, and the additional relations are imposed among these three,

$$l_i = v_i, v_i - 2, \ldots, 0 \text{ or } 1 \tag{2.32a}$$

$$m_i = l_i, l_i - 1, \ldots, 1 - l_i, -l_i \tag{2.32b}$$

---

* Appendix V lists most of the pertinent polynomials and the equations from which they arise. It should be kept in mind that it is not here important what the polynomial is. What is important is that the polynomial helps to describe the behavior of this vibrator.

These restrictions arise naturally during the solution of the differential equations which yield the eigenfunctions of Eq. (2.30).

The solution of Eq. (2.26a) for the eigenfunctions yields at the same time the eigenvalues of the energy:

$$E_i = h\nu_i\left(v_i + \frac{1}{2}\right) \tag{2.33a}$$

$$E_i = h\nu_i\,(v_i + 1) \tag{2.33b}$$

$$E_i = h\nu_i\left(v_i + \frac{3}{2}\right) \tag{2.33c}$$

Eqs. (2.33a), (2.33b), and (2.33c) are the eigenvalues of the non-degenerate, twofold degenerate, and threefold degenerate oscillators, respectively. If we let $d_i$ denote the degeneracy of the $i$-th mode, we may write the zeroth-order vibrational energy of the molecule as:

$$E_{0v} = \sum_i h\nu_i\left(v_i + \frac{d_i}{2}\right) \tag{2.34}$$

The completion of the zeroth-order problem now rests in the solution of the rotational portion of this problem. It is apparent from Eqs. (2.9) that one of three possible problems depending on the symmetry of the nuclear distribution will arise.

The eigenfunctions for the three cases may be written down as:

$$\psi_{JKM}(\vartheta,\varphi) = N_{JM}e^{\pm iM\varphi}P_J^M(\cos\vartheta) \tag{2.35a}$$

$$\psi_{JKM}(\vartheta,\chi,\varphi) = N_{JKM}\Theta(\vartheta)e^{\pm iK\chi}e^{\pm iM\varphi} \tag{2.35b}$$

$$\psi_{JM\tau}(\vartheta,\chi,\varphi) = \sum_{K=-J}^{+J} C_{JKM}^{(\tau)}\psi_{JKM}(\vartheta,\chi,\varphi) \tag{2.35c}$$

Eqs. (2.35a), (2.35b), and (2.35c) are the eigenfunctions for the spherical rotator, the symmetrical rotator,* and the asymmetrical rotator,† respectively.

Three quantum numbers, $J$, $K$, and $M$ occur. $J$ specifies the total angular momentum of the rotator. $K$ specifies the projection of the angular momentum vector on the molecular figure axis. It is perhaps worthy of note that $K$ does not occur in Eq. (2.35a). This appears reasonable in that all axes of a spherical rotator are equivalent with respect to symmetry. $M$ specifies the projection of the angular momentum vector on the space-fixed $z$-axis. The cognomen, magnetic quantum number, has been applied to $M$ since this quantum number obviously has no significance except when a unique space-fixed axis is established by the imposition of a magnetic or electric field on the system.

$P_J^M(\cos\vartheta)$ is the associated Legendre function and $\Theta(\vartheta)$ consists principally of hypergeometric functions.

The eigenfunction of the asymmetrical rotator is obtained as an expansion in terms of the complete orthogonal set of eigenfunction of the symmetric rotator. The $C_{JKM}^{(\tau)}$ are simply the constants of this expansion. $\tau$ is not really a quantum number.

The relations among the various rotational quantum numbers may be written down as:

$$J = 0,1,2,\ldots \tag{2.36a}$$

$$K,M,\tau = J,J-1,\ldots,1-J,-J \tag{2.36b}$$

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* See References 28, 90, 149, 151.

† See References 51, 87, 88, 132, 145, 188, 197.

The eigenvalues for the spherical and symmetric rotators may be expressed as:

$$E_{0R} = \frac{\hbar^2}{2I_{0x}} J(J+1) \tag{2.37a}$$

$$E_{0R} = \frac{\hbar^2}{2I_{0x}} J(J+1) + \left(\frac{1}{I_{0z}} - \frac{1}{I_{0x}}\right)\frac{K^2\hbar^2}{2} \tag{2.37b}$$

The eigenvalues of the asymmetric rotator cannot be written down in the concise, closed form of Eqs. (2.37),* and, in addition, more than one expression for them has been put forward. Let us simply assume their existence.

The total molecular energy in zeroth-order is then:

$$E_0 = \sum_i h\nu_i \left(v_i + \frac{d_i}{2}\right) + E_{0R} \tag{2.38}$$

Eq. (2.38) characterizes the molecule as possessing the dual, non-interacting properties of (1) a non-rotating particle system carrying out simple harmonic vibrations and (2) a rotating rigid body. Although this is quite apparently an extremely idealized solution, it admirably satisfies the two requirements for the zeroth-order in that (a) it does provide the exact solution and (b) these effects make the largest contribution to the molecular rotation-vibration energies.

## 2.6. THE FIRST AND SECOND ORDER PROBLEMS

Eq. (2.26a) has thus been provided with a solution, and the next and obvious steps are the successive solutions of Eqs. (2.26b) and (2.26c). Since these solutions amount essentially to the modification of the simple model of the preceding paragraph, and since the detail involved attains rather voluminous proportions which would add little to this sketchy presentation, we will not follow through the solution of these higher order approximations. Nielsen[133]† has carried out the first- and second-order perturbations in the general case, and Shaffer et al** have furnished the field with many specific examples of this calculation.

When the first- and second-order solutions have been carried out, a more reasonable description of the molecule emerges.

(1) The vibrations are no longer harmonic, since the ideal case of the Hooke's law potential has been replaced by an anharmonic potential.

(2) The molecule no longer rotates as a rigid body, but undergoes a centrifugal stretching or separation of its constituent particles which is dependent, as one might expect, through $J$ and $K$ on the degree of excitation of the rotational motion.

(3) The moments of inertia are no longer constants, but depend through $v$ on the degree of excitation of the vibrational motion.

(4) Coriolis interactions arise between the internal angular momenta and the total angular momenta. The internal angular momenta may arise from the degenerate vibrations or from the coupling of different vibrations.

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* For these eigenvalues see References 51, 87, 88, 132, 145, 188, 197.

† It may be noted that Nielsen's Eq. (4) for the kinetic energy differs slightly from Eq. (2.6). This is due to a slightly different method of setting up the problem. In Eq. (2.6) let $\rho = 0$, that is, let the origins of the inertial and moving frames coincide. Then the two equations coincide term for term where $\Omega_x$ is the $x$-component of $\Sigma m_i \, r_i \times v_i$, and so on.

** See References 24, 91, 134, 135, 162 through 170.

Simply as an example of these effects, let us briefly consider Nielsen's expression for the energy through second order of the symmetric molecule.

$$\frac{E}{hc} = \frac{E_v}{hc} + \frac{E_{rot}}{hc} \mp \frac{h}{4\pi^2 c I_{0x}} \sum_i \zeta l_i K \tag{2.39}$$

where:

$$\frac{E_{rot}}{hc} = J(J+1)B_v - K^2(B_v - C_v) - J^2(J+1)D_J - J(J+1)K^2 D_{JK} - K^4 D_K \tag{2.40a}$$

$$B_v = B_e - \alpha_0 - \sum_i \left(v_i + \frac{d_i}{2}\right) \alpha_i \tag{2.40b}$$

$$C_v = C_e - \gamma_0 - \sum_i \left(v_i + \frac{d_i}{2}\right) \gamma_i \tag{2.40c}$$

$$B_e = \frac{h}{8\pi^2 c I_{0x}} \qquad\qquad C_e = \frac{h}{8\pi^2 c I_{0z}} \tag{2.40d}$$

Eq. (2.39) has been expressed in wave numbers instead of the energy units previously utilized (ergs, ton-miles$^2$ -months$^{-2}$, etc.) as the denominator on the left of Eq. (2.39) indicates.

$E_v/hc$ is a rather complicated expression for the anharmonic vibrational energy. The third term on the right of Eq. (2.39) is the energy of Coriolis interaction. $\zeta_i$ is the Coriolis parameter, and the quantum numbers are as previously described. It might be of interest to note that when $l_i$, the quantum number which furnishes a measure of the angular momentum associated with a degenerate mode, is zero, the Coriolis term is likewise zero. The summation is over all vibrational modes where $l_i$ is related to the degree of excitation of the vibration by Eq. (2.32a). $\zeta_i$ will be zero for non-degenerate vibrations.

Eq. (2.40a) illustrates the newly introduced dependence of the moment of inertia on $v_i$. The last three terms on the right of this equation result from the centrifugal stretching whose dependence on the rotational excitation is illustrated.

This is as far as our rough description of the rotation-vibration energy levels and their associated eigenfunctions and eigenvalues need be carried, since, save for the inversion doubling effect,* the material which we have considered is all that will be needed in our line broadening studies.

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* See *infra*, Chap. 8 and Appendix VI.

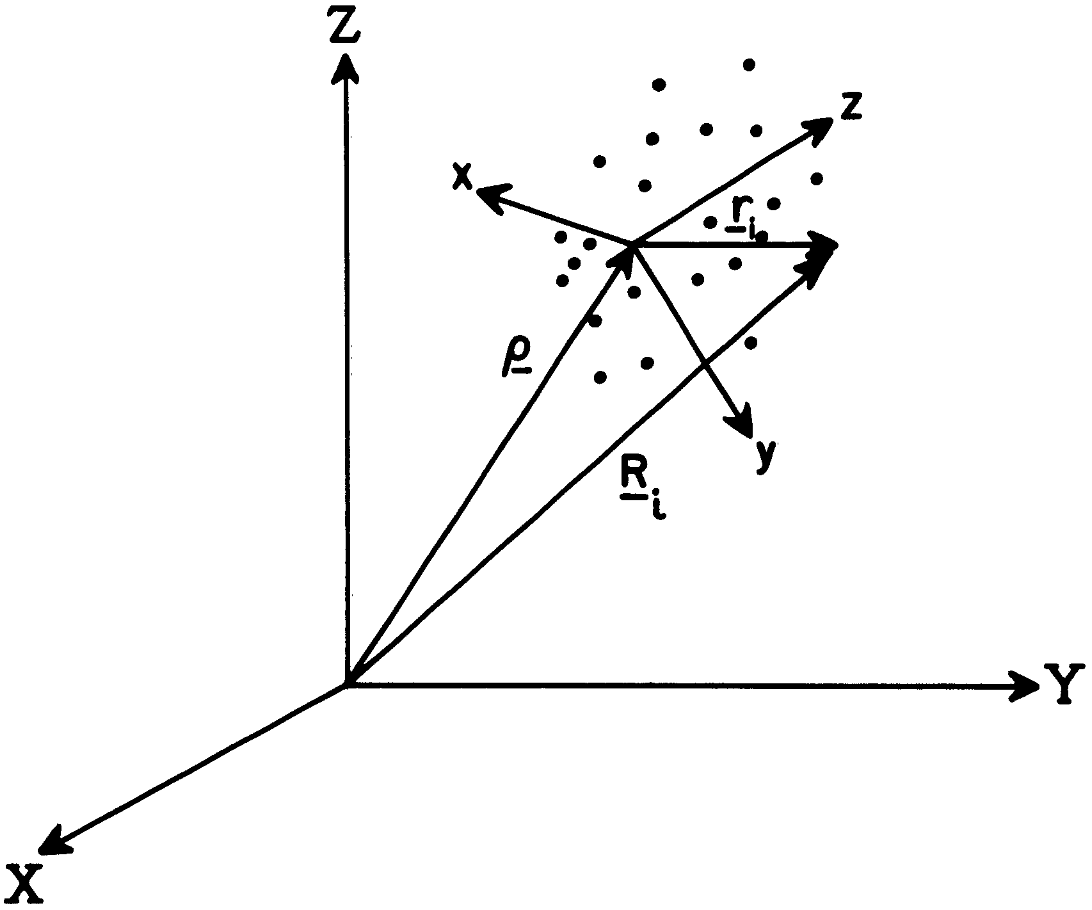

Fig. (2.1). Reference system for a collection of nuclei. The XYZ frame is an inertial one, the xyz frame a moving one.

# CHAPTER 3

# ELECTRODYNAMICS

In this chapter we shall devote ourselves to a rather sketchy treatment of those portions of electrodynamics which it will be imperative that we utilize during our considerations of line broadening theory. Since all of line broadening is intimately associated with the behavior of radiation during absorption and emission processes, the need for these considerations should be apparent.

## 3.1. LORENTZ INVARIANCE

Let us begin by supposing there to be a group of $l$-dimensional coordinate systems $x^a$, $\bar{x}^a$, etc. Now if we have $l^{m+n}$ functions $A^{a_1a_2\ldots a_m}_{b_1b_2\ldots b_n}$ in the $x$-system, $\bar{A}^{a_1a_2\ldots a_m}_{b_1b_2\ldots b_n}$ in the $\bar{x}$-system, and so on, which are interrelated (or which transform) as follows:

$$\bar{A}^{a_1a_2\ldots a_m}_{b_1b_2\ldots b_n} = \sum A^{c_1c_2\ldots c_m}_{d_1d_2\ldots d_n} \frac{\partial\bar{x}^{a_1}}{\partial x^{c_1}} \frac{\partial\bar{x}^{a_2}}{\partial x^{c_2}} \cdots \frac{\partial\bar{x}^{a_n}}{\partial x^{c_m}} \frac{\partial x^{d_1}}{\partial\bar{x}^{b_1}} \cdots \frac{\partial x^{d_n}}{\partial\bar{x}^{b_n}} \tag{3.1}$$

then these $l^{m+n}$ functions are the components in their coordinate system of a mixed tensor of contravariant order $m$ and covariant order $n$. Finally, the aggregate of these sets of $l^{m+n}$ components is the mixed tensor of the à propos contravariant and covariant order. The obvious modification of this definition for simple contravariant or covariant tensors follows.

A four dimensional coordinate system consisting of the three space coordinates $x_1$ $x_2$ $x_3$ and the coordinate $x_4 = ict$ may surely be defined. Now if $x_a$ is one such system and $x_a$ another, Lorentz invariance so-called requires that:

$$x_1^2 + x_2^2 + x_3^2 - c^2t^2 = \bar{x}_1^2 + \bar{x}_2^2 + \bar{x}_3^2 - c^2\bar{t}^2 \tag{3.2}$$

This relation will then establish the Lorentz transformation between the two coordinates. As an example, if in three space one frame is moving in the direction of its $x$-axis and in such a manner that its axes remain parallel to those of another frame, then in four space:

$$\bar{x}_1 = \frac{x_1 + i\beta x_4}{\sqrt{1-\beta^2}}, \bar{x}_2 = x_2;\ \bar{x}_3 = x_3;\ \bar{x}_4 = \frac{x_4 - i\beta x_1}{\sqrt{1-\beta^2}} \tag{3.3}$$

or, simply:

$$x_a = \sum_b x_b \frac{\partial x_b}{\partial\bar{x}_a}$$

where

$$\beta = v/c$$

From Eq. (3.1) it is apparent that Eq. (3.3) defines a covariant tensor of order one or a vector. Now any set of four functions $A_a$ which transforms according to Eq. (3.3), that is,

$$\bar{A}_a = \sum_b A_b \frac{\partial x_b}{\partial\bar{x}_a} \tag{3.4}$$

is designated a "four vector."

We might note the inherent invariance of scalars or numbers, since surely they should be unaffected by a change of reference frame. In four space time is not a scalar. Thus, the scalar product $\Sigma A_i B_i$ which may be defined in analogy to the scalar product of two three vectors is invariant. We may also show that the four volume element $dx_1\, dx_2\, dx_3\, dx_4$, the four divergence,

$$\Sigma \frac{\partial A_i}{\partial x_i} \tag{3.5a}$$

and the four atled square

$$\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} = \Sigma \frac{\partial^2}{\partial x_i^2} \tag{3.5b}$$

are Lorentz invariant. Procurement of an invariant time element $dT$ appears to be in order. Taking the length of an infinitesimal vector product and dividing by $(dt)^2$ yields:

$$\frac{\Sigma dx_i^2}{(dt)^2} = -\left(\frac{d\gamma}{dt}\right)^2 = \sum_{i=l}^{3}\left(\frac{dx_i}{dt}\right)^2 + c^2 = -c^2 + v^2 = -c^2(1-\beta^2)$$

or:

$$dT = cdt\sqrt{1-\beta^2} \tag{3.6}$$

namely, an invariant time element $dT$, the "proper time."

We have obtained a few basic relations which will be useful in the first task, that is, the setting up of the Maxwell equations in invariant form.

## 3.2. MAXWELL'S EQUATIONS IN LORENTZ INVARIANT FORM

It seems reasonable to begin by supposing charge invariant. Now an element of charge in a volume element is surely:

$$de = \rho dx_1\, dx_2\, dx_3$$

We know the four dimensional volume element to be invariant, so that if $de$ is invariant, $\rho$ must correspond to the fourth component of a four vector. We let:

$$ic\rho = i_4 \tag{3.7}$$

The $x$-component of the current density can be related as follows (we still assume relative motion of the $x$-axes for simplicity):

$$i_x = \rho v_x = \rho\frac{dx_1}{dt} = i_4\frac{dx_1}{dx_4} \tag{3.8}$$

It follows from the occurrence of $i_4$ in the equation for $i_x$ that $i_x$ will transform like the component of a four vector. Thus, we may take the charge and current density as forming a Lorentz invariant four vector:

$$i_1 = \rho v_x;\quad i_2 = \rho v_y;\quad i_3 = \rho v_z$$

$$i_4 = ic\rho \tag{3.9}$$

Now let us consider the wave equations for the scalar and vector potentials which arise as follows. We begin with Maxwell's equations:

$$\nabla \times \mathbf{E} = -\frac{1}{c}\dot{\mathbf{H}} \tag{3.10a}$$

$$\nabla \times \mathbf{H} = \frac{4\pi}{c}\rho\mathbf{v} + \frac{1}{c}\dot{\mathbf{E}} \tag{3.10b}$$

$$\nabla \cdot \mathbf{E} = 4\pi\rho \tag{3.10c}$$

$$\nabla \cdot \mathbf{H} = 0 \tag{3.10d}$$

The absence of any magnetic poles as indicated by Eq. (3.10d) leads to the vector potential solution for **H**:

$$\mathbf{H} = \nabla \times \mathbf{A} \tag{3.11}$$

which when substituted into Eq. (3.10a) yields:

$$\nabla \times \left(\mathbf{E} + \frac{1}{c}\dot{\mathbf{A}}\right) = 0 \longleftrightarrow \mathbf{E} = -\frac{1}{c}\dot{\mathbf{A}} - \nabla\varphi \tag{3.12}$$

where $\varphi$ is a scalar potential. When Eq. (3.12) is substituted into Eqs. (3.10b) and (3.10c) there results:

$$\nabla \cdot \frac{1}{c}\dot{\mathbf{A}} + \nabla^2\varphi + 4\pi\rho = 0 \tag{3.13a}$$

$$\frac{1}{c}\ddot{\mathbf{A}} - \nabla^2\mathbf{A} + \nabla\left(\nabla \cdot \mathbf{A} + \frac{1}{c}\dot{\varphi}\right) = \frac{4\pi}{c}\rho\mathbf{v} \tag{3.13b}$$

and when we let:

$$\nabla \cdot \mathbf{A} + \frac{1}{c}\dot{\varphi} = 0$$

Eqs. (3.13a) and (3.13b) become:

$$\frac{1}{c^2}\ddot{\mathbf{A}} - \nabla^2\mathbf{A} = \frac{4\pi}{c}\rho\mathbf{v} \tag{3.14a}$$

$$\frac{1}{c^2}\ddot{\varphi} - \nabla^2\varphi = 4\pi\rho \tag{3.14b}$$

Eq. (3.5b) tells us that the operator $\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2$ which occurs on the left of each of Eqs. (3.14) is invariant. A comparison of the right sides of these equations with Eq. (3.9) for the charge-current four vector serves to show the similarity. The fact that such a combination of the right sides of these equations has already been obtained leads us to consider the combination of the vector and scalar potentials appearing on the left. Such a combination is a happy one, and we obtain a four vector transforming in the desired manner if we take for our components:

$$A_1 = A_x;\quad A_2 = A_y;\quad A_3 = A_z;\quad A_4 = i\varphi \tag{3.15}$$

Now the Lorentz relation:

$$\nabla \cdot \mathbf{A} + \frac{\dot{\varphi}}{c} = 0 \tag{3.16a}$$

may be written as the invariant four divergence:

$$\sum_i \frac{\partial A_i}{\partial x_i} = 0 \tag{3.16b}$$

and the potentials are still restricted thereby.

Surely, from Eq. (3.15)

$$iE_x = -\frac{i}{c}\dot{A}_x - i\frac{\partial\varphi}{\partial x} = \frac{\partial A_1}{\partial x_4} - \frac{\partial A_4}{\partial x_1} \tag{3.17a}$$

$$H_x = (\nabla \times \mathbf{A})_x = \frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} \tag{3.17b}$$

Let us investigate the set of derivatives of a four vector,

$$\frac{\partial A_i}{\partial x_k} = f_{ki}' \tag{3.18}$$

According to Eq. (3.4) these derivatives transform as follows:

$$\frac{\partial \bar{A}_i}{\partial \bar{x}_k} = \sum_{l,j} \frac{\partial A_j}{\partial x_l}\frac{\partial x_l}{\partial \bar{x}_m}\frac{\partial x_j}{\partial \bar{x}_i} \tag{3.19a}$$

so that:

$$\bar{f}_{ki}' = \sum_{l,j} f_{lj}' \frac{\partial x_l}{\partial \bar{x}_k}\frac{\partial x_j}{\partial \bar{x}_i} \tag{3.19b}$$

According to Eq. (3.1) $f_{ki}'$ in Eq. (3.19b) transforms tensorially, and as a consequence, the derivatives of the four vector are the components of a tensor of order two.

Since, for example:

$$(\bar{A}^a_{bc} + \bar{B}^a_{bc}) = \Sigma\,(A^i_{jk} + B^i_{jk})\,\frac{\partial \bar{x}^a}{\partial x^i}\frac{\partial x^j}{\partial \bar{x}^b}\frac{\partial x^k}{\partial \bar{x}^c} \tag{3.20a}$$

then the sum or difference of two tensors of the same type is a tensor of like type. Thus:

$$\frac{\partial A_i}{\partial x_k} - \frac{\partial A_k}{\partial x_i} = f_{ki}' - f_{ik}' = f_{ki} = -f_{ik} \tag{3.20b}$$

is a skew symmetric tensor component. This tells us that the right sides of Eq. (3.17) are tensor components so that, by Eq. (3.20b):

$$H_x = f_{23}; \quad H_y = f_{31}; \quad H_z = f_{12}$$

$$iE_x = f_{41}; \quad iE_y = f_{42}; \quad iE_z = f_{34} \tag{3.21}$$

and we might remark that there are $1^{m+n} = 4^2 = 16$ components as required.

Two of Maxwell's equations:

$$\nabla \cdot \mathbf{E} = 4\pi\rho\,;\ \nabla \times \mathbf{H} - \frac{1}{c}\mathbf{E} = \frac{4\pi}{c}\rho\mathbf{v} \tag{3.22a}$$

may now be written as:

$$\sum_l \frac{\partial f_{kl}}{\partial x_l} = \frac{4\pi}{c} i_k \tag{3.22b}$$

where summing over the derivative amounts to contracting the tensor from order two to order one, a vector, which is requisite for the equality. The remaining two Maxwell equations

$$\nabla \cdot \mathbf{H} = 0;\ \nabla \times \mathbf{E} + \frac{1}{c}\dot{\mathbf{H}} = 0 \tag{3.23a}$$

may be written as:

$$\frac{\partial f_{23}}{\partial x_1} + \frac{\partial f_{31}}{\partial x_2} + \frac{\partial f_{12}}{\partial x_3} = 0$$

$$\frac{\partial f_{43}}{\partial x_2} + \frac{\partial f_{24}}{\partial x_3} + \frac{\partial f_{32}}{\partial x_4} = 0 \tag{3.23b}$$

Now after the same fashion in which we proved $f_{ki}'$ a tensor of order two, we may prove $\frac{\partial f_{ik}}{\partial x_l} = t_{ikl}$ a tensor of order three. Thus Eq. (3.23b) becomes:

$$t_{ikl} + t_{kli} + t_{lik} = 0 \tag{3.23c}$$

which sum is also a tensor by Eq. (3.20a). Thus, Maxwell's equations have been expressed as tensors and four vectors according to Eqs. (3.22b) and (3.23c). Since these type quantities are Lorentz invariant, Maxwell's equations are Lorentz invariant.

## 3.3. THE RELATIVISTIC HAMILTONIAN OF A PARTICLE

The Lorentz density of force acting on the charge density is given by:

$$\mathbf{k} = \rho\left(\mathbf{E} + \frac{1}{c}\mathbf{v} \times \mathbf{H}\right) \tag{3.24a}$$

where the first term is due to the electric field, and the second term is the well known magnetic effect. If Eq. (3.24a) is also Lorentz invariant, things are progressing very nicely indeed. Now for example:

$$\begin{aligned} ck_x &= c\rho E_x + \rho(v_y H_z - H_y v_z) \\ &= f_{14}i_4 + f_{12}i_2 + f_{13}i_3 \\ &= \sum_k f_{ik}i_k \end{aligned}$$

by Eqs. (3.9) and (3.21) since $f_{11} = 0$. In general, Eq. (3.24a) may be written for $i = 1,2,3$:

$$k_i = \frac{1}{c}\sum_k f_{ik}i_k \tag{3.24b}$$

where $k_4$ does not arise directly out of Eq. (3.24a), but is defined by Eq. (3.24b) as:

$$k_4 = \frac{i}{c}\rho(\mathbf{E} \cdot \mathbf{v})$$

the work done by the field on the charge per unit of volume per unit of time. If we substitute for $i_4$ from Eq. (3.22b) in Eq. (3.24b) there results:

$$k_i = \frac{1}{4\pi}\sum_{k,l} f_{ik} \frac{\partial f_{kl}}{\partial x_l} \tag{3.24c}$$

or:

$$k_i = \sum_k \frac{\partial T_{ik}}{\partial x_k} \tag{3.24d}$$

where:

$$T_{ik} = \frac{1}{4\pi}\left[\sum_l f_{il}f_{lk} + \frac{1}{4}\delta_{ik}\sum_{l,m} f_{lm}^2\right]$$

$$= \begin{pmatrix} T_{xx} & T_{xy} & T_{xz} & -\frac{i}{c}S_x \\ T_{yx} & T_{yy} & T_{yz} & -\frac{i}{c}S_y \\ T_{zx} & T_{zy} & T_{zz} & -\frac{i}{c}S_z \\ -\frac{i}{c}S_x & -\frac{i}{c}S_y & -\frac{i}{c}S_z & u \end{pmatrix} \tag{3.25}$$

which is defined as the "generalized tension tensor."

We define the diagonal and off-diagonal elements of the Maxwell tension tensor as:

$$4\pi T_{xx} = \tfrac{1}{2}(E_x^2 - E_y^2 - E_z^2 + H_x^2 - H_y^2 - H_z^2)$$
$$4\pi T_{xy} = 4\pi T_{yx} = E_xE_y + H_xH_y \tag{3.26}$$

and agree that $\mathbf{S} = c\mathbf{E} \times \mathbf{H}$ is the Poynting vector. The last symbol $u$ is the energy per unit of volume given, as we may recall, by

$$\frac{E^2 + H^2}{8\pi}$$

Now we note that S is the energy passing through unit area per unit time. Thus, we may define density of field momentum as $\frac{1}{c^2}\mathbf{S}$. Finally, we shall refer to the quantity $\frac{1}{c}\mathbf{S}$ as momentum. From these considerations the energy and momentum of the field in a certain volume is:

$$U = \frac{1}{8\pi}\int (E^2 + H^2)dt = \int u dt \tag{3.27a}$$

$$\mathbf{G} = \int \mathbf{g}d\tau = \frac{1}{c}\int \mathbf{S}d\tau = \frac{1}{4\pi}\int \mathbf{E} \times \mathbf{H}d\tau \tag{3.27b}$$

Let us write, for example, from Eq. (3.24d):

$$k_x = \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} + \frac{1}{it}\ \frac{\partial T_{x4}}{\partial t} = \nabla_x \cdot T - \frac{1}{c}\frac{\partial g_x}{\partial t} \tag{3.28}$$

Integrating over all space we obtain:

$$\int k_x d\tau = -\frac{1}{c}\ \frac{\partial G_x}{\partial t} + \oint T_{xi} d\sigma = K_x \tag{3.29a}$$

by Eq. (3.23b) and by Gauss' theorem equating the divergence of a tensor integrated over a volume to the tensor components normal to the volume-enclosing surface integrated over the surface.

Since K is the force acting on the charge in the volume over which integration has been carried out, it must be equivalent to the time rate of change of the mechanical momentum of the charges, $u = mvc$, where we recall our definition of momentum as $c$ times the momentum in the normal sense. Thus

$$\mathbf{K} = \frac{d}{dt}(m\mathbf{v}) = \frac{1}{c}\frac{d\mathbf{u}}{dt}$$

and Eq. (3.29a) becomes:

$$\frac{d}{dt}(u_x + G_x) = c\oint T_{xi}\, d\sigma \tag{3.29b}$$

This equation stipulates momentum conservation by requiring that the time rate of change of particle momentum $u$ plus field momentum $G$ in the volume is equal to the momentum that flows through the surface, an apparently reasonable assertion.

In like manner Eq. (3.24d) yields:

$$\frac{c}{i}\int k_4 d\tau = \int \rho\mathbf{E} \cdot \mathbf{v}d\tau = -\oint S_i d\sigma - \frac{\partial U}{\partial t} \tag{3.30a}$$

by Eqs. (3.25) and (3.27a) and Gauss' theorem. Or, since $\frac{\partial T}{\partial t} = \int \mathbf{k} \cdot \mathbf{v}d\tau$

$$\frac{d}{dt}(T + U) = -\oint S_i d\sigma \tag{3.30b}$$

gives the requisite energy conservation. Thus Eq. (3.24d) guarantees the desired energy and momentum conservation. Now again from Eq. (3.24d):

$$c\int k_x d\tau dt = c\int K_x dt = u_x = u_1 \tag{3.31a}$$

$$c\int k_4 d\tau dt = i\int \rho(\mathrm{E}\cdot \mathrm{v})d\tau dt = iT \tag{3.31b}$$

so that if we consider the group of charged particles or charges in the volume in question as a particle — or if we simply consider our volume as containing one particle — the momentum $u$ and kinetic energy $T$ of this particle make up a four vector, $u_i$. Now the following is invariant:

$$-\Sigma u_i^2 = T^2 - (u_x^2 + u_y^2 + u_z^2) = \mu^2 \tag{3.32}$$

and a consideration of this equation tells us that $\mu$ represents the rest energy of the particle, that is, the energy for $u_x = u_y = u_z = 0$.

The four vector made up of $u$ and $T$ transforms according to Eqs. (3.3) and (3.4), and, if we assume the particle at rest in the $\bar{x}$ system, the "Einstein formulae" for $u$ and $T$ result:

$$u_x = \frac{\mu\beta}{\sqrt{1-\beta^2}} \tag{3.33a}$$

$$T = \frac{\mu}{\sqrt{1-\beta^2}} \tag{3.33b}$$

Since, for $v \ll c$, $u_x$ must equal $mv_x c$;

$$\mu = mc^2 \tag{3.33c}$$

In analogy to the non-relativistic case in which we equate the time derivative of the momentum to the force due to the field acting on the particle,

$$\mathrm{K} = e\left(\mathrm{E} + \frac{1}{c}\mathrm{v}\times \mathrm{H}\right)$$

we write, according to Eq. (3.33a):

$$K_x = \frac{1}{c}\frac{du_x}{dt} = \frac{d}{dt}\frac{mv_x}{\sqrt{1-\beta^2}} = e\left(E_x + \frac{1}{c}(\mathrm{v}\times \mathrm{H})_x\right) \tag{3.34}$$

and dividing through $\sqrt{1-\beta^2}$ there results:

$$\frac{du_i}{dT} = \frac{e}{\mu}\Sigma f_{ik}u_k \tag{3.35}$$

from Eqs. (3.6), (3.21), and (3.33). We have thus obtained the equation for the relativistic motion of a particle in an external field.

Now if $T$ is the kinetic energy of our particle, the total energy $E$ may be represented by $T + e\varphi$ where $\varphi$ is the scalar potential of the external field. Hence, from the sum of the two four vectors defined by Eqs. (3.15) and (3.31) we may form the four vector:

$$p_i = u_i + eA_i$$

or:

$$p_1 = u_x + eA_x;\quad p_2 = u_y + eA_y;\quad p_3 = u_z + eA_z;\quad p_4 = iE = i(T + e\varphi) \tag{3.36}$$

We shall designate the space components of $u_i$ and $p_i$ as kinetic momentum and total momentum respectively. Finally, Eqs. (3.32) and (3.36) may be combined to yield:

$$\Sigma u_i^2 = \Sigma(p_i - eA_i)^2 = -\mu^2 \tag{3.37a}$$

We agree that the straightforward expansion of Eq. (3.37a) is:

$$(p_1 - eA_1)^2 + (p_2 - eA_2)^2 + (p_3 - eA_3)^2 - T^2 = -\mu^2 \tag{3.37b}$$

and using Eq. (3.37b) for the momentum-energy relation we shall accept as the Hamiltonian the following:

$$H = V + T = e\varphi + \sqrt{\mu^2 + (\mathbf{p} - e\mathbf{A})^2} \tag{3.38a}$$

By the binomial theorem:

$$H = e\varphi + \mu\sqrt{1 + \frac{(\mathbf{p} - e\mathbf{A})^2}{\mu^2}} = e\varphi + \mu + \frac{1}{2}\frac{(\mathbf{p} - e\mathbf{A})^2}{\mu} + \dots$$

$$\doteq e\varphi + \frac{(\mathbf{p} - e\mathbf{A})^2}{\mu} \tag{3.38b}$$

for $v \ll c$, i.e., for the non-relativistic case and where the constant term $\mu$ is neglected.

## 3.4. THE RELATIVISTIC HAMILTONIAN FOR PARTICLES PLUS FIELD

Now the fields which we shall utilize in Eqs. (3.38) must include the field produced by the charge with which the field is interacting, this latter interaction producing the self-force.

Eqs. (3.38) then give the Hamiltonian in which the particle-field interaction is included for a charged particle in the relativistic or non-relativistic cases.

Now let us obtain a Hamiltonian for our field. To begin with "gauge invariance" tells us that **E** and **H** are not changed when **A** and $\varphi$ are replaced by $\mathbf{A}' = \mathbf{A} + \nabla\xi$ and $\varphi' = \varphi - \dot{\xi}/c$, and we utilize this fact by choosing $\xi$ such that $\varphi'$ is zero. Then from Eqs. (3.13a) and (3.13b) we obtain, instead of Eqs. (3.14), the following:

$$\frac{1}{c}\nabla . \dot{\mathbf{A}} + 4\pi\rho = 0 \tag{3.39a}$$

$$\frac{1}{c^2}\ddot{\mathbf{A}} - \nabla^2\mathbf{A} + \nabla(\nabla \cdot \mathbf{A}) = \frac{4\pi}{c}\rho\mathbf{v} \tag{3.39b}$$

and we shall only concern ourselves with this vector potential. Let us suppose we may express $\mathbf{A}(xyzt)$ as:

$$\mathbf{A}(xyzt) = \Sigma q_i\,(t)\mathbf{A}_i(xyz) \tag{3.40}$$

Let us consider the $i$-th homogeneous form of Eq. (3.39b) for $\mathbf{A}_i$:

$$\nabla^2\mathbf{A}_i + \frac{\nu_i^2}{c^2}\,\mathbf{A}_i = 0 \tag{3.41}$$

according to Eq. (3.40).

If we confine the field to a cube of side $l$ and admit the boundary conditions,

$$\mathbf{A}_i(oyz) = \mathbf{A}_i(lyz), \text{ etc.}$$

$$\nabla \cdot \mathbf{A}_i = 0$$

the solution to Eq. (3.37) is surely:

$$\mathbf{A}_i = \mathbf{e}_{ij}\sqrt{\frac{4\pi c^2}{l^3}}\sin\frac{2\pi}{l}(n_1x + n_2y + n_3z) = \mathbf{e}_{ij}\sqrt{\frac{4\pi c^2}{l^3}}\ \sin\,(\mathbf{k}_i \cdot \mathbf{r})$$

$$\mathbf{A}_i = \mathbf{e}_{ij}\sqrt{\frac{4\pi c^2}{l^3}}\ \cos\,(\mathbf{k}_i \cdot \mathbf{r})$$

or finally:

$$\mathbf{A}_i = \mathbf{e}_{ij}\sqrt{\frac{4\pi c^2}{l^3}}\exp\Big[i(\mathbf{k}_i \,.\, \mathbf{r})\Big] \tag{3.42a}$$

where $r$ is a position vector and $k_i$ is now in the direction of motion of this $i$-th plane wave. In addition, the $A_i$ have been normalized to unity in the box such that

$$\int \mathbf{A}_i \cdot \mathbf{A}_j d\tau = 4\pi c^2 \delta_{ij}$$

Eq. (3.42a) simply serves to illustrate insofar as we are concerned that an expansion in plane waves at least has the cursory appearance of a reasonable procedure.

$$\Sigma q_{ij} \mathbf{A}_i = \Sigma q_{ij} \mathbf{u}_{ij} \tag{3.42b}$$

Now we let the subscript $i$ refer to the direction of propagation — $i$ opposite to $-i$ — and $j$ prescribe the direction of polarization (the direction of E), $j = 1$ indicating a longitudinal wave and $j = 2,3$ a transverse wave. Thus:

$$\begin{aligned} \mathbf{A} &= \sum_{ij} q_{ij} \mathbf{u}_{ij} \\ &= \mathbf{A}_l + \mathbf{A}_t = \Sigma q_l \mathbf{u}_l + \Sigma q_t \mathbf{u}_t \end{aligned} \tag{3.43}$$

where A has been separated into longitudinal and transverse components.

Now, remembering that $\nabla^2 \mathbf{u}_{ij} = -\frac{\nu_i^2}{c^2} \mathbf{u}_{ij} + \nabla(\nabla \cdot \mathbf{u}_l) = \nabla^2 \mathbf{u}_l$

— since $\nabla \times \nabla \times = -\nabla^2 + \nabla(\nabla \cdot \;)$ — Eq. (3.39b) becomes:

$$\frac{1}{c^2} \Sigma (\ddot{q}_t + \nu_t^2 q_t) \mathbf{u}_t + \frac{1}{c^2} \Sigma \ddot{q}_l \mathbf{u}_l = \frac{4\pi}{c} \rho \mathbf{v} \tag{3.44a}$$

or after multiplication by $\overline{\mathbf{u}}_t$ or $\overline{\mathbf{u}}_l$ and integration over our box:*

$$\ddot{q}_t + \nu_t^2 q_t = \frac{1}{c} \int \rho \overline{\mathbf{u}}_t \cdot \mathbf{v} dv \tag{3.44b}$$

$$\ddot{q}_l = \frac{1}{c} \int \rho \overline{\mathbf{u}}_l \cdot \mathbf{v} dv \tag{3.44c}$$

by Eq. (3.39b).

Let us note that, since Eq. (3.41b) corresponds to forced oscillation, the transverse wave may be quantized, but, since Eq. (3.41c) corresponds to a free particle motion under the influence of a force not dependent on the position coordinate, the longitudinal component may not be so quantized.

It can be shown — we shall not do so, but it is a quite straightforward procedure — that the Hamilton equations which can be obtained from Eqs. (3.44b) and (3.44c) arise from the Hamiltonian:

$$H = \sum_t \tfrac{1}{2}(p_t \bar{p}_t + \nu_t^2 \bar{q}_t q_t) + \sum_l \tfrac{1}{2} \bar{p}_l p_l + \sum_k \sqrt{\mu_k^2 + [\mathbf{p}_k - e_k \mathbf{A}_k]^2} \tag{3.45}$$

where the third term corresponds to that occurring in Eq. (3.38a). The appearance of this term should not come as a surprise since Eq. (3.10c) allows the presence of charged particles in the cube under consideration.

We may rewrite the second sum[198a] as the Coulomb interaction between the particles. Thus, the contribution of the longitudinal wave to the Hamiltonian drops out.† Finally, when we add the portion of the Hamiltonian due to an external field there results:

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* The orthonormality of the $\mathbf{u}_i$ set yields the result.

† The contribution of these waves to $A$ within the bracket in the third term also disappears.

$$H = \sum_k [\mu_k^2 + (\mathbf{p}_k - e_k \sum_i q_{ij}\mathbf{u}_{ij} - e_k\mathbf{A}^e)^2]^{\frac{1}{2}} + \tfrac{1}{2}\sum_t (\bar{p}_t p_t + \nu_t^2 \bar{q}_t q_t)$$

$$+ \tfrac{1}{2}\sum_{ik} \frac{e_i e_k}{r_{ik}} + \sum_k e_k \varphi^e(k) \tag{3.46}$$

The four terms in Eq. (3.46) represent (1) the kinetic energy of the particles and the interaction of these particles with the light waves, (2) the energy of the light waves, (3) electrostatic interaction between the particles, and (4) the interaction between the particles and the external field.

From Eq. (3.46):

$$H_t = \tfrac{1}{2}(\bar{p}_t p_t + \nu_t^2 \bar{q}_t q_t) \tag{3.47a}$$

At this point, it behooves us to rewrite a portion of Eq. (3.43) as:

$$A = \sum_t (q_t u_t + \bar{q}_t \bar{u}_t) + \sum_l (q_l u_l + \bar{q}_l \bar{u}_l) \tag{3.48}$$

Now, however, $q_t$ and $\bar{q}_t$ are not canonical in that they do not satisfy the canonical equations of Hamilton. This requires the introduction of the new canonical variables:

$$Q_t = q_t + \bar{q}_t \tag{3.49a}$$

$$P_t = -i\nu_t(q_t - \bar{q}_t) = Q_t \tag{3.49b}$$

Substitution of these equations into Eq. (3.47a) yields:

$$H_t = \tfrac{1}{2}(P_t^2 + \nu_t^2 Q_t^2) \tag{3.47b}$$

This is the Hamiltonian of a harmonic radiation oscillator, and it is apparent that its energy eigenvalues must correspond to those of the well known harmonic oscillator.

$$E_t = (n_t + \tfrac{1}{2})h\nu_t \tag{3.50}$$

This equation tells us that each one of the infinite number of radiation oscillators in our volume possesses a zero point energy of $\frac{1}{2}h\nu_t$ so that even for each of the oscillators in the ground state the volume is possessed of an infinite energy. Assuming this difficulty to be a formal one, we write simply for $H^{153a}$:

$$H = \sum_k [\mu_k^2 + (\mathbf{p}_k - e_k \sum_i (q_i \mathbf{u}_{ij} + \bar{q}_i \mathbf{u}_{ij}) - e_k \mathbf{A}^e)^2]^{\frac{1}{2}} + \sum_t n_t h\nu_t$$

$$+ \tfrac{1}{2}\sum_{i \neq k} \frac{e_i e_k}{r_{ik}} + \sum_k e_k \varphi^e \tag{3.51}$$

## 3.5 REEXPRESSION AND UTILIZATION OF THE COMPLETE HAMILTONIAN

In order to put Eq. (3.51) in an oft-encountered form, we note that:

$$\frac{dx_k}{dt} = v_{xk} = \frac{\partial H_k}{\partial p_x} = \frac{c(p_{xk} - e_k A_x)}{[\mu_k^2 + (\mathbf{p}_k - e_k\mathbf{A})^2]^{\frac{1}{2}}} \text{ ; etc.} \tag{3.52a}$$

according to Hamilton's equations, and, if we square and add the $v$-components given by Eq. (3.52a), we can obtain:

$$p - eA = \frac{mvc}{\sqrt{1 - \beta^2}} \tag{3.52b}$$

Utilizing Eqs. (3.52) we may write $H_k$ as:

$$H_k = e_k\varphi + \frac{1}{c}\mathbf{v}_k \cdot (\mathbf{p}_k - e_k\mathbf{A}) + \mu_k\sqrt{1 - \beta_k^2} \tag{3.53}$$

which, according to Dirac, satisfies the equation:

$$(E_k - e_k\varphi)\psi_k = [\underline{\alpha}_k \cdot (\mathbf{p}_k - e_k\mathbf{A}) + \gamma_k\mu_k]\,\psi_k \tag{3.54}$$

where now $\underline{\alpha}_k$ and $\gamma_k$ are matrices satisfying the following commutation relations:

$$\alpha_x\gamma + \gamma\alpha_x = 0 \qquad\qquad \alpha_x\alpha_y + \alpha_y\alpha_x = 0$$

$$\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \gamma^2 = 1 \tag{3.55a}$$

Specifically, these matrices are:

$$\underline{\alpha} = \begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} \qquad\qquad \gamma = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \tag{3.55b}$$

with each element representing a two by two matrix, the $\underline{\sigma}$ being the well known Pauli spin matrices:

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad\qquad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_y = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \qquad\qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{3.55c}$$

We might pause for a moment to give a portion of Eq. (3.54) specifically. Suppose $\psi = u(s)u(\mathbf{r})$ where $u(s)$ is a function only of the spin coordinates and $u(\mathbf{r})$ a function of only the space coordinates. Then:

$$[\alpha_x p_x - e\alpha_x A_x + \ldots]\;\psi = \alpha_x p_x\psi + \ldots$$

$$= -ic\hbar\begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} u(s)\,\frac{\partial u(\mathbf{r})}{\partial x} + \ldots$$

where the $\sigma_x$ are given by Eq. (3.55c) and the remainder of the equation takes an analogous form.

According to Eq. (3.53), Eq. (3.51) takes on the form:

$$H = \sum_k [\underline{\alpha}_k \cdot (\mathbf{p}_k - e\mathbf{A}) + \gamma_k\mu_k + e_k\varphi^e] + \tfrac{1}{2}\sum_{i \neq k} \frac{e_ie_k}{r_{ik}} + \sum_t n_t\hbar\nu_t \tag{3.56}$$

and we are now in a position to separate this Hamiltonian into a perturbed and an unperturbed portion such that:

$$H = H_0 + H' \tag{3.57a}$$

We select these parts of the Hamiltonian as:

$$H_0 = \sum_k [\underline{\alpha}_k \cdot (\mathbf{p}_k - e_k\mathbf{A}^e) + \gamma_k\mu_k + e_k\varphi^e] + \tfrac{1}{2}\sum_{i \neq k} \frac{e_ie_k}{r_{ik}} + \Sigma n_t\hbar\nu_t = H_p + H_f \tag{3.57b}$$

$$H' = -\sum_k e_k\underline{\alpha}_k \cdot \mathbf{A} = H_{pf} \tag{3.57c}$$

where $H_p$ is the Hamiltonian of the particle, $H_f$ is the Hamiltonian of the field, and $H_{pf}$ is the Hamiltonian of the interaction between the particle and the field. We might note that the $\mathbf{A}^e$ and $\varphi^e$ remaining in the particle Hamiltonian are associated only with the external field.

If we now revert to the non-relativistic approximation of Eq. (3.38b) we obtain:

$$H_k = \frac{1}{2\mu_k}(\mathbf{p}_k - e_k\mathbf{A})^2 \tag{3.58a}$$

from which:

$$H_p = \sum_k \frac{1}{2\mu_k}(p_k^2 - 2e_kp_k \cdot \mathbf{A}^e + e_k^2A_e^2 + e_k\varphi^e) \tag{3.57b'}$$

$$H' = -\sum_k \frac{1}{2\mu_k}(2e_k\mathbf{p}_k \cdot \mathbf{A} - e_k^2A^2) \tag{3.57c'}$$

Let us now consider $H'$ as given by Eq. (3.57c′) since we shall be primarily concerned with this non-relativistic case. Where the unperturbed Hamiltonian allows for no change in the number of photons in the field — note this through the term $\sum_t n_t \hbar \nu_t$ — the perturbing portion of the Hamiltonian does just this. This is of no little importance, for, since this term gives the interaction between radiation and matter, it follows that no changes in this photon number may occur in the absence of matter.[*] The first term in Eq. (3.57c′) refers to absorptions or emissions of one photon — by matter — in a given process, while the second term refers to absorptions or emissions of two photons or the simultaneous absorption and emission of two photons — one each way.

From Eq. (3.48) the first term in Eq. (3.57c′) becomes:

$$H'_{(1)} = -\sqrt{\frac{4\pi c^2}{l^3}} \sum_{ki} \frac{e_k}{\mu_k} \mathbf{p}_k \cdot (q_i \mathbf{A}_i + \bar{q}_i \bar{\mathbf{A}}_i) \tag{3.58}$$

Now before doing anything more with this equation, let us consider the eigenfunctions of the operator $H$. We surely expect these eigenfunctions to describe the system particles plus field. Let us take one particle for simplicity and suppose the quantum number $n$ to describe the state of this particle, while the quantum numbers $n_1, n_2, n_3, \ldots$ describe the state of the denumerably infinite number of radiation oscillators in the volume. Then:

$$\psi_N = \psi_{nn_1n_2n_31} \ldots (qq_1q_2q_3 \ldots) = \psi_n(q)\psi_{n_1}(q_1)\psi_{n_2}(q_2) \ldots .$$

and the matrix elements of $H_{(1)}'$ are:

$$(H_{(1)}')_{NM} = \int \ldots \int \overline{\psi_n(q)\psi_{n_1}(q_1) \ldots}\, H_{(1)}' \psi_m(q)\psi_{m_1}(q_1) \ldots d\tau dq_1 \ldots \tag{3.60}$$

Due to the behavior of the Hermite polynomials which go to make up the harmonic oscillator eigenfunctions, the matrix elements of $q_i$ may be found as the familiar ones:

$$(q_i)_{n_i m_i} = \int q_i \psi_{n_i} \psi_{m_i} dq_i = \begin{cases} \sqrt{\dfrac{\hbar}{2\nu_i}(n_i + 1)} & \text{for } m_i = n_i + 1 \\ 0 & \text{for } m_i = n_i - 1 \end{cases} \tag{3.61a}$$

$$(\bar{q}_i)_{n_i m_i} = \int \bar{q}_i \psi_{n_i} \psi_{m_i} dq_i = \begin{cases} 0 & \text{for } m_i = n_i + 1 \\ \sqrt{\dfrac{\hbar}{2\nu_i} n_i} & \text{for } m_i = n_i - 1 \end{cases} \tag{3.61b}$$

In the general manner of wave mechanics $\mathbf{p}$ must be replaced by $-ihc\,\nabla$. Thus the dot product $(\mathbf{p} \cdot \mathbf{A}_i)$ is the gradient in the direction of $\mathbf{A}_i$ according to Eq. (3.39b). Now, we recall that $(\mathbf{k}_i \cdot \mathbf{r})$ is, in essence, the projection of $\mathbf{r}$ on the wave propagation direction, which direction in turn is perpendicular to $\mathbf{A}_i$. Thus, operating on $\exp i(\mathbf{k}_i \cdot \mathbf{r})$ with $-i\hbar c\,\nabla_i$ yields zero so that the following is valid:

$$(-i\hbar c\,\nabla_i) \exp [i(\mathbf{k}_i \cdot \mathbf{r})]\psi_m(q) = \exp [i(\mathbf{k}_i \cdot \mathbf{r})](-i\hbar c\,\nabla_i)\psi_m(q) + 0 \tag{3.62}$$

Finally, utilizing Eqs. (3.61) and (3.62) we obtain:

$$(H_{(1)}')_{nn_1 \ldots n_i \ldots ; mn_i \ldots n_i \pm 1 \ldots}$$
$$= \frac{e}{\mu}\sqrt{\frac{4\pi c^2}{l^3}} \int \bar{\psi}_n(q) \left\{ \begin{matrix} \sin \\ \cos \end{matrix} (\mathbf{k}_i \cdot \mathbf{r}) \right\} (-i\hbar c\,\nabla_i)\psi_m(q) d\tau \sqrt{\frac{\hbar}{2\nu_t}} \left\{ \begin{matrix} \sqrt{n_i + 1} \\ \sqrt{n_i} \end{matrix} \right\}$$

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[*] Some of the "thinkers" ruminations on matter models tend to cloud this appearancewise straightforward statement but we shall content ourselves with "leaving it where it is." "Things are precisely what they seem." Indignatius.

$$= -\frac{e}{\mu}\sqrt{\frac{hc^2}{\nu_i L^3}}\begin{Bmatrix}\sqrt{n_i+1} \\ \sqrt{n_i}\end{Bmatrix}(\mathbf{Q}_i)_{nm} \tag{3.63a}$$

Eq. (3.63a) then gives us the matrix elements of the first order — in *e* — interaction between the light field and the particle for the non-relativistic case. The result is appearancewise the same if we let $(\mathbf{Q}_i)_{nm}$ be given by:

$$(\mathbf{Q}_i)_{nm} = \frac{\mu}{c}\sum_s\int\bar{\psi}_{ns}(q)\,\exp\,[i(\mathbf{k}\cdot\mathbf{r})]\,\alpha^i\psi_{ms}(q)d\tau \tag{3.63b}$$

# CHAPTER 4

# STARK BROADENING

We turn now to a consideration of the broadening of spectral lines by the electric fields of the molecules which surround the emitting molecule.

## 4.1. PRELIMINARY CONSIDERATIONS

Before doing so, however, let us touch briefly on the Stark splitting of a spectral line by an external electric field. In Chapter 2 the magnetic quantum number $M$, which specifies the spatial orientation of the angular momentum vector, has arisen. It is qualitatively apparent and quantitatively confirmable that, in the absence of a field of force, $M$ has no effect on the level energies but, as we have seen, serves only as one of the level degeneracy parameters. There is, in fact, no reason that spatial orientation should affect level energy when no unique direction in space, which may be used to differentiate between various orientations, exists.

Let us now impose an electric field **E** on the gas, thus establishing the requisite unique axis in space. Suppose, for example, the gas to consist of linear dipole molecules. Classically then, the dipoles will be under the influence of a force which tends to align them with the electric field, the magnitude of this force being dependent on the angle between **E** and the dipole axis. Quantum mechanically, we may consider this angle as a discontinuous function of $M$. Hence in the case of a linear dipole rotator, the unique $J$ levels will be split into several levels for which the energy displacement from that of the original level will be dependent on the value of $M$. The spectral lines arising from transitions among levels split in this manner will, of course, also be split.

Stark[213] originally suggested applying this principle to the broadening of a spectral line, and later Holtsmark[65, 66] carried out the first analytical attack on the problem.*

Holtsmark felt that Fuchtbauer and Hoffmann's investigation,[43] for one, of the broadening of the *Cs* and *Na* lines by $N$ at high pressure left something to be desired in the Lorentz theory of pressure† broadening, since this experiment showed a much larger line width than was prophesied by that theory. Holtsmark also advanced the premise that " . . . according to the new conception of light emission as pertaining to quanta, the plausibility of the Lorentz explanation decreases, because it becomes entirely improbable that emission results from oscillating electrons."[66] These would appear to be valid reasons** for a new approach to the problem of pressure broadening, and Holtsmark's approach led to a Stark-effect explanation of this phenomenon.

We begin, with Holtsmark, by considering an emitting atom which is assigned the label 0. This emitter

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*In order to alleviate the anguish which this remark may cause some of the more diligent perusers of the literature, a word of clarification would appear to be in order. In several portions of the literature one finds References 65 and/or 66 attributed to Debye. This is simply not correct, but the probable reason for the error may be deduced. Debye wrote a two-page, semi-quantitative article[38] on the subject of Stark broadening which immediately preceded Holtsmark's article in the Physicalische Zeitschrift for 1919, and it would appear that this juxtaposition has considerably confused the reference situation ever since.

†This is a poor term which we shall replace by "foreign gas" or "self" wherever possible.

**The latter perhaps not too much so, since we could " . . . appeal to correspondences. . . " (See *infra*, Chap. 6.)

is surrounded by a large number $N_1$ of disturbing molecules (or ions) with assigned labels $1, \ldots, N_1$ in general $n$. Each of these surrounding molecules will contribute to an electric field at the location of 0, and this field will thus be the sum of these $N_1$ components. Were these perturbing atoms at rest, there would be a constant electric field at 0, and a Stark splitting of the emitted lines would result. The molecular motions change this situation, however. By virtue of these motions of the broadening molecules various molecular system configurations will exist from time to time, and these with varying probabilities. To each of these various configurations will correspond a field strength at the emitter which will occur with the probability of the molecular configuration. Quite obviously then, various Stark splittings may occur with these varying probabilities and, in a manner which will be more apparent after a study of the mathematics of the situation, a line broadening, instead of a simple line splitting, should result.

## 4.2. THE PROBABILITY OF AN ELECTRIC FIELD STRENGTH AT THE EMITTER

Holtsmark[65*] began with the assumption that the probability of a particular field strength $E_0$ is a function of $E_0$ and set out to determine this probability.

Let the components of the field strength at 0 due to the $n$-th perturber be $X_n$, $Y_n$, $Z_n$. The components of $E_0$ will then be given by:

$$X_0 = \sum_{1}^{N_1} X_n \; ; \quad Y_0 = \sum_{1}^{N_1} Y_n \; ; \quad Z_0 = \sum_{1}^{N_1} Z_n \tag{4.1}$$

We desire the probability that

$$\begin{aligned} &X_0 \text{ lies between } X_0 \text{ and } X_0 + dX_0 \\ &Y_0 \text{ lies between } Y_0 \text{ and } Y_0 + dY_0 \\ &Z_0 \text{ lies between } Z_0 \text{ and } Z_0 + dZ_0 \end{aligned} \tag{4.2}$$

Let the position of the $n$-th broadener be specified by the $m$ coordinates $x_{1n}, x_{2n}, \ldots, x_{mn}$. Then the $X_n$, $Y_n$, $Z_n$ are functions of these $m$ coordinates. It follows that the $X_0$, $Y_0$, $Z_0$ of Eq. (4.1) are functions of the $N_1m$ coordinates belonging to the $N_1$ surrounding atoms. An $N_1m$ dimensional space is next set up, and to each point in this space there now corresponds a stipulated field strength. These points will be distributed in space according to some probability law or, what amounts to the same thing, some density function.

The probability that $x_{1n}, x_{2n}, \ldots, x_{mn}$ lie in the range $dx_{1n}, dx_{2n} \ldots dx_{mn}$ may be expressed as:

$$\sigma_n dx_{1n} dx_{2n} \ldots dx_{mn} \tag{4.3}$$

where $\sigma_n$ is a function of the $x_{1n}, x_{2n}, \ldots x_{mn}$. It follows that the probability that all $N_1m$ coordinates lie in the range $dx_{11}\, dx_{21} \ldots dx_{mN_1}$ is:

$$\sigma_1 \ldots \sigma_{N_1}\, dx_{11} dx_{12} \ldots dx_{1m} dx_{21} \ldots dx_{N_1m} \tag{4.4}$$

It should be noted that this coordinate distribution establishes our electric field strength within a certain small range.

In certain portions of our $N_1m$ dimensional space the range requirements for the field components as given by Eq. (4.2) will be satisfied. On the other hand, it is apparent that these requirements will not be satisfied in certain portions of space. It follows from these considerations that, with Holtsmark, we must now obtain the probability of meeting the requirements of Eq. (4.2).

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[*] The editorial or typesetting errors which appear in this article are so numerous that the author feels they should be brought to the attention of those who may feel inclined to study the original. In almost all cases they can be picked up rather readily by considering the development which immediately precedes and follows them, but, nonetheless, they do create a certain aura of confusion without forewarning.

If Eq. (4.4) is integrated over those portions of space satisfying Eq. (4.2) and this result is divided by the integral of Eq. (4.4) over all space, the field strength probability function is obtained:

$$W\left(X_0, Y_0, Z_0\right) = \frac{1}{V_{N_1}} \underset{\substack{\text{all}\\ \text{space}}}{\int \ldots \int} \sigma_1 \sigma_2 \ldots \sigma_{N_1}\, dx_{11} \ldots dx_{mN_1} \tag{4.5a}$$

where:

$$V_{N_1} = \int \ldots \int \sigma_1 \sigma_2 \ldots \sigma_{N_1}\, dx_{11} \ldots dx_{mN_1} \tag{4.5b}$$

$W(X_0, Y_0, Z_0)$ may be defined by interpreting $W(X_0, Y_0, Z_0)\, dX_0 dY_0 dZ_0$ as the probability that $X_0, Y_0, Z_0$ satisfy Eq. (4.2).

We might consider Eq. (4.5a) more specifically since it is a rather important one in this development. The integrand provides us with the probability that a volume element which satisfies Eq. (4.2) will be occupied by a system point — a point which specifies a certain configuration of the atomic system of perturbers. $V_{N_1}$ serves to normalize this probability, the need for which normalization is apparent.

The evaluation of Eq. (4.5a) now becomes of major importance. Holtsmark used what might be considered a modified form of the method developed by Markoff[211] for this evaluation.

The first step is the multiplication of Eq. (4.5a) by the proper Dirichlet factors in order to transform this integral into an integral over all space. The Dirichlet factors for this transformation are:

$$H(X) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\sin \alpha \xi}{\xi} e^{i \Upsilon \xi} d\xi \tag{4.6a}$$

$$H(Y) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\sin \beta \eta}{\eta} e^{i \epsilon \eta} d\eta \tag{4.6b}$$

$$H(Z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\sin \gamma \zeta}{\zeta} e^{i \chi \zeta} d\zeta \tag{4.6c}$$

where:

$$\alpha = \tfrac{1}{2} dX_0 \ ; \ \Upsilon = \sum_{1}^{N_1} X_n \left(x_{1n} \ldots x_{mn}\right) - X_0 \tag{4.7a}$$

$$\beta = \tfrac{1}{2} dY_0 \ ; \ \epsilon = \sum_{1}^{N_1} Y_n \left(x_{1n} \ldots x_{mn}\right) - Y_0 \tag{4.7b}$$

$$\gamma = \tfrac{1}{2} dZ_0 \ ; \ \chi = \sum_{1}^{N_1} Z_n \left(x_{1n} \ldots x_{mn}\right) - Z_0 \tag{4.7c}$$

Certain relations among the factors in Eqs. (4.6) may be written as follows:

$$-\alpha < \Upsilon < \alpha \tag{4.8a}$$

$$-\beta < \epsilon < \beta \tag{4.8b}$$

$$-\gamma < \chi < \gamma \tag{4.8c}$$

If Eq. (4.8a) is valid, Eq. (4.6a) is equal to one. If Eq. (4.8a) is not valid, Eq. (4.6a) is zero. A consideration of Eq. (4.7a) will show that this is simply another way of stating Eq. (4.2). In like manner the validity of Eqs. (4.8b) and (4.8c) control the values of Eqs. (4.6b) and (4.6c) according to Eqs. (4.7b) and (4.7c).

By Eqs. (4.7) $\alpha$, $\beta$, and $\gamma$ are infinitely small so that:

$$\frac{\sin \alpha\xi}{\xi} = \alpha \; ; \qquad \frac{\sin \beta\eta}{\eta} = \beta \; ; \qquad \frac{\sin \gamma\zeta}{\zeta} = \gamma \tag{4.9}$$

If Eqs. (4.7) and (4.9) are substituted into Eqs. (4.6) the result is:

$$H(X) = \frac{1}{2\pi} dX_0 \int_{-\infty}^{+\infty} e^{i\xi(\sum_1^{N_1} X_n - X_0)} d\xi \tag{4.10a}$$

$$H(Y) = \frac{1}{2\pi} dY_0 \int_{-\infty}^{+\infty} e^{i\eta(\sum_1^{N_1} Y_n - Y_0)} d\eta \tag{4.10b}$$

$$H(Z) = \frac{1}{2\pi} dZ_0 \int_{-\infty}^{+\infty} e^{i\zeta(\sum_1^{N_1} Z_n - Z_0)} d\zeta \tag{4.10c}$$

Now multiply Eq. (4.5a) by Eqs. (4.10):

$$W(X_0, Y_0, Z_0)dX_0dY_0dZ_0 = \frac{1}{8\pi^3} dX_0dY_0dZ_0 \iiint_{-\infty}^{+\infty} d\xi d\eta d\zeta$$

$$\cdot\, e^{i(\xi X_0 + \eta Y_0 + \zeta Z_0)} \frac{1}{V_{N_1}} \underset{\substack{\text{all}\\ \text{space}}}{\int \cdots \int} \sigma_1 \ldots \sigma_{N_1} e^{i(\xi \Sigma X_n + \eta \Sigma Y_n + \zeta \Sigma Z_n)} dx_{11} \ldots dx_{mN_1} \tag{4.11}$$

The $X_n$, $Y_n$, $Z_n$ are functions of the $x_{1n} \ldots x_{mn}$ while the $X_0$, $Y_0$, $Z_0$ are constants in all the integrations. It should be stipulated now that all the broadening molecules are considered the same, that is, the Stark broadening is not treated for the case where, for molecules, more than one compound (element) acts as a broadening agent. In this event, identical electric field strength components $X_n$, $Y_n$, $Z_n$ will be the same functions of $x_{1n}, x_{2n}, \ldots, x_{mn}$. Let us briefly consider the reason for this. Suppose the broadening molecules may be considered as quadrapoles insofar as the field which they produce is concerned. Then, since the field produced will be a function of the quadrapole moment and the coordinates of the molecule, and since the quadrapole moments for like molecules will be the same, the field strength components will differ only for differing $x_{1n}, x_{2n}, \ldots x_{mn}$. It also follows from these considerations that for identical $X_n$, $Y_n$, $Z_n$, $\sigma_1, \sigma_2, \ldots, \sigma_{N_1}$ will all be equal.

These equalities among the coordinates and their probability functions lead to a very fortunate simplification of Eq. (4.11). The inner integral can be broken up into the product of $N_1$ identical integrals, each of which is integrated only over the $m$ coordinates of a single molecule. The result is:

$$J^{N_1} = \frac{1}{V^{N_1}} \Bigg[ \underset{\substack{\text{all}\\ \text{space}}}{\int \cdots \int} e^{i(\xi X + \eta Y + \zeta Z)} \sigma dx_1 dx_2 \ldots dx_m \Bigg]^{N_1} \tag{4.12}$$

In Eq. (4.12) the principle enumerated in the preceding paragraph has been applied to $V_{N_1}$. Thus Eq. (4.11) becomes:

$$W(X_0, Y_0, Z_0) = \frac{1}{8\pi^3} \int_{-\infty}^{+\infty} \cdots \int d\xi d\eta d\zeta e^{-i(\xi X_0 + \eta Y_0 + \zeta Z_0)} \frac{1}{V^{N_1}} \Bigg[ \int_{\text{all space}} \cdots \int e^{i(X\xi + Y\eta + Z\zeta)} \sigma dx_1 \ldots dx_m \Bigg]^{N_1} \tag{4.13}$$

It is at this stage of the development that Holtsmark departed from the Markoff method and proceeded with an integral evaluation scheme which he attributed to Debye.

## 4.3. THE INTRODUCTION OF SPECIFIC FIELD PRODUCERS

Let us form the dot product $\mathbf{s} \cdot \mathbf{E}$ where:

$$\mathbf{E} = \mathbf{i}X + \mathbf{j}Y + \mathbf{k}Z \tag{4.14a}$$

$$\mathbf{s} = \mathbf{i}\xi + \mathbf{j}\eta + \mathbf{k}\zeta \tag{4.14b}$$

It might be mentioned that $\xi, \eta, \zeta$ will be constants for the integration over $x_1, \ldots, x_m$.

Eq. (4.12) may now be transformed into spherical polar coordinates and integrated after an expression for E has been obtained.

A molecule we here consider as something or other which is made up of a number of charges, $e_s$. Let us establish a moving reference frame at the center of the molecule and determine the potential which would exist at the point $x, y, z$ due to these charges. If $\mathbf{r}$ is the position vector of the point $x, y, z$, $\mathbf{r}_s$ is the positions vector of the $s$-th charge, and $\mathbf{R}_s$ the sum of these two vectors, then the fact that

$$\begin{aligned} R_s^2 &= (x - x_s)^2 + (y - y_s)^2 + (z - z_s)^2 \\ &= r^2\left[1 + \left(\frac{r^2}{r}\right)^2 - \frac{2(r - r_s)}{r^2} + \ldots\right] \end{aligned} \tag{4.15}$$

yields the potential:

$$\begin{aligned} \varphi = \sum \frac{e_s}{R_s} &= \frac{\Sigma e_s}{r} - \frac{(\mathbf{r} \cdot \Sigma e_s \mathbf{r}_s)}{r^3} - \frac{1}{2r^3}\left\{\Sigma e_s r_s^2 - 3\Sigma\left[e_s \frac{(\mathbf{r} \cdot \mathbf{r}_s)^2}{r^2}\right]\right\} + \ldots \\ &= \frac{\Sigma e_s}{r} - \frac{1}{r^2}\left[\frac{\mathbf{r}}{r} \cdot \Sigma e_s \mathbf{r}_s\right] - \frac{1}{2r^3}\left\{\Sigma e_s x_s^2\left(1 - \frac{3x^2}{r^2}\right) + \Sigma e_s y_s^2\left(1 - \frac{3y^2}{r^2}\right)\right. \\ &\quad + \Sigma e_s z_s^2\left(1 - \frac{3z^2}{r^2}\right) - \frac{6\Sigma e_s x_s y_s xy}{r^2} - \frac{6\Sigma e_s y_s z_s yz}{r^2} \\ &\quad \left. - \frac{6\Sigma e_s z_s x_s zx}{r^2}\right\} - \ldots \end{aligned} \tag{4.16}$$

in which the final form of the potential is the most informative. The rapid convergence of the final series in Eq. (4.16) is generally considered as assured by the assumption $r \gg r_s$. When one considers the small portion of space encompassed by the atom, this assumption appears reasonably valid. It is true, however, that the question as to what transpires when the broadener closely approaches the emitter is a rather embarrassing one.

Holtsmark deals with the three cases (a) none of the terms disappears (b) the first term disappears (c) the first and second terms disappear. The rapid convergence of the series tells us that we may neglect all terms but the first in case (a) and all but the second in case (b). Case (c) would appear to be self-explanatory with respect to ignoration. Thus, these three cases yield the following field producers:

1. Ions
2. Dipoles
3. Quadrupoles

An ion may be defined as a charged molecule. A dipole may be defined as a system of charges which gives rise to the second term in Eq. (4.16) but not to the first. A quadrupole is defined by the third term in this equation.

For these three cases we must now specify $\mathbf{s} \cdot \mathbf{E}$ where $\mathbf{E}$ is the electric field strength and $\mathbf{s}$ is the position vector.

For the ion we have:

$$\varphi = \frac{\Sigma e_s}{r} = \frac{\epsilon}{r} \longleftrightarrow \mathbf{E} = \nabla\varphi = -\frac{\epsilon}{r^3}\mathbf{r}$$

which gives:

$$\mathbf{s} \cdot \mathbf{E} = -\frac{\epsilon}{r^3}(\mathbf{r} \cdot \mathbf{s}) = -\frac{\epsilon}{r^2} s \cos\vartheta \tag{4.17}$$

In Eq. (4.17) $s = |\mathbf{s}|$, and $\vartheta$ is the angle between $\mathbf{r}$ and $\mathbf{s}$. The dipole potential is

$$\varphi = \frac{\mathbf{r} \cdot \Sigma e_s \mathbf{r}_s}{r^3} = \frac{\mathbf{r} \cdot \underline{\mu}}{r^3} \tag{4.18}$$

where $\underline{\mu}$ is the dipole moment, a definition of convenience. Hence:

$$\mathbf{E} = \nabla\varphi = \nabla\frac{\mathbf{r} \cdot \underline{\mu}}{r^3} = \frac{1}{r^3}\nabla(\mathbf{r} \cdot \underline{\mu}) - \frac{3}{r^5}\mathbf{r}(\mathbf{r} \cdot \underline{\mu}) = \frac{\underline{\mu}}{r^3} - \frac{3\mathbf{r}(\mathbf{r} \cdot \underline{\mu})}{r^5} \tag{4.19}$$

So that:

$$\mathbf{s} \cdot \mathbf{E} = \frac{1}{r^2}(\mathbf{s} \cdot \underline{\mu}) - \frac{3}{r^5}(\mathbf{r} \cdot \underline{\mu})(\mathbf{s} \cdot \mathbf{r}) \tag{4.20}$$

In Eq. (4.20) we may write:

$$\mathbf{s} \cdot \underline{\mu} = s\mu \cos\alpha; \quad \mathbf{r} \cdot \underline{\mu} = r\mu \cos\beta; \quad \mathbf{s} \cdot \mathbf{r} = sr \cos\gamma$$

Now consider Fig. (4.1).

Spherical coordinates may be introduced as follows. $\mathbf{s}$ is taken as the polar axis. $\alpha$ and $\gamma$ are then the polar angles $\vartheta_1$ and $\vartheta_2$ respectively, and the azimuth angles $\varphi_1$ and $\varphi_2$ are as indicated. $\beta$, the angle between $\underline{\mu}$ and $\mathbf{r}$, is given by:

$$\cos\beta = \cos\vartheta_1 \cos\vartheta_2 + \sin\vartheta_1 \sin\vartheta_2 \cos(\varphi_1 - \varphi_2) \tag{4.21}$$

Substitution of Eq. (4.21) into Eq. (4.20) yields:

$$\mathbf{s} \cdot \mathbf{E} = \frac{1}{r^3} s\mu \left[\cos\vartheta_1 - 3\cos\vartheta_2\left(\cos\vartheta_1 \cos\vartheta_2 + \sin\vartheta_1 \sin\vartheta_2 \cos(\varphi_1 - \varphi_2)\right)\right] \tag{4.22}$$

Finally, the quadrupole potential must be considered. This potential — the term in braces in Eq. (4.16) — may be simplified by a rotation of the coordinate system which has been attached to the molecule. The quadrupole moment is analogous to the rotary inertia tensor, and we may diagonalise the matrix of this moment by a rotation of the coordinate axes to which it is referred, thus eliminating terms of the type $\Sigma e_s x_s y_s$. We can assume this operation to have been carried out so that only the diagonal constants of the quadrupole remain.

$$\Theta_1 = \Sigma e_s x_s^2; \quad \Theta_2 = \Sigma e_s y_s^2; \quad \Theta_3 = \Sigma e_s z_s^2 \tag{4.23}$$

If an atom is symmetric about some axis we obtain an analogy to the symmetric rotator case of the moments of inertia. Holtsmark assumed this simplification so that $\Theta_1 = \Theta_2$. Hence:

$$\varphi = -\frac{1}{2r^3}\left[\Theta_2\left(1 - \frac{3x^2}{r^2}\right) + \Theta_2\left(1 - \frac{3y^2}{r^2}\right) + \Theta_3\left(1 - \frac{3z^2}{r^2}\right)\right]$$

$$= \frac{1}{2r^5}(\Theta_3 - \Theta_2)(-x^2 - y^2 + 2z^2) = \frac{A\beta^2}{2r^5} \tag{4.24}$$

where:

$$A = \Theta_3 - \Theta_2; \quad \beta^2 = -x^2 - y^2 + 2z^2$$

From Eq. (4.24)

$$E_x = \frac{\partial\varphi}{\partial x} = -\frac{Ax}{2r^5}\left(2 - 5\frac{\beta^2}{r^2}\right)$$

$$E_y = \frac{\partial\varphi}{\partial y} = -\frac{Ay}{2r^5}\left(2 - 5\frac{\beta^2}{r^2}\right); \quad E_z = \frac{\partial\varphi}{\partial z} = \frac{Az}{r^5}\left(2 - 5\frac{\beta^2}{r^2}\right) \tag{4.25}$$

Again spherical polar coordinates are adopted as shown in Fig. (4.2).

$c$ is the molecular figure axis. It follows that:

$$\begin{aligned} s_x &= s \sin\vartheta_1 \cos\varphi_1 & x &= r \sin\vartheta_2 \cos\varphi_2 \\ s_y &= s \sin\vartheta_1 \sin\varphi_1 & y &= r \sin\vartheta_2 \sin\varphi_2 \\ s_z &= s \cos\vartheta_1 & z &= r \cos\alpha_2 \end{aligned} \tag{4.26}$$

Utilizing Eq. (4.26), we obtain:

$$\mathbf{s}\cdot\mathbf{E} = s_xE_x + s_yE_y + s_zE_z = \frac{A_z}{2r^4}\left\{2\cos\vartheta_1\cos\vartheta_2 - \sin\vartheta_1\sin\vartheta_2\cos(\varphi_1 - \varphi_2)\right\}(7 - 15\cos^2\vartheta_2) \tag{4.27}$$

A consideration of Eqs. (4.17), (4.22), and (4.27) indicates that these three cases may all be represented by:

$$\mathbf{s}\cdot\mathbf{E} = \frac{s}{r^p}w_p \tag{4.28}$$

where $w_p$ is a function of the angles and $p$ may take on the values 2, 3, or 4.

Eq. (4.28) may now be substituted into Eq. (4.12) to obtain:

$$J = \frac{1}{V}\int \underset{\substack{\text{all}\\ \text{space}}}{\cdots} \int e^{i\frac{sw_p}{r^p}}\,\sigma\,dx_1dx_2\ldots dx_m \tag{4.29}$$

The transformation of the coordinates $x_1, \ldots, x_m$ to the coordinates $r_1, \vartheta_1, \vartheta_2, \varphi_1, \varphi_2$ is in order. After the transformation all positions are referred to the center of the molecule and, further, all directions of a vector from this center are equally probable. Thus, since the molecular distribution is a random one:

$$\sigma dx_1dx_2\ldots dx_m = r^2dr\sin\vartheta_1d\vartheta_1\sin\vartheta_2d\vartheta_2d\varphi_1d\varphi_2 \tag{4.30}$$

The limits of integration are taken as $\vartheta$ from 0 to $\pi$, $\varphi$ from 0 to $2\pi$, and $r$ from 0 to $R$, thus enclosing the gas in a sphere of radius $R$.

It follows that:

$$V = \int\ldots\int r^2dr\sin\vartheta_1d\vartheta_1\sin\vartheta_2d\vartheta_2d\varphi_1d\varphi_2 = \frac{16\pi^2}{3}R^3 \tag{4.31}$$

Now the transformation to solid angles is made by utilizing the relations:

$$d\Omega = \sin\vartheta_1d\vartheta_1d\varphi_1\ ; \quad d\Omega' = \sin\vartheta_2d\vartheta_2d\varphi_2 \tag{4.32}$$

so that Eq. (4.29) becomes:

$$J = \frac{1}{V} \int_{\Omega}\int_{\Omega'} d\Omega d\Omega' \int_0^R r^2 e^{i\frac{sw_p}{r^p}} dr \tag{4.33}$$

If we let $u = \frac{sw_p}{r^p}$ then $\left(\frac{sw_p}{p}\right)^{3/p} du = r^2dr$ and Eq. (4.33) becomes:

$$J = \frac{3R^3}{16\pi^2} \int_{\Omega}\int_{\Omega'} d\Omega d\Omega' \left(\frac{sw_p}{p}\right)^{3/p} \int_{\alpha}^{\infty} e^{iu} u^{-\frac{3+p}{p}} du \tag{4.34}$$

where $\alpha = \frac{sw_p}{R^p}$.

Eq. (4.34) cannot be carried further for the general case, but rather, it is necessary to consider it separately for the ion, the dipole, and the quadrupole. These three cases will now be considered in this order.

## 4.4. THE SPECIAL CASE OF THE ION

In the case of the ion $p = 2$, and the integral in $u$ may be successively integrated by parts to obtain:

$$\int_{\alpha}^{\infty} e^{iu} u^{-5/2} du = \frac{2}{3} \alpha^{-3/2} e^{iu} + \frac{4}{3} i\alpha^{-1/2} + \frac{4}{3} i^2 \int_{\alpha}^{\infty} e^{iu} u^{-1/2} du \tag{4.35}$$

The integral on the right of Eq. (4.35) may be evaluated as:

$$\begin{aligned}\int_{\alpha}^{\infty} e^{iu} u^{-1/2} du &= \int_0^{\infty} e^{iu} u^{-1/2} du - \int_0^{\alpha} e^{iu} u^{-1/2} du \\ &= e^{i\frac{\pi}{4}} \Gamma\left(\tfrac{1}{2}\right) - \int_0^{\alpha} \left(1 + iu + \tfrac{1}{2} i^2u^2 + \ldots\right) u^{-1/2} du \\ &= \sqrt{\pi}\, e^{i\frac{\pi}{4}} - 2\alpha^{1/2} - \frac{2}{3} \alpha^{3/2} - \frac{2}{5} \cdot \frac{1}{2} i^2 \alpha^{5/2} \ldots\end{aligned} \tag{4.36*}$$

This series for $\alpha$ appears reasonably well justified in consideration of the small value of $\alpha$. A straightforward substitution of Eqs. (4.35) and (4.36) into Eq. (4.34) yields:

$$\begin{aligned} J = \frac{3}{16\pi^3 R^3} \int d\Omega d\Omega' \frac{\alpha^{3/2}}{2} R^3 \Bigg[ &\frac{2}{3} \alpha^{-3/2} e^{i\alpha} + \frac{4}{3} i\alpha^{1/2} e^{i\alpha} \\ &+ \frac{4}{3} i^2 \left(\sqrt{\pi} e^{i\frac{\pi}{4}} - 2\alpha^{1/2} - \frac{2}{3} \alpha^{3/2} - \ldots\right)\Bigg] \end{aligned} \tag{4.37}$$

All terms in Eq. (4.37) with the exception of the first term in the bracket and the first term in the parenthesis are now dropped as small so that, after developing $e^{i\alpha}$ as a power series, one obtains:

$$J = \frac{1}{16\pi^2} \int\int d\Omega d\Omega' \left[ 1 + i\alpha + 2i^2 \sqrt{\pi}\, e^{i\frac{\pi}{4}} \alpha^{3/2} + \ldots \right] \tag{4.38}$$

A rather appalling number of terms have been thrown out in the last few operations, but the facts that (a) one is forced to pursue this course in order to solve the problem, and (b) the development has been predicated on large $R$, do tend to justify the ignoration.

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*By definition $\Gamma(s + 1) = \int_0^{\infty} u^s e^{-u} du = s!$

$w_2$ is a cosine function. Thus, $\alpha$, which is a function of $w_2$ integrated over $\Omega$ and $\Omega'$ is zero. Eq. (4.38) then becomes on partial integration:

$$J = 1 + 2i^2 \sqrt{\pi}\, e^{i\frac{\pi}{4}} \frac{1}{16\pi^2} \int\int d\Omega d\Omega' \alpha^{3/2} \tag{4.39}$$

If we set $\bar{w}_2 = \frac{1}{16\pi^2} \int\int d\Omega d\Omega' w_2{}^{3/2}$ Eq. (4.39) becomes:

$$J = 1 - 2\sqrt{\pi}\, e^{i\frac{\pi}{4}}\, \bar{w}_2 s^{3/2} \frac{4\pi}{3} \frac{N}{N_1} \tag{4.40}$$

$N_1$ is obviously a large number. Then since $\left(1 - \frac{X}{N_1}\right)^{N_1} \doteq e^{-X}$, we may write:

$$J^{N_1} = \exp\left(-\sqrt{\pi}\, e^{i\frac{\pi}{4}} s^{3/2} \frac{2}{3}\, 4\pi N \bar{w}_2\right) \tag{4.41}$$

Also,

$$\bar{w}_2 = \frac{1}{16\pi^2} \int\int\int \epsilon^{3/2} \cos^{3/2}\vartheta_1 \sin \vartheta_1 d\vartheta_1 d\varphi_1 d\Omega = \epsilon^{3/2}\, \tfrac{1}{2} \int_0^{\pi} \cos^{3/2}\vartheta_1 \sin \vartheta_1 d\vartheta_1$$

$$+ \epsilon^{3/2}\, \tfrac{1}{2} \int_{\pi/2}^{\pi} \cos^{3/2}\vartheta_1 \sin \vartheta_1 d\vartheta_1 = \epsilon^{3/2} \frac{1}{5} (1 - i) \tag{4.42}$$

So that, when it is recalled that $e^{i\frac{\pi}{4}} = \frac{i+1}{2}$, Eq. (4.31) becomes:

$$J^{N_1} = \exp\left(-\frac{8\sqrt{2\pi}}{15} \pi N s^{3/2} \epsilon^{3/2}\right) = e^{-4.21 N s^{3/2} \epsilon^{3/2}} \tag{4.43}$$

## 4.5. THE SPECIAL CASE OF THE DIPOLE

We turn now to the calculation of $J^{N_1}$ for the dipole. The integral in $u$ in Eq. (4.34) is:

$$\int_{\alpha}^{\infty} e^{iu} u^{-2} du = \alpha e^{i\alpha} + i \int_{\alpha}^{\infty} e^{iu} u^{-1} du = \alpha e^{i\alpha} + i\left[\int_0^{\infty} e^{iu} u^{-1} du - \int_0^{\alpha} e^{iu} u^{-1} du\right] \tag{4.44}$$

where here $\alpha = \frac{s w_3 \mu}{R^3}$

We replace $-1$ in Eq. (4.44) by $-1 + \Lambda$ where $\Lambda$ is very small and may be set equal to zero in the limit. This gives:

$$f(\alpha,\Lambda) = \int_0^{\infty} e^{iu} u^{-1+\Lambda} du - \int_0^{\alpha} e^{iu} u^{-1+\Lambda} du$$

$$= \frac{\Gamma(\Lambda)}{i^{\Lambda}} - \int_0^{\alpha} u^{-1+\Lambda} \left[1 + iu + \tfrac{1}{2} i^2 u^2 + \ldots\right] du$$

$$= \frac{\Gamma(\Lambda)}{i^{\Lambda}} - \left[\frac{\alpha^{\Lambda}}{\Lambda} + i \frac{\alpha^{1+\Lambda}}{1+\Lambda} + \frac{i^2}{2} \frac{\alpha^{2+\Lambda}}{2+\Lambda} + \ldots\right] \tag{4.45}$$

By MacLaurin expansion:

$$\frac{\alpha^{\Lambda}}{\Lambda} = \frac{1 + \Lambda \log \alpha + \ldots}{\Lambda} = \frac{1}{\Lambda} + \log \alpha + \ldots \tag{4.46}$$

From the relations:

$$\Gamma(\Lambda)\Gamma(1 - \Lambda) = \frac{\pi}{\sin \Lambda\pi}$$

$$\Gamma(1 - \Lambda) = \Gamma(1) - \Lambda\Gamma'(1)$$

$$i^{-\Lambda} = i^{-i\frac{\pi}{2}\Lambda} = \left(1 - i\frac{\pi}{2}\Lambda\right)$$

one obtains:

$$\frac{\Gamma(\Lambda)}{i^{\Lambda}} = \frac{\pi}{\sin \pi\Lambda} \frac{\left(1 - i\frac{\pi}{2}\Lambda\right)}{[\Gamma(1) - \Lambda\Gamma'(1)]} + \frac{1}{\Lambda}\left[\Gamma'(1) - \frac{\pi}{2} i\right] \tag{4.47}$$

Substitute Eqs. (4.46) and (4.47) into Eq. (4.45) and pass to the limit $\Lambda = 0$ to obtain:

$$f(\alpha,\Lambda) = \Gamma'(1) - i\frac{\pi}{2} - \log \alpha - i\,\alpha - \frac{i^2}{2}\frac{\alpha^2}{2} - \ldots \tag{4.48}$$

Eq. (4.48) in conjunction with Eq. (4.45) yields:

$$J = \frac{1}{V}\iint d\Omega d\Omega' \frac{sw_3\mu}{3}\left[\alpha^{-1}e^{i\alpha} + i\left(\Gamma'(1) - i\frac{\pi}{2} - \log \alpha - i\alpha - \frac{i^2}{2}\frac{\alpha^2}{2}\ldots\right)\right] \tag{4.49}$$

Develop $e^{i\alpha}$ in a power series; insert the value for $V$ and for $\alpha R^3 = \mu s w_3$ and utilize the fact that $\iint \alpha \, d\Omega d\Omega' = 0$ to rewrite Eq. (4.49) as follows:

$$J = 1 - i\frac{3R^3}{16\pi^2 R^3 3}\iint d\Omega d\Omega' \left[\alpha \log \alpha + (i + \tfrac{1}{2})\,\alpha^2 + \ldots\right] \tag{4.50}$$

The expression for $\alpha$ is substituted into Eq. (4.50) and all terms of higher order than $\alpha \log \alpha$ are dropped as small.

$$J = 1 - \frac{i}{16\pi^2}\iint \frac{\mu s w_3}{R^3} 3 \left(\log w_3 + \log \frac{\mu s}{R^3}\right) d\Omega d\Omega' \tag{4.51}$$

In Eq. (4.51) $\log \frac{\mu s}{R^3}$ will be a constant for the integration so that this term, due to the periodicity of $w_3$, will be zero after integration as has occurred in the previous development. Again the number of atoms per unit of volume will be $N$ so that:

$$N_1 = \frac{4}{3}\pi R^3 N \tag{4.52}$$

Also let:

$$\bar{w}_3 = \frac{1}{16\pi^2}\iint w_3 \log w_3 \, d\Omega d\Omega' \tag{4.53}$$

Using Eqs. (4.52) and (4.53) in Eq. (4.51) and applying the approximation $\left(1 - \frac{x}{N_1}\right)^{N_1} = e^{-x}$ we obtain:

$$J^{N_1} = e^{-\frac{4}{3}\pi\mu s i N \bar{w}_3} \tag{4.54}$$

where $\bar{w}_3$ is defined by Eqs. (4.53) and (4.22). Holtsmark evaluated Eq. (4.53) graphically and obtained $\bar{w}_3 = -0.345\pi i$. Thus Eq. (4.54) becomes:

$$J^{N_1} = e^{-\frac{4}{3}\pi^{3/2}(0.345)\mu N} = e^{-4.54s\mu N} \tag{4.55}$$

## 4.6. THE SPECIAL CASE OF THE QUADRUPOLE

Finally, $J^{N_1}$ for the quadrupole where $p = 4$ must be evaluated. For the quadrupole:

$$J = \frac{1}{v}\int\int \frac{(Asw_4)^{3/4}}{2^{3/4}\cdot 4}\int_{\alpha}^{\infty} e^{iu}u^{-7/4}\,du\; d\Omega d\Omega' \tag{4.56}$$

The integral in $u$ is evaluated in the same manner as was done for the ion.

$$\int_{\alpha}^{\infty} e^{iu}u^{-7/4}du = \frac{4}{3}\left[e^{i\alpha}\alpha^{-3/4} + ie^{i\frac{\pi}{3}}\Gamma(\tfrac{1}{4}) - 4i\alpha^{1/4} - \frac{4i^2}{5}\alpha^{5/4} - \ldots\right] \tag{4.57}$$

where $\alpha = \dfrac{Asw_4}{2R_0^4}$

Hence:

$$J = \frac{1}{6\pi^2}\int\int d\Omega d\Omega'\left[1 + e^{i\frac{5}{8}\pi}\Gamma(\tfrac{1}{4})\left(\frac{Asw_4}{2}\right)^{3/4}\frac{1}{R_0^3}\right] \tag{4.58}$$

In Eq. (4.58) higher order terms have been dropped as in the ion and dipole cases. We then obtain:

$$J^{N_1} = \exp\left[e^{i\frac{5}{8}\pi}\Gamma(\tfrac{1}{4})\frac{4\pi}{3}N\left(\frac{As}{2}\right)^{3/4}\bar{w}_4{}^{3/4}\right] \tag{4.59}$$

where, as usual:

$$\bar{w}_4{}^{3/4} = \frac{1}{16\pi^2}\int\int d\Omega d\Omega' w_4{}^{3/4}$$

Utilizing Eq. (4.27), Holtsmark graphically evaluated $\bar{w}_4{}^{3/4}$ to obtain $\bar{w}_4{}^{3/4} = .70\ (1 + i^{3/2})$.*

Hence:

$$J^{N_1} = \exp\left[e^{i\frac{5}{8}\pi}\Gamma(\tfrac{1}{4})\frac{4\pi}{3}.70\left(1 + e^{i\frac{3}{4}\pi}\right)N\left(\frac{As}{2}\right)^{3/4}\right]$$

Note that:

$$e^{i\frac{5}{8}\pi}(1 + e^{i\frac{3}{4}\pi}) = e^{i\frac{5}{8}\pi} + e^{i\frac{5}{8}\pi}\cdot e^{i2\pi} = e^{i\frac{5}{8}\pi} + e^{-i\frac{5}{8}\pi} = 2\cos\tfrac{5\pi}{8} = -0.7665$$

$$\Gamma(\tfrac{1}{4}) = 3.6256$$

Hence:

$$J^{N_1} = e^{-4.87N(As)^{\frac{3}{4}}} \tag{4.60}$$

Eqs. (4.43), (4.55), and (4.60) thus provide $J^{N_1}$ for the three cases under consideration. We may now turn our attention to the evaluation of $W(X_0Y_0Z_0)$ as given by Eq. (4.13).

$$W(X_0Y_0Z_0) = \frac{1}{8\pi^3}\int\int\int_{-\infty}^{+\infty} d\xi d\eta d\zeta\, e^{-i(\xi X_0+\eta Y_0+\zeta Z_0)}J^{N_1} \tag{4.61}$$

---

*In his first paper on the subject[66] Holtsmark gave the value $1.66\,(1 + i^{3/2})$. He later reported[67] an error as a result of this value which indicates that the correct value of $w_4{}^{3/4}$ should be as given above.

### 4.7. THE FIELD PROBABILITY FUNCTION FOR THE THREE SPECIAL CASES

Holtsmark chose the dipole case for the first evaluation, since, in Eq. (4.55) $s$ has the exponent one. For the dipole then:

$$W(X_0Y_0Z_0) = \frac{1}{8\pi^3}\iiint_{-\infty}^{+\infty} d\xi d\eta d\zeta e^{-i(\xi X_0+\eta Y_0+\zeta Z_0)}e^{-c_3 s} \tag{4.62}$$

where: $c_3 = 4.54\,\mu N$.

In Eq. (4.62) $X_0Y_0Z_0$ can be taken as the components of a vector $\mathbf{E}_0$ which is independent of $\mathbf{s}$, the vector with components $\xi\eta\zeta$. Then the exponent in Eq. (4.62) is obviously the dot product $\mathbf{E}_0 \cdot \mathbf{s} = E_0 s \cos\vartheta$ where here $\vartheta$ is the angle between $\mathbf{E}_0$ and $\mathbf{s}$. Now transform from the rectangular coordinates $\xi\eta\zeta$ to the spherical polar coordinates $s\vartheta\varphi$.

$$d\xi d\eta d\vartheta = s^2 \sin\vartheta d\vartheta d\varphi ds$$

Eq. (5.57) thus becomes:

$$W(X_0Y_0Z_0) = \frac{1}{8\pi^3}\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} \sin\vartheta d\vartheta d\varphi s^2 ds e^{-iE_0 s\cos\vartheta}e^{-c_3 s} \tag{4.63}$$

Integrate over $\vartheta$ and $\varphi$ to obtain:

$$W(X_0Y_0Z_0) = \frac{1}{4\pi^2}\int_0^{\infty} s^2 ds e^{-c_3 s}\frac{2}{E_0 s}\sin(E_0 s) \tag{4.64}$$

We write $\sin(E_0 s)$ as an exponential and take the imaginary part.

$$W(X_0Y_0Z_0) = \frac{1}{2\pi^2}\mathfrak{J}\left\{\int_0^{\infty}\frac{s}{E_0}e^{(-c_3+E_0 i)s}ds\right\} \tag{4.65}$$

Let $-t = (-c_3 + E_0 i)$ so that the integral in Eq. (4.65) becomes a gamma or factorial function.

$$W(X_0Y_0Z_0) = \frac{1}{2\pi^2}\mathfrak{J}\left\{\left[\frac{\Gamma(2)}{(-c_3+E_0 i)^2 E_0}\right]\right\} = \frac{1}{\pi^2}\frac{c_3}{(c_3^2+E_0^2)^2} \tag{4.66}$$

Eq. (4.66) gives us for the dipole the field strength probability function which we have been seeking. A "Normalfeldstarke" may be defined as:

$$E_n = c_3 = 4.54\mu N \tag{4.67}$$

Let $\beta$ give the relation between this "Normalfeldstarke" and the actual field strength.

$$\beta = \frac{E_0}{E_n} \tag{4.68}$$

Now we replace the volume element $dX_0dY_0dZ_0$ by $4\pi E_0^2dE_0$. From Eq. (4.66):

$$W(X_0Y_0Z_0) = \frac{1}{\pi^2}\frac{1}{\left(1+\frac{E_0^2}{c_3^2}\right)^2}\frac{1}{c_3^3} = \frac{1}{\pi^2}\frac{1}{(1+\beta^2)^2}\frac{1}{c_3^3} \tag{4.69}$$

Hence:

$$\begin{aligned} W(E_0)dE_0 &= 4\pi E_0^2 W(X_0Y_0Z_0)dE_0 \\ &= \frac{4}{\pi}\frac{1}{(1+\beta^2)^2}\frac{E_0^2}{c_3^3}dE_0 = \frac{4}{\pi}\frac{\beta^2 d\beta}{(1+\beta^2)^2} \end{aligned} \tag{4.70a}$$

Fig. (4.3) furnishes a plot of $W(E_0)$ vs. $\beta$ as given by Eq. (4.70a). After we have obtained $W(E_0)$ for the ion and the quadrupole, we can consider the significance of these plots.

The case of the ion may be taken up next. As in the case of the dipole, let

$$\mathbf{E}_0 \cdot \mathbf{s} = E_0 s \cos \vartheta \tag{4.71a}$$

$$d\xi d\eta d\vartheta = s^2 \sin \vartheta d\vartheta d\varphi ds \tag{4.71b}$$

$$J^{N_1} = e^{-4.21 N \epsilon^{3/2} s^{3/2}} = e^{-c_2 s^{3/2}} \tag{4.71c}$$

After integration over $\vartheta$ and $\varphi$ the equation which corresponds to Eq. (4.64) is obtained as:

$$W(X_0Y_0Z_0) = \frac{1}{4\pi^2} \int_0^\infty s^2 ds e^{-c_2 s^{3/2}} \frac{2}{E_0 s} \sin (E_0 s) \tag{4.72*}$$

The integral in Eq. (4.72) is not directly evaluable, so that a series development of sin $(E_0 s)$ is called for.

Let:

$$E_0 s = v^{2/3};\ ds = \frac{2}{3}\frac{1}{E_0} dv\, v^{-1/3};\ \beta = \frac{E_0}{c_2^{2/3}} \tag{4.73a}$$

and:

$$\sin v^{2/3} = v^{2/3} - \frac{1}{6} v^{6/3} + \frac{1}{120} v^{10/3} - \frac{1}{5040} v^{14/3} + \ldots \tag{4.73b}$$

Upon substitution of Eqs. (4.73) into Eq. (4.72) we obtain:

$$W(X_0Y_0Z_0) = \frac{1}{3\pi^2 E_0^3} \int_0^\infty e^{-\frac{c_2}{E_0^{3/2}} v} \left[ v - \frac{1}{6} v^{7/3} + \frac{1}{120} v^{11/3} - \frac{1}{5040} v^{14/3} + \ldots \right] dv \tag{4.74}$$

It is apparent that each term in Eq. (4.74) can be expressed as a gamma function.

If:

$$\frac{1}{\beta^{3/2}} = \frac{c_2}{E_0^{3/2}} = \left(\frac{E_n}{E_0}\right)^{3/2}$$

Then:

$$E_n = c_2^{3/2} = 2.61 N^{2/3} \epsilon \tag{4.75}$$

If we take as the mean separation of two of the particles $r_0$, then $\frac{4}{3} \pi r_0^3 N = 1$ where $N$ is, as usual, the particle density. This mean particle separation would then give about the same result for a normal field strength, namely, for $E_n' = 2.60\ N^{2/3}\ \epsilon$.

Again we take the "Normalfeldstarke" as the unit of field strength. Eq. (4.74) becomes:

$$W(X_0Y_0Z_0) = \frac{1}{3\pi^2 E_0^2} \left[ \Gamma(2)\beta^3 - \frac{1}{6}\Gamma\left(\frac{10}{3}\right)\beta^5 + \frac{1}{120}\Gamma\left(\frac{14}{3}\right)\beta^7 - \frac{1}{5040}\Gamma(6)\beta^9 + \ldots \right] \tag{4.76a}$$

Or:

$$W(X_0Y_0Z_0) = \frac{1}{3\pi^2 E_0^3} [\beta^3 - 0.4628\beta^5 + 0.1227\beta^7 - 0.02325\beta^9 + \ldots] \tag{4.76b}$$

In analogy with the dipole case:

$$W(E_0)dE_0 = W(X_0Y_0Z_0)\ 4\pi E_0^2 dE_0 = \frac{4}{3\pi} \beta^2 d\beta (1 - 0.4628\beta^2 + 0.1227\beta^4 - 0.02325\beta^6 + \ldots) \tag{4.76b}$$

---

*If we now let $v = E_0 s$ we obtain Unsold's Eq. (55) [103] developed by Verweij[104], namely, $W(\beta) = \frac{2}{\pi\beta} \int_0^\infty v \sin v e^{-\left(\frac{v}{\beta}\right)^{3/2}} dv$.

A consideration of Eq. (4.70b) shows that the series converges only for small $\beta$. For the case of large $\beta$, Holtsmark wrote $\sin(E_0 s)$ in Eq. (4.67) as an exponential taking the imaginary part and expressed $e^{-c_2 s^{3/2}}$ as a series to obtain:

$$W(X_0Y_0Z_0) = \frac{1}{4\pi^2 E_0}\,\Im\left\{\int_0^\infty ds\,s\,e^{iE_0 s}\left[1 - c_2 s^{3/2} + \frac{c_2^2}{2}s^3 - \frac{c_2^3}{6}s^{9/2} + \frac{c_2^4}{24}s^6 - \ldots\right]\right\} \tag{4.77}$$

Eq. (4.77) may be expressed as a series of gamma functions if we let $iE_0 s = -t$.

$$W(X_0Y_0Z_0) = \frac{1}{4\pi^2 E_0}\,\Im\left[\frac{\Gamma(2)}{(i_0E_0)^2} + \frac{ic_2}{(iE_0)^{7/2}}\Gamma\left(\frac{7}{2}\right) - \frac{1}{2}\,\frac{c_2^2}{(iE_0)^5}\Gamma(5) + \frac{1}{6}\,\frac{c_2^3}{(iE_0)^{13/2}}\Gamma\left(\frac{13}{2}\right) + \ldots\right] \tag{4.78}$$

Hence:

$$W(E_0)dE_0 = \frac{d\beta}{\beta^{5/2}}\,1.496\left(1 + \frac{2.555}{\beta^{3/2}} + \frac{14.43}{\beta^3} + \frac{0}{\beta^{9/2}} + \ldots\right) \tag{4.70c*}$$

The plot resulting from Holtsmark's incorrect versions of Eqs. (4.70b) and (4.70c) is given in Fig. (4.3).

Finally, the probability of a field strength $E_0$ must be calculated for the quadrupole. As in the two preceding cases, integration is first carried out over $\vartheta$ and $\varphi$ to obtain the following:

$$W(X_0Y_0Z_0) = \frac{1}{2\pi^2}\int_0^\infty s^2 ds\,e^{-c_4 s^{3/4}}\,\frac{\sin(E_0 s)}{E_0 s} \tag{4.79}$$

We make the substitutions $v = E_0 s$ and $\beta = \dfrac{E_0}{c_4^{4/3}}$ which yield:

$$W(X_0Y_0Z_0) = \frac{1}{2\pi^2 E_0^3}\int_0^\infty e^{-\left(\frac{v}{\beta}\right)^{3/4}}\,v\sin v\,dv \tag{4.80}$$

When the exponential is expanded in a series and sinv is expressed as the imaginary part of an exponential, Eq. (4.80) becomes:

$$W(X_0Y_0Z_0) = \frac{1}{2\pi^2 E_0^3}\,\Im\left\{\int_0^\infty v e^{iv}\left[1 - \left(\frac{v}{\beta}\right)^{3/4} + \frac{1}{2!}\left(\frac{v}{\beta}\right)^{6/4} - \frac{1}{3!}\left(\frac{v}{\beta}\right)^{9/4} + \frac{1}{4!}\left(\frac{v}{\beta}\right)^{12/4} + \ldots\right]dv\right\} \tag{4.81}$$

The series in Eq. (4.81) will not be properly convergent for small values of $\beta$. Each term in Eq. (4.81) is a gamma function. A straightforward arithmetical calculation after the substitution of $\beta$ and the gamma functions yields:

$$W(E_0)dE_0 = \frac{4}{\pi}\,\frac{d\beta}{\beta^{7/4}}\,0.805\left[1 - \frac{0.730}{\beta^{3/4}} - \frac{0.328}{\beta^{3/2}} + \frac{0.621}{\beta^{9/4}} - \frac{0.163}{\beta^3} + \ldots\right] \tag{4.70d}$$

The factor $\dfrac{4}{\pi}$ has been inserted for comparison with the previous Eqs. (4.70). Again $\beta = \dfrac{E_0}{E_n}$ where $E_n = c_4^{4/3}$.

For $0 < \beta < 1$, Holtsmark utilized graphical integration to obtain:

$$W(E_0)dE_0 = \frac{4}{\pi}\,\beta^2 d\beta\,\frac{4}{3}\left(1 - 2.44\beta^2 + 11.25\beta^4 - 72\beta^6 + \ldots\right) \tag{4.70e}$$

---

*Holtsmark obtained

$$W(E_0)dE_0 = \frac{d\beta}{\pi\beta^{5/2}}\,2.350\left[1 + \frac{5.106}{\beta^{3/2}} - \frac{7.4375}{\beta^3} + \ldots\right]$$

but a check of the work preceding is sufficient to show that this is not correct. Also, see Verweij[174] as reported by Unsold[26] which is almost correct. Holtsmark's equation corresponding to our Eq. (4.78) is also slightly in error.

Eqs. (4.70d) and (4.70e) yield the quadrupole curve in Fig. (4.3).

Fig. (4.3) tells us that, since the probability of zero field strength is zero, we must expect some broadening due to the Stark effect under any conditions. The maxima of the three curves give us the most probable field strengths in the three cases, and it may be noted that the slopes of these probability curves vary. The positions of the maxima indicate that the ion yields the greatest relative broadening, the dipole the intermediate, and the quadrupole the least. It should be recalled, however, that, since $\beta$ depends on a different "Normalfeldstarke" $E_n$ in each case, these comparative considerations cannot be directly carried over to comparisons of broadened lines in the three cases.

Eqs. (4.70) now give the probability $W(E_0)$ for the existence at a certain time of the field $E_0$ due to one of three causes. As has been mentioned earlier, there is a continuously varying field, so that we must specify a certain time at which there is a probability $W(E_0)$ that $E_0$ exists. The broadening of the spectral lines due to one of these fields may now be determined.

## 4.8. GENERAL INTENSITY DISTRIBUTION IN A STARK BROADENED LINE

Let us assume that a spectral line is emitted at the time when the field $E_0$ exists. $E_0$ will then split the line according to the Stark effect. Let the intensity in this split line be given by:

$$Id\nu = I(E_0,\nu)\,d\nu \tag{4.82}$$

$I$ is then the intensity in any relative units for the frequency $\nu$ and the field strength $E$. If we multiply this intensity distribution by the probability for the field strength $E$ and integrate over all $E$, we obtain the intensity distribution in the broadened line as follows:

$$Id\nu = d\nu \int_0^\infty I(E,\nu)\,W(E)\,dE \tag{4.83}$$

Instead of attempting to utilize an accurate but overcomplicated expression for $I(E,\nu)$, Holtsmark makes a rectangular assumption for the broadened spectral line, that is, he assumes $I(E,\nu)$ to be a constant within the limits of the line and zero outside. Thus, for a particular field strength $E$ we have a rectangle of height $h$ and width $2\nu_m$ where $2\nu_m$ is the separation of the outermost Stark components. The area of this rectangle, which is the integrated intensity, is taken as a constant which is independent of $E$. This is an approximation, but a reasonably good one. We would, of course, obtain rectangles of different width — different $2\nu_m$ — for different values of $E$. The integrated intensity of the line is:

$$f = 2\nu_m h = 2\nu_m I(E,\nu) \tag{4.84}$$

Thus:

$$I(E,\nu) = \frac{f}{2\nu_m} \text{ inside } 2\nu_m\text{, and: } I(E,\nu) = 0 \text{ outside } 2\nu_m \tag{4.85}$$

Let us take $\nu_0$ as the frequency of the line before splitting. Then it follows that all rectangles for which $\nu_m \geqslant |\,\nu - \nu_0\,|$ will contribute toward the intensity at the frequency $\nu$. In order to obtain the total intensity, integration is carried out for all rectangles which are wider than $2\nu_m$:

$$Id\nu = d\nu \int_{E'}^\infty \frac{f}{2\nu_m} W(E)dE \tag{4.86}$$

$E'$ is that field strength which causes the splitting $2(\nu - \nu_0)$, and $\nu_m$ is given by:

$$2\nu_m = cE \tag{4.87}$$

where $c$ is simply a proportionality factor. Eq. (4.86) becomes:

$$Id\nu = d\nu \int_{E'}^{\infty} \frac{f}{cE} W(E)dE \tag{4.88}$$

The evaluation of Eq. (4.88) for the three cases yields the desired broadening. First, we consider the case of the dipole.

## 4.9. LINE SHAPE AND HALF WIDTHS ACCORDING TO THE EARLY STARK THEORY

When Eq. (4.70a) is substituted into Eq. (4.88), the result is:

$$Id\nu = d\nu \frac{4}{\pi} \int_{\beta'}^{\infty} \frac{f}{cE_n} \frac{\beta d\beta}{(1+\beta^2)^2} = d\nu \frac{f}{2cE_n} \frac{4}{\pi} \frac{1}{(1+\beta'^2)} \tag{4.89}$$

in which $\beta' = \dfrac{2(\nu-\nu_0)}{cE_n} = \dfrac{2\Delta\nu}{cE_n}$, so that:

$$I(\nu) = \frac{2f}{\pi} \frac{cE_n}{c^2E_n^2 + 4(\nu - \nu_0)^2} \tag{4.90}$$

The half-width of the line can be seen to be:

$$\delta_{sd} = cE_n = c\, 4.54\, N\mu \tag{4.91}$$

An interesting sidelight seems worthy of introduction at this point. Let us set our integrated intensity $f$ equal to $S$, a trivial but legitimate move. Then let us substitute Eq. (4.91) into Eq. (4.90) to obtain:

$$I(\nu) = \frac{S}{\pi} \frac{(\delta_{sd}/2)}{(\nu - \nu_0)^2 + (\delta_{sd}/2)^2} \tag{4.92}$$

Eq. (4.92), the line shape equation for an emission line which has been Stark broadened by a dipole field, is identical to Eq. (1.78), the line shape equation for a Lorentz broadened absorption line. Holtsmark made no mention of the relation and his final equation was in the form of Eq. (4.89).

The dependence of the line half-width on the electric dipole moment and the gas density is apparent from Eq. (4.92). With which comment we turn our attention to the ion and the quadrupole.

Eqs. (4.87) and (4.88) may be rewritten as:

$$2\nu_m = cE_n\beta \tag{4.93}$$

$$Id\nu = d\nu \frac{f}{cE_n} \int_{\beta'}^{\infty} \frac{W(\beta)d\beta}{\beta} \tag{4.94}$$

Holtsmark evaluated Eq. (4.94) graphically for the cases of the ion and the quadrupole. Fig. (4.4), after Holtsmark, represents his results for the intensity distribution for all three cases. In Fig. (4.4) the abscissae have been changed for the three perturbers so that the half-widths coincide, thus giving a curve shape comparison. The half-intensity $\beta$'s for the ion and the quadrupole may be obtained from the curve as 1.25 and 0.67, respectively. These values of $\beta$ yield the half-widths:

Ion: $\delta_{si} = 1.25cE_n = 3.25cN^{2/3}\epsilon$ (4.95a)

Quadrupole: $\delta_{sq} = 0.67cE_n = 5.53cN^{4/3}A$ (4.95b)

### 4.10. REVIEW OF HOLTSMARK'S EARLY STARK BROADENING THEORY

Let us rapidly review this development before beginning its refinement. We began with the assumption that a spectral line is broadened by a Stark effect which arises from a rapidly varying field produced at the emitter by (a) ions, (b) dipoles or (c) quadrupoles.* We assumed that the probability $W(E_0)$, that a field strength $E_0$ exists at the emitter at a certain time, is a function of $E_0$. A rather laborious derivation yielded Eqs. (4.70a) through (4.70c), the equations for these probabilities for the three cases under consideration. A linear Stark effect, $2\nu_m = cE$, was assumed. $I(E,\nu)$ was assumed constant for a given field strength within the outermost Stark components and zero outside. Thus, each field strength yielded a rectangle of different width, but the same area. For a given frequency then, we integrated over all rectangles whose width is such that they contribute to the intensity at this frequency. Eq. (4.88) for the intensity distribution within the Stark-broadened line resulted. For the dipole Eq. (4.88) yielded the line shape:

$$I(\nu) = \frac{S}{\pi}\frac{(\delta_{sd}/2)}{(\nu - \nu_0)^2 + (\delta_{sd}/2)^2} \tag{4.92}$$

which is identical with Eq. (1.78). Eq. (4.88) does not lend itself so readily to evaluation for the ion and quadrupole cases.

$$\delta_{si} = 3.25cN^{2/3}\epsilon \tag{4.95a}$$

$$\delta_{sd} = 4.54cN\mu \tag{4.91}$$

$$\delta_{sq} = 5.53cN^{4/3}A \tag{4.95b}$$

Eqs. (4.95a), (4.91), and (4.95b) show the dependence of the half-width on the electrical properties of the perturbing molecule through $\epsilon$ (charge), $\mu$ (dipole moment), or $A$ (quadrupole constant) and also on the gas density through $N$ (the number of perturbers per unit of volume).

These equations are also the ones through which Holtsmark sought experimental verification of his theory. Since the theory is to undergo further development, there does not appear to be any particular reason to enumerate Holtsmark's comparisons of it with experiment at this point, although he did meet with some success in these comparisons.

### 4.11. NEED FOR FINITE MOLECULAR DIAMETERS IN THE HOLTSMARK THEORY

It may be recalled that we have essentially considered the molecules involved in the theory as points, in that, when the integration was carried out over the molecular positions in space, no portions of space were excluded on the basis of previous occupancy. In 1920 Debye,[26] while in the process of deriving a mean square value for the quadrupole electric field strength due to an atomic collection, commented on this punktformig assumption. "Zur Bestimmung von $\bar{\mathcal{E}}^2$ kaum man nicht die von J. Holtsmark, diese Zeitschrift *20*, 162, 1919, entwickelte Wahrscheinlichkeitsformel benutzen. An jener Stelle wurde nämlich der Durchmesser der Moleküle zu O angenommen und dem entspricht es, dass aus den Holtsmarkschen Formeln $\bar{\mathcal{E}}^2 = \infty$

---

*Debye[26] obtained approximate expressions for these field strengths and hence, an idea as to the behavior of the half-widths as follows. Electric charge is taken as $5 \times 10^{-10}$ gm.$^{1/2}$ −cm.$^{3/2}$ −sec.$^{-1}$ and the radius of the molecule as $10^{-8}$ cm. We assume that (a) the ion has charge $5 \times 10^{-10}$ gm$^{1/2}$ −cm$^{3/2}$ −sec$^{-1}$ (b) the moment of the dipole is $5 \times 10^{-18}$ gm$^{1/2}$ −cm$^{5/2}$sec$^{-1}$ and (c) the quadrupole constant is $5 \times 10^{-26}$ gm$^{1/2}$ −cm$^{7/2}$ −sec$^{-1}$. Since the electric field has the units gm$^{1/2}$ −cm$^{1/2}$ −sec$^{-1}$, and since we may assume the field to be the product of either (a), (b), or (c) and some power of $N$ (molecules − cm$^{-3}$), this power of $N$ may be adjusted so that the product has the proper units, thus yielding approximate expressions for the electric field in each of the three cases. Hence, we obtain for (a) $E = \epsilon N^{2/3}$, for (b) $E = \mu N$, and for (c) $E = \theta N^{4/3}$ or 4500 ESU, 135 ESU, and 4 ESU respectively. Multiplicative constants would yield the values obtained by Holtsmark.

folgt. Es möge in diesem Zusammenhange bemerkt werden, dass auch bei dem von Holtsmark behandlten Problem eine Berücksichtigung der Endlichkeit der Durchmesser erwünscht wäre, um so mehr, als dadurch die Druckabhänigkeit des Verbreiterungseffekts beeinflusst werden dürfte."[26] This appears to be a reasonable assertion, and so Holtsmark evidently considered it, for in 1924, he attacked the problem again,[67] this time with finite diameters assigned the molecules under consideration. Gans[49] had approached the problem earlier under the assumption of finite diameters for the emitting molecules, but he had retained the point assumption for the broadening molecules. As Holtsmark noted, this would be a good assertion for the case where ions are the field producers, since we would normally expect the ions to make up only a small portion of the total number of molecules present. On the other hand, these assumptions would not appear to be valid for the dipole or quadrupole case. Gans further found a Gaussian distribution for very high field strengths, " . . . wie zu erwarten war."[67]

In this development, Holtsmark retained the simplifying assumption which classifies the broadening molecules as ions, dipoles, or quadrupoles, that is, he again took only the first term in the series for the potential. Since these assumptions are predicated on large $R$, it is apparent that when the gas density or pressure is high, $R$ no longer remains large enough to justify them. How high "high" is, is, of course, a matter for discussion.* For these "high" densities the calculations cannot be carried out, but the field strength distribution in these cases is assumed Gaussian.[49] Holtsmark thus limits himself to those gas densities where the first term in the potential series does give a good approximation of the electric field.

### 4.12. THE FIELD STRENGTH PROBABILITY FUNCTION WITH FINITE MOLECULAR DIAMETERS

We begin with Eq. (4.11) written in a slightly different form, since the modifications in the development will occur at a later stage.

$$W(X_0Y_0Z_0) = \frac{1}{8\pi^3}\iiint_{-\infty}^{+\infty} d\xi d\eta d\zeta e^{-i(\xi X_0+\eta Y_0+\zeta Z_0)} \int \sigma e^{i(\xi\Sigma X_n+\eta\Sigma Y_n+\zeta\Sigma Z_n)} d\tau \Big/ \int \sigma d\tau \tag{4.96}$$

Again:

$$\xi X_0 + \eta Y_0 + \zeta Z_0 = sE_0 \cos\vartheta_s \,;\; d\xi d\eta d\zeta = s^2 ds \sin\vartheta_s d\vartheta_s d\varphi_s \tag{4.97}$$

where in this case E$_0$ has been taken as the polar axis and s has been referred to it. Substitute Eq. (4.97) into Eq. (4.96) and integrate over $\vartheta_s$ and $\varphi_s$ to obtain:

$$W(E_0) = \frac{2E_0}{\pi}\int_0^\infty ds\, s \sin(E_0 s)\frac{L(s)}{M(s)} \tag{4.98}$$

where:

$$L(s) = \int d\tau\, \sigma\, e^{i\Sigma(\xi X_n+\eta Y_n+\zeta Z_n)} \tag{4.99}$$

$$M(s) = \int s d\tau \tag{4.100}$$

If $\chi$ is the angle between s and E$_n$

$$\Sigma(\xi X_n + \eta Y_n + \zeta Z_n) = s\Sigma E_n \cos\chi_n \tag{4.101}$$

---

*In a somewhat similar consideration, Spitzer (see *infra*, this Chap.) takes as a limit a pressure such that $R > 10r_0$ where $r_0$ is the radius of the Bohr orbit.

Now in the computation of $L(s)$ and $M(s)$, the finiteness of the molecular diameters is to be taken into account. In the earlier computation, it was possible to transform Eq. (4.16) into Eq. (4.18), a product of identical integrals. This was legitimate, due to the independency of the molecules, in that the motion of one molecular point is not interfered with by the other molecular points. This integral product is no longer admissible after finite diameters have been assigned the molecules, for we may not now allow the center of a molecule to be separated from the center of another molecule by less than this molecular diameter. We let:

$$\Xi_n = e^{isE_n \cos \chi_n} \tag{4.102}$$

so that:

$$L(s) = \int_k d\tau\sigma \prod_{k-1}^{N_1} \Xi_n$$

$$= \int_{k_1} \Xi_1\sigma_1 d\tau_1 \int_{k_2} \Xi_2\sigma_2 d\tau_2 \ldots \int_{k_{N_1}} \Xi_{N1}\sigma_{N1} d\tau_{N1} \tag{4.103}$$

where the first integral is carried over the space not occupied by the other $(N_1 - 1)$ molecules and the 0-th molecule (emitter). Thus, the first integral is dependent on the coordinates of the other molecules and must be included under the integral sign of the second integral, and so on. This fact obviously does not simplify matters. The difficulty may be eliminated, however, by selecting a suitable initial distribution for molecules. This selection would appear to be justified, since our results should not depend on the arbitrary initial distribution of the molecules. "Thus, we choose the initial positions of the atoms such that they are all united in space at an arbitrary position which, however, is constant for the duration of the $N - 1$ first integrations. . . ."[67] The position of the first molecule was chosen for this union. After locating the molecules in this manner, we may move molecule $N_1$ about space in the process of the integration, while keeping the remaining molecules at position one. This process is carried out for $N_1 - 1$ of the molecules. Thus, we see that the first integral contains coordinates which require that it be included only under the integral sign for molecule one — we are working backwards, one might say, from molecule $N_1$ to molecule one. The happy situation prevails for the first $N_1 - 1$ integrals. Let the integral over all space except that portion occupied by the emitter be:

$$\int_{k_n} \Xi_n\sigma_n d\tau_n = H \tag{4.104}$$

Further, let the integral over that portion occupied by the $N_1$ remaining molecules at position one be:

$$\int_{nk} \Xi_n\sigma_n d\tau_n = H_n \tag{4.105}$$

This notation yields for the first integration:

$$(H - H_{N_1 - 1})$$

After $N_1 - 1$ integrations we have:

$$L(s) = \int \sigma_1 d\tau_1\, \Xi_1 \prod_{n=1}^{N_1-1} (H - H_n) \tag{4.106}$$

where Eq. (4.106) is to be integrated over the entire coordinate range excepting that portion occupied by the emitter.

Substitute Eq. (4.30) into Eq. (4.105) to obtain:

$$H_n = \int_{nk} \Xi_n r^2 \sin \vartheta_1 d\vartheta_1 \sin \vartheta' d\vartheta' d\varphi_1 d\varphi' dr$$

$$\doteq \Xi_1 n \int_0^d \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} r^2 dr \sin \vartheta_1 d\vartheta_1 \sin \vartheta' d\vartheta' d\varphi_1 d\varphi' = n\Xi_1 4\pi k \tag{4.107}$$

where $k$ is eight times the volume of a molecule; $n$ is the number of molecules at position one; $\Xi_1$ is the value of $\Xi$ at the position of the first molecule, and $d$ is the diameter (closest separation of two molecular centers) of a molecule. This approximation is only a good one if $nk \ll V$, the total volume; and also only at some distance from the emitter, since $\Xi$ could not be taken as the constant $\Xi_1$ for the integration for position one close to the emitter.

If we let $V$ differ from its previous value by a factor of $4\pi$ we may write an analogy to Eq. (4.29) as:

$$H = 4\pi VJ \tag{4.108}$$

We substitute Eqs. (4.107) and (4.108) into Eq. (4.106) to obtain:

$$L(s) = (4\pi VJ)^{N_1 - 1} \int_{kn} \Xi_1 \sigma_1 d\tau_1 \prod_{n=1}^{N_1-1} \left(1 - n\frac{k\Xi_1}{VJ}\right) \tag{4.109}$$

$M(s)$ may now be calculated in a similar manner. Integration over the $N_1$-th atom yields $4\pi(V - (N_1 - 1)k)$, and so on up to the last integration. We obtain:

$$M(s) = (4\pi V)^{N'} \prod_{n=1}^{N_1-1} \left(1 - \frac{nk}{V}\right) \tag{4.110}$$

Now let:

$$K(s)J^{N_1-1} = \frac{L(s)}{M(s)} = \frac{1}{4\pi V} J^{N_1-1} \frac{\int_{kn} \Xi_1 \sigma_1 d\tau_1 \prod_{n=1}^{N_1-1} \left(1 - n\frac{k\Xi_1}{VJ}\right)}{\prod_{n=1}^{N_1-1} \left(1 - \frac{nk}{V}\right)} \tag{4.111}$$

We have assumed $nk \ll V$ so that $N_1 \frac{k\Xi_1}{VJ} = N_1\epsilon \ll 1$. This fact allows the approximation:

$$\log \prod_{n=1}^{N_1-1} (1 - n\epsilon) \doteq \sum_1^{N_1-1} n\epsilon \doteq -\frac{N_1^2}{2}\epsilon \longleftrightarrow \prod_{n=1}^{N_1-1} (1 - n\epsilon) = e^{-\frac{N_1}{2\epsilon}} \tag{4.112}$$

Hence:

$$K(s) = \frac{1}{k_n} \int_{kn} \Xi_1 d\tau_1 e^{-\left(\frac{N_1^2 k}{2} \frac{\Xi_1}{V} + \frac{N_1^2 k}{2V}\right)}$$

$$= \frac{e^\alpha}{k_n} \int_{kn} \Xi_1 \sigma_1 d\tau_1 e^{-\alpha\Xi_1} \tag{4.113}$$

where: $\frac{2\alpha}{N_1} = \frac{N_1 k}{V}$, eight times the ratio of molecular to total volume.

A transformation of coordinates at this point facilitates continuation of the calculation. Let:

$$\sigma_1 d\tau_1 = r_1^2 dr_1 \sin \chi_1 d\chi_1 \sin \gamma_1 d\gamma_1 \tag{4.114a}$$

so that:

$$k_n = \frac{4}{3} R^3 \tag{4.114b}$$

where $r_1$ is the radius vector of molecule one; $\chi_1$ is the angle between $s$ and $E_1$, and $\gamma_1$ is the angle between $r_1$ and the molecular axis. The legitimacy of this transformation is assured, since we may recall that we are now integrating over the entire volume. $E_1$ is a function of $r_1$, $\gamma_1$, and the electrical constants of the molecule. Holtsmark limited his calculations to dipoles as field producers, since he felt that in the case of finite diameters the complexity of the calculations for ions or quadrupoles was too great, if, indeed, a reasonable result could be obtained.

From Eq. (4.19):
$$E_1 = \frac{\mu}{r^3}\, w = \frac{\mu}{r^3}\sqrt{1 + 3\cos^2\gamma} \tag{4.115}$$

Let:
$$z = sE_1 = s\frac{\mu}{r^3}\, w \tag{4.116a}$$

Hence:
$$K(s) = \frac{3e^{\alpha}}{4R^3}\int_0^R\int_0^{\pi}\int_0^{\pi} e^{is\cos z}e^{-\alpha e^{is\cos z}}\, r_1^2 dr_1 \sin\chi_1 d\chi_1 \sin\gamma_1 d\gamma_1 \tag{4.117}$$

where the lower limit $r = 0$ introduces " . . . no noticeable errors." Integration over $\chi$ yields:

$$K(s) = e^{\alpha}\frac{3}{2R^3}\int_0^{\pi}\sin\gamma_1 d\gamma_1\int_0^R r_1^2\, dr_1 \frac{1}{\alpha z}\, e^{-\alpha\cos z}\sin(\alpha\sin z)$$

$$= \frac{e^{\alpha}}{\alpha}\,\frac{3}{2R^3}\,\mathfrak{J}\left\{\int_0^{\pi}\sin\gamma_1 d\gamma_1\int_0^R r_1^2 dr_1\frac{1}{z}\, e^{-\alpha(\cos z - i\sin z)}\right\} \tag{4.118}$$

where the imaginary part of the exponential has been substituted for sin ($\alpha$ sin $z$).

From Eq. (4.116a):
$$r_1^2 dr_1 = -s\mu w z^{-2} dz \tag{4.116b}$$

Hence:
$$K(s) = \frac{e^{\alpha}}{2\alpha}\int_0^{\pi} d\gamma_1 \sin\gamma_1 \cdot z_1 \cdot \mathfrak{J}\left\{\int_{Z_1}^{\infty} dz z^{-3}e^{-\alpha u}\right\}$$

$$= P_1\,\tfrac{1}{2}\int_0^{\pi} d\gamma_1\sin\gamma_1 \tag{4.122}$$

where:
$$u = e^{-iz} = \cos z - i\sin z \tag{4.123}$$

Instead of integrating Eq. (4.122) along the axis of reals from $z_1$ to $\infty$, Holtsmark integrated around a path in the complex plane ($z = x + iy$) — which, it may be noted, includes no singular points — as shown in Fig. (4.5).

We desire only the imaginary portion of the result. The integral along $BC$ is real, so that it contributes nothing to Eq. (4.122). The integrals along $CD$ and $DE$ disappear for $Y = \infty$ and $z_2 = \infty$ respectively. Thus, by Cauchy's theorem,* the integral with limits $z_1$ and $\infty$, which we desire, is equal to the integral along $AB$.

Let:
$$z = z_1e^{-i\varphi} \longleftrightarrow dz = -z_1ie^{-i\varphi}d\varphi$$

Since $z_1, \alpha \ll 1$,

Let:
$$u = e^{-iz} = 1 - iz_1e^{-i\varphi} + \ldots \doteq 1 - iz_1e^{-i\varphi}$$

And:
$$e^{\alpha}e^{-\alpha u} = e^{i\alpha z_1 e^{-i\varphi}} = 1 + i\alpha z_1e^{-i\varphi} - \frac{\alpha^2 z_1^2}{2}e^{-2i\varphi} - i\frac{\alpha^3 z_1^3}{6}e^{-3i\varphi} - \ldots \tag{4.124}$$

---

*Cauchy's theorem states that the integral around a closed path in the complex plane which includes no singular points is zero.

Eq. (4.124) yields for $P_1$ after integration:

$$P_1 = 1 + \frac{\pi}{4}\alpha z_1 + \frac{\alpha^2 z_1^2}{6} + \dots \tag{4.125}$$

So that:

$$K(s) = \frac{1}{2}\int_0^{\pi} d\gamma_1 \sin\gamma_1 \left(1 + \frac{\pi}{4}\alpha z_1 + \frac{\alpha^2 z_1^2}{6} + \dots\right) \tag{4.126}$$

Let:

$$\frac{N_1 k}{2v} = b;\ \frac{N_1}{v} = N \longleftrightarrow \alpha z_1^2 = \frac{4}{3}\pi b N \mu s w \tag{4.127}$$

We now substitute Eqs. (4.127) into (4.126) and drop all terms after the second in the series in the resulting equation to obtain:

$$K(s) = 1 + \frac{\pi^2}{6} bN\mu s \int_{-1}^{+1} \sqrt{1 + 3x^2dx} = 1 + 4.54\, bN\mu s \tag{4.128}$$

where $x = \cos\gamma_1$.

An objection to taking the upper limit of $z$ as infinity ($r = 0$) may well be raised for this would mean that the molecules are point masses in that the emitter is infinitely close to the broadener for $z = \infty$. Holtsmark felt that "... For the cases which are encountered in practice, this effect is insignificant."[67]

We have assumed large $N_1$ and, essentially:

$$\frac{L(s)}{M(s)} = K(s) \lim_{N_1 \to \infty} J^{N_1 - 1} \tag{4.129}$$

The quantity $\lim\limits_{N_1 \to \infty} J^{N_1-1}$ is nearly the same as has been given earlier for the ion, dipole, and quadrupole, respectively by Eqs. (4.43), (4.55), and (4.60). Instead of integrating from 0 to $R$ to obtain $J^{N_1-1}$, we must here take into account the finite diameters by integrating from a finite lower limit which is taken as the mean of the gas kinetic diameters of the emitting and broadening atoms. If we let:

$$a = 4\pi N d^3\ ;\quad z = \frac{K_p s}{d^p} \tag{4.130}$$

where $K_p$ is $\epsilon$, $\mu$, or $A$ for $p$ equal to 2, 3, or 4 respectively, we may write Gans'[40] result as:

$$J^{N_1-1} = e^{-aG_p(s)} \tag{4.131}$$

Eq. (4.131) yields Eqs. (4.43), (4.55), and (4.60) as a first approximation with $a \ll 1$. In second approximation one obtains for the dipole:

$$J^{N_1-1} = e^{4.54\mu N s} e^{a/3} \tag*{(4.132)*}$$

Thus, a constant factor has been introduced which depends on the mean molecular diameters. This would also be the case for the ion and the quadrupole. Eq. (4.98) now becomes:

$$\begin{aligned} W(E_0) &= e^{a/3}\frac{2E_0}{\pi}\int_0^{\infty} dss \sin(E_0 s)\, e^{-4.54\mu N s}\,(1 + 4.54bN\mu s) \\ &= e^{a/3}\frac{2E_0}{\pi}\,\mathfrak{J}\left\{\int_0^{\infty} dss e^{(-4.54\mu N s + iE_0 s)}\,(1 + 4.54bN\mu s)\right\} \end{aligned}$$

---

[*] As Debye[38] pointed out, this equation does not hold for $E_0 = \infty$ since $W(E_0)$ decreases too slowly for very high field strengths, thus yielding an infinite mean value of $E_0$. Gans found a Gaussian distribution for these large $E_0$.

$$= \left[\frac{4}{\pi}\frac{E_0^2 E'}{(E'^2 + E_0^2)}\right] e^{a/3}\left\{1 + b\,\frac{3E'^2 - E_0^2}{E'^2 + E_0^2}\right\} \tag{4.133}$$

where $E' = 4.54N\mu$.

The factor in brackets in Eq. (4.133) is identical to Eq. (4.70a) the probability for the case of point atoms, while the remaining factors essentially correct it for finite diameters. Gans had already obtained the corrective factor $e^{a/3}$ which, it may be noted, is independent of field strength, and thus does not take into account any field strength changes, and, as a consequence, this factor will not influence the broadening. We should remember that Eq. (4.133) breaks down for very large field strengths, and the Gaussian probability function must be utilized. Eq. (5.133) may be written as:

$$W(\eta) = \frac{4}{\pi}\,\frac{\eta^2}{(\eta^2 + 1)^2}\,e^{a/3}\left\{1 + b\,\frac{3 - \eta^2}{1 + \eta^2}\right\} \tag{4.134}$$

where: $\eta = \dfrac{E_0}{E'}$.

A simple calculation shows the maximum of the probability curve to fall at $\eta = 1 - b$, while this maximum is at $\eta = 1$ for the dipole on the uncorrected curve. The resulting line width is changed "... by the same per centile amount."[67]

## 4.13. DIPOLE LINE SHAPE FROM REFINED STARK BROADENING THEORY

Although Holtsmark did not work out the line shape for this corrected case, let us make the short calculation necessary to obtain an idea of this shape. We shall utilize Eq. (4.94) and assume that for $\eta' \leqslant \eta \leqslant \eta''$. Eq. (4.134) yields the correct form of $W(\eta)$ while for $\eta'' \leqslant \eta \leqslant \infty$ Erf $(\eta)$ yields the correct $W(\eta)$. We are assuming $\eta''$ very large. Eq. (4.94) becomes:

$$I(\nu)d\nu = d\nu e^{a/3}\,\frac{4}{\pi}\,\frac{f}{cE_n}\int_{\eta'}^{\eta''}\frac{\eta}{(1 + \eta^2)^2}\left\{1 + b\,\frac{3 - \eta^2}{(1 + \eta^2)}\right\}d\eta + d\nu\,\frac{4}{\pi}\,\frac{f}{cE_n}\int_{\eta''}^{\infty}\mathrm{Erf}\,(\eta)\,d\eta$$

$$= d\nu e^{a/3}\,\frac{4}{\pi}\,\frac{f}{cE_n}\left[\int_{\eta'}^{\infty}\frac{\eta}{(1 + \eta^2)^2}\left\{1 + b\,\frac{3 - \eta^2}{(1 + \eta^2)}\right\} - \int_{\eta''}^{\infty}\frac{\eta}{(1 + \eta^2)^2}\left\{1 + b\,\frac{3 - \eta^2}{(1 + \eta^2)}\right\}d\eta + \int_{\eta''}^{\infty}\mathrm{Erf}\,(\eta)d\eta\right]$$

$$I(\nu) = \frac{4}{\pi}\,\frac{f}{cE_n}\,\frac{e^{a/3}}{4}\,\frac{(2 + 5b) + (2 + 4b)\eta'^2}{(1 + \eta'^2)^2} + K(\eta'') \tag{4.135}$$

The spectral line given by Eq. (4.135) neglecting the $K(\eta'')$ term will still be symmetrical about the line center. For small $b$, and $b$ has been assumed small, the curve shape as given by Eq. (4.135) is very nearly identical with the shape given by Eq. (4.89). A good approximation for values of $b$ up to 0.0020 is:

$$I(\nu) = \frac{4}{\pi}\,\frac{f}{2cE_n}\,e^{a/3}\,\frac{1 + 2b}{(1 + \eta'^2)} = \frac{2f}{\pi}\,e^{a/3}\,\frac{(1 + 2b)\,cE_n}{c^2E_n^2 + 4(\nu - \nu_0)^2}$$

$$= \frac{f}{\pi}\,e^{a/3}\,\frac{(1 + 2b)\,(\delta/2)}{(\nu - \nu_0)^2 + (\delta/2)^2} \tag{4.136}$$

Holtsmark calculated $b$ for four monatomic and four diatomic gases on the basis of Debye's work[26] and obtained values of $b < 0.0020$ in all but one instance.

## 4.14. LINE SHIFT AND QUADRATIC STARK EFFECT

We might now, with Holtsmark, consider another form of broadening which may arise. Suppose the line is not split to give a band for the field strength $E$ as was assumed in deriving Eqs. (4.89) and (4.136), but that it is simply displaced by a frequency $\Delta\nu$. Now for a linear Stark effect the right (or left) side of the $W(E_0)$ curve is the intensity distribution curve for the broadened spectral line, since the probabilities of the various field strengths will give the probabilities for a shift of the line by an amount corresponding to this field strength, and hence, the relative intensities at those frequencies. If $\gamma$ is the line shift for unit field strength, we may read the shifts of the line intensity maxima directly from Fig. (4.3) as:

$$\Delta\nu = 1.5\ \gamma E_n \text{ Ion} \tag{4.137a}$$

$$\Delta\nu = 1.0\ \gamma E_n \text{ Dipole} \tag{4.137b}$$

$$\Delta\nu = 0.65\ \gamma E_n \text{ Quadrupole} \tag{4.137c}$$

Thus, this type of consideration gives an asymmetrical spectral line whose maximum intensity has undergone a frequency shift. Qualitative examples of this shift and asymmetry had been given by Takamine and Kokubu[181] for certain *He* lines and for "many metal lines" by Takamine.[180]

Fig. (4.6) shows a calculation of this same effect made by Holtsmark under the assumption of a quadratic Stark effect. Holtsmark calculated the widths of the *H* line broadened by the quadrupole field of hydrogen for pressures ranging from 0.3 cm to 20 cm., added the Doppler broadening correction to them, and compared the resulting half-widths to those observed by Michelson. Not more than an order of magnitude agreement can be claimed.

## 4.15. A COMPARISON WITH SOME EXPERIMENTAL RESULTS

A consideration of the displacements of *Zn* lines as observed by Swaim[18] shows that the theory gives slightly better results for an ion field than a quadrupole where air is assumed as the broadening agent. When Holtsmark attempted to apply this result to the broadening by air of the *Li* line λ 4602 in a light arc as observed by Stark,[213] he found a variation of the observed from the calculated by a factor of 380, a goodly variation.

Two possibilities arise from these comparisons of theory with experiment. (1) The Stark effect, if it is a factor, is not the only factor which contributes to the broadening of a spectral line. (2) Simultaneous broadening by both ions and quadrupoles or dipoles occurs, especially in the case of a light arc, and the fields produced may be inhomogeneous ones.

A further comment in definition of this inhomogeneity may be in order. Let us consider, say, an alkali atom in which we may only be concerned with the spectrum-producing valence electron. For our purposes here we can deal either with a Bohr orbit for this electron or those regions of space where $\bar{\psi}\psi d\tau$ is relatively high for the electron. Then in order that the fields producing Stark broadening be homogeneous for this case these fields must be essentially constant over the region of the orbit or of high $\bar{\psi}\psi d\tau$.

We have restricted our gas to low pressure in order that the results may be valid, and another restriction has been inferred but not actually stipulated. If a given field $E$ at time $\tau$ is to broaden a line into one of the rectangles which have been assumed for the various values of $E$, then $E$ must be a constant for a time interval sufficient to allow the molecule to emit under conditions which will produce this rectangle. The field at the emitter varies due to the motion of the molecular broadeners, and this then means that an upper limit, which depends on the lifetime of the upper of the two quantum states involved in the emission, must be placed on these molecular velocities, and hence, the gas temperature.

In 1925 Holtsmark and Trumpy[71] measured the half-widths of several of the emission lines of Li, Ag, Cu, and Ni. For all four of these elements the broadening field producers were considered as ions. For Li, Eq. (4.95a) was assumed for the half-widths of the lines. The constant $c$ was obtained from the measurements of Takamine[180] except where otherwise noted in Table (4.1). Thus, when the line half-widths had been measured experimentally $E_n$ was computed for the lines. This is not direct proof of the theory, but, if, for all the lines, $E_n$ is the same, it is in indirect support of it.

| λ A | Designation | Separation of outermost Stark components for 38000 volts/cm | c ESU | Half Width A | $E_n$ v/cm |
|---|---|---|---|---|---|
| 4273 | $2p - 4s$ | 0.36[177] | 0.00284 | — | — |
| 3986 | $2p - 5s$ | perhaps 1.00[108] | 0.00950 | 1.26 | 32000 (inacc.) |
| 4603 | $2p - 4d$ | 4.67 | 0.0369 | 3.56 | 23200 |
| 4132 | $2p - 5d$ | 8.54 | 0.0678 | 6.95 | 24600 |
| 3915 | $2p - 6d$ | 13.62 | 0.1076 | 10.05 | 22400 |
| 4148 | $2p - 5d$ | 7.80[67]* | — | — | — |

Table 4.1

It is apparent that the three field strengths fall within a relatively narrow range, although it would not appear that the number of measurements is great enough to allow the drawing of too many conclusions. Holtsmark and Trumpy rounded off 24600 and 22400 to 24500 and 22500 respectively.

Takamine[180] had shown, as we have noted, that certain Ag, Cu, and Ni lines show the Stark displacement effect which yields the half-widths as given by Eq. (4.137a). Holtsmark and Trumpy calculated $E_n$ for several lines of these elements again assuming ions as the broadening field producers. The $\gamma$'s as given in Table (4.2) were taken from Takamine's measurements.[180]

| Element | A | Designation | $\gamma$ A | Half-Width | $E_n$ v/cm | Current Amp |
|---|---|---|---|---|---|---|
| Ag | 4476 | $2p_2 - 3s$ | 0.00021 | — | — | 10 |
| | 4226 | — | 0.0125 | 0.65 | 10400 | 10 |
| | 4211 | $2p_1 - 4d_1$ | 0.0431 | 1.95 | 9000 | 10 |
| | 4055 | $2p_2 - 4d_2$ | 0.0458 | 2.70 | 11800† | 10 |
| Cu | 4531 | $2p_1 - 3s$ | 0.000272 | — | — | 15 |
| | 4481 | $2p_2 - 3s$ | 0.000614 | — | — | 15 |
| | 4062 | $2p_1 - 4d_1$ | 0.00546 | 0.66 | 24000 | 15 |
| | 4023 | $2p_2 - 4d_2$ | 0.00418 | 0.53 | 25400 | 15 |
| Ni | 4411 | — | 0.00138 | — | — | 20 |
| | 3934 | — | 0.00300 | 0.85 | 54000 | 20 |
| | 4018 | — | 0.0080 | 2.04 | 51000 | 20 |
| | 3984 | — | 0.0112 | 2.72 | 48500 | 20 |

Table 4.2

In this case again, we see that, for the various currents, the $E_n$ fall within fairly narrow ranges.

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*This is for a field of 80000 volts/cm.

†Holtsmark and Trumpy gave 8100.

## 4.16. THE STARK EFFECT IN PARABOLIC COORDINATES

Although Holtsmark's theory of Stark broadening is basically a statistical one and, as a result, may be associated with the statistical theory of Margenau,* we shall continue to treat Stark broadening separately. Under this delineation we must proceed from a consideration of Holtsmark's work in 1924 to Spitzer's studies[173, 174] of 1939. Before doing so, however, let us consider the Stark broadening of the spectral lines of hydrogen from a quantum mechanical point of view. In doing this we shall very rapidly sketch the theory as presented by Epstein[34] and Bethe.[6]

To begin with we suppose the electron to be moving in the field of its nucleus of charge $e$ under the influence of the potential $-e^2/r$. A homogeneous field of strength $E$ is imposed along the $z$-axis resulting in the addition of $-eEz$ to the potential. Finally, we transform to parabolic coordinates by utilizing the relations:

$$x = \sqrt{\xi\eta}\cos\varphi \ ; \quad y = \sqrt{\xi\eta}\sin\varphi \ ; \quad z = \frac{\eta - \xi}{2}$$

$$0 \leqslant \xi \leqslant \infty \ ; \quad 0 \leqslant \eta \leqslant \infty \ ; \quad 0 \leqslant \varphi \leqslant 2\pi \tag{4.138}$$

If we utilize Eq. (4.138) and the potential energy expression which we have obtained, the Schrodinger equation may be written as:

$$\frac{\partial}{\partial\eta}\left(\eta\frac{\partial\psi}{\partial\eta}\right) + \frac{\partial}{\partial\xi}\left(\xi\frac{\partial\psi}{\partial\xi}\right) + \frac{1}{4}\left(\frac{1}{\eta}+\frac{1}{\xi}\right)\frac{\partial^2\psi}{\partial\varphi^2} + \frac{\mu}{2\hbar^2}\left[E_n(\eta+\xi) + 2e^2 - \frac{eE(\eta^2-\xi^2)}{2}\right]\psi = 0 \tag{4.139}$$

This equation must be solved by the methods of perturbation theory, and, since the carrying out of the solution involves large quantities of mathematical spadework which do not directly contribute to our line broadening considerations, we shall simply give the first and second order energy results. For other information concerning the Stark effect which we shall utilize we may treat the problem in more general terms.

The zeroth-order solution of Eq. (4.139) simply yields the unperturbed energies of the hydrogen atom. The first-order solution yields the energy perturbation of the linear Stark effect:

$$E^{(1)} = \frac{3h^2E}{2\mu e}\, n\,(k_2 - k_1) \tag{4.140a}$$

The second-order solution results in the energy perturbation of the quadratic Stark effect:

$$E^{(2)} = -\frac{E^2}{16\mu^2}\left(\frac{\hbar}{e}\right)^4 n^4\,[17n^2 - 3\,(k_2 - k_1) - 9m^2 + 19] \tag{4.140b}$$

In Eqs. (4.140) $n = k_1 + k_2 + m$ is the total quantum number, while $k_1$, $k_2$, and $m$ are the quantum numbers associated with the parabolic coordinates $\xi$, $\eta$, and $\varphi$ respectively. We might note that $\varphi$ corresponds exactly to the $\varphi$ of spherical polar coordinates. This means that the quantum number $m$ is the magnetic quantum number specifying angular momentum about the atomic figure axis in parabolic as well as in polar coordinates. As a consequence, the selection rules for the $m$ of parabolic coordinates will correspond to those for the $m$ of polar.

The eigenfunctions of hydrogen in parabolic coordinates will be written down at a later point when their utilization will be required.

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*See *infra*, Chap. 5.

## 4.17. A GENERAL TREATMENT OF THE STARK EFFECT

Now let us consider the problem in a more general form. To begin with the imposition of the external electric field, which is the Stark effect producer, will present us with a problem in perturbation theory if we consider the case of the isolated hydrogen atom as the unperturbed problem. The perturbation introduced will be $eEr \cos \vartheta$, if, as in the last section, we take the field along the $z$-axis and set up the problem in spherical polar coordinates. Let us assume our familiarity with the solution of this unperturbed problem in these coordinates and specify the solution by $\psi_{nlm}$. The symbols $n$, $l$, and $m$ we take to indicate the principal, the orbital angular momentum, and the magnetic quantum numbers respectively, and for convenience of notation, we further suppose the numbers $n$ and $l$ to be represented by $n$ and the number $m$ by $j$. Now a different energy eigenvalue corresponds to each eigenfunction going with a different value of $n$. For a given value of $n$, however, there are a set of eigenfunctions corresponding to the various possible values of $j$ to which set there corresponds but one energy eigenvalue, namely, $E_n$.* This means that the energy level of energy $E_n$ is degenerate. The perturbation, which is to be introduced, will tend to remove this degeneracy, that is, solutions to higher order problems of the form Eqs. (2.26) will result in energy dependences on $j$. This fact will require us to treat the perturbation problem in a slightly different manner from that of Chapter 2.

In zeroth-order there are, say, $i$ eigenfunctions which satisfy the Schrodinger equation for energy $E_n$. It follows then that the complete solution of the differential equation for the state under consideration is a linear combination of these $i$ eigenfunctions:

$$\psi_{nj}^{(0)} = \sum_{j'} c_{nj'} \psi_{nj'}^{(0)} \tag{4.141}$$

This result may be substituted into Eqs. (2.25):

$$H = H^0 + H' \tag{4.142a}$$

$$\psi_{nj} = \sum_{j'} c_{nj'} \psi_{nj'}^{(0)} + \epsilon \psi_{nj}^{(1)} + \epsilon^2 \psi_{nj}^{(2)} + \ldots \tag{4.142b}$$

$$E_{nj} = E_n^{(0)} + \epsilon E_{nj}^{(1)} + \epsilon^2 E_{nj}^{(2)} + \ldots \tag{4.142c}$$

Eqs. (4.142) are next utilized to obtain the analog of Eqs. (2.26) from $H\psi_n = E_n\psi_n$ as:†

$$H^0 \sum_{j'} c_{nj'} \psi_{nj'}^{(0)} = E_n^{(0)} \sum_{j'} c_{nj'} \psi_{nj'}^{(0)} \tag{4.143a}$$

$$(H^0 - E_n^{(0)}) \psi_n^{(1)} = \sum_{j'} c_{nj'} (E_n^{(1)} - H') \psi_{nj'}^{(0)} \tag{4.143b}$$

$$H'\psi_{nj}^{(1)} + H^0 \psi_{nj}^{(2)} = E_n^{(0)} \psi_{nj}^{(2)} + E_{nj}^{(1)} \psi_{nj}^{(1)} + \sum_{j'} c_{nj'} E_{nj}^{(2)} \psi_{nj'}^{(0)} \tag{4.143c}$$

We agree that the $\psi_{nj}$ are a complete orthonormal set. This unanimity of viewpoint allows us to introduce the expansions:

$$\psi_{nj}^{(1)} = \sum_{n'j'} a_{njn'j'} \psi_{n'j'}^{(0)} \; ; \quad \psi_{nj}^{(2)} = \sum_{n'j'} b_{njn'j'} \psi_{n'j'}^{(0)} \tag{4.144}$$

with the result, after slight rearrangement:

$$\sum_{n'j'} a_{njn'j'} (H^0 - E_n^{(0)}) \psi_{n'j'}^{(0)} = \sum_{j'} c_{nj'} (E_{nj}^{(1)} - H') \psi_{nj'}^{(0)} \tag{4.143b$'$}$$

$$\sum_{n'j'} b_{njn'j'} (H^0 - E_n^{(0)}) \psi_{n'j'}^{(0)} + \sum_{n'j'} a_{njn'j'} (H' - E_{nj}^{(1)}) \psi_{n'j'}^{(0)} = \sum_{j'} c_{nj'} E_{nj}^{(2)} \psi_{nj'}^{(0)} \tag{4.143c$'$}$$

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*Concerning this magnetic quantum number see *supra*, Sec. (2.5) where $m = M(m \sim j)$.

†For the simpler non-degenerate case see *infra*, Chap. 5.

If Eq. (4.143b′) is multiplied through on the left by $\bar{\psi}_{nj}^{(0)}$ and integrated over all space, the result is:

$$\sum_{n'j'} a_{njn'j'} \int \bar{\psi}_{nj}^{(0)} (E_{n'}^{(0)} - E_{n}^{(0)}) \psi_{n'j'}^{(0)} \, d\tau = \sum_{j'} c_{nj'} \int \bar{\psi}_{nj}^{(0)} (E_{nj}^{(1)} - H') \bar{\psi}_{nj'}^{(0)} \, d\tau \tag{4.144}$$

according to Eq. (4.143a). Orthonormality decrees:*

$$\int \bar{\psi}_{nj}^{(0)} \psi_{n'j'}^{(0)} \, d\tau = \delta_{nn'} \delta_{jj'} \tag{4.145}$$

Thus, if $n \neq n'$ or $j \neq j'$ or if both inequalities hold, the left side of Eq. (4.145) goes to zero. If, on the other hand, $n = n'$, it is apparent that the difference $E_{n'}^{(0)} - E_{n}^{(0)}$ is zero. Under any condition then:

$$\sum_{j'} c_{nj'} \int \bar{\psi}_{nj}^{(0)} (E_{nj}^{(1)} - H') \psi_{nj'}^{(0)} \, d\tau = 0 \tag{4.146}$$

which, according to Eq. (4.145) further reduces to:

$$\sum_{j'} c_{nj'} (\delta_{jj'} E_{nj}^{(1)} - H'_{jj'}) = 0 \tag{4.147}$$

by virtue of the fact that $\int \bar{\psi}_{nj}^{(0)} E_{nj}^{(1)} \psi_{nj'}^{(0)} \, d\tau = E_{nj}^{(1)} \int \bar{\psi}_{nj}^{(0)} \psi_{nj'}^{(0)} \, d\tau$ and where we have introduced the matrix element:

$$H'_{jj'} = \int \bar{\psi}_{nj}^{(0)} H' \psi_{nj'}^{(0)} \, d\tau$$

Eq. (4.147) yields a set of equations from which, in theory at least, the $c_{nj}$ may be obtained.

Let us consider the matrix of $E_{nj}^{(1)} - H'_{jj'}$ for hydrogen:

| nlm \ nlm | (100) | (200) | (210) | (211) | (21-1) | . . . |
|---|---|---|---|---|---|---|
| (100) | $E^{(1)}$ | 0 | 0 | 0 | 0 | . . . |
| (200) | 0 | $E^{(1)}$ | $-H_{12}'$ | 0 | 0 | . . . |
| (210) | 0 | $-H_{12}'$ | $E^{(1)}$ | 0 | 0 | . . . |
| (211) | 0 | 0 | 0 | $E^{(1)}$ | 0 | . . . |
| (21-1) | 0 | 0 | 0 | 0 | $E^{(1)}$ | . . . |
| ⋮ | ⋮ | ⋮ | ⋮ | ⋮ | ⋮ | |

Table 4.3

First we may consider the reason for the disappearance of the various matrix elements. To begin with we have forbidden† the appearance of thematrix elements between states of different $n$ in obtaining Eq. (4.144). Next the angle $\varphi$ does not appear in $H'$ so that integrals of the form $\int_0^{2\pi} e^{i(m-m')\varphi} d\varphi$ will cause $H'$ to disappear for $m \neq m'$. Finally the presence of $\cos \vartheta$ in $H'$ is responsible through $\int_0^{\pi} \Theta_l(\vartheta)\Theta_{l'}(\vartheta) \cos \vartheta \cdot \sin \vartheta \, d\vartheta$ for the disappearance of $H'$ except for $l' = l \pm 1$ by virtue of the orthogonality of the associated Legendre functions.

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*$\delta_{nn}$ is the Kronecker delta of definition $\delta_{nn'} = \begin{matrix} 0 \text{ for } n \neq n' \\ 1 \text{ for } n = n' \end{matrix}$

†Failure to forbid this leads to the same result, i.e., in first order levels of different $n$ are still separated by the amount of zeroth-order.

The matrix tells us several important facts about the Stark effect. To begin with we see that the linear Stark effect has no "effect" on the energy of the ground state. Secondly, the matrix elements for $m \neq m'$ disappear. Finally, a twofold degeneracy corresponding to $m = \pm 1$ still exists in the state with $n = 2$. We might remark that for $n = 3$ the states with $m = \pm 1$ have the same energy, as do the states with $m = \pm 2$, and so on for the higher values of $n$.

Now let us return to Eq. (4.143b′), multiply through on the left by $\psi_{ml}$ and integrate over all space where we take $n' = m \neq n$ and $l = j'$. The result is:

$$a_{njn'j'} = \frac{\sum\limits_{j''} c_{nj''} H'_{n'j'nj''}}{(E_{n'}^{(0)} - E_n^{(0)})} \quad ; \quad n' \neq n \tag{4.148}$$

If Eq. (4.143c) is multiplied through on the left by $\bar{\psi}_{nj}^{(0)}$ and integrated over all space the result is:

$$C_{nj}E_{nj}^{(2)} = \sum_{n'j'} a_{njn'j'} \int \bar{\psi}_{nj}^{(0)} H' \psi_{n'j'}^{(0)} d\tau \tag{4.149}$$

From Eqs. (4.148) and (4.149) we obtain:

$$E_{nj}^{(2)} = - \sum_{n'j'} \frac{\sum\limits_{j''} c_{nj''} H'_{n'j'nj''}}{c_{nj}(E_{n'}^{(0)} - E_n^{(0)})} H'_{njn'j'}$$

$$= -E^2 \sum_{n'j'} \frac{\sum\limits_{j''} c_{nj''}(n'j' \mid er \cos \vartheta \mid nj'')}{c_{nj}(E_{n'}^{(0)} - E_n^{(0)})} (nj \mid er \cos \vartheta \mid n'j') \tag{4.150*}$$

Eq. (4.150) tells us the second order energy of our perturbed degenerate system. We may glean a few factors of importance from this equation. First it may be noted that this energy correction is proportional to the square of the electric field, or a quadratic Stark effect has been obtained. Next, matrix elements of $H'$ are still non-vanishing only for $\Delta l = \pm 1$ and $\Delta m = 0$. Finally, a fact which will be of some importance later is that now the matrix elements for changes in the principal quantum number will not disappear.

### 4.18. PRELIMINARY APPROXIMATIONS FOR THE QUANTUM BROADENING PROBLEM

Let us return to Spitzer's theory of the broadening of hydrogen lines by the electric fields of neighboring ions.[173,174] This author began with three simplifying assumptions: "(1) the matrix elements of the interaction potential between states of different total quantum number may be neglected, and . . . the other matrix elements may be computed on the assumption that the atom is in a homogeneous field of strength $Ze^2/r$ . . . (2) Each collision . . . may be assumed isolated from all others. (3) The mass of the colliding particles may be taken infinitely large."[173]

First we might point out that the "total quantum number" to which Spitzer refers is the $n$ of Eqs. (4.140), not the principal, radial quantum number $n$. The two are more or less comparable, however, and, as we may see from a comparison of Table (4.3) and Eq. (4.150), the neglect of the matrix elements for a change in the principal quantum number infers a linear Stark effect as does Assumption (1) above. We shall justify this in a moment.

The remainder of Assumption (1) supposes a homogeneous field $E$ over the "boundaries" of the atom, or, say, over the electron orbit. We have supposed this to be the case in our considerations of the Stark effect, and, if a field is imposed from "outside," there can be little objection to this. Now, however, we are

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*The alternate expression for the matrix element $(a \mid z \mid b) = \int \bar{\psi}_a z \psi_b d\tau$ is here introduced.

supposing our field to be produced by an ion, and, if the separation of the hydrogen and the ion, $r$, is not large compared to the average distance of the electron from the hydrogen nucleus, $\bar{r}_e$, this approximation surely breaks down. Thus, some lower limit $R$ must be set on $r$, and Spitzer chooses this limit as $R > 10\bar{r}_e$, although at this separation "... the perturbing electric force may deviate from its average value by as much as 20 percent."[173] Now $\bar{r}_e$ may have as its maximum value $3na_0^2/2$ — $a_0$ is the radius of the first Bohr orbit — so that $R > 8.0 \times 10^{-8}\, n^2$ where $n$ is the total quantum number. The exchange integrals, which we have not mentioned, as well as quadratic Stark effects will be small for these distances as we may show by Eqs. (4.140).

$$\frac{\Delta\nu_1}{\Delta\nu_2} = \frac{E^{(1)}}{E^{(2)}} = \frac{24n(k_1 - k_2)R^2}{n^4[17n^2 - 3(k_2 - k_1)^2 - 9m^2 + 19]a^2}$$

When $k_2 - k_1$ is set equal to $n/2$ and $m$ and 19 are neglected, the result is:

$$\frac{\Delta\nu_1}{\Delta\nu_2} \doteq \frac{3R^2}{4a^2n^4} = \frac{27}{16}\left(\frac{R}{\bar{r}_e}\right)^2 > 150$$

Assumption (2) is the binary assumption which, together with the third assumption, will become familiar ones. It is certainly obvious that the treatment of a two particle interaction is far simpler than the treatment of a three or more particle interaction. In addition, it is rather apparent that at the lower pressures the approximation should be a reasonable one by virtue of the following: The highest probability is that the separation of a single one of the surrounding molecules from the emitter is sufficiently small to insure that its interaction overshadows that of the remaining broadeners. It might be said that, although Assumption (3) is reasonable for heavy particles, this will certainly not be true where the ions are electrons.

### 4.19. THE STATE GROWTH EQUATION FOR THE ADIABATIC APPROXIMATION

To begin with, we consider the change in the potential as adiabatic so that the quantum state of the system will remain unchanged during a collision. Let us digress for just a moment on the subject of adiabatic processes, since we shall encounter them continuously in our further consideration of line broadening theories.

One is accustomed to consider an adiabatic process as one in which the entropy of the system — or the degree of disorder thereof — remains unchanged. Now if the probability that a molecule is in state $X$ has the value unity before and after the occurrence of some phenomenon which affects the molecule "system," the degree of disorder of this system remains unchanged and hence, the occurrence of the phenomenon constitutes an adiabatic process. On the other hand, if the probability for state $X$ is unity at the initiation of the process and changes by virtue of the occurrence of this process to .6 for state $X$, .3 for state $Y$, and .1 for state $Z$, the degree of system disorder has changed, and in consequence, a non-adiabatic process has occurred.

In the present adiabatic case, a two state atom with an upper state $A$ and a lower state $B$ are considered where $E_A$ and $E_B$ respectively are the energy of the two states.

Since the electric field is assumed directed along the $z$-axis of the emitting hydrogen atom, and since this electric field is radial from the perturber to the emitter — this, of course, would only be strictly correct for the one perturber assumed — the coordinate system will rotate with the passage of the ion so that the $z$-axis is always directed toward the ion. Adiabaticity requires that this rotation occur for the following reason. The quantum number $m$ specifies the projection of the angular momentum on the electric field of the ion. In order that $m$ remain constant as required by the adiabatic hypothesis the molecule must rotate with the changing direction of the ionic field.

In the state $A$ the molecule has energy $E_A(t)$ and there are no photons in the radiation field so that the unperturbed eigenfunction for the system molecule plus field is:

$$\Psi_a^{(0)} = \psi_a^{(0)}\, e^{-\frac{i}{\hbar}\int_0^t E_A(t)dt} \tag{4.151a}$$

In the state B the molecule has energy $E_B(t)$ and a photon of frequency $\nu_i$ is present in the field. The unperturbed eigenfunction is:

$$\Psi_{b_i}^{(0)} = \psi_{b_i}^{(0)}\, e^{-\frac{i}{\hbar}\int (E_B(t)+h\nu_i)dt} \tag{4.151b}$$

If Eqs. (4.151) are substituted into:

$$H\psi = i\hbar\frac{\partial}{\partial t}\psi \tag{4.152}$$

the time dependent form of the Schrodinger equation, the more familiar form of this equation results:

$$H\psi_a^{(0)} = E_A(t)\, \psi_A^{(0)}(t) \tag{4.153a}$$

$$H\psi_{b_i}^{(0)} = (E_B(t) + h\nu_i)\, \psi_{b_i}^{(0)}(t) \tag{4.153b}$$ [*]

In Eqs. (4.153) $t$ is a parameter, and $E_A(t)$ and $E_B(t)$ are the molecular level energies *as perturbed by the linear Stark effect of the ionic field.*

We now wish to introduce the molecule-field interaction[†] and ascertain the solution to Eq. (4.152) under the influence of this perturbation. The result of this perturbation will be to smear out the probability of finding the molecule-field system in state $\Psi_a^{(0)}$, $\Psi_{b_1}^{(0)}$, $\Psi_{b_2}^{(0)}$, etc. This prognostication leads us to assume a solution of the perturbed problem of the form:

$$\psi_n = a(t)\, \Psi_a^{(0)} + \sum_i b_i(t)\, \Psi_{b_i}^{(0)} \tag{4.154a}$$

Eq. (4.153) tells us that, if the system is initially unperturbed and subsequently perturbed for a time $t$, the probability that the system is in the state $\Psi_a^{(0)}$ is $|\, a(t)\, |^2$, in the state $\Psi_{b_i}^{(0)}$ is $|\, b_i(t)\, |^2$, and so on. Thus, these coefficients may well be dubbed "state growth coefficients," for this they are. Finally then, the solution of the Schrodinger equation amounts to nothing more nor less than the procuring of these coefficients. Since $\left| a(t) \exp\left(\frac{i}{h}\int_0^t E_A(t)dt\right)\right|^2 = |\, a(t)\, |^2$ and $\left| b_i(t) \exp\left[\frac{i}{\hbar}\int_0^t (E_B(t) + h\nu_i)dt\right]\right|^2 = |\, b_i(t)\, |^2$, we prefer to write Eq. (4.152a) in the equivalent form:

$$\psi_n = a(t)e^{\frac{i}{\hbar}\int E_A(t)dt}\Psi_a^{(0)} + \sum_i b_i(t)\, e^{\frac{i}{\hbar}\int (E_B(t)+h\nu_i)dt}\Psi_{b_i}^{(0)} \tag{4.154b}$$

If the molecule-field interaction Hamiltonian is taken as $H'$, Eq. (4.154b) may be substituted into Eq. (4.152) with the result:

$$a(H^0 + H')e^{\frac{i}{\hbar}\int E_A dt}\ \Psi_a^{(0)} + \sum_i b_i(H^0 + H')e^{\frac{i}{\hbar}\int (E_B+h\nu_i)dt}\ \Psi_{b_i}^{(0)} = i\hbar\dot{a}e^{\frac{i}{\hbar}\int E_A dt}\ \Psi_a^{(0)}$$

$$- E_A a e^{\frac{i}{\hbar}\int E_A dt}\ \Psi_a^{(0)} + i\hbar a e^{\frac{i}{h}\int E_A d}\frac{\partial}{\partial t}\Psi_a^{(0)} + i\hbar\sum_i \dot{b}_i e^{-\frac{i}{\hbar}\int (E_B+h\nu_i)dt}\Psi_{b_i}^{(0)}$$

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[*] For the Hamiltonian used here see *supra* Eq. (3.57b).

[†] See *supra* Chap. 3.

$$- \sum_i (E_B + h\nu_i) b_i \Psi_{b_i}^{(0)} e^{-\frac{i}{\hbar}\int (E_B + h\nu_i) dt} + ih \sum_i b_i e^{-\frac{i}{\hbar}\int (E_B + h\nu_i) dt} \Psi_{b_i}^{(0)} \tag{4.155}$$

Certain terms drop out, since $H^0 \Psi_r = ih \frac{\partial}{\partial t} \Psi_r$. In order to determine $a(t)$, let us then multiply through on the left by $\overline{\Psi}_a^{(0)}$ and integrate over all space to obtain:

$$aH'_{aa} e^{\frac{i}{\hbar}\int E_A dt} + \Sigma\, b_i H'_{ab_i} e^{\frac{i}{\hbar}\int E_A dt} = i\hbar \dot{a} e^{\frac{i}{h}\int E_A dt} - E_A a e^{\frac{i}{\hbar}\int E_A dt} \tag{4.156}$$

According to Eqs. (3.61a) and (3.63a) the diagonal matrix elements, such as $H'_{aa}$, of the field-molecule interaction disappear. Eq. (4.156) then becomes:

$$i\hbar \dot{a} = E_A(t) a(t) + \sum_i H_{ab_i} b_i(t) \tag{4.157a}$$

The multiplication of Eq. (4.155) by $\overline{\Psi}_{b_i}^{(0)}$ in like manner results in:

$$i\hbar \dot{b}_i = \{E_B(t) + h\nu_i\} b_i(t) + H_{b_i a} a(t) \tag{4.157b}$$

Eqs. (4.157) are the so-called "state growth equations," since they tell us the manner in which the state probabilities $| a(t) |^2$ and $| b_i(t) |^2$ change with time.

## 4.20. THE STARK BROADENED SPECTRAL LINE FOR THE ADIABATIC CASE

Let us assume that at time $t = 0$, the atom is in the state $A$ with no radiation present in the field. Thus, $| a(0) |^2$ is unity, and the $| b_i(0) |^2$ are zero. These requirements and Eq. (4.157a) are satisfied by:

$$a(t) = e^{-\frac{1}{2}\Gamma t} \exp\left\{ -\frac{i}{\hbar} \int_0^t E_A(\tau) d\tau \right\} \tag{4.158}$$

Now let us consider Eq. (4.157b). From the fact that the right side of this equation is a sum of two terms we may infer that $b_i(t)$ is a product of two functions. Hence:

$$b_i(t) = f(t) g(t) \tag{4.159}$$

From Eqs. (4.157b) and (4.159) we obtain:

$$g(t) \frac{df(t)}{dt} = \frac{1}{i\hbar} \left\{ E_B(t) + h\nu_i \right\} g(t) f(t) \tag{4.160a}$$

$$f(t) \frac{dg(t)}{dt} = H_{b_i a} a(t) \frac{1}{i\hbar} \tag{4.161a}$$

The solution of Eq. (4.160a) is:

$$f(t) = \exp\left\{ -2\pi i \nu_i t - \frac{1}{h} \int_0^t E_B(\tau) d\tau \right\} \tag{4.160b}$$

If we now substitute Eqs. (4.158) and (4.160b) into Eq. (4.161a) we may solve the resulting equation to obtain:

$$g(t) = -\frac{iH_{b_i a}}{\hbar} \int^t e^{-\frac{1}{2}\Gamma T} dT \exp\left\{ 2\pi i \nu_i T + \frac{i}{\hbar} \int_0^T (E_B(\tau) - E_A(\tau)) d\tau \right\} \tag{4.161b}$$

Eqs. (4.160b) and (4.161b) may now be substituted into Eq. (4.159) to yield:

$$b_i(t) = -\frac{iH_{bia}}{\hbar}\exp\left\{-2\pi i\nu_i t - \frac{i}{\hbar}\int_0^T E_B(\tau)d\tau\right\}.$$

$$\cdot\int_0^t e^{-\frac{1}{2}\Gamma T}dT\exp\left\{2\pi i\nu_i T + \frac{i}{\hbar}\int_0^T (E_B(\tau) - E_A(\tau))d\tau\right\} \tag{4.162}$$

By time $t = \infty$ the emitter will certainly be in the ground state, and a photon of frequency $\nu_i$ will be in the field. The intensity distribution in the spectral line is surely given by $| b_{i(\nu)}(\infty) |^2$, since this will represent the probabilities for the appearance of these various frequencies. If we call $I'(\nu)$ the intensity of the frequency $\nu$ there results:

$$I'(\nu) = \frac{(H_{bia})^2}{\hbar^2}\left|\int_0^\infty e^{-\frac{1}{2}\Gamma T}dT\exp\left\{2\pi i\nu_i T + \frac{i}{\hbar}\int_0^T (E_B(\tau) - E_A(\tau))d\tau\right\}\right|^2 \tag{4.163}$$

If we let $E_{A0}$ and $E_{B0}$ be the unperturbed energies of te $A$ and $B$ states respectively, we may utilise the equations:

$$\Delta_A(t) = \left\{E_A(t) - E_{A0}\right\}\Big/\hbar \tag{4.164a}$$

$$\Delta_B(t) = \left\{E_B(t) - E_{B0}\right\}\Big/\hbar \tag{4.164b}$$

$$x = 2\pi(\nu - \nu_{AB}) \tag{4.164c}$$

to transform Eq. (4.163) to:

$$I(x) = \frac{\Gamma}{2\pi}\left|\int_0^\infty e^{i(x+\frac{1}{2}i\Gamma)T}dT\exp\left\{-i\int_0^T (\Delta_A(\tau) - \Delta_B(\tau))d\tau\right\}\right|^2 \tag{4165}$$

where $I(x)dx$ over all $x$ has been normalized to unity.

From Eq. (4.140a):

$$\Delta_A(t) = \frac{3hn_A}{2\,me}E\,(k_{2A} - k_{1A}) \tag{4.166}$$

We have supposed the field $F$ to be produced by an ion of, say, charge $Ze$ at distance $r(t)$. We assume straight paths for the perturbing ions, and we now let $v$ be the ionic velocity, $R$ the distance of closest approach and $t_0$ the time of closest approach. The results:

$$E = \frac{Ze}{r^2(t)} \tag{4.167a}$$

$$r^2(t) = R^2 + v^2(t - t_0)^2 \tag{4.167b}$$

$$\Delta_A(t) - \Delta_B(t) = \frac{g/h}{R^2 + v^2\,(t - t_0)^2} \tag{4.167c}$$

$$g/\hbar = 3hgZ/2m = 1.73gZ \tag{4.167d}$$

$$g = n_A(k_{2A} - k_{1A}) - n_B(k_{2B} - k_{1B}) \tag{4.167e}$$

Eqs. (4.167c) may be integrated as follows:

$$\int_{t_0}^{T} \left\{ \Delta_A(\tau) - \Delta_B(\tau) \right\} d\tau = \frac{g}{\hbar R v} \tan^{-1} \frac{v(T - t_0)}{R} \tag{4.168}$$

Now surely if we allow $T$ in Eq. (4.168) to have the limits $-\infty$ and $+\infty$, we will obtain the total phase shift of the emitted radiation due to a collision. The result of taking these limits is, of course, a shift of $\pi\Upsilon$ where:

$$\Upsilon = \frac{g}{\hbar R v} \tag{4.169}$$

It may be noted that in Eq. (4.165) we desire the limits 0 and $T$ on the integral in the exponential, whereas, we have taken the limits $t_0$ and $T$ in Eq. (4.168). A reasonable approximation is to assume that between 0 and $t_0$ one half of our total phase shift will occur so that if we subtract $\frac{1}{2}\pi\Upsilon$ from Eq. (4.168) we shall obtain the desired result for Eq. (4.165). Let us now substitute Eq. (4.168) into Eq. (4.165) and integrate by parts to obtain:

$$I(x) = \frac{\Gamma}{2\pi} \frac{1}{(x^2 + (\frac{1}{2}\Gamma)^2)} \Bigg| \left\{ e^{i(x+\frac{1}{2}i\Gamma)T} \exp\left[ -i\Upsilon \tan^{-1} \frac{v(T - t_0)}{R} \right] \right\}_0^{\infty}$$

$$+ e^{-\frac{1}{2}i\pi\Upsilon} \frac{v\Upsilon}{R} \int_0^{\infty} \frac{1}{1 + \frac{v^2(T - t_0)^2}{R^2}} e^{i(x+\frac{1}{2}i\Gamma)T} \exp\left[ -i\Upsilon \tan^{-1} \frac{v(T - t_0)}{R} \right] dT \Bigg|^2 \tag{4.170a}$$

Since: $$e^{i(x+\frac{1}{2}i\Gamma)T} \exp\left[ -i\Upsilon \tan^{-1} \frac{v(T - t_0)}{R} \right] \Bigg|_0^{\infty} = e^{-\frac{1}{2}\Gamma\infty} e^{ix\infty} e^{-i\gamma\frac{\pi}{2}} - e^0 e^{i\gamma\pi} = 0 - 1$$

Eq. (4.170a) becomes:

$$I(x) = \frac{\Gamma}{2x} \frac{1}{[\pi^2 + (\frac{1}{2}\Gamma)^2]} \left| i + \frac{\Upsilon v}{R} e^{-\frac{1}{2}i\pi\gamma} \int_0^{\infty} \frac{e^{i(x+\frac{1}{2}i\Gamma)T} \exp\left[ -i\Upsilon \tan^{-1} \frac{v(T-t_0)}{R} \right]}{1 + \frac{v^2(T - t_0)^2}{R^2}} dT \right|^2 \tag{4.170b}$$

Now let us take a factor $\exp\,(x + \frac{1}{2}\,i\Gamma)\,t_0$ out of the integral and partially complete the absolute square to obtain:

$$I(x) = \frac{\Gamma}{2\pi[x^2+(\frac{1}{2}\Gamma)^2]} \left\{ 1 + e^{-\Gamma t_0} \frac{\Upsilon^2 v^2}{R^2} \left| \int_{-t_0}^{\infty} \frac{e^{i(x+\frac{1}{2}i\Gamma)t} \exp\left[ -i\Upsilon \tan^{-1} \frac{v\tau}{R} \right] d\tau}{1 + \frac{v^2\tau^2}{R^2}} \right|^2 \right\} \tag{4.170c}$$

where $T = \tau + t_0$, and where, "... unless $x$ is comparable with $\Gamma$, the process of averaging over $t_0$ will remove the cross product when the square of the absolute value is taken in. . . ."[173] Eq. (4.170b). Now let us extend the lower limit to $-\infty$, — this will have little effect — assume $x \gg \Gamma$ and neglect the damping factor under the integral to yield:

$$I(x) = \frac{\Gamma}{2\pi x^2} \left\{ 1 + e^{-\Gamma t_0} \frac{\Upsilon^2 v^2}{R^2} \left| \int_{-\infty}^{+\infty} \frac{e^{ix\tau} \exp\left[ -i\Upsilon \tan^{-1} \frac{v\tau}{R} \right]}{1 + \frac{v^2\tau^2}{R^2}} d\tau \right| \right\} \tag{4.170d}$$

We now let:

$$u = \frac{v\tau}{R} \tag{4.171a}$$

$$\xi = \frac{xR}{v} \tag{4.171b}$$

and integrate Eq. (4.170d) over $t_0$ to obtain, if $\Omega(\Upsilon, \xi) = \frac{v}{R}$ is the number of collisions per second:

$$I(x) = \frac{\Gamma}{2\pi x^2}\left\{1 + \frac{\Omega(\Upsilon, \xi)}{\Gamma}\Upsilon^2 f_\Upsilon^2\ (\xi)\right\} \tag{4.172}$$

where

$$f_\Upsilon(\xi) = \int_{-\infty}^{+\infty} \frac{e^{i(\xi u - \gamma \tan^{-1} u)}}{1 + u^2}\, du \tag{4.173}$$

Let us first consider the result of the two limiting cases (1) $\xi$ very large and (2) $\xi$ approaches zero. In order to consider Case (1) let us integrate Eq. (4.173) by parts:

$$\lim_{\xi \to \infty} f_\Upsilon(\xi) = \lim_{\xi \to \infty}\left\{\frac{e^{-i\Upsilon \tan^{-1} u} e^{i\xi u}}{i\xi}\Bigg|_{-\infty}^{+\infty} + \frac{\Upsilon}{\xi}\int_{-\infty}^{+\infty} \frac{e^{i\xi u}\, e^{-i\Upsilon \tan^{-1} u}}{(1+u^2)^2}\, du\right\} = 0$$

From this result it is apparent that $f_\Upsilon(\xi)$ goes to zero for sufficiently large $\xi$, and, as a result, the line profile is independent of the number of collisions for $x$ large enough. For Case (2) straight integration for $\xi = 0$ yields $\Upsilon f_\Upsilon(0) = 2 \sin \frac{\Upsilon\pi}{2}$. Thus $\Upsilon^2 f_\Upsilon^2(0) = 4 \sin^2 \frac{\Upsilon\pi}{2}$ and the average value of this expression is, of course, two. If $\Omega_{1/\pi}$ is the total number of collisions for which the phase shift is greater than unity or $\Upsilon > 1/\pi$ as required by the Weisskoff theory, we obtain, by neglecting the unity in Eq. (4.172), the Weisskoff line shape for $\xi$ small.

$$I(x) = \frac{\Omega_{1/\pi}}{\pi x^2} \tag{4.174}$$

These are the two limiting results for Eq. (4.172), but Eq. (4.173) may be integrated, if rather laboriously. To begin with:

$$e^{-i\tan^{-1} u} = \cos(\tan^{-1} u) - i \sin(\tan^{-1} u) =$$

$$= \cos[\tan^{-1} u]\,[1 - iu] = \frac{(1 - iu)}{(1 + u^2)^{\frac{1}{2}}} \tag{4.175}$$

Substituting Eq. (4.175) into Eq. (4.173) and expanding $(1 - iu)^\Upsilon$ according to the binomial theorem we obtain:

$$f_\Upsilon(\xi) = \int_{-\infty}^{+\infty} \frac{e^{iu\xi}}{(1+u^2)^{1+\frac{1}{2}\Upsilon}}\, du \left[1 - i\Upsilon u + \frac{\Upsilon(\Upsilon - 1)\,(-iu)^2}{2!} + \ldots + (-iu)^\Upsilon\right] \tag{4.176}$$

Now since the first integral in Eq. (4.176) is an even function we may surely write:

$$\int_{-\infty}^{+\infty} \frac{e^{iu\xi}}{(1+u^2)^{1+\frac{1}{2}\Upsilon}}\, du = 2\int_{0}^{\infty} \frac{\cos u\xi}{(1+u^2)^{1+\frac{1}{2}\Upsilon}}\, du$$

Basset has shown that:*

$$K_l(xz) = \frac{\Gamma(l+\frac{1}{2})\,(2z)^l}{x^l\Gamma(\frac{1}{2})}\int_0^\infty \frac{\cos xu\,du}{(u^2+z^2)^{l+\frac{1}{2}}} \tag{4.177a}$$

where $K_l(xz)$ is the Bessel function of the second kind. If we let $g\Upsilon(\xi)$ be the first integral in Eq. (4.176), we obtain:

$$g\Upsilon(\xi) = \frac{2^{\frac{1}{2}(1-\Upsilon)}\sqrt{\pi}}{\Gamma(\frac{1}{2}\Upsilon+1)}\,\xi^{\frac{1}{2}(1+\Upsilon)}K_{\frac{1}{2}(1+\Upsilon)}(\xi) \tag{4.177b}$$

Eq. (4.176) then becomes:

$$f_\Upsilon(\xi) = g_\Upsilon(\xi) \mp \Upsilon\frac{d}{d\xi}g_\Upsilon(\xi) + \frac{\Upsilon(\Upsilon-1)}{2!}\,\frac{d^2}{d\xi^2}\,g_\Upsilon(\xi) \mp \ldots \tag{4.178}$$

If, in the expression for the hypergeometric function $F(a,b,c,z)$ we set $bz = x$ and allow $b$ to approach infinity, we obtain the confluent hypergeometric function (series):[209]

$${}_1F_1(\alpha,\gamma,x) = 1 + \frac{\alpha}{\gamma}x + \frac{\alpha(\alpha+1)}{2!\gamma(\gamma+1)}x^2 + \ldots$$

Now if $\Upsilon$ is an even positive integer, we may use an expression due to Oltramare:† [180]

$$\int_0^\infty \frac{\cos xu}{(u^2+z^2)^n}\,du = \frac{(-1)^{n-1}\pi}{z^{2n-1}(n-1)!}\left[\frac{d^{n-1}}{dp^{n-1}}\,\frac{e^{-xzp}}{(1+p)^n}\right]_{\gamma=1}$$

to obtain for Eq. (4.176):

$$f_{2\alpha}(\xi) = 2\pi\,(-1)^{\alpha-1}\xi\,e^{-\xi}{}_1F_1(1-\alpha,\,2,\,2\xi) \tag{4.179}$$

An inspection of Eq. (4.176) for $f_\Upsilon(\xi)$ is sufficient to show that the integral of $f_\Upsilon^2(\xi)$ over $\xi$ is independent of $\Upsilon$. Now surely:

$$\int_{-\infty}^{+\infty} f_\Upsilon^2(\xi)d\xi = \iiint_{-\infty}^{+\infty} \frac{e^{i\xi(u-u')}}{(1+u^2)\,(1+u'^2)}\,du\,du'd\xi \tag{4.180}$$

Let us write out the Fourier transform of $f(x) = f_\Upsilon^2(\xi)$ as follows:

$$f(x) = \frac{1}{2\pi}\iint_{-\infty}^{+\infty} f(\zeta)e^{ik(x-\zeta)}\,dk d\zeta \tag{4.181}$$

If in Eq. (4.180) we take $f(u') = \dfrac{1}{(1+u^2)\,(1+u'^2)}$, then in essence we have, from Eq. (4.180), $2\pi f(u)$ integrated over $u$. Thus, Eq. (4.180) becomes:

$$\int_{-\infty}^{+\infty} f_\Upsilon^2(\xi)d\xi = \int_{-\infty}^{+\infty} 2\pi f(u)du = 2\pi\int_{-\infty}^{+\infty}\frac{du}{(1+u^2)^2} = \pi^2 \tag{4.182}$$

This then will essentially be a normalizing factor for our spectral line.

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*See also reference 215.

† We could probably also use a relation obtained by Malmstén[169]

$$\int_0^\infty \frac{\cos ax}{(1+x^2)^{n+1}}\,dx \sim \frac{\pi e^{-a}}{2^{2n+1}n!}\left[(2a)^n + {}_nC_1\,(n+1)\,(2a)^{n-1} + {}_nC_2\,(n+1)(n+2)\,(2a)^{n-2} + \ldots\right] \text{ for the same result.}$$

Fig. (4.7) gives the results of Spitzer's calculations for several values of $\Upsilon \cdot x_{\max}$ is nothing more than $q/\hbar R^3$. The limiting value for $\Upsilon = \infty$ corresponds, of course, to zero velocity according to Eq. (4.169). Thus, this value of $\Upsilon$ should yield the line shape as given by the Statistical theory.* Spitzer obtains the limiting value of $\Upsilon f_\Upsilon^2(\xi)$ from the Statistical theory rather than from Eq. (4.173) going back to Eq. (4.167b) to do so. The result is:

$$\lim_{\Upsilon \to \infty} \Upsilon f_\Upsilon^2(\xi) = \frac{2\pi(x-1)^{1/2}}{x_{\max}^{1/2}} \tag{4.183}$$

which together with Eq. (4.172) will give the inverse 3/2 dependence on $x$ as predicted by the Statistical theory.

In obtaining Eq. (4.172) we have assumed that the change in the potential may be considered adiabatic, and we shall now proceed to demonstrate that the breakdown of the adiabatic hypothesis results in a change in $f_\Upsilon(\xi)$.

## 4.21. THE EFFECT OF A NON-ADIABATIC ASSUMPTION

We may recall that the interaction between the radiation field and the atom resulted in the appearance, of $\Gamma$, and, since we have assumed $x > \frac{1}{2}\Gamma$ at any rate, we neglect, with Spitzer, this interaction. For this case:†

$$i\hbar\frac{\partial\Psi}{\partial t} = H(t)\Psi \tag{4.184a}$$

where

$$\Psi = \sum_r a_r(t)\,\psi_r(t) \tag{4.184b}$$

We substitute Eq. (4.184b) into Eq. (4.184a), multiply through on the left by $\bar{\psi}_s(t)$, and integrate over all space to obtain

$$-\dot{a}_s = i\,\frac{E_s(t)}{\hbar}\,a_s(t) + \sum_r k_{sr}a_r(t) \tag{4.185a}$$

since: $H(t)\psi_r(t) = E_r(t)\psi_r(t)$ instantaneously,
where:

$$k_{sr}(t) = \int \bar{\psi}_s(t)\,\frac{\partial\psi_r(t)}{\partial t}\,d\tau \tag{4.185b}$$

We may obtain $k_{sr}$ in slightly different form by first differentiating Eq. (4.156) to obtain:

$$\left(\frac{\partial H}{\partial t} - \frac{\partial E_r}{\partial t}\right)\psi_r = \left[E_r(t) - H(t)\right]\frac{\partial\psi_r}{\partial t} \tag{4.186a}$$

If Eq. (4.186a) is multiplied through on the left by $\bar{\psi}_s(t)$ and integrated over all space, the result is:

$$\left(\frac{\partial H}{\partial t}\right)_{sr} = [E_r(t) - E_s(t)]\,k_{sr};\; s \neq r \tag{4.186b}$$

where the $E_s(t)$ may be obtained due to the Hermitian** quality of $H(t)$, that is $\bar{H}_{rs} = H_{sr}$. Since $k_{ss} = 0$, Eq. (4.186b) is sufficient.

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*See *infra* Chap. 5.

† The derivation carried out here was first performed in an identical fashion for this case by Guttinger.[illegible]

** We may recall that an Hermitian matrix is self adjoint, that is, $\| A \|^{+} = \| \tilde{A} \| = \| A \|$.

Eq. (4.167a) gives the field, and we assume that the ion is moving in the $y_e z_e$ plane where the subscript $e$ refers to the electronic coordinates of the emitter. In addition, the ion is supposed moving parallel to the $Y$ axis. For simplicity, let us consider Fig. (4.8).

If $\underline{\mu}$ is the electric dipole moment of the molecule, the interaction is $\underline{\mu} \cdot \mathbf{E} = \mu_x E_x + \mu_y E_y + \mu_z E_z$. Then from Fig. (4.8), the time dependent portion of this Hamiltonian is $\mu_z E_z = -\dfrac{z_e Ze^2}{r^2(t)}$

It is further apparent from the figure that:

$$r^2 = R^2 + v^2(t - t_0)^2 \quad \longleftrightarrow \quad \frac{dr}{dt} = \frac{v^2(t - t_0)}{r} \tag{4.187a}$$

since $R$ is a constant $t$. An inertial $Y$-axis is taken as shown in Fig. (4.8) and an inertial $Z$-axis is taken as corresponding to $R$. A study of the figure tells us that.

$$Y_e = z_e \sin \vartheta + y_e \cos \vartheta$$

$$Z_e = z_e \cos \vartheta - y_e \sin \vartheta$$

Differentiation of these relations, multiplication of the first by $\sin \vartheta$ and the second by $\cos \vartheta$, and addition of the resulting expressions yields:

$$\frac{dz_e}{dt} = y_e \frac{d\vartheta}{dt}$$

but:

$$\frac{d\vartheta}{dt} = \frac{v \cos \vartheta}{r} = \frac{vR}{r^2}$$

so that:

$$\frac{\partial z_e}{\partial t} = \frac{y_e vR}{r^2} \tag{4.187b}$$

Utilizing Eqs. (4.187a) and (4.187b) we may find:

$$\frac{\partial H}{\partial t} = -Ze^2 \frac{\partial}{\partial t} \frac{z_e}{r^2} = \frac{2Zz_e e^2}{r^3} \frac{dr}{dt} - Z\frac{e^2}{r^2} \frac{\partial z_e}{\partial t}$$

$$= \frac{Ze^2 v}{r^4(t)} \left\{ 2z_e v (t - t_0) - y_e R \right\} \tag{4.187c}$$

and we need only the $y_e R$ term since we may recall that for states of the same total quantum number, the matrix of $z_e$ is diagonal.

From Eq. (4.184a):

$$i\hbar \frac{\partial \psi_s}{\partial t} = E_{ss} = H(t) \psi_s$$

so that, when we multiply through on the left by $\bar{\psi}_s$, and integrate over all space, we obtain:

$$E_s = (H(t))_{ss} = (\underline{\mu} \cdot \mathbf{E})_{ss} = -\frac{Ze^2 z_{ss}}{r^2(t)} \tag{4.188}$$

Combining Eqs. (4.186b), (4.187), and (4.188) we obtain

$$R_{sr} = \frac{vR}{r^2(t)} \frac{y_{sr}}{z_{rr} - z_{ss}} \tag{4.189}$$

Now letting,

$$\left\{ v^2 (t - t_0)^2 + R^2 \right\} dw = vRdt \tag{4.190a}$$

$$w = \tan^{-1} \frac{v(t - t_0)}{R} \tag{4.190b}$$

in Eq. (4.185a), and substituting for $r^2(t)$ from Eq. (4.188) we obtain:

$$\frac{da_s}{dw} + i\Upsilon_{ss}a_s + \sum_{r \neq s} \frac{y_{sr}}{z_{rr} - z_{ss}} a_r = 0 \tag{4.191a}$$

where:

$$\Upsilon_{ss} = -\frac{Ze^2 z_{ss}}{\hbar vR} \tag{4.191b}$$

Eq. (4.191a) for the coefficients $a$ may be solved for any specific case given a solver with sufficient time and patience. Spitzer's time and patience extended through the first excited state of hydrogen, and we shall now consider his example.

In obtaining Table (4.3) we found $\Delta m = 0$ since, in our operator, $\varphi$ did not occur due to the lone presence of $z$. In those cases in which our operator contains $y$ or $x$, however, $\varphi$ will appear and we find, for example, since $y = r \sin \vartheta \sin \varphi$:

$$\int_0^{2\pi} e^{-im\varphi} \sin \varphi \, e^{im'\varphi} \, d\varphi = \frac{1}{2i} \int_0^{2\pi} [e^{-i(m-m'-1)} - e^{-i(m-m'+1)}] \, d\varphi$$

Thus, the matrix elements of $y$ fail to disappear only for $\Delta m = \pm 1$.

Let us write down the deferred eigenfunctions of hydrogen in parabolic coordinates:

$$\psi_{k_1k_2m} = \frac{1}{\sqrt{2\pi}} u_1(\xi) u_2(\eta) \, e^{im\varphi} \tag{4.192a}$$

$$u_1(\eta) = \frac{\sqrt{k_1!}}{k_1 + (m!)^{3/2}} e^{-\frac{1}{2}\epsilon\eta} \, \eta^{\frac{1}{2}m} \, \epsilon^{\frac{1}{2}(m+1)} \, L^m_{k_1+m}(\epsilon\eta) \tag{4.192b}$$

$$u_2(\xi) = \frac{\sqrt{k_2!}}{k_2 + (m!)^{3/2}} e^{-\frac{1}{2}\epsilon\xi} \, \xi^{\frac{1}{2}m} \, \epsilon^{\frac{1}{2}(m+1)} \, L^m_{k_2+m}(\epsilon\xi) \tag{4.192c}$$

Our first excited state has the possible functions $\psi_{100}$, $\psi_{00-1}$, $\psi_{010}$, and $\psi_{001}$ which we may designate as $\psi_1$, $\psi_3$, $\psi_4$, and $\psi_2$. The matrix elements of $z$ will be the matrix elements of $\frac{\eta - \xi}{2}$ according to Eq. (4.138). As an example of the type of relation which we desire we may consider the following:

$$\left(\frac{\eta - \xi}{2}\right)_{11} = z_{11} = \frac{A}{2\pi} \int e^{-\epsilon\eta} \, \epsilon\eta \, [L_1{}^0(\epsilon\eta)]^2 \, d\eta \int u_2{}^2(\xi) \, d\xi \int d\varphi - \frac{A}{2\pi} \int u_1{}^2(\xi) \, d\xi$$

$$\cdot \int e^{-\epsilon\xi} \, \epsilon\xi \, [L_0{}^0(\epsilon\xi)]^2 \, d\xi \int d\varphi = -\left[\frac{A}{2} \int e^{-\epsilon\eta} \, \epsilon\eta \, [L_0{}^0(\epsilon\eta)]^2 \, d\eta \int u_2{}^2(\xi) \, d\xi \int d\varphi\right.$$

$$\left. - \frac{A}{2\pi} \int u_1{}^2(\eta) \, d\eta \int e^{-\epsilon\xi} \, \epsilon\xi \, [L_1{}^0(\epsilon\xi)]^2 \, d\xi \right] = -z_{44} = -\left(\frac{\eta - \xi}{2}\right)_{44}$$

In this manner we arrive at the relations:

$$z_{11} = -z_{44} \; ; \quad z_{22} = z_{33} = 0$$

$$y_{12} = y_{21} = y_{13} = \ldots = y_{34} = -\tfrac{1}{2}z_{11}$$

Eqs. (4.169) and (4.167) tell us that for the case where the lower state involved in a transition is unperturbed — which the ground state certainly is — $\Upsilon_{ss} = \Upsilon$. Using this fact together with Eq. (4.193) in Eq. (4.191) we obtain:

$$\frac{da_1}{dw} + i\Upsilon a_1 + \tfrac{1}{2}\left(a_2 + a_3 + \tfrac{1}{2}a_4\right) = 0 \tag{4.194a}$$ *

$$\frac{da_2}{dw} - \tfrac{1}{2}\left(a_1 - a_4\right) = 0 \tag{4.194b}$$

$$\frac{da_3}{dw} - \tfrac{1}{2}\left(a_1 - a_4\right) = 0 \tag{4.194c}$$

$$\frac{da_4}{dw} - i\Upsilon a_4 - \tfrac{1}{2}\left(\tfrac{1}{2}a_1 + a_2 + a_3\right) = 0 \tag{4.194d}$$

In the usual manner we may assume $a(t) = a(t_0)\exp(i\,\sigma\,w)$ to obtain the secular determinant for the $a_i$:

$$\begin{vmatrix} i(\sigma + \Upsilon) & \tfrac{1}{2} & \tfrac{1}{2} & \tfrac{1}{4} \\ -\tfrac{1}{2} & i & 0 & \tfrac{1}{2} \\ -\tfrac{1}{2} & 0 & i & \tfrac{1}{2} \\ -\tfrac{1}{4} & -\tfrac{1}{2} & -\tfrac{1}{2} & i(\sigma - \Upsilon) \end{vmatrix} = 0$$

whose solution is $\sigma = 0, 0, \pm(\Upsilon^2 + \frac{17}{16})^{1/2}$. If the coefficients of $a_4$ in Eq. (4.194a) and $a_1$ in Eq. (4.194d) were zero the solution would be $\sigma = 0, 0, \pm(\Upsilon^2 + 1)^{1/2}$. The $a_i$ themselves could now be found.

We shall defer the proof until Chapter 6, but Weisskopf[193] had attempted to show that the line profile is given by the absolute square of the Fourier transform of the state function. (There are certainly objections to this proof, but since one of them applies to Spitzer's approach as well,† these objections can reasonably be overlooked here.) Of these state functions it is quite obvious we shall have three, one corresponding to $\sigma = 0$, the second given by:

$$a(t) = a(t_0)\exp\left[i\sigma w\right] = a(t_0)\exp\left\{i\left(\Upsilon^2 + \frac{17}{16}\right)^{1/2}\tan^{-1}\frac{v(t - t_0)}{R}\right\} \tag{4.195}$$

and the third the complex conjugate of the second. Thus the lowest hydrogen line has been split into three components.

If we utilize Weisskopf's assertion, a comparison of Eq. (4.195) with Eq. (4.170d) tells us that the line profile will still be given by Eq. (4.172) where now $f_r(\xi)$ is replaced by $f_\sigma(\xi)$. This then is essentially the effect of the breakdown of the adiabatic hypothesis on the profile of the lowest hydrogen line.

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*Spitzer leaves $\frac{1}{2}a_4$ out of this equation, although Eq. (4.191a) would appear to require it:

$$\frac{y_{14}}{z_{44} - z_{11}}\,a_4 = \frac{-\frac{1}{2}z_{11}}{-z_{11} - z_{11}}\,a_4 = \tfrac{1}{2}a_4$$

† The principal objection is the use of rectilinear motion in a central force problem.

## 4.22. THE BORN APPROXIMATION FOR THE STARK BROADENING PROBLEM

Now let us take as our Hamiltonian:

$$H_a + H_f + V + H' = H \tag{4.196}$$

where $H_a$ is the unperturbed atomic Hamiltonian, $H_f$ the unperturbed field Hamiltonian, $H'$ the atom-field interaction, and $V$ the ionic field Hamiltonian. We suppose there to be two upper states $A_1$ and $A_2$ of equal unperturbed energy $E_{A0}$ and two lower states $B_1$ and $B_2$ of equal unperturbed energy $E_{B0}$. We let $\Gamma$ be the probability coefficient for a transition from $A_1$ to $B_1$ per unit time.

We assume that our perturbed eigenfunction may be expanded in terms of the four unperturbed eigenfunctions of the states which we are considering as:*

$$\psi = a_1\psi_1 + a_2\psi_2 + b_1\psi_1 + b_2\psi_2 = \sum_i c_i\psi_i \tag{4.197}$$

Although it will prove a somewhat laborious procedure, let us, for clarity's sake, work out the equation for $\dot{a}_1$ specifically.

To begin with Eqs. (3.57b), (3.57b′), and (3.57c′) tell us our non-relativistic Hamiltonian for radiation plus particles. To this, of course, we must needs add $H'$.

Into the equation:

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi$$

we substitute (neglecting the second term in Eq. (3.57b)) Eqs. (4.196) and (4.197) to obtain:

$$ih\,(\sum_i \dot{c}_i\psi_i + \sum_i c_i\dot{\psi}_i) = \sum_i c_iH\psi_i \tag{4.198a}$$

In the usual manner we multiply through on the left by $\bar{\psi}_1$ and integrate over all space. First, it is apparent from Eq. (3.57b) that the contributions of $H_f$ will disappear either due to eigenfunction orthogonality or due to the fact that in state $a_1$ we assume no photons in the field so that all $n$ in $\sum_t n_th\nu_t$ are zero. Secondly the $H_a$ and the $E_a$ diagonal term will obviously disappear. We are thus left with, after orthogonality has relieved us of several terms of the form $\dot{c}_i\psi_i$ and $c_i\psi_i$ $(i \neq 1)$:

$$i\hbar\dot{a}_1 = a_1H_{11}' + a_2H_{12}' + b_1H_{13}' + b_2H_{14}' + \sum_i c_iV_{1i} \tag{4.198b}$$

Now $b_1V_{13}$ and $b_2V_{14}$ disappear due to the fact that the matrix elements of the ionic field disappear for changes in the total quantum number. Finally Eq. (3.63a) tells us that $a_1H_{11}'$ and $a_2H_{12}'$ disappear so that Eq. (4.198b) becomes:

$$i\hbar\dot{a}_1 = a_1V_{11} + a_2V_{12} + b_1H_{13}' + b_2H_{14}' \tag{4.198c}$$

Let us notice that Eq. (4.158) infers a value $-\frac{1}{2}\,i\hbar\Gamma a(t)$ for the sum on the right of Eq. (4.157a). In essence we again make the same assumption — $b_1H_{13}' + b_2H_{14}'$ corresponds to the sum in question — to obtain:

$$i\hbar a_1 = \hbar\Delta_{A1}\,(t)a_1 + \hbar K_A\,(t)a_2 - \tfrac{1}{2}\,i\hbar\Gamma a_1 \tag{4.198d}$$

where we have let $\hbar\Delta_{A1}(t)$ be the diagonal and $\hbar K_A(t)$ the off-diagonal matrix elements of $V$ as in Eqs. (4.164). In like manner we let $\hbar\Delta_{A2}(t)$be the other diagonal matrix element in the upper state, $\hbar\Delta_{B1}(t)$ and $\hbar\Delta_{B2}(t)$ the diagonal matrix elements of the lower state, and $\hbar K_B(t)$ the off-diagonal matrix elements of the lower

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*In doing this we tacitly infer that only four states exist.

state. Thus, we obtain for $\dot{a}_1$, and analogously for the time derivatives of the other state growth coefficients, the following:

$$\dot{a}_1 = -i\Delta_{A1}(t)a_1 - iK_A(t)a_2 - \tfrac{1}{2}\Gamma a_1 \tag{4.199a}$$

$$\dot{b}_{1s} = -i(x + \Delta_{B1}(t))b_{1s} - iK_B(t)b_{2s} - iH'_{AB_s}a_1 \tag{4.199b}$$

$$\dot{b}_{2s} = -i(x + \Delta_{B2}(t))b_{2s} - i\,\overline{K_B(t)}\,b_{1s} \tag{4.199c}$$

where $x$ is still given by Eq. (4.164c).

From Eq. (4.199a) it is apparent that $a_1(t)$ will be of the form:

$$a_1(t) = e^{-\frac{1}{2}\Gamma(t)}\,h_1(t) \tag{4.200a}$$

and differentiation shows that Eq. (4.199a) is satisfied if we take for $h_1(t)$ the following:

$$h_1(t) = \exp\,(-i\int_0^t \Delta_{A1}(\tau)\,d\tau)\,\{\,h_1(0) - i\int_0^t K_A(\mathrm{T})a_2(\mathrm{T})\cdot$$

$$\cdot\exp\,(i\int_0^{\mathrm{T}} \Delta_{A1}(\tau)d\tau - \tfrac{1}{2}i\Gamma\mathrm{T})d\mathrm{T}\} \tag{4.200b)*}$$

Eqs. (4.200) surely satisfy the boundary condition $a_1(0) = h_1(0)$.

From Eqs. (4.199b) and (4.199c) there then results:

$$b_{1s}(t) = -i\overline{p_1(t)}\int_0^t p_1(\mathrm{T})d\mathrm{T}\,\{H_{AB_s}{}'e^{-\frac{1}{2}\Gamma t}\,h_1(\mathrm{T}) + -K_B(\mathrm{T})b_{2s}(\mathrm{T})\} \tag{4.201a}$$

$$b_{2s}(t) = -i\overline{p_2(t)}\int_0^t p_2(\mathrm{T})\,d\mathrm{T}\,\overline{K_B(\mathrm{T})}\,b_{1s}(\mathrm{T}) \tag{4.201b}$$

where:

$$p_1(t) = \exp\,\{\,ixt + i\int_0^t \Delta_{B1}(\tau)d\tau\} \tag{4.201c}$$

$$p_2(t) = \exp\,\{\,ixt + i\int_0^t \Delta_{B2}(\tau)d\tau\} \tag{4.201d}$$

We shall not go through the succeeding steps in detail, but merely sketch them in. Spitzer next assumed, say, $b_{1s}(t)$ as a "series of successive approximations,"

$$b_{1s}(t) = b_{1s}{}^{(0)}(t) + b_{1s}{}^{(1)}(t) + b_{1s}{}^{(2)}(t) + \ldots \tag{4.202}$$

$b_{1s}{}^{(0)}(t)$ is obtained from Eq. (4.201a) by neglecting $K_B$ and integrating by parts. This result is substituted into Eq. (4.201b) to obtain $b_{2s}{}^{(1)}(t)$, and this latter result finally utilized to find $b_{1s}{}^{(2)}(t)$. In addition $b_{2s}{}^{(0)}$, $b_{1s}{}^{(1)}$, and $b_{2s}{}^{(2)}$ are shown to vanish. There ultimately results:

$$|\,b_{1s}(\infty)|^2 + |\,b_{2s}(\infty)|^2 = \frac{|\,H_{AB_s}{}'\,|^2}{x^2 + (\frac{1}{2}\Gamma)^2}\Big[\,|\,h_1(0)\,|^2\,\{\,1 + |\int_0^\infty l(\mathrm{T})d\mathrm{T}\,|^2$$

$$- 2\,R\,[\int_0^\infty l(\tau)d\tau\int_0^\infty \overline{l(\mathrm{T})}d\mathrm{T}\,]\,\} + \left|\int_0^\infty p_1(\mathrm{T})e^{-\frac{1}{2}\Gamma\mathrm{T}}d\mathrm{T}\left\{\frac{dh_1}{d\mathrm{T}} + i\Delta_{B1}h_1\right\}\right|^2$$

$$+ |\int_0^\infty p_2(\mathrm{T})e^{-\frac{1}{2}\Gamma\mathrm{T}}d\mathrm{T}K_Bh_1\,|^2\Big] \tag{4.203a}$$

where:

$$l(t) = K_B(t)p_1(t)\overline{p_2(t)} \tag{4.203b}$$

It can be shown that the double integral cancels the term immediately preceding it in Eq. (4.203a). In addition, the changes in $h_1$ and $h_2$ during a collision are neglected so that these quantities are taken outside

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*Spitzer gives $+\frac{1}{2}\Gamma\mathrm{T}$ instead of $-\frac{1}{2}\Gamma\mathrm{T}$, but this would not appear to cancel the exp $(-\frac{1}{2}\Gamma\mathrm{T})$ in $a$ when the second term on the right of Eq. (4.199a) is being obtained.

the integral signs and the mean square of each equated to unity. Finally $\exp(-\frac{1}{2}\Gamma T)$ is taken outside the integral and $x$ is assumed $\gg \frac{1}{2}\Gamma$. Again we recall that Eq. (4.203a) should give the intensity distribution. Thus:

$$I(x) = \frac{\Gamma}{2\pi x^2}\left[1 + \exp(-\Gamma t_0)\left\{\left|\int_0^\infty e^{ixT}(\Delta_{A1} - \Delta_{B1})dT\right|^2 + \left|\int_0^\infty e^{ixT}K_A dT\right|^2 + \left|\int_0^\infty e^{ixT}\bar{K}_B dT\right|^2\right\}\right] \tag{4.204}$$

The integrals of $\Delta_{B1}$ and $\Delta_{B2}$ may be noted to have disappeared, and this is by virtue of their first expected appearance in fourth order. Use has also been made of the fact that the phases of $h_1$ and $h_2$ are arbitrary which would lead to the disappearance of their cross product terms in the main (occurrence with equal probability of positive and negative signs).

Now we take the $z_e$ axis as parallel to the direction of rectilinear motion of the perturbing ion and the $y_e z_e$ plane as the plane of perturber motion. If, as usual, $\vartheta$ is the angle between the distance of closest broadener approach and the instantaneous emitter-broadener separation, then the $z_e$ component of the field produced by the perturbing ion will be given by $E \sin\vartheta$ and the $y_e$ component by $E\cos\vartheta$. Under these conditions Eqs. (4.167) tell us that the diagonal matrix elements of the ionic field yield:

$$\Delta_{A1}(T) - \Delta_{B1}(T) = q\,\frac{\sin\vartheta}{\hbar r^2}$$

On the other hand the matrix of $z_e$ is diagonal. Thus, we should expect the contributions to the off-diagonal elements of the ionic field, $K_A$ and $K_B$ to arise from the matrix of $y_e$ alone so that, if we let $K_A$ be some constant the off-diagonal element $K_A$ will be given by $K_A \cos\vartheta/\hbar r^2$. According to the conventions introduced:

$$\sin\vartheta = \frac{v(T - t_0)}{r}\,;\ \cos\vartheta = \frac{R}{r} \tag{4.205}$$

so that from Eqs. (4.167):

$$\int_0^\infty e^{ixT}(\Delta_{A1} - \Delta_{B1})dT = \Upsilon\int_{-\infty}^{+\infty} e^{i\xi u}\frac{u\,du}{(1 + u^2)^{3/2}} \tag{4.206a}$$

$$\int_0^\infty e^{ixT}K_A dT = \frac{K_A}{\hbar R v}\int_{-\infty}^{+\infty} e^{i\xi u}\frac{du}{(1 + u^2)^{3/2}} \tag{4.206b}$$

Integrals of the form Eqs. (4.206) have already been quite handily disposed of in Eq. (4.176) and subsequent, and when the result of such disposition is substituted into Eq. (4.204) the result:

$$I(x) = \frac{\Gamma}{2\pi x^2}\left\{1 + 4\exp(-\Gamma t_0)\,\xi^2\left[\Upsilon^2 K_0^2(\xi) + \frac{K_A{}^2 + K_B{}^2}{\hbar^2 R^2 v^2}K_1^2(\xi)\right]\right\} \tag{4.207}$$

It appears reasonably evident that when the $y_e$ and $z_e$ axes are interchanged, the roles of the $K$'s and the $\Delta$'s will be interchanged resulting in the interchange of $K_0^2$ and $K_1^2$. "When $J(x)$ is summed over all possible components of a particular hydrogen line $n$ — weighting $J(x)$ for each component by the oscillator strength* of that component — the result must clearly be independent of the choice of axes." This appears physically sensible, and it is to be admitted that, if such is the case, the weighted sum over $\Upsilon$ must equal the weighted sum over $K_A{}^2$ and $K_B{}^2$ in Eq. (4.207). With the understanding then that the sum in question

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*See Appendix VII for a discussion of Oscillator Strengths.

is to be taken, it is legitimate to replace $(K_A^2 + K_B^2)/\hbar^2R^2v^2$ by $\Upsilon^2$. If we again specify the number of collisions as in Eq. (4.172), we obtain this latter equation for Eq. (4.207) where now $f_\Upsilon(\xi)$ is replaced by:

$$f_0'(\xi) = 2\xi\,[K_1^2(\xi) + K_0^2(\xi)]^{1/2} \tag{4.208}$$

From Eq. (4.179):

$$f_1(\xi) = 2\xi\,[K_1(\xi) \pm K_0(\xi)] \tag{4.209}$$

so that we see that $f_0'^2(\xi)$ is nothing more nor less than the average of $f_1^2(\xi)$ over plus and minus values.

We may now draw some conclusions which will tend to show that which we have been attempting to prove, namely, " . . . the change in the atomic wave functions becomes appreciable and the Born approximation becomes invalid in the same region as that in which the adiabatic approach becomes approximately valid. . . ."[173]

The replacement of $f_\Upsilon(\xi)$ by $f_\sigma'(\xi)$ in Eq. (4.172) is somewhat similar to the replacement by $f_\sigma(\xi)$ earlier. Now the change in $f_\sigma(\xi)$ as $\Upsilon$ goes from one to zero is small. On the other hand $\Upsilon$ is of the order of $2\,K_B/\hbar vR$ which in turn is approximately equal to the square of the time integral of $K_B(t)$. This latter quantity tells us approximately the probability of the molecule changing its state from $B_1$ to $B_2$, i.e., of invalidating the Born approximation. This rather tenuous line of reasoning leads us to the conclusion that as $\Upsilon$ gets large enough to allow the use of the adiabatic approximation as a good assumption, the Born approximation is no longer valid.

## 4.23. REVIEW OF THE QUANTUM STARK BROADENING THEORY

In the last few sections then we have (1) considered the effect on a hydrogen spectral line of an adiabatic collision of specific optical collision diameter and perturber velocity to obtain Eq. (4.172) for the intensity distribution in the broadened line, (2) considered the deviations from this adiabatic hypothesis of (1) for the specific case of the first Lyman lines and found that $f_\Upsilon(\xi)$ must be replaced by $f_\sigma(\xi)$ to account for the non-adiabaticity, and (3) utilized what corresponded to the Born approximation to obtain a line shape (as given by Eq. (4.207)) and in this derivation the transitions considered were more general than (2) since they could take place between any two perturbed levels. In toto then (2) and (3) have indicated the necessity of replacing Eq. (4.172) by:

$$I(x) = \frac{\Gamma}{2\pi x^2}\left\{1 + \frac{\Omega(\Upsilon,\xi)}{\Gamma}\,\Upsilon^2 f_\Upsilon^2(\xi)\right\} \tag{4.210a}$$

where:

$$\sigma^2 = 1 + \Upsilon^2 \tag{4.210b}$$

and the remainder of the symbols are defined, as before, by Eqs. (4.167), (4.169), and (4.171).

The problem which remains then is one of integrating over all values of $\Upsilon$ and $\xi$, that is, all values of $v$ and $\rho$, the distance of closest approach in order to obtain a comprehensive picture of the intensity distribution in the spectral line.

## 4.24. INCLUSION OF DIFFERENT TYPES OF COLLISIONS

In order to accomplish this integration, we first suppose $\Omega_m'(\rho,v)d\rho dv$ to be the number of times per second (essentially a probability) that a hydrogen atom undergoes an optical collision of diameter between $\rho$ and $\rho + d\rho$ with an ion of mass $M_m$, charge $Z_me$ and having a relative velocity between $v$ and $v + dv$. Then an integration of Eq. (4.210a) over $\rho$ and $v$ together with a summation over $m$, the types of ions, will yield the expression desired.

$$I(x) = \frac{\Gamma}{2\pi x^2}\left\{1 + \frac{1}{\Gamma}\sum_m \int_0^\infty dv \int_0^S \Omega_m'(\rho,v)\Upsilon^2 f_\sigma^2(\xi)d\rho\right\} \tag{4.211}$$

The upper limit of integration over the collision diameter is simply given by:

$$\frac{4}{3}\pi S^3 = \frac{1}{N}$$

where $N$ has its usual meaning. This upper limit of $\rho$ amounts to a " . . . consideration of successive, isolated, single encounters. . . ."[174] and indicates that collisions of greater diameter than the average molecular separation will tend to be "completely screened." Of course, this means the ignoration of distant encounters which, in connection with the Weisskopf theory, we shall see in Chapter 6 means loss of any line shift. Although Spitzer was naturally well aware of the fallacy in considering the lower limit zero as meaningful, he thought that it was a " . . . better procedure . . . to include an admittedly inaccurate value for the contribution from these close encounters rather than to neglect them entirely."[174] The extension of the limit to zero actually makes very little difference.

For the distribution of velocities a Maxwell-Boltzmann distribution was assumed, and for the optical collision diameter — distance of closest approach — the simple probability $2\pi\rho v N_m$ was assumed so that:

$$\Omega'_m(\rho,v) = (2\pi\rho v N)\,(4 l_m^{3/2}\pi^{-\frac{1}{2}} v^2 \exp\,[-l_m v^2]) \tag{4.212a}$$

where

$$l_m = \frac{1}{2k\mathrm{T}}\,\frac{M_m m_H}{M_m + m_H} \tag{4.212b}$$

with $m_H$ the hydrogen atom mass.

When Eq. (4.212a) is substituted into Eq. (4.211) $\xi$ is reintroduced, and $u$ is substituted for $l_m v^2$, there results:

$$I(x) = \frac{\Gamma}{2\pi x^2}\left\{1 + \frac{4\pi^{1/2}}{\Gamma x^{1/2}} \sum_m \frac{N_m {q_m}^{3/2}}{\hbar^{3/2}}\, {\gamma_1}^{1/2} H_m(x)\right\} \tag{4.213a}$$

where:

$$H_m(x) = \int_0^\infty e^{-u} du \int_0^{\gamma_1/\gamma_2 u^{\frac{1}{2}}} f_\sigma^2(\xi)\,\frac{d\xi}{\xi} \tag{4.213b}$$

$$\gamma_1 = \frac{q_m l_m x}{\hbar}\;; \qquad \gamma_2 = \frac{q_m {l_m}^{1/2}}{\hbar s} \tag{4.213c}$$

and finally:

$$\sigma^2 = 1 + \frac{{\gamma_1}^2}{u^2\xi^2} \tag{4.213d}$$

from Eq. (4.210b). We might note that the quantity $q_m/\hbar$ is the Stark shift which results from placing a charge $Z_m e$ unit distance from a hydrogen atom. We shall have more to say about $\gamma_1$ and $\gamma_2$ later.

The main problem which Spitzer faced in carrying the theory forward to completion from this point was the evaluation of the integral occurring in Eq. (4.213b). The difficulty arising here is largely due to the fact that $f_\sigma(\xi)$ (as we may recall from Eq. (4.179)) has only been evaluated for integral values of T and hence $\sigma$. Spitzer avoids the difficulty presented by this situation by taking, for $x/x_{\max}$ less than 1/16:

$$f_\sigma(\xi) = \begin{cases} f_1(\xi) & 1 < \sigma < 1.5 \\ f_2(\xi) & 1.5 < \sigma < 3 \\ f_4(\xi) & 3 < \sigma < 5 \\ f_\infty(\xi) & 5 < \sigma \end{cases} \tag{4.214a}$$

and for $x/x_{\max}$ greater than 1/16:

$$f_\sigma(\xi) = f_\sigma(0) \tag{4.214b}$$

We shall not consider the intervening steps in detail but simply give the solution as:

$$H_m(x) = 4ln\,\frac{1}{\gamma_2} - 2.33 + 61\gamma_1 + 6.7\,\frac{\gamma_1}{\gamma_2} \tag{4.215}$$

which is accurate to within ten percent for $\gamma_1$ less than $\gamma_2/10$ and $\gamma_2$ less than 0.2. The asymptotic value of $H_m(x)$ for large values of $\gamma_2$ is apparent from this equation. For $x/x_{\max}$ less than 1/16 this asymptotic result holds for $H_m(x)$. Finally with $\gamma_1$ large ($\gamma_2$ still assumed small) $H_m(x)$ is given by $H_m'(x)$ where:

$$H_m'(x) = 4ln\,\frac{1}{\gamma_1} - 3.02 + 61\gamma_1 \tag{4.216}$$

These then are the values of $H_m(x)$ which are to be utilized in Eq. (4.213a) in order to obtain the intensity distribution for one component of the hydrogen line. Since we are desirous of obtaining the intensity distribution in an actual observed line, we now sum contributions of the form Eq. (4.213a) from the various components weighted by the oscillator strengths of the components concerned. The result is:

$$I(x) = \frac{1}{2\pi x^2}\left\{\sum_j \Gamma_j\,\varphi_j + 4\frac{\pi^{1/2}}{x^{1/2}\beta^{3/2}}\sum_j \varphi_i \sum_m N_m q_{mj}^{3/2}\gamma^{1/2}\left(H'_{mj}(x) - H^2_{mj}(x)\right)\right\} \tag{4.217}$$

where the $\varphi_j$ are the normalized oscillator strengths:

$$\varphi_j = \frac{f_j}{\sum_j f_j} \tag{4.218}$$

This is the desired solution, and let us now consider a few of the ramifications of it, as well as the restrictions and approximations involved in it.

## 4.25. APPROXIMATIONS IN THE QUANTUM STARK BROADENING THEORY

The two parameters $\gamma_1$ and $\gamma_2$ can tell us a good deal about the reduction of the equations for line shape obtained here to those of the Statistical and Interruption theory. We first consider $\gamma_1$. For an ion with the most probably relative velocity, $L_m^{-1/2}$, $\gamma_1 = \Upsilon^2 \cdot x/x_{\max}$. Now then, if $\gamma_1$ is small, the parameter $\Upsilon$ will be greater than one only for $x/x_{\max}$ small. Then, as we have already demonstrated in connection with Eq. (4.173),

$$f_\sigma(\xi) = \frac{2\sin\left(\frac{\pi\sigma}{2}\right)}{\sigma}$$

and from Eq. (4.210a) we obtain the Interruption theory shape as was obtained in Eq. (4.174). On the other hand, if $\gamma_1$ is large, $\Upsilon$ is large, and ergo, Eq. (4.183) and the Statistical theory again. A similar line of reasoning leads to the reduction to the Statistical theory for large $\gamma_2$.

Before continuing, let us remark that Holtsmark's $\beta$ is essentially equivalent to $x/x_{\max}$ for $\rho$ equal to $s$. This will now be useful in certain comparisons which are to be made with the Holtsmark theory. In order to make these comparisons Spitzer first shifted from $I(x)$ to $W(\beta)$ by the rather straightforward relation:

$$W(\beta)d\beta = I(x)\,dx \tag{4.219a}$$

where now:

$$\beta = \frac{xs^2h}{q} = \frac{\gamma_1}{\gamma_2^2} \tag{4.219b}$$

When Eq. (4.219a) is multiplied by $\beta^2$ and the indicated substitutions made, there results, according to Eq. (4.213a) and the relation between $s$ and $N$:

$$\beta^2 W(\beta) = 2I(x)\,\frac{x^2 s^2 \hbar}{q} = \frac{3}{\pi^{3/2}} \sum_m \frac{\gamma_2 H_m(x) N_m}{N} \tag{4.220}$$

where the first term in Eq. (4.213a) has been assumed negligible and the right side of the equation has been multiplied by two for agreement with the Statistical theory. Fig. (4.9) gives the curves of log $\beta^2 W(\beta)$ vs. log $\beta$ for several values of the parameter. We may note that for the case $\gamma_2 = \infty$ (the solid line) Verweij's calculation[185] based on Holtsmark's earlier work has been used, since the present theory reduces to this Statistical theory for this situation, as we have seen.

Next Eq. (4.174) may be considered. For the $\Omega_{1/\pi}$ which appears in this equation, we substitute the integral of Eq. (4.212a) over $\rho$ from zero to $\rho'$ and subsequently integrate over all values of $v$ with the result:

$$I(x) = \frac{2}{\sqrt{\pi}} \sum_m \frac{\pi^2 q^2 \sqrt{l_m}\, N_m}{\hbar^2 x^2}$$

so that, according to Eq. (4.220):

$$\beta^2 W(\beta) = 3\sqrt{\pi} \sum_m \frac{\gamma_2 N_m}{N} \tag{4.221}$$

The horizontal lines in Fig. (4.9) represent the Interruption result — the oft-called Weisskopf result — for several values of $\gamma_2$. The actual asymptotic result for $\beta^2 W(\beta)$, which one might expect to agree with the Interruption result, agrees with Eq. (4.221) only for $\gamma_2 = 0.047$. This is another demonstration of the error involved in the Interruption theory's failure to include the effect of distant collisions and nonadiabaticity. We mention this fact with no special emphasis, since we shall go into a much more detailed consideration of these facets of the Interruption theory in Chapter 6.

One other rather obvious point seems worthy of mention in connection with Fig. (4.9). Eq. (4.213c) tells us that $\gamma_2$ is directly proportional to the density, since it is inversely proportional to the mean molecular separation which is in turn inversely proportional to the particle density. The result is that as the density increases the theory tends toward the Statistical theory, and conversely, as the pressure decreases the theory tends toward the Interruption theory. This may be seen directly from Fig. (4.9). These are facts which we shall encounter on several subsequent occasions, but this seems a particularly simple way to demonstrate these facts about the two types of theories. One more item of interest may be garnered from a perusal of the figure in question. The parameter $\gamma_2$, in addition to being density dependent, is inversely velocity dependent through $l_m$ (see Eq. (4.212b)). Firstly then, it is rather obvious that we tend toward the Statistical theory with decreasing velocity — this too we shall later divine from different considerations. In an assemblage of equal numbers of electrons and ions the latter may be expected to move slowly, and our previous consideration tells us that we then expect the statistical effect. Au contraire, as far as the electrons are concerned, however, since their velocities may be expected to be much higher. Another look at Fig. (4.9) then tells us that the contribution of the electrons to the line width should be negligible.

Let us now review the main points in Spitzer's development of his Stark broadening theory.

### 4.26. SUMMARY OF THE QUANTUM BROADENING THEORY AND ERROR EVALUATION

Spitzer began with three assumptions, namely, (A) THE STARK EFFECT IS LINEAR AND THE ELECTRIC FIELD PRODUCING IT IS HOMOGENEOUS, (B) COLLISIONS ARE BINARY, and (C) THE MASS OF THE COLLIDING PARTICLES MAY BE TAKEN AS INFINITELY LARGE.* Let us consider these.

First, Spitzer's approximate evaluation of the error involved in Approximation (A). The coordinates of the photoelectron we shall designate with the subscript *e*. The distance from this electron to the ion is taken as *d*, its position vector as $\mathbf{r}_e$, and the separation of the emitter nucleus and the ion we take as *R*. These quantities are related as follows:

$$d^2 = R^2 + r_e^2 - 2z_eR$$

so that the potential at the electron due to the ionic charge is:

$$V = -\frac{Ze^2}{d} = -\frac{Ze^2}{R}\left\{1 + \frac{Ze}{R} + \frac{1}{2R^2}(3z_e^2 - r_e^2)\ldots\right\} \tag{4.222}$$

Now the upper levels of the photoelectron are broadened by the largest amount (see for example Eq. (4.166)), and, from the point of view of the Bohr theory especially, they have the largest values of $z_e$. For large $z_e$:

$$< r_e^2 > \doteq < z_e^2 > \doteq < z_e >^2$$

so that:

$$< V > = -\frac{Ze^2}{R^2} < z_e > \left\{1 + \frac{< z_e >}{R}\right\} \tag{4.223}$$

It is apparent that the maximum value for $z_e$ is $r_e$ so that, since the second term in Eq. (4.223) gives the error, the maximum value of the error due to the assumption of a homogeneous ionic field is $r_e/R$. We should remark, however, that this method of determining the error breaks down for *R* less than three or four $< r_e >$.

Eq. (4.223) points up one more fact of importance. Since $z_e$ is an average, its sign will not change. As a consequence, the sign of the correction term $< r_e >/R$ will not change so that an asymmetry in the line will result, since the mean perturbation will not cancel out.

We consider next Approximation (B). It is intuitively apparent that multiple collisions at short distances of approach will have a low probability. On the other hand, a close, binary collision will screen out, at least partially, the effects of distant multiple collisions. We may expect then for large $\gamma_2$ that this approximation is not too serious a one. As $\gamma_2$ decreases (with the density) on the other hand, one would expect the probability of a multiple collision to decrease. Spitzer specifies the value 1/5 for $\gamma_2$ as an upper limit in order that the binary approximation may be a good one.

Assumption (C) would be a particularly serious one only for electrons, and we have made note of the fact that the ions, not the electrons are generally the important broadening agents.

Having made these assumptions the problem was set up assuming, as the intermolecular interaction the linear Stark effect. Firstly, a quantum mechanical solution of the adiabatic — the quantum state of the system remains unchanged — problem was carried out. We begin with the basic equations for the state growths, Eqs. (4.157). The fact that the absolute square of the coefficient $b_{s(\nu)}(\infty)$ is the probability that the atom is in a state, in order to get to which it had to emit a photon of frequency $\nu$, means that the absolute square of this coefficient must also be the intensity of this frequency in the spectral line. This line of reason-

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*We should recall that we consider this mass as infinite only insofar as any effects which the intermolecular interaction may have on the perturber motion.

ing leads to Eq. (4.163) for the line shape of one component due to one type of collision. The problem is then carried through to the adiabatic solution of Eq. (4.172) for the line shape. During the mathematical manipulation leading to this solution two additional approximations are introduced, namely, (D) THE PERTURBER MOTION IS RECTILINEAR AND CLASSICAL and (E) THE FREQUENCY IN QUESTION IS MUCH FARTHER OUT IN THE LINE WINGS THAN THE NATURAL LINE WIDTH — NAMELY, $x^2 \gg \Gamma$. We shall encounter ample comment on Approximation (D) later, and Approximation (E) simply restricts the validity of the results to the line wing.

Further, as concerns the purely adiabatic hypothesis, we noted the manner in which Spitzer's results reduced to the Interruption solution for $\Upsilon$ small and the Statistical solution for $\Upsilon$ large.

Next a nonadiabatic solution of the problem for the lowest Lyman lines was carried through, and it was discovered that Eq. (4.172) held true for this case if $\Upsilon$ was replaced by $\sigma$ where $\sigma^2$ was approximately $(1 + \Upsilon)^2$.

Finally, the problem was considered from the Born point of view. The solution in this case, which breaks down at approximately the point where the adiabatic approximation becomes valid, is given by Eq. (4.207).

The next step consists of an averaging of our modified Eq. (4.163) over the distance of closest approach and velocity. This result is given in Eqs. (4.213). Finally, the weighted summation over the various components results in the final form Eq. (4.217).

Let us take note of two more remarks of Spitzer's in conclusion. To begin with, he was able to show by a judicious utilization of Eqs. (4.167) that for close collisions, that is, for $R$ as small as $10 < r_e >$, the value of $\Upsilon$ will be quite large so that, since replacing it by $\sigma$ is of little or no import, the collisions may be considered as adiabatic.

By an approximate calculation Spitzer placed the following limits on the validity of Eq. (4.217): (1) Excluding the error due to the inhomogeneity of the ionic field for the moment, Spitzer obtained an error due to the method of calculation of Eq. (4.215) as not more than 10 percent and the equation is asymptotically correct except for the case $0.2 < \gamma_2 < 2$ and $\gamma_1 < 1$ which Spitzer refers to as intractable. (2) A consideration of the inhomogeneous ionic field, on the other hand, adds a correction for the Statistical theory reduction. For the case where the theory reduces to the Interruption approximation the error is about 13 percent for temperature of under 30000°. (3) The theory breaks down completely for $\Delta \lambda_{AB} > 135 n_B^4/n_A^2$.

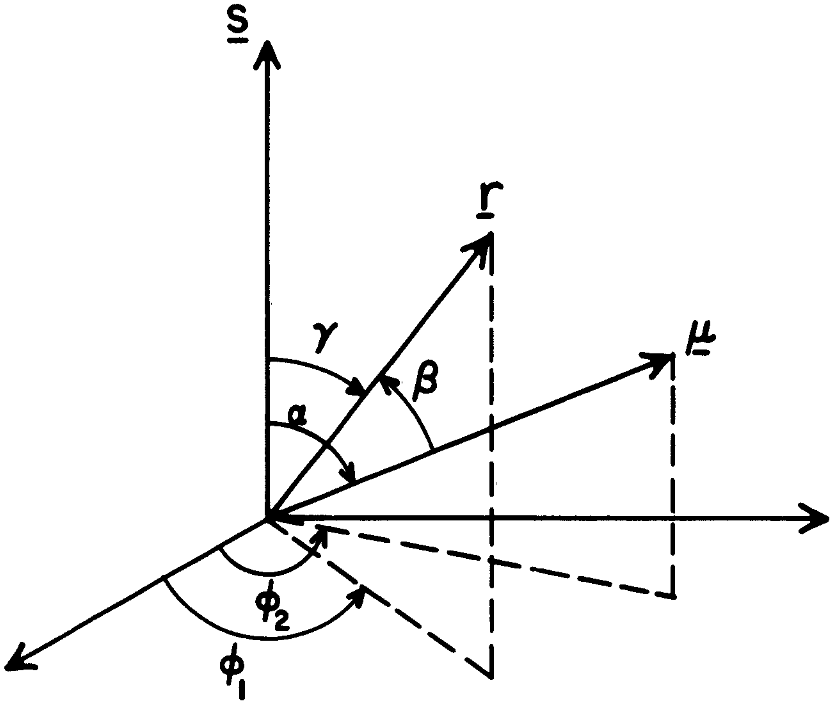

Fig. (4.1). Introduction of polar coordinates for the dipole broadener case. S is the polar axis.

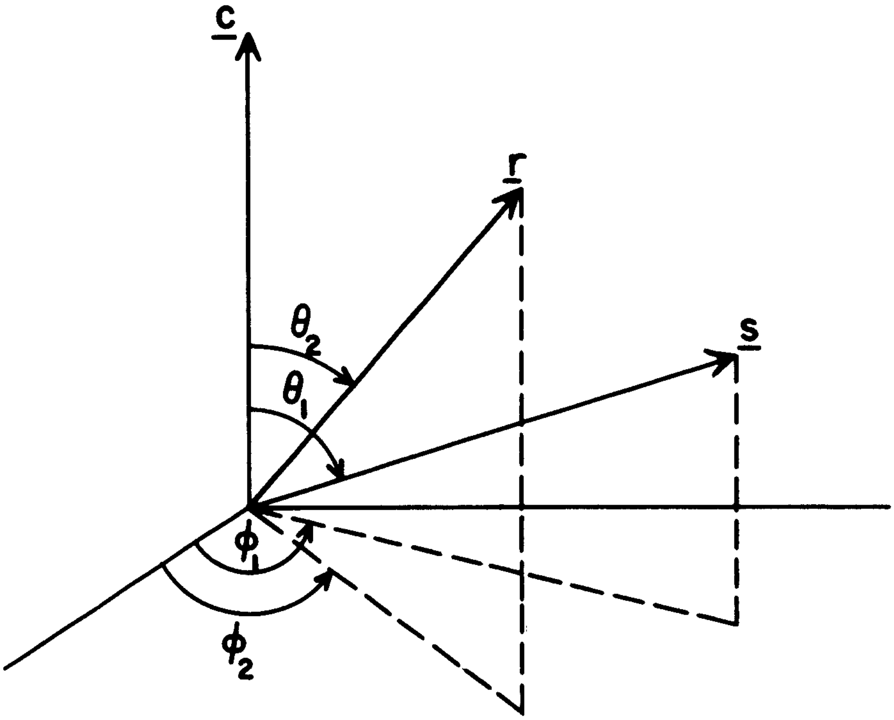

Fig. (4.2). Polar coordinates for the quadrupole broadener.

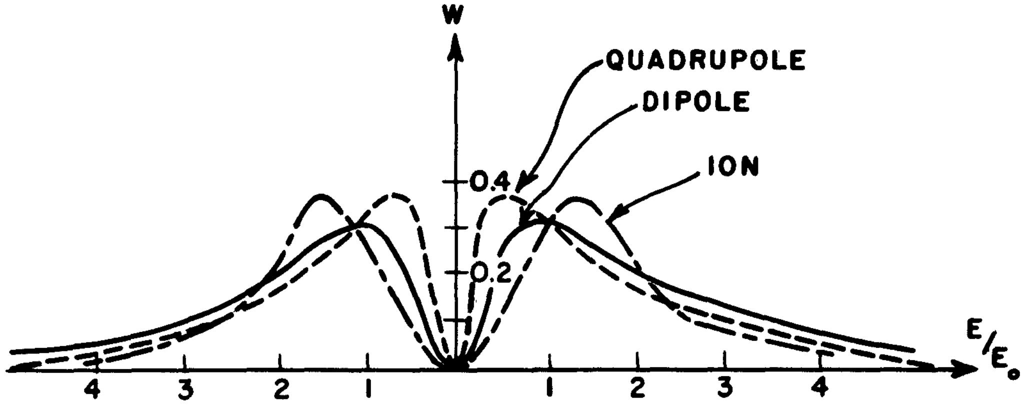

Fig. (4.3). The field strength probability function. (After Holtsmark[65]).

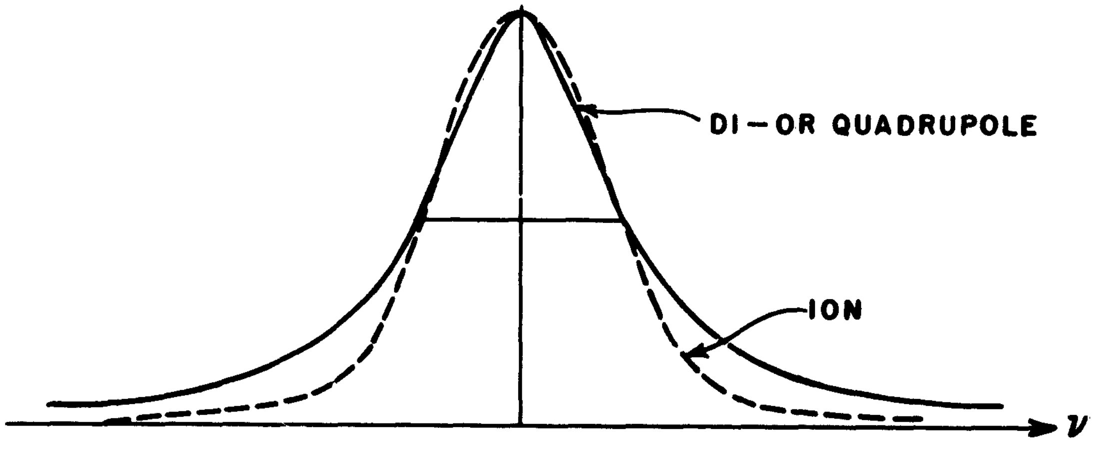

Fig. (4.4). The Stark Theory line shape. (After Holtsmark[65]).

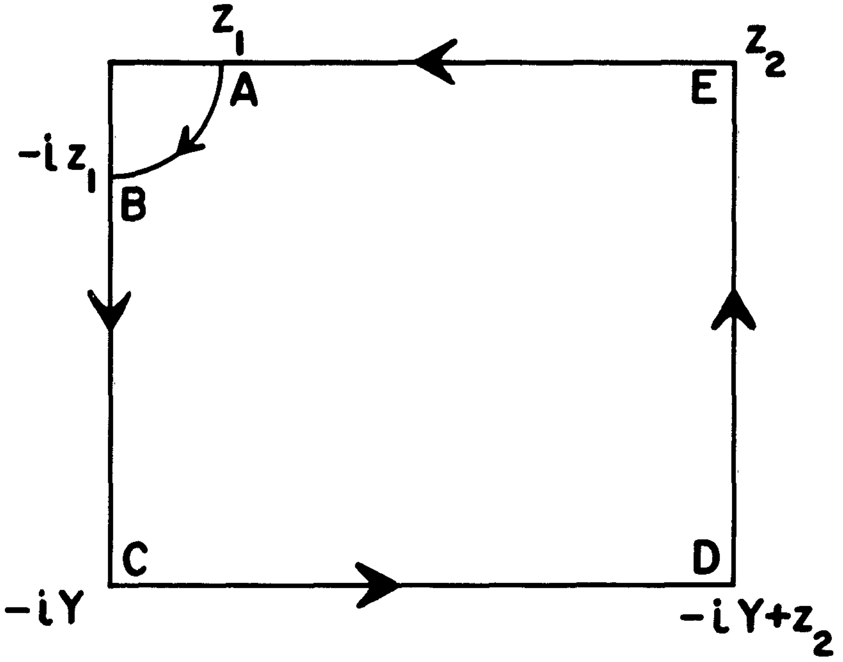

Fig. (4.5). Path in the complex plane used for the evaluation of Eq. (4.122).

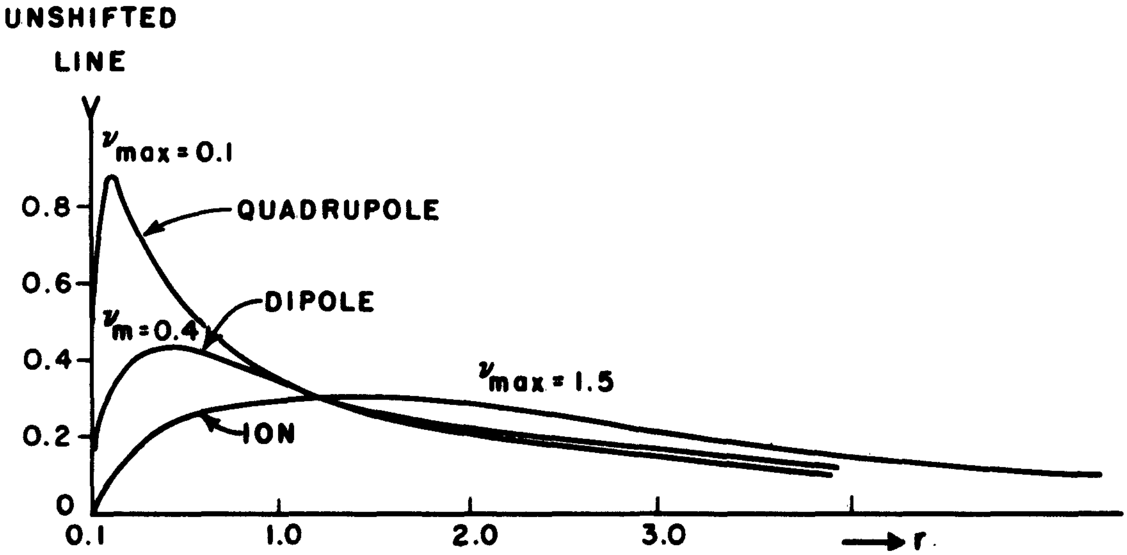

Fig. (4.6). The line shape due to the quadratic Shark effect. (After Holtsmark[67].)

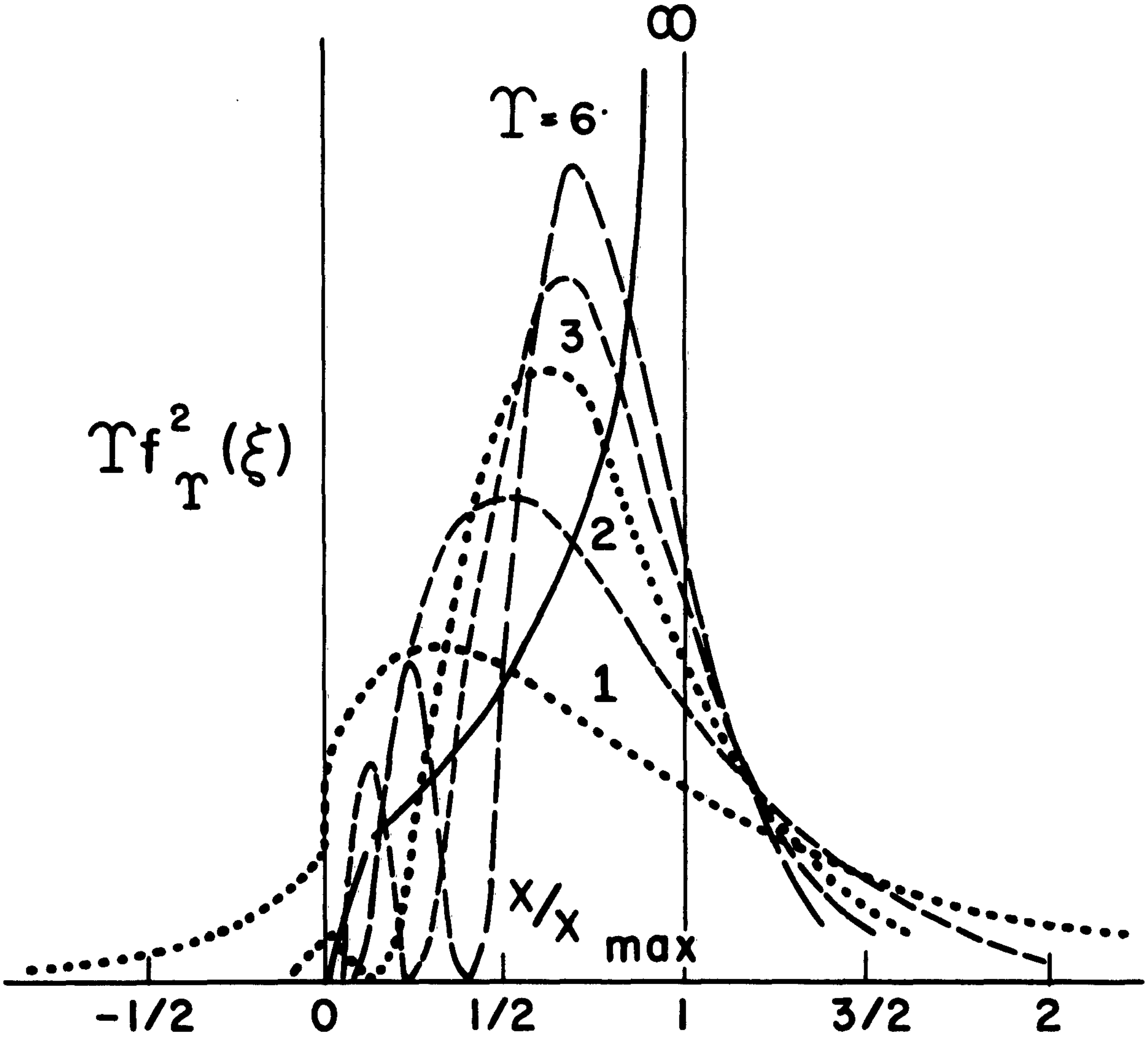

Fig. (4.7). Stark effect line shapes for various collision phase shifts. (After Spitzer.[173])

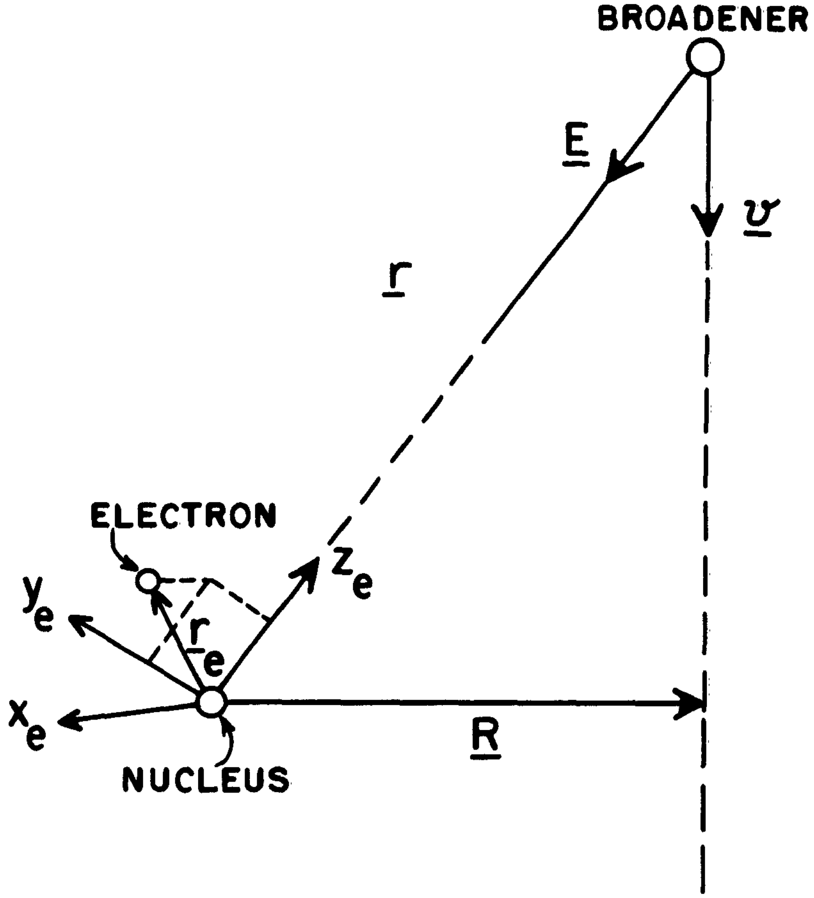

Fig. (4.8). The physical conditions for the non-adiabatic collision. The broadener and the emitter nucleus are in the $y_e z_e$ plane.

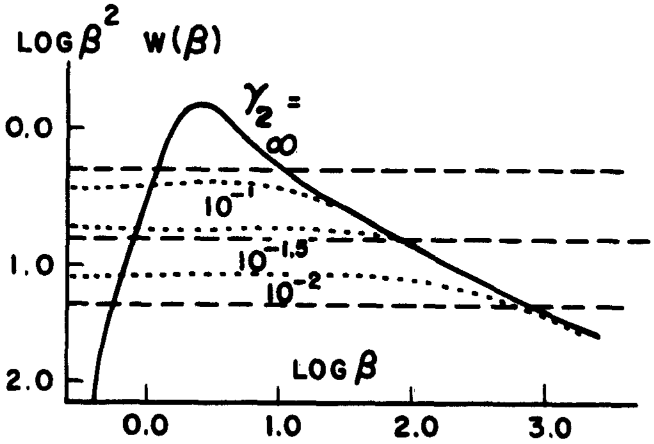

Fig. (4.9). Line shapes for a single H line component. The solid line is the Holtsmark result. The dashed lines are the Weisskopf results. (After Spitzer.[174])

# CHAPTER 5

## STATISTICAL BROADENING

In 1926 Franck[39] presented a paper to the Faraday Society in which he sketched for the first time the tenets of what is now the well-known Franck-Condon principle.

### 5.1. THE FRANCK-CONDON PRINCIPLE

In order to consider his conception, let us imagine a molecule which for convenience we may take as diatomic. Let us further neglect the rotational motion and consider only the electronic and vibrational energies. We suppose this molecule to be initially in a vibrational ground state. An electronic transition now takes place to, say, some higher electronic state. Now let us consider Fig. (5.1).

In Fig. (5.1) the curves for two electronic states — between which our transition is assumed to take place — are given in which the molecular energy as a function of nuclear separation has been plotted. In essence, Franck hypothesized that the transition takes place vertically between these two curves. This means that the nuclei have the same separation immediately after the electronic transition as they did before even though the potential curve which governs the nuclear behavior has been changed by the transition. Since in general, as is illustrated by Fig. (5.1), the new separation of the nuclei will not correspond to the equilibrium position of this electronic state, the molecule will no longer be in a vibrational ground state, and it will begin to vibrate, or it may be dissociated.

Shortly after the publication of these views, Condon[20] suggested the manner in which this principle could be used to predict intensities, one might say qualitatively. Let us roughly consider his graphical method by considering Fig. (5.2). We are utilizing the quantum mechanical energy levels of a vibrator, but we shall consider the intensity question classically.

Consider vibrational level "A" of the initial state. Classically speaking, the internuclear separation during the vibration (corresponding to an energy of "A") could neither be less than "a" nor greater than "b". Further, the molecule will most often be found with an internuclear separation in the neighborhood of "a" or "b", since we may recall that "b" is the separation at which stretching has ceased and contraction is to begin. Thus we may say that the most probable, and hence, the most intense transitions correspond to "a" and "b". If at the time of the electronic transition the internuclear distance corresponds to "b", the transition will proceed vertically to the curve for the upper electronic state, and then, since the vibrational energies are, of course, quantized, would proceed to the closest vibrational level "B". Thus, the most intense transitions from level "A" will be to levels "B" and "C".

Condon[21] later modified this principle to strictly include the wave mechanics, and essentially this modification has the effect of adding an indeterminacy to the principle so that if, for example, $A \rightarrow B$ is favored in Fig. (5.2), we will now have a band around the frequency corresponding to this frequency rather than the frequency itself.

The foundation for a theory of spectral line broadening had thus been laid by Franck and Condon and the theory itself was first qualitatively developed by Jablonski.[74]

## 5.2. FIRST APPLICATION OF FRANCK CONDON TO LINE BROADENING

For the interaction energy of two atoms in a molecule Jablonski stated the Franck-Condon principle as: "At the moment of the electron jump (1) the reciprocal separation of the atomic nuclei and (2) the velocity of the nuclei are not noticeably changed."[74] It need hardly be considered stretching a point to carry this principle over to the case of two free molecules, an absorber (emitter) and a broadener.

Let us consider, with Jablonski, the potential curves for two free molecules as given in Fig. (5.3). These curves are repulsion curves, but for the principles involved the curve type is of no import. The potential energy of the two particle system is given as a function of the molecular separation. If the broadening molecule is an infinite distance from the absorber, the unperturbed spectral line of frequency corresponding to $E'_\infty - E_\infty$ would be absorbed. In the event that the molecular separation were $r_a$ at the time of absorption, the frequency of the line would have some different value corresponding to $E'_{r_a} - E_{r_a}$. We here neglect the lack of sharpness which would be present in $r_a$.* With the aid of Fig. (5.3) let us consider this absorbing transition in slightly greater detail.

Firstly, we have assumed that energy is conserved so that we have the $T$, $V$, and $E$ curves as shown for the two molecules in the initial state. Now the transition takes place at the separation $r_a$. In accordance with the Franck-Condon principle, the relative velocity of the molecules is not changed by this transition so that immediately after the transition the point "$x$" on the $T$-curve still gives the relative velocity. Now, however, the total energy is $E'$ and this too is to be conserved. Hence, as shown by the $T'$-curve the relative kinetic energy of the particles after separation will be increased, and this increase is at the expense of the incident radiation. The reverse effect could also occur, that is, the "effective" incident radiation could be increased at the expense of the final kinetic energy. These interactions between collisions and radiation had been considered by Oldenberg[137] [138] and later by Minkowski.[129]

Thus, we see how radiation differing in frequency from that characteristic for the molecular transition may be absorbed Qualitatively at least, it follows directly that ". . . the intensity distribution (and the line width) is dependent on the profiles of the potential curves and the probability of different $r$ values."[74] Thus, the most probable $r$ values would correspond to the most intense frequencies of the spectral line. Since the probability of a given $r$ would depend on the relative velocity of the "collision partners," the variable relative velocity which may be inferred from the $T$-curve in Fig. (5.3) must needs be considered. Theoretically at least, one might now determine the line profile by utilizing gas kinetic theory.

It is apparent that almost any form of asymmetry of the spectral line could be obtained, depending on the relative profiles of the potential curves. Before considering the matter of line shift, it might be well to emphasize that the line frequency (corresponding to a specific $r_a$) rapidly approaches the unperturbed line frequency with increasing $r$ regardless of the type of interaction curves under consideration. Thus, it follows that, with increasing probability of small $r$, there will be an increasing displacement or shift of the line intensity maximum. Small $r$ would become more probable with increasing pressure.

In what has preceded we have considered the perturbing effect of only one molecule. In "reality" many molecules would contribute to the disturbance, but Jablonski's ruminations do give a qualitative

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* This lack of sharpness of $r_a$ will be considered at a later point. If the transition took place in an infinitely small time interval or if the relative velocities of the partners were infinitely small, this lack of sharpness would not be present, and the transition indicated on Fig. (5.3) would accurately represent the situation. However, the transition time is always finite. Thus, we obtain a diffuseness which is caused by the fact that the molecular velocities are not infinitely small and results from the exchange of radiation and kinetic energy[139, 137, 138] *during* the process of emission. We shall see that this results in Margenau's "velocity distribution."

idea as to how this type of spectral line broadening and shift are brought about. He envisioned it as applicable to any type of interaction curves — "... it can be exchange- as well as Coulomb dipole-, quadrupole-, etc. forces ..."[74]

## 5.3. CALCULATION OF THE VAN DER WAALS FORCES INVOLVED IN BROADENING

In 1932 Margenau[111] utilized, for the first time, the van der Waals forces[*] between two atoms of different, types to explain the shift and broadening of spectral lines. Since "... numerous causes which can neither be well controlled experimentally nor accurately corrected for by theory ... may play an important role in the phenomenon ..."[111] of broadening in emission, he considered only absorption.[†]

Van der Waals forces may exist among neutral molecules, so that an immediately apparent advantage of considering these forces as the cause of broadening in preference to the Stark type lies in the possibility of explaining that broadening caused by molecules which possess no permanent poles. The first step then lies in the calculation of these broadening forces.

Margenau first applied himself to the case of foreign gas broadening in which the absorbing atom is in its lowest $p$-state and the broadening atom is in its normal state.

Let us consider Fig. (5.4).

The atomic nuclei are at ($a$) and ($b$), and the centers[**] of negative charge are at $(x_1y_1z_1)$ and $(x_2y_2z_2)$ where the $x$-axis of the coordinate system to which the system is referred coincides with $r$, the separation of the two nuclei. We here assume that $r$ is large so that no electron interchange[††] effect need be considered. For example, one could take as eigenfunctions for, say, two $H$ atoms $\psi = \psi_a(1)\,\psi_b(2)$ instead of $\psi = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)$, etc.

The interaction potential energy of the system will be given by:

$$V = e^2\left(\frac{1}{r}+\frac{1}{r_{12}}-\frac{1}{r_{a2}}-\frac{1}{r_{b1}}\right)$$

$$= \frac{e^2}{r}+\frac{e^2}{r}\left[\frac{1}{\sqrt{\dfrac{(y_1-y_2)^2}{r^2}+\dfrac{(z_1-z_2)^2}{r^2}+\dfrac{(x_1^2+x_2^2-2x_1x_2-2x_1r+2x_2r)}{r^2}+1}}\right]$$

$$-\frac{e^2}{r}\left[\frac{1}{\sqrt{\dfrac{y_2^2}{r^2}+\dfrac{z_2^2}{r^2}+\dfrac{(x_2^2+2x_2r)}{r^2}}}\right]-\frac{e^2}{r}\left[\frac{1}{\sqrt{\dfrac{y_1^2}{r^2}+\dfrac{z_1^2}{r^2}+\dfrac{(x_1^2-2x_1r)}{r^2}+1}}\right]$$

$$= \frac{e^2}{r^3}\,(y_1y_2+z_1z_2-2x_1x_2)+\frac{3}{2}\,\frac{e^2}{r^4}\,[r_1^2x_2-r_2^2x_1+(2y_1y_2+2z_1z_2-3x_1x_2)\,(x_1-x_2)]$$

$$+\frac{3}{4}\,\frac{e^2}{r^5}\,[r_1^2r_2^2-5r_2^2x_1^2-5r_1^2x_2^2+2(y_1y_2+z_1z_2+4x_1x_2)^2]+\dots$$

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[*] Margenau[119] has cryptically but delightfully defined the van der Waals force as "... that force which gives rise to the constant $a$ in van der Waals equation ..."

[†] For the equivalence of emission see *infra*, Sec. (6.13).

[**] If an atom possesses no dipole moment, to say nothing of the absence of a quadrupole moment, the centers of positive and negative charge would normally coincide. Since we are not assuming the existence of any permanent poles, this apparent anomaly should be explained. We assume here that a mutual polarization — that is, a drawing apart of the centers of positive and negative charge — occurs, and we are then free to consider these charge centers.

[††] See *infra*, Chap. 7.

since $r$ has been assumed large.* The first term is the dipole-dipole interaction term, the second the dipole-quadrupole, and so on. Margenau utilized only the first term, so that the perturbing potential for the system is:

$$V = \frac{e^2}{r^3}(y_1y_2 + z_1z_2 - 2x_1x_2) \tag{5.1}$$

so that: $H = E_0 + V_0 + V = H_0 + H'$

Eqs. (2.26b) and (2.26c) may be written down for this case as:

$$H^0\psi_n' + H'\psi_n^0 = E_n^0\psi_n' + E_n'\psi_n^0 \tag{2.26b'}$$

$$H^0\psi_n'' + H'\psi_n' = E_n^0\psi_n'' + E_n'\psi_n' + E_n^0\psi_n'' \tag{2.26c'}$$

We now replace† $\psi_n'$ by $\sum\limits_k a_{nk}\psi_k^0$ and $\psi_n''$ by $\sum\limits_k b_{nk}\psi_k^0$, replace $H^0\psi_k^0$ by $E_k^0\psi_k^0$, multiply both equations on the left by $\psi_m^0$, and integrate over all space to obtain:

$$a_{nm}E_k^0\delta_{mk} + \int\bar{\psi}_m^0H'\psi_n^0d\tau = E_n^0a_{nm}\delta_{mk} + E_n'\delta_{mn} \tag{5.2a}$$

$$b_{nm}E_m^0\delta_{nk} + \sum_k a_{nk}\int\bar{\psi}_m^0H'\psi_k^0d\tau = E_n^0b_{nm}\delta_{mk} + E_n'a_{nm}\delta_{mk} + E_n''\delta_{nm} \tag{5.2b}$$

These equations yield the first and second order energy corrections:

$$E_{10}' = \int\bar{\psi}_m^0H'\psi_m^0d\tau = 0$$

$$E_{10}'' = \sum_k a_{nk}\int\bar{\psi}_n^0H'\psi_k^0d\tau = \sum_k{}' \frac{\int\bar{\psi}_1^0(a)\bar{\psi}_0^0V\psi_A^0(a)\psi_B^0(b)d\tau\int\bar{\psi}_A^0(a)\bar{\psi}_B^0(b)V\psi_1^0(a)\psi_0^0(b)d\tau}{(E_n^0 - E_k^0)} \tag*{(5.3)**}$$

$$= -\sum{}' \frac{|V_{10,AB}|^2}{E_A - E_1 + F_B - F_0} \tag{5.4}$$

In Eq. (5.4) the $E_A$ are the energy levels of the absorbing atom, $E_1$ being the energy of the initial $p$-state, and the $F_B$ are the energy levels of the broadening atom, $F_0$ being the energy of the initial $s$-state. $V_{10,AB}$ may now be written out as:

$$V_{10,AB} = \int\bar{\psi}_{AB}V\psi_{10}d\tau = \int\bar{\psi}_A(1)\bar{\psi}_B(2)V\psi_1(1)\psi_0(2)d\tau_1d\tau_2 \tag{5.5}$$

since, as mentioned earlier, no electron exchange is considered. If, in the symbolism of Margenau, we let, for example, $x_{1A}(1) = \int\bar{\psi}_A(1)x\psi_1(1)d\tau_1$, $|V_{10,AB}|$ may be written as:

$$|V_{10,AB}| = \frac{e^4}{r^6}[y_{1A}^2(1)y_{0B}^2(2) + z_{1A}^2(1)x_{0B}^2(2) + 4x_{1A}^2(1)x_{0B}^2(2) + 2y_{1A}(1)z_{1A}(1)y_{0B}(2)z_{0B}(2)$$

$$- 4x_{1A}(1)y_{1A}(1)x_{0B}(2)y_{0B}(2) - 4x_{1A}(1)z_{1A}(1)x_{0B}(2)z_{0B}(2)] \tag{5.6}$$

Margenau utilized hydrogen like wave functions for both atoms which, in general, may be represented as:

$$\psi_{nlm} = R_{nl}(r)P_l^m(\vartheta)e^{im\varphi} \tag{5.7}$$

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* This is merely a different form of Eq. (4.16) which will be more useful here.

† See *supra*, Eq. (4.144) and preceding.

** $E_{10}' = \int\bar{\psi}_1^0(a)x\psi_1^0(a)d\tau_1\int\bar{\psi}_0^0(b)x\psi_0^0(b)d\tau_2 + \ldots = \int\bar{\psi}_1^0(a)x\psi_1^0(a)d\tau_1\iiint[R_{n0}]^2r^3\sin^2\vartheta\cos\varphi drd\vartheta d\varphi + \ldots$
$= \int\{\ \}d\tau_1\iint[R_{n0}]^2r^3\sin^2\vartheta\, drd\vartheta\cdot 0 + \ldots = 0$, since $\int_0^{2\pi}\cos\varphi d\varphi = 0$, and so on.

in which l is the orbital angular momentum quantum number; $m$ is the magnetic quantum number, and $n$ is the orbital quantum number.

The following relations exist among the matrix elements associated with the broadening atom:

$$\sum_m x_{0B}y_{0B} = \sum_m x_{0B}z_{0B} = \sum_m y_{0B}z_{0B} = 0 \tag{5.8a}$$

$$\sum_m x_{0B}{}^2(2) = \sum_m y_{0B}{}^2(2) = \sum_m z_{0B}{}^2(2) = \frac{1}{3} r_{0B}{}^2(2)\delta_{l1} \tag{5.8b}$$

We have summed over the quantum number $m$ in Eqs. (5.8) since it has no effect on the level energies, but remains a spatial degeneracy parameter. $r_{0B}$ (2) is to be defined below. Let us prove a portion of Eq. (5.8a) as an example.

$$\sum_m x_{0B}y_{0B} = \sum_m \int \overline{\psi}_B(2)x\psi_0(2)d\tau \int \overline{\psi}_B(2)y\psi_0(2)d\tau$$

$$= \sum_{m=-l}^{+l} \int\int\int R_{10}\, R_{nl}\, e^{im\varphi}\, P_l^m r^3 \sin^2\vartheta \cos\varphi\, dr d\vartheta d\varphi \int\int\int R_{10}\, R_{nl}\, P_l^m e^{im\varphi}\, r^3 \sin^2\vartheta \sin\varphi\, dr d\vartheta d\varphi$$

$$= \sum_{m=-l}^{+l} \frac{1}{4i} \int\int\int R_{10}R_{nl}P_l^m \sin^2\vartheta\, (e^{i(m+1)\varphi} - e^{i(m-1)\varphi})r^3 dr d\vartheta d\varphi \int\int\int \ldots \tag{5.9}$$

The integral over $\varphi$ in Eq. (5.9) is zero unless $m = \pm 1$, while when $m = \pm 1$ the sum of all such integrals over $m$ goes to zero. The remaining portion of Eqs. (5.8) may be evaluated in a similar manner. An inspection of Eq. (5.9) also tells us that, in Eq. (5.8b):

$$r_{0B}{}^2(2) = [\int_0^\infty R_{n0}(r)R_{nB}(r)r^3 dr]^2 \tag{5.8c}$$

Certain relations may also be written down among the matrix elements associated with the absorbing atom. Here the state is the $p$-state and hence $m_1 = 0, \pm 1$. For the emitter then:

For $m_1 = 0$:

$$\sum_m x_{1A}{}^2(1) = r_{1A}{}^2(1)\left[\frac{1}{3}\delta_{l0} + \frac{4}{15}\delta_{l2}\right] \tag{5.10a}$$

$$\sum_m y_{1A}{}^2(1) = \sum_m z_{1A}{}^2(1) = r_{1A}{}^2(1)\frac{1}{5}\delta_{l2} \tag{5.10b}$$

For $m_1 = \pm 1$

$$\sum_m x_{1A}{}^2(1) = r_{1A}{}^2(1)\frac{1}{5}\delta_{l2} \tag{5.10c}$$

$$\sum_m y_{A1}{}^2(1) = \sum_m z_{1A}{}^2(1) = r_{1A}{}^2(1)\left[\frac{1}{6}\delta_{l0} + \frac{7}{30}\delta_{l2}\right] \tag{5.10d}$$

Eqs. (5.8) and (5.10) may now be utilized to obtain $| V_{10,AB}|^2$ summed over all values of the magnetic quantum numbers for the states $A$ and $B$. The result may be written as:

For $m_1 = 0$:

$$\sum_{m_A m_B} | V_{10,AB}|^2 = \frac{e^4}{r^6} r_{1A}{}^2(1)r_{0B}{}^2(2)\left[\frac{22}{45}\delta_{l_A2} + \frac{4}{9}\delta_{ll}\right]\delta_{l_B1} \tag{5.11a}$$

For $m_1 = \pm 1$:

$$\sum_{m_A m_B} |V_{10,AB}|^2 = \frac{e^4}{r^6} r_{1A}^2(1) r_{0B}^2(2) \left[\frac{19}{45}\delta_{l_A 2} + \frac{1}{9}\delta_{l_B 0}\right]\delta_{l_B 1} \tag{5.11b}$$

Margenau expressed the interaction energy in terms of "dispersion-$f$-values"* which are proportional to the absorbing transition probability. If we denote the $f$-values for the emitting atom by $f_{1A}$ and for perturbing atom by $g_{0B}$, we obtain:

$$\begin{aligned} f_{1A} &= \frac{8\pi^2 m}{3h^2}(E_A - E_1) \sum_{m_1} [x_{1A}^2(1) + y_{1A}^2(1) + z_{1A}^2(1)] \\ &= \frac{8\pi^2 m}{3h^2}(E_A - E_1) r_{1A}^2(1) \left[\frac{2}{3}\delta_{l_A 2} + \frac{1}{3}\delta_{l_A 0}\right] \end{aligned} \tag{5.12}$$

$$g_{0B} = \frac{8\pi^2 m}{3h^2}(F_B - F_0) r_{0B}^2(2)\, \delta_{l_A 1} \tag{5.13}$$

If we now let $f_{1A'}$ be the $f$-value for the $d$-states where $l_A = 2$ and $f_{1A}''$ be the $f$-values for those states where $l_A = 0$, the substitution of Eqs. (5.12) and (5.13) into Eqs. (5.11) and the subsequent substitution of Eqs. (5.11) into Eq. (5.4) yields:

For $m_1 = 0$:

$$E_{10} = -\frac{1}{r^6}\frac{3}{4m^2}\left(\frac{he}{2\pi}\right)^4 \left\{\frac{11}{5}\sum_{A'B}\frac{f_{1A'}g_{0B}}{D_{A'B}} + 4\sum_{A''B}\frac{f_{1A''}g_{0B}}{D_{A''B}}\right\} \tag{5.14a}$$

For $m_1 = \pm 1$:

$$E_{10} = -\frac{1}{r^6}\frac{3}{4m^2}\left(\frac{he}{2\pi}\right)^4 \left\{\frac{19}{10}\sum_{A'B}\frac{f_{1A'}g_{0B}}{D_{A'B}} + \sum_{A''B}\frac{f_{1A''}g_{0B}}{D_{A''B}}\right\} \tag{5.14b}$$

It is thus apparent that "... the interaction energy between one atom in a $p$-state and another in an $s$-state depends on the orientation of the former ..."[111] through the value of the magnetic quantum number for the $p$-state.

Eqs. (5.14) may be rewritten as:

$$E_{10} = -\frac{1}{r^6}\frac{3}{4_m^2}\left(\frac{he}{2\pi}\right)^4 \left\{\frac{22 - 3m_1^2}{10}\sum_{A'B}\frac{f_{1A'}g_{0B}}{D_{A'B}} + (4 - 3m_1^2)\sum_{A''B}\frac{f_{1A''}g_{0B}}{D_{A''B}}\right\}$$

and if, ignoring the dependence of the energy on the orientation, we sum over $m_1$ and divide by three, we obtain, as average $E_{10}$:

$$\langle E_{10}\rangle = -\frac{1}{r^6}\frac{3}{2m^2}\left(\frac{he}{2\pi}\right)^4 \left\{\sum_{A'B}\frac{f_{1A'}g_{0B}}{D_{A'B}} + \sum_{A''B}\frac{f_{1A''}g_{0B}}{D_{A''B}}\right\}$$

This equation obviously has the same coefficients for the $f_{1A'}$ and $f_{1A''}$ so that we may write our expression for the interaction energy as follows:

$$\langle E_{10}\rangle = -\frac{1}{r^6}\frac{3}{2m^2}\left(\frac{he}{2\pi}\right)^4 \sum_{AB}\frac{f_{1A}g_{0B}}{D_{AB}} \tag{5.15}$$

This corresponds to the more general form for the interaction energy which had been obtained by London[108] as:†

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* Another name for oscillator strengths.

† We shall discuss London's interaction considerations in some detail in Chap. 8.

$$<E_{A'B'}> = -\frac{1}{r^6}\frac{3}{2m^2}\left(\frac{he}{2\pi}\right)^4 \sum_{A'B} \frac{f_{A'A}g_{B'B}}{D_{ABA'B'}} + S \tag{5.15'}$$

In this equation $S$ refers to the terms which would enter if interactions of higher order than the dipole were included in the perturbing potential. Margenau[110] had investigated the effect of these higher order terms on the van der Waals forces.

Eq. (5.15) may be simplified by applying the London approximation [108] that the summation of $g_{0B}$ over $B$ may be replaced by the multiplicative factor $\alpha\Delta F$ where $\alpha$ is the polarizability of the broadening atom and $\Delta F$ is the mean energy difference for a transition with the resultant absorption of electric dipole radiation by the broadener. As Margenau notes "... Except in the case of rare gases, this will introduce considerable errors ..."[111] since, for rare gases, "... the transition from the lowest state to the next higher state ... involves an energy which is an appreciable portion of the ionization energy."[111] Eq. (5.15) thus becomes:

$$<E_{k0}> = -\frac{1}{r^6}\frac{3}{2m}\left(\frac{he}{2\pi}\right)^2 \alpha\Delta F \sum_A \frac{f_{kA}}{(E_A - E_k)(\Delta F + E_A - E_k)} \tag{5.16}$$

If we consider the sign of $<E_{k0}>$ we find that it is dependent on the sign of $(\Delta F + E_A - E_k)$, that is, on whether the transition is an absorbing or emitting one, since $f_{kA}/(E_A - E_k)$ is always positive and the sign of the remaining factors is obviously always positive. This fact leads to (a) a negative value for $E$ and hence an attractive interaction force for $k = 0$, the absorbing atom initially in the ground state or (b) the appearance of negative terms in the summation for $E_{k0}$ when $k \neq 0$. Let us assume, however, that $<E_{00}>$ and $<E_{10}>$ are negative so that the ground and first-excited states of the absorber — we consider here only this transition — are distorted into energy curves which are functions of the atomic separation $r$, and similar to those shown in Fig. (5.5).

In Fig. (5.5), $E$ would correspond to the frequency of the absorbed radiation when the absorber is not perturbed by the broadener. The separation of the two curves at lesser values of $r$ would correspond to the frequency of radiation which is absorbed when the absorbing and broadening atoms are separated by these values of $r$. There is, as has been mentioned, a lower limit to be imposed on $r$. For example, in the case of the broadening of *Na* lines by *K*, Margenau felt that the equations for the interaction energies "... certainly fail at distances of the order of 5 or 6*A*."[111]

Having obtained rather detailed information as to the forces which, in the present theory, are to act as broadening (or shifting) agents, let us proceed to a consideration of the manner in which these forces are presumed to give rise to this broadening and shift.

### 5.4. LINE SHIFT ACCORDING TO THE EARLY STATISTICAL THEORY

To begin with, the following assumptions were made:

"1. Atom I (the absorber) is surrounded only by individuals of type II (broadeners).

"2. The mutual attraction between structures II will be neglected* ...

"3. Internal electronic changes of atom I, caused by absorption of light, occur adiabatically with respect to its surroundings....

"4. The transition probability of atom I is independent of the configuration of the perturbing atoms ..."[111]

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* This is similar to the assumption of point broadeners (see *supra*, Chap. 4).

We now establish a coordinate system whose origin lies at the absorbing atom and to which the position vectors $r_1, \ldots, r_n$ of the $n$ broadening atoms are referred. If we let the interaction energy between the absorber in its ground state and the $i$-th broadener be $\epsilon(r_i)$, the system energy is $\sum_i \epsilon(r_i)$. In like manner the energy after a transition becomes $E + \eta(r_i)$ where $\eta$ is as given in Fig. (5.5). Thus, the change in the energy due to the transition is given by:

$$\Delta(r_1 \ldots r_n) = E + \sum_i [\eta(r_i) - \epsilon(r_i)] \tag{5.17}$$

From Eq. (5.17) we may obtain the average energy change as:

$$<\Delta> = \int e^{-\sum_i \epsilon(r_i)/kT} \{ E + \sum_i [\eta(r_i) - \epsilon(r_i)] \} d\Omega / \int e^{-\sum_i \epsilon(r_i)/kT} d\Omega \tag{5.18}$$

In Eq. (5.18) we have, in the numerator, integrated the energy difference over the entire $3N$-dimensional space. In this integration the energy difference has been weighted by the Boltzmann factor for each $d\Omega$ range in the $3N$-dimensional space for the ground state energy. Each point in this space will, as in the Stark broadening consideration, correspond to a certain configuration of the system. "The integration in the denominator is performed over the space of each individual separately and yields approximately $V^n$, $V$ being the total volume of the assembly; for $\epsilon(r)$ is known to be different from zero only in a very small sphere about the origin, so that in the remainder of the volume of each individual the integrand is one."[111] The disappearance of $\epsilon(r)$ is, of course, predicated on the fact that the curve of this function is virtually a straight line except near the origin. The assumption pertaining to the integration is strictly true if all atoms are considered point masses or if the density is very low as seen in Chapter 4. In the event of finite atomic diameters, previous occupancy would exclude certain portions of space from the integration for each particle. The errors introduced, however, are probably not as great as those introduced by other necessary approximations. Let us consider the numerator.

$$\begin{aligned}\int e^{-\sum_i \epsilon(r_i)/kT} \{ E + \sum_i [\eta(r_i) - \epsilon(r_i)] \} d\Omega &= EV^n + \int e^{-\epsilon(r_1)/kT} \ldots e^{-\epsilon(r_n)/kT} [\eta(r_1) + \ldots + \eta(r_n) - \epsilon(r_1) \\ &- \ldots - \epsilon(r_n)] d\Omega = EV^n + V^{n-1} [ \int e^{-\epsilon(r_1)/kT} [\eta(r_1) - \epsilon(r_1)] dx_1 dx_2 dx_3 + \ldots \\ &+ \int e^{-\epsilon(r_n)/kT} [\eta(r_n) - \epsilon(r_n)] dx_1 dx_2 dx_3 \\ &= EV^n + V^{n-1} \, n \int e^{-\epsilon(r)/kT} [\eta(r) - \epsilon(r)] \, dx_1 dx_2 dx_3 ]\end{aligned}$$

Thus, Eq. (5.18) becomes:

$$<\Delta> = E + \frac{n}{V} \int e^{-\epsilon(r)/kT} [\eta(r) - \epsilon(r)] \, dx_1 dx_2 dx_3 ] \tag{5.19}$$

Now if we assume that $r > r_1$, $\eta$ may be replaced by $E_{10}$ for $R_1 \leqslant r \leqslant \infty$ and the dotted curve given in Fig. (5.5) results. In like manner $\epsilon$ is replaced by $E_{00}$ within these limits. For $r < r_1$ we assume a statistical weight of zero for $\Delta$. If we let $E_{10} = -b/r^6$ and $E_{00} = -a/r^6$, we obtain:

$$\eta(r) - \epsilon(r) = \frac{(a - b)}{r^6} = \frac{(b - a)}{a} E_{00}$$

so that the line shift becomes:

$$D = 4\pi \frac{b - a}{a} \frac{n}{V} \int_{R_1}^{\infty} E_{00} e^{-E_{00}/kT} \, r^2 dr \tag{5.20}$$

which is simply the Maxwell-Boltzmann weighted average of the energy shifts.

The dependence of the pressure shift on the density of the broadening gas which had been found experimentally by Fuchtbauer, Joos, and Dinkelacker[45] is given by Eq. (5.20). The differentiation of Eq. (5.20) with respect to the temperature yields the following approximate dependence of the shift change on the temperature change:

$$\frac{1}{D}\frac{\partial D}{\partial T} = \frac{1}{kT^2}\frac{\int_{R_1}^{\infty}\epsilon^2 e^{-\epsilon/kT} r^2 dr}{\int_{R_1}^{\infty}\epsilon e^{-\epsilon/kT} r^2 dr} \doteq -\frac{1}{3kT^2}\frac{a}{R_1^6} \tag{5.21}$$

Up to this point we have closely followed the approach utilized in Margenau's[111] first paper on the subject of broadening,* but it behooves us now to use a later and more general work[112] for the continued development.

## 5.5 EARLY ATTEMPTS TO OBTAIN STATISTICAL LINE SHAPE

The fundamental hypothesis on which the theory will be developed was stated by Margenau as "... the chance that the energy of transition of the atom lies within the range $V - \frac{1}{2}dV$ to $V + \frac{1}{2}dV$ is proportional to the length of time which the system spends on that part of curve $\eta$ or $\epsilon$ whence a transition within the range of energies can occur."[112] This hypothesis, when advanced as the basis of spectral line broadening, was, of course, in disagreement with the theory which Weisskopf[103]† had recently advanced.**

This chance of the transition energy corresponds to the intensity of the associated frequency interval in the broadened line. We denote the intensity by $I(V)$, and it follows that:

$$I(V)dV = c\int_V dt \tag{5.22}$$

In Eq. (5.22) $c$ is simply a constant, and we are integrating the time over the energy range, $dV$, under consideration, "... the length of time which the system spends on that part of curve $\eta$ or $\epsilon$ whence a transition with the range of energies can occur."[112] A repetitive but important statement.

Before proceeding, we add two conditions to those already in force. (a) In considering the $n$ foreign perturbing atoms we neglect the Maxwell-Boltzmann spatial distribution factor, and (b) we consider the motion as uniform between two collisions. We may neglect the Boltzmann factor, which would be $e^{-\epsilon(r)/kT}$ for the initial state distribution, "... for $\epsilon(r)$ is known to be different from zero only in a very small sphere about the origin ..."[111] as we have seen earlier. The reason for assumption (b) above will become apparent in what is to follow.

Now let the radial coordinates — referred to the origin of coordinates which has been established at the absorber — be given by $r_1, r_2, \ldots, r_n$ for the $n$ perturbing atoms. Thus, under the assumptions (a) and (b) above, Eq. (5.22) becomes:††

$$\begin{aligned} I(V)dV &= c\int_{r_1\sim V}\cdots\int_{r_n\sim V}\int_{\vartheta_1}\cdots\int_{\vartheta_n}\int_{\varphi_1}\cdots\int_{\varphi_n} r_1^2\ldots r_n^2 \sin\vartheta_1\ldots\sin\vartheta_n\, dr_1\ldots dr_n\, d\vartheta_1\ldots d\vartheta_n\, d\varphi_1\ldots d\varphi_n \\ &= c(4\pi)^n\int\cdots\int_V r_1^2\ldots r_n^2\, dr_1\ldots dr_n \end{aligned} \tag{5.23a}$$

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* It should be mentioned that Kulp[96] independently covered much the same ground as did Margenau at about the same time.

† See *infra*, Chap. 6.

** In the process of advancing, Weisskopf hurled a rather blunt verbal harpoon at Jablonski's theory[74] which after all forms the basis for the considerations of this chapter. Margenau's return thrust[113] will be discussed at a later point.

††Instead of "time" being now the determining factor for our $dV$ "chance", spatial distribution is the factor due to the assumption of uniform motion.

where $r_1 \ldots r_n$ are integrated over that range which gives the desired $dV$. $dV$ now refers to the difference between the perturbed energy and the unperturbed energy $V_\infty$ . It is apparent that $c$ is simply the normalizing factor $v^{-n}$ so that we obtain:

$$I(V)dV = \left(\frac{4\pi}{v}\right)^n \int \ldots \int_V r_1^2 \ldots r_n^2 \, dr_1 \ldots dr_n \tag{5.23b}$$

Let us refer back to Eq. (5.16). For the lower state we let $V_\epsilon = -a/r_i^6$, and for the upper state we let $V_\eta = -b/r_i^6$. Then for the interaction energy change due to the $i$-th perturber we obtain $(b - a)/r_i^6$ so that the total line perturbation becomes:

$$V = (b - a) \sum_{i=1}^{n} \frac{1}{r_i^6} = \beta \sum_{i=1}^{n} \frac{1}{r_i^6} \tag{5.24}$$

It would be convenient to rewrite Eq. (5.23) as an integral over all configuration space. As in the Stark effect considerations, we may accomplish this by multiplying it by a Dirichlet factor which has the value one for $-\frac{1}{2}dV \leqslant V \leqslant \frac{1}{2}dV$ and zero for all other values of $V$. After the suitable Dirichlet factor has been chosen, Eq. (5.23) becomes:

$$I(V)dV = \frac{1}{\pi}\left(\frac{4\pi}{v}\right)^n \int \ldots \int \int_{-\infty}^{+\infty} d\Upsilon \, \frac{\sin\left(\frac{1}{2}\Upsilon dV\right)}{\Upsilon} \exp\left[-iV\Upsilon + i\beta\Upsilon \sum \frac{1}{r_j^6}\right] r_1^2 \ldots r_n^2 \, dr_1 \ldots dr_n$$

$$= \frac{1}{\pi}\left(\frac{4\pi}{v}\right)^n \int_{-\infty}^{+\infty} \frac{\sin\left(\frac{1}{2}\Upsilon dV\right)}{\Upsilon} \, e^{-iV\Upsilon} \left[\int_{R_1}^{R} e^{i\beta\Upsilon/r^6} r^2 dr\right]^n d\Upsilon \tag{5.25}$$

The limits which have been placed on $r$ in Eq. (5.25) call for clarification. We have mentioned the necessity for putting a lower limit on $r$, and this is, of course, $R_1$, since we cannot expect our potential curves to be valid at very small $r$. $R$ is defined by $v = 4/3\ \pi\ R^3$, the volume of gas under consideration. In Eq. (5.25) we have also rewritten the product of the $n$ integrals as the product of $n$ identical integrals as was done in obtaining Eq. (5.19).

By virtue of the "smallness" with which the definition of a differential vests it, we may replace $\sin\left(\frac{1}{2}\Upsilon\, dV\right)$ by $\left(\frac{1}{2}\Upsilon\, dV\right)$ in Eq. (5.25). If we let:

$$E = \frac{\beta}{r^6}; \quad u(E) = -\frac{2}{3}\frac{\pi}{v}\frac{\beta^{1/2}}{E^{3/2}}$$

Eq. (5.20) becomes:

$$I(V)dV = \frac{dV}{2\pi} \int_{-\infty}^{+\infty} e^{-iV\Upsilon} \left[\int_{\beta/R^6}^{\beta/R^6} e^{i\Upsilon E} u(E) dE\right]^n d\Upsilon \tag{5.26}$$

If we now let:

$$f(\Upsilon) = -\frac{2\pi}{3v}\beta^{1/2} \int_{\gamma}^{\beta/R^6} \frac{e^{i\Upsilon E}}{E^{3/2}} dE \tag{5.27}$$

where $\gamma = \beta/R_1^6$, we obtain:

$$I(V) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-iV\Upsilon} [f(\Upsilon)]^n d\Upsilon \tag{5.28}$$

Now let $\Upsilon\gamma = x$, $v_1 = 4/3\,\pi R_1^3$, and $u = \Upsilon E$. We now integrate by parts to obtain:

$$f(x) = \frac{2\pi}{3v}\left(\frac{\beta x}{\gamma}\right)^{1/2}\left\{ \left.\frac{e^{iu}}{u^{1/2}}\right|_{x}^{xR_1^6/R^6} - 2i\int_{x}^{xR_1^6/R^6} \frac{e^{iu}}{u^{1/2}}\,du \right\} \doteq 1 - \frac{v_1}{v}e^{ix} - i\,\frac{v_1}{v}x^{1/2}\int_{x}^{0}\frac{e^{iu}}{u^{1/2}}\,du \tag{5.29}$$

The remaining integral in Eq. (5.29) is a combination of Fresnel integrals which Margenau obtained from Jahnke and Emde,[208a] so that:

$$f(x) = 1 - \frac{v_1}{v}\left[\sqrt{2\pi x}\,S(x) + \cos x\right] + i\,\frac{v_1}{v}\left[\sqrt{2\pi x}\,C(x) - \sin x\right] \tag{5.30}$$

From Eq. (5.29), it is apparent (we recall that $v_1$ is a small sphere of radius $R_1$) that $|f(x)| < 1$. This fact justifies the replacement of Eq. (5.30) by $\exp\left[-\frac{nv_1}{v}\left\{\sqrt{2\pi x}\,S(x) + \cos x - i\sqrt{2\pi x}\,C(x) + i\sin x\right\}\right]$ since the right side of Eq. (5.30) may be considered as the first two terms of the McLaurin expansion of the exponential before raising it to the $n$-th power. Eq. (5.28) thus becomes:

$$I(V) = \frac{1}{2\pi\gamma}\int_{-\infty}^{+\infty}\exp\left[-\frac{nv_1}{v}\left\{\sqrt{2\pi x}\,S(x) + \cos x - i\sqrt{2\pi x}\,C(x) + i\sin x\right\} - i\,\frac{v}{\gamma}x\right]dx$$

Since $C(-x) = iC(x)$ and $S(-x) = -iS(x)$, this equation becomes:

$$I(V) = \frac{1}{\pi\gamma}\int_{0}^{\infty}\cos\left[\frac{nv_1}{v}\left[\sqrt{2\pi x}\,C(x) - \sin x\right] - \frac{v}{\gamma}x\right]\exp\left[-\frac{nv_1}{v}\left\{\sqrt{2\pi x}\,S(x) + \cos x\right\}\right]dx \tag{5.31}$$

Eq. (5.31) gives the intensity distribution in our asymmetrically broadened, shifted spectral line, but it has the undesirable trait of responding only to graphical integration. Margenau[112] carried out the requisite graphical integration for $n/v$ corresponding to 50 atmospheres, $\beta = 47$ volts $\times\,A^6$, and $R_1 = 5.6A$. His results are given by the dotted line curve in Fig. (5.6). The solid line curve is the $Hg$ 2537 line as obtained by Fuchtbauer, Joos, and Dinckelacker[46] for broadening by 50 atmospheres of $N_2$.

It is apparent from Fig. (5.6) that the theory shows poorest agreement with experiment on the blue side of the line, since no agreement at all may be considered relatively poor. Eq. (5.31) allows no broadening to the blue (or shift), and the theoretical intensity always goes to zero at the unperturbed line position. The reason for this becomes apparent when we consider the fact that we have not allowed transitions at separations less than $R_1$, thus neglecting those portions of the potential curves which give rise to blue shifts of the frequency. "Furthermore, the assumption of uniform motion between collisions does particular violence to transitions taking place on the inner portions of the curves."[112]

An approximate calculation[112*] yielded a symmetrical line

$$I(V) = \frac{1}{\sqrt{2\pi n}}\,e^{-(n<E> - V)^2/2ns^2} \tag{5.32}$$

where $$<E> = \frac{4\pi\beta}{3vR_1^3},\quad s^2 = \frac{4\pi\beta^2}{9vR_1^9},\ \text{and a half width:}$$

$$\delta = \frac{1.36}{h}\left(\frac{n}{v}\,\frac{4\pi}{3}\,R_1^3\right)^{\frac{1}{2}}\frac{\beta}{R_1^6} \tag{5.33}$$

---

[*] We will not reproduce this calculation since it does not contribute overly to the flow of the development.

Margenau[113] next considered various shapes of interaction curve in an attempt to obtain from Eq. (5.25) various spectral line forms. First, we consider Eq. (5.25) in a one-dimensional form for simplicity. Then we assume the $\epsilon$-curve in Fig. (5.5) to be flat, so that we may replace $\beta\Sigma\frac{1}{r_i^6}$ by $\Sigma f(x_i)$ where $f(x_i)$ is the $\eta$-curve for the $i$-th particle. Eq. (5.25) then becomes:

$$I(V)dV = \frac{L^{-n}}{\pi}\int_{-\infty}^{+\infty} d\Upsilon\left[\frac{\sin(\frac{1}{2}\Upsilon dV)}{\Upsilon}\right] e^{-i\nu\Upsilon}\int_0^L\ldots\int_0^L e^{i\Upsilon\Sigma f(x_i)}\,dx_1\ldots dx_n \qquad (5.34)$$

It may be noted that in Eq. (5.34) the lower limits of the $r$-integration are zero. This may be interpreted as the distance of closest approach of the broadener rather than separation zero.

Figs. (5.7a), (5.7c), and (5.7e) give the $f(x)$ curves which allow the evaluation of Eq. (5.34) in a closed form to yield the line shapes given by Figs. (5.7b), (5.7d) and (5.7f).

Our theory has now developed to the point where an explanation of the line shift has been obtained As we have mentioned, Fuchtbauer, Joos, and Dinkelacker[45] had found a linear dependence of the line shift on the pressure, and the theory appears to have yielded this through Eq. (5.20). In addition, the theory has yielded the line shape through Eq. (5.31). This equation has not yet proven amenable to evaluation in closed form, and this closed form evaluation would appear to be the next step. At about this stage in the evolution of the theory, however, Kuhn[92] and Kuhn and London[94] brought up certain additional difficulties to be resolved in and features to be incorporated into the theory.

### 5.6. SOME OBJECTIONS TO THE STATISTICAL THEORY

Kuhn and London[94] pointed out that the statistical distribution of intensity — what they termed the "occurrence distribution" — only agrees with the actual distribution in the case of infinitely small values of the molecular velocities. For finite velocities each point on the distribution curve should be assigned a diffuseness as has been mentioned* in connection with Jablonski's first paper[74] and subsequently ignored.

Kuhn[92] investigated shift and broadening in a semi-quantitative manner with a view toward using these phenomena to determine intermolecular forces. As a result of this investigation he felt that (a) the theory yields a line shift dependence on the square of the pressure rather than on the pressure as had been advanced, (b) the intensity in the long wave length wing of the line should vary as $(\Delta\nu)^{-3/2}$ and (c) the interaction energy $-\beta/r^6$ might well be replaced by $-\beta r^p$ for certain cases.

Let us consider and dispose of (c) above first. As Margenau[87] pointed out $-\beta/r^6$ yields reasonable results above a certain separation; whereas, higher powers of $r$ become appreciable only at small distances of separation. If a dependence on $r^{-p}$ is assumed the outer and major portion of the potential curve is falsified, and certainly no improvement is obtained. The ideal but impractical solution would, of course, be the use of $r^{-6}$ and higher power terms.

As concerns (b) above Kuhn concludes that "... the proportionality to $N$ ... is ... illusory ..."[92], and we may follow his reasoning by considering Eq. (5.20) which may be slightly rewritten by neglecting the Maxwell-Boltzmann factor as:

$$D = \frac{4}{3}(a - b)\pi\frac{n}{V}\frac{1}{R_1^3} \qquad (5.35)$$

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* See *supra*, p. 94.

"Identification of . . . $(D)$ with $\nu_0 - \nu_{max}$ is only possible if $R$ is made equal or proportional to the average distance of the atoms, i.e., if $1/R$ is proportional to $n/V$ which makes . . . $(D)$ proportional to $(n/V)^2$."[93] This proportionality between the shift and the square of the density brings about a disagreement with the results of Fuchtbauer, Joos, and Dinckelacker,[45] the resolution of which we will defer. Since we have so far only obtained the intensity distribution in integral form, (b) above as yet presents no contradictions. Insofar as the method by which Kuhn obtained the intensity dependence on $\Delta\nu$ is concerned, it is so qualitative as to render its inclusion here of no particular moment.

## 5.7. THE STATISTICAL LINE SHAPE

In Eq. (5.25) let us, with Margenau,[114] replace $V$ by $\Delta\nu$, where $\Delta\nu$ is the frequency separation from the line center, to obtain:

$$I'(\Delta\nu)\, d(\Delta\nu) = \frac{1}{\pi}\left(\frac{4\pi}{v}\right)^n \int \ldots \int r_1^2 \ldots r_n^2 dr_1 \ldots dr_n \int_{-\infty}^{+\infty} d\Upsilon \, \frac{\sin\left(\frac{1}{2}\Upsilon\, d(\Delta\nu)\right)}{\Upsilon} \, e^{-i(\Delta\nu)\Upsilon + i\beta\Upsilon\Sigma r_i^{-6}} \tag{5.36}$$

where the limits of integration are the same as those which have been applied to Eq. (5.25). It is certainly legitimate to replace $e^{-i\beta\Upsilon/r^6}$ by $1 - (1 - e^{i\beta\Upsilon/r^6})$, and, after expressing Eq. (5.36) by the product of $n$ identical integrals and replacing $\sin\left(\frac{1}{2}\Upsilon\, d(\Delta\nu)\right)$ by $\frac{1}{2}\Upsilon\, d(\Delta\nu)$ as has been done previously, this yields:

$$I'(\Delta\nu) = \frac{1}{2\pi}\left(\frac{4\pi}{v}\right)^n \int_{-\infty}^{+\infty} d\Upsilon e^{-i(\Delta\nu)\Upsilon} \left\{ \int \left[1 - (1 - e^{i\beta\Upsilon/r^6})\right] r^2 dr \right\}^n \tag{5.37}$$

Now let us consider the term in braces in Eq. (5.37). The integration should be carried from the closest separation $R_1$ to a maximum separation $d$ which is, of course, related to the volume of gas under consideration by $v = (4/3)\,\pi\, d^3$. Since $R_1$ is small, it is apparent that only a very small error will be introduced by integrating $r^2dr$ from the lower limit zero. On the other hand, the error which we shall introduce by taking lower limit zero for the remainder of the integrand in the braces will require discussion later. We may write $(1 - e^{i\beta\Upsilon/r^6})$ as $-\dfrac{i\beta\Upsilon}{r^6} + \dfrac{\beta^2\Upsilon^2}{2r^{12}} - \ldots$, from which it is apparent that, since $d$ is large, we may take infinity as the upper limit of $\int (1 - e^{i\beta\Upsilon/r^6})\, r^2dr$ with no appreciable error. Thus we obtain:

$$\int\left[1 - (1 - e^{-i\beta\Upsilon/r^6})\right] r^2dr = \frac{V}{4\pi}\left(1 - \frac{4\pi V'}{V}\right) \tag{5.38}$$

where $V' = \int_0^\infty (1 - e^{i\beta\Upsilon/r^6}) r^2dr$. In raising the braced expression in Eq. (5.37) to the $n$th power Margenau ". . . allows the volume of the gas to increase indefinitely while maintaining $N = n/V$ constant."[114] This amounts to the same procedure as allowing $d$ to approach infinity, while keeping the density constant. Since $\lim\,(1 - 4\pi\, NV'/n)^n = e^{-4\pi NV'}$, Eq. (4.37) then becomes:

$$I'(\Delta\nu) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\Upsilon e^{-i(\Delta\nu)\Upsilon}\, e^{-4\pi NV'(\Upsilon)} \tag{5.39}$$

when the factor $\left(\dfrac{4\pi}{V}\right)^n$ in Eq. (5.36) has been cancelled by the reciprocal of this factor in Eq. (5.38).

Now let $x = \beta T/r^6$ in $V'$ and rewrite $V'$ slightly as:

$$V'(T) = -\frac{(\beta T)^{1/2}}{6}\int_0^\infty\left(\frac{\cos x}{x^{3/2}} + i\frac{\sin x}{x^{3/2}}\right)dx = \frac{(\beta T)^{1/2}}{3}\int_0^\infty\left(\frac{\sin x}{x^{1/2}} - i\frac{\cos x}{x^{1/2}}\right)dx = \frac{\sqrt{2\pi\beta T}}{6}(1 - i) \quad (5.40)$$

where an integration by parts followed by the reasonably intelligent use of an integral table yields the result. Substitute Eq. (5.40) into (4.39) to obtain:

$$I'(\Delta\nu) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dT\left\{ e^{-i(\Delta\nu)T}\, e^{-2/3\, N\pi^{3/2}\beta^{1/2}T^{1/2}}\, e^{i2/3\, N\pi^{3/2}\beta^{1/2}\tau^{1/2}}\right\}$$

$$= \frac{1}{2\pi}\int_{-\infty}^{0} dT\,\{\,\} + \frac{1}{2\pi}\int_0^\infty dT\,\{\,\} = \frac{1}{2\pi}\int_0^\infty dT e^{i(\Delta\nu)T}\, e^{-i2/3\, N\pi^{3/2}\beta^{1/2}T}\, e^{-2/3\, N\pi^{3/2}\beta^{1/2}T^{1/2}}$$

$$+ \frac{1}{2\pi}\int_0^\infty dT e^{i(\Delta\nu)T}\, e^{-2/3\, N\pi^{3/2}\beta^{1/2}T/^{1/2}}\, e^{i2/3\pi^{3/2}\beta^{1/2}T^{1/2}}$$

$$= \frac{1}{\pi}\int_0^\infty \exp\left[-\frac{2\pi}{3}N\sqrt{2\pi\beta T}\right]\cos\left[(\Delta\nu)T - \frac{2\pi}{3}N\sqrt{2\pi\beta T}\right]dT$$

$$= \frac{2}{3}\pi\beta^{1/2}N(\Delta\nu)^{-3/2}\exp\left[-\frac{4}{9}\frac{\pi^3\beta N^2}{\Delta\nu}\right] \quad (5.41)$$

from the tables.

If we let $\gamma = \frac{2}{3}\pi\beta^{1/2}N$ for convenience of notation, this equation becomes:

$$I'(\Delta\nu) = \gamma(\Delta\nu)^{-3/2}\, e^{-\pi\gamma^2/\Delta\nu} \quad (5.42)$$

It should be made clear here that positive $\Delta\nu$ refers to a displacement from the unperturbed line position toward the red, that is, negative frequency displacements. As Kuhn[92] had predicted, the intensity in the wing of the line where the exponential has become small varies as $(\Delta\nu)^{-3/2}$. We may further note from Eq. (5.42) that the poor correspondence between the predicted and the experimental curves on the blue side of the shifted line remains, and that the intensity again goes to zero at the position of the unperturbed line as in Eq. (5.31). The superposition of the velocity distribution on this statistical distribution tends to alleviate this non-agreement. We shall continue to defer a consideration of this superposition.

## 5.8. THE STATISTICAL SHIFT AND HALF-WIDTH

The shift of the intensity maximum of the line may be found by equating the first derivative of Eq. (5.42) to zero as:

$$\Delta\nu_{\max} = \frac{2}{3}\pi\gamma^2 = \left(\frac{2}{3}\pi\right)^3\beta N^2 \quad (5.43)$$

The noteworthy feature in Eq. (5.43) is the dependence of the shift on the square of the density in agreement with Kuhn.[92] This leads us to a contradiction of Fuchtbauer, Joos, and Dinkelacker's results, or does it? Fuchtbauer et al's observations were made on the *Hg*2537 line broadened by pressures up to 50 atmospheres. Margenau and Watson[121] had also found a linear relationship between pressure and line shift in the case of the *Na D* lines for relative densities[*] around 10. Later the same authors reported[122] departures from this linear shift behavior in the case of the *K* resonance lines at relative densities above 20. From these investigations Margenau[114] concluded that Fuchtbauer[45] et al's measurements and the later ones of Watson and himself[121] had not been carried to sufficiently high pressure to show the quadratic dependence on the gas density. This is, of course, not completely conclusive at this point.

Also from Eq. (5.42) or its plot, we may obtain the half-width of the shifted line as:

$$\delta = 1.85\,\pi\gamma^2 \tag{5.44}$$

Before leaving Eq. (5.42) let us briefly consider the effect of taking lower limit zero in Eq. (5.38). — This effect is indirectly connected with the simple assumption of a potential curve of the form $r^{-6}$ which, as we have noted, is increasingly inaccurate as the optical impact separation (distance of closest approach) falls farther below 10*A*. – The effect of allowing these atomic separations of such small magnitude is to overly lengthen the tail of the line by permitting unwarrantedly large values of $\Delta\nu$. It is apparent that the intensity should be practically zero for $\Delta\nu > \Delta\nu_1 = \beta/R_1{}^6$ for the true statistical distribution. Thus the ratio $\Delta\nu_1/\Delta\nu_{\max}$ should give us a rough measure of the validity of Eq. (5.42). If we assume $R_1 \sim 5A$

$$\frac{\Delta\nu_1}{\Delta\nu_{\max}} = \frac{1}{(5A)^6\left(\frac{2}{3}\pi\right)^2 N^2} \doteq \frac{10^4}{N'^2} \tag{5.45}$$

where $N'$ is measured in units of relative density. Thus, the ratio varies from $10^4$ at relative density unity to 10 at relative density 30, so that the validity of the theoretical line wing decreases in this manner. At relative density 30, the intensity corresponding to $\Delta\nu_1$ is 10 percent of the maximum so that the error due to our lower limit of integration will be less than 10 percent for this pressure.

## 5.9. SUMMARY OF THE EARLY STATISTICAL THEORY

Up to this point the development has been primarily classical. We have assumed that an interaction which is proportional to $r^{-6}$ takes place between the absorber and its perturbers, this interaction being different for the ground and excited states of the absorber. Thus, say, unique electronic transitions result not in the absorption of radiation of a unique frequency but rather in the absorption of a band of frequencies, the frequency absorbed being dependent on the separation of the absorber from its perturbers. The intensity of any given frequency in this line is now taken proportional to the probability of a configuration of the perturbers such that the system, absorber + perturbers occupies the position on the interaction potential curves corresponding to this frequency. Thus, we see the semi-classical approach which has so far been exclusively applied.

## 5.10. THE JABLONSKI THEORY AND PERTURBED TRANSITION PROBABILITY

Jablonski[75] felt that a wave mechanical theory† of line broadening should be developed and that "... derartige Theorie soll im engsten Abschluss an die Wellenmechanische Theorie der Bandenintensitäti-

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[*] Margenau and Watson had defined the unit of the "relative density" as "... the amount of perturbing gas used in the experiment at 0°C. and 1 atm."[121]

† The Jablonski theory is the sole quantum broadening theory which does not utilise the assumption of the "classical path," that is, it is the only theory which treats the translational motion quantum mechanically.

verteilung entwickelt werden."[75] To this end Jablonski's paper of 1937[75] and those which followed[76-79] were devoted.*

We begin, with Jablonski,[75] by assuming that our absorber (emitter) and the $N_1$ perturbers, whose perturbing influence shall be responsible for the broadening of the spectral line, go to make up a very large, $(N_1 + 1)$-atomic molecule.

We are interested in the two eigenfunctions of this molecule which are associated with the two states between which the radiating transition is to take place. Let these eigenfunctions be designated $\psi(E,q,r)$ and $\psi'(E',q,r)$. $E$ and $E'$ are the energies of the two states; $q$ represents the totality of all electron coordinates, and $r$ is the aggregate of the nuclear coordinates. In order to avoid the use of eigendifferentials, the atomic system is restricted to a finite volume $V$ so that $\psi(E,q,r) = \psi'(E',q,r) = 0$ for $r \geqslant R$, where we have referred all $r_i$ to a coordinate system at the emitter and have placed the emitter at the center of a sphere. This restriction to a finite volume, of course, quantizes the nuclear translational (molecular vibrational) motions although our level density will be great enough so that we shall closely approach the continuous curves of our earlier considerations.

The first approximation, that of the separability of electronic and nuclear motions, is now introduced.

$$\psi(E,q,r) = \psi_e(E_e, q)\psi_k(E_k,r); \quad E = E_e + E_k \tag{5.46a}$$

$$\psi'(E',q,r) = \psi_e'(E_e',q)\psi_k'(E_k,r); \quad E' = E_e' + E_k' \tag{5.46b}$$

If we consider an electronic transition, Eqs. (5.46) yield for the matrix element of $E \longleftrightarrow E'$:

$$\begin{aligned} D_{EE}' &= \int \bar{\psi}'(E_e', q) D\psi_e(E_e, q)d\tau_q \int \bar{\psi}_k'(E_k, r)\psi_k\,(E_k, r)d\tau_r \\ &= M \int \bar{\psi}_k'(E_k', r)\psi_k(E_k, r)d\tau_r \end{aligned} \tag{5.47}$$

In the first approximation $M$ is independent of $r$, and we may note that this is merely a restatement of the Franck-Condon principle in that this infers that the nuclear motion is momentarily unaffected by the electronic transition. Were we to proceed to the second approximation we would there find $M$ a linear function of $r$.

We must now find these nuclear eigenfunctions and in order to do this, we first recall an assumption which has already been utilized. It is assumed that the perturbing forces are additive, which means that the nuclear eigenfunction for the system may be represented as a product of nuclear eigenfunctions as follows:

$$\psi = \prod_{i}^{N_1} \psi_i \tag{5.48}$$

The reason that this product results may be found in the separability of the Schrodinger equation which results from a potential energy of the form $U(r) = \sum\limits_i U_i(r_i)$, where $r_i$ is the radius vector linking the emitter and the $i$-th disturber. Thus, Eq. (5.48) would yield $N_1$ equations of the form:

$$\left[\frac{\hbar^2}{2\mu} \nabla_i^2 + E_i - U_i(r_i)\right]\psi_i = 0 \tag{5.49}$$

where $i$ refers to the $i$-th perturber. Let us obtain Eq. (5.49) after the manner of Bethe.[6]

We consider a system consisting of the emitter and one perturber. Let the mass of the emitter be $M$

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* One of these articles[77] was not available to the author. The material contained in this article, however, is covered by subsequent papers which were consulted.

and that of the perturber $m$. Let the coordinates of the emitter be $(x_1^{(1)}, x_2^{(1)}, x_3^{(1)})$ and of the disturber $(x_1^{(2)}, x_2^{(2)}, x_3^{(2)})$. Then the emitter-broadener separation is $r^2 = \sqrt{x_1^2 + x_2^2 + x_3^2}$ where:

$$x_i = x_i^{(2)} - x_i^{(1)} \tag{5.50a}$$

and the coordinates of the center of mass of the system are:

$$X_i = \frac{\mu}{m} x_i^{(1)} + \frac{\mu}{M} x_i^{(2)} \tag{5.50b}$$

The Hamiltonian of the system is:

$$H = \frac{p_1^2}{2M} + \frac{p_2^2}{2m} + U(r)$$

which yields the Schrodinger equation:

$$\frac{\hbar^2}{2M} \nabla_1^2 \psi + \frac{\hbar^2}{2m} \nabla_2^2 \psi + (E - U(r))\, \psi = 0 \tag{5.51}$$

where $\nabla_i^2 = \sum_{j=1}^{3} \frac{\partial^2}{\partial x_j^{(i)2}}$. The eigenfunction $\psi$ is a function of the six $x_i^{(j)}$. Utilising Eqs. (5.50), we may easily show that, since $\psi = \psi(X_1\,(x_1^{(1)}, x_1^{(2)}), x_1\,(x_1^{(1)}, x_1^{(2)}) \ldots)$:

$$\frac{\partial^2}{\partial x_j^{(1)2}} = \left(\frac{\mu}{m_j}\right)^2 \frac{\partial^2}{\partial X_j^2} + (-1)^i\, 2 \frac{\mu}{m_j} \frac{\partial^2}{\partial x_j \partial X_j} + \frac{\partial^2}{\partial x_j^2}\,;\; m_j = \begin{matrix} m \text{ for } j = 1 \\ M \text{ for } j = 2 \end{matrix} \tag{5.52}$$

where $\mu = \frac{mM}{m + M}$. Utilising Eq. (5.52) we may now transform Eq. (5.51) to the following:

$$\frac{\hbar^2}{2(M+m)} \sum_{j=1}^{3} \frac{\partial^2 \psi}{\partial X_j^2} + \frac{\hbar^2}{2\mu} \sum_{j=1}^{3} \frac{\partial^2 \psi}{\partial x_j^2} + [E - U(r)]\, \psi = 0 \tag{5.53}$$

If we neglect the center of mass motion as given by the first term in Eq. (5.53) — separability allows us to do so, and, in addition, this has no effect on our problem — we obtain Eq. (5.49), and this equation describes the behavior of one of our broadeners with respect to the emitter.

Now let $k^2 = \frac{2\mu E}{\hbar^2}$ and $U(r) = \frac{2\mu}{\hbar^2} V(r)$ in Eq. (5.49) to obtain:

$$\nabla^2 \psi + [k - U(r)]\, \psi = 0 \tag{5.54}$$

The solution* to this equation, after setting it up in spherical polar coordinates, is:

$$\psi_k = \sum_{l=0}^{\infty} A_l P_l (\cos \Theta)\, L_{kl} (r) \tag{5.55}$$

where $rL_{kl}(r) = G_{kl}(r)$ satisfies the equation:

$$\frac{d^2 G_{kl}}{dr^2} + \left[k^2 - U(r) - \frac{l\,(l + 1)}{r^2}\right] G_{kl} = 0 \tag{5.56a}$$

Each radial eigenfunction $L_{kl}$ refers to a broadening atom of energy $\frac{k^2\hbar^2}{2\mu}$ and relative angular momentum

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* See *infra*, Eq. (9.34) and subsequent.

$\sqrt{l(l+1)}\hbar$. In solving a Schrodinger equation for a given $U(r)$, one obtains a set of orthogonal eigenfunctions, but in the case of this system we have $U(r)$ and $U'(r)$ for the two states between which our transition is to take place, and the $L_{kl}$ and $L'_{k'l'}$ resulting from these different nuclear potential functions for the two states are not generally orthogonal. We may then write:

$$\int \psi_k \psi_{k'}' d\tau = 2\pi \int_0^\pi \int_0^\infty \sum_l \sum_{l'} A_l A_{l'}' \, P_l(\cos \Theta) \, P_{l'}(\cos \Theta) \, L_{kl}(r) L'_{k'l'}(r) \cdot \sin \Theta d\Theta dr \tag{5.57}$$

In Eq. (5.57) the integral is zero unless $l = l'$ due to the orthogonality of the Legendre polynomials which amounts to another restatement of the Franck-Condon principle in that the relative angular momentum remains constant during the radiating transition.

The Wentzel-Kramers-Brillouin (WKB)* approximation yields the following solutions for Eq. (5.56):

$$rL_{kl} = \begin{cases} \dfrac{c}{\sqrt{p_{kl}(r)}} e^{-\frac{1}{\hbar}\int_r^{r_0} |p_{kl}(r)| dr} & \text{for } r < r_0 \\[2ex] \dfrac{c}{\sqrt{p_{kl}(r)}} 2 \cos \left[ \dfrac{1}{\hbar} \displaystyle\int_{r_0}^{r} p_{kl}(r) dr - \dfrac{\pi}{4} \right] & \text{for } r > r_0 \end{cases} \tag{5.58}$$

where $p_{kl}(r) = \sqrt{k^2 - U(r) - \dfrac{l(l+1)}{r^2}}$, the radial component of the relative momentum. $r_0$ is the collision partner separation for which $p_{kl}(r) = 0$.

Now let us consider Eq. (5.56a) for the case of large $r$ where $k^2 \ll U(r) + \dfrac{l(l+1)}{r^2}$. In this asymptotic case we should expect a solution of the form $G_{kl} = A(kr + \Upsilon)$, the solution to:

$$\frac{d^2 G_{kl}}{dr^2} + k^2 G_{kl} = 0 \tag{5.56b}$$

Upon the evaluation of $A$ and $\Upsilon^{104}$ one obtains, for $r \gg r_0$ †:

$$L_{kl} = \frac{c}{r} \sin\left(kr - \frac{l\pi}{2} + \eta_l\right) \tag{5.59}$$

where $\eta_l$ is the phase difference. We may now apply our boundary condition $\psi_k = 0$ for $r = R$ to obtain:

$$\frac{C}{R} \sin\left(kR - \frac{l\pi}{2} + \eta_l\right) = 0$$

or

$$kR - \frac{l\pi}{2} + \eta_l = \eta\pi \tag{5.60}$$

where $n$ is an integer. From Eq. (5.60) we may evaluate $k$ and subsequently the energy:

$$E_l = \frac{k^2\hbar^2}{2\mu} = \frac{\left(n\pi + \frac{l}{2}\pi - \eta_l\right)^2}{2\mu R^2} \hbar^2 \tag{5.61}$$

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* See Appendix VIII.

† Jablonski chose the lower limit of $r$ as $\sim 10^{-7}$ cm.

Let us determine from Eq. (5.61) the energy level density. Differentiation of Eq. (5.61) yields:

$$\frac{dn}{dE_l} = \frac{\sqrt{2\mu}\,R}{2\hbar\pi\sqrt{E_l}} + \frac{1}{\pi}\frac{d\eta_l}{dE_l} \tag{5.62}$$

as the number of levels per unit of energy appropriate to the angular momentum $\sqrt{l(l+1)}\,\hbar$. Eq. (5.62) is valid for the level density for $R$ large compared to the range in which $U(r) + \frac{l(l+1)}{r^2}$ is not small compared to $k^2$.

We now form the overlap integral:

$$\int_0^R \cdots \int_0^R \prod_i^{N_1} L_{inl}\, L'_{in'l}\, r_1^2\, dr_1 \ldots dr_n = \prod_i^{N_1} \int_0^R G_{inl}\, G'_{in'l}\, dr_i \tag{5.63}$$

If we now let

$$\prod_i^{N_1} P_{inn'l} = \prod_i^{N_1} \left| \int_0^R G_{inl}(r)\, G'_{in'l}(r)\, dr \right|^2 \tag{5.64}$$

$P_{inn'l}$, the square of the matrix element for the $i$-th broadener, is the probability that the nuclear state will proceed from $n,l$ to $n',l$ as a result of the electronic radiating transition of the emitter. The product given by Eq. (5.64) is the probability that all perturbers will undergo this change in nuclear state due to the radiating transition. We normalize the probability of finding a perturber somewhere in the region $0 \leqslant r \leqslant R$ in the usual manner:

$$\int_0^R |G_{inl}(r)|^2\, dr = 1 \tag{5.65a}$$

Since except for a small region ($r < 10^{-7}$ cm.) $G_{inl}(r) = rL_{inl} = c\sin\left(kr - \frac{l\pi}{2} + \eta_l\right)$, we satisfy Eq. (5.65a) as follows:

$$c^2 \int_0^R \sin^2\left(kr - \frac{l\pi}{2} + \eta_l\right) dr = c^2\,\frac{R}{2} = 1 \tag{5.65b}$$

thus evaluating $c$. We now let:

$$P_{inn'l} = \frac{A_{inn'l}}{R^2} \tag{5.66}$$

If we multiply Eq. (5.66), the relative transition probability, by Eq. (5.62), the level density, in which we neglect $\eta_l$ as small, we obtain:

$$P_{iEE'l} = \frac{A_{iEE'l}}{R}\,\frac{\sqrt{\mu}}{\hbar\pi\sqrt{2E_l}} \tag{5.67}$$

Eq. (5.67) gives us the probability distribution for the various energy changes. It is now of importance to determine the statistical weight of an initial state $E, l$.

Let $\rho$ be the closest distance of approach of a broadening atom. Classically then our angular momentum at closest approach, where $|\mathbf{r} \times \mathbf{v}| = |\mathbf{r}||\mathbf{v}|$, will be given by $\sqrt{2\mu E_l}\,\rho$, and the quantum equivalent

$\sqrt{l(l+1)}\,\hbar$.* If we equate, square, and differentiate these two expressions for the angular momentum, we obtain:

$$h^2\,(2l+1)\,dl = 2\mu E_l \cdot 2\rho d\rho \tag{5.68}$$

The Maxwell-Boltzmann distribution yields as the number of disturbers whose energy lies between $E$ and $E + dE$:

$$N_E = N\frac{\sqrt{E}}{(\pi kT)^{3/2}}\,e^{-E/kT}\,dE \tag{5.69}$$

where $N = N_1/V$. We now desire the number of perturbing atoms of the above mentioned energy whose angular momentum is between $\sqrt{2\mu E}\,\rho$ and $\sqrt{2\mu E}\,(\rho + d\rho)$. Consider Fig. 5.8.

In Fig. (5.8) the emitter is at 0. $d\Omega$ is a solid angle and $dV = r^2 dr d\Omega$ is a volume element, a distance $r$ from the emitter. Then the number of molecules of energy between $E$ and $E + dE$ in this volume element is $N_E r^2 dr d\Omega$. Now the number of molecules in this volume element of optical collision diameter between $\rho$ and $\rho + d\rho$ — that is, the number which will pass the emitter with separation between $\rho$ and $\rho + d\rho$ — is the fraction $\dfrac{2\pi\rho d\rho.}{r^2 d\Omega}$ We integrate the latter denominator for agreement with the Jablonski result to obtain the number of molecules in this volume element which are moving inward with impact parameters between $\rho$ and $\rho + d\rho$ as $N_E r^2 dr d\Omega\, 2\pi\rho\, d\rho/4\pi r^2$. Jablonski used this value for $N_E$ in his first paper[76] while he felt later [78] that he should have utilized twice this value since there will be an equal number moving outward. In following the development of the first paper we shall make this correction.

We then obtain from Eq. (5.69):

$$N_{E\rho} = N\,\frac{\sqrt{E}}{(\pi kT)^{3/2}}\,e^{-E/kT}\,\frac{4\pi\rho d\rho}{4\pi r^2}\,dEdV \tag{5.70}$$

Eq. (5.70) is now integrated over the entire volume of the container with the exception of a small excluding sphere of radius $r'(\sim 10^{-7}$ cm.). The result of this integration is $(R - r')$, and we simply drop $r'$ as small. Substitution for $\rho d\rho$ from Eq. (5.68) into this result yields:

$$m_{(E,E+\Delta E),\,l} = \pi N\int_{E}^{E+\Delta E}\frac{e^{E/kT}}{(\pi kT)^{3/2}}\,\frac{(2l+1)}{\mu\sqrt{E}}\,\hbar^2\,RdE \tag{5.71}$$

Eq. (5.71) gives the number of broadeners whose energy lies between $E$ and $E + \Delta E$ and whose angular momentum quantum number is $l$ or the statistical weight of $E_l$ in Eq. (5.67). Eq. (5.71) then gives us the number of factors in:

$$\prod_{i}^{N_1} P_{inn'l} = \prod_{i}^{N_1} P_{iEE'l}(E - E') \tag{5.64}$$

Let us neglect consideration of the restrictions which we must impose on Eq. (5.71) temporarily. We divide the terms in Eq. (5.64) into groups, each group having the same $l$ and energies restricted to a small range $\Delta E$. Now the distribution of the total energy change in each group may be computed, and as a result the distribution corresponding to all $E$, $l$ groups may be obtained.

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* This equating of the quantum and classical angular momentum is predicated on the preponderant importance of large angular momenta (high $l$) where the Bohr Correspondence Principle applies.

## 5.11. A PARTICULAR PROBABILITY DISTRIBUTION

The following problem is posed: "The probability distributions $P_1(x_1), P_2(x_2), \ldots, P_{N_1}(x_{N_1})$ of certain quantities $x_1, x_2, \ldots, x_{N_1}$ being given, calculate the probability distribution of:"[79]

$$X = \sum_{i=1}^{N_1} x_i \tag{5.72}$$

The "quantities" here are $x_i = E_i' - E_i$, and the method of solution of this problem will be taken from a later paper of Jablonski.[79]

We assume that the $P_i(x_i)$ are independent of each other in accordance with our earlier assumption of independence of the broadening molecules. The form of the probability distribution $P_i(x_i)$ is:

$$\int P_i(x_i)dx_i = \int_{\Delta x_i} [(1 - \epsilon)\delta(x_i) + W(x_i)]dx_i \tag{5.73}$$

Eq. (5.73) is based on the assumption of a probability $1 - \epsilon$ for $x_i = 0$*, and for $x_i \neq 0$, the probability of $x_i$ being within $\Delta x_i$ is:

$$\int_{\Delta x_i} W(x_i)dx_i \doteqdot W(x_i)\Delta x_i$$

Also from Eq. (5.73), recalling the delta function behavior:

$$\int_{-\infty}^{+\infty} P_i(x_i)dx_i = \int_{-\infty}^{+\infty} [(1 - \epsilon)\delta(x_i) + W(x_i)]dx_i = 1$$

so that:

$$\epsilon = \int_{-\infty}^{+\infty} W(x_i)dx_i$$

We consider $P_1(x_1) = P_2(x_2) = \ldots = P_{N_1}(x_{N_1})$, and we now desire:

$$\int_{\Delta X} P_{E,l}(X)dX \tag{5.74}$$

where $X$ is given by Eq. (5.72). In order to find Eq. (5.74) Jablonski essentially utilizes mathematical induction.

We assume the probability distribution of a sum of $N_1 - 1$ quantities to be known:

$$P_{1,2,\ldots(N_1-1)}\left(\sum_{i=1}^{N_1-1} x_i\right)$$

Then the probability distribution $P(X)$ of the $N_1$ quantities:

$$X = \sum_{i=1}^{N_1} x_i = \sum_{i=1}^{N_1-1} x_i + x_{N_1}$$

is surely:

$$P_{E,l}(X) = \int_{-\infty}^{+\infty} P_{1,2,\ldots,(N_1-1)}\,(X - x_{N_1})\,P_{N_1}(x_{N_1})dx_{N_1} \tag{5.75}\dagger$$

Now let us return to Eq. (5.74). We let $W^{(1)}(X) \equiv W(x_1)$ and $\int_{\Delta X} W^{(m)}(X)dX$ is the probability that

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* $\delta(x_i)$ is the delta function where by definition $\int_{-\infty}^{+\infty} \delta(x_i)dx_i = 1$.

† The $x_i$ have been assumed continuous with a range $-\infty$ to $+\infty$.

the sum of $m$ quantities, none of which vanish, lies between $X$ and $X + dX$. Then in analogy to Eq. (5.75):

$$W^{(m)}(X) = \int_{-\infty}^{+\infty} W^{(M-1)}\,(X - x_i) W^{(1)}(x_i)dx_i \tag{5.76}$$

or for the case $N_1 = 2$:

$$W^{(2)}(X) = \int_{-\infty}^{+\infty} W^{(1)}(X - x_i)\,W^{(1)}(x_i)dx_i \tag{5.77}$$

From Eqs. (5.75) and (5.77) and in analogy with Eq. (5.73) we obtain:

$$\begin{aligned}\int_{\Delta X} P_{E,l}(X)dX &= \int_{\Delta X}\int_{-\infty}^{+\infty} P_1(X - x_i)P_2(x_i)dx_i dX\\ &= \int_{\Delta X}\int_{-\infty}^{+\infty} [(1 - \epsilon)\delta(X - x_i) + W^{(1)}(X - x_i)][(1 - \epsilon)\delta(x_i) + W^{(1)}(x_i)]\;dXdx_i\\ \int_{\Delta X} P_{E,l}(X)dX &= \int_{\Delta X}\int_{-\infty}^{+\infty} [\delta(X - x_i)\delta(x_i)(1 - \epsilon)^2 + W^{(1)}(X - x_i)\delta(x_i)(1 - \epsilon)\\ &\quad + \delta(X - x_i)(1 - \epsilon)W^{(1)}(x_i) + W^{(1)}(X - x_i)W^{(1)}(x_i)]\,dXdx_i\\ &= \int_{\Delta X}\left[\delta(X)(1 - \epsilon)^2 + \binom{2}{1}W^{(1)}(X)(1 - \epsilon) + W^{(2)}(X)\right]dX\end{aligned} \tag{5.78*}$$

since $\int_{-\infty}^{+\infty} [\delta(X - x_i)\delta(x_i)(1 - \epsilon)^2]dx_i = \delta(X)(1 - \epsilon)^2$, etc., again by virtue of the delta function definition.

We may repeat the procedure for successively higher values of $N_2$ to obtain for $N_1$ quantities:

$$\int_{\Delta X} P_{E,l}(X)dX = \int_{\Delta X}\left[\delta(X)(1 - \epsilon)^{N_1} + \sum_{m=1}^{N_1}\binom{N_1}{m}W^{(m)}(X)(1 - \epsilon)^{N_1-m}\right]dX \tag{5.79a}$$

Jablonski's inductive proof is completed by showing that Eq. (5.79a) holds for $N_1 + 1$ quantities. No useful purpose would be served here by writing out this final phase of the proof.

For $\epsilon = 1$, all the terms save the last in Eq. (5.79a) vanish, and for $\epsilon \ll 1$ we obtain:

$$\int_{\Delta X} P(X)dX = \int_{\Delta X}\left[\delta(X)e^{-\epsilon N_1} + \sum_{m=1}^{N_1}\binom{N_1}{m}W^{(m)}\,(X)e^{-\epsilon(N_1-m)}\right]dX \tag{5.79b}$$

Now let us consider more carefully what Eq. (5.79a) tells us about our atomic system.

To begin with $\int_{\Delta X} P_{E,l}(X)dX$ is the probability distribution for the translational energy of the $N_1 + 1$ perturbers in the $E,l$ group plus the radiator, and $\int_{\Delta x_i} W(x_i)dx_i$ is the probability of a change, $x_i = E_i' - E_i$ in the energy of the $i$-th perturber. We next consider the various terms in the bracketed integrand. The first term is the probability for no translational energy change in the system; the first term in the sum gives the contribution to the probability distribution of a collision of one perturber with the emitter (two body collision), the second term the contribution by a three body collision, etc.†

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* The symbol $\binom{n}{m}$ is generally defined as $\frac{n!}{m!(n - m)!}$ as in $\binom{2}{1}$.

† In his first paper Jablonski[75] obtained the equation corresponding to Eq. (5.79a) for the case $P_1(x_1) \neq P_2(x_2) \neq \ldots \neq P_{N_1}(x_{N_1})$. Since, however, he only utilized the simpler form Eq. (5.79a), we do not reproduce it here.

It now is necessary to construct $P(X)$ for all $l$ and all energy increments $\Delta E$ — we have obtained $P_{l,E}$ $(X)$ for the various $l,\Delta E$ groups. The intensity distribution in an absorption line then becomes:

$$P(X) = I(\hbar\omega_0 + X) \tag{5.80a}$$

and in an emission line:

$$P'(X) = I'(\hbar\omega_0 - X) \tag{5.80b}$$

From the foregoing considerations we might have been led to expect the same intensity distribution* in an absorption line as in an emission line, but this is not the case. $A_{EE'}$ $(X)$ is equal to $A_{E'E}$ $(-X)$ but due to the different distributions of the energy of nuclear motion before and after collisions $P(X)$ is only approximately equal to $P(-X)$.

In Eqs. (5.80) $\omega_0$ denotes the frequency of the unperturbed spectral line.

This would appear to be an apropos point in the development for a resume of just what we have obtained.

## 5.12. REVIEW OF THE JABLONSKI THEORY TO THIS POINT

After taking for our system a large "molecule" made up of $N_1$ perturbers and an emitter (absorber) restricted to a volume $V$, we applied Condon's first approximation to separate the electronic motion whose state changes result in our radiation (absorption) from the nuclear motion (Approximation I). We further considered the perturber motions to be independent of one another (Approximation II). Next Eq. (5.55) was obtained for the eigenfunctions of this motion, and the overlap integral Eq. (5.57) resulted. This overlap integral, as a result of the Condon approximation, yielded the selection rule $l = l'$ for the angular momentum quantum number (Approximation III). From the asymptotic solution (Approximation IV) to Eq. (5.56) we obtained the density of our nuclear energy states Eq. (5.62). As a result of Approximation III the matrix element of a nuclear transition is given in terms of the radial eigenfunctions. The square of the matrix element of a nuclear transition — and hence the probability of the transition — between states $n,l$ and $n',l$, we found as Eq. (5.66). As a result, the probability of an energy change $E \longleftrightarrow E'$ was found as Eq. (5.67), the product of Eq. (5.66) and Eq. (5.62), the nuclear state density. $E_l$ on the right of Eq. (5.67) furnishes the basis for the difference in the absorption and emission lines as given by Eqs. (5.80). It should be kept in mind that Eq. (5.67) is only the intensity or probability due to one perturber. We next found $N_{E\rho}$ (Eq. 5.70) the number of perturbers with energy between $E$ and $E + dE$ and angular momentum between $\sqrt{2\mu E}\rho$ and $\sqrt{2\mu E}(\rho + d\rho)$. In finding this density we assumed the equivalence of classical and quantum angular momentum (Approximation V). We proceeded to find $m_{(E,E+\Delta E),l}$, the number of disturbers with quantum number $l$ and energy between $E$ and $E + \Delta E$, the statistical weight of $E_l$ in Eq. (5.67). This yielded the number of factors in the product Eq. (5.64). This product was divided into $E,l$ groups and $P_{E,l}$ $(X)$ where $X$ as given by Eq. (5.72) was determined from the $P_{iEl}$ $(x_i)$. From these considerations we obtained Eq. (5.79a) for $P_{E,l}$ $(X)$, and subsequently the intensity distribution in the absorption and emission lines. An example might further clarify the meaning of the $W^{(m)}$ $(X)$. As we have mentioned, the first term in the sum in Eq. (5.79a) is the probability distribution resulting from single perturbing atom transits. This term is analogous to Eq. (5.67):

$$W^{(1)}(X) = W^{(1)}(E_{n'} - E_n) = \frac{A^2{}_{EE'l}}{R^2}\frac{dn}{dE_l}m_{(E,E+\Delta E),l} \tag{5.81}$$

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* Compare *infra*, Sec. 6.

The evaluation of $A^2_{E'El}$, the square of the matrix element of the translational motion, now poses the biggest problem. In his later papers [78, 79] on the subject Jablonski carried out a calculation which yielded an approximation for these matrix elements.

## 5.13. LIMITING CASES AND THE MATRIX ELEMENT A

Before considering this approximate evaluation of $A$, we might mention two limiting cases of the theory which Jablonski[76] pointed out. The theory will reduce to the limiting case of a distribution of the type*:

$$I(\omega)_{w \neq w_0} = \frac{\Sigma D_i^2}{\hbar(\omega - \omega_o)^2} \tag{5.82}$$

but with no "damping constant" — an additional term in the denominator which prohibits a complete resonance condition — for small differences in the potential curves for the two electronic states involved in the radiating transition.

The other limiting case which essentially corresponds to high densities, leads to the statistical distribution (occurrence distribution) smeared out, a conception which we have mentioned earlier but not enlarged upon, with a half width:

$$\delta = \frac{1}{2}\sqrt{v_r \frac{dv}{dr}} \tag{5.83}$$

which compares favorably with the smearing half-width of Kuhn and London[94]:

$$\delta = \frac{1}{\pi}\sqrt{\pi \frac{dv}{dx}} \tag{5.84}$$

Let us now return to the evaluation of $A$.

Jablonski evaluated $A$, sometimes referred to as the "Condon integral," in two papers [78, 79], but, since the second is the more comprehensive evaluation and differs only slightly from the first, we shall simply consider it.

For the eigenfunction we take the $WKB$ approximation for $r > r_0$ in the form given by Eq. (5.58) with $c$ as given by Eq. (5.65b). We must insert the additional normalization factor $\sqrt{p_{kl(\infty)}} = \sqrt{2\mu E_{nl}}$. The eigenfunction is then:

$$\begin{aligned}\psi_{nl} &= \left(\frac{2}{R}\right)^{1/2}\left[\frac{2\mu E_{nl}}{2\mu(E_{nl} - V(r)) - h^2\dfrac{l(l+1)}{r^2}}\right]^{1/4} \cos\left\{\frac{1}{h}\int_{r_0}^{r}\left[2\mu(E_{nl} - V(r)) - h^2\frac{l(l+1)}{r^2}\right]^{1/2} dr + \Upsilon\right\} \\ &= \left(\frac{2p(\infty)}{Rp(r)}\right)^{1/2}\cos\left[\frac{1}{\hbar}\int_{r_0}^{r} p(r)dr + \Upsilon\right]\end{aligned} \tag{5.85}$$

Where, as has been previously noted, $U(r) = \frac{2\mu}{\hbar^2} V(r)$ and $p(r) = \sqrt{2\mu(E_{nl} - V(r)) - \frac{l(l+1)\hbar^2}{r^2}}$. $p(r)$ is, of course, the radial component of the relative linear momentum. The phase $\Upsilon$ has already arisen

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* See *infra*, Chap. 6.

in the solution of Eq. (5.56b). If we let $r_t$ be the classical turning point or reversal point where $p(r_t) = 0$ then Eq. (5.85) is only valid for $r > r_0 = r_t$.*

By utilizing Eq. (5.85) we may form the matrix element:

$$A_{n'n''l} = \int \bar{\psi}_{n'l}\, \psi_{n''l}\, d\tau \doteq \frac{2}{R} \int_0^R \left(\frac{p'(\infty)}{p'(r)}\right)^{1/2} \cos\left[\int_{r_t}^{r} \frac{p'(r)}{\hbar}\, dr + \Upsilon'\right] \left(\frac{p''(\infty)}{p''(r)}\right)^{1/2} \cos\left[\int_{r_t}^{r} \frac{p''(r)}{h}\, dr + \Upsilon''\right] dr$$

$$= \frac{1}{R} \int_{r_t}^{R} \left(\frac{p'(\infty)p''(\infty)}{p'(r)p''(r)}\right)^{1/2} \left[\cos\left(\int_{r_t}^{r} \frac{p'(r) - p''(r)}{\hbar}\, dr + \Upsilon' - \Upsilon''\right)\right.$$

$$\left. + \cos\left(\int_{r_t}^{r} \frac{p'(r) + p''(r)}{\hbar}\, dr + \Upsilon' + \Upsilon''\right)\right] dr \tag{5.86}$$

In Eq. (5.86) a single prime denotes a quantity going with one of the electronic states and a double prime a quantity going with the other.

Since the sums involved in the second cosine term in Eq. (5.86) will increase or decrease more rapidly than the differences involved in the first cosine term, the second term will fluctuate much more rapidly than the first with $r$. Thus, the contribution of the second cosine term to the integral in Eq. (5.86) will be much less in the region of maximum contribution of both terms. On this basis, Jablonski considered only the first. It may also be seen that the region of maximum contribution of this first term is the neighborhood of the so-called "Condon point" where $p'(r_c) = p''(r_c)$.†

It follows immediately that $(A_{n'n''l})^2$ ". . . is the probability of change of translational energy by $X = E_{n'} - E_{n''}$ equal to that resulting from the classical *FCP* for the transition in $r_c''$:[79]

$$X = V'(r_c) - V''(r_c) = \hbar(\omega_0 - \omega) = \hbar\Delta\omega$$

We now break up the integral within the cosine from one with limits $r_t$ and $r$ into one with limits $r_t$ and $r_c$ and another with limits $r_c$ and $r$. The second of these two integrals may be expanded in a Taylor series about $r_c$ in a straightforward manner to yield:

$$A_{n'n''l} = \frac{1}{R} \int_{r_t}^{R} \left[\frac{p'(\infty)p''(\infty)}{p'(r)p''(r)}\right]^{1/2} \cos\left\{\frac{1}{\hbar} \int_{r_t}^{r_c} p'(r) - p''(r)\, dr + \Upsilon' - \Upsilon''\right.$$

$$\left. + \frac{1}{\hbar} \int_{r_c}^{r} \left[p'(r) - p''(r_t) + \left[\frac{d}{dr}(p'(r) - p''(r))\right]_{r=r_c} (r - r_c) + \dots\right] dr\right\} dr \tag{5.87}$$

If all terms beyond the second in the series be now neglected; $r - r_c$ be replaced by $\xi$, and the approxi-

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* "The difficulty arising from the failure of the *WKB* approximation in the region of the point of closest approach of the colliding atoms (classical turning point) is not surmounted by Weisskopf's treatment, but merely completely camouflaged."[79]

† This nomenclature has its origin in the "classical" conception of the *FCP* where it is assumed that the relative nuclear velocities remain constant during an electronic transition.

mation $p'(r) = p''(r) = p(r_c)$ be made in the denominator of the factor in front of the cosine,* Eq. (5.87) becomes:

$$A_{n'n''l} = \frac{[p'(\infty)p''(\infty)]^{\frac{1}{2}}}{Rp(r_c)} \int_{-\infty}^{+\infty} \cos(\alpha \pm \beta\xi^2)\,d\xi = \frac{[p'(\infty)p''(\infty)]^{\frac{1}{2}}}{Rp(r_c)} \left(\frac{\pi}{\beta}\right)^{\frac{1}{2}} \cos\left(\alpha \pm \frac{\pi}{4}\right) \tag{5.88†}$$

where:

$$\alpha = \frac{1}{\hbar}\int_{r_0}^{r_c} [p'(r) - p''(r)]\,dr + \Upsilon' - \Upsilon'' \tag{5.89a}$$

and:

$$\begin{aligned}\beta = \frac{1}{2\hbar}\left|\frac{d}{dr}[p'(r) - p''(r)]\right|_{r=r_c} = \frac{1}{2\hbar}\Bigg| &\frac{-\mu\dfrac{dV'(r)}{dr}}{\left[2\mu(E_{nl} - V'(r)) - \hbar^2\dfrac{l(l+1)}{r^2}\right]^{1/2}} \\ &-\left(\mu\frac{dV''(r)}{dr}\right)\Bigg/\left[2\mu(E_{n'l} - V''(r)) - \hbar^2\frac{l(l+1)}{r^2}\right]^{1/2}\Bigg|_{r=r_c} = \mu\left|\frac{dU(r)}{dr}\right|_{r=r_c}\Bigg/p(r_c)\end{aligned} \tag{5.89b}$$

where $U(r) = X = V'(r) - V''(r)$.

We may first note that the term $p'(r_c) - p''(r_c)$ in Eq. (5.87) is zero by definition. $\beta\xi$ results from the first integration, since $(r - r_c)^2{}_{r=r_c}$ is obviously zero, thus simply leaving the upper limit of this integral. In addition, an obvious approximation has been made in Eq. (5.88) by taking the limits $-\infty$ and $+\infty$. Extending the limits in this manner is predicated on the assumption that the integrand only contributes significantly to the integral in the region $r = r_c$.

Substitution of Eq. (5.89b) into Eq. (5.88) yields:

$$A_{n'n''l} = A_X = \frac{1}{R}\left(\frac{p'(\infty)p''(\infty)}{p(r_c)\mu\left|\dfrac{dU}{dr}\right|_{r=r_c}}\right)^{1/2}\cos\left(\alpha \pm \frac{\pi}{4}\right) = \frac{1}{R}\left(\frac{p'(\infty)p''(\infty)2\pi\hbar}{p(r_c)\mu\left|\dfrac{\partial X}{\partial r}\right|_{r=r_c}}\right)^{1/2}\cos\left(\alpha \pm \frac{\pi}{4}\right) \tag{5.90}$$

Eq. (5.90) is an approximation to the matrix element which we have been seeking. Before further utilization of Eq. (5.90), let us consider the additional ramifications of the earlier theory which Jablonski[79] introduced in 1945.

## 5.14. THE GENERAL SYSTEM ENERGY CHANGE PROBABILITY

It will perhaps be most straightforward to simply replace Eq. (5.81) by:

$$W^{(1)}(X) = W^{(1)}(E_{n'} - E_{n''}) = \sum_{l=0}^{l_{\max}} Q(l)\frac{D^2{}_{n'n''l}}{\sum\limits_{n'=1}^{\infty} D^2{}_{n'n''}}\frac{dn'}{dE_{n'}} \doteq \int_0^{l_{\max}} Q(l)\frac{D^2{}_{n'n''l}}{S}\frac{dn'}{dE_{n'}}\,dl \tag{5.91}$$

and explain the reason for so doing. $D^2{}_{n'n''l}$ is defined as before by Eq. (5.47), and $\dfrac{dn'}{dE_{n'}}$ is the energy level density which we have also previously encountered. $Q(l)$ is the probability of occurrence of a certain $l$ which replaced the statistical weight found earlier. The approximation of a high $l$ density has been made

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* Jablonski[79] refers to this approximation as crude. The approximation appears to get "cruder" the closer $r_c$ lies to $r_t$.

† In his earlier paper [78] Jablonski had defined $\beta$ as an absolute value so that there was every reason for taking $\pm\beta\xi^2$. In the later paper [79] he kept the $\pm$ signs but failed to define $\beta$ as an absolute value. This, of course, was not correct.

so that the summation may be replaced by the integration. If a single prime is taken to mean the upper state, Eq. (5.91) refers to an absorption line. The emission line would replace $\frac{dn'}{dE_{n'}}$ by $\frac{dn''}{dE_{n''}}$.

Now if Eq. (5.91) were substituted into Eq. (5.79a) or (5.79b), the intensity distribution (normalized to unity) in the spectral line — natural and Doppler widths neglected — would be obtained. Needless to remark, this has not been done. The Condon approximation yields:

$$S = M_0^2; \; D_{n'n''l} = M_0 A_{n'n''l}$$

and Eq. (5.91) may be written:

$$W^{(1)}(X) \doteq \int_0^{l_{\max}} Q(l) A^2_{n'n''l} \frac{dn'}{dE_{n'}} \, dl \tag{5.92}$$

where $\frac{dn}{dE_n}$ is given by Eq. (5.62), and $A_{n'n''l}$ is given by Eq. (5.90). $Q(l)$, however, remains to be determined.

$Q(l)$ is certainly proportional to the statistical weight due to the spatial degeneracy ($m_l$) of the state $l$;

$$Q(l) = g(2l + 1) \tag{5.93}$$

On the basis used for obtaining Eq. (5.68),

$$\rho = h[l(l+1)/2\mu E]^{1/2} \tag{5.94}$$

and

$$Q(l)dl \doteq Q'(\rho)d\rho \tag{5.95}$$

for large $l$.

In Fig. (5.9), one-half the molecules may be considered as moving toward (or across) the plane $A—A$ from the left, while the remainder proceed toward the plane from the right. The probability, that a collision of optical collision diameter $\rho$ between $\rho$ and $\rho + d\rho$ occurs, is thus the volume of the tube shell of thickness $d\rho$ divided by the total volume available to the broadeners. This follows from the assumption of a random distribution in space. We suppose the assemblage to be confined to a sphere of radius $R$. In consequence:

$$Q'(\rho)d\rho = \frac{2\int_0^{r_{\max}} 2\pi\rho d\rho dr}{\frac{4}{3}\pi R^3} = \frac{3}{R^3} r_{\max} \rho d\rho$$

Now by definition $r = r_{\max}$ when $r' = R$ so that:

$$Q'(\rho)d\rho = \frac{3}{R^3}(R^2 - \rho^2)^{1/2} \rho d\rho \tag{5.96a}$$

or for the case under consideration $\rho \ll R$ so that:

$$Q'(\rho)d\rho = \frac{3}{R^2}\rho d\rho = \frac{3}{2R^2} d(\rho^2) \tag{5.96b}$$

By substituting from Eq. (5.94) for $\rho$ in Eq. (5.96b) we obtain:

$$Q'(\rho)d\rho = \frac{3h^2}{4R^2\mu E}(2l + 1)dl$$

Now using Eq. (5.95) this yields:

$$Q(l) = \frac{3\hbar^2}{4R^2\mu E}(2l+1) \tag{5.97}$$

For convenience, we rewrite Eq. (5.62) slightly, recalling that the equation was obtained for $r = R$, to obtain:

$$\frac{dn}{dE_n} = \frac{(\mu)^{1/2}R}{\pi\hbar(2E_n)^{1/2}} = \frac{\mu R}{\pi\hbar p_n(\infty)} \tag{5.62}$$

If Eqs. (5.97), (5.62), and (5.90) are substituted into Eq. (5.92) the desired expression for the case of an absorption line is:

$$W^{(1)}(X) = \int_0^{l_1} \frac{3}{4}\,\frac{\hbar^2}{R^2\mu E_{n''}}\,\frac{(2l+1)\mu R p'(\infty)p''(\infty)}{\pi\hbar p'(\infty)R^2p'(r_c)}\,\frac{2\pi\hbar}{\mu\left|\frac{dX}{dr}\right|_{r=r_c}}\cos^2\left(\alpha \pm \frac{\pi}{4}\right)dl + \zeta(X + l_t)$$

$$= \frac{3}{4}\,\frac{\hbar^2}{\mu E_{n''}R^3\left|\frac{dX}{dr}\right|_{r=r_c}}\int_0^{l_1}\frac{2(l+1)\;2\cos^2(\alpha \pm \pi/4)}{\left(1 - \frac{V''(r_c)}{E_{n''l}} - \hbar^2\frac{l(l+1)}{2\mu E_{n''l}r_c^2}\right)^{1/2}}\,dl + \zeta(X,l_t) \tag{5.98}$$

where $$\frac{p''(\infty)}{p(r_c)} = \frac{(2\mu E_{n''l})^{1/2}}{\left[2\mu(E_{n''l} - V''(r)) - \hbar^2\frac{l(l+1)}{r^2}\right]^{1/2}} = \frac{1}{\left(1 - \frac{V''(r_c)}{E_{n''l}} - \hbar^2\frac{l(l+1)}{2\mu E_{n''l}r_c^2}\right)^{1/2}}$$

At the classical turning point the following relation holds:

$$2\mu\left[E_{n''l} - V''(r_c)\right] - \hbar^2\frac{l_t(l_t+1)}{r^2} = p''^2(r_c) = 0 \tag{5.99}$$

From Eq. (5.99) we may obtain:

$$1 - \frac{V''(r_c)}{E_{n''l}} = \frac{\hbar^2 l_t(l_t+1)}{2\mu r^2E_{n''l}} \tag{5.100}$$

When Eq. (5.100) is substituted into the denominator under the integral sign in Eq. (5.98) the result is:

$$W^{(1)}(X) = \frac{3}{2}\,\frac{r_c^2\left(1 - \frac{V''(r_c)}{E_{n''l}}\right)^{1/2}}{l_t(l_t+1)R^3\left|\frac{dX}{dr}\right|_{r=r_c}}\int_0^{l_1}\frac{(2l+1)\;2\cos^2\left(\alpha \pm \frac{\pi}{4}\right)}{\left[1 - \frac{l(l+1)}{l_t(l_t+1)}\right]^{1/2}}\,dl + \zeta(X,l_t) \tag{5.101}$$

The $\zeta(X,l_t)$ is a correction term which is added due to the choice of upper limit $l_1 < l_t$. This upper limit must be less than $l_t$ since the *WKB* approximation fails in the region of the classical turning point, and $\zeta(X,l_t)$ is then to correct for this low limit choice. "The more accurate calculations involving eigenfunctions valid in the regions of turning points and outside the classical range of motion would be very tedious unless carried out by the aid of the differential analyzer."[79]

If $|X| = |E_{n'} - E_{n''}|$ is large enough, that is, if we are considering frequencies sufficiently far out in the wing of the line then $\cos\left(\alpha \pm \frac{\pi}{4}\right)$ is a rapidly oscillating function of $l$, as we may see from Eq. (5.88) and Eq. (5.89a). In this case we may replace $\cos^2\left(\alpha \pm \frac{\pi}{4}\right)$ by its average value $\frac{1}{2}$. Eq. (5.101) then becomes:

$$W^{(1)}(X) = \frac{3}{2}\,\frac{r_c^2\left(1 - \dfrac{V''(r_c)}{E_{n''}}\right)^{1/2}}{l_t(l_t+1)R^3\left|\dfrac{dX}{dr}\right|_{r=r_c}} \int_0^{l_1} \frac{2l+1}{\left[1 - \dfrac{l(l+1)}{l_t(l_t+1)}\right]^{1/2}}\,dl + \zeta(X,l_t)$$

$$= \frac{3r_c^2}{R^3\left|\dfrac{dX}{dr}\right|_{r=r_c}}\left(1 - \frac{V''(r_c)}{E_{n''}}\right)^{1/2}\left[1 - \left(1 - \frac{l_1(l_1+1)}{l_t(l_t+1)}\right)^{1/2}\right] + \zeta(X,l_t) \tag{5.102}$$

for an absorption line. We simply replace the double prime by a prime in Eq. (5.102) for the emission line.

The asymptotic form ($l_1 = l_t$) for $W^{(1)}(X)$ is:

$$W^{(1)}(X) = \frac{3r_c^2(1 - V''(r_c)/E_{n''})^{1/2}}{R^3\left|\dfrac{dX}{dr}\right|_{r=r_c}} \tag{5.103}$$

and corresponding for an emission line.

Next, let us show that Eq. (5.103) reduces to Kuhn's distribution[92] — Margenau's distribution without the exponential — for certain interactions. Before doing so, however, let us mention a consideration which we have so far neglected.

## 5.15. DOUBLE INTERACTION CURVES AND REDUCTION TO THE MARGENAU LINE SHAPE

It has been tacitly assumed that there is one interaction curve for the upper electronic state and one for the lower. This is not generally the case, for there may well be several interaction curves for each electronic state, and for single encounters we would then have various $W_i^{(1)}(X)$ for the various pairs of curves. Our $W^{(1)}(X)$ would then have the form:

$$W^{(1)}(X) = a_1W_1^{(1)}(X) + a_2W_2^{(1)}(X) + \cdots \equiv \Sigma a_iW_i^{(1)}(X) \tag{5.104}$$

where $a_i$ would denote the "... relative abundance of transitions between two particular potential curves ..."[79] with which $W_i^{(1)}(X)$ is associated. It is also apparent that, since $A_{n'n''l}$ or $D_{n'n''l}$ would be different for each $W_i^{(1)}(X)$, each $A_{n'n''l}$ would have to comprise a separate calculation for each $W_i^{(1)}(X)$. When one considers that we have here discussed only single encounters, the complexity of the accurate computation for multiple collisions appears rather staggering. Let us return to the limiting case of Kuhn's (Margenau's) distribution.

According to the classical *FCP*:

$$X = V'(r_c) - V''(r_c) = \hbar(\omega - \omega_0) = \hbar\Delta\omega$$

From this equation $\Delta\omega = f(r_c)$ so that $r_c = f(\Delta\omega)$. Let $n = \frac{4}{3}\pi R^3 N$. Utilizing these relations and Eqs. (5.103) and (5.104) we obtain for an absorption line:

$$I(\omega) = \Sigma a_i \, 4\pi N f^3(\Delta\omega) \frac{\left(1 - \frac{V''(r_c)}{E_{n''}}\right)}{\left|\frac{d(\Delta\omega)}{dr_c}\right|} \tag{5.105}$$

We now make the approximation $E = \frac{3}{2}kT$, although $I(\omega)$ should be averaged over all $E$ which occur in the gas. Finally, an assumption of one electronic curve for each electronic state is introduced. We let:

$$V'(r_c) = -\frac{c'}{r_c^{\eta}} \; ; \; V''(r_c) = -\frac{c''}{r_c^{\eta}} \tag{5.106}$$

so that:

$$\Delta\omega = \frac{1}{\hbar}\frac{c' - c''}{r_c^{\eta}} = \frac{K}{r_c^{\eta}} ; \, r_c = f(\Delta\omega) = \left(\frac{K}{\Delta\omega}\right)^{1/\eta} ; \, V''(r_c) = \frac{c''}{K}\Delta\omega \tag{5.107}$$

Substitution of Eq. (5.107) into Eq. (5.105) yields:

$$I(\omega) = \frac{4\pi N K^{3/\eta}}{\eta(\Delta\omega)^{(\eta+3)/\eta}}\left(1 + \frac{2c''\Delta\omega}{3KkT}\right) \tag{5.108*}$$

which corresponds to the Kuhn form for $2c''\Delta\omega/(3KkT) \ll 1$. The agreement of this limiting form of the theory with the earlier work of Kuhn;[92] and Margenau[114] would tend to imply a corroboration of either this theory or one of the earlier ones depending, of course, on who is pointing out the corroboration.

As Foley[38] has remarked, the divergence of the intensity at line center as given by Eq. (5.108) should hardly come as a surprise when the method of obtaining this equation is considered. The reason for the divergence lies in the fact that the perturber will only spend an infinitesimal portion of its time within the range of the forces, for the case of a large combining volume, when only a single perturbing atom has been initially considered, and then the resulting expression averaged over all possible transitions. This fact results in an infinite probability for the unperturbed line center frequency. The argument is without any particular significance, however, as far as line wing theory validity is concerned.

Insofar as it has been possible to ascertain, this is as far as Jablonski has carried his quantum mechanical broadening theory. Our only concrete results are then given by Eq. (5.108) which had already been given by Margenau's statistical theory (or Kuhn's if you will) with the exception of the small factor in the bracket. This is only a limiting case of the wave mechanical theory and serves no immediately apparent purpose save the wave mechanical verification of the statistical theory. Before a further discussion of this theory, let us review the approximations which we have made in addition to those listed before Eq. (5.81).

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* This differs by a factor two from that obtained by Jablonski in an earlier paper.[78] Since the calculation is in principle the same but in actuality somewhat different — for example, he obtained $\frac{1}{R}\sqrt{\frac{\pi}{\beta}}\cos\left(\alpha \pm \frac{\pi}{4}\right)$ in the previous paper in place of Eq. (5.88) — we shall not go into the detail of this difference. The approximate derivation which we have given here would appear to be the better of the two.

## 5.16 THE APPROXIMATIONS OF THE JABLONSKI THEORY*

First, let us mention that we have improved Approximation V. Eq. (5.95) certainly holds for very large $l$. Thus, if we obtain it as we did we should have an approximation for $Q(l)$ which is very close to the true state of affairs.

We have replaced our previous Approximation IV by one in which we assume the *WKB* approximate eigenfunction (Approximation IV). The second term in the integral of Eq. (5.86) has been neglected (Approximation VI). We have neglected all terms beyond the second in the series in Eq. (5.87) (Approximation VII). It was then assumed that $p'(r) = p''(r) = p(r_c)$ in the denominator of Eq. (5.87) (Approximation VIII). The limits in Eq. (5.88) have been extended from 0 and $R$ to $-\infty$ and $+\infty$ (Approximation IX). The approximation of Eq. (5.91) — replacing the summation over $l$ by an integration — is probably a trivial one in most cases (Approximation X). Eq. (5.62) is an approximation, but perhaps one of the closest ones (Approximation XI). The limits on Eq. (5.98) are, of course, an approximation, but this one is such a direct result of IV that it may well be included in it. We replaced $\cos^2\left(\alpha \pm \frac{\pi}{4}\right)$ by its average value (Approximation XII). The obvious approximations resulting in Eqs. (5.103) and (5.108) need not be discussed. We should add, however, that without additional approximations it is apparent that no actual line intensity distribution can be obtained for the case of several potential curves for each state — $\Sigma a_i W_i^{(1)}(X)$ instead of simply $W_i^{(1)}(X)$ — and multiple collisions.

As a result of the approximations which have been introduced, we are left with Eq. (5.103) which is only (a) valid in the wing of the line and (b) valid for heavy broadeners. In addition, no information has been afforded about line shift.

Approximation IV is a serious limitation, but one the alternative to which would be the specific and extensive use of some computing device. As a direct result of this approximation, the asymptotic form Eq. (5.103) of $W^{(1)}(X)$ is larger than the true $W^{(1)}(X)$. The reason for this becomes apparent when we recall that the *WKB* eigenfunctions and hence the $A^2_{n'n''l}$ become infinite for $l = l_t$, that is, at the classical turning point. These considerations have the direct effect of making the asymptotic intensity distribution inapplicable to the case of broadening by light particles. Let us investigate the reason for this.

It can be shown† that in order for the *WKB* approximation to be valid,

$$\Delta l = (l_t - l) \gg \frac{[l_t(l_t+1)]^{2/3}}{2l_t+1} = \kappa(l_t) \tag{5.109**}$$

Table 5.1 gives the values of $l_t$ and $\kappa$ for the broadening of *Hg* lines by *A* and *He*.

| *T* | 1000 *K* | | 300 *K* | |
|---|---|---|---|---|
| Perturber | | | | |
| *A* | 158 | 2.7 | 86 | 2.3 |
| *He* | 25 | 1.5 | 14 | 1.2 |

Table 5.1. Values of $l_t$ and $\kappa$ corresponding to $r_c = 3.3A$ for *Hg-A* and *Hg-He*.
(After Jablonski[79])

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* See *supra*, Sec. 5.12.

† An attempt to avoid this phrase has been made, but the calculation which would be involved is not particularly enlightening.

** In Jablonski's article[79] the exponent is given as 3/2 instead of 2/3, but his table — corresponding to our Table 5.1 — affirms this to be a misprint.

From Table 5.1 we can see that we are restricted to very low values of $l_1$ where $l_1 = l_t - \Delta l$ if we assume Eq. (5.109) to be satisfied by, say, $\Delta l \geqslant 10Kl_t$ and in the case of 300°$K$ the limits on our integral would be 0 and 2. From these considerations the necessity for restricting Eq. (5.103) to heavy broadeners becomes immediately apparent. Another approximation which we have made tends to lead to the same result.

In order to make Approximation VI it was necessary for us to assume that there is only a noticeable contribution to Eq. (5.86) in the region of the Condon point. This is the same approximation which earlier had restricted the statistical theory to heavy particles (low velocities) by neglecting the intrinsic diffuseness in $r_c$.

Now let us consider Approximation IX. It is essentially predicated on the assumption of a maximum contribution to the integral for $A$ in the neighborhood of the Condon point. If this is the case we may, with the introduction of small error, extend these limits as has been done. In addition, this means that the phase of the cosine term must increase by at least $\pi$ as $\xi$ increases from 0 to $r$. This would automatically require that $\beta r_c^2 > \pi$ which yields:

$$r_c > \left( \frac{2\pi \cancel{K} p(r_c)}{\mu \left| \dfrac{dX}{dr} \right|_{r=r_c}} \right)^{1/2} \tag{5.110a}$$

or for $|X| = hK/r^\eta$

$$r_c < \left( \frac{\eta K \mu}{2\pi p(r_c)} \right)^{1/(\eta-1)} \tag{5.110b}$$

Eq. (5.110a) essentially restricts the validity of our solution to the wing where the frequency displacement is relatively large, due to the restrictions imposed by this equation against distant encounters. We might add that Approximation XII also restricts our solution to the line wing.

Jablonski's theory, in its present form, cannot then be said to give any new results insofar as the shape which we are to expect in a spectral line is concerned, but it certainly does provide at least the basis for a complete wave mechanical theory of line broadening. Perhaps the exact calculation of the $A$'s or some not immediately apparent approximations will draw more information from it.

## 5.17. A MILD CONTROVERSY, LORENTZ-JABLONSKI EQUIVALENCE

Subsequent developments found Foley[37] investigating the manner in which Jablonski's theory could be shown to lead to a Lorentz type intensity distribution and Jablonski[80] objecting to certain of Foley's demonstrations and concluding that, "One has either to demonstrate rigorously that the Lorentz formula can be obtained from the quantum mechanical theory proposed by the writer or to modify (or to reject) one of these theories."[80] We shall consider this in slightly greater detail.

Initially, Foley remarked that the overlap integral which Jablonski utilised may be written, using *WKB* functions, as:

$$\frac{1}{R_0} \int_0^{R_0} dR \cos \left\{ \frac{1}{\cancel{K}} \int_0^{R} [p(R) - p'(R)]\, dR + \eta - \eta' \right\} \tag{5.111a)*$$

---

* Let us note that this is the less exact form which Jablonski utilized in an earlier consideration.[78] The more exact form is, of course, given by Eq. (5.86) from a later work.

Eq. (5.111a) indicates that Foley had already inferred the approximation which negated the second term on the right of Eq. (5.86). Foley next wrote down:

$$\int_{\rho}^{R_0} dR \frac{c^2}{p(R)} \cos\left\{ \int_{\rho}^{R} \frac{m}{\hbar} \frac{\Delta E - \Delta U(R)}{p(R)} dR \right\} \tag{5.111b}$$

In order to obtain this, let us again consider Eq. (5.86). Let us introduce the approximation which we utilized subsequent to Eq. (5.87), namely, $p'(r) \doteq p''(r) \doteq p(r_c)$. This leads us to:

$$\begin{aligned} p'(r) - p''(r) &= \sqrt{2\mu(E' - U'(r)) - \frac{l(l+1)\hbar^2}{r^2}} - \sqrt{2\mu(E'' - U''(r)) - \frac{l(l+1)\hbar^2}{r^2}} \\ &\doteq \frac{p(r_c)}{p(r_c)}\left\{ 2\mu(E' - U'(r)) - \frac{l(l+1)\hbar^2}{r^2} - 2\mu(E'' - U''(r)) + \frac{l(l+1)}{r^2}\hbar^2 \right\} \\ &\doteq 2\mu \frac{(\Delta E - \Delta U(r))}{p(r)} \end{aligned}$$

This result, with the $\eta$'s dropped, gives us Eq. (5.111b) wherein the two is neglected. Now at the boundary of the container $p(R_0) = \sqrt{K^2 - U(R_0) - \frac{l(l+1)}{R_0^2}} \rightarrow K$ so that Eq. (5.60) becomes:

$$\frac{p(R_0) \,.\, R_0}{\hbar} - \frac{l\pi}{2} + \eta = n\pi = \tfrac{1}{2}(2n' + 1)\pi$$

in Foley notation so that:

$$[p'(R_0) - p''(R_0)]\frac{R_0}{\hbar} + \eta' - \eta'' = m\pi \tag{5.112}$$

Surely, the substitution

$$dt = \frac{mdR}{p(R)} = \frac{mdR}{\sqrt{2m}\sqrt{E - U(R) - \frac{l(l+1)h^2}{2mR^2}}} \tag{5.113*}$$

may be utilized and, in addition, the approximation† $l(l + 1) = m^2v^2\rho^2$ may be introduced to change the integral within the braces in Eq. (5.111b) to:

$$\frac{2}{h}\int_{\rho}^{R} (\Delta E - \Delta U)dR \doteq \frac{2}{\hbar}\int_{0}^{T_i} (\Delta E - \Delta U)dR = 2\,\frac{\Delta e_i}{\hbar}T_i - 2\int_{0}^{T_i}\frac{\Delta U}{\hbar}\,dt = m\pi$$

at the boundary according to Eq. (5.112) when $Tv = R_0$. Or:

$$2\Delta\omega_i T_i - 2\int_{0}^{T_i} \frac{\Delta U}{h}\, dt = m\pi \tag{5.114a**}$$

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* Foley used $l^2$ instead of $l(l + 1)$, but this is of no particular import.

† See the discussion of this preceding Eq. (5.68).

** Foley lacked the factor two.

where now the $i$ refers to the $i$-th perturber. As a consequence Eq. (5.111b) becomes:

$$\frac{c^2}{m}\int_0^{T_i} dt_i \cos 2\left[\omega_i t_i - \int_0^t \frac{\Delta U_i(t)}{\hbar}\, dt\right] \tag{5.114b}$$

The similarity between Eq. (5.114b) and, say, Eq. (7.5a)* would indicate that under the proper manipulations the Lorentz form could probably be obtained from the former equation. Foley proceeds to obtain this form; Jablonski proceeds to criticize the obtention;[80] following which Foley continues to proceed, this time justifying it.[38] Whether or not anything has been proven by this succession of events depends primarily on the justifiability of the approximations involved. Now Foley essentially voiced the opinion that Jablonski's method of evaluating Eq. (5.111b) is only correct in the static or slow motion case. This is as it may be, but Foley had to assume the Franck-Condon principle, a static affair, in order to obtain Eq. (5.111b) in the first place (evidently). Jablonski's theory breaks down (in the sense that generality can no longer be maintained and the development continued) following Eq. (5.86). The flaw in the Jablonski theory seems to lie, not in the fact that it is a special case of the Foley considerations,† but in the obvious difficulties inherent in obtaining results in any but the simplest cases — binary collisions and Franck-Condon.

We now conclude our theoretical considerations of statistical broadening — except for equivalence and reduction considerations in subsequent chapters — with Margenau's latest investigation[119] in the field. The advances which this work encompassed were threefold (1) the theory was broadened to allow almost any interaction law dependent on some inverse power of the atomic separation, (2) forces which change sign were allowed for by the introduction of a spin interaction, and (3) a more concise** and elegant development was attained.

## 5.18. A MORE SOPHISTICATED STATISTICAL THEORY

Our basic theory remains, of course, the same, and we again begin by inquiring, as in, say, Eq. (5.22) and subsequent, what the probability is that a configuration of perturbers will exist such that a change in the energy perturbation of $V = \Sigma V_i$ between the two levels under consideration will result. This $V$ shift, as we may recall, results in the emission of radiation which is shifted in frequency by this amount. We suppose that the dependence of $V$ on molecular separation will be of the form $cr^{-m}$, and now we augment this potential with a spin interaction (separable) $u(\xi)$. Thus there results:

$$V_i = cr_i^{-m}\, u\,(\xi_i) \tag{5.115a}$$

Firstly, the function $u(\xi_i)$ must vanish in the mean. On this basis Margenau chose for $u(\xi_i)$:

$$u(\xi_i) = \begin{matrix} -\,1 \text{ for } \xi_i \leqslant 0 \\ +\,1 \text{ for } \xi_i > 0 \end{matrix}\;;\; -1 \leqslant \xi \leqslant 1 \tag{5.115b}$$

which may lead to different numerical factors than would the accurate spin function, but nothing else.

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* See *infra*.

† See *infra*, Chap. 6.

** This conciseness can be carried too far.

On a random basis the occupation probability for $r$, where $\frac{4}{3}\pi R^3$ is the volume occupied by the gas, is:

$$\frac{dV}{V} = \frac{r^2 \sin\vartheta d\vartheta d\varphi dr}{\frac{4}{3}\pi R^3} \longleftrightarrow p(r)\,dr = \frac{3}{R^3} r^2\,dr \tag{5.116a}$$

and in like manner for the spin:

$$p(\xi)\,d\xi = \frac{dl}{l} = \frac{d\xi}{2} = \tfrac{1}{2}d\xi \tag{5.116b}$$

Now we have the requisite elements for the determination of $W_n(V)$, the probability that with $n$ perturbers present the shift at the emitter will amount to $V$. In complete analogy to Eq. (4.13) and the reasoning which led to it, we may obtain:

$$W_n(V) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-isV} A_n(s)\,ds \tag{5.117a}$$

where:

$$A_n(s) = \left\{ \int p(\xi)\,d\xi \int p(r)\,dr \exp\left[ is\,cr^{-m} u(\xi) \right] \right\}^n \tag{5.117b}$$

Since such complete analogy has been claimed, two differences in factors should be explained. We have $\frac{1}{2\pi}$ occurring in Eq. (5.117a) instead of $\left(\frac{1}{2\pi}\right)^3$ as in Eq. (4.13), since only one Dirichlet factor of the form Eq. (4.10) has been introduced. Also $\frac{1}{V^n}$ fails to appear in Eq. (5.117a) since its equivalent is contained in $p(r)p(\xi)$.

Using no subterfuge whatever, Eq. (5.117b) may be rewritten as:

$$A_n(s) = \left[1 - 3B(s)/2R^3\right]^n \tag{5.118a}$$

where:

$$B(s) = \int_{-1}^{+1} d\xi \int_0^l \left\{1 - \exp\left[iscr^{-m} u(\xi)\right]\right\} r^2 dr \tag{5.118b}$$

Eq. (5.118a) may surely be expanded according to the binomial theorem. In the result we allow $R$ to approach infinity which in turn means $n$ approaches infinity, since $n = \frac{4}{3}\pi R^3 N$. This converts our binomial expansion into the infinite MacLaurin series for:

$$A(s) = \exp\left[-2\pi NB(s)\right] \tag{5.118c}$$

so that our Eq. (5.117a) becomes:

$$W(V) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \exp\left[-isV - 2\pi NB(s)\right] ds \tag{5.119}$$

Next, Eq. (5.118b) may be integrated over $\xi$ so that:

$$B(s) = 2\int_0^{+\infty} (1 - \cos sv) r^2 dr \tag{5.120a}$$

where:

$$v = cr^{-m} \tag{5.120b}$$

If we let,

$$sv \equiv t \tag{5.120c}$$

$B$ may be written as:

$$B = \frac{2}{3}(c|s|)^{3/m} \int_0^{\infty} (1 - \cos t) d(t^{-3/m})$$

$$= \frac{2}{3}(c|s|)^{3/m} \left[ t^{-3/m}(1 - \cos t) \Big|_{t^{-3/m}=0}^{t^{-3/m}=\infty} - \int_0^{\infty} t^{-3/m} \sin t \, dt \right]$$

$$= \frac{2}{3}(c|s|)^{3/m} \int_0^{\infty} t^{-3/m} \sin t \, dt \tag{5.121}$$

where integration by parts has been utilized and l'Hospital's rule applied. This application of l'Hospital's rule results in the restriction of $m$ such that $m > \frac{3}{2}$. This is actually no restriction on the theory, since none of our interaction laws will require a value of less than 3/2.

For convenience, let:

$$\frac{\pi 4}{3} c^{3/m} \int_0^{\infty} t^{-3/m} \sin t \, dt = g_m \tag{5.122a}$$

so that:

$$2\pi B(s) = g_m |s|^{3/m} \tag{5.122b}$$

Our probability $W(V)$ is a real affair, and the utilization of this reality and Eq. (5.122b) in Eq. (5.119) yields:

$$W(V) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp\left[- N g_m s^{3/m}\right] \cos(sV) ds = \frac{1}{\pi} \int_0^{\infty} \exp\left[- N g_m s^{3/m}\right] \cos(sV) ds \tag{5.123}$$

since the integrand is an even function.

By evaluating Eq. (5.123) for the case $V = 0$ (no shift)

$$W(O) = \frac{m}{3\pi} \Gamma\left(\frac{m}{3}\right) \frac{1}{(N g_m)^{m/3}} \tag{5.124}$$

Margenau demonstrates the interesting result that the line center intensity decreases as $N^{-m/3}$.

If we define a function $I_m$ as,

$$I_m(X) = \int_0^{\infty} \exp\left[ - \left(\frac{u}{K}\right)^{3/m} \right] \cos u \, du \tag{5.125a}$$

then Eq. (5.123) may quite readily be written as:

$$W(V) = \frac{1}{\pi\,|V|}\,I_m\left(\frac{V}{V_0}\right) \tag{5.125b}$$

where:

$$V_0 = (Ng_m)^{m/3} \tag{5.125c}$$

All of which leads us to the departure point of special cases, and, with Margeneau, we shall consider three, namely, broadening by (1) permanent dipoles, (2) quadrupoles, and (3) forces which do not change sign.

In the dipole case we have $m = 3$* so that from Eqs. (5.125c), (5.122), and (5.125a):

$$V_0 = \frac{2}{3}\pi^2 Nc\,;\; I_3(X) = \frac{x}{1 + x^2}$$

so that Eq. (5.125b) becomes:

$$W(V) = \frac{V_0}{\pi(V^2 + V_0^2)} \tag{5.126a}$$

or, when we recall that $V = \hbar(\omega_0 - \omega)$:

$$W(\omega) = \frac{V_0/\pi\hbar^2}{(\omega_0 - \omega)^2 + V_0^2/\hbar^2} \tag{5.126b}$$

This is of some interest, since it is the Michelson-Lorentz or dispersion form of the line shape.†

A consideration of Eq. (5.122a) and Eq. (5.125a) should suffice to justify the statement that numerical calculations or series expansions are requisite for the evaluation of the integrals in these equations for other values of $m$. Margenau has carried out this numerical evaluation for the quadrupole case, $m = 5$, and the resulting curve $\frac{I_5(x)}{x}$ is compared to the one for the dipole in Fig. (5.10).

Let us note the symmetry which is displayed by the two line representations of Fig. (5.10) which we have not previously encountered in statistical broadening. The reason for this difference becomes clear when we neglect sign change through spin interaction as we shall now proceed to do. If we simply let $u = 1$ we obtain in place of Eq. (5.120a) the following:

$$B(s) = 2\int_0^\infty (1 - e^{-isv})r^2 dr \tag{5.127a}$$

from Eq. (5.118b) and

$$B(s) = -\,i\,\frac{2}{3}(c\,|s|)^{3/m}\int_0^\infty t^{-3/m}e^{it}dt = g \equiv g' + ig'' \tag{5.127b}$$

as in Eq. (5.121).

Then from Eqs. (5.127) and (5.119) we obtain as the form of the intensity (probability) distribution:

$$W(V) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \exp\,(-\,Ng's^{3/m})\cos\,(Vs + Ng''s^{3/m})\,ds \tag{5.128}$$

---

* See *supra*, Eq. (5.3).

† See *supra*, Chap. 1 and *infra*, Chap. 6.

Eq. (5.128), of course, will lead us to the type of results we have obtained earlier for van der Waals force, as an example of the same sign forces.

In the case of van der Waals interaction $m = 6$ so that:

$$g' = -g'' = \frac{2}{3}\pi\sqrt{2\pi C}$$

and, ergo, Eq. (5.41).

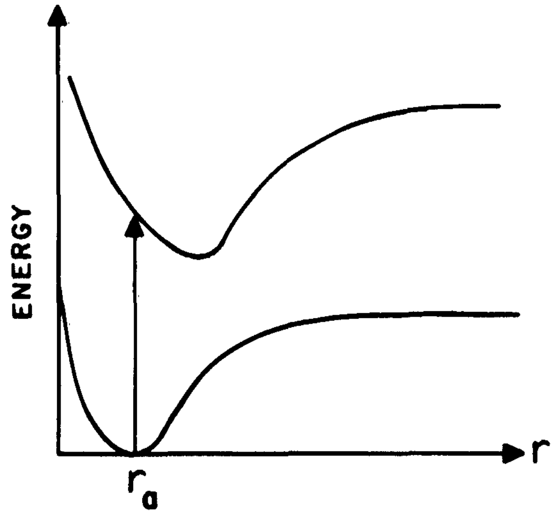

Fig. (5.1). The transition between two electronic states according to Franck.

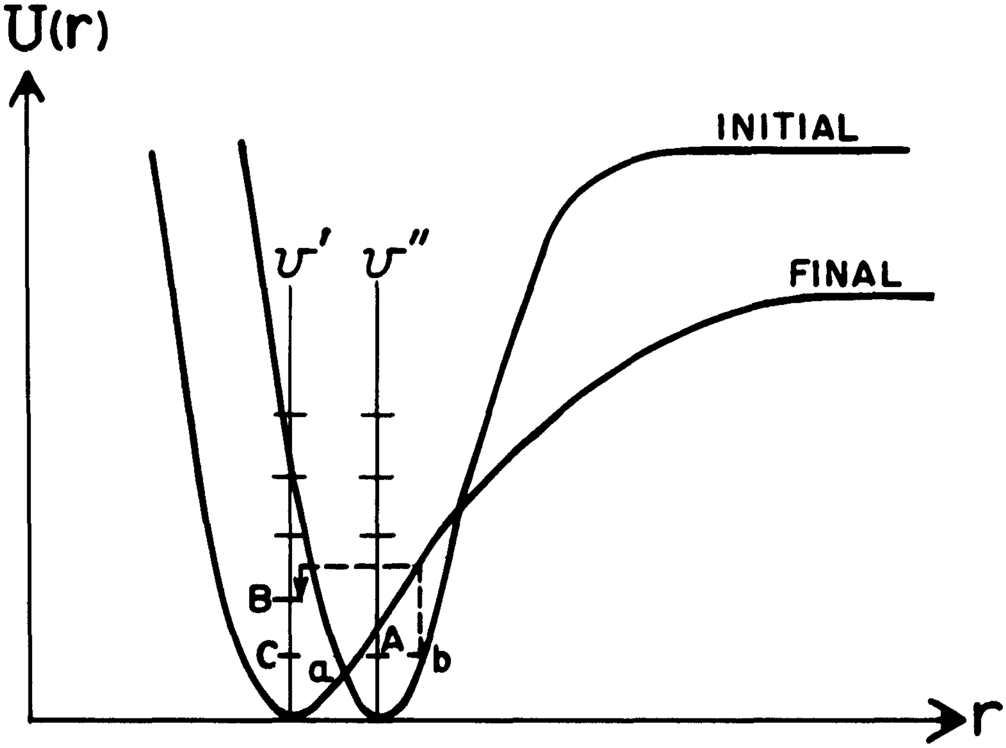

Fig. (5.2). The electronic transition with the indication of the most probable (intense) accompanying vibrationaltransitions. (After Condon.$^{20}$)

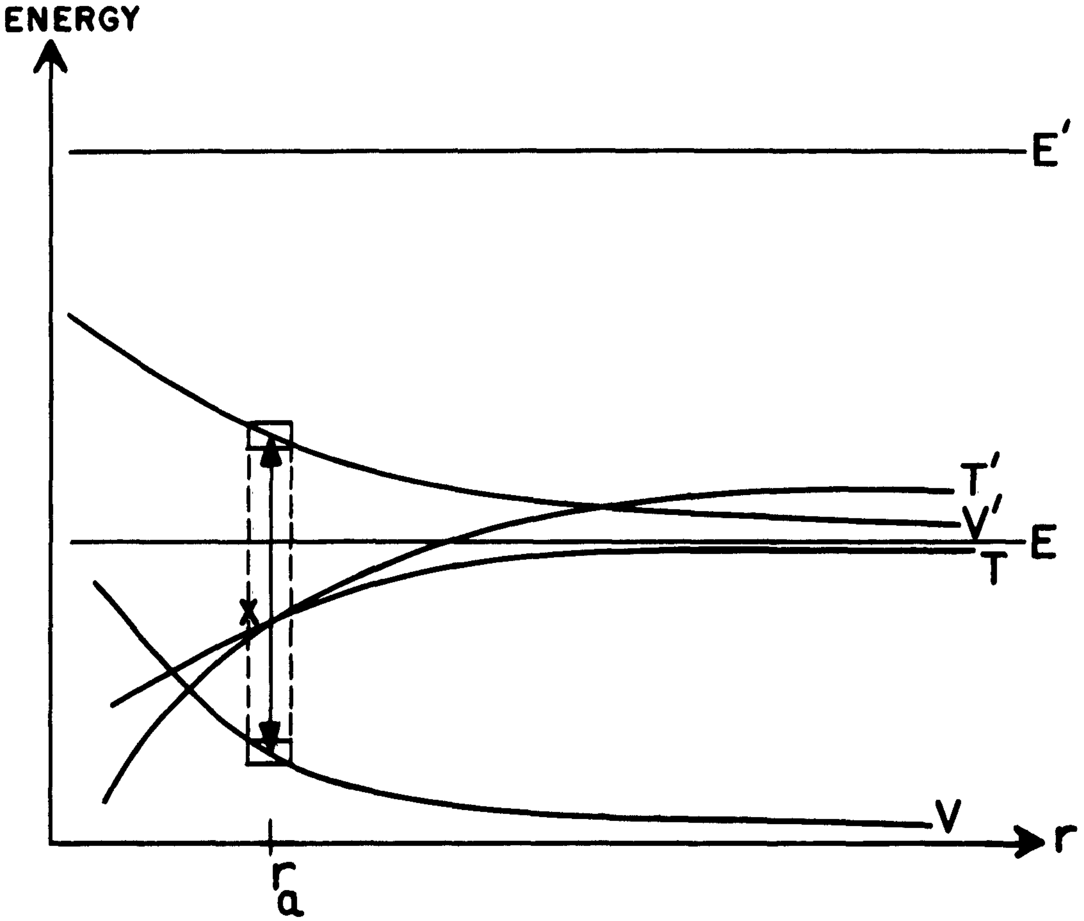

Fig. (5.3). An electronic transition in which translational velocity is unchanged during transition.

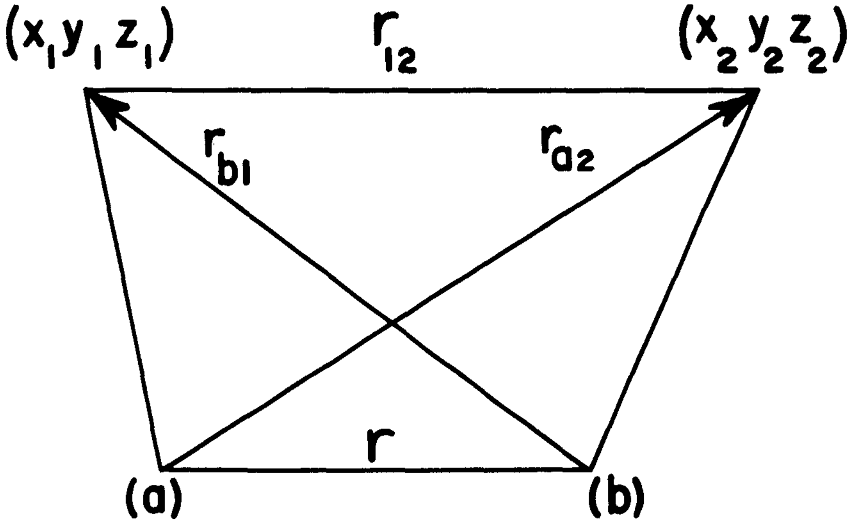

Fig. (5.4). The configuration for the Margenau van der Waals' force calculation. The nuclei are at (a) and (b) and the photoelectrons at $(x_1y_1z_1)$ and $(x_2y_2z_2)$.

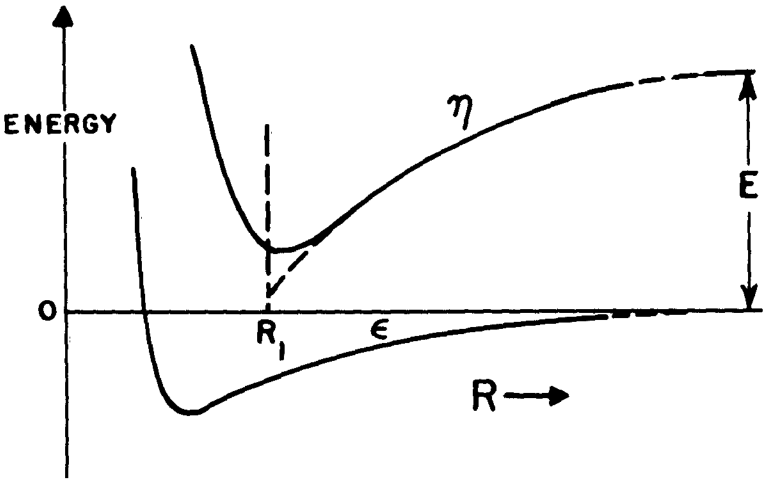

Fig. (5.5). The state curves of the statistical theory indicating the cutoff separation $R_1$. (After Margenau[111].)

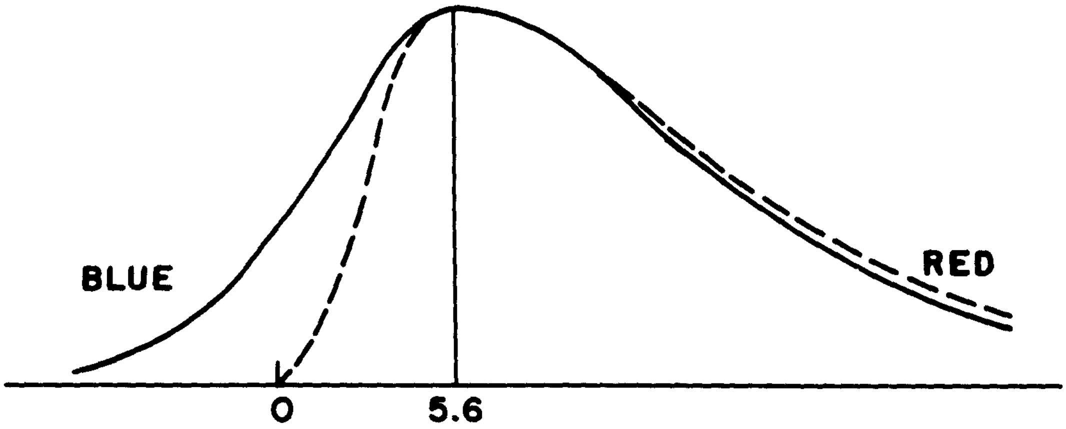

Fig. (5.6). The Hg 2537 line. The solid curve was obtained by Fuchtbauer, Joos, and Dinckelacker[45] for 50 atmospheres $N_2$. The dotted line is the Margenau result. (After Margenau[112].)

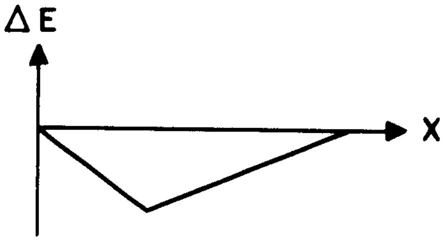

Fig. (5.7a)

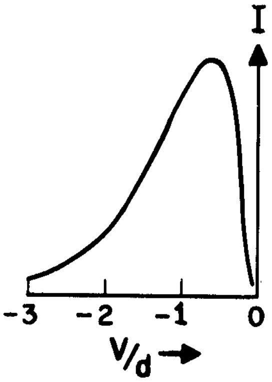

Fig. (5.7b)

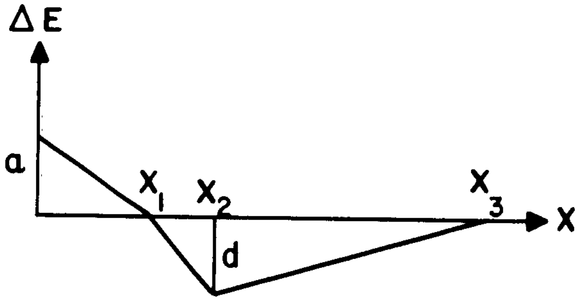

Fig. (5.7c)

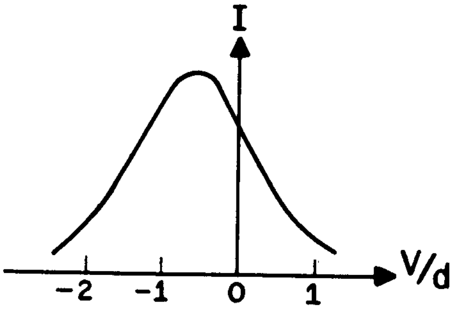

Fig. (5.7d)

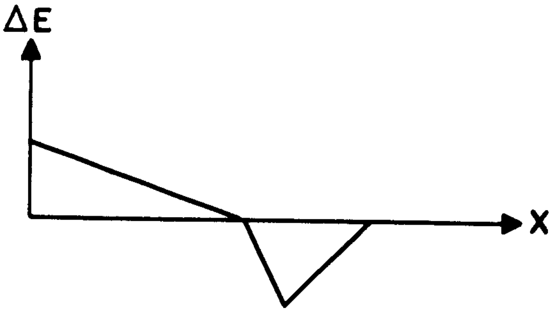

Fig. (5.7e)

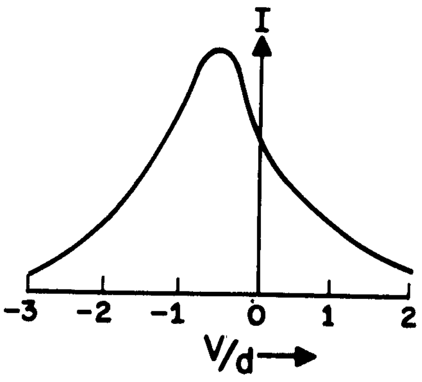

Fig. (5.7f)

Figs. (b), (d), and (f) give the results of evaluating Eq. (5.34) for Figs. (a), (c), and (e) respectively. (After Margenau.[113])

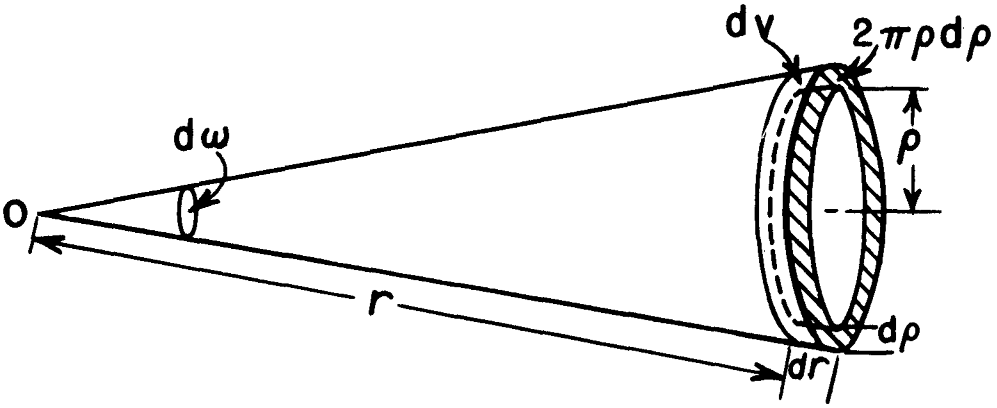

Fig. (5.8). The volume involved in a computation of the random probability (dV/V) of molecules having energies E to E + dE and optical collision diameters $\rho$ to $\rho$ + d$\rho$.

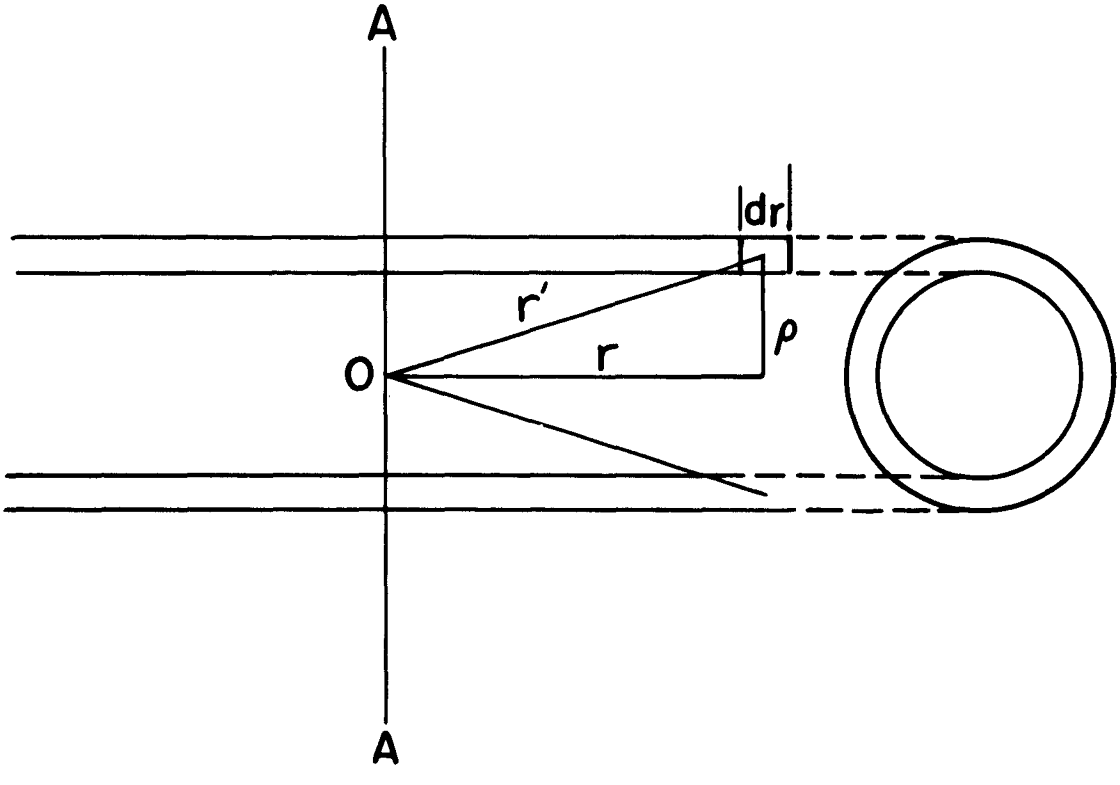

Fig. (5.9). The physical situation involved in the calculation of Q′ ($\rho$) fc Eq. (5.95).

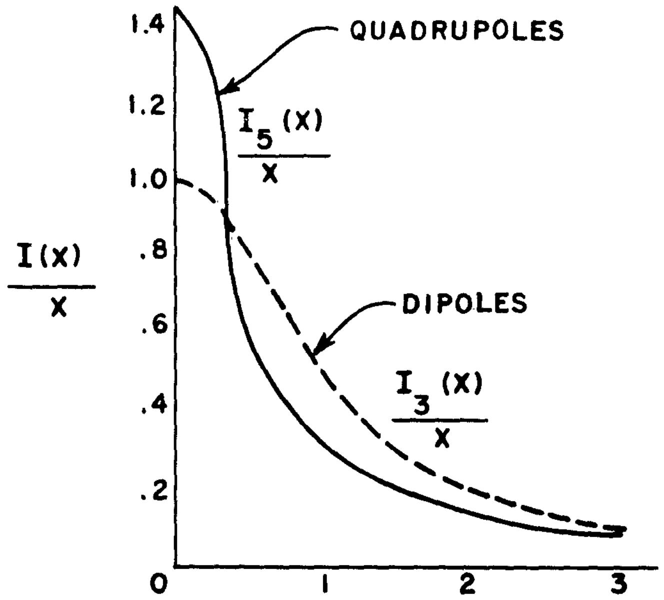

Fig. (5.10). Line shapes according to the Statistical Theory. (After Margenau.[119])

# CHAPTER 6

## INTERRUPTION BROADENING

We shall now deal with what amounts to a different approach to the question of the broadening of a spectral line by molecules of a type different from the emitter (absorber). In actuality, we shall find that we are not really dealing with a different phenomenon, but rather a different mathematical approach to the same phenomenon. No matter what approach to the problem of broadening by foreign gas atoms we may take, the basic phenomenon that causes this broadening is some sort of perturbing influence which arises from an interaction between broadener and emitter and which causes some usually time dependent distortion of the two energy levels between which the radiating transition takes place. We have considered several different attempts to mathematically describe the results of this interaction, and we shall now turn to the consideration of still another.

### 6.1. THE LENZ APPEAL TO CORRESPONDENCES

In 1924 Lenz[98] began what may be considered a post-quantum mechanical continuation of the work of Michelson and Lorentz on "pressure" broadening.* As we shall see, this work as well as a comfortable majority of the succeeding work on Interruption broadening consisted largely in attempts at quantum mechanical justification of the classical approach utilized. This article paved the way to a fertile field of disagreement.

We begin, with Lenz, by considering two types of molecular interaction which lead to a broadening of the spectral line:

(1) An interaction of a type such that all energy is radiated, that is, none of the radiation energy is transformed into translational energy of the molecules. The Stark effect due to the external fields of the surrounding atoms is an example of this type.

(2) A collision of the second kind in which excitation energy is completely transformed into translational energy.

In the quantum mechanical case of a radiating gas, a certain percentage of the atoms present undergo radiating transitions. The remainder of the excited atoms lose their excitation energy not by a radiating transition, but by a collision in which the excitation energy is transformed into translational energy.† On the other hand, a classical oscillator radiates a portion of its energy and loses the rest on collision. Lenz appeals to the Bohr correspondence principle to equate the overall amounts of scattered and heat converted energy in the two cases. We may obtain the desired amount of heat transformed energy in the classical case by a suitable selection of molecular diameter. It is apparent that we could obtain this amount by adjusting the molecular diameter to yield the required collision frequency. Now under these conditions we consider a collision to have occurred when two molecular centers have approached each other to within this adjusted molecular diameter. It may then be assumed that the wave train which is being emitted is cut off at the collision. Then as in the Lorentz case a broadening which is proportional to the density results.

These considerations were essentially based on type (2) interactions. Lenz then advanced the hypothesis

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* See *supra*, Chap. 1.

† This "black or white" assumption does not allow for the case of radiation with partial transformation to translational energy which we have previously considered (Chapter 5), but this is a minor point at this stage.

that type (1) interactions would yield the same result. Let us now consider the type (1) interactions from the Lenz point of view.

The assumption is first made that outside a certain minimum separation of the two atoms, the field of one atom* produces no Stark frequency perturbing effect on the emitter. At this minimum separation, however, the frequency of the emitted radiation is instantaneously disturbed by a large amount. Let us further call the occurrence of this closest approach an optical collision. Then, between two such collisions the atom will radiate undisturbed. During the short time of the optical collision on the other hand — that is, during the time during which the broadener is separated from the emitter by the amount or less than the amount of this minimum separation — radiation of a very different frequency is emitted. We simply neglect this "undefined emission" during collision, and assume that radiation ceases at collision and commences again after collision. Thus, we obtain the same type situation as that with which we have already dealt. Again a series of wave trains of length dependent on the time between collisions is emitted. According to this theory, the force laws which govern the interaction between emitter and broadener are of no specific importance. We must again — as in type (2) collisions — appeal to the Bohr correspondence principle for justification of our considerations.

This, in essence, is the theory that Lenz proposed, and it might be noted that it is more a justification for Michelson's treatment of pressure broadening than for Lorentz's, at least insofar as the computational portion of it is concerned.

Let us then replace our radiating atom by a classical oscillator. An equivalent form of Eq. (1.6b) gives for the amplitude:

$$J(\nu) = \text{const} \int_{-\tau/2}^{\tau/2} e^{2\pi i(\nu_0-\nu)t}\, dt = \text{const}\, \frac{\sin \pi\,(\nu_0 - \nu)\tau}{\pi(\nu_0 - \nu)} \tag{6.1}$$

The square of Eq. (6.1) would yield Eq. (1.12). If the square of this equation is averaged over all collision times, where the probability of a collision time between $\tau$ and $\tau + d\tau$ is given by $f(\tau)d\tau$ as in Eq. (1.56) the result is:

$$I(\nu) = \text{const} \int_0^\infty \frac{\sin^2 [\pi(\nu_0 - \nu)\tau']}{\pi^2(\nu_0 - \nu)^2}\, d\tau e^{-\tau'/\tau_0} = \text{const} \frac{(1/2\pi\tau)}{(\nu_0 - \nu)^2 + (1/2\pi\tau)^2} \tag{6.2}$$

Eq. (6.2) is, of course, equivalent to Eq. (1.78). The proportionality between the pressure and the half-width is apparent from Eq. (6.2) through the inverse proportionality between mean time between collisions, $\tau_0$, and half-width.

## 6.2. THE PHASE SHIFT DEFINITION OF A COLLISION AND HALF-WIDTH

Weisskopf first attacked the problem of Interruption broadening by foreign gas atoms in 1932.[193] In this paper he also discussed the case of broadening by like molecules.† He, too, considered the radiating molecule as replaced by a classical oscillator.

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* We could theoretically extend these considerations to an emitter and several broadeners which would, of course, be the case for multiple collisions. A single broadener, however, offers a conceptually convenient method of consideration.

† See *infra*, Chap. 7.

Let us assume that $\omega_0(t)$ is the natural frequency of this oscillator as a function of time. $\omega_0(t)$ is a constant during the so-called transit time — the time interval between two optical collisions. $\omega_0(t)$ changes, however, during what Weisskopf considered the very short time of the collision. Let us develop a slightly more general equation than we would need for this case.

The varying electric dipole moment* of the oscillator is for this case:

$$M(t) = A(t) \exp \left[i \int_0^t \omega_0(\tau)\, d\tau\right] \tag{6.3}$$

The Fourier integral of Eq. (6.3) is then:

$$M(t) = \int_{-\infty}^{+\infty} J(\omega) e^{i\omega t}\, d\omega \tag{6.4}$$

so that the amplitude is given by

$$J(\omega) = \int_{-\infty}^{+\infty} M(t) e^{-i\omega t}\, dt = \int_{-\infty}^{+\infty} A(t) \exp \left\{ i \left[ \int_0^t \omega_0(\tau)\, d\tau - \omega t \right] \right\} dt \tag{6.5a}$$

Weisskopf gave this equation as:

$$J(\omega) = \text{const} \int \exp \left[ i \int_0^t \omega_0(\tau)\, d\tau - i\omega t \right] dt \tag{6.5b}$$

The intensity distribution in the spectral line would then be given by the absolute square of Eq. (6.5b).

As Lenz had previously done, Weisskopf considered $\omega_0(t)$ a constant during the transit time and completely neglected the behavior during the short time of the collision itself. Now let us consider again Lenz's type (1) broadening.

An interaction between broadener and emitter exists such that the frequency of the oscillator is shifted by $\Delta(r)$ where $r$ is the emitter-broadener separation. It then follows that the phase shift in the undisturbed frequency during the optical collision is given by:

$$\Theta = \int_0^t \Delta(r)\, dt \tag{6.6}$$

Here $t$, the upper limit of the integral, is the time of collision.

When $\Theta$ has attained some value or other, an optical collision is assumed to have taken place, that is, we consider one wave train as terminated, and another completely independent wave train as initiated. Weisskopf arbitrarily assumes a value of $\Theta \sim 1$ for the phase shift required for the definition of an optical collision.

In order to qualitatively justify this assumption, let $r_0$ be the separation at closest approach of the two molecules and $v$ their relative velocity and write:

$$r = \sqrt{|\mathbf{r}|^2} = \sqrt{<v^2>\, t^2 + r_0^2 + 2\, \mathbf{r}_0 \cdot \mathbf{v}t} = \sqrt{<v^2> t^2 + r_0^2}$$

since $\mathbf{r}_0$ is perpendicular to $\mathbf{v}$.

Thus, Eq. (6.6) becomes:

$$\Theta = \int_{-\infty}^{+\infty} \Delta\left(\sqrt{v^2 t^2 + r_0^2}\right) dt \tag{6.7}$$

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* In Chap. 1 we considered the vibration of the photoelectron (Lorentz theory). Essentially, this amounts to the same thing. When this electron vibrates, it causes the noted variation in the dipole moment.

Weisskopf used the mean relative velocity squared here $<v>^2$ while Margenau and Watson[200] used the mean square relative velocity $<v^2>$. As is well known, these two quantities differ by a factor $\frac{3\pi}{8}$.

Now Weisskopf assumed an interaction $\Delta(r) = C/r^6$ where $C$ is given by $\alpha_1\alpha_2 V$. $\alpha_1$ and $\alpha_2$ are the polarizabilities of the emitter and the broadener, respectively. From the Stark effect of the *Na-D* lines he took $\alpha_1 = 9.5 \times 10^{-23}$, and he assumed $\alpha_2 = 10^{-24}$. Finally, $V$ was taken as four volts. If we let $x = \frac{vt}{\rho}$ we may rewrite Eq. (6.7) as:

$$\Theta = \int_{-\infty}^{+\infty} \frac{C dt}{\rho^6\left(\frac{v^2t^2}{\rho^2} + 1\right)^3} = \frac{C}{\rho^5 v} \int_{-\infty}^{+\infty} \frac{dx}{(x^2+1)^3} \backsim 1 \qquad (6.8)^*$$

where the assumption that $\Theta = 1$ determines an optical collision has been introduced. From Eq. (6.8) we may obtain for $\rho$:

$$\rho = J\left(\frac{C}{v}\right)^{1/5} \qquad (6.9)\dagger$$

where

$$J = \left(\int_{-\infty}^{+\infty} \frac{dx}{(1+x^2)^3}\right)^{1/5} = \left(\frac{3\pi}{8}\right)^{1/5} \doteq 1$$

Finally, for a temperature 500 and for values of the constants as given above Weisskopf obtained an optical collision-diameter $\rho = 6.8$A for the *Na-D* lines for $\Theta = 1$ which he considered a "plausible value." Actually, since we cannot strictly specify a phase shift which rigidly determines an optical collision, $\Theta = 1$ is probably as good a value as any.

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* For our future utilization let us write this as:

$$\eta = 2\pi\Theta = \frac{2\pi C}{v\rho^{n-1}} C_n \qquad (6.8a')$$

where

$$C_n = \int_{-\pi/2}^{\pi/2} \cos^{n-2}\varphi \, d\varphi = \sqrt{\pi}\, \frac{\Gamma\left(\frac{n-1}{2}\right)}{\Gamma\left(\frac{n}{2}\right)}$$

In these equations $\varphi$ is the angle between the distance of closest approach $\rho$ and the emitter-perturber direction. (See, for example, Fig. (6.1)). From Eq. (6.8a') we may write:

$$\rho = \left(\frac{2\pi C c_n}{v\eta_o}\right)^{1/n-1} \qquad (6.8b')$$

so that $\gamma$ becomes:

$$\gamma = \frac{2}{\tau} = 2\pi\left(\frac{2\pi C c_n}{v\eta}\right)^{2/n-1} vN$$

$$= C^{2/n-1}\, v^{\frac{n-3}{n-1}}\, N\, (2\pi)^{\frac{n+1}{n-1}}\, c_n^{\frac{2}{n-1}}\, \eta_o^{-\frac{2}{n-1}}$$

† In frequency units $\nu$ (as opposed to angular frequency units $\omega$):

$$\rho = \left(\frac{3\pi^2 C}{4v}\right)^{1/5} \qquad (6.9')$$

The shape of the broadened spectral line is still given by Eq. (6.2).

Before dealing with the controversy which arose here between the Statistical and the Interruption theories, and which we have touched briefly in Chapter 5, let us consider Weisskopf's attempt at quantum mechanical justification of this basically classical theory.

## 6.3. WEISSKOPF'S QUANTUM JUSTIFICATION OF THE FOURIER ANALYSIS

As does Jablonski,* Weisskopf considered the broadening of the spectral line by foreign gas molecules as an analogy to the Condon treatment of electronic-vibration bands of diatomic molecules. He began by assuming that all the broadening atoms are fixed in space and considered the motion of a single emitter among the members of this assemblage.

Weisskopf wrote the Schrodinger equation for the translational motion of the emitter with respect to a broadener as:

$$\nabla^2 \psi_n(\mathbf{r}) + \frac{8\pi^2 m}{h^2}[E - V_n(\mathbf{r})]\psi_n(\mathbf{r}) = 0 \tag{6.10}$$

In Eq. (6.10) $n$ represents the electronic state of the emitter and $E$ is the translational energy of the emitter. $V_n(\mathbf{r})$ "... is known to be different from zero only in a very small sphere about the ..."[111] broadener. Inside this small sphere, of course, $V_n(\mathbf{r})$ represents the interaction potential between the emitter and a broadener. The interaction is a function of the electronic state $n$.

A point should certainly be made here about Eq. (6.10). Weisskopf did not introduce any conditions which quantize the translational motion of the emitter. He simply wrote down Eq. (6.10). Jablonski noted that "Weisskopf treats the continuous translational energy spectrum as a discrete one should be treated thus omitting an important factor in the final intensity formula."[79] In a footnote he adds in explanation that "In the case of continuous eigenvalues, eigendifferentials instead of eigenfunctions must be used. If, by using a limited space, the continuous spectrum is transformed into a discrete one, a factor, denoting the density of energy levels, appears in the intensity distribution formula. This factor being omitted in Weisskopf's considerations, an incorrect dependence of the width of the line on energy of collision (i.e., of the temperature of the gas) is obtained."[79]

The Condon principle of separability of electronic and nuclear motion may now be utilized in analogy to Eq. (5.47) to obtain the transition probability for a change of electronic state from $n$ to $n'$ and translational energy from $E$ to $E'$.

$$\begin{aligned} D_{EE'} &= \int q\varphi_n(q)\psi_n(\mathbf{r},E)\overline{\varphi}_{n'}(q)\overline{\psi}_{n'}(\mathbf{r},E')\,dq\,dr \\ &= A_{nn'}\int \psi_n(\mathbf{r},E)\overline{\psi}_{n'}(\mathbf{r},E')\,d\mathbf{r} \end{aligned} \tag{6.11}$$

In Eq. (6.11) $q$ are the coordinates of the electron relative to the center of mass of the emitter; $\varphi_n(q)$ is the electronic eigenfunction, and $\psi_n(\mathbf{r},E)$ is the translational eigenfunction for the emitter in the electronic state $n$.

Now as in our considerations of Eq. (5.57) if $V_n(\mathbf{r}) = V'_{n'}(\mathbf{r})$ orthogonality decrees that $E = E'$; whereas, if $V_n(\mathbf{r}) \neq V'_{n'}(\mathbf{r})$ we may have $E \neq E'$. In the latter case Eq. (6.11) squared yields the probability that "... the emitted light departs from the Bohr frequency $\omega_{nn'}$ of the $n \rightarrow n'$ transition by $\frac{2\pi}{h}(E - E')$. The thus computed intensity distribution is identical to the collision damping (distribu-

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* See *supra*, Chap. 5.

tion).”[193] The last statement in the quotation is given by Weisskopf without further justification and appears to be open to question. We should recall that Lenz's appeal to the Bohr correspondence principle is so far the only quantum mechanical justification which we have for the Interruption broadening theory. Weisskopf next introduced a further justification.

Let us simplify Eq (6.11) by considering it as unidimensional.* Several additional assumptions are now made. Firstly, we assume there to be no direction change on collision. Next, it is to be assumed that the collision consists in a passage by the broadener through the outer portions of the sphere of effective $V(r)$. These collisions would certainly occur more frequently than the very close approaches or the central collisions. Finally, it is to be inferred that the change in $V(r)$ during the collision is small compared to the translational energy.

These assumptions Weisskopf used to justify his utilization of the one dimensional form of Eq. (5.58) (where $x > x_0$) as the eigenfunction.

$$\psi_n(x,E) = \frac{\text{const}}{\sqrt{p}} e^{-\frac{2\pi i}{h}\int_0^x p dx} \tag{6.12a}$$

where: $p = \sqrt{2m(E - V_n)}$.

Here $r_0$ may be taken as the radius of the sphere whereon $V_n(\mathbf{r}) = E$ or in this case the distance $x_0$. In the space between atoms ($V_n(\mathbf{r}) = 0$) Weisskopf takes for his eigenfunction:†

$$\psi_n\,(x,E) = \text{const}\; e^{\frac{2\pi i}{h}\sqrt{2mE}x + i\Upsilon} \tag{6.12b}$$

When Eq. (6.12a) is substituted into Eq. (6.11), the matrix element for a change in the translational energy from $E$ to $E'$ becomes:

$$\text{const} \int \frac{1}{\sqrt{pp'}} e^{\frac{2\pi i}{h}\int (p'-p)dx} dx \tag{6.13}$$

Now surely $dx = vdt$, and since we assumed that the change in $V(r)$ is much less than the translational energy, $p - p' = \sqrt{2mT} - \sqrt{2mT'} \ll p = \sqrt{2mT}$ in which $T$ is the kinetic energy of the translational motion since $E = T + V$. From this follows: $(p - p')\,v = (\sqrt{2mT} - \sqrt{2mT'})\sqrt{\frac{2T}{m}} = 2T - 2\sqrt{TT'} \doteq 2(T - T')$.** On substituting these quantities into Eq. (6.13) we obtain:

$$\frac{\text{const}}{m} \int e^{\frac{4\pi i}{h}\int_0^t (T'-T)dt} dt \tag{6.14a}$$

Instead of Eq. (6.14a) Weisskopf obtained

$$\frac{\text{const}}{m} \int e^{\frac{2\pi i}{h}\int_0^t (T-T')dt} dt \tag{6.14b}$$

since he said $(p - p')v = T - T'$. We must show his proof using Eq. (6.14b) since (6.14a) simply will not yield the desired results. Although the statement is rather shaky, we shall content ourselves by justifying

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* "The assumption of rectilinear motion is incompatible with the fact that the atomic collision problem is a central force problem."[79] It would seem that this assumption should provide a reasonable first approximation, however.

† We should here keep in mind Jablonski's comment on quantization, eigenfunctions, and eigendifferentials.

** Weisskopf leaves out the factor 2.

the utilization of the relation: $2(T - T') \doteq T - {}_{\bullet}T'$. Insofar as order of magnitude is concerned $2\Delta T$ is the same as $\Delta T$.

It is apparent that Eqs. (6.14b) and (6.5b) are identical if $\frac{2\pi}{h}(T' - T) = \omega_0(t) - \omega$. This identity is what should be shown, since the absolute square of the matrix element given by Eq. (6.14b) yields the intensity, and we wish to show that it reduces to Eq. (6.5b).

It is certainly true that $T' - T = E' - E + V_n - V_{n'}$. In addition, the emitted frequency must be $\omega = \omega_{nn'} + \frac{2\pi}{h}(E - E')$. From these three relations we obtain:

$$\omega_0(t) = \omega_{nn'} + \frac{2\pi}{h}[V_n(x) - V_{n'}'(x)] \tag{6.15}$$

Eq. (6.15)* is a statement of the Franck-Condon principle. We are thus free to conclude that Eqs. (6.14b) and (6.7b) are identical, and, subject to certain limitations, this provides a further support for the theory of Interruption broadening.

At this point it would be à propos to consider the objection which Weisskopf raised in his first article on Interruption broadening to Jablonski's earlier theory[74] of spectral line broadening.

We may recall* Jablonski's and later Margenau's utilization of the Franck potential curves for the formulation of a broadening theory. In considering Weisskopf's objection to Jablonski's utilization of these Franck curves let us refer to Eq. (5.58). Since Weisskopf's objections were stated in a very few words, we shall quote them in their entirety.

"One must distinguish here between eigenfrequencies and emitted or absorbed frequencies. If $\omega_0$ is time variable, then the intensity of the emitted frequency $\omega$ is given by (14).† Hence, frequencies can be emitted which have not at any time been eigenfrequencies of the atom. This is the reason why Jablonski in his considerations can never find the collision damping. From the Franck curves he determines the occurrence of the various $\omega_0$ -values from which in general nothing regarding the intensity distribution of the radiation can result."[193]**

It is here understood that the "various $\omega_o(t)$" are the "eigenfrequencies of the atom" which are referred to. One comment certainly appears to be in order. The conclusions drawn above are wholly dependent on whether or not sufficient quantum mechanical justification has been afforded Eq. (6.5b).

Under the assumption that Eq. (6.5b) has been satisfactorily justified, then the statistical considerations of Chapter 5 are now in need of justification in view of Weisskopf's remarks. Margenau[112] succeeded in doing this by showing that in actuality a correspondence does exist between the Statistical and Interruption theories.

## 6.4. CORRESPONDENCE BETWEEN STATISTICAL AND INTERRUPTION THEORIES

According to the statistical theory:

$$I(V)dV = c\int_V dt \tag{5.22}$$

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* See *supra*, Chap. 5.

† This is our Eq. (6.5b).

** These remarks appear as a footnote in Reference 193.

Now we shall only consider this in one dimension.* The following Dirichlet factor has the value one for $V - \frac{1}{2}dV \leqslant V(t) \leqslant V + \frac{1}{2}dV$ and the value zero for $V$ anything else:

$$\frac{1}{\pi}\int_{-\infty}^{+\infty} \sin\left(\tfrac{1}{2}\, xdV\right) e^{i[V - V(t)]x}\, \frac{dx}{x} \tag{6.16}$$

$V(t)$ in Eq. (6.16) is defined by Eq. (5.24). Thus Eq. (6.16) allows us to extend the limits on Eq. (5.22) so that it becomes:

$$I(V)dV = c\int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} \sin\left(\tfrac{1}{2}\, xdV\right) e^{i[V - V(t)]x}\, \frac{dx}{x} \tag{6.17}$$

We suppose that during the "time of sojourn" in the appropriate configuration, the emitted frequency will have a magnitude in the neighborhood of $\omega = V/\hbar$. Then from Eq. (6.17):

$$I(\omega)d\omega = c\int\int dt\, \frac{dx}{x} \sin\left(\tfrac{1}{2}xd\omega\right) e^{i\omega x - i\omega_0(t)x} \tag{6.18}$$

According to Eq. (6.5b) the intensity due to $\omega$ may be written as:

$$I(\omega)d\omega = \int_{\omega - d\omega/2}^{\omega + d\omega/2} |J(\omega)|^2\, d\omega = c \iiint_{\omega - d\omega/2}^{\omega + d\omega/2} \exp\left[\, i\int_0^t \omega_0(\tau)d\tau - i\int_0^{t'} \omega_0(\tau)d\tau + i\omega(t' - t)\right] dtdt'd\omega$$

$$= \int\int dtdt' \exp\left[i\int_0^t \omega_0(\tau)d\tau - i\int_0^{t'} \omega_0(\tau)d\tau + i\omega(t' - t)\right] \frac{\sin\left[\frac{1}{2}(t' - t)d\omega\right]}{(t' - t)} \tag{6.19}$$

The last integral in the exponential is of small value unless $x = t' - t$ is small. In addition, $\omega_0(t)$ should certainly be a continuous function so that the integral may be expanded in a Maclaurin series in $t' - t$. The result is:

$$-\, i\int_0^{t'} \omega_0(\tau)d\tau = -\, i\left[\int_0^{t} \omega_0(\tau)d\tau + \omega_0(t)(t' - t) + \omega_0\,(t)\,\frac{(t' - t)^2}{2} + \ldots\right] \tag{6.20}$$

If the series in Eq. (6.20) is cut off after the first two terms and the result substituted into Eq. (6.19), we obtain:

$$I(\omega)d\omega = \int\int dtdt' e^{i\omega(t' - t) - i\omega_0(t)(t' - t)}\, \frac{\sin\left[\frac{1}{2}(t' - t)d\omega\right]}{(t' - t)} \tag{6.21}$$

Then if we let $x = t' - t$, Eqs. (6.18) and (6.21) are identical. Thus, the time derivatives of $\omega_0(t)$ must be very small in order that the Interruption distribution reduces to the Statistical distribution. This in turn means that the broadeners must move very slowly with respect to the emitter in order that the distribution may so reduce.

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* "What's sauce for the goose . . ."

So far, then, we have considered Lenz's and Weisskopf's quantum mechanical justification for the theory of Interruption broadening which they supported, and the correspondence (mathematically at least) of this theory with the Statistical theory under certain limiting conditions. Let us reconsider now the physical theory implicit in our development.

## 6.5. THE PHYSICAL PHENOMENON IMPLIED BY THE LENZ-WEISSKOPF THEORY

For conceptual clarity, let us refer to Fig. (6.1). In this figure we have represented the emitter path by the arrow, and the perturbers by the small circles. At point "b" on the emitter path the radiation of a "new" wave train is initiated, since under the Michelson-Lenz-Weisskopf theory a terminating optical collision has just been undergone by the emitter. As the emitter travels along its path toward point "c" it is perturbed by the surrounding atoms according to some potential interaction "law" of the form $Cr^{-n}$ and small phase changes occur. The "A" perturbers in Fig. (6.1), however, are too distant to cause an optical collision in the Weisskopf sense (phase change of unity) so we ignore them. The effects of this ignoration we shall discuss later. When we arrive at the point "c" the second "B" perturber is now within the range requisite for inducing a phase change of unity. At this point, then, we cut off the emitted wave train and perform a Fourier analysis of the radiation emitted between points "b" and "c." Thus, we can see that, among other possible omissions, we have neglected (a) the effect of distant collisions and (b) the effect of phase changes greater than unity. Let us consider Omission (b) and defer our consideration of Omission (a) until a more à propos time.

When we fail to consider phase changes greater than unity, as we implicitly do in the Weisskopf theory, we essentially neglect values of $\omega$ farther from line center than some value $\omega_l$ in the line wing. In essence, then, we can only expect legitimate application of the theory near line center. We shall see from Lindholm's later work the manner in which we actually get a statistical distribution joining the interruption distribution in the line wing. It is apparent that the limit of applicability of the interruption distribution in the line wing will be given by $\Delta\omega = 2\pi Cr^{-n}$ where $r = \rho_0$. Then from Eq. (6.8a′) we obtain for the limit on $\Delta\omega$:

$$\Delta\omega \leqslant \left(\frac{v^n}{2\pi C c_n{}^n}\right)^{1/n-1}; \quad \eta_0 = 1 \tag{6.22}$$

From a slightly different viewpoint we shall later obtain about the same restriction.

Let us now return to the continued development of the Interruption theory.

## 6.6. THE TIME OF COLLISION INCLUDED (LENZ THEORY)

Our line shape is given by Eq. (6.2), and a consideration of this equation shows us that two of the important effects on a spectral line which arise out of the presence of foreign gas atoms are strikingly absent. These missing effects are (1) the shift of the line intensity maximum and (2) any asymmetry in the broadened line. An attempt to refine the theory so as to include these effects was made by Lenz[99] in 1933.

In essence, Lenz felt that in order to obtain a line shift and asymmetry " . . . we must not limit ourselves to the interval between collisions but must include the effect of the collisions in calculating the distribution."[99] In the past, we have limited ourselves in that we have considered $\omega_0$ a constant during the time between collisions and ignored its behavior during the actual collision.

Let us suppose that $\tau_0$ is the mean time between collisions and, further, that $2\tau$ is the time of collision.

We take $f_0(d)$ to be the frequency change per unit time during the time of collision $2\tau$ where $\rho$ is the optical collision diameter. As did Weisskopf, Lenz defined this diameter as the molecular separation at which the phase of "the classically substituted oscillators" has changed by one. Then the change of phase during collision is:

$$\vartheta = 2\tau f_0(d) \tag{6.23}$$

The oscillator frequency is given by:

$$\omega_0(t) = \omega_0 + f(t) \tag{6.24}$$

We may express the amplitude as:

$$x = x^0 e^{i\omega_0 t + i\vartheta(t)} \tag{6.25}$$

where:

$$\vartheta(t) = \int^{t} f(t)dt$$

The amplitude in a Fourier expansion of Eq. (6.25) we may find from an analogy to Eq. (6.5b) as:

$$J(\omega) = \int_{-\infty}^{+\infty} e^{i(\omega_0 - \omega)t + i\vartheta(t)}\, dt \tag{6.26}$$

From Eq. (6.26) the intensity corresponding to the frequency $\omega$ is:

$$I(\omega) = |\, J(\omega)\, |^2 = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{i(\omega_0 - \omega)(t' - t) + i[\vartheta(t') - \vartheta(t)]}\, dt dt' \tag{6.27}$$

The variable is next changed to $T = t' - t$ where still $t = t$. Thus, Eq. (6.27) becomes:

$$I(\omega) = \int_{-\infty}^{+\infty} dT e^{i(\omega_0 - \omega)T} \int_{-\infty}^{+\infty} e^{i\Delta\vartheta(t,T)}\, dt \tag{6.28a}$$

where

$$\Delta\vartheta(t,T) = \vartheta(t + T) - \vartheta(t) \tag{6.28b}$$

Now let $\mathbf{r}$ be the position vector of the oscillator-emitter and let $\mathbf{r}_k$ be the position vector of the $k$-th disturber. Lenz considered all disturbers the same, and the frequency disturbance due to the $k$-th disturber as $\varphi(\mathbf{r} - \mathbf{r}_k)$, simply some function of their separation. Then he let the perturbations due to various broadeners be additive so that:

$$f(t) = \sum_k \varphi(\mathbf{r} - \mathbf{r}_k) \tag{6.29}$$

although he noted that " . . . in the case of very large densities of disturbing gas this assumption is probably not good."[99] The rectilinear velocities of the emitter and the $k$-th disturber are given by $\mathbf{v}$ and $\mathbf{v}_k$ respectively. The position vectors at time $t = 0$ are taken as $\mathbf{r}^a$ and $\mathbf{r}_k{}^a$. Finally, Lenz assumed that close or central collisions are not of importance compared to those in the neighborhood of the optical collision diameter. By the above definitions:

$$\varphi(\mathbf{r} - \mathbf{r}_k) = \varphi[(\mathbf{r}^a - \mathbf{r}_k{}^a) + (\mathbf{v} - \mathbf{v}_k)t] \tag{6.30}$$

so that, by Eqs. (6.28b), (6.29), and (6.30):

$$\Delta\vartheta(0,T) = \Sigma\Delta\vartheta_k(0,T) = \Sigma\int_0^T \varphi\, [\mathbf{r}^a - \mathbf{r}_k{}^a + (\mathbf{v} - \mathbf{v}_k)\alpha]\, d\alpha \tag{6.31}$$

Lenz assumed that the second integral in Eq. (6.28a) is the statistical time mean value of $e^{i\Delta\vartheta(t,T)}$. This assumption provides a device for the evaluation of the integral.

Let us digress for a moment from the matter at hand in order to justify Lenz's next step.

If we are considering the behavior of a collection of $N_1$ particles, we may first conveniently set up a $2N_1$ dimensional phase space, the coordinates of which are the $2N_1$ position coordinates and conjugate momenta of the $N_1$ particles. Any point in this phase space will now represent a certain momentum and spatial configuration for the $N_1$-particle system, and this point is generally referred to as a representative point. The behavior of this representative point conveniently tells us the behavior of our system, and Boltzmann's impressively titled "ergodic hypothesis" tells us what we may expect this behavior to be. The ergodic hypothesis* states that the representative point will successively pass through all points in phase space compatible with the total energy of the system. We cannot prove from this hypothesis, but we can certainly infer from it that the statistical time mean value of a quantity will be the same as the statistical mean value of the quantity.

Thus, the second integral in Eq. (6.28a) which Lenz has assumed to be the time mean of the integrand may be evaluated by finding the mean of the integrand.

If we take $u_k$, $v_k$, $w_k$ as our components of $\mathbf{v}_k$ and $x_k{}^a$, $y_k{}^a$, $z_k{}^a$ as our components of $\mathbf{r}_k{}^a$, the volume element of the phase space of our broadeners will be:

$$dV = \Pi\, dx_k{}^a\, dy_k{}^a\, dz_k{}^a\, du_k\, dv_k\, dw_k$$

Now let us assume a Maxwell-Boltzmann distribution, and we then obtain:

$$\int_{-\infty}^{+\infty} e^{i\Delta\vartheta} dt = \langle e^{i\Delta\vartheta} \rangle = \frac{\int e^{i\Delta\vartheta(0,T)} e^{E/kT}\, dV}{\int e^{E/kT}\, dV} \tag{6.32}$$

We have made the assumption that all broadeners are the same. On this basis, Lenz wrote Eq. (6.32) as the product of $N_1$ identical integrals. Although Lenz does not mention it, we should always keep in mind that all such transformations to integral products are not wholly justified by the assumption of identical particles. As has been mentioned,† previous occupancy of certain portions of space by other broadeners would still limit the integration for any one broadener to the unoccupied portions of space. Thus, in cases of this kind, an additional assumption must be made to the effect that these previously occupied parts of space need not be excluded.**

We let:

$$E = \Sigma \frac{m_k}{2} (\mathbf{v}_k \cdot \mathbf{v}_k) \qquad \text{(6.33a)††}$$

$$|\,\mathbf{v}\,| = c\,;\ |\,\mathbf{v}_k\,| = c_k\,;\ c_0{}^2 = \frac{2kT}{m_k}\,;\ m_i = m_k = m_0 \tag{6.33b}$$

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* To be quite technically correct, we should probably introduce the so-called quasi-ergodic hypothesis, but the ergodic one will be sufficient to our purposes.

† See *supra*, Chaps. 5 and 6.

** This is also implied by Eq. (6.39), that is, by neglecting interactions between broadeners.

†† Kinetic energy is here taken as total energy.

Utilizing Eqs. (6.33) the $k$-th identical integral becomes, after integration of the denominator in Eq. (6.32):

$$\frac{1}{\pi^{3/2} V c_0^3} \int_{-\infty}^{+\infty} e^{-c_k^2/c_0^2 + i\Delta\vartheta_k(0,T)}\, dx_k\, dy_k\, dz_k\, du_k\, dv_k\, dw_k \tag{6.34}$$

Next it is assumed that $\Delta\vartheta_k\ (0,T)$ is very small except in the immediate neighborhood of the emitter. Now let:

$$\int e^{i\Delta\vartheta_k(0,T)}\, dx_k\, dy_k\, dz_k = V + \Upsilon_k \tag{6.35}$$

where $V$ is the volume in the configuration space of the $k$-th emitter, and $\Upsilon_k$ is the integral of $e^{i\Delta\vartheta_k(0,T)}$ over. the spheres of effective $\Delta\vartheta_k\ (0,T)$. Utilizing this in Eq. (6.34), we obtain:

$$1 + \frac{1}{\pi^{3/2} V c_0^3} \int_{-\infty}^{+\infty} \Upsilon_k e^{-c_k^2/c_0^2}\, du_k\, dv_k\, dw_k = 1 + \frac{N\Upsilon}{N_1} \tag{6.36a}$$

where:

$$\Upsilon = \frac{1}{\pi^{3/2} c_0^3} \int_{-\infty}^{+\infty} \left[e^{i\Delta\vartheta_k(0,T)} - 1\right] e^{-c_k^2/c_0^2}\, dx_k \ldots dw_k \tag{6.36b}$$

Thus, when Eq. (6.32) is considered as the product of $N_1$ identical integrals of the form Eq. (6.36), the result is:

$$\int_{-\infty}^{+\infty} e^{i\Delta\vartheta}\, dt = \int_{-\infty}^{+\infty} e^{N\Upsilon - \frac{mc^2}{m_0 c_0^2}}\, du\, dv\, dw \tag{6.37}$$

In Eq. (6.37) we have finally integrated over the velocity space of the emitter after having introduced the Boltzmann factor $e^{-mc/m_0 c_0^2}$ for the emitter. The approximation: $1 + \dfrac{N\Upsilon}{N_1} \doteq e^{N\Upsilon/N_1}$ has been used, $1 + \dfrac{N\Upsilon}{N_1}$ being the first two terms in the power series expansion of $e^{N\Upsilon/N_1}$. In addition $m$ is the mass of the emitter.

The integral of Eq. (6.37) may only be evaluated by graphical methods. Lenz considered certain special cases.

The limits on Eq. (6.31) may as well be $-\frac{1}{2}T$ and $+\frac{1}{2}T$. Then:

$$\Delta\vartheta_k\ (0,\ -T) = -\Delta\vartheta_k\ (0,T) \tag{6.38}$$

from Eqs. (6.31) and (6.35). Now, in order to carry out the integration in Eq. (6.35), let the $x$-axis of our spatial coordinate system correspond to $\mathrm{v} - \mathrm{v}_k$, and define quantities as follows:

$$\rho^2 = (y - y_k)^2 + (z - z_k)^2 \tag{6.39a}$$

$$\rho\beta = x^a - x_k^a + |\mathrm{v} - \mathrm{v}_k|\,\alpha \tag*{(6.39b)*}$$

$$\rho\xi = x^a - x_k^a \tag{6.39c}$$

$$\rho\eta = |\mathrm{v} - \mathrm{v}_k|\,T \tag{6.39d}$$

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* Lenz gave $\rho\beta$ as $x - x_k + |\mathrm{v} - \mathrm{v}_k|\,\alpha$ in place of the above.

Thus, $r^2 = \rho^2(1 + \beta^2)$ where **r** is the emitter-broadener separation, $\beta$ is the cotangent of the angle between **r** and the $x$-axis, while $\xi$ is the tangent of this angle.

We assume an interaction potential function of the form $\varphi = -ar^{-p}$. Then by virtue of Eqs. (6.39), Eq. (6.31) becomes:

$$\Delta\vartheta_k(0,T) = -\int_{-T/2}^{T/2} ar^{-p}d\alpha = -a\int_{\xi-\eta/2}^{\xi+\eta/2} [\rho^2(1+\beta^2)]^{-p/2}\left[\frac{\rho d\beta}{|\mathbf{v}-\mathbf{v}_k|}\right]$$

$$= -g\int_{\xi-\eta/2}^{\xi+\eta/2}\frac{d\beta}{(1+\beta^2)^{p/2}} \tag{6.40a}$$

where

$$g = \frac{1}{\rho^{p-1}}\,\frac{a}{|\mathbf{v}-\mathbf{v}_k|} \tag{6.40b}$$

On the basis of the high $p$ normally present the simplification may be made:

$$\psi\,(\zeta) = \int_{-\infty}^{\zeta}\frac{d\beta}{(1+\beta^2)^{p/2}} \tag{6.41}$$

Now Eq. (6.41) is very small for $\zeta$ less than around $-1$, a constant for $\zeta$ greater than around $+1$, and nearly rectilinear for intermediate $\zeta$. We then take for $\psi\,(\zeta)$:

$$\psi(\zeta) = \begin{cases} 0 \text{ for } \zeta < -\kappa \\ \chi(\zeta+\kappa) \text{ for } -\kappa \leqslant \zeta s + \kappa \\ 2\kappa\mu \text{ for } \zeta > \kappa \end{cases} \tag{6.42}$$

Lenz found by graphical integration that for $6 \leqslant p \leqslant 10$, $\kappa$ has a value of 0.75 and $\kappa\mu$ ranges between 0.57 and 0.44.

We may take $dx_k\,dy_k\,dz_k = 2\pi\rho^2\,d\rho\,d\xi$ so that from Eq. (6.35):

$$\Upsilon_k = -\int_0^\infty 2\pi\rho^2 d\rho \int_{-\infty}^{+\infty}[e^{i\Delta\vartheta_k(0,T)}-1]\,d\xi \tag{6.43}$$

In integrating over $\xi$ we need only consider $\eta > 0$ according to Eq. (6.38). Also, due to Eqs. (6.41) and (6.42) the integral reduces to one in the two regions $\xi + \frac{\eta}{2} \geqslant -\kappa$ and $\xi - \frac{\eta}{2} \leqslant +\kappa$. Now integration over $\xi$ gives for the two cases shown:

$$\text{for } \eta \geqslant 2\kappa \; : \; 2\kappa + \eta + (2\kappa - \eta)e^{-2ig\chi\kappa} + \frac{2}{ig\chi}\,(e^{-2ig\chi\kappa} - 1) \tag{6.44a}$$

$$\text{for } \eta \leqslant 2\kappa \; : \; 2\kappa + \eta - (2\kappa - \eta)e^{-ig\chi\eta} + \frac{2}{ig\chi}\,(e^{-2ig\chi\eta} - 1) \tag{6.44b}$$

In attempting to carry out the remaining integral, Lenz divided the integrand into two parts corresponding to Eqs. (6.44a) and (6.44b).* Thus:

$$\Upsilon_k = \Upsilon_k^{(1)} + \Upsilon_k^{(2)} \tag{6.45}$$

Let $\rho_0$ be the optical collision diameter. From Eqs. (6.40b), (6.33b), and (6.42) Lenz expressed $\rho_0$ as:

$$\rho_0 = 2\kappa\left(\frac{a}{c_0}\right)^{1/p-1} \tag*{(6.46)†}$$

which is arrived at by assuming a phase change of 1 (or $2\pi$) to have occurred at $\rho_0$ separation. Now let:

$$\Lambda = \frac{c_0 T}{\rho_0} \; ; \; \sigma = \frac{|\mathbf{v} - \mathbf{v}_k|}{c_0} \tag{6.47}$$

At the boundary between the regions of Eqs. (6.44), from Eqs. (6.39d) and (6.47) $2\kappa\rho_{\text{lim}} = \sigma\Lambda\rho_0$. Thus, we get for the value of Eq. (6.40a) at the boundary:

$$\gamma_0 = 2\kappa\chi g_{\text{lim}} = \frac{2\kappa\chi}{\sigma^p\Lambda^{p-1}} \tag{6.48}$$

Due to the high powers present in the denominator of Eq. (6.48) $\gamma_0$ is either $\ll 1$ or $\gg 1$ except in a small transition region.

From Eqs. (6.39d), (6.40b), and (6.47):

$$\eta = \sigma\Lambda\frac{\rho_0}{\rho} \; ; \quad g = \frac{1}{\sigma}\left(\frac{\rho_0}{2\kappa\rho}\right)^{p-1} \tag{6.49a}$$

and let:

$$\gamma_1 = 2\kappa\chi g = \frac{2\kappa\chi}{\sigma}\left(\frac{\rho_0}{2\kappa\rho}\right)^{p-1} ; \gamma_2 = \chi g\eta = 2\kappa\chi\Lambda\left(\frac{\rho_0}{2\kappa\rho}\right)^{p} \tag{6.49b}$$

Further:

$$2\pi\left(\frac{2\kappa}{\rho_0}\right)^3\rho^2 d\rho = -\frac{2\pi}{p-1}\left(\frac{2\kappa\chi}{\sigma\gamma_1}\right)^{3/p-1}\frac{d\gamma_1}{\gamma_1} = -\frac{2\pi}{p}\left(\frac{2\kappa\chi\Lambda}{\gamma_2}\right)\frac{d\gamma_2}{\gamma_2} \tag{6.49c}$$

We may thus introduce Eqs. (6.49) into Eqs. (6.44) and then introduce the result into Eq. (6.43) to obtain:

$$\frac{\Upsilon_k}{\rho_0^3} = \varphi_1(\gamma_0)\sigma^{-3/(p-1)} + \psi_1(\gamma_0)\Lambda\sigma^{1-2/(p-1)} \tag{6.50a}$$

$$\frac{\Upsilon_k}{\rho_0^3} = \varphi_2(\gamma_0)\Lambda^{3/p} + \psi_2(\gamma_0)\sigma\Lambda^{1+2/p} \tag{6.51a}$$

$$\varphi_1(\gamma_0) = -\frac{2\pi}{p-1}\frac{(2\kappa\chi)^{3/(p-1)}}{(2\kappa)^2}\int_{\gamma_0}^{+\infty}(1 - e^{-i\gamma_1})\frac{d\gamma_1}{\gamma_1^{1+3/(p-1)}} \tag{6.50b}$$

$$\psi_1(\gamma_0) = -\frac{2\pi}{p-1}\frac{(2\kappa\chi)^{2/(p-1)}}{(2\kappa)^2}\int_{\gamma_0}^{+\infty}(1 - e^{-i\gamma_1})\frac{d\gamma_1}{\gamma_1^{1+2/(p-1)}} \tag{6.50c}$$

$$\varphi_2(\gamma_0) = -\frac{2\pi}{p}\frac{(2\kappa\chi)^{3/p}}{(2\kappa)^2}\int_0^{\gamma_0}(1 - e^{-i\gamma_2})\frac{d\gamma_2}{\gamma^{1+3/p}} \tag{6.51b}$$

$$\psi_2(\gamma_0) = -\frac{2\pi}{p}\frac{(2\kappa\chi)^{2/p}}{(2\kappa)^2}\int_0^{\gamma_0}\left[(1 + e^{-i\gamma_2}) + \frac{2}{i\gamma_2}(e^{-i\gamma_2} - 1)\right]\frac{d\gamma_2}{\gamma_2^{1+2/p}} \tag{6.51c}$$

---

* $\eta$ goes from $\infty$ to 0 as $\rho$ goes from 0 to $\infty$.

† It would appear that we should have $(2\kappa)^{1/p-1}$ here instead of $2\kappa$. We simply use the Lenz result above, however.

An inspection of the above integrals indicates that they are properly convergent. If we now let $z = \sigma\Lambda^{1-1/p}$ then, since $z\kappa\chi \sim 1$ (see Eq. (6.42)) $\Upsilon_0 \sim z^{-p}$ according to Eq. (6.48). If $\sigma$, $\Lambda$, and, as a consequence, $z$ take values from 0 to $\infty$ then $\gamma_0$ is obviously $\ll 1$ or $\gg 1$ except right around $z = 1$. In the case $\gamma_0 \ll 1$, it is apparent that we may neglect Eq. (6.51a) compared to Eq. (6.50a), and in the case $\gamma_0 \gg 1$ the reverse is true. Thus, there results:

$$\frac{\Upsilon_k^{(1)}}{\rho_0^3} = A_1\sigma^{-3/(p-1)} + B_1\Lambda\sigma^{1-2/(p-1)} \text{ for } \sigma\Lambda^{1-1/p} > 1 \tag{6.52a}$$

$$\frac{\Upsilon_k^{(2)}}{\rho_0^3} = A_2\Lambda^{3/p} + B_2\sigma\Lambda^{1+2/p} \text{ for } \sigma\Lambda^{1-1/p} < 1 \tag{6.52b}$$

where:

$$A_1 = \varphi_1(0);\ B_1 = \psi_1(0);\ A_2 = \varphi_2(\infty);\ B_2 = \psi_2(\infty) \tag{6.52c}$$

Eqs. (6.52a) and (6.52b) are not valid near the indicated limits, and in addition "cumbersome expressions" must be introduced for the transition region. These expressions are neglected as "keine Rolle spielen."

This essentially completes the evaluation of $\Upsilon_k$. Now it will be necessary to integrate over $T$ in Eq. (6.28a) and over velocity space in the transformed version of the second integral in Eq. (6.28a) in order to obtain the intensity distribution. Integration over $T$ infers integration over $\Lambda$ in the equations for $\Upsilon_k$.*

Lenz established a polar coordinate origin at the endpoint of $\mathbf{v}$. We let the angle between $\mathbf{v}$ and $\mathbf{v} - \mathbf{v}_k$ be $\varphi$ and take this angle as our polar angle. Then we take $\mathbf{v} - \mathbf{v}_k$ as the radial coordinate and $\vartheta$ as the azimuthal coordinate. Our volume element in the velocity space of the $k$-th emitter becomes:

$$du_k dv_k dw_k = -(\,|\mathbf{v} - \mathbf{v}_k|\,)^2\, d(\,|\mathbf{v} - \mathbf{v}_k|\,)\, d\vartheta\, d(\cos\varphi) = -2\pi c_0^3\sigma^2 d\sigma\, d(\cos\varphi) \tag{6.53}$$

where, since our integral will possess azimuthal symmetry, we have integrated over $d\vartheta$, and where Eq. (6.47) has been used for the substitution for $\mathbf{v} - \mathbf{v}_k$. Now let us apply the law of cosines to the vector triangle consisting of $\mathbf{v}$, $\mathbf{v}_k$, and $\mathbf{v} - \mathbf{v}_k$ where the absolute values of the three vectors are given by Eqs. (6.33b) and (6.47).

$$c_k^2 = c^2 + c_0^2\sigma^2 - 2cc_0\sigma\cos\varphi$$

or

$$\left(\frac{c_k^2}{c_0^2}\right) = \sigma^2 + \sigma_0^2 - 2\sigma\sigma_0\cos\varphi;\ \sigma_0 = \frac{c}{c_0} \tag{6.54}$$

We next substitute Eqs. (6.53) and (6.54) into Eq. (6.36a) and integrate over cos from $-1$ to $+1$ to obtain:

$$\Upsilon = \frac{1}{\sqrt{\pi}\sigma_0}\int_0^\infty \left[e^{-(\sigma-\sigma_0)^2} - e^{-(\sigma+\sigma_0)^2}\right] \Upsilon_k(\sigma)\sigma\, d\sigma \tag{6.55}$$

Now the following function is formed:

$$F_j(\sigma_0) = \frac{1}{\sqrt{\pi}\sigma_0}\int^\infty \left[e^{-(\sigma-\sigma_0)^2} - e^{-(\sigma+\sigma_0)^2}\right] \sigma^{j+1}\, d\alpha \tag{6.56}$$

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* See *supra*, Eq. (6.47).

When Eqs. (6.52) are utilized in Eq. (6.55) integrals of the form of Eq. (6.56) will result, and the relevant values of $j$ will be: $j = -\frac{3}{p-1}, 0, 1 - \frac{2}{p-1}, 1$. Since we may expect large $p$ values, $j$ is always between $-1$ and 1 in value. In order to find $F_j(0)$, apply l'Hospital's rule to Eq. (6.56) to obtain:

$$F_j(\sigma_0) = \lim_{\sigma_0 \to 0} \left\{ \frac{1}{\sqrt{\pi}} \int_0^\infty [2(\sigma - \sigma_0)e^{-(\sigma-\sigma_0)^2} + 2\,(\sigma + \sigma_0)e^{-(\sigma+\sigma_0)^2}]\, \sigma^{j+1}\, d\sigma \right\}$$

$$= \frac{4}{\sqrt{\pi}} \int_0^\infty e^{-\sigma^2}\, \sigma^{j+2}\, d\sigma = \frac{2}{\sqrt{\pi}} \Gamma\left(1 + \frac{j+1}{2}\right) \tag{6.57a}$$

Eq. (6.57) holds then for $\sigma_0 = 0$ which in turn means that $c = 0$ and we consider the disturbers at rest. Now for the $p$ values which may arise $F_j(0)$ has values between 1.13 and 1. The other limiting case of $F_j(\sigma_0)$ arises for $\sigma_0 \gg 1$. In this case, the second term in Eq. (6.56) drops out as small. The integral only has appreciable value near $\sigma = \sigma_0$ so that:

$$F_j(\sigma_0) = \sigma_0^j \quad ; \quad \sigma_0 \gg 1 \tag{6.57b}$$

where $\sigma_0 = 4$ is large enough.

Lenz allowed Eq. (6.57a) to suffice, and, further, on the assumption of low gas densities, he neglected the region of Eq. (6.52b) and simply used Eq. (6.52a). We shall not show this, but it might be mentioned here that at pressures of more than one atmosphere Eq. (6.52b) must be utilized. Now from Eqs. (6.52b) and (6.52a) we may obtain:

$$N\Upsilon = N\rho_0^3\,[A_1F_{j_1}(\sigma_0) + \Lambda B_1F_{j_2}(\sigma_0)] \tag{6.58a}$$

$$j_1 = -\frac{3}{p-1} \quad ; \quad j_2 = 1 - \frac{2}{p-1} \tag{6.58b}$$

The Doppler effect is next introduced by replacing $\omega$, the natural frequency of our substituted oscillator by $\omega_c = \omega_0(1 - u/c_2)$, the frequency shifted by an emitter velocity of $u$ in the $x$-direction.*

Eqs. (6.58a) and (6.37) yield for Eq. (6.28a) the following:

$$I(\omega) = \Re\left\{\int_0^\infty e^{i\frac{\Lambda}{l}+N\Upsilon-\frac{m}{m_0}\sigma_0^2}\, du\, dv\, dw\, d\Lambda\right\} \tag{6.59}$$

The real part has been taken here, since by Eq. (6.38) we may take the real part, and then take as lower integral limit zero instead of minus infinity. Also in Eq. (6.59) $\frac{1}{l} = (\omega_c - \omega)\frac{\rho_0}{c_0} = (\omega_c - \omega)\,T_0$, $m_0$ is the mass of a broadener, and $m$ is the mass of the emitter. Integration has been taken over $\Lambda$ which replaces $T$ according to Eq. (6.47). Integration of Eq. (6.59) may be carried out over $\Lambda$ if Eq. (6.58a) is kept in mind. The result is:

$$I(\omega) = \Re\left\{\int_0^\infty e^{-\frac{m}{m_0}\sigma_0^2}\, du\, dv\, dw\, G(\sigma_0)\right\} \tag{6.60a}$$

where:

$$G(\sigma_0) = e^{N\rho_0^3A_1F_{j_1}(\sigma_0)} / i(\omega_c - \omega)T_0 + N\rho_0^3\, B_1\, F_{j_2}(\sigma_0) \tag{6.60b}$$

---

* Cf. *supra*, Sec. 1.5.

The real part of $B_1$ is negative. Lenz considered the special case of $Hg$ where $\sigma_0 < 1$ so that in Eq (6.60a) $J(\omega) \doteq \mathfrak{R}[G\,(0)]$. In addition, for the case $\frac{m}{m_0} \sim 1$, the integrand of Eq. (6.60a) may be regarded as a "Zackenfunction" whose only appreciable value occurs for $\sigma_0 \sim \frac{m_0}{m}$. Lenz took $\sigma_{0_{\max}} = 2$ and disregarded the Doppler effect. The result is:

$$I(\omega) = \mathfrak{R}\left[G\left(\sqrt{\frac{m_0}{m}}\right)\right] \tag{6.61a}$$

Let us develop the exponential in Eq. (6.61a) in a series and take only the first two terms to obtain:

$$I(\omega) = \mathfrak{R}\left\{\frac{1 + N\rho_0^3\,F_{j_1}\,[\mathfrak{R}(A_1) + i\,\mathfrak{J}(A_1)]}{i(\omega_0 - \omega)\,T + N\rho_0^3\,F_{j_2}\,[\mathfrak{R}(B_1) + \mathfrak{J}(B_1)]}\right\} = \frac{1 + \epsilon\,(\omega_0 - \Delta\omega_j - \omega)\,T_0}{(\omega_0 + \Delta\omega_0 - \omega)^2 + (\delta/2)^2} \tag{6.61a}$$

$$T_0\,\Delta\omega_0 = N\rho_0^3\,F_{j_2}(\sigma_m)\,\mathfrak{J}\,[B_1]\,;\ \frac{T_0}{2}\,\delta = N\rho_0^3\,F_{j_2}\,(\sigma_m)\,\mathfrak{R}\,[B_1] \tag{6.61b}$$

$$\epsilon = \frac{\mathfrak{J}[A_1]}{\mathfrak{R}[B_1]}\,\frac{F_{j_1}(\sigma_m)}{F_{j_2}(\sigma_m)};\ T_0 = \frac{\rho_0}{c_0};\ \sigma_m = \sqrt{\frac{m_0}{m}} \tag{6.61c}$$

We can see by a consideration of Eq. (6.61a) that this very restricted line shape equation does yield a shift as given by $\Delta\omega_0$ of the intensity maximum and an asymmetrical line, a measure of whose asymmetry is given by $\epsilon$. As in other dispersion type line shapes $\delta$ is the half-width of the broadened spectral line. Finally, $T_0$ is the time that a collision lasts, and it can be seen that as this goes to zero the line loses its asymmetrical shape and the shift disappears.

## 6.7. A SPECIFIC EVALUATION OF THE LENZ HALF-WIDTH

The half-width may well be evaluated more precisely for future comparison. From Eqs. (6.52c) and (6.50c) we may write:

$$B_1 = \psi_1\,(0) = -\frac{2\pi}{p-1}\,\frac{(2\kappa\chi)^{2/(p-1)}}{(2\kappa)^2}\int_0^\infty (1 - e^{-i\gamma_1})\,\frac{d\gamma_1}{\gamma_1^{1+2/(p-1)}}$$

$$= -\frac{2\pi}{5}\,\frac{(2\kappa\chi)^{2/5}}{(2\kappa)^2}\int_0^\infty (1 - e^{-i\gamma_1})\,\frac{d\gamma_1}{\gamma_1^{7/5}}$$

We shall only sketch the method developed by Jensen[82] for the evaluation of an integral of this type. The integral is first transformed as follows:

$$\int_0^\infty (1 - e^{i\gamma_1})\;\frac{d\gamma_1}{\gamma_1^{1+2/(p-1)}} = \frac{i}{2/(p-1)}\;\varphi\left(\frac{2}{p-1}\right)$$

where:

$$\varphi\left(\frac{2}{p-1}\right) = (-i)^{1-\frac{2}{p-1}}\int_0^\infty e^{-ix}\,x^{\frac{2}{p-1}}\,dx = \lim_{\epsilon\to 0}\,\lim_{a\to\infty}\int_\epsilon^a e^{-ix}\,x^{-\frac{2}{p-1}}\,dx$$

On the substitution $\gamma_1 = iw$, we obtain for $\varphi$:

$$\varphi = (-i)^{1-2/(p-1)} \lim_{\epsilon \to 0} \lim_{a \to \infty} \int_{w=\epsilon i}^{w=ai} e^{-w} \; w^{-2/(p-1)} \; dw$$

We consider $\varphi$ in the complex plane where $\varphi$ would be an integration along the axis of imaginaries. By using Cauchy's Integral Theorem we may equate this to the sum of integrals (a) along a circular path about the origin from $i\epsilon$ to $\epsilon$, (b) along the axis of reals from $\epsilon$ to $a$, and (c) along a circular path from $a$ to $ia$. After carrying out these operations we finally obtain:

$$\varphi\left(\frac{2}{p-1}\right) = (-i)^{1-2/(p-1)}\,\Gamma\left(1 - \frac{2}{p-1}\right) = \frac{\pi\left(\frac{2}{p-1}\right)}{\sin\left[\pi\left(\frac{2}{p-1}\right)\right]}\;\frac{(-i)^{1-2/(p-1)}}{\Gamma\left(1+\frac{2}{p-1}\right)}$$

so that $$\int_0^\infty (1 - e^{i\gamma_1})\,\frac{d\gamma_1}{\gamma_1^{\,1+2/(p+1)}} = \frac{\pi}{\sin\left[\pi\left(\frac{2}{p-1}\right)\right]}\;\frac{\exp\left[i\frac{\pi}{2}\left(\frac{2}{p-1}\right)\right]}{\Gamma\left(1+\frac{2}{p-1}\right)} = \frac{\pi}{\sin\left(\frac{2}{5}\pi\right)}\;\frac{e^{i\pi/5}}{\Gamma\left(\frac{7}{5}\right)}$$

and $$\mathfrak{R}\,(B_1) = -\,3.7845\,\frac{(2\kappa\chi)^{2/5}}{(2\kappa)^2}$$

On substitution from Eqs. (6.61c) and (6.46), Eq. (6.61b) becomes:

$$\delta = 7.977\,N\,(c_0)^{3/5}\,(a)^{2/5}\,F_{j_2} \tag{6.62}$$

where we have utilized the value $\kappa\chi = .57$ since $p = 6$.*

Although Lenz has introduced into the Interruption theory a consideration of the time of collision, thus obtaining a line which is shifted and asymmetrical, he has obtained an equation for this line which is only valid in a very restricted domain. As has been mentioned, the considered equation is only valid for pressures up to one atmosphere and for frequencies near the line center. The line center restriction is partly due to the fact that the intensity and hence numerator must be greater than zero. This in turn would mean that $|\,\omega_0 - \omega\,|$ must not become too large.

Although Lenz's results are not very generally applicable, he certainly demonstrated that successful modification of the Interruption theory was dependent at least to some extent on the inclusion of the time of collision, and the inclusion of this time in a more successful manner awaited Lindholm's later attack[102, 103] on the problem. Lindholm's avowed intent was "... to perform the Fourier analysis without the limitations that reduce the validity of Lenz's paper."[103]

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* See *supra*, Eq. (6.42) and subsequent.

### 6.8. LINE SHIFT WITHOUT COLLISION TIME

In analogy to Eq. (6.27) we begin with the equation:

$$
\begin{aligned}
I(\nu) &= \left| \int e^{2\pi i(\nu-\nu_0)t+i\Delta(t)} dt \right|^2 \\
&= \int\!\!\int_{-\infty}^{+\infty} e^{2\pi i(\nu-\nu_0)(t''-t')+i[\Delta(t'')-\Delta(t')]} dt\, dt' \\
&= \int_{-\infty}^{+\infty} e^{2\pi i(\nu-\nu_0)t} dt \int_{-\infty}^{+\infty} e^{i[\Delta(t+t')-\Delta(t')]} dt'
\end{aligned}
\qquad (6.63)
$$

As had Lenz, Lindholm considered the second integral as the statistical time mean value of the integrand and set this time mean equal to $\exp(-A(t) + iB(t))$ so that:

$$I(\nu) = \int_0^\infty e^{-A(t)} \cos [2\pi(\nu - \nu_0)t + B(t)]dt \qquad (6.64a)$$

Next it is assumed that but three different phase changes occur on collision.* These we shall designate as $\eta_a$, $\eta_b$, $\eta_c$. This in turn would mean that three different "differential collision cross-sections," $\sigma_i$, occur, where:

$$\sigma_i = \int | J(\eta_i) |^2 \sin \vartheta \, d\vartheta \qquad (6.65)$$

The total cross-section is $\sigma = \sigma_a + \sigma_b + \sigma_c$, and the mean time between collisions is $\tau$. The probability of $n + m + l$ collisions during the time $t$ is then:

$$\frac{1}{(n+m+l)!} \left(\frac{t}{\tau}\right)^{n+m+l} e^{-t/\tau} \qquad (6.66a)$$

and the probability that, of these $(n + m + l)$ collisions, $n$ will be of type $a$ corresponding to a phase shift $\eta_a$ $m$ will be type $b$, and $l$ will be type $c$ is:

$$\frac{(n+m+l)!}{n!\, m!\, l!} \left(\frac{\sigma_a}{\sigma}\right)^n \left(\frac{\sigma_b}{\sigma}\right)^m \left(\frac{\sigma_c}{\sigma}\right)^l \qquad (6.66b)$$

Thus, the probability that $n$ $a$-collisions, $m$ $b$-collisions, and $l$ $c$-collisions will occur in time $t$ is:

$$\left(\frac{\sigma_a}{\sigma}\right)^n \left(\frac{\sigma_b}{\sigma}\right)^m \left(\frac{\sigma_c}{\sigma}\right)^l \frac{1}{n!\, m!\, l!} \left(\frac{t}{\tau}\right)^{n+m+l} e^{-t/\tau} \qquad (6.67)$$

As in Lenz' considerations:

$$\Delta(t + t') - \Delta(t') = \sum_k [\Delta_k(t + t') - \Delta_k(t')] = n\eta_a + m\eta_b + l\eta_c \qquad (6.68)$$

In this case then the mean value of $e^{i[\Delta(t+t')-\Delta(t')]}$ which Lindholm assumed equal to the second integral in Eq. (6.63) is given by:

$$\left\langle e^{i[\Delta(t+t')-\Delta(t')]} \right\rangle = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \sum_{l=0}^{\infty} \left(\frac{\sigma_a}{\sigma}\right)^n \left(\frac{\sigma_b}{\sigma}\right)^m \left(\frac{\sigma_c}{\sigma}\right)^l \frac{1}{n!\, m!\, l!} \left(\frac{t}{\tau}\right)^{n+m+l} e^{-t/\tau} \left\{ e^{i[n\eta_a+m\eta_b+l\eta_c]} \right\} \qquad (6.69a)$$

---

* As we shall see, we could initially assume some other number and later extend the number of allowed phase changes as desired.

No normalizing denominator is needed in Eq. (6.69a), since the factor multiplying the exponential is already a normalized probability. Since: $\sum_{n=0}^{\infty}\left(\frac{\sigma_a t e^{i\eta_a}}{\sigma\tau}\right)^n \frac{1}{n!} = \exp\left[\frac{\sigma_a t}{\sigma\tau} e^{i\eta_a}\right]$, etc., Eq. (6.69a) becomes

$$\left\langle e^{i[\Delta(t+t') - \Delta(t')]} \right\rangle = e^{\frac{t}{\tau\sigma}\left[\sigma_a e^{i\eta_a} + \sigma_b e^{i\eta_b} + \sigma_c e^{i\eta_c}\right]} e^{-t/\tau} \tag{6.69b}$$

Utilizing Eq. (6.69b) in Eq. (6.63) we obtain:

$$\begin{aligned} I(\nu) &= \Re \left\{ \int e^{2\pi i(\nu - \nu_0)t} e^{\frac{t}{\tau\sigma}\left[\sum_i \sigma_i(\cos\eta_i + i\sin\eta_i) - \sigma\right]} dt \right\} \\ &= \int e^{-\frac{t}{\tau\sigma}\sum_i [\sigma - \sigma_i \cos\eta_i]} \cos\left[\frac{t}{\tau\sigma}\sum_i \sigma_i \sin\eta_i + 2\pi(\nu - \nu_o)t\right] dt \end{aligned} \tag{6.64b}$$

where we have taken the real part of exp(isin $\eta_i$) since the intensity is a real quantity. Thus, from Eqs. (6.64) there results:

$$A = t\sum_i \frac{\sigma_i}{\sigma\tau}\left[\sigma - \sigma_i \cos\eta_i\right] = \alpha t \tag{6.70a)*}$$

$$B = t\sum_i \frac{\sigma_i}{\sigma\tau} \sin\eta_i = \beta t \tag{6.70b}$$

and Eq. (6.64) becomes:

$$\begin{aligned} I(\nu) &= \int_0^{\infty} e^{-\alpha t} \cos\left\{\left[2\pi(\nu - \nu_0) + \beta\right] t\right\} dt \\ &= \frac{\text{const.}}{\left[(\nu - \nu_0) + \frac{\beta}{2\pi}\right]^2 + \left[\frac{\alpha}{2\pi}\right]^2} \end{aligned} \tag{6.71}$$

In obtaining Eq. (6.71) the collision time has been neglected in that we simply took the various phase changes as having occurred. A comparison of Eq. (6.71) with Eq. (6.61a), however, shows that this neglect of collision time has only effected a change from Lenz' result insofar as the line asymmetry is concerned. Eq. (6.71), of course, yields no line asymmetry. This difference between the two equations arises principally from the approximations which Lenz was obliged to utilize.

It might also be noted that we restricted ourselves to three phase changes $\eta_a$, $\eta_b$, and $\eta_c$, in setting up Eq. (6.67), but there is no reason to restrict Eqs. (6.70) for the shift and half-width in this manner.

## 6.9. REASON FOR WEISSKOPF THEORY FAILURE TO YIELD SHIFT†

Let us digress for a moment in order to consider an interesting aspect of the situation which has been mentioned by Burkhardt[15] and Unsold.[203] To begin with, let us rewrite Eqs. (6.70) as:

$$\alpha = vN\sum_i \sigma_i\left(1 - \frac{\sigma_i}{\sigma}\cos\eta_i\right) \doteq vN\sum_i 2\sigma_i \sin\frac{2\eta_i}{2} \tag{6.72a}$$

$$\beta = vN\sum_i \sigma_i \sin\eta_i \tag{6.72b}$$

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* Lindholm gives $[1 - \sigma_i \cos\eta_i]$.

† Cf. *supra*, Sec. 6.5.

From Eqs. (6.71) and (6.72a) it is apparent that the damping constant $\gamma$ may be written as:

$$\gamma = 2\alpha \dotplus 2vN\sum_i 2\sigma_i \sin^2 \frac{\eta_i}{2} \tag{6.73}$$

If, as usual, the distance of closest approach is taken as $\rho$, then the cross section $\sigma_i$ for a phase change $\eta_i$ can be taken as $2\pi$ where we now suppose there to be a continuum of cross sections instead of the discrete set of Eqs. (6.72). In addition, the assumption of this continuum replaces the summations in Eqs. (6.72) by integrations. These changes in Eqs. (6.72) together with the substitution for $\eta_i$ of Eq. (6.8a′) into these equations yield:

$$\gamma \doteq 2vN \int_0^\infty 4\pi\, \rho\, d\rho \sin^2 \frac{2\pi C c_n}{v\rho^{n-1}}$$

$$= C^{\frac{2}{n-1}}\, v^{\frac{n-3}{n-1}}\, N\, 8\pi^{\frac{n+1}{n-1}}\, c_n^{\frac{2}{n-1}} \int_0^\infty \sin^2 \frac{1}{x^{n-1}}\, x\, dx \tag{6.74a}$$

$$\beta = \omega_o - \omega_m = vN \int_0^\infty 2\pi\, \rho\, d\rho \sin \frac{2\pi C c_n}{v\rho^{n-1}}$$

$$= C^{\frac{2}{n-1}}\, v^{\frac{n-3}{n-1}}\, N\, 2\pi^{\frac{n+1}{n-1}}\, c_n^{\frac{2}{1-n}} \int_0^\infty \sin \frac{2}{x^{n-1}}\, x\, dx \tag{6.74b}$$

where now:

$$\frac{\eta}{2} = \frac{\pi C c_n}{v\rho^{n-1}} = \frac{1}{x^{n-1}}$$

Now let us consider the case of $n = 4$ as illustrating a rather interesting circumstance relating to the Weisskopf theory. (We note that in order to obtain agreement between Eqs. (6.9) and (6.74a) we must needs choose $\eta_0 = 0.64$.)

We may recall the failure of the Weisskopf theory to yield a line shift under any conditions.* What we propose to demonstrate is that the neglect on the part of the Weisskopf theory of collisions resulting in phase changes of less than unity, while accounting for most of the broadening, is responsible for the absence of a line shift.

To begin with, let us plot xsin² $\frac{1}{x^3}$ (from Eq. (6.74a)) and xsin $\frac{2}{x^3}$ (from Eq. (6.74b)) against $\rho/\rho_o$. The result appears in Fig. (6.2), and let us consider this figure. The vertical line in about the center of the figure is the Weisskopf collision radius. Now the area under the upper curve gives us the integral in Eq. (6.74a) and is hence a measure of the broadening. In like manner, the area under the lower curve is a measure of the shift. The Weisskopf theory only considers those areas to the left of the ordinate specifying the Weisskopf collision radius. It thus becomes quite apparent that with the adoption of this radius we obtain almost all

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* This is not true for his more detailed theory for which see *infra*, Chap. 7. This theory does not appear to have been applied, however.

No normalizing denominator is needed in Eq. (6.69a), since the factor multiplying the exponential is already a normalized probability. Since: $\sum_{n=0}^{\infty}\left(\frac{\sigma_a t e^{i\eta_a}}{\sigma\tau}\right)^n \frac{1}{n!} = \exp\left[\frac{\sigma_a t}{\sigma\tau} e^{i\eta_a}\right]$, etc., Eq. (6.69a) becomes

$$\left\langle e^{i[\Delta(t+t') - \Delta(t')]}\right\rangle = e^{\frac{t}{\tau\sigma}[\sigma_a e^{i\eta_a} + \sigma_b e^{i\eta_b} + \sigma_c e^{i\eta_c}]}\, e^{-t/\tau} \tag{6.69b}$$

Utilizing Eq. (6.69b) in Eq. (6.63) we obtain:

$$I(\nu) = \Re\left\{\int e^{2\pi i(\nu-\nu_0)t}\, e^{\frac{t}{\tau\sigma}[\sum_i \sigma_i(\cos\eta_i + i\sin\eta_i) - \sigma]}\, dt\right\}$$

$$= \int e^{-\frac{t}{\tau\sigma}\sum_i[\sigma - \sigma_i\cos\eta_i]} \cos\left[\frac{t}{\tau\sigma}\sum_i \sigma_i \sin\eta_i + 2\pi(\nu - \nu_o)t\right] dt \tag{6.64b}$$

where we have taken the real part of exp(isin $\eta_i$) since the intensity is a real quantity. Thus, from Eqs. (6.64) there results:

$$A = t\sum_i \frac{\sigma_i}{\sigma\tau}[\sigma - \sigma_i\cos\eta_i] = \alpha t \tag{6.70a}^{*}$$

$$B = t\sum_i \frac{\sigma_i}{\sigma\tau}\sin\eta_i = \beta t \tag{6.70b}$$

and Eq. (6.64) becomes:

$$I(\nu) = \int_0^{\infty} e^{-\alpha t}\cos\left\{[2\pi(\nu - \nu_0) + \beta]\,t\right\} dt$$

$$= \frac{\text{const.}}{\left[(\nu - \nu_0) + \frac{\beta}{2\pi}\right]^2 + \left[\frac{\alpha}{2\pi}\right]^2} \tag{6.71}$$

In obtaining Eq. (6.71) the collision time has been neglected in that we simply took the various phase changes as having occurred. A comparison of Eq. (6.71) with Eq. (6.61a), however, shows that this neglect of collision time has only effected a change from Lenz' result insofar as the line asymmetry is concerned. Eq. (6.71), of course, yields no line asymmetry. This difference between the two equations arises principally from the approximations which Lenz was obliged to utilize.

It might also be noted that we restricted ourselves to three phase changes $\eta_a$, $\eta_b$, and $\eta_c$, in setting up Eq. (6.67), but there is no reason to restrict Eqs. (6.70) for the shift and half-width in this manner.

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$$\alpha = vN\sum_i\sigma_i\left(1 - \frac{\sigma_i}{\sigma}\cos\eta_i\right) \doteq vN\sum_i 2\sigma_i \sin\frac{2\eta_i}{2} \tag{6.72a}$$

$$\beta = vN\sum_i \sigma_i\sin\eta_i \tag{6.72b}$$

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* Lindholm gives $[1 - \sigma_i\cos\eta_i]$.

† Cf. *supra*, Sec. 6.5.

From Eqs. (6.71) and (6.72a) it is apparent that the damping constant $\gamma$ may be written as:

$$\gamma = 2\alpha \doteq 2vN\sum_i 2\sigma_i \sin^2 \frac{\eta_i}{2} \tag{6.73}$$

If, as usual, the distance of closest approach is taken as $\rho$, then the cross section $\sigma_i$ for a phase change $\eta_i$ can be taken as $2\pi$ where we now suppose there to be a continuum of cross sections instead of the discrete set of Eqs. (6.72). In addition, the assumption of this continuum replaces the summations in Eqs. (6.72) by integrations. These changes in Eqs. (6.72) together with the substitution for $\eta_i$ of Eq. (6.8a′) into these equations yield:

$$\begin{aligned} \gamma &\doteq 2vN \int_0^\infty 4\pi\, \rho\, d\rho \sin^2 \frac{2\pi C c_n}{v\rho^{n-1}} \\ &= C^{\frac{2}{n-1}}\, v^{\frac{n-3}{n-1}}\, N\, 8\pi^{\frac{n+1}{n-1}}\, c_n^{\frac{2}{n-1}} \int_0^\infty \sin^2 \frac{1}{x^{n-1}}\, x\, dx \end{aligned} \tag{6.74a}$$

$$\begin{aligned} \beta = \omega_o - \omega_m &= vN \int_0^\infty 2\pi\, \rho\, d\rho \sin \frac{2\pi C c_n}{v\rho^{n-1}} \\ &= C^{\frac{2}{n-1}}\, v^{\frac{n-3}{n-1}}\, N\, 2\pi^{\frac{n+1}{n-1}}\, c_n^{\frac{2}{1-n}} \int_0^\infty \sin \frac{2}{x^{n-1}}\, x\, dx \end{aligned} \tag{6.74b}$$

where now:

$$\frac{\eta}{2} = \frac{\pi C c_n}{v\rho^{n-1}} = \frac{1}{x^{n-1}}$$

Now let us consider the case of $n = 4$ as illustrating a rather interesting circumstance relating to the Weisskopf theory. (We note that in order to obtain agreement between Eqs. (6.9) and (6.74a) we must needs choose $\eta_0 = 0.64$.)

We may recall the failure of the Weisskopf theory to yield a line shift under any conditions.* What we propose to demonstrate is that the neglect on the part of the Weisskopf theory of collisions resulting in phase changes of less than unity, while accounting for most of the broadening, is responsible for the absence of a line shift.

To begin with, let us plot $x\sin^2 \frac{1}{x^3}$ (from Eq. (6.74a)) and $x\sin \frac{2}{x^3}$ (from Eq. (6.74b)) against $\rho/\rho_o$. The result appears in Fig. (6.2), and let us consider this figure. The vertical line in about the center of the figure is the Weisskopf collision radius. Now the area under the upper curve gives us the integral in Eq. (6.74a) and is hence a measure of the broadening. In like manner, the area under the lower curve is a measure of the shift. The Weisskopf theory only considers those areas to the left of the ordinate specifying the Weisskopf collision radius. It thus becomes quite apparent that with the adoption of this radius we obtain almost all

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* This is not true for his more detailed theory for which see *infra*, Chap. 7. This theory does not appear to have been applied, however.

the broadening effects (insofar as this theory is concerned) while we obtain almost none of the shift effects. In addition, these curves serve to illustrate the relative importance of near and distant collisions in broadening and shift.

If the $\eta_i$ are very small then, since $\sin \eta_i \doteq \eta_i$:

$$\omega - \omega_m = \beta \doteq vN\Sigma\, \sigma_i \eta_i \tag{6.75}$$

In Fig. (6.3) is illustrated a wave train during whose emission strong collisions ($\eta > 1$), which lead primarily to broadening, and weak collisions ($\eta < 1$), which lead primarily to shift, have been undergone by the emitter. Let us suppose the wave train to be essentially rendered completely incoherent at a strong collision insofar as Fourier analysis is concerned, and let us determine the mean frequency between two strong collisions separated by a time interval $T$. In order to do this, it would appear quite reasonable to add to the number of vibrations of the natural frequency, $\omega_0 T$, the number of additional vibrations due to the weak collisions $TvN \underset{\eta_i<1}{\Sigma} \sigma_i \eta_i$ to obtain:

$$\omega_m = \frac{1}{T}\left\{ \omega_0\, T + TvN \underset{\eta_i<1}{\Sigma} \sigma_i\, \eta_i \right\} \tag{6.76}$$

The most cursory glance serves to show the agreement between Eqs. (6.75) and (6.76).

Finally, a consideration of Table 6.1 yields values for shift and width from Eqs. (6.74) according to this theory. The case $n = 2$, in addition to yielding a symmetrical line yields:

$$\gamma_2 = 8\pi^5 \frac{C^2 N}{v}\left\{ 0.923 - \ln \eta_m + \frac{\eta_m^{\,2}}{24} - \cdots \right\} \tag{6.77}$$

the reason for its exclusion from the table being self evident. In addition, the table gives the $\eta_0$ necessary for agreement with the Weisskopf theory.

| $n_n$ | $\gamma_n$ | $\eta_{0n}$ | $\beta_n$ | $\gamma_n/\beta_n$ |
|---|---|---|---|---|
| 3 | $4\pi^2\, CN$ | 0.64 | —— | —— |
| 4 | $3.88\ C^{2/3}\, v^{1/3}\, N$ | 0.64 | $33.4\ C^{2/3}\, v^{1/3}\, N$ | 1.16 |
| 6 | $17.0\ C^{2/5}\, v^{3/5}\, N$ | 0.61 | $6.16\ C^{2/5}\, v^{3/5}\, N$ | 2.80 |

Table 6.1

## 6.10. LINDHOLM GENERAL THEORY TO INCLUDE COLLISION TIME

Next Lindholm considered the problem with the collision time included. Let the collision time be $s_i$, and the phase change per unit of time during the collision be $k_i$. Then, if we assume the phase to change linearly during the collision, the total phase change on collision will be $\eta_i = k_i s_i$. Let us consider Fig. (6.4). $x$ and $y$ measure times back to $t'$ to $t''$ respectively as shown. The five arrows below the time axis represent five different collisions whose duration is represented by the respective arrow lengths. Only those collisions which occur at least partly during $t''-t'$ are to be included.

In analogy to Eq. (6.67) the probability that $n_{xi}$ collisions will begin during the time interval $dx$ is:

$$\left(\frac{\sigma_i}{\sigma}\frac{dx}{\tau}\right)^{n_{xi}} \frac{1}{n_{xi}!\,e^{dx/\tau}} \tag{6.78a}$$

It can be seen directly from our definitions that these collisions will contribute to $e^{i[\Delta(t'')-\Delta(t')]}$ the factor

$$e^{in_{xi}k_i\varphi(s_i-x)} \tag{6.79a}$$

where:

$$\begin{aligned} \varphi(s_i - x) &= 0 \qquad \text{for } s_i - x < 0 \\ \varphi(s_i - x) &= s_i - x \text{ for } 0 < s_i - x < t'' - t' \\ \varphi(s_i - x) &= t \qquad \text{for } t'' - t' < s_i - x \end{aligned} \tag{6.79b}$$

Eq. (6.79b) is merely a restatement of our restriction of the collision such that at least a portion of it occurs within $t'' - t'$.

In analogy with Eq. (6.78a) we get for the $n_{yi}$ probability:

$$\left(\frac{\sigma_i}{\sigma}\frac{dy}{\tau}\right)^{n_{yi}} \frac{1}{n_{yi}!\, e^{dy/\tau}} \tag{6.78b}$$

and in analogy to Eq. (6.79a) we obtain:

$$e^{in_{yi}k_i\psi(s_i-y)} \tag{6.79c}$$

where:

$$\begin{aligned} \psi(s_i - y) &= s_i \text{ for } s_i - y < 0 \\ \psi(s_i - y) &= y \text{ for } 0 < s_i - y \end{aligned} \tag{6.79d}$$

From Eqs. (6.79a) and (6.79c) and in analogy with Eq. (6.69a), we now obtain the mean value of $e^{i[\Delta(t'')-\Delta(t')]}$ as:

$$\begin{aligned} <e^{i[\Delta(t'')-\Delta(t')]}> = \sum_{n_{x_11}=0}^{\infty} \cdots \sum_{n_{x_j1}=0}^{\infty} \sum_{n_{x_21}=0}^{\infty} \cdots \sum_{n_{y_ji}=0}^{\infty} \prod_{i} \prod_{dx_l} \prod_{dy_j} \frac{1}{n_{x_li}!\, e^{dx_l/\tau}} \left(\frac{\sigma_i}{\sigma}\frac{dx_l}{\tau}\right)^{n_{x_li}} \cdot \\ \cdot \frac{1}{n_{y_ji}!\, e^{\frac{dy_j}{\tau}}} \left(\frac{\sigma_i}{\sigma}\frac{dy_j}{\tau}\right)^{n_{y_ji}} e^{i[n_{x_li}k_i\varphi(s_i-x)+n_{y_ji}k_i\psi(s_i-y)]} \end{aligned} \tag{6.80}$$

In Eq. (6.80) the $x_l$ represent the possible $dx$ time intervals during which included collisions may originate. The $y_j$ represent the possible $dy$ time intervals during which included collisions may originate. Thus, $n_{x_l1}$is the number of collisions of the type one originating with some probability during the $dx_l$ time interval. Again we can see that the summations in Eq. (6.80) are the MacLaurin series expansion for the exponential. We, of course, have such an exponential for each $dx_l$ (or $dy_j$) interval, and they are all to be multiplied together. Let us consider the $dx_l$ intervals. We have a long series of exponentials corresponding to the various $dx_l$ intervals which are to be multiplied together. This is the same as adding the exponents of these exponentials, and, since we may define $dx_l$ as small as we like, we may change this sum of exponents to an integral over $x$. The same holds true for $y$, and, when we have summed over $i$ in the exponent, we obtain as the contribution to our mean value:

$$\begin{aligned} \exp \sum_i \Bigg[ \int_0^{\infty} \left( \frac{\sigma_i dx}{\sigma\tau} e^{ik_i\varphi(s_i-x)} - \frac{dx}{\tau} \right) \\ + \int_0^{t} \left( \frac{\sigma_i dy}{\sigma\tau} e^{ik_i\psi(s_i-x)} - \frac{dy}{\tau} \right) \Bigg] \end{aligned} \tag{6.81a}$$

In the second integral of Eq. (6.81a) we do not extend the upper limit beyond $t$ since this would then duplicate the values given by the $x$-integral. Since $\sum_i \sigma_i = \sigma$ the following relation holds:

$$\sum_i \int \frac{dx}{\tau} = \sum_i \int \frac{\sigma_i}{\sigma} \frac{dx}{\tau}$$

Finally let us sum over all collision times $s_i$, and neglect the summation over $i$ which may be introduced at any subsequent point. Our mean value is then:

$$< e^{i[\Delta(t'') - \Delta(t')]} > = \exp \sum_{s_i = 0}^{\infty} \left[ \int_0^{\infty} \left( \frac{\sigma_i dx}{\sigma \ \tau} e^{ik_i \varphi(s_i - x)} - \frac{\sigma_i dx}{\sigma \tau} \right) \right.$$

$$\left. + \int_0^{t} \left( \frac{\sigma_i dy}{\sigma \tau} e^{ik_i \Psi(s_i - y)} - \frac{\sigma \ dy}{\sigma \tau} \right) \right] \qquad (6.81b)$$

From Eqs. (6.64a) and (6.81b) we now obtain:

$$A = \sum_{s_i=0}^{\infty} \left[ \int_0^{\infty} \left( \frac{\sigma_i dx}{\sigma \tau} \cos \left[ k_i \varphi \left( s_i - x \right) \right] - \frac{\sigma_i dx}{\sigma \tau} \right) \right.$$

$$\left. + \int_0^{t} \left( \frac{\sigma_i dy}{\sigma \tau} \cos \left[ k_i \psi \left( s_i - y \right) \right] - \frac{\sigma_i dy}{\sigma \tau} \right) \right] \qquad (6.82a)$$

$$B = \sum_{s_i=0}^{\infty} \left\{ \int_0^{\infty} \frac{\sigma_i dx}{\sigma \tau} \sin \left[ k_i \varphi(s_i - x) \right] + \int_0^{t} \frac{\sigma_i dy}{\sigma \tau} \sin \left[ k_i \psi(s_i - y) \right] \right\} \qquad (6.83a)$$

Our function $\varphi(s_i - x)$ has been defined by Eq. (6.79b). As an example this equation yields for the first integration Eq. (6.82a)

$$\sum_{s_i=0}^{\infty} \int_0^{\infty} \left( \frac{\sigma_i dx}{\sigma \tau} \cos \left[ k_i \ \varphi(s_i - x) \right] - \frac{\sigma_i dx}{\sigma \tau} \right) = \sum_{s_i=0}^{t} \int_t^{\infty} \left( \frac{\sigma_i dx}{\sigma \tau} \cos \left[ k_i \cdot 0 \right] - \sigma_i \frac{dx}{\sigma \tau} \right)$$

$$+ \sum_{s_i=0}^{t} \int_0^{t} \left( \frac{\sigma_i dx}{\sigma \tau} \cos \left[ k_i (s_i - x) \right] - \frac{\sigma_i dx}{\sigma \tau} \right) + \sum_{s_i=t}^{\infty} \int_{s_i}^{\infty} \left( \frac{\sigma_i dx}{\sigma \tau} \cos \left[ k_i \cdot 0 \right] - \sigma_i \frac{dx}{\sigma \tau} \right)$$

$$+ \sum_{s_i=t}^{\infty} \int_{s_i-t}^{s_i} \left( \frac{\sigma_i dx}{\sigma \tau} \cos \left[ k_i (s_i - x) \right] - \frac{\sigma_i dx}{\sigma \tau} \right) + \sum_{s_i=t}^{\infty} \int_0^{s_i-t} \left( \frac{\sigma_i dx}{\sigma \tau} \cos \left[ k_i (s_i - t) \right] - \sigma_i \frac{dx}{\sigma \tau} \right)$$

In this manner we obtain Eqs.(6.82b) and (6.83b)

$$A = \sum_{s_i=0}^{t} \frac{\sigma_i}{\sigma\tau}\left[(1 - \cos\eta_i)(t - s_i) - \sin\eta_i \frac{2}{k_i} + 2s_i\right]$$

$$+ \sum_{s_i=t}^{\infty} \frac{\sigma_i}{\sigma\tau}\left[(1 - \cos k_i t)(s_i - t) - \sin k_i t \frac{2}{k_i} + 2t\right] \tag{6.82b}$$

$$B = \sum_{s_i=0}^{t} \frac{\sigma_i}{\sigma\tau}\left[(1 - \cos\eta_i)\frac{2}{k_i} + \sin\eta_i (t - s_i)\right]$$

$$+ \sum_{s_i=t}^{\infty} \frac{\sigma_i}{\sigma\tau}\left[(1 - \cos k_i t)\frac{2}{k_i} + \sin k_i t (s_i - t)\right] \tag{6.83b}$$

The direct substitution of Eqs. (6.82b) and (6.83b) into Eq. (6.64a) would now give us an expression, if a rather cumbersome one, for the intensity distribution, but before doing this, let us digress for the purpose of simplification.

## 6.11. SPECIFICATION OF AND APPROXIMATIONS TO THE GENERAL THEORY

First we shall assume, with Lindholm, that all perturbers possess the same velocity relative to the emitter and let this velocity be the relative mean velocity $<v>$.* Next, it is assumed that the perturber paths are straight lines.† The frequency perturbation is taken as the van der Waals interaction $\Delta\nu = -bR^{-6}$ where $R$ is the broadener-emitter separation. If the distance of closest approach is $\rho$, and the phase change as before is $\eta_i$, we obtain from Eq. (6.7):

$$\eta_i = 2\pi \int_{-\infty}^{+\infty} \Delta\nu dt = 2\pi b \int_{-\infty}^{+\infty} \frac{dt}{(<v>^2 t^2 + \rho^2)^3} = \frac{3\pi^2 b}{4<v>\rho^5} \tag{6.84a}$$

The "length in space of the collision" we now take as proportional to $\rho$ and as given by $2\kappa\rho$. Let:

$$x = \rho\left[\frac{8<v>}{3\pi^2 b}\right]^{1/5} ; \; y = \frac{<v>t}{2\kappa}\left[\frac{8<v>}{3\pi^2 b}\right]^{1/5} \tag{6.85}$$

so that Eq. (6.84) becomes:

$$\eta_i = \frac{2}{x^5} \tag{6.84b}$$

In addition:

$$s_i = \frac{2\kappa\rho}{<v>} = \frac{2\kappa}{<v>}\left[\frac{3\pi^2 b}{8<v>}\right]^{1/5} x \tag{6.86a}$$

$$k_i = \frac{\eta_i}{s_i} = \frac{<v>}{\kappa}\left[\frac{8<v>}{3\pi^2 b}\right]^{1/5} \cdot \frac{1}{x^6} \tag{6.86b}$$

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* We may recall that in the Lenz derivation not a constant velocity but a Maxwell-Boltzmann distribution of the $u_k$, $v_k$, and $w_k$ was assumed. We shall see that this apparently has little effect.

† If Jablonski's criticism[79] of Weisskopf's one dimensional assumption — to the effect that such an assumption is incompatible with the central force problem involved — was valid, it is applicable here.

$$t = \frac{2\kappa}{<v>}\left[\frac{3\pi^2 b}{8<v>}\right]^{1/5} y \tag{6.86c}$$

$$\sigma_i = 2\pi\,\rho\,d\rho = 2\pi\left[\frac{3\pi^2 b}{8<v>}\right]^{2/5} x\,dx \tag{6.86d}$$

where Eqs. (6.86) follow from Eq. (6.85) and the definitions of the various quantities. Also let:

$$l = N4\,\pi\kappa\left[\frac{3\pi^2 b}{8<v>}\right]^{3/5} ;\; k = (\nu - \nu_o)\,\frac{4\pi\kappa}{<v>}\left[\frac{3\pi^2 b}{8<v>}\right]^{1/5} \tag{6.86e}$$

where $N$ is the number of perturbers per unit of volume.

Now, if, in a straightforward if somewhat laborious manner, we substitute the results of Eqs. (6.82b), (6.83b), (6.85), and (6.86) into Eq. (6.64a) we obtain:

$$I(\nu) = \int_0^\infty e^{-l\Phi(y)} \cos\left[ky + l\Psi(y)\right] dy \tag{6.87}$$

where:

$$\Phi(y) = \int_0^y \left[\left(1 - \cos\frac{2}{x^5}\right)(y - x) - \sin\frac{2}{x^5}x^6 + 2x\right] x\,dx$$

$$+ \int_y^\infty \left[\left(1 - \cos\frac{2y}{x^6}\right)(x - y) - \sin\frac{2y}{x^6}\,x^6 + 2y\right] x\,dx \tag{6.88a}$$

$$\Psi(y) = \int_0^y \left[\left(1 - \cos\frac{2}{x^5}\right)x^6 + \sin\frac{2}{x^5}\,(y - x)\right] x\,dx$$

$$+ \int_y^\infty \left[\left(1 - \cos\frac{2y}{x^6}\right)x^6 + \sin\frac{2y}{x^6}\,(x - y)\right] x\,dx \tag{6.89a}$$

The fact that $\Phi(y)$ and $\Psi(y)$ may not be evaluated directly should hardly come as a surprise. Let us consider $\Phi(y)$. We may transform this function into a sum of the form $\int_0^\infty + \int_y^\infty$. The integral with limits zero and infinity may be evaluated exactly after Jensen.[82] The other integral may be expanded in a series, and it can then be shown that for $y > 1$ this integral may be neglected. The integrals in $\Phi(y)$ may also be written as $\int_0^\infty + \int_0^y$. Again the integral with limits zero and infinity may be directly evaluated, and it is found that, when the latter integral is expanded in a series, this remaining integral is small for $y < 0.5$. The integrals were numerically evaluated by Lindholm for $0.5 < y < 1$, and he concluded that the result for $y < 0.5$ could be extended up to approximately $y = 1$. In this way Eqs. (6.88) were found to be:

$$\Phi(y) = 0.795\,y + 0.165 \qquad \text{for } y > 1 \tag{6.88b}$$

$$\Phi(y) = 0.369\,y^{4/3} + 0.591\sqrt{y} \qquad \text{for } y < 1 \tag{6.88c}$$

$$\Psi(y) = 0.577\,y + 0.227 \qquad \text{for } y > 1 \tag{6.89b}$$

$$\Psi(y) = 0.213\,y^{4/3} + 0.591\sqrt{y} \qquad \text{for } y < 1 \tag{6.89c}$$

When Eqs. (6.88b), (6.88c), (6.89b), and (6.89c) are substituted into Eq. (6.87) the result is:

$$I(\nu) = I_0 + I_\infty \tag{6.90a}$$

where:

$$I_0 = \int_0^1 e^{-l[0.369y^{4/3}+0.591\sqrt{y}]} \cos\left[ky + l(0.213y^{4/3} + 0.591\sqrt{y})\right] dy \tag{6.90b}$$

$$\begin{aligned} I_\infty &= e^{-l[0.165]} \int_1^\infty e^{-l[0.795y]} \cos\left[y(k + 0.577\,l) + 0.227\,l\right] dy \\ &= e^{-0.960l}\, \frac{0.795l\cos(0.804l + k) - (k + 0.579l)\sin(-0.804l + k)}{(0.795l)^2 + (k + 0.577l)^2} \end{aligned} \tag{6.90c}$$

Numerical calculation is required for Eq. (6.90b), and in a general form this is as far as Lindholm carried the calculation. Let us now consider some of the special cases of Eq. (6.90a).

For very high pressures $l$, as given by Eq. (6.86e), is obviously very large. It is apparent from Eq. (6.90c) that we may neglect $I_\infty$ under these conditions. In Eq. (6.90b) the integrand, due to the behavior of the exponential with large $l$, will be very small unless $y$ is very small. When $y$ is small $y^{4/3} \ll y^{1/2}$ so that we may write:

$$\begin{aligned} I(\nu) = I_0 &= \int_0^\infty e^{-l[0.591\sqrt{y}]} \cos\left[ky + l(0.591\sqrt{y})\right] dy \\ &= \sqrt{\frac{\pi}{2}}\, \frac{0.591\,l}{(-k)^{3/2}} \exp\left[-\frac{(0.591l)^2}{2(-k)}\right] = c_1 N <v>^{6/5} (\Delta\nu)^{-3/2} e^{-N^2C_2/\Delta v} \end{aligned} \tag{6.91}$$

for $k < 0$. $I(\nu) = 0$ for $k > 0$ which means that the line is displaced to the red, and the intensity falls to zero at the frequency of the undisplaced line. In addition to this agreement with Margenau's statistical predictions, a comparison of Eq. (6.91) with Eq. (6.42) shows that Lindholm's line shape has reduced to Margenau's statistical shape for the case of high pressure. If we let $\kappa = \frac{16}{3\pi} = 1.7$ instead of 0.75 as given after Eq. (6.42) we obtain exact agreement between the exponentials in Eqs. (5.42) and (6.91). Since the statistical theory had yielded such excellent agreement with experiment at high pressure Lindholm chose $\frac{16}{3\pi}$ as the value for $\kappa$ on the basis of this resulting agreement. Lindholm justified his disagreement as follows:

First, let us recall that the time duration of the collision is essentially $2\kappa$ and consider Fig. (6.5). Curve (a) in this figure is the actual curve for the phase integral $2\pi b \int_{-\infty}^{t} \frac{dt}{(v^2t^2 + \rho^2)^3}$. Curve (b) is the Lenz approximate curve where $\kappa = 0.75$, and curve (c) is the Lindholm curve where $\kappa = 1.7$. Lindholm felt that the larger $\kappa$ value is more justified in that it includes the slow frequency shifts at either end of the true curve (a).

Now let us consider the special case of Eq. (6.90a) corresponding to Lenz' calculation for low pressure and spectral positions near line center. Lindholm took $N$ and $(\nu - \nu_0)$ small enough so that Eq. (6.86e) goes to zero, and as a result, Eq. (6.90b) becomes $I_0 = 1$. Now let us expand Eq. (6.90e) in a series and keep only second order terms in $l$ and $k$. The result is:

$$I_\nu = I_0 + I_\infty = 1 + (1 - .960\,l)\,\frac{[(.795\,l) - (k + .577\,l)\,(k + .804\,l)]}{(.795\,l)^2 + (k + .577\,l)^2}$$

$$= .795\,\frac{1 - (k + .577\,l)\,\dfrac{.227}{.795} - .165\,l}{(.795\,l)^2 + (.577\,l + k)^2} \tag{6.92}$$

A comparison of Eq. (6.61a) and (6.92) is in order. It can be seen that, from the above equation and Eq. (6.86e), the line shift and half-width are given by:

$$\Delta = \frac{.577}{\dfrac{2\pi\kappa}{<v>}\left[\dfrac{3\pi^2 b}{8<v>}\right]^{1/5}} = \frac{.577\,l}{c} = .097\,N{<}v{>}^{3/5}\,b^{2/5} \tag{6.93a}$$

$$\delta/2 = \frac{.795\,l}{c} = 2.68\,N{<}v{>}^{3/5}\,b^{2/5} \tag{6.93b}$$

The linear dependence on the pressure and the dependence on the temperature through $<v>$ of both the shift and the half-width may be noted from Eqs. (6.93). We may compare this with Eq. (6.62). Before doing so, however, it will be necessary to rewrite Eq. (6.62) slightly. The constant $b$ differs from the constant $a$ in the latter equation by virtue of the fact that Lenz used units of angular velocity $\omega$ while Lindholm utilized units of frequency $\nu$.

Thus Eq. (6.62) must be multiplied by the factor $\frac{1}{2\pi}\cdot(2\pi)^{2/5}$, and one obtains 2.65 instead of 7.977. The difference between these two equations arises chiefly from the fact that Lindholm used only the mean relative velocity, while Lenz used a distribution of velocities. A reasonable basic agreement exists between the two theory results, however.

Having considered the Lenz and Margenau limiting cases, let us turn our attention to the behavior of Eqs. (6.90b) and (6.90c) in the wings of the line. We consider Eq. (6.87). Using Eqs. (6.88b), (6.88c), (6.89b), and (6.89c) this equation may be written as:

$$\begin{aligned} I(\nu) = {} & \int_0^\infty e^{-l[0.369y^{4/3}+0.591\sqrt{y}]}\cos\left[ky + l(0.213y^{4/3} + 0.591\sqrt{y})\right]dy \\ & - \int_1^\infty e^{-l[0.369y^{4/3}+0.591\sqrt{y}]}\cos\left[ky + l(0.213y^{4/3} + 0.591\sqrt{y})\right]dy \\ & + \int^\infty e^{-l[0.795y+0.165]}\cos\left[ky + l(0.577y + 0.277)\right]dy \end{aligned} \tag{6.94}$$

For $k$ very large the cosine function, and hence the integrand will fluctuate very rapidly for large $y$ resulting in the usual cancellation effect. Thus, we may restrict ourselves to small $y$. As a result of this restriction, the first integral in Eq. (6.94) makes the greatest contribution to $I(\nu)$. In evaluating this integral — a rather lengthy operation — Lindholm utilized the substitution $ky = z^2$ which allowed him to expand certain portions of the integrand in power series to arrive at integrals of the form:

$$\int_0^\infty e^{-sz+iz^2} z^\alpha\,dz = \tfrac{1}{2}\sum_{n=0}^{\infty}(-1)^n (i)^{\frac{\alpha+1+n}{2}}\,\Gamma\left(\frac{\alpha+1+n}{2}\right)\frac{s^n}{n!}$$

He thus obtained the following two equations for the red and violet wings of the line respectively:

$$I(\nu) = \frac{0.741\,l}{(-k)^{3/2}} + \frac{0.254\,l}{(-k)^{7/3}} - \frac{0.129\,l^3}{(-k)^{5/2}} + \frac{0.532\,l^2}{(-k)^{17/6}} \tag{6.95a}$$

$$I(\nu) = \frac{0.507\,l}{k^{7/3}} - \frac{0.614\,l^2}{k^{17/6}} + \frac{0.320\,l^3}{k^{10/3}} + \cdots \tag{6.95b}$$

Eqs. (6.95) result from the evaluation of only the first integral in Eq. (6.94). Lindholm found by evaluation of the remaining two integrals in Eq. (6.94) that the largest contribution of the neglected integrals amounted to $\frac{0.07\,l}{k^3}$. Thus, error in Eqs. (6.95) amounts to around $\frac{0.07\,l}{k^3}$.

If the first term in Eq. (6.95a) is taken as the expression for the intensity in the red wing, agreement with the expressions of Kuhn[92] and Margenau[114] is, of course, obtained. The earlier verification of Kuhn's expression for the intensity distribution in the red wing in the case of *Na* broadened by *A* as obtained by Minkowski[130] and in the case of *Hg* broadened by *A* as obtained by Kuhn[93] provides experimental justification for the Lindholm result.

Let us assume that the first term in Eq. (6.95b) is sufficient to describe the intensity distribution in the violet wing. When a comparison of this expression with the measurements of Minkowski[130] for the violet wing of the $Na\ D_2$ line broadened by *A* is made, really excellent agreement is obtained. It might be mentioned here that, although the $(\Delta\nu)^{-3/2}$ dependence had been previously obtained for the red wing, the $(\Delta\nu)^{-7/3}$ dependence had certainly not been previously obtained for the violet wing. Minkowski[130] had attempted to use a $(\Delta\nu)^{-2}$ dependence without the success which attended Lindholm's utilization of $(\Delta\nu)^{-7/3}$.

It should be recalled here that the results which have been obtained are predicated on the assumption of a van der Waals interaction between emitter and broadener.

Lindholm obtained more general results than Lenz had obtained primarily because he assumed the same relative velocity for all perturbers, a not very serious approximation. Thus, his method of including the time of collision in the Fourier analysis yielded, for the case of van der Waals forces, Eqs. (6.90) which can be evaluated for specific cases.

Kleman and Lindholm [87a] experimentally investigated the broadening of *Na* lines by *A* and obtained excellent agreement in shift, half-width, and line contour with this theory.

## 6.12. A MAXWELL DISTRIBUTION OF DIPOLE MOMENTS AFTER COLLISION

The reader may have noted with some alarm the manner in which we have blithely bypassed the important work of Spitzer[175] on the subject of Interruption (impact, collision, velocity, etc.) broadening. We might perhaps explain the basis for our continued deferment of this discussion.

To this point it should be quite apparent that our Interruption considerations have been almost wholly classical ones. In addition, we shall find that several more classical considerations of the phenomenon await our perusal. Spitzer's attack on the other hand, is launched from a primarily quantum mechanical point of view. Thus, it appears reasonable to defer the work of Spitzer, as well as that of Foley[47] and Karplus and Schwinger[84] until we have completed the preponderantly classical theories of certain other authors. On this basis we shall next consider a 1945 paper of Van Vleck and Weisskopf.[187]

We have called attention to the fact that the Lorentz theory is technically not a Fourier transform of either the motion of an electronic oscillator or a broken off light wave — and we might just as well be technically correct where our limited capacity allows — but we have also noted the general tendency to attribute this Michelson type treatment to this author. In the paper which we shall now consider, van Vleck and Weisskopf set out to consider certain phases of Lorentz' theory, and indeed they do consider Lorentz' theory. These authors are of the opinion that, "The literature of collision broadening is dominated by two names — those of Lorentz and Debye. . . . "[187] and they proceed to set about a revision of Lorentz' development such that an agreement between the work of these two "dominating" figures is obtained. In essence this revision consisted in substituting for the Lorentz distribution of $x$ and $\dot{x}$[*] after collision the Maxwell-Boltzmann distribution. Let us be specific.

Van Vleck and Weisskopf defined two types of collisions, strong and, yes, weak ones. Following a strong collision the molecule retains no " 'hangover' or memory" of its precollision orientation. Adiabaticity is also assumed here, and in this connection, the adiabatic character assures us that the electric field of the light is a constant during the very short time of the collision, i.e.:

$$\mathrm{E}\cos(\omega t) = \mathrm{E}\cos(\omega t_0)$$

The difference between this and the Lindholm theory is apparent. Weak collisions, on the other hand, leave the molecule with a hangover. The assumption of strong collision yielded Eq. (1.86) which we write down:

$$\alpha = \frac{\omega}{c}\,\frac{4\pi N\mu^2}{3kT}\,\frac{\omega\tau}{1+\omega^2\tau^2} \tag{1.86}$$

This is Debye's equation for the linear absorption coefficient which we obtained in Chapter 1 after the fashion of Van Vleck and Weisskopf. Let us recall that $\omega$ appearing in Eq. (1.86) relates only to the frequency of the incident radiation, and that nowhere does any natural frequency of the electronic vibration (in the classical sense) appear. Thus, one might consider Eq. (1.86) to broaden a line of zero frequency through a collision mechanism. Van Vleck and Weisskopf regard this as " . . . a theory of spectral shape for a non-resonant line . . ."[187] In order to determine the quantum mechanical analog of Eq. (1.86) we may recall that, instead of integrating over cos $\omega t$ as in Eq. (1.86), we sum over the various quantum states. We obtain the same result, however, since here also $<\cos^2\vartheta> = 1/2$. Thus, we need only consider Eq. (1.86).

From the Lorentz theory we obtained in Chapter 1:

$$\alpha = \frac{2\pi Ne^2}{mc}\left(\frac{\omega}{\omega_0}\right)\left[\frac{1/\tau}{(\omega-\omega_0)^2+(1/\tau)^2} - \frac{1/\tau}{(\omega+\omega_0)^2+(1/\tau)^2}\right] \tag{1.78a}$$

The equations,[†]

$$s = \frac{4\pi^2}{3}\,\frac{e^2}{\hbar c}\,\omega_{ij}\,|\,\mathrm{x}_{ij}\,|^2 I_0(\omega) \tag{6.96a}$$

$$s = \frac{2\pi^2e^2}{mc}\,I_0(\omega) \tag{6.96b}$$

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[*] See *supra*, Chap. 1.

[†] See Appendix VII.

tell us that we must needs replace $1/m$ by $\frac{4}{3}\frac{\pi}{\hbar}\nu_{ij} \mid \mathbf{x}_{ij} \mid^2$ in Eq. (1.78a) in order to arrive at a quantum analog of this equation. In Eq. (6.96a) $e\mathbf{x}_{ij}$ is, of course, the matrix element of the electric dipole moment* — if it is electric dipole radiation that we are considering — between the states $i$ and $j$. In addition, it is apparent that a temperature distribution of the molecules over the various stationary quantum states according to the applicable Maxwell-Boltzmann law must be imposed and a subsequent summing over the possible transitions introduced. These three modifications in Eq. (1.78a) result in:

$$\alpha = \left(\frac{4\pi\nu Ne^2}{3hc}\right) \frac{\sum\limits_{j}\sum\limits_{i} \mid \mathbf{x}_{ij} \mid^2 f(\nu_{ij}, \nu) e^{-W_j/kT}}{\sum\limits_{j} e^{-W_j/kT}} \tag{6.97a}$$

where the "shape factor" is given by:

$$f(\nu_{ij},\nu) = \frac{1}{\pi}\left[\frac{\Delta\nu}{(\nu_{ij} - \nu)^2 + (\Delta\nu)^2} - \frac{\Delta\nu}{(\nu_{ij} + \nu)^2 + (\Delta\nu)^2}\right] \tag{6.97b}$$

$$\Delta\nu = 1/2\pi\tau \tag{6.97c}$$

Let us write:

$$\sum_{j}\sum_{i} \mid \mathbf{x}_{ij} \mid^2 f(\nu_{ij},\nu) e^{-W_j/kT} = \sum\sum_{j \neq i} [\mid \mathbf{x}_{ij} \mid^2 f(\nu_{ij}, \nu) e^{-W_j/kT}$$

$$+ \mid \mathbf{x}_{ji} \mid^2 f\,(\nu_{ji}, \nu) e^{-W_j/kT}] = \sum_{i}\sum_{j} \mid \mathbf{x}_{ij} \mid^2 f(\nu_{ij}, \nu)\, \frac{h\nu_{ij}}{2kT} e^{-W_j/kT}$$

since:

$$\nu_{ij} = -\nu_{ji}\,;\ f(\nu_{ij}, \nu) = -f\,(\nu_{ji}, \nu);\ \mid \mathbf{x}_{ij} \mid = \mid \mathbf{x}_{ji} \mid \tag{6.98a}$$

and:

$$(e^{-y} - e^{-x-y}) \doteq \tfrac{1}{2}x(e^{-y} + e^{-x-y}) \text{ for } x \ll 1 \tag{6.98b}$$

so that Eq. (6.97a) becomes:

$$k = \left(\frac{4\pi\nu N}{6\hbar c}\right) \frac{h}{kT} \frac{\sum\limits_{j}\sum\limits_{i} \mid \mathbf{x}_{ij} \mid^2 \nu_{ij} f(\nu_{ji}, \nu) e^{-W_j/kT}}{\sum\limits_{j} e^{-W_j/kT}} \tag{6.99}$$

with the shape factor still given by Eq. (6.97b).

Now if Eqs. (1.86) and (6.97a) are truly equivalent, as it would appear they should be, Eq. (6.97a) should reduce to Eq. (1.86) for $\nu_{ij} = 0$. It is apparent that instead of this reduction we simply obtain zero for Eq. (6.97a). This discrepancy was remedied by Van Vleck and Weisskopf by utilizing a Maxwell-Boltzmann distribution for $x$ and $\dot{x}$ instead of Eq. (1.57) as a basis for obtaining the constants $C_1$ and $C_2$ in:

$$x = \frac{Ee}{m(\omega_0{}^2 - \omega^2)} e^{i\omega t} + C_1 e^{i\omega_0 t} + C_2 e^{i\omega_0 t} \tag{1.52}$$

From Eqs. (1.49) the Hamiltonian for our vibrating electron is surely:

$$H(t) = \frac{p^2}{2m} + \tfrac{1}{2}\,(\omega_0 x)^2 m - ex\,E \cos \omega t \tag{6.100}$$

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* Van Vleck-Weisskopf allow either magnetic or electric moment.

Then the right side of Eq. (1.58a) instead of being zero will be $x$ averaged over the Maxwell-Boltzmann distribution for Eq. (6.100). The right side of Eq. (1.58b) will still be zero, however, since:

$$\frac{\int\!\!\int_{-\infty}^{+\infty} p \exp\left[-H(t_0)/kT\right] dxdp}{\int\!\!\int_{-\infty}^{+\infty} \exp\left[-H(t_0)/kT\right] dxdp} = \frac{\int_{-\infty}^{+\infty} pe^{-\frac{p^2}{2mkT}} dp \int_{-\infty}^{+\infty} f(x)dx}{\int\!\!\int_{-\infty}^{+\infty} f(x,p)\, dxdp}$$

$$= \frac{-mkTe^{-\frac{p^2}{2mkT}} \Big|_{-\infty}^{+\infty} . \int_{-\infty}^{+\infty} f(x)dx}{\int\!\!\int_{-\infty}^{+\infty} f(x,p)\, dx\, dp} = 0$$

Thus, Eqs. (1.58) now become:

$$\frac{Ee}{m(\omega_0^2 - \omega^2)} e^{i\omega(t-\vartheta)} + C_1' e^{i\omega_0(t-\vartheta)} + C_2' e^{-i\omega_0(t-\vartheta)} = A = \frac{\int\!\!\int_{-\infty}^{+\infty} x \exp\left[-H(t_0)/kT\right] dx\, dp}{\int\!\!\int_{-\infty}^{+\infty} \exp\left[-H(t_0)/kT\right] dx\, dp} \tag{6.101a}$$

$$\frac{Eei\omega}{m(\omega_0^2 - \omega^2)} e^{i\omega(t-\vartheta)} + C_1' i\omega_0 e^{i\omega_0(t-\vartheta)} - i\omega_0 C_2' e^{i\omega_0(t-\vartheta)} = 0 \tag{6.101b}$$

Eqs. (6.101) may be solved in a very straightforward manner to yield:

$$C_1' = C_1 + \Delta C_1 = C_1 + \frac{A}{2} e^{i\omega_0 t_0} \tag{6.102a}$$

$$C_2' = C_2 + \Delta C_2 = C_2 + \frac{A}{2} e^{i\omega_0 t_0} \tag{6.102b}$$

where the $C$ are now given by Eqs. (1.59) and $t_0 = t - \vartheta$.

Letting $a = \dfrac{1}{2mkT}$, $b = \dfrac{m\omega_0^2}{2kT}$, $c = \dfrac{eE \cos \omega t}{kT}$, we may integrate $A$ by parts as follows:

$$A = \frac{\int_{-\infty}^{+\infty} xe^{-bx^2+cx} dx \int_{-\infty}^{+\infty} e^{-ap^2} dp}{\int_{-\infty}^{+\infty} e^{-bx^2+cx} dx \int_{-\infty}^{+\infty} e^{-ap^2} dp} = \frac{\int_{-\infty}^{+\infty} xe^{-bx^2+cx} dx}{\int_{-\infty}^{+\infty} e^{-bx^2+cx} dx}$$

$$= -\frac{1}{2b} e^{cx} e^{-bx^2} \Big|_{-\infty}^{+\infty} + \frac{C}{2b} \frac{\int_{-\infty}^{+\infty} e^{-bx^2+cx} dx}{\int_{-\infty}^{+\infty} e^{-bx^2+cx} dx} = \frac{C}{2b} = \frac{2eE \cos \omega t}{m\omega_0^2} \tag{6.103}$$

As a result of Eq. (6.101):

$$\Delta C_1 e^{i\omega_0 t_0} = \Delta C_2 e^{-i\omega_0 t_0} = \frac{eE \cos \omega t_0}{m\omega_0^2}. \tag{6.104}$$

It is now evident that to Eq. (1.60) is next added the term

$$\frac{Ee}{m\omega_0^2} \cos(\omega t_0) \cos \omega_0(\epsilon - t_0) = \frac{Ee}{2m\omega_0^2} \Re \left[e^{i\omega(t-\vartheta)} \left(e^{i\omega_0\vartheta} + e^{-i\omega_0\vartheta}\right)\right] \tag{6.105}$$

and the thus amended version of Eq. (1.60) yields, according to Eq. (1.61):

$$<x> = \Re \left[ \frac{eEe^{i\omega t}}{m(\omega_0^2 - \omega^2)} \left\{ 1 - \frac{(\omega_0 + \omega)\, \omega/\omega_0^2\tau}{2\,[1/\tau - i(\omega_0 - \omega)]} + \frac{(\omega_0 - \omega)\omega/\omega_0^2\tau}{2\,[1/\tau + i(\omega_0 + \omega)]} \right\} \right] \qquad (6.106)$$

In analogy to the method of obtaining Eq. (1.78a) we may then obtain:

$$\alpha = \frac{2\pi Ne^2}{mc} \left(\frac{\omega}{\omega_0}\right)^2 \left[ \frac{1/\tau}{(\omega - \omega_0)^2 + (1/\tau)^2} + \frac{1/\tau}{(\omega + \omega_0)^2 + (1/\tau)^2} \right] \qquad (6.107)$$

In analogy to the manner of obtaining Eqs. (6.97b) and (6.99) from Eq. (1.78a) we may now obtain Eq. (6.99) from Eq. (6.107) where here:

$$f(\nu_{ij},\nu) = \frac{1}{\pi} \frac{\nu}{\nu_{ij}} \left[ \frac{\Delta\nu}{(\nu_{ij} - \nu)^2 + (\Delta\nu)^2} + \frac{\Delta\nu}{(\nu_{ij} + \nu)^2 + (\Delta\nu)^2} \right] \qquad (6.108)$$

Utilizing Eqs. (6.99) and (6.108), we do indeed obtain Eq. (1.86) for the case of zero resonant frequency, $\nu_{ij} = 0$, and $e^2\Sigma \mid x_{ij} \mid^2 = \mu^2$ which at least is of import in resolving the paradox in the low frequency region. Eq. (6.107) on the other hand, offers little change in the visible region, the $\left(\frac{\omega}{\omega_0}\right)^2$ factor yielding slightly more line asymmetry.

In the treatment so far we have discussed the case of strong, hangover-free collisions where the Maxwell-Boltzmann distribution may be imposed after the collision. Van Vleck and Weisskopf somewhat after the fashion of Kauzmann[85] and Kronig[52, 89] obtained the Debye formula for the polarization for the case of "collisions of arbitrary strength." We shall not detail this calculation, since it essentially is a treatment for the limiting case of $\nu_{ij} = 0$. We might mention the basic premises involved, however.

$A_{\omega\omega'}d\omega'$ is the probability that after collision the dipole which originally was oriented in the solid angle $d\omega$ is oriented in the solid angle $d\omega'$. In the absence of the field $A_{\omega\omega'}$ is a function $f(\vartheta)$ only of the angle $\vartheta$ between $d\omega$ and $d\omega'$. The following situation applies: For a strong collision $f(\vartheta)$ is independent of $\vartheta$, and in the case of weak collisions, since a strong carry-over effect is assumed, $f(\vartheta)$ is only appreciable for small $\vartheta$. Finally, in the presence of the external field, we assume the states $\omega$ and $\omega'$ to be Maxwell-Boltzmann weighted and the usual "detailed balance" or equal in-out relation,

$$A_{\omega\omega'} \exp\,(\mu E \cos\psi \cos\omega t/kT) = A_{\omega'\omega} \exp\,(\mu E \cos\psi' \cos\omega t/kT)$$

holds.

Van Vleck and Weisskopf also make mention of (1) adiabaticity and (2) dispersion of $\tau$ as limiting factors on our Eq. (6.105).

Reference (1), we should recall that here we have specifically defined adiabaticity as the condition in which the frequency of the light wave is much smaller than the reciprocal of the duration of the collision, $\nu \ll 1/\tau_c$ so that during a collision $E\cos\omega t \doteq E\cos\omega t_0$. This condition allows our dipoles to settle down sufficiently after the collision so that the Maxwell-Boltzmann distribution may be applied to this pseudo-equilibrium configuration. Although the point is not stressed by these two authors, this is certainly an approximation which obviously could not be fulfilled immediately after a collision. It would appear to be a reasonable one, however. If, on the other hand, one considers regions other than the microwave (in which regions these authors appear primarily interested) where $\nu \sim 1/\tau_c$ then it would seem more acceptable to maintain the Lorentz approximation, especially since said retention makes no very appreciable difference, $<x> = 0$ leading to Eq. (1.78a).

With respect to (2) Van Vleck and Weisskopf felt that if the molecules of the assemblage were distributed over various classes relegated to varying values of $\tau$ then the final averaging of the formula over this $\tau$ distribution would yield line shapes more nearly corresponding to those observed. This may be the case.

In toto this theory seems to have contributed the idea of Maxwell-Boltzmann distribution to the Lorentz theory, that is, insofar as line broadening is concerned. From our point of view, we have not much affected the final result, but have perhaps placed it on a more firm foundation in the microwave region. We shall later consider Karplus and Schwinger's work [84] which established a quantum-mechanical basis for this same theory.

## 6.13. DETAILED BALANCING

Now let us complete our classical consideration of Interruption broadening with the refinements introduced by Van Vleck and Margenau.[186] The ruminations of these authors did not serve to actually change the shape of the proposed absorption line, but they did finally show that the shapes of the spectral lines* are the same in emission as in absorption, a point of no mean import. At any rate, since we accept the thesis that the integrated absorption and emission balance each other — in a Rayleigh-Jeans radiation field, which we shall mention in a moment — detailed balance of emission and absorption results from this equivalence of absorption and emission line shapes. That is, a given frequency interval absorbs as much as it emits. The balance was obtained by a hitherto untried technique, that is, the summing of the work done on the oscillator by the electric field at collision as well as during the intercollision intervals. This yielded the same frequency by frequency power as that emitted between two collisions.

If our oscillator motion is described by $x(t) = x_0 \cos(\omega_0 t + \varphi)$ where $\varphi$ is, of course, the phase constant, then Eqs. (6.4) and (6.5a) with $M(t) = x(t)$ yield the Fourier analysis of $x(t)$. We may then integrate the expression for $x(\omega)$ (corresponding to $J(\omega)$ in Eq. (6.5a)) and average $|x(\omega)|^2$ over a random distribution of $\varphi$ to obtain a result which when utilized for $x$ in Eq. (1.61) yields:†

$$|x(\omega)|^2 = \frac{x_0^2}{4\pi}\left[\frac{1}{a^2 + (\omega_0 - \omega)^2} + \frac{1}{a^2 + (\omega_0 + \omega)^2}\right] \tag{6.109}$$

where now $a = 1/\tau$.

A point charge $e$ which is oscillating in one dimension radiates power of amount:**

$$\frac{dW}{dt} = \frac{2}{3}\frac{e^2}{c^3}\ddot{x}^2$$

From the equation for simple harmonic motion $\ddot{x} = -\omega^2 x$. In addition, normalization of the Fourier components requires:

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* These authors refreshingly refer these spectral lines to the classical harmonic oscillator, and one is then presumably free to accept Weisskopf's proof of oscillator-atom equivalence or not as one sees fit.

† In evaluating Eq. (6.5a) we have taken the limits 0 and $\vartheta$ where $\vartheta$ is the time between two collisions, thus integrating $x_0 \cos(\omega t + \varphi)$ over the time between two collisions to obtain $x(\omega)$.

** See Appendix IX.

$$\int_{-\infty}^{+\infty} [x(t)]^2 \, dt = \int_{-\infty}^{+\infty} | \, x(\omega) \, |^2 \, d\omega = 2 \int_{0}^{\infty} | \, x(\omega) \, |^2 \, d\omega$$

so that:

$$\ddot{x}^2 = -\omega^4 \, | \, x(t) \, |^2 = -\omega^4 \, | \, x(\omega) \, |^2$$

We thus obtain for the power emitted by the oscillator in the frequency interval between $\omega$ and $\omega + d\omega$:

$$P_E{}' (\omega) \, d\omega = \frac{2e^2}{3c^3} \, 2\omega^4 \, | \, x(\omega) \, |^2 \, d\omega \tag{6.110a}$$

This must be modified to include the intervals between all collisions over a long period $T$, however, since the Fourier analysis has only been carried out over one such period. As a result, Eq. (6.110a) becomes:

$$P_E (\omega) \, d\omega = \frac{aTP_E{}' (\omega) \, d\omega}{T} = \frac{2e^2}{3c^3} \, 2\omega^4 \, | \, x(\omega) \, |^2 \, a \, d\omega \tag{6.110b}$$

Substitution of Eq. (6.109) into Eq. (6.110b) then yields:

$$P_E (\omega) = \frac{e^2 x_0{}^2}{3\pi c^3} \, \omega^4 \left[ \frac{a}{a^2 + (\omega_0 - \omega)^2} + \frac{a}{a^2 + (\omega_0 + \omega)^2} \right] \tag{6.111}$$

Now in order to obtain detailed balancing, we must needs show that $P_A(\omega)$, the power absorbed at the frequency $\omega$, corresponds to this.

Let us suppose the electric vector of the incident radiation to be given by Ecos $(\omega t + \varphi)$, and, in addition, collisions to occur at $t = t_1, t_2, \ldots$ If the velocity proportional viscous drag force $g\dot{x}$ is dropped from Eq. (1.49b) the Van Vleck-Margenau equation is obtained as:

$$\ddot{x} + \omega_0{}^2 \, x = \frac{eE_x}{m} \, x \cos (\omega t + \varphi)$$

and a solution of the form:

$$x = \begin{cases} x_1 \text{ for } t_1 \leqslant t \leqslant t_2 \\ x_2 \text{ for } t_2 \leqslant t \leqslant t_3 \\ \text{etc.} \end{cases}$$

is sought under the Lorentz boundary conditions $x_j(t_j) = \dot{x}_j(t_j) = 0$. The following integral forms satisfy the boundary conditions and the equations of motion:

$$x_j = \frac{eE_x}{m\omega_0} \int_{0}^{t-t_j} \cos (\omega t - \omega \Lambda + \varphi) \sin \omega_0 \Lambda \, d\Lambda \tag{6.112a}$$

$$\dot{x}_j = \frac{eE_x}{m} \int_{0}^{t-t_j} \cos (\omega t - \omega \Lambda + \varphi) \cos \omega_0 \Lambda \, d\Lambda \tag{6.112b}$$

It appears rather obvious that the work done by the field on the oscillator of charge *e between* collisions is

$$W = \sum_j \int_{t_j}^{t_{j+1}} eE_x \cos(\omega t + \varphi)\ \dot{x}_j\, dt \tag{6.113a}$$

or, by Eq. (6.112b)

$$W = \frac{e^2E_x^2}{m} \sum_j \int_0^{\vartheta_j} \cos(\omega t + \varphi_j)\, dt \int_0^t \cos[\omega(t - \Lambda + \varphi_j)] \cos \omega_0 \Lambda\, d\Lambda \tag{6.113b}$$

where:

$$\vartheta_j = t_{j+1} - t_j \text{ and } \varphi_j = \omega t_j + \varphi$$

The total time of observation can be chosen as, say, $T$, and the distribution function for the inter-collision times may again be taken as $ce^{-a\vartheta}\, d\vartheta$ in analogy to Eq. (1.61). We may evaluate $c$ from:

$$T = c \int_0^\infty e^{-a\vartheta}\, \vartheta d\vartheta = \frac{c}{a^2}$$

and subsequently substitute $a^2T \int_0^\infty e^{-a\vartheta}\, d\vartheta$ for the sum in Eq. (6.113b). Then, using the well known trigonometric relations for $\cos(a \pm b)$ and $\sin(a \pm b)$ and a large sheet of paper, one may reduce the resulting equation to one which, when integrated over a random distribution of the $\varphi_j$, yields:

$$W = \frac{e^2E_x^2}{2m}\, a^2\, T \int_0^\infty e^{-a\vartheta}\, d\vartheta \int_0^\vartheta dt \int_0^t \cos \omega\Lambda \cos \omega_0 \Lambda\, d\Lambda \tag{6.114*}$$

We shall accept the formula:

$$a \int_0^\infty e^{-a\vartheta}\, d\vartheta \int_0^\vartheta f(\Lambda)\, d\Lambda = \int_0^\infty e^{-a\vartheta} f(\Lambda)\, d\Lambda$$

by means of which Eq. (6.114) may be integrated to obtain the work done by the field between collisions. As a consequence, the average power or work per unit time is:

$$\frac{W}{T} = \frac{e^2E_x^2}{4m} \left[\frac{a}{a^2 + (\omega - \omega_0)^2} + \frac{a}{a^2 + (\omega + \omega_0)^2}\right] \tag{6.115}$$

The work done by the field *at* collision will be obtained. The Lorentz boundary conditions require that $x_j(t_{j+1})$ be zero. Since the oscillator will have some displacement $x_j(t_{j+1})$ probably not zero, an instantaneously infinite velocity of the oscillator is required so that the displacement change may occur in zero time. Since the authors do not appear to claim that this corresponds closely to physical reality, it would not appear that too much complaint against it as a mathematical device is in order. At any rate, in complete analogy to Eq. (6.113a) we obtain:

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* Van Vleck and Margenau give $a$ here in place of $a^2$, but their previous calculations together with those that follow tend to indicate a misprint.

$$W_c = \lim_{\Upsilon\to 0} \int_{t_{j+1}-\Upsilon}^{t_{j+1}+\Upsilon} eE_x \cos(\omega t + \varphi)\, x_j dt$$

$$= \lim_{\Upsilon\to 0} \sum_j \Big[ eE_x \cos(\omega t + \varphi) x_j \Big]_{t_{j+1}-\Upsilon}^{t_{j+1}+\Upsilon} + \lim_{\Upsilon\to 0} \sum_j \int_{t_{j+1}-\Upsilon}^{t_{j+1}+\Upsilon} \omega e E_x \sin[\,\omega t + \varphi]\, x_j dt$$

$$= \lim_{\Upsilon\to 0} \sum_j \left[ eE_x \cos(\omega t + \varphi) x_j(t_{j+1} + \Upsilon) - eE_x \cos(\omega t + \varphi) x_j\,(t_{j+1} - \Upsilon)\right] + 0$$

$$= \; - \sum_j eE_x \cos(\omega t + \varphi)\, x_j(t_{j+1}) \tag{6.116}$$

by virtue of integration by parts and the fact that as $t \longrightarrow t_{j+1}$ minus, $x \longrightarrow x_j(t_{j+1})$ while as $t \longrightarrow t_{j+1}$ plus, $x \longrightarrow 0$. Eq. (6.112a) then tells us that we must add the term

$$-\frac{e^2 E_x^2}{m\omega} \sum_j \cos(\omega\vartheta_j + \varphi_j) \int_0^{\vartheta_j} \cos[\omega(\vartheta_j - \Lambda) + \varphi_j] \sin \omega_0 \Lambda \, d\Lambda$$

to the right side of Eq. (6.113b). This equation may now be dealt with as was Eq. (6.113b) to obtain the power term:

$$\frac{e^2 E_x^2 a}{4\, m\omega} \left[ \frac{\omega - \omega_0}{a^2 + (\omega - \omega_0)^2} - \frac{\omega + \omega_0}{a^2 + (\omega + \omega_0)^2} \right] \tag{6.117}$$

which when added to Eq. (6.115) yields:

$$P_A(\omega) = \frac{W}{T} = \frac{e^2 E_x^2 \omega}{4 m\omega_0} \left[ \frac{a}{a^2 + (\omega - \omega_0)^2} - \frac{a}{a^2 + (\omega + \omega_0)^2} \right] \tag{6.118}$$

A consideration of Eqs. (6.111) and (6.118) is sufficient to show that detailed balance has not been obtained if for no other reason than that the shape factors as given by the brackets in the two equations differ. Van Vleck and Margenau overcame this difficulty by passing from the Lorentz to the Van Vleck-Weisskopf boundary conditions on $x$ and $\dot{x}$ at collision. We have shown in some detail how this transition added the terms as given by Eq. (6.102) to $x$ and subsequently added to the absorption coefficient resulting in Eq. (6.105). It should suffice here to say that a similar computation adds the term:

$$\frac{e^2 E_x a}{4\, m\omega^2} \left[ \frac{\omega^2 - \omega\omega_0}{a^2 + (\omega - \omega_0)^2} + \frac{\omega^2 + \omega\omega_0}{a^2 + (\omega + \omega_0)^2} \right] \tag{6.119}$$

to Eq. (6.118) to arrive at the power absorbed from the light wave as a function of frequency.

We let $\Upsilon(\omega)d\omega$ be the energy density in the field for the frequency interval $\omega$ to $\omega + d\omega$. Then this quantity is given by

$$\Upsilon(\omega)d\omega = \frac{E^2}{4\pi} = \frac{1}{4\pi} <E^2> <\sin^2 \omega t>$$

$$= \frac{1}{8\pi} <E^2>$$

when we substitute for the mean value of the sine squared term. $E^2$ is averaged over the directions of polarization. We agree that:

$$E^2 = E_x^2 + E_y^2 + E_z^2$$

so that: $$<E_x^2> = 3\ E_x^2$$

which yields: $$\Upsilon(\omega)d\omega = \frac{3}{8\pi}\ E_x^2$$

Let us diverge for a moment.

We might recall that the principle of equipartition requires that the mean kinetic energy associated with a degree of freedom by $\frac{1}{2}\ kT$. Then since the mean kinetic energy, $<\frac{1}{2}m\omega_0^2x_0^2 \cos^2 \omega_0 t>$, is the same as the mean potential energy, $<\frac{1}{2}\ m\omega_0^2x_0^2 \sin^2 \omega_0 t>$, for the oscillator we may reasonably expect the mean total energy of oscillation to be $kT$. Likewise, $\frac{1}{2}\ m\omega_0^2x_0^2\ (\sin^2 \omega_0 t + \cos^2 \omega_0 t) = kT$, so that

$$x_0^2 = 2\ \frac{kT}{m\omega_0^2}$$

Jeans' number, which specifies the allowed number of proper vibrations in a wave number interval, will prove useful here. Let us recall the solution $\sin\left(2\pi k \frac{x}{X}\right) \sin\left(2\pi l \frac{y}{Y}\right) \sin\left(2\pi m \frac{z}{Z}\right)$ to the wave equation $\nabla^2\ \psi - \frac{1}{c^2}\ \psi = 0$ when we impose the boundary conditions, standing waves in a box of sides $X$, $Y$, and $Z$. Surely our wave numbers will be:

$$\bar{\nu}_x = \frac{k}{X}\ ;\ \ \bar{\nu}_y = \frac{l}{Y}\ ;\ \ \bar{\nu}_z = \frac{m}{Z}$$

and we form a three space of these wave number components. It would appear to follow that the number of different proper vibrations in the wave number interval $d\bar{\nu}_x\ d\bar{\nu}_y\ d\bar{\nu}_z$ (Jeans' number) is:

$$d\mathfrak{Z} = dkdldm = d\bar{\nu}_x d\bar{\nu}_y d\bar{\nu}_z XYZ = d\tilde{V} \cdot V \tag{6.120a}$$

where $d\tilde{V}$ is a volume element in wave number space and $V$ is, of course, a volume in ordinary space.

Now surely $d\tilde{V} = 4\pi^2\bar{\nu}^2 d\bar{\nu}$, so Eq. (6.120a) becomes:

$$d\mathfrak{Z} = V4\pi^2\bar{\nu}^2 d\bar{\nu} \tag{6.120b}$$

We, of course, recall that $\nu = \bar{\nu}c$ and also that electromagnetic radiation is possessed of two transverse components. Utilizing these two facts we obtain from Eq. (6.120b):

$$d\mathfrak{Z} = V\frac{8\pi^2\nu^2}{c^3}\, d\nu \tag{6.120c}$$

Eq. (6.120c) gives us Jeans' Number for the number of proper vibrations in the frequency interval $d\nu$, but we still desire an expression for the energy density of the radiation. It would certainly appear reasonable that we could obtain this quantity by multiplying $d\mathfrak{Z}$ by the mean energy for each proper vibration, which we may recall is $kT$. Thus:

$$\mathfrak{T}(\nu)d\nu = \frac{d\mathfrak{Z}}{V}\, kT = \frac{8\pi\nu^2}{c^3} kTd\nu$$

or: $$\mathfrak{T}(\omega)d\omega = \frac{\omega^2 kT}{\pi^2 c^3}\ d\omega \tag{6.121}$$

Eq. (6.121) is the well known Rayleigh-Jeans radiation law.

Thus, we replace $E_x^2$ by,

$$E_x^2 = \frac{4}{3}\frac{m\omega^2\omega_0^2}{\pi c^3}x_0^2 \tag{6.122}$$

in the sum of Eqs. (6.118) and (6.119) to obtain:

$$P_A(\omega) = \frac{c^2x_0^2}{3\pi c^3}\omega^4\left[\frac{a}{a^2+(\omega_0-\omega)^2}+\frac{a}{a^2+(\omega_0+\omega)^2}\right] \tag{6.123}$$

A comparison of Eqs. (6.111) and (6.123) shows that a detailed balance condition between absorption and emission has indeed been obtained by considering, in absorption, the work done by the field (a) between collisions and (b) at collisions and by including the Maxwell-Boltzmann boundary conditions. In essence a choice of methods was available for obtaining $x$ for Eq. (6.110a). We could have (a) taken $\omega^2$ times the Fourier analysis of $x$ (as we did) or (b) taken the Fourier analysis of $\ddot{x}$ for $x$. As Van Vleck and Margenau note, method (b) would not have implicitly included the infinite accelerations at the time boundaries, and, as a consequence, detailed balancing would not have been obtained.

We have remarked that the boundary conditions especially are an approximation. In an actual molecular system, of course, finite collision times would have to be considered. In addition, the Planck radiation law would more logically replace the Rayleigh-Jeans law. In the limit of low frequency, however, the former reduces to the latter, so that, as in the case of the earlier van Vleck-Weisskopf considerations, the results are particularly applicable to the microwave region.

## 6.14. ADIABATICITY LIMITATIONS AND ELECTRONIC STATE ROTATION

This essentially completes our classical considerations of interruption broadening, and we may now turn our attention to some of the more quantum mechanical attacks on the problem.

We begin with Spitzer's considerations which consisted of a demonstration of the errors introduced into the theory by (1) the adiabatic assumption and (2) the neglect of the rotation of the electronic quantum states. Let us first consider Approximation (2).

We consider the case of one perturber and one emitter. We further suppose the perturber to produce an electric field due to its possession of a permanent or an induced dipole moment, quadrupole moment, etc. This field will be radial about the perturber. We recall that the quantum number $M$ specifies the component of the angular momentum on some space fixed axis. This axis is now fixed by the electric field, and, since the field is radial, will be directed toward the perturber. Then as the perturber moves by the emitter, this axis — and incidentally the remainder of the reference frame — will rotate so as to remain directed toward the perturber. Finally, if $M$ is to remain unchanged the atom must rotate with this reference frame. Thus is the rotation with the perturber passage obtained. Now let us consider Fig. (6.6).

The perturber motion is assumed rectilinear of velocity v as indicated in the figure. The angle $\vartheta$ is the angle that the $z$-axis of the emitter frame makes with its direction at time of closest approach, $R$.

Now the radiation (we presume) is observed in the stationary frame $(x'y'z')$, and if one neglects rotation — as had been done in the past — one would simply take the matrix elements of the electronic coordinates $(xyz)$. When one considers the rotation, however, the matrix elements of $x\sin\vartheta + z\cos\vartheta$, $y$, and $z\sin\vartheta - x\cos\vartheta$ are desired instead.* This then is the source of error which is introduced when rotation

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* The transformation involved is apparent from Fig. (6.6).

is not considered. Classically, one can see that if a linear oscillator is rotated by 180° a phase change of $\pi$ in the emitted radiation occurs. This in turn leads us from Spitzer's objection to Approximation (2) to his objection to Approximation (1).

We define an adiabatic collision here as before.* Extremely close and distant encounters present two possible violations of this. We have noted, for instance, that the quadratic Stark effect which allows transitions between states of different unperturbed energy, is only important for close optical collisions.† On the other hand, a distant encounter in which the interaction is very weak may be considered. If during such a passage adiabaticity is maintained, the oscillator rotates through 180° and the $\pi$ phase change results regardless of the weakness of the interaction. Thus, as Unsold[203] has noted, the assumption of adiabaticity for such distant collisions is an absurdity.

Spitzer, utilizing Schwinger's computations[161] for the matrix elements, $\dot{\vartheta}^{-1}\int \bar{\psi}_s \frac{\partial \psi_r}{\partial t} d\tau$, in a rotating coordinate system, carried out a calculation which led him to a minimum value for the phase shift on collision which would allow the reasonable utilization of the adiabatic approximation.

The adiabatic equations

$$H(t)\psi_s(t) = E_s(t)\psi_s(t)$$

are assumed to have the eigenvalues

$$E_s(t) = \frac{q_s}{[r(t)]^n}$$

so that the adiabatic phase shift is given by:

$$\varphi_{as} = \int_{-\infty}^{+\infty} \frac{2\pi E_s(t)}{h}\, dt = \frac{q_s}{h} \int_{-\infty}^{+\infty} \frac{dt}{(R^2 + v^2t^2)^{n/2}}$$

Spitzer showed that the adiabatic approximation is valid if

$$\varphi_{as} > c_n K_{sr} \left| \frac{\Lambda_s}{\Lambda_s - \Lambda_r} \right| \tag{6.124a}$$

and invalid if

$$\varphi_{as} < c_n \left| \frac{\Lambda_s}{\Lambda_s - \Lambda_r} \right| \tag{6.124b}$$

where:

$$c_n = \frac{\sqrt{\pi}\, \Gamma[\frac{1}{2}(n-1)]}{\Gamma(\frac{1}{2}n)}$$

$$K_{sr} = \cdot^{-1} \int \bar{\psi}_s \frac{\partial \psi r}{\partial t}\, d\tau$$

$$q_s = \Lambda_s q_s \,;\; |\Lambda_s - \Lambda_r| = 1 \text{ (lowest value)}$$

Eqs. (6.124) then give the Spitzer criteria for the utilization of the adiabatic hypothesis when the rotating electronic states are utilized. We might remark that when the rotation is ignored and adiabaticity is assumed, the two incorrect approximations tend to compensate each other.

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* See *supra*, Sec. (4.19).

† See *supra*, Chap. 4.

Finally, Spitzer obtained* also a limit for the applicability of the Interruption analysis

$$|\,\nu - \nu_0\,| < \frac{P}{2\pi}\left(\frac{hv^n}{c_n q_s}\right)^{1/n-1} \tag{6.125}$$

which restricts the validity in the line wings. The symbol $P$ is the only previously undefined one in Eq. (6.125) and this a rather arbitrary allowable error that is inserted.

Let us note that if we let $P = 1$, $q_s/\hbar = 2\pi C$, Eq. (6.125) very nearly ($C_n{}^n \neq C_n$) corresponds to Eq. (6.22), the earlier obtained wing limit for the Interruption theory.

Having determined the limits of applicability of the adiabatic hypothesis, we shall, with Foley,[37] ignore them in obtaining the Fourier integral expression for the line profile on the basis of the quantum radiation theory. In addition, we shall now consider Foley's phase shift solutions of the resulting Fourier integral in which development the intriguingly entitled Correlation Function† will arise.

## 6.15. THE FOLEY PHASE SHIFT SOLUTION

As has been our wont, we shall continue to treat the translational and hence the relative, motions of the molecules classically. Now we are faced with precisely the problem we encountered, for example, in Chapter 4. Eq. (4.196) will give us, when rewritten in Foley notation:

$$H = H_1(p_l,q_l) + H_2(p_l,q_l,Q_i(t)) + H_3(p_l,q_l,p_s,q_s) + H_4(p_s,q_s) \tag{6.126}$$

where, as usual, $H_1$ is the unperturbed Hamiltonian of the molecules, $H_2$ that of the molecular interactions responsible for our broadening, $H_3$ that of the molecule-field interaction, and $H_4$ is the Hamiltonian of the unperturbed field. Our procedure now is similar to that which we utilized in Chapter 4 subsequent to Eq. (4.196) except that now the matrix elements of $H_2$ will hardly be those of the linear Stark effect. Utilizing the correspondence, however, it is surely apparent that we will obtain equations corresponding to Eq. (4.199a) as solutions:

$$\dot{a}_n = -\frac{i}{\hbar}V_{mn}(t)a_m\,(t)\exp\left[-i(E_m - E_n)t/\hbar\right] \tag*{(6.127a)**}$$

and equations corresponding to Eq. (4.199a) as solutions:

$$a_f = S_{if}a_i \exp\left[-\frac{i}{\hbar}(E_i - E_f - h\omega_s)t\right] - \frac{i}{\hbar}V_{nf}(t)a_n(t)\exp\left[-\frac{i}{\hbar}(E_n - E_f)t\right] \tag{6.127b}$$

In Eqs. (6.127) the $V_{kj}$ are the matrix elements of the molecular interactions and the $S_{kj}$ are the matrix elements of the molecule-field interaction. Now under the adiabatic collision assumption Eq. (6.127a) yields:

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* Spitzer first outlined the method that should be used in determining the line profile as follows: (1) Set up and solve by finding the $a_i(t)$ the problem of a radiating atom perturbed by a passing particle — ion, or molecule. (2) Determine the Fourier transform for the $a_i(t)$ and sum over all such transforms squared to find the line profile due to a single encounter. (Multiple encounters are neglected throughout.) (3) Finally, all such encounters are integrated over all collision velocities and closest approach distances. Spitzer generally utilizes the method and then determines the error in simplifying this procedure so as to obtain the Weisskopf result. This error is, of course, given by Eq. (6.125).

† The author encountered some difficulty in ascertaining just what this function was correlated with when correlated. It quite obviously was correlated with something, however, since people have been recorrelating it ever since.

** This equation implies the sole existence of the two states $m$ and $n$.

$$a_n(t) = \frac{V_{mn}(t)a_m(t)}{E_m - E_n}\exp\left[-\frac{i}{\hbar}(E_m - E_n)t\right] \tag{6.128}$$

We shall substitute for $V_{nf}$ in Eq. (6.127b) from Eq. (6.128) to obtain:

$$a_f = S_{if}a_i \exp\left[-\frac{i}{\hbar}(E_i - E_f - h\omega_s)t\right] - \frac{i}{\hbar}a_f P_f(t) \tag{6.129}$$

where $P_i(t) = E_n - E_f$.

In analogy to Eq. (4.158) we now choose $a_i$ as:

$$a_i = e^{-\gamma t}e^{-\frac{i}{\hbar}\int\limits_0^t P_i(t)dt} \tag{6.130}$$

and we may now solve Eq. (6.129) for the probability amplitude for the emission of a quantum of frequency $\omega_s$:

$$A_{\omega_s}(T) = \exp\left[-\frac{i}{\hbar}\int\limits_0^T P_f dt\right]\int\limits_0^T dt\, S_{if}\exp\left[-\gamma T - \frac{i}{\hbar}\int^t (P_i(t) - P_f(t)\, dt + i\omega t\right] \tag{6.131}$$

where $\omega = \omega_{if} - \omega_s$.

If the natural line width factor $\gamma$ is neglected and the time of collision $T$ is extended to infinity, we essentially obtain the Weisskopf expression for the Fourier amplitude.

As we have noted on several occasions, the Fourier amplitude may be written as:

$$A(\omega) = \sqrt{N}\int\limits_0^\infty dt \exp\left[-i\int\limits_0^t P(x)dx + i\omega t\right] \tag{6.132}^*$$

where $P(t) = P_i(t) - P_f(t)$ from which:

$$I(\omega) = N\int\limits_0^\infty dt_1 \int\limits_0^\infty dt_2 \exp\left[-i\int\limits_{t_2}^{t_1} P(x)dx + i\omega(t_1 - t_2)\right] \tag{6.133a}$$

which becomes, when we let $t_1 - t_2 = \tau$ and $t_2 = t_0$:

$$I(\omega) = N\int\limits_{-\infty}^{+\infty} d\tau \int\limits_0^\infty dt_0 \exp\left[-i\int\limits_{t_0}^{t_0+\tau} P(x)dx + i\omega\tau\right]$$

$$= \Re\left\{N\int\limits_0^\infty d\tau\int\limits_0^\infty dt \exp\left[-i\int\limits_{t_0}^{t_0+\tau} P(x)dx + i\omega\tau\right]\right\} \tag{6.133b}$$

Now let us introduce the so-called correlation function as:

$$\exp\left[-i\int\limits_{t_0}^{t_0+\tau} P(x)dx\right] \tag{6.134a}$$

where now, from Eq. (6.133b)

$$\langle y(\tau)\rangle = \int\limits_0^\infty dt_0 \exp\left[-i\int\limits_{t_0}^{t_0+\tau} P(x)dx\right] \tag{6.134b}^\dagger$$

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* We have given Foley's derivation of the state growth equations. Let us remark that Eq. (6.132) could have been obtained with no difficulty whatever by simply rewriting Eq. (4.162) very slightly.

† Cf. *supra*, Eq. (6.32).

is a "... measure of the average correlation ..." of Eq. (6.134a) over the interval $\tau$. The integral in Eq. (6.134a) may surely be approximated by the phase shift approximation as:

$$\int_{t_0}^{t_0+\tau} P(x)dx = \sum_{i=1}^{n} \alpha_i \tag{6.135}$$

under the assumptions that (1) the time interval involved is long in comparison to the duration of the collision (2) which is vanishingly small. These then result in the approximation of the sum of an integral number of collision phase shifts as given by Eq. (6.135). The fact that this approximation is applicable to the case of low densities and high velocities arises out of assumption (1).

Let us first refer to Eq. (1.56) for the probability that the molecule will undergo a collision during $\tau$ where as always $\tau_0$ is the mean time between collisions. Note that $\frac{\tau}{\tau_0} = A$ the number of collisions during time $\tau$.* As in Eq. (6.66a) the probability of $n$ collisions in time $\tau$ is given by $\left(\frac{\tau}{\tau_0}\right)^n \frac{1}{n!} e^{-\tau/\tau_0}$. From Eqs. (6.134b) and (6.135) the average value of the correlation function for this case of $n$ collisions is:

$$\int dt_0 \exp\left[ - i \sum_{i=1}^{n} \alpha_i\right] = \prod_{i=1}^{n} \int_{-\infty}^{+\infty} d\alpha\, p(\alpha)\, (\cos\alpha - i \sin\alpha) = (A - iB)^n \tag{6.136}$$

the $p(\alpha)d\alpha$ being the distribution in phase shifts. Thus, $A$ and $B$ are the average values ($A = \int d\alpha p(\alpha) \cos\alpha$, etc.) of $\cos\alpha$ and $\sin\alpha$ respectively.

Now Foley established a cut-off distance $\rho_0$, time $\tau_0$, and phase shift $\alpha_0$ for the intermolecular forces which may later be extended. We have already averaged over $n$ collisions, and Foley completed the calculation and obtained $<y(\tau)>$ by averaging over the various possible values of $n$ as follows:†

$$<y(\tau)> = \sum_{n=0}^{\infty} \frac{e^{-\tau/\tau_0}}{n!} \left(\frac{\tau}{\tau_0}\right)^n (A - iB)^n = \exp\left[\frac{A - iB}{\tau_0}\tau - \frac{\tau}{\tau_0}\right] \tag{6.137}$$

since the series is the well known one for the exponential.

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* Jablonski[80] objected to Foley's utilization of $\frac{1}{\tau_0} e^{-\tau/\tau_0}$ for the distribution of collisions. He felt that a Maxwell-Boltzmann distribution was called for, but, as Foley[38] pointed out, the random distribution for the broadening case seems to have precedent if nothing else, as justification. This would not appear to be entirely conclusive.

† Mizushima[131] raised the objection that "... His derivation of ... Eq. (6.138) ... is inadequate in that he replaced the sum of averages by the average of sums ..."[131] A little consideration serves to clarify Mizushima's contention. On the left side of Eq. (6.136) there is obviously a sum over $\alpha$. Now the individual terms of this sum are not reproduced by assigning various values to $n$, but, traced back through Eq. (6.136), various sums result in Eq. (6.137). Thus, the average in Eq. (6.137) is one over sums, as Mizushima noted. Mizushima carried through this calculation in what appears to be the more proper order to obtain:

$$I(\nu) = \frac{c}{\pi} \frac{\delta}{(\nu_s - \nu_0 - \Delta)^2 + \delta^2} \tag{6.137a'}$$

where:

$$\delta = \int F(s)\,(1 - \cos\alpha_s)\, ds/2\pi \tag{6.137b'}$$

$$\Delta = \int F(s) \sin\alpha_s\, ds/2\pi \tag{6.137c'}$$

and $F(s)ds$ is the number of collisions with collision parameter between $s$ and $s + ds$ per unit time.

The direct substitution of Eq. (6.137) into Eq. (6.133b) yields:

$$I(\omega) = \Re\left\{ N \int_0^8 d\tau \exp\left[\frac{A-1}{\tau_0}\,\tau - i\,\frac{B-\omega}{\tau_0}\,\tau\right]\right\}$$

$$= \frac{(1-A)/\pi\tau_0}{[(1-A)/\tau_0]^2 + [B/\tau_0 - \omega]^2} \qquad (6.138)$$

It is quite apparent from Eq. (6.138) that we have obtained a line center shift of $B/\tau_0$. The half-width is, of course, $\frac{2(1-A)}{\tau_0}$. Since $\tau_0$ appears in both shift and width results, it follows that a linear density proportionality exists. The constants occurring in Eq. (6.138) may be evaluated in a quite straightforward manner.

We commence by supposing interactions of the form $V = \beta h\gamma^{-p}$ so that the phase shift $\alpha$ is given by:

$$\alpha = \int_{-\infty}^{+\infty} \frac{V_i - V_f}{h}\,dt = \int_{-\infty}^{+\infty} \frac{\beta_i - \beta_f}{(\rho^2 + v^2t^2)^{p/2}}\,dt = \frac{\gamma}{v\rho^{p-1}} \qquad (6.139)$$

where $v$ is, as usual, the relative velocity and $\rho$ the distance of closest approach.

Eq. (1.13) tells us that:

$$\frac{1}{\tau_0} = \frac{v}{l} = N\pi\rho^2 v \qquad (6.140a)$$

where $v$ is the mean relative velocity and $l$ is the mean free path. Now, however, let us introduce a normalized distribution of velocities $f(v)dv$ and a distribution of interaction force constants $g$ (not a continuous distribution). The reason for the latter distribution should become apparent when we recall the dependence of this interaction constant on the molecular states involved. When these two distributions are applied and averaged over, Eq. (6.140a) becomes:

$$\frac{1}{\tau_0} = N \sum_k \int_0^\infty dv\, f(v)\, g_k\, \pi\, \rho_{vk}^2\, v \qquad (6.140b)$$

which is surely the expression for the number of collisions which produce a phase shift greater than our cut-off phase shift $\alpha_0$. Eq. (6.140b) may be rewritten according to Eq. (6.139) as:

$$\frac{1}{\tau_0} = N \sum_k \int_0^\infty dv\, f(v)\, g_k\, \pi\, \frac{{\gamma_k}^{2/(p_k-1)}\, v^{(p_k-3)/(p_k-1)}}{\alpha^{2/(p_k-1)}}$$

$$= N\pi \sum_k g_k \left< v^{(p_k-3)/(p_k-1)} \right> \frac{\gamma^{2/(p_k-1)}}{\alpha^{2/(p_k-1)}} \qquad (6.140c)$$

The line half-width has been determined as $\frac{2(1-A)}{\tau_0}$ or:

$$= \frac{2}{\tau_0}\left[1 - \int_{-\infty}^{+\infty} \cos\alpha\, p(\alpha)\, d\alpha\right] = \frac{2}{\tau_0}\left[1 + \int_{-\infty}^{+\infty}\left[2\sin^2\frac{\alpha}{2} - 1\right] p(\alpha)\, d\alpha\right]$$

$$= \frac{4}{\tau_0}\int_{-\infty}^{+\infty} \sin^2\frac{\alpha}{2}\, p(\alpha)\, d\alpha \qquad (6.141a)$$

Since:

$$\int_{-\infty}^{+\infty} p(\alpha)\, d\alpha = 1$$

Foley took $\frac{1}{\tau_0}\, p(\alpha)\, d\alpha$ as:

$$\frac{1}{\tau_0}\, p(\alpha)\, d\alpha = \frac{D\, {\gamma_k}^{2/(p_k-1)}\, g_k\, f(v)\, v^{(p_k-3)/(p_k-1)}}{\alpha^{(p_k+1)/(p_k-1)}\,(p_k-1)}\, d\alpha \qquad (6.142)^*$$

where $D$ is a normalization factor.

When Eq. (6.142) is substituted into Eq. (6.141a) the result is:

$$\delta = 8\,\pi\, N \sum_k g_k\, \frac{\gamma^{2/p_k-1}}{(p_k-1)} < v^{(p_k-3)/(p_k-1)} > \int_0^\infty \frac{d\,\alpha\, \sin^2\alpha/2}{|\,\alpha\,|^{(p_k+1)/(p_k-1)}} \qquad (6.143)†$$

Integration may be carried out from zero to infinity (and the result doubled) in the case of all phase shifts positive. If this is not the case the complete integration must, of course, be carried out.

Eq (6.142) may be again used to obtain the phase shift as:

$$\frac{B}{\tau_0} = \frac{1}{\tau_0}\int \sin\alpha\, p(\alpha)\, d\alpha$$

$$= 2\pi N \sum_k g_k\, \frac{\gamma^{2/(p_k-1)}}{(p_k-1)} < v^{p_k-3/p_k-1} > \int_0^\infty \frac{d\alpha\, \sin\alpha}{|\,\alpha\,|^{(p_k+1)/(p_k-1)}} \qquad (6.144)$$

where again only positive phase shifts have been assumed.

The integrals in Eqs. (6.143) and (6.144) are amenable to evaluation in terms of gamma functions. For foreign gas broadening in molecular spectra to which we are restricting ourselves here, an interaction of the form $\beta/r^p$ yields a shift to width ratio of:

$$\delta/\Delta = \tfrac{1}{2}\cot\left\{\frac{p-3}{2(p-1)}\,\pi\right\} \qquad (6.145)$$

---

* Foley wrote $p(\alpha)\, d\,\alpha = \frac{D{\gamma_k}^{2/(p_k-1)} g_k\, f(v)\, v^{(p_k-3)/(p_k-1)}}{\alpha^{(p_k+1)/(p_k-1)}\,(p_k-1)}$ but it would be a bit difficult to obtain his result with this expression.

† Foley gave $\sin^2\alpha$ instead of $\sin^2\frac{\alpha}{2}$.

Thus, Foley's investigations into the phase shift solution of the Fourier integral have yielded line shapes which have the admirable attribute of possessing a shift, although no asymmetry would appear to be present. These results have, of course, been obtained classically after the quantum adiabatic hypothesis was utilized to obtain the Fourier integral. We might now sketch Foley's investigation of the error involved in the adiabatic hypothesis.* In order to do this, we shall find an expression for the probability of non-adiabatic transitions.

### 6.16. THE ALLOWABILITY OF THE ADIABATIC APPROXIMATION

To begin with, we expand the eigenfunction for the system in terms of the instantaneous solutions to:

$$H(t)\psi_n(t) = E_n(t)\psi_n(t) \tag{6.146}$$

as:

$$\Psi(t) = \sum_n a_n(t) \exp\left[-\frac{i}{\hbar}\int_0^t E_n(t)\,dt\right]\psi_n(t) \tag{6.147}$$

Eq. (6.146) is, of course, the solution to:

$$H(t)\Psi(t) = i\hbar\frac{\partial}{\partial t}\Psi(t) \tag{6.148}$$

If we let, for convenience, $A = -\frac{i}{\hbar}\int_0^t E_n(t)dt$, the substitution of Eq. (6.146) into (6.147) yields:

$$ih\sum_n \dot{a}_n(t)\exp(A)\,\psi_n(t) + i\hbar\sum_n a_n(t)\exp(A)\,\frac{\partial\psi_n(t)}{\partial t} + \sum_n a_n(t)\exp(A)\,E_n(t)\,\psi_n(t)$$

$$= \sum_n a_n(t)\exp(A)\,H(t)\psi_n(t) = \sum_n a_n(t)\exp(A)\,E_n(t)\psi_n(t) \tag{6.149†}$$

The $\sum_n a_n(t)\exp(A)\,E_n(t)\,\psi_n(t)$ terms will obviously cancel out of Eq. (6.148). Subsequently, the multiplication through on the left by $\bar{\psi}_k$ and integration over all space leads to the rate of state growth equation:

$$\dot{a}_k = -\sum_n a_n(t)\left(\bar{\psi}_k \mid \frac{\partial\psi_n}{\partial t}\right)\exp\left[-\frac{i}{\hbar}\int_0^t (E_n - E_k)dt\right] \tag{6.150}$$

The time dependent portion of the Hamiltonian is included** in the collision interaction. Thus, we may temporarily treat Eq. (6.146) as a time independent perturbation problem in order to find the $\psi_n(t)$. Foley utilized the first order eigenfunction which for this problem we have not as yet obtained.

If, in Eq. (5.1) we let $m = k$ there results:

$$a_{nk} = \frac{(k \mid H' \mid n)}{(E_n - E_k)} \tag{6.151}$$

---

* Since the treatment is slightly different from Spitzer's (cf. *supra*, Chap. 5) we shall give it here.

† Now note that this will give us a different expression for the $a_n$ than Eq. (4.185a) (Spitzer's or Guttinger's equation). This is because Spitzer absorbed the exponential into the $\psi_r(t)$ in Eq. (4.184b).

** Cf. *supra*, Eq. (6.150).

for the coefficients of the first-order perturbed eigenfunction in the expansion in terms of the unperturbed eigenfunctions. Thus, we obtain for the present case:

$$\begin{aligned} \psi_n(t) &= \psi_n{}^0 + \sum_i \frac{(n \mid H'(t) \mid i)}{E_i - E_n} \psi_i{}^0 \\ &= \psi_n{}^0 + \psi_n{}'(t) \end{aligned} \tag{6.152}$$

where:

$$\psi_n{}^0 = u_n e^{i/\hbar(E_n t)}$$

Now for Eq. (6.147) let us write:

$$\Psi(t) = \sum_n a_n(t)\psi_n(t) = \sum_n a_n(t)\psi_n{}^0 + \sum_n a_n(t)\psi_n{}'(t) \tag{6.153}$$

and substitute this equation into Eq. (6.148) to obtain:

$$\left(H + H'(t) - i\hbar\frac{\partial}{\partial t}\right) \sum_n a_n(t)\, \psi_n(t) = \left(H + H' - i\hbar\frac{\partial}{\partial t}\right)\left(\sum_n a_n(t)\psi_n{}^0 + \sum_n a_n(t)\psi_n{}'(t)\right) = 0$$

or:

$$\left(H + H' - i\hbar\,\frac{\partial}{\partial t}\right) \sum_n a_n\, \psi_n{}^0 = 0 \tag{6.154a}$$

$$\left(H + H' - i\hbar\,\frac{\partial}{\partial t}\right) \sum_n a_n\, \psi_n{}' = 0 \tag{6.154b}$$

Eq. (6.154a) tells us that:

$$i\hbar \sum_n \dot{a}_n(t)\, \psi_n{}^0 = \sum_n a_n(t)\, H'(t)\, \psi_n{}^0$$

and multiplication through on the left by $\overline{\psi_n}{}^0$ and integration over all space yields:

$$\dot{a}_k(t) = -\frac{i}{\hbar} \sum_n (k \mid H'(t) \mid n) \exp\left[\frac{i}{\hbar}\,(E_k - E_n)\right] a_n(t) \tag{6.155a}$$

We suppose the system to be originally in the state $m$ — before the collision — so that $a_m(0) = 1$; all other $a_n(0) = 0$. Eq. (6.155a) becomes:

$$\begin{aligned} \dot{a}_k\,(0) &= -\frac{i}{\hbar}\,(k \mid H'(t) \mid m) \exp\,[i\omega_{km}t] \\ &= -\frac{i\,\omega_{km}}{E_n - E_m}\,(k \mid H'(t) \mid m) \exp\,[i\omega_{km}t] \end{aligned} \tag{6.155b}$$

where $\omega_{km} = (E_k - E_m)/\hbar$

In a general problem of this nature we would suppose the $a_n$ to change sufficiently slowly so that in obtaining a specific $a_n$ we would integrate Eq. (6.155) from time zero to time $t$. In this case, however, we imagine the collision perturbation to only proceed during the time 0 to $t$ with the consequence that the extension of the integration to include all times previous and subsequent to this time interval has no effect on the result. These machinations produce:

$$a_k = \frac{-i\,\omega_{km}}{E_k - E_m} \int_{-\infty}^{+\infty} (k|H'(t)|m) \exp\,[i\omega_{km}t]\, dt \tag{6.156}$$

$H'(t)$ is generally the dipole-dipole interaction as in, say, Eq. (5.1), but we should note that its matrix element will not disappear here, since we are not taking it over one state as was done in this earlier case. Thus:

$$(k \mid H'(t) \mid m) = \frac{(k \mid \beta \mid m)}{(\rho^2 + v^2t^2)^{3/2}} \tag{6.157}$$

Now if we let $K = \rho \, \frac{\omega_{km}}{r}$ we may rewrite Eq. (6.156) as:

$$a_k = \frac{(k \mid \beta \mid m)}{\rho^3(E_k - E_m)} \, H_1(iK) \tag{6.158}$$

where $H_1(iK)$ is the first order Hankel function.

Eq. (6.158) will give us an idea as to how important the non-adiabatic transitions are. Specifically, we can consider the numerator of this equation as a facile guide to this importance. The level energy difference appearing in this numerator would indicate that the non-adiabatic transitions will be of negligible importance for optical spectra where the level separations are large, but in the infrared region this is not the case. In the event of the occurrence of such a transition, the radiation of the line under consideration will cease. Thus, Foley suggested the introduction into the phase shift distribution $p(\alpha)$ of a probability for these arbitrary phase shifts equivalent to the total probability for the non-adiabatic transitions. This has not been carried out specifically.

Eq. (6.143) indicates that, in order to accurately calculate the line width, we need a detailed knowledge of the interactions between emitter and absorber in the upper and lower states so that $\gamma$ may be properly evaluated. The shift to width ratio of Eq. (6.155) should be independent of $\gamma$ — dependent only on the power of the interaction law — and should thus provide either (a) a test of the interaction law or (b) a test of the theory. Here, of course, the oft encountered indeterminism of a check of theory against experiment arises, since, in the case of non-agreement between the two, one may legitimately ask the questions: Is (a) wrong? or Is (b) wrong? or Are they both wrong? At any rate, Foley obtained 0.363 for $\delta/\Delta$ for the case $p = 6$ and compared this result with the experimental results of several authors for foreign gas broadening. The compared ratios are given in Table (6.2).

The wide divergence of the experimental results both from each other and from Foley's theoretical predictions is apparent, but the average, as Foley noted, of the values in Table (6.2), 0.375, agrees well with the value given by Eq. (6.145). Practically speaking, however, this does not of necessity mean much, since the statistical sampling obtainable from the table is not great enough for one to be able to say that, on the average, the shift will be 0.375 any more than 0.175 or 0.575.

## 6.17. THE DENSITY MATRIX

Before considering the Karplus-Schwinger[84] derivation of Eq. (6.107), let us again consider the representative point in phase space which we mentioned preceding Eq. (6.32). We specify the density in phase space by $\Upsilon$, and we suppose this density to be a measure of the probability that the representative point is in the volume element corresponding to a certain configuration and momentum state per unit phase volume. Since the representative point is of necessity somewhere in phase space:

| Spectral Line | Perturber | Ratio | Reference |
|---|---|---|---|
| Hg 2537 | A | 0.39 | 45 |
| | $N_2$ | 0.45 | 45 |
| | $O_2$ | 0.47 | 45 |
| Na 5890 | A | 0.35 | 121 |
| | $N_2$ | 0.44 | |
| K 7665 | $N_2$ | 0.47 | 121a |
| | | 0.37 | 73a |
| 7699 | $N_2$ | 0.50 | 121a |
| | | 0.44 | 73a |
| 4044 | $N_2$ | 0.50 | 121a |
| 4047 | $N_2$ | 0.57 | 121a |
| Hg 2537 | $CO_2$ | 0.25 | 45 |
| | $H_2O$ | 0.22 | 45 |
| | $H_2$ | 0.16 | 45 |
| Na 5890 | $H_2$ | 0.23 | 121 |
| K 7665 | A | 0.36 | 73a |
| 7699 | A | 0.42 | 73a |
| Rb 4216 | He | 0.33 | |
| 4202 | He | 0.23 | |
| 4216 | Ne | 0.17 | |
| 4202 | Ne | 0.22 | 136a |
| 4216 | A | 0.56 | |
| 4202 | A | 0.39 | |
| Cs 4555 | He | 0.30 | |
| | Ne | 0.23 | |
| | A | 0.42 | 42 |
| | $N_2$ | 0.62 | |
| 3876 | He | 0.62 | |
| | Ne | 0.37 | |
| | A | 0.77 | |
| | $N_2$ | 0.32 | |

Table 6.2. After Foley.[37]

$$\int \dots \int \Upsilon \, dq_1 \dots dq_{3N'} \, dp_1 \dots dp_{3N'} \tag{6.159a}$$

and the mean value of a quantity $F$ is defined as:

$$<F> = \int \dots \int F \, \Upsilon \, dq_1 \dots dp_{3N'} \tag{6.159b}$$

in accordance with the definition of a mean value under the aegis of any other distribution function.

For convenience, let us now take a collection of $N$ such representative points in the phase space, representing a system of systems. Here $\Upsilon$ will be the actual system density, and we could replace one by $N$ in Eq. (6.159a). Corresponding to this density in phase space, we may obtain and utilize a "density matrix" as the quantum mechanical analog.

From expansions of the form, say, Eq. (6.153), we may define the components of this density matrix as:

$$\Upsilon_{nm} = \frac{1}{N'} \sum_{i=1}^{m} \bar{a}_{im}(t)\, a_{in}(t) = <\bar{a}_m a_n> \tag{6.160}$$

Now, as usual, the average value of some observable $F$ over one of the systems is:

$$<F> = \int \bar{\Psi} F \Psi d\tau = \sum_{m,n} \int \bar{a}_m \bar{\psi}_m F a_n \psi_n d\tau$$

$$\sum_{m,n} F_{mn}\, \bar{a}_m\, a_n \tag{6.161a}$$

so that the average value of $F$ over all systems is:

$$<F> = \sum_{m,n} F_{mn} <\bar{a}_m a_n> = \sum_{m,n} F_{mn}\, \Upsilon_{nm} \tag{6.161b}$$

which, according to the rules of matrix multiplication is:

$$<F> = \sum_{n} (\Upsilon F)_{nn} = Tr \, \| \Upsilon F \| \tag{6.162}$$

In Eq. (6.162) "Tr" is the trace or diagonal sum of the product matrix $\| \Upsilon F \|$. Thus, the density matrix provides an averaging medium which we shall utilize subsequently.

We may obtain another useful relation by recalling the state growth equation which we have noted on several occasions:

$$\frac{\partial a_n}{\partial t} = -\frac{i}{\hbar} \sum_k H_{nk}\, a_k \tag{6.163}$$

From Eq. (6.163) we may infer that:

$$\frac{\partial \Upsilon_{nm}}{\partial t} = \frac{\partial}{\partial t} <\bar{a}_m a_n> = \left\langle \bar{a}_m \frac{\partial a_n}{\partial t} \right\rangle + \left\langle \frac{\partial \bar{a}_m}{\partial t} a_n \right\rangle$$

$$= -\frac{i}{\hbar} \sum_k (\bar{H}_{nk} <\bar{a}_m a_k> - \bar{H}_{mk} <\bar{a}_k a_n>)$$

$$= -\frac{i}{\hbar} \sum_k (H_{nk}\Upsilon_{km} - \Upsilon_{nk}H_{km}) = -\frac{i}{\hbar}[(H\Upsilon)_{nm} - (\Upsilon H)_{nm}]$$

or in matrix form:

$$i\hbar \frac{\partial}{\partial t} \| \Upsilon \| = \| H \| \, \| \Upsilon \| - \| \Upsilon \| \, \| H \| \tag{6.164}$$

We now revert to the quantum mechanical derivation of Eq. (6.107).

### 6.18. ANOTHER QUANTUM JUSTIFICATION OF THE LORENTZ EQUATION

To begin with, the absorption coefficient for the absorption by a gas may be represented as:

$$\alpha = 4\pi \frac{\omega}{c} N \left[\mathfrak{I}(\chi)\right] \tag{6.165a}$$

where $\omega$ is the frequency of the absorbed radiation and $\chi$ is either the electric or magnetic susceptibility. We may recall that the induced dipole moment is related to the susceptibility by

$$\underline{\mu}(t) = \mathfrak{R}\left[\chi\, \mathbf{F} e^{-i\omega t}\right] \tag{6.165b}$$

where we now suppose our electric field to be:

$$\mathbf{F}(t) = \mathbf{F} \cos \omega t = \mathfrak{R}\left[\mathbf{F}\, e^{-i\omega t}\right] \tag{6.165c}$$

Now our general procedure here will be to (a) find the average value $\underline{\mu}(t)$ using Eq. (6.162), (b) ascertain $\chi$ from Eq. (6.165b) by a utilization of the results of (a), and (c) find $\alpha$ by an insertion of the results of (b) in Eq. (6.165), an apparently straightforward sequence of operations.

We must begin by gaining some knowledge of $\Upsilon$, and the physical conditions of the problem will furnish us this information. To begin with, we recall the Van Vleck-Weisskopf distribution of $\underline{\mu}(t)$ — through the amplitude distribution — as an application of the Maxwell-Boltzmann energy distribution. This leads us to our averaging density matrix at time $t_0 = t - \vartheta$ where $t_0$ is the time of collision:

$$\| \Upsilon_0(t_0) \| = e^{\sigma/kT} \| e^{-H(t_0)/kT} \| = \| e^{-H(t_0)/kT} \| \tag{6.166a}$$

and the normalizing condition:

$$Tr \, \| \Upsilon \| = 1$$

tells us that:

$$1/C = e^{-\sigma/kT} = Tr \, \| e^{-H(t_0)/kT} \| \tag{6.166b}$$

In addition, Eq. (6.98) in a more general form yields:

$$\| H(t) \| = \| H_0 \| - \| \underline{\mu} \| \cdot \mathbf{F}(t) = \| H_0 \| + \| V \| \cos \omega t \tag{6.167}$$

where now $H_0$ is the Hamiltonian of the isolated molecule and the dipole moment operator is given by $\| \underline{\mu} \|$.

We are now in a position to utilize Eq. (6.162) for finding the average value of $\| \underline{\mu}(t) \|$ as:

$$< \underline{\mu}(t) > = Tr \, \| \underline{\mu} <\Upsilon(t)> \| \tag{6.168}$$

The density matrix is to be averaged over the random distribution $\frac{1}{\tau} e^{-\vartheta/\tau}\, d\vartheta$ of times $t_0 = t - \vartheta$ since the last collision, an obviously necessary procedure. Insofar as $\| \Upsilon \|$ is concerned, it certainly may be presumed dependent on the time of the last collision $t_0$ such that $\| \Upsilon \| = \| \Upsilon(t, t_0) \|$. In addition $\| \Upsilon(t, t_0) \|$ must satisfy Eq. (6.164) and Eq. (6.166) through:

$$\| \Upsilon(t_0, t_0) \| = \| \Upsilon_0(t_0) \| \tag{6.169}$$

Firstly then

$$\| <\Upsilon(t)> \| = \frac{1}{\tau} \int_0^\infty \| \Upsilon(t, t - \vartheta) \| \, e^{-\vartheta/\tau} d\vartheta \tag{6.170}$$

and since:

$$\left[ \frac{\partial}{\partial t} \| \Upsilon(t, t_0) \| \right]_{t_0 = t - \vartheta} = \frac{\partial}{\partial t} \| \Upsilon(t, t - \vartheta) \| + \frac{\partial}{\partial \vartheta} \| \Upsilon(t, t - \vartheta) \|$$

we may obtain from Eq. (6.170):

$$\begin{aligned}
\frac{\partial}{\partial t}\|<\Upsilon(t)>\| &= \int_0^\infty \left[\frac{\partial}{\partial t}\,\|\,\Upsilon(t,t_0)\,\|\right]_{t_0=t-\vartheta} \frac{e^{-\vartheta/\tau}}{\tau}\,d\vartheta - \int_0^\infty \frac{\partial}{\partial\vartheta}\|\,\Upsilon(t,t-\vartheta)\,\|\,\frac{e^{-\vartheta/\tau}}{\tau}\,d\vartheta \\
&= -\frac{i}{\hbar}\int_0^\infty [\|\,H(t)\,\|\,\|\,\Upsilon(t,t-\vartheta)\,\| - \|\,\Upsilon(t,t-\vartheta)\,\|\,\|\,H\,(t)\,\|]\,\frac{e^{-\vartheta/\tau}}{\tau}\,d\vartheta \\
&\quad - \|\,\Upsilon(t,t-\vartheta)\,\|\,\frac{e^{-\vartheta/\tau}}{\tau}\Bigg|_0^\infty - \frac{1}{\tau^2}\int_0^\infty \|\,\Upsilon(t,t-\vartheta)\,\|\,e^{-\vartheta/\tau}\,d\vartheta \\
&= -\frac{i}{\hbar}[\|\,H(t)\,\|\,\|<\Upsilon(t)>\| - \|<\Upsilon(t)>\|\,\|\,H(t)\,\|] - \frac{1}{\tau}[\|<\Upsilon(t)>\| - \|\,\Upsilon_0(t)\,\|]
\end{aligned} \tag{6.171}$$

by Eq. (6.164) and an integration by parts.

Next the transformation:

$$\|\,D(t)\,\| = \|\,<\Upsilon(t)>\,\| - \|\,\Upsilon_0(t)\,\| \tag{6.172}$$

may be introduced into Eq. (6.171). $\|\,D(t)\,\|$ is essentially a measure of the variation of the density matrix $\|\,\Upsilon(t)\,\|$ from a density matrix describing a condition of instantaneous thermal equilibrium.

Under this transformation Eq. (6.171) becomes:

$$\frac{\partial}{\partial t}\,\|\,D(t)\,\| = -\frac{i}{\hbar}\,[\|\,H(t)\,\|\,\|\,D(t)\,\| - \|\,D(t)\,\|\,\|\,H(t)\,\|] - \frac{1}{\tau}\,\|\,D(t)\,\| - \frac{\partial}{\partial t}\|\,\Upsilon_0(t)\,\| \tag{6.173}$$

Let us write out a typical matrix element of $\frac{\partial}{\partial t}\,\|\,D(t)\,\|$ from Eq. (6.173):

$$\frac{\partial}{\partial t}\,D_{mn} = -\frac{i}{\hbar}\sum_k\,[H_{mk}\,D_{kn} - D_{mk}\,H_{kn}] - \frac{i}{\tau}\,D_{mn} - \frac{\partial}{\partial t}\,(\Upsilon_0(t))_{mn} \tag{6.174a}$$

We may surely assume that $\|\,H_0\,\|$ has been diagonalized so that Eq. (6.174a) becomes:

$$\begin{aligned}
\frac{\partial}{\partial t}\,D_{mn} &= -\frac{i}{\hbar}\sum_k\,[H_{mk}{}^0\,D_{km}\,\delta_{mk} - D_{mk}\,H_{kn}{}^0\,\delta_{kn} + (V_{mk}\,D_{kn} - D_{mk}\,V_{kn})\cos\omega t] \\
&\quad - \frac{1}{\tau}\,D_{mn} - \frac{\partial}{\partial t}(\Upsilon_0\,(t))_{mn} \\
&= -\frac{i}{\hbar}(H_{mm}{}^0 - H_{nn}{}^0)\,D_{mn} + \cdots
\end{aligned}$$

$$\frac{\partial}{\partial t}\,D_{nm} = -\frac{i}{\hbar}(E_m{}^0 - E_n{}^0)\,D_{mn} - \frac{i}{\hbar}\sum_k\,[V_{mk}\,D_{kn} - D_{mk}\,V_{kn}] - \frac{1}{\tau}D_{mn} - \frac{\partial}{\partial t}\,(\Upsilon_0(t))_{mn} \tag{6.174b}$$

From Eq. (6.174b) we may obtain simply by rearrangement:

$$\frac{\partial}{\partial t} + i\omega_{mn} + \frac{1}{\tau}\, D_{mn}(t) = -\frac{\partial}{\partial t}\,(\Upsilon_0(t))_{mn} - \frac{i}{\hbar}\sum_k (V_{mk}\, D_{kn} - D_{mk}\, V_{kn}) \cos \omega t \tag{6.175}$$

This is the apropos point in the development for the introduction of necessary restriction to a weak incident radiation field. This approximation allows us to drop the summation on the right of Eq. (6.175) due to the resultant smallness of the $V_{nm}$. In addition, this assumption means that the density matrix $\| \Upsilon_0(t) \|$ should not be very different from the density matrix for an isolated molecule at temperature T. Now this latter density matrix is given by:

$$\| \Upsilon^{(0)} \| = C^{(0)} \| e^{-H_0/kT} \| \,;\; 1/C^{(0)} = Tr \| e^{-H_0/kT} \| \tag{6.176a}$$

and, since we have presupposed $\| H_0 \|$ diagonal:

$$\Upsilon_{mn}^{(0)} = \Upsilon_m^{(0)}\, \delta_{mn} \,;\; \rho_m^{(0)} = \frac{e^{-E_m/kT}}{Tr \| e^{-E_n/kT} \|} \tag{6.176b}$$

Karplus and Schwinger demonstrated the manner in which an operator of the form $\| e^{A+B} \| = \| e^{H(t)/kT} \|$ could be expanded in a series. The weakness of the field and the consequent smallness of the $V_{mn}$ was then their basis for cutting off this expansion after the second term with the result:

$$\left(e^{-H(t)/kT}\right)_{mn} = e^{-E_m/kT}\, \delta_{mn} + \frac{e^{-E_m/kT} - e^{-E_n/kT}}{E_m - E_n}\, V_{mn} \cos \omega t \tag{6.177a}$$

$$1/C = Tr \| e^{-H(t)/kT} \| + Tr \| e^{-H_0/kT} \| + \frac{1}{kT}\, Tr \| e^{-H_0/kT}\, \underline{\mu} \cdot \mathbf{F} \| \cos \omega t \tag{6.177b}$$

Finally, the utilization of Eqs. (6.176) and (6.177) in Eq. (6.166a) yields:

$$(\Upsilon_0(t))_{mn} = \Upsilon_m^{(0)}\, \delta_{mn} + (\Upsilon_m^{(0)} - \Upsilon_n^{(0)}) \frac{V_{mn}}{\hbar\omega_{mn}} \cos \omega t \tag{6.178}$$

The substitution of Eq. (6.178) into Eq. (6.175), recalling that the sum has been dropped in this latter equation, now results in:

$$\left(\frac{\partial}{\partial t} + i\omega_{mn} + \frac{1}{\tau}\right) D_{mn}(t) = \omega(\Upsilon_m^{(0)} - \Upsilon_n^{(0)})\, \frac{V_{mn}}{\hbar\omega_{mn}} \cos \omega t \tag{6.179}$$

An integrating factor may be utilized after the normal fashion to obtain the steady state solution to this first order equation as:

$$D_{mn}(t) = \frac{\omega}{\omega - \omega_{mn} + i/\tau}\, (\Upsilon_n^{(0)} - \Upsilon_m^{(0)})\, \frac{V_{mn}}{2\hbar\omega_{mn}}\, e^{-i\omega t}$$

$$+ \frac{\omega}{\omega - \omega_{mn} - i/\tau}\, (\Upsilon_n^{(0)} - \Upsilon_m^{(0)})\, \frac{V_{mn}}{2\hbar\omega_{mn}}\, e^{i\omega t} \tag{6.180}$$

To Eq. (6.180) we add $\| \Upsilon_0(t) \|$ as indicated by Eq. (6.172) to obtain:

$$<\Upsilon_{mn}(t)> = \Upsilon_m^{(0)}\,\delta_{mn} + \left(\frac{\omega}{\omega - \omega_{mn} + i/\tau} - 1\right)(\Upsilon_n^{(0)} - \Upsilon_m^{(0)})\,\frac{V_{mn}}{2\hbar\omega_{mn}}\,e^{-i\omega t}$$

$$+ \left(\frac{\omega}{\omega - \omega_{mn} - i/\tau} - 1\right)(\Upsilon_n^{(0)} - \Upsilon_m^{(0)})\,\frac{V_{mn}}{2\hbar\omega_{mn}}\,e^{i\omega t} \tag{6.181}$$

The simple substitution of Eq. (6.181) into Eq. (6.168) yields:

$$\mu(t) = \sum_{m,n} \underline{\mu}_{nm}\,\underline{\mu}_{mn}\cdot \mathbf{F}\,e^{-i\omega t}\left(1 - \frac{\omega}{\omega - \omega_{mn} + i/\tau}\right)\frac{\Upsilon_n^{(0)} - \Upsilon_m^{(0)}}{2\hbar\omega_{mn}}$$

$$+ \sum_{m,n} \underline{\mu}_{mn}\,\underline{\mu}_{nm}\cdot \mathbf{F}\,e^{i\omega t}\left(1 - \frac{\omega}{\omega - \omega_{mn} - i/\tau}\right)\frac{\Upsilon_n^{(0)} - \Upsilon_m^{(0)}}{2\hbar\omega_{mn}} \tag{6.182}$$

Now, due to the spherical symmetry of the isolated molecule, $\underline{\mu}_{nm}\,\underline{\mu}_{mn}\cdot\mathbf{F}$ may be replaced by $\frac{1}{3}\,\underline{\mu}_{nm}\cdot\underline{\mu}_{mn}\,\mathbf{F} = \frac{1}{3}\,|\,\underline{\mu}_{nm}\,|^2\,\mathbf{F}$. When the substitution has been made in Eq. (6.182) we may use the resulting equation and Eq. (6.165b) to obtain:

$$\chi = \sum_{m,n} \tfrac{1}{3}\,|\,\underline{\mu}_{mn}\,|^2\left(1 - \frac{\omega}{\omega - \omega_{mn} + i/\tau}\right)\frac{\Upsilon_n^{(0)} - \Upsilon_m^{(0)}}{h\omega_{mn}} + \cdots$$

$$= \sum_{m,n} \tfrac{1}{6}\,|\,\underline{\mu}_{mn}\,|^2\left(2 - \frac{\omega}{\omega - \omega_{mn} + i/\tau} + \frac{\omega}{\omega + \omega_{mn} + i/\tau}\right)\frac{\Upsilon_n^{(0)} - \Upsilon_m^{(0)}}{\hbar\omega_{mn}} \tag{6.183a}$$

from which:

$$\mathfrak{J}\,[\chi] = \sum_{m,n}\frac{1}{6h}\,|\,\underline{\mu}_{mn}\,|^2\,\frac{\omega}{\omega_{mn}}\left[\frac{1/\tau}{(\omega - \omega_{mn})^2 + 1/\tau^2} + \frac{1/\tau}{(\omega + \omega_{mn})^2 + 1/\tau^2}\right](\Upsilon_n^{(0)} - \Upsilon_m^{(0)}) \tag{6.183b}$$

Eqs. (6.183b) and (6.165a) then may be combined to give:

$$\alpha = \frac{2\pi}{3}\,\frac{\omega^2}{c}\,\frac{N}{kT}\sum_{m,n}|\,\underline{\mu}_{mn}\,|^2\left[\frac{1/\tau}{(\omega - \omega_{mn})^2 + 1/\tau^2} + \frac{1/\tau}{(\omega + \omega_{mn})^2 + 1/\tau^2}\right]\frac{1 - e^{-\hbar\omega_{mn}/kT}}{\hbar\omega_{mn}/kT}\,\Upsilon_n^{(0)} \tag{6.184}$$

This equation is generally the same as Eq. (6.107).

The Lorentz absorption coefficient equation has thus been afforded still another quantum justification* subject, of course, to the approximations introduced.

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* Jablonski has not commented.

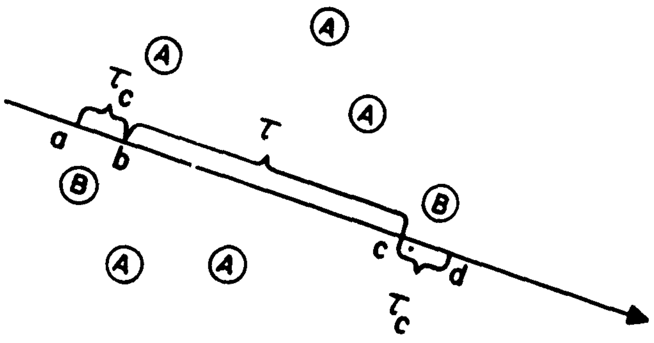

Fig. (6.1). A model of the physical conceptions inherent in the Weisskopf Interruption Theory.

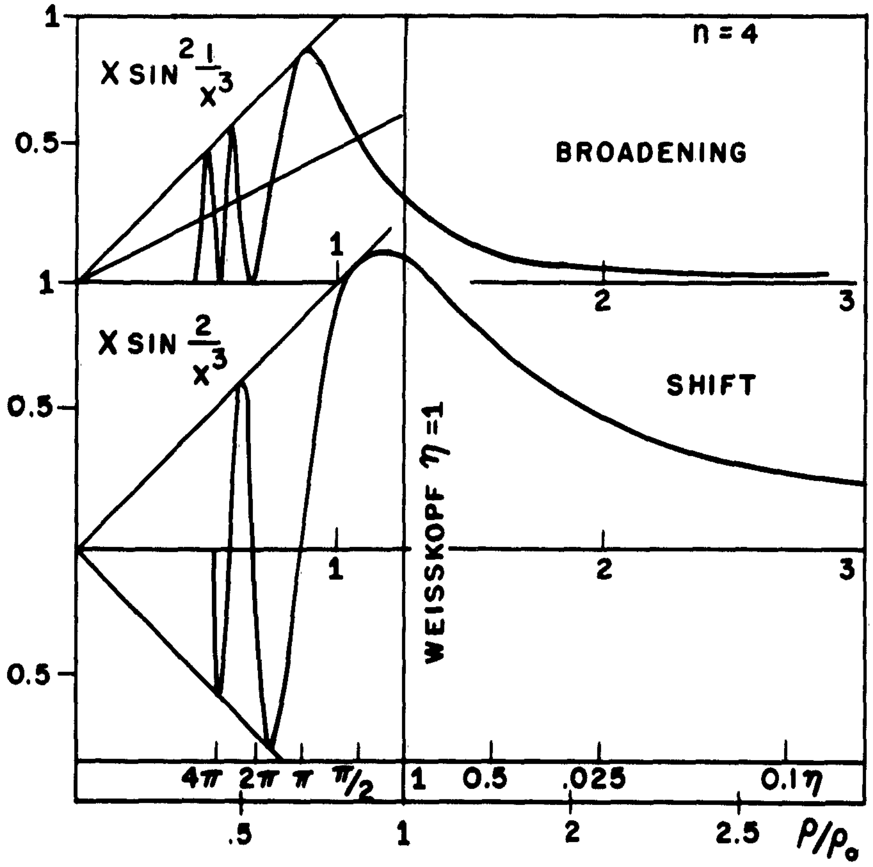

Fig. (6.2). The broadening and shift contributions with collision phase shift for n = 4. (After Unsold[203] and Lindholm.[102a])

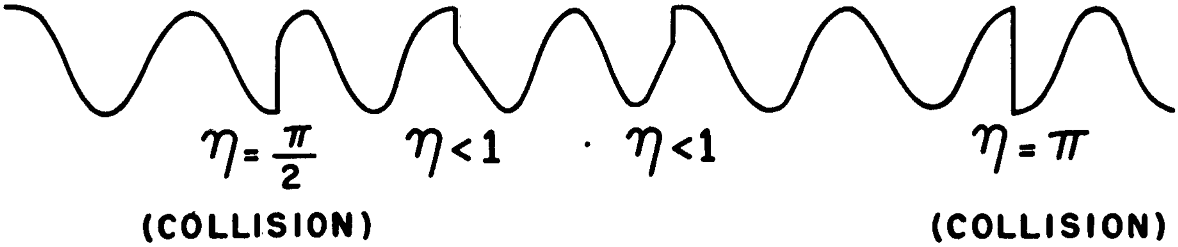

Fig. (6.3). An illustration of the phase shifts induced by collision. (After Unsold[203] and Lindholm.[102a])

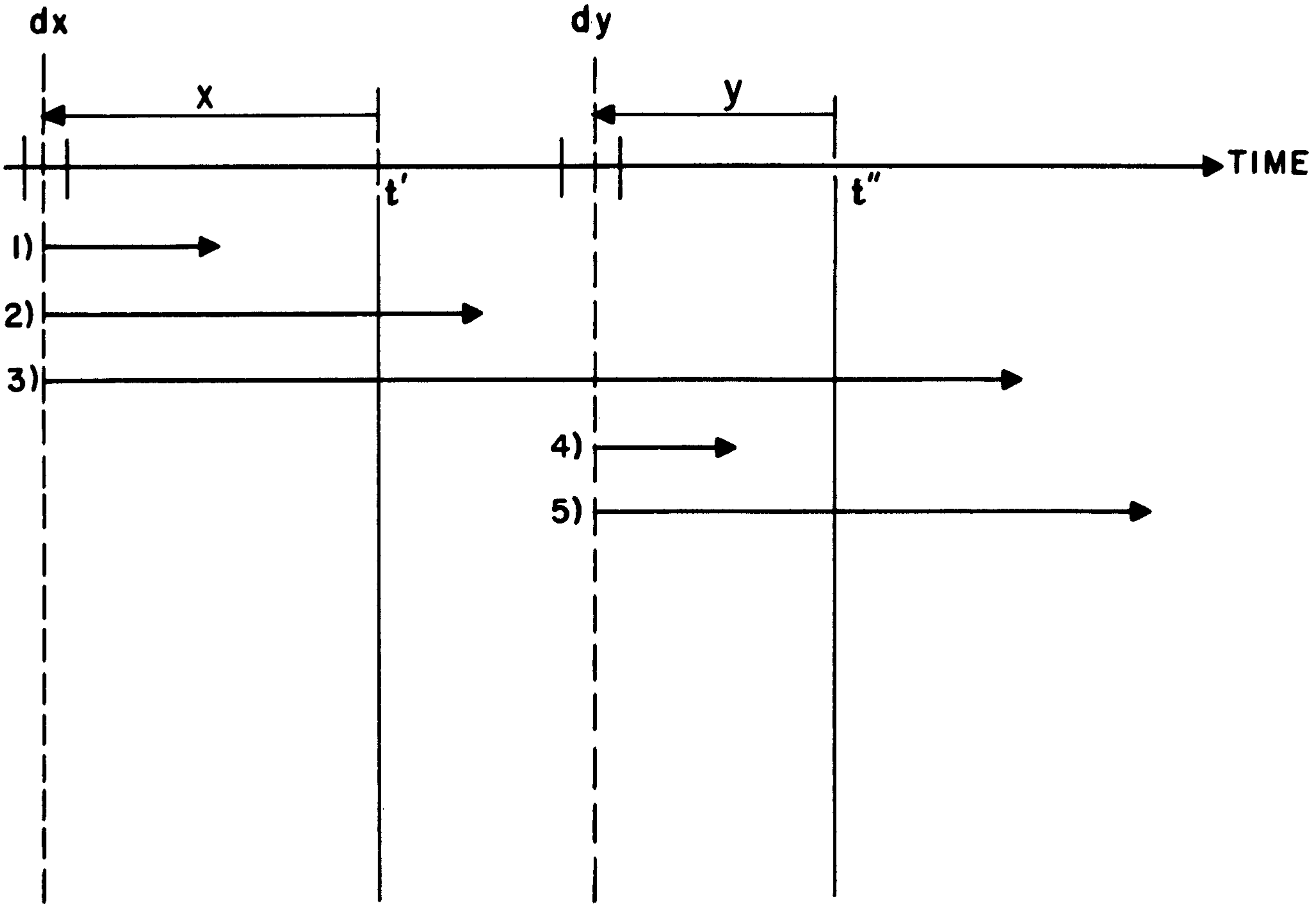

Fig. (6.4). Various possible collisions classifiable as to duration. (After Lindholm.[103])

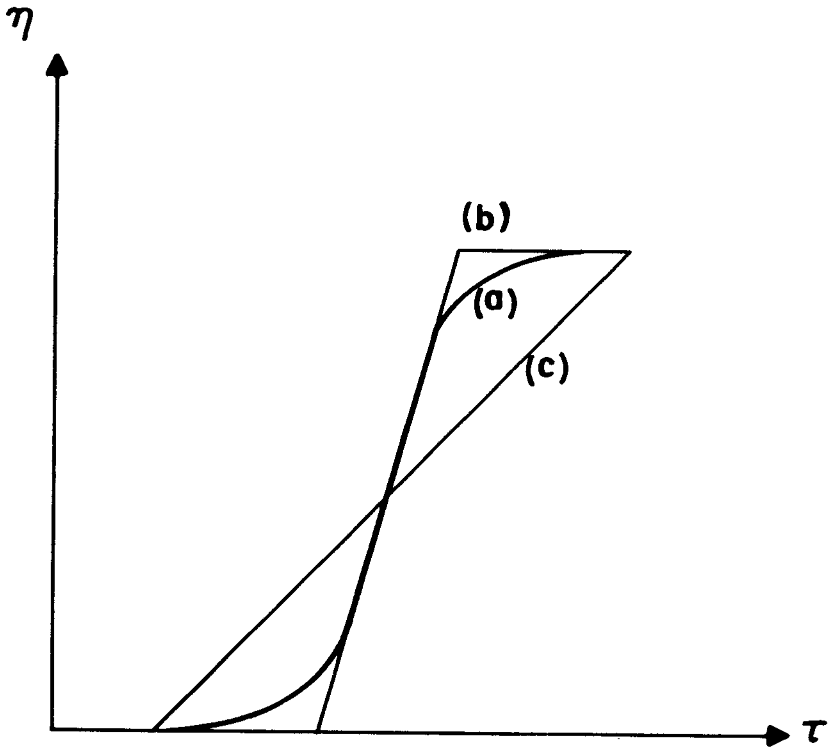

Fig. (6.5). The Lenz and Lindholm approximations of the course of the phase change. (After Lindholm.[103])

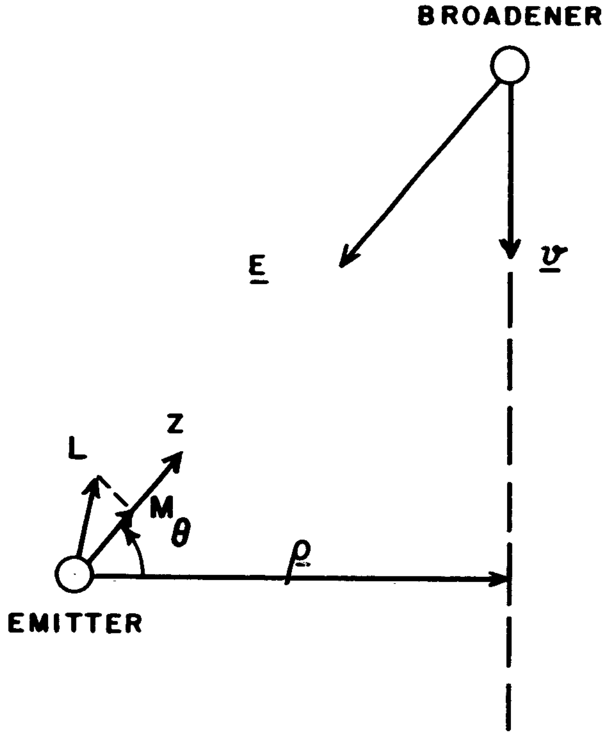

Fig. (6.6). Adiabaticity in Collisions. The angular momentum vector L has the allowed projection M on the Z-axis. The Z-axis orientation is determined by the radial electric field $\underline{E}$ of the broadener.

# CHAPTER 7

# RESONANCE BROADENING

We have considered the broadening of spectral lines resulting from the presence of other molecules in the neighborhood of the emitter only for those cases which arise when the broadening molecules are molecules of a different type than the emitter. As we have seen, this broadening by foreign gases arises from an interaction of, say, the Stark or van der Waals type between the emitter and broadener which results in the distortion of the energy levels of the former with the consequent spreading and shifting of the spectral line. We now devote our attention to the case of resonance or self broadening in which the width of the spectral line arises from the presence of molecules of the same type as the emitter. As was early recognized, this type of broadening is much stronger than that caused by foreign molecules. The reason for this greater broadening can be qualitatively understood either by considering the situation from a classical or quantum viewpoint.

## 7.1. THE QUALITATIVE BASIS OF SELF BROADENING

We have noted repeatedly that, excepting Doppler and natural line width, broadening is caused by an interaction between the emitting molecule and a neighbor. In the classical sense, the similar molecules of a radiating gas are made up of a collection of like oscillators of the same natural frequency. Due to the sameness of this natural frequency, a strong coupling of these oscillators may be expected to occur in the usual classical manner given some basic, say electrostatic, coupling force. This in turn will cause a spread of the coupled oscillator frequencies about the natural frequency of a single oscillator.

From a quantum mechanical sense, the same strong broadening can be inferred. Let us hypothesize a two molecule system in which the level degeneracy resulting from the sameness of the molecules results in an energy perturbation dependent on the inverse cube of the molecular separation. We recall that under the same interaction force two unlike molecules result in an inverse sixth power dependence on the molecular separation. Thus, obviously greater broadening will result from the presence of like molecules. We shall later discuss the reduction in state lifetime for the case of resonance broadening which results in a broadening of the spectral line, but the state degeneracy which we have mentioned above we shall allow to suffice as an introductory consideration.

## 7.2. THE HOLTSMARK THEORY OF COUPLED OSCILLATORS

The first attack on the problem of resonance broadening was made by Holtsmark[68] in 1925.* This author considered the problem from a classical point of view which depicted the molecules of the absorbing, self-broadening gas as classical oscillators.

Now we suppose a coupling force, dependent on the electric dipole moment of the molecules, to be present. Let us begin by considering two of these classical oscillators each consisting primarily of a "quasi-elastically bound" electron. If $x_1$ is the vibrational coordinate† of the first oscillator and $x_2$ that of the

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* At about the same time Mensing[126] attacked the problem on much the same general basis, utilizing the "old" quantum theory. Since little is to be gained by carrying through the problem using the "old" and then again using the "new" quantum theory, we shall begin our quantum theoretical considerations of the problem with the work of Frenkel[40] in 1930.

† Cf. *supra*, Sec. 2.2.

second, then the Lagrangian for the problem is surely:

$$L = T - V = (\tfrac{1}{2} m\dot{x}_1^2 + \tfrac{1}{2} m\dot{x}_2^2) - (\tfrac{1}{2} k_1 x_1^2 + \tfrac{1}{2} k_2 x_2^2 + k_3 x_1 x_2) \tag{7.1}$$

where, as usual, $k_1 = m\omega_1^2$ and $k_2 = m\omega_2^2$, $\omega_1$ and $\omega_2$ being the natural frequencies of the two oscillators which have now been coupled through $k_3$. We have assumed a quadratic potential energy expression, thus inferring harmonic oscillation. If we now apply Lagrange's equations we obtain:

$$m\ddot{x}_1 + m\omega_1^2 x_1 + k_3 x_2 = 0 \tag{7.2a}$$

$$m\ddot{x}_2 + m\omega_2^2 x_2 + k_3 x_1 = 0 \tag{7.2b}$$

Utilizing the standard assumptions $x_1 = c_1 e^{i\omega t}$ and $x_2 = c_2 e^{i\omega t}$ we obtain Lagrange's secular determinant:

$$\begin{vmatrix} \omega^2 - \omega_1^2 & -\dfrac{k_3}{m} \\ -\dfrac{k_3}{m} & \omega^2 - \omega_2^2 \end{vmatrix} = 0$$

which yields for the two frequencies of the now coupled oscillators:

$$\omega^2 = \frac{1}{2}\left(\omega_1^2 + \omega_2^2 \pm \sqrt{(\omega_1^2 - \omega_2^2) + 4\left(\frac{k_3}{m}\right)^2}\right) \tag{7.3}$$

If the two atoms are unlike then $|\omega_1^2 - \omega_2^2| \gg \frac{k_3}{m}$ and we obtain:

$$\omega^2 - \omega_{1,2}^2 = \pm \frac{k_3^2}{m^2(\omega_1^2 - \omega_2^2)} \tag{7.4}$$

whereas, in the case $\omega_1 = \omega_2 = \omega_0$ (like molecules), we obtain:

$$\omega^2 - \omega_0^2 = \pm \frac{k_3}{m} \tag{7.5}$$

A consideration of Eqs. (7.4) and (7.5) serves to illustrate the much larger frequency shift accompanying the coupling of like oscillators since $k_3$ is always small. This essentially forms the basis for Holtsmark's considerations. Let us first determine, with Holtsmark, $k_3$, and then proceed with the problem.

We have assumed our coupling force to arise from the electric dipole moments of the oscillators, and we now specify these moments by $\mathbf{p}_k(t) = ex_k$.

Eq. (4.19) may be rewritten slightly if we let the unit vector in the direction of $\mathbf{r}$ be given by $\mathbf{r}_0 = \frac{\mathbf{r}}{|\mathbf{r}|}$:

$$\mathbf{E}_i = \frac{1}{r^3}[\,\mathbf{p}_i - 3\mathbf{r}_0\,(\mathbf{r}_0 \cdot \mathbf{p}_i)] \tag{4.19}$$

which is the electric field at distance $r$ (in the direction of $\mathbf{r}_0$) due to the electric dipole $\mathbf{p}_i$. Then the potential due to the interaction of a dipole $\mathbf{p}_k$ at distance $r$ is:

$$V = \mathbf{E}_i \cdot \mathbf{p}_k = \frac{1}{r^3}[\mathbf{p}_i \cdot \mathbf{p}_k - 3(\mathbf{r}_0 \cdot \mathbf{p}_i)(\mathbf{r}_0 \cdot \mathbf{p}_k)] \tag{7.6a}$$

If we utilize the coordinates of Fig. (5.4) here, we obtain Eq. (5.1) from this. Eq. (7.6a) may be rewritten as:

$$V = \frac{e^2}{r^3}\,[r_i r_k \cos\gamma_{ik} - 3r_i r_k \cos\gamma_i \cos\gamma_k] \tag{7.6b}$$

In Eq. (7.6b) $r_i$ and $r_k$ are the axes of the dipoles of molecule one and molecule two respectively; $\gamma_{ik}$ is the angle between the two dipoles, and $\gamma_i$ and $\gamma_k$ are the angles between $\mathbf{r}$ and $\mathbf{p}_i$ and $\mathbf{p}_k$ respectively. Holtsmark assumed the special case $\mathbf{p}_i \parallel \mathbf{p}_k$ so that he obtained:

$$V = \frac{e^2}{r^3}\,[1 - 3\cos^2\gamma_{ik}]\,x_i x_k \tag{7.6c}$$

where $\gamma_{ik}$ is now the angle between either $\mathbf{p}_i$ or $\mathbf{p}_k$ and $\mathbf{r}$.

Then the force on molecule $i$ due to the field produced by molecule $k$ is, since $\mathbf{F} = -\nabla V$:

$$F = \frac{e w_{ik} p_k(t)}{r_{ik}^3} = \frac{e^2 w_{ik}}{r_{ik}^3}\,x_k$$

so that:

$$k_3 = \frac{e^2 w_{12}}{r_{12}^3}$$

We may let:

$$a_{ik} = \frac{e^2 w_{ik}}{m r_{ik}^3} \tag{7.7}$$

Now if we consider a system of $N_1$ atoms instead of our original two atomic system we may obtain, after the same fashion as we obtained Eq. (7.2), $N_1$ equations of the form:

$$\ddot{x}_i + \omega_0^2 x_i + \Sigma\, a_{ik} x_k = 0 \qquad \begin{array}{l} k \lessgtr i \\ i = 1, 2, \ldots, N_1 \end{array} \tag{7.8}$$

In arriving at Eq. (7.8) we must, of course, assume that all the atoms of our system are identical and, as a result, possess the same natural frequency.

From Eq. (7.8) we may obtain the secular determinant for the problem:

$$\begin{vmatrix} \Lambda & a_{12} & a_{13} & \ldots & a_{1N_1} \\ a_{21} & \Lambda & a_{23} & \ldots & a_{2N_1} \\ a_{31} & a_{32} & \Lambda & \ldots & a_{3N_1} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{N_1 1} & a_{N_1 2} & a_{N_1 3} & \ldots & \Lambda \end{vmatrix} = 0 \tag{7.9}$$

where the abbreviation $\Lambda = \omega^2 - \omega_0^2$ has been utilized.

To this point the development has been on quite firm ground, but Holtsmark's continuation of the problem has been seriously disputed by, among others, Weisskopf[204], Lenz[99], and Margenau and Watson.[200] The difficulty arises out of Holtsmark's attempts on the rather appalling determinant of Eq. (7.9).

Eq. (7.9) will have $N_1$ roots, the determinant resulting in an $N_1$-th order equation. The $N_1$ roots $\Lambda_r$ will be of the form:

$$\Lambda_r = \omega_r^2 - \omega_0^2 \tag{7.10}$$

Thus, the absorbing atoms are now capable of absorbing the $N_1$ frequencies $\omega_r$ instead of simply the natural frequency $\omega_0$ so that we obtain an absorption line of a definite width.

The equation resulting from the determinant of Eq. (7.9) will have no $\Lambda^{N_1-1}$ term. Now in an $N_1$-th order equation in which the coefficient of the $N_1$-th power term is unity the coefficient of the $(N_1 - 1)$-st power term is equivalent to the sum of the roots of the equation. This fact leads us to the conclusion that in this case:

$$\sum_{r=1}^{N_1} \Lambda_r = 0$$

In addition, the relations between the roots and coefficients of a polynomial are such that the coefficient of the $(N_1 - 2)$-rd power term is given by:

$$A_2 = -\sum_{\substack{i=1\\ i<k}}^{N_1} \sum_{k=2}^{N_1} \Lambda_i \Lambda_k = -\sum_{\substack{i=1\\ i<k}}^{N_1} \sum_{k=2}^{N_1} a_{ik}\, a_{ki} \tag{7.11}$$

The term on the extreme right of Eq. (7.11) is the coefficient of the $(N_1 - 2)$nd power term resulting from the expansion of the determinant.

A secular determinant arising from a vibrational problem of this nature is automatically symmetric since $a_{ik}$ and $a_{ki}$ are each equal to one half of the constant for some individual coordinate cross product term in the quadratic potential energy expression for the problem. Thus $a_{ik} = a_{ki}$.

Holtsmark now makes the assumption* that the summation over $a_{ik}a_{ki}$ in Eq. (7.11) may be replaced by an integration. When one considers the large number of molecules involved and the large distribution of $a_{ik}$ as given by Eq. (7.7) this would appear to be a reasonable assumption. Let us take the probability that $a_{ik}$ lies between $a_{ik}$ and $a_{ik} + da_{ik}$ in value as:

$$w(a_{ik})\, da_{ik}$$

Then if a random spatial distribution of the molecules is assumed:

$$w(a_{ik})\, da_{ik} = \frac{2\pi}{V}\, r^2 dr \sin \gamma_{ik}\, d\gamma_{ik} \tag{7.12}$$

where $\gamma_i$ and $\gamma_k$ are the angles between the axes of the $i$-th and $k$-th molecules and the line joining these molecules, respectively. We thus may take $\gamma_{ik}$ as the polar angle in our volume element. Since $a_{ik} = a_{ki}$ we may replace $a_{ik}a_{ki}$ by $a_{ik}^2$, and, when we integrate $a_{ik}$ and Eq. (7.12) over all space we will obtain the

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* Lenz[99] comments that "It is true that Holtsmark misled by a complex determinant scheme finds . . ." What Holtsmark finds is as yet of no great import, but the validity of this statement certainly is. If Holtsmark utilized assumptions whose invalidity is glaringly apparent or if an error appears in the development, the statement is, of course, justified. The converse follows. More important criticisms will be discussed later.

mean value of $a_{ik}^2$. Now there are $\frac{N_1(N_1-1)}{2} \doteq \frac{N_1^2}{2}$ of the $a_{ik}^2$ terms in Eq. (7.11) so that the results of this integration must be multiplied by $\frac{N_1^2}{2}$ to obtain $A_2$.

Thus:

$$A_2 \doteq -\frac{N_1^2}{2}\int w(a_{ik})\,a^2{}_{ik}\,da_{ik} = -\frac{N_1^2}{V}\frac{e^4\pi}{m^2}\int_{\gamma_0}^{\infty}\int_0^{\pi}\frac{(1-\cos^2\gamma_{ik})}{r_{ik}^4}\sin\gamma_{ik}\,d\gamma_{ik}\,dr_{ik}$$

$$= -\frac{8\pi}{15}\frac{e^4}{m^2}\frac{NN_1}{\rho_0^3} \tag{7.13}$$

since $V = \frac{N_1}{N}$. $\rho_0$ is here taken as the closest distance of approach of two molecular centers.

Since — as we have deduced from the fact that the equation resulting from the determinant has no $\Lambda^{N_1-1}$ term — the sum of the $\Lambda_\tau$ is zero, it is true that:

$$\sum_{i=1}^{N_1}\sum_{\substack{k=2\\ i<k}}^{N_1}\Lambda_i\Lambda_k = -\tfrac{1}{2}\sum_{\tau=1}^{N_1}\Lambda_\tau^2$$

Thus, according to Eq. (7.11) we may now write for Eq. (7.13):

$$\Sigma\,\Lambda_\tau^2 = \frac{16\pi}{15}\frac{e^4}{m^2}\frac{NN_1}{\rho_0^3} \tag{7.14}$$

According to Eq. (7.10) this becomes:

$$\frac{\Sigma\Lambda^2{}_\tau}{N_1} = <(w_\tau^2-\omega_0^2)^2> = \frac{16\pi}{15}\frac{e^4}{m^2}\frac{N}{\rho_0^3} \tag{7.15}$$

If we let $\omega - \omega_0 = \omega_\tau'$ then

$$\omega_\tau^2 - \omega_0^2 = \omega_\tau\omega_\tau' + \omega_0\omega_\tau' \doteq 2\omega_0\omega_\tau'$$

since we have assumed $(\omega_\tau - \omega_0) \ll \omega_0$. We now obtain from Eq. (7.15):

$$\sqrt{<\omega_\tau'^2>} = \sqrt{\frac{16\pi}{15}}\,\frac{e^2}{m}\,\frac{1}{\rho_0^{3/2}}\sqrt{N}\,\frac{1}{2\omega_0} \tag{7.16}$$

At this point Holtsmark makes the assumption that the distribution of $\omega_\tau'$ and hence the resulting intensity distribution in the spectral line is a Gaussian error curve. It is particularly with this assumption that Weisskopf[204] and later Margenau and Watson[200] find themselves in disagreement. In the development to this point there is no more basis for the choice of a Gaussian error curve than there is for any other reasonably conceivable curve. In addition, the experimental evidence does not provide much support for the assumption. Be this as it may, however, when this assumption is made there results:

$$W(\omega')d\omega' = \frac{1}{\sqrt{2\pi<\omega'^2>}}\,e^{-\omega'^2/<\omega'^2>}\,d\omega' \tag{7.17}$$

and for the half-width:

$$2\omega' = 2.36\sqrt{<\omega'^2>} = 103.5\times10^7\,\frac{\sqrt{N}}{\rho_0^{3/2}}\,\frac{1}{2\omega_0} \tag{7.18}$$

In essence, then, the theory yields a half-width which is directly proportional to "... the root of the number of absorbing centers ..." [68] and inversely proportional to a distance $\rho_0$ which is rather arbitrary and may be likened to the optical collision diameter of the Lorentz-Lenz-Weisskopf-etc. theory. This half-width is predicated on a line shape which could just as justifiably have been assumed at the beginning of the formulation as at the end.

The theory is certainly important, however, in that it provided the entree into the field of resonance broadening, and it can only be classified as unfortunate that the guardian inside the gate to this field was Eq. (7.9).

A few years after the presentation of this theory by Holtsmark, Frenkel[40] attacked the problem on the basis of the quantum theory, although the physical considerations were essentially the same.

## 7.3. QUANTUM RESONANCE IN BINARY INTERACTIONS

Let us begin, with Frenkel, by considering a system of two molecules. The interaction energy when the two molecules are unlike has already been given by Eq. (5.15). Now for the case of two like molecules, let us again use Holtsmark's potential $k_3x_1x_2$ for comparison. We find ourselves dealing with a case of quantum mechanical degeneracy.

Let us assume that one member of our two particle system will proceed from a state of energy $E_1$ to the ground state of energy $E_0$ with accompanying radiation. The two molecules of the system we designate as 1 and 2, and the eigenfunctions for the first molecule alone in the ground and first excited states as $\psi_0(1)$ and $\psi_1(1)$ respectively. Then, the unperturbed eigenfunction for the system in the ground state is:

$$\Psi_0 = \psi_0(1)\psi_0(2) \tag{7.19}$$

$\Psi_0$ is the eigenfunction going with the state having energy $E_0$. On the other hand, if the system is possessed of energy $E_1$, the eigenfunction may be:

$$\psi_{11} = \psi_1(1)\psi_0(2) \quad \text{or} \quad \psi_{21} = \psi_0(1)\psi_1(2)$$

Since either of these two eigenfunctions satisfies the Schrodinger equation for energy $E_1$, the eigenfunction for the state is a linear combination of the two possibilities:

$$\Psi_{1j} = c_1\psi_{11} + c_2\psi_{21} = \sum_{j'} c_{1j'}\psi_{1j'} \tag{7.20}$$

In addition, the two states $\psi_{11}$ and $\psi_{21}$ of equal energy indicate that a quantum degeneracy problem* has arisen, and Eq. (4.147) yields two equations for the $c_{1j'}$. These equations have a solution, according to Cramer's rule, only if:

$$\begin{vmatrix} E_1^{(1)} - H_{11}' & -H_{12}' \\ -H_{12}' & E_1^{(1)} - H_{22}' \end{vmatrix} = 0 \tag{7.21}$$

$H_{11} = H_{22} = 0$ so that:†

$$E_1^{(1)} = \pm H'_{12} \tag{7.22}$$

We substitute Eq. (7.22) into an equation of the form Eq. (4.147) to obtain:

$$c_{11} = \pm c_{12}$$

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* See *supra*, Sec. 4.17.

† Cf. *supra*, Eq. (5.1).

so that Eq. (7.20) becomes:

$$\Psi_{1_s} = c_{11}\psi_{11} + c_{11}\psi_{21} \tag{7.23a}$$

$$\Psi_{1_a} = c_{11}\psi_{11} - c_{11}\psi_{21} \tag{7.23b}$$

To find $c_{11}$ we normalize Eq. (7.23a):

$$c_{11}^2\int|\psi_{11}|^2d\tau + c_{11}^2\int|\psi_{21}|^2d\tau + 2c_{11}^2\int\psi_{11}\psi_{21}d\tau = c_{11}^2 + c_{11}^2 + 0 = 1$$

due to the orthonormality of the original eigenfunctions. From this, it is apparent that $c_{11} = 1/\sqrt{2}$.

An inspection of Eq. (7.23a) shows it to be symmetric with respect to exchange of the two molecules while Eq. (7.23b) is antisymmetric. In the case of electric dipole radiation in which the transition proceeds from state one to the ground state the matrix element is:

$$M_{10} = \int \overline{\Psi}_1\mathbf{M}\Psi_0 d\tau \tag{7.24}$$

$\Psi_0$ has been given by Eq. (7.19) and is symmetrical with respect to an exchange of the two molecules, as is also the electric dipole moment in this case. Since an integrand is nothing more nor less than a number after integration, it must surely be symmetrical. On this basis we throw out Eq. (7.23b) and merely retain (7.23a).

We have thus found our first excited state eigenfunction for the system. The first order energy is given by:

$$\begin{aligned} E_1^{(1)} &= \int \overline{\Psi}_{1_s} H'\Psi_{1_s}d\tau \\ &= k_3\int x_1x_2\,\overline{\psi_1(1)\psi_0(2)}\,\psi_0(1)\psi_1(2)d\tau_1d\tau_2 \\ &= +\,k_3\,|x_{01}|^2 \end{aligned} \tag{7.25}$$

Eq. (7.25) tells us that the presence of one molecule shifts the spectral line by the amount:

$$\nu' = +\frac{k_3}{m}|x_{01}|^2 \tag{7.26a}$$

Let us rewrite Eq. (7.5) slightly for comparison:

$$\omega - \omega_0 = \pm\frac{k_3}{(\omega + \omega_0)m} \doteq \pm\frac{k_3}{2\omega_0 m}$$

or

$$\nu' \doteq \pm\frac{k_3}{8\pi^2 m\nu_0} = \pm\frac{e^2}{r^3}\frac{(1 - \cos^2\gamma)}{8\pi^2 m\nu_0} \tag{7.26b}$$

The quantum mechanical equation (7.26a) apparently yields one shifted frequency, but we shall see that when the different possible values of the magnetic quantum number are considered two frequencies will result.

Under the assumption in $k_3$ that:

$$<(1 - 3\cos^2\gamma)^2> = 1 - <6\cos^2\gamma> + <9\cos^4\gamma> = 1 - 2 + \frac{9}{5} = \frac{4}{5}$$

Frenkel obtains for the root mean square value of $\nu'$:

$$\sqrt{<\nu'^2>} = \frac{2}{\sqrt{5}}\frac{e^2}{r^3}\frac{|x_{10}|^2}{h} \tag{7.27}$$

In addition, Frenkel utilizes the more exact expression Eq. (7.6a) instead of Eq. (7.6c) for $V$ to obtain:

$$\sqrt{<\nu'^2>} = \sqrt{\frac{2}{3}}\,\frac{1}{r^3}\,\frac{|\mathbf{p}_{10}|^2}{h} \tag{7.28}$$

As Margenau and Watson[200] have done, we may also use Eq. (5.1) for $V$. If we take hydrogen-like wave functions and use precisely the method of calculation which we have utilized in obtaining Eq. (7.25) we obtain for $E_1$:

$$E_1^{(1)} = h\nu' = \begin{cases} -\dfrac{2}{3}\dfrac{e^2}{r^3}|r_{12}|^2 \text{ for } m = 0 \\[2ex] +\dfrac{1}{3}\dfrac{e^2}{r^3}|r_{12}|^2 \text{ for } m = \pm 1 \end{cases} \tag{7.29a}$$

where, as usual, $m$ is the magnetic quantum number, and where:

$$|r_{12}|^2 = \frac{3h}{8\pi^2 m\nu_0} f_{12}$$

so that:

$$\nu' = \begin{cases} -\dfrac{e^2}{r^3}\dfrac{2}{8\pi^2 m\nu_0} f_{12} \quad \text{for} \quad m = 0 \\[2ex] +\dfrac{e^2}{r^3}\dfrac{1}{8\pi^2 m\nu_0} f_{12} \quad \text{for} \quad m = \pm 1 \end{cases} \tag{7.29b}$$

which compares at least reasonably well with Eq. (7.26b), although the symmetry is obviously lacking.

## 7.4. THE STATISTICAL RESONANCE RESULT

Eq. (7.29b) may be rewritten as:

$$\mathrm{E}^{(1)} = h\nu' = \gamma\left(\frac{e^2 h f_{12}}{8\pi^2 m\nu_0}\right)\frac{1}{r^3} \tag{7.30'}$$

where $\gamma$ is the statistical weight factor associated with $m$. After the fashion of Margenau and Watson,[200] let us equate $\gamma$ to unity. We consider this an averaging process over the possible molecular orientations.[*] The result is:

$$V = E^{(1)} = cr^{-m} = \left(\frac{e^2 h f_{12}}{8\pi^2 m\nu_0}\right) r^{-3} \tag{7.31a'}$$

so that:

$$c = \frac{e^2 h f_{12}}{8\pi^2 m\nu_0} \tag{7.31b'}$$

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[*] Cf. *supra*, Eqs. (5.14) and subsequent.

From Eq. (5.126b) the half width of the resonance broadened spectral line is:

$$\delta = \frac{2V_0}{h} = \frac{4}{3}\frac{\pi^2}{h}Nc$$

so that:

$$\delta = \frac{e^2 f_{12}}{6m\nu_0}N \tag{7.32'}$$

Eq. (7.32′) was originally obtained by Margenau and Watson[200] in a slightly different manner.

## 7.5. RESONANCE BROADENING BY MANY MOLECULES (FRENKEL)

Let us now turn our attention, with Frenkel, to a system of $N_1$ like molecules. Again we are only interested in the ground state for the system in which none of the $N_1$ molecules is excited and the first excited state for the system in which one of the $N_1$ molecules is excited. Our first excited state eigenfunction is given by Eq. (7.20), and the $c_{jn}$ are given by $N_1$ equations of the form Eq. (4.147). In Eq. (4.147)— again utilizing Eq. (7.6c) for $V$— the $H'_{lj}$ are given by:

$$H_{lj}' = \sum_{\substack{l' \\ l'<j'}}\sum_{j'} k_{l'j'} \int \ldots \int x_{l'}\, x_{j'}\, \psi_{l'}\, \psi_{j'}\, d\tau_1 \ldots d\tau_{N_1} \tag{7.30a}$$

where here $H' = \sum\limits_{l<j} k_{lj}\, x_l\, x_j$.

It would appear to be worthwhile from the point of view of clarity to illustrate this equation with an example.

Let us suppose that we have a three molecular system, and let the eigenfunctions for the three molecules in the ground state be given by $\psi_1(0)$, $\psi_2(0)$, and $\psi_3(0)$. In the first excited state we shall replace 0 by 1. Then the first excited state for the system must be a linear combination of the following functions:

$$\begin{aligned} \psi_1 &= \psi_1(1)\ \psi_2(0)\ \psi_3(0) \\ \psi_2 &= \psi_1(0)\ \psi_2(1)\ \psi_3(0) \\ \psi_3 &= \psi_1(0)\ \psi_2(0)\ \psi_3(1) \end{aligned} \tag{7.31}$$

From Eq. (7.31) we may obtain Eq. (7.30a) for this case as, for example:

$$\begin{aligned} H_{12}' &= \int\ (k_{12}x_1x_2 + k_{13}\, x_1\, x_3 + k_{23}\, x_2\, x_3)\, \psi_1\, \psi_2\, d\tau_1\, d\tau_2\, d\tau_3 \\ &= k_{12} \int\ x_1\, \psi_1(1)\, \psi_1(0)\, d\tau_1\ \int x_2\, \psi_2(0)\, \psi_2(1)\, \mathrm{d}\tau_2 \int \psi_3(0)\, \psi_3(0)\, d\tau_3 \\ &\qquad + k_{13} \int x_1\, \psi_1(1)\, \psi_1(0)\, d\tau_1 \int \psi_2(0)\, \psi_2(1)\, d\tau_2 \int x_3\, \psi_3(0)\, \psi_3(0)\, d\tau_3 \\ &\qquad + k_{23} \int \psi_1(1)\, \psi_1(0)\, d\tau_1 \int x_2\, \psi_2(0)\, \psi_2(1)\, d\tau_2 \int x_3\, \psi_3(0)\, \psi_3(0)\, d\tau_3 \\ &= k_{12}\, |x_{10}|^2 + 0 + 0 = k_{12}\, |x_{10}|^2 \end{aligned} \tag{7.32}$$

In general, Eq. (7.30a) may be written:

$$H_{lj}' = k_{lj}|x_{10}\,|^2 \tag{7.30b}$$

Now let us rewrite Eq. (7.8) under the assumption that $x_i = x_i e^{i\omega t}$ — the assumption which leads to the secular determinant.

$$(\omega^2 - \omega_0^2)\, x_l = \frac{1}{m}\, \Sigma k_{lj}\, x_j$$

or:

$$(\nu - \nu_0) x_l \doteq \frac{1}{8\pi^2 m \nu_0}\, \Sigma k_{lj}\, x_j \tag{7.33}$$

Eq. (7.33) is the classical analog of Eq. (4.147) in the same fashion as Eq. (7.26b) is the analog of Eq. (7.26a).

Frenkel used this analogy as his basis for replacing $\frac{1}{8\pi^2 m\nu_0}$ by $\frac{1}{h}\, |x_{10}|^2$ in Eq. (7.16) to obtain the quantum mechanical equivalent of this equation:

$$\sqrt{<\nu'^2>} = 4\sqrt{\frac{\pi}{15}}\, \frac{\sqrt{N}}{\rho_0^{3/2}}\, \frac{e^2\, |x_{10}|^2}{h} \tag{7.34a}$$

Frenkel also uses Eq. (7.6a) instead of Eq. (7.6c) to obtain:

$$\sqrt{<\nu'^2>} = \frac{2}{3}\sqrt{\frac{2\pi N}{\rho_0^3}}\, \frac{1}{h}\, |\mathbf{p}_{10}|^2 \tag{7.34b}$$

Even if Eq. (7.34b) holds without question we still have no information about the half-width, since the assumption of the Gauss error curve is not very well justified. Eq. (7.34b) does not hold without question, however, as we may now show.

We have $N_1$ eigenfunctions of the form Eq. (7.20) for the first excited state of the system. We have one eigenfunction for the ground state. The probability of a transition from a state going with one of these $N_1$ eigenfunctions and the ground state is given by the square of the matrix element of the electric dipole moment. Thus, in order to find the root mean square frequency shift, the proper weights must be given to each of these shifts. The intensity distribution also would result from the calculation of these weighted eigenvalues which, as in Eq. (7.29a), would each have three different values according as $m = 0, \pm 1$. Frenkel did launch an attack on this problem, but with no notable success.

The question of resonance broadening is again confronted by the obstacle presented to progress by Eq. (7.9).

Whether or not the methods used by Holtsmark and Frenkel to obtain their results are correct, the results themselves as given by Eqs. (7.15) and (7.31) are open to serious question in that these equations claim a dependence of the half-width on the root of the density. A consideration of these equations will probably indicate to the reader, however, that $\rho_0$ offers a bonnet out of which we might possibly produce a different pressure dependence. This is admittedly a posteriori reasoning, since Schutz-Mensing[160] (nee Mensing) has done just this.

## 7.6. A LINEAR RELATION BETWEEN HALF-WIDTH AND DENSITY

From Eq. (7.11) and the fact that $2\omega_0\omega_r' \doteq \omega_r^2 - \omega_0^2$ we may write:

$$\tfrac{1}{2}\Sigma\, 4\omega_0^2\, \omega_r'^2 = \left(\frac{e^2}{m}\right)^2 \sum_{i\neq k} b_{ik}^2 \tag{7.35a}$$

where $b_{ik} = \dfrac{(1 - 3\cos^2\gamma_{ik})}{r^3_{ik}}$. Eq. (7.35a) may be rewritten as:

$$\Sigma\, \omega_r'^2 = \frac{2}{4\omega_0^2}\left(\frac{e^2}{m}\right)^2 \sum_{i\neq k} b_{ik}^2$$

or:

$$<\nu'^2> = \frac{\Sigma \nu_r'^2}{N} = \frac{2}{4(2\pi)^4\,\nu_0^2}\left(\frac{e^2}{m}\right)^2 \frac{1}{N}\sum_{i\neq k} b_{ik}^2 \tag{7.35b)*$$

Now we recall that Holtsmark replaced the sum in Eq. (7.35b) by a weighted integration over $b_{ik}^2$ Schutz-Mensing considers only the $i$-th molecule initially and replaces the summation over $k$ by an integration and multiplication by $N_1$, there now being $(N_1 - 1)$ instead of $N_1(N_1 - 1)/2$ terms.
As in Eq. (7.13):

$$\sum_k a^2_{ik} \doteq 2\pi\, \frac{N_1}{V}\int\limits_{\rho_i}^{\infty}\int\limits_{0}^{\pi} \frac{1}{r_i^4}\,(1 - 3\cos^2\gamma_i)^2 \sin\gamma_i\, d\gamma_i\, dr_i = \frac{16\pi}{15}\,\frac{N}{\rho_i^2} \tag{7.36}$$

We may note that the lower limit has been designated by $\rho_i$. $\rho_i$ is taken as the separation of the $i$-th molecule and the closest adjoining molecule, and is hence a variable. Finally, Schutz-Mensing takes the average $\rho_i$ to obtain the complete summation in Eq. (7.35b).

$$\sum_{ik} b_{ik}^2 \doteq (\tfrac{1}{2})\,\frac{16\pi}{15}\,\frac{NN_1}{<\rho>^3} \tag{7.37)†$$

In her earlier work, Schutz-Mensing had calculated a value $0.55N^{-1/3}$ for $<\rho>$. Thus, Eq. (7.35b) becomes:

$$<\nu'^2> = \frac{16\pi}{15}\, 6\, \frac{1}{4(2\pi)^4\nu_0^2}\left(\frac{e^2}{m}\right)^2 N^2 \tag{7.35c}$$

Thus, it is apparent that, should we now use Eq. (7.18) for the half-width, we would obtain a linear dependence on the density.

She also carried through a calculation in which an integration is carried out over the probability that $\rho$ lies between $\rho$ and $\rho + d\rho$ to obtain:

$$\Sigma\, b_{ik}^2 = -\frac{64}{15}\,\pi^2 N^2 N_1 \left[ - c - \log\left(\frac{4\pi}{3}\,\rho_0^3 N\right)\right] \tag{7.38}$$

where the bracketed term is the first term in the expansion of the exponential integral $Ei\left(-\dfrac{4\pi}{3}\,\rho_0^3\, N\right)$.

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* A minor point to the effect that Schutz-Mensing left out the 2 in the numerator of this equation might be mentioned.

† Schutz-Mensing does not obtain the factor 1/2, but since there are only a total of $N_1^2/2$ terms arising out of the summation over $b$, it would seem paradoxical to end by obtaining a total of $N_1$. This appears true even though, when only the latter portion of Eq. (7.36) is considered, there do remain $(N_1 - 1)$ to occupy the space point a distance $\rho_i$ from the $i$-th molecule. It should finally be noted that the two in the numerator of Eq. (7.35b) and the one-half in Eq. (7.37) do combine to yield Eq. (7.18) with $\rho_0$ replaced by $<\rho>$.

After the Frenkel manner, Schutz-Mensing next considered the replacement of $\frac{1}{8\pi^2 \nu_0 m}$ by the square of the matrix element divided by $h$ to obtain the "corresponding" quantum mechanical cases.

The lack of success attendant on the method of attack utilized by Holtsmark[68] and Frenkel[40] was perhaps the reason that Weisskopf[193] considered the problem from a different viewpoint. As has been mentioned previously, Weisskopf objected to Holtsmark's use of a Gaussian error curve with the resulting relation between the half-width and the mean square of the deviation $<\Delta\omega^2>$. He pointed out that in the case of an intensity distribution of the form $\frac{\gamma}{\pi}\frac{1}{(\Delta\omega)^2+\gamma^2}$ the half-width is $\gamma$ but $<\Delta\omega^2>$ is infinite. In addition, Weisskopf felt that Holtsmark should have included the natural width, although it should be mentioned that above pressures of a few millimeters this would not be of too great import.

## 7.7. THE WEISSKOPF RESONANCE BROADENING THEORY

Let us first obtain the Lorentz-Lorenz relation. From Maxwell's equations we obtain the following relation between the electric displacement $D$, the electric field $E$, and the polarization $I$:

$$D = \epsilon E = E + 4\pi I \tag{7.39a}$$

where $\epsilon$ is the dielectric constant for the medium. Now the force on a unit charge in a polarizable medium may be shown to be:

$$F = E + 4\pi I \tag{7.39b}$$

If the polarizability of a molecule is $\alpha$, then the induced electric dipole moment of the molecule is:

$$p = \alpha F \tag{7.39c}$$

From Eq. (7.39c) the polarization or the electric moment per unit of volume is:

$$I = Np = N\alpha F = N\alpha\left(E + \frac{4\pi}{3} I\right) \tag{7.40}$$

where $N$ is the number of molecules per unit of volume. If we eliminate $I$ between Eqs. (7.39a) and (7.40) we obtain the Lorentz-Lorenz relation:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} N\alpha \tag{7.41a}$$

or, if we recall that the dielectric constant for a medium is the square of the refractive index:

$$\frac{n_c^2 - 1}{n_c^2 + 2} = \frac{4}{3}\pi N\alpha \tag{7.41b}$$

where $n_c = n(1 + i\kappa)$.

Weisskopf asserted that the "... width is given completely by the course of the absorption coefficient $n$ ..."[193] in Eq. (7.41b), and he based this assertion on the manner of the development of this equation by

Oseen,[140] Ewald,[34] and Bothe.[14] These authors had treated the molecules of a gas as classical oscillators and had obtained the equation in question after a computation in which the "reciprocal effect" of the oscillators on one another had been included. Thus, Weisskopf felt that Eq. (7.41b) included the coupling effect.

Now let us make the usual approximation to the effect that in our gas $n_c \doteq 1$ and $n_c^2 - 1 \doteq 2(n_c - 1)$ so that Eq. (7.41b) becomes:

$$n_c - 1 \doteq 2\pi N\alpha \tag{7.41c}$$

Next, we must needs find $N\alpha$, and, since $\alpha E = \Sigma e x_k$, $N\alpha$ is given by:

$$N\alpha = \frac{N}{E}\Sigma\, e x_k \tag{7.42}$$

We set up Newton's equation for the amplitude $x_k$ under the assumption that the electron of mass $m$ possesses the natural frequency $\omega_0$, is subject to a velocity proportional damping force, the constant of proportionality being $m\gamma$, and is acted upon by a force $eE$ due to the presence of the electric field $E$. The resulting equation is:

$$m\ddot{x}_k = - m\gamma\dot{x}_k - m\omega_0^2 x_k + eE \tag{7.43}$$

If we suppose the time dependent portion of $x_k$ to be the same as that of $E$, the solution of Eq. (7.43) for the time independent portion of the amplitude is:

$$x_k = \frac{e}{m}\frac{E_0}{\omega_k^2 - \omega^2 + i\omega\gamma} \doteq \frac{e}{m\omega_k}\frac{E_0}{\omega_k - \omega + i\gamma}$$

so that:

$$N\alpha = \frac{Ne^2}{m\omega_0}\frac{1}{\omega_0 - \omega + i\gamma}f_{nm} \tag{7.44}$$

Here $f_{mn}$ is the so-called oscillator strength for the transition from level $m$ to level $n$. In this case $f_{mn}$ will give the number of dispersion electrons belonging to the transition under consideration. From Eqs. (7.41c) and (7.44c) we obtain:

$$n_c = 1 + \frac{2\pi Ne^2}{m\omega_0}\frac{1}{\omega_0 - \omega + 2\gamma}f_{mn} \tag{7.45}$$

$n\kappa$ is the imaginary part of Eq. (7.45) so that:

$$n\kappa = - \frac{2\pi Ne^2\gamma}{m\omega_0}\frac{1}{(\omega_0 - \omega)^2 + \gamma^2}f_{mn} \tag{7.46}$$

$\gamma$ may be considered as $\gamma_1 + \gamma_2$ where $\gamma_1$ and $\gamma_2$ are the radiation and collision damping respectively. We may neglect $\gamma_2$ in the case of very low pressures to simply obtain the effects of the natural line width. We again consider Eq. (7.41). This may be rewritten as:

$$n_c^2 - 1 = \frac{4\pi N\alpha}{(1 - \frac{4}{3}\pi N\alpha)} \tag{7.47}$$

where we have not assumed $n \doteq 1$. If we substituted the value of $N\alpha$ from Eq. (7.44) into Eq. (7.47) and let $A = \frac{Ne^2}{m\omega_0} f_{mn}$ we obtain:

$$n_c^2 - 1 = \frac{4\pi A}{\omega_0 - \omega - \frac{4}{3}\pi A + i\gamma} \tag{7.48}$$

If:

$$B = 4\pi A \ ; \ \bar{\omega}_0 = \omega_0 - \frac{4}{3}\pi A \ ; \ \overline{\Delta\omega} = \omega - \omega_0 \tag{7.49a}$$

Eq. (7.48) becomes:

$$n_c^2 = x + iy = \frac{(-\overline{\Delta\omega} + i\gamma + B)(\overline{\Delta\omega} + i\gamma)}{(\overline{\Delta\omega})^2 + \gamma^2} \tag{7.50}^*$$

If the transformation:

$$b = \frac{B}{\gamma} \ ; \ \Delta = \frac{\overline{\Delta\omega}}{\gamma} \tag{7.49b}$$

is utilized in Eq. (7.50) the result is:

$$n_c^2 = x + iy = -\frac{(-\Delta + b + i)(\Delta + i)}{\Delta^2 + 1} \tag{7.51}$$

The imaginary part of the root of $n_c^2$ is $n\kappa$, and this is desired. It may be recalled that:

$$\sqrt{n_c^2} = r^{1/2} e^{i\left(\frac{\vartheta + 2k\pi}{2}\right)}$$

where:

$$r = \sqrt{x^2 + y^2} \ ; \ \vartheta = \text{arc tan} \frac{y}{x}$$

Thus, we may obtain from Eq. (7.51):

$$n\kappa = \mathfrak{J}\sqrt{n_c^2} = \sqrt[4]{\frac{(\Delta - b)^2 + 1}{\Delta^2 + 1}} \sin\left\{\frac{1}{2}\arctan\left(\frac{b}{(\Delta - b)\Delta + 1}\right)\right\} \tag{7.52}^\dagger$$

for the absorption coefficient.

For the case $\Delta \gg b$, that is, in the wings of the spectral line, Eq. (7.52) reduces to Eq. (7.46).

It might be mentioned at this point that our half-width as given by $\gamma_1 + \gamma_2$ will be directly proportional to the pressure — above those pressures at which $\gamma_1$ noticeably affects the sum — through $\gamma_2$. In this theory, which is directly connected to Weisskopf's foreign gas broadening theory,** the optical collision diameter must be taken a good bit larger than in the case of foreign gas broadening. As an example Weisskopf estimated a value of 44A for the optical collision diameter in the case of the $Na$-$D_1$ line.

Weisskopf himself was not very happy about the results of his considerations for in the final analysis he was forced to ignore the coupling of the atoms " . . . since for the present no way to treat (this) is

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* Weisskopf gave $(\overline{\Delta\omega} + i\gamma + B)$ instead of $(-\overline{\Delta\omega} + i\gamma + B)$ in his first paper[193] but corrected it in his second.[193a]

† Weisskopf obtained $(\Delta + b)^2 + 1$ under the root instead of $(\Delta - b)^2 + 1$ in his first paper.[193]

** See *supra*, Chap. 7.

apparent . . ."[193] As we have mentioned Weisskopf's main conclusion is his assumption that ". . . the collisions cause an enlargement in the damping of the individual oscillators . . .,"[193] an enlargement of greater magnitude than in the case of foreign gas broadening.*

We may write out our half width for purposes of consideration if we let the mean free path as given by Eq. (1.13) be $l$:

$$\delta = \gamma = \frac{2}{\tau} = \frac{<v>}{l} = 2\pi\rho^2 <v> N \tag{7.53}$$

where $<v>$ is taken by Weisskopf as the mean relative velocity. We have here the optical collision diameter as an essentially unknown and conveniently adjustable parameter. We may calculate a value for it, however, if we again assume† that a phase change of unity defines an optical collision. Eq. (6.7) may be written for this case as:

$$\Delta(r) = \Delta(\sqrt{v^2t^2 + \rho^2}) = \frac{K}{r^3}\ ;\ \Theta = \int_{-\infty}^{+\infty} \frac{Kdt}{(v^2t^2 + \rho^2)^{3/2}} \sim 1 \tag{7.54a}$$

Now if we let $dx = vdt/\rho$ we obtain from Eq. (7.53):

$$K\int_{-\infty}^{+\infty} \frac{\rho dx}{\rho^3 v(x^2 + 1)^{3/2}} = \frac{K}{v\rho^2}\int_{-\infty}^{+\infty} \frac{dx}{(x^2 + 1)^{3/2}} = 1$$

or:

$$\rho = J\sqrt{\frac{K}{v}} \tag{7.54b)**}$$

where:

$$J = \left(\int_{-\infty}^{+\infty} \frac{dx}{(1 + x^2)^{3/2}}\right)^{1/2} = \sqrt{2} \tag{7.55}$$

A consideration of Eq. (7.31a′), for example, serves to evaluate $K$.

$$\begin{aligned}\Delta\omega &= \left(\frac{e^2 f_{nm}}{4\pi m\nu_0}\right) r^{-3} \\ &= \frac{e^2}{2m\omega_0 r^3} f_{nm} = \frac{K}{r^3}\end{aligned} \tag{7.56}$$

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* Weisskopf also included Doppler broadening in one stage of the development. To do this one simply replaces $\omega$ in Eq. (7.44) by $\omega + \Upsilon$ — $\Upsilon$ is the frequency displacement due to the Doppler effect —, multiplies by the probability of the displacement, namely, the Maxwell-Boltzmann probability $\frac{1}{\Upsilon_0\sqrt{\pi}} \exp(-\Upsilon^2/\Upsilon_0^2)d\Upsilon$ to obtain, in place of Eq. (7.44):

$$N\alpha = \frac{A}{\Upsilon_0\sqrt{\pi}} \int_{-\infty}^{+\infty} \frac{\exp[-\Upsilon^2/\Upsilon_0^2]\, d\Upsilon}{(\omega_0 - \omega - \Upsilon) + i\gamma}$$

† Cf. *supra*, Sec. 6.2.

** In frequency units $\nu : \rho = \sqrt{\frac{4\pi\kappa}{v}}$ (7.54b′)

where we have averaged over the angle function and multiplied by the oscillator strength of the transition giving rise to the line under consideration. Utilization of Eqs. (7.54) and (7.55) in Eq. (7.53) yields:

$$\delta = 2\pi \frac{e^2}{m\omega_0} f_{mn} N \tag{7.57}$$

In a short paper on the subject Weisskopf[193a], plotted Eq. (7.52) for the case $b = 4$ and the collision width much greater than the natural width. Weisskopf's figure is reproduced in Fig. (7.1), and a consideration of the figure serves to illustrate the shift and symmetry provided by the theory.

### 7.8. REVIEW OF SELF-BROADENING TO THIS POINT

Thus far then we have considered two theories as to the origin of the resonance interactions resulting in self broadening and four theories propounded for the purpose of explaining this self broadening as such. The first of these interaction theories as advanced by Holtsmark considered the self broadening gas as a collection of coupled oscillators whose coupling resulted in a splitting of the frequency about the unperturbed line position. Unfortunately, the calculational difficulties involved in this theory led to results which were questionable. In particular we refer to Eq. (7.9). Without too much justification Holtsmark used his interaction results within the assumption of a Gaussian line shape to obtain Eq. (7.18) for the line half width.

The quantum mechanical analog of this coupled-oscillator-interaction theory provided the other resonance interaction. This quantum mechanical analog was essentially predicated on the degeneracy resulting from the presence of $N_1$ identical particles any one of which may be excited. It too faced extreme difficulties of computation. As a consequence, although the basic theory appears sound, the possibility of obtaining results from this theory would seem remote. At any rate, on an appeal to correspondences Frenkel obtained, in analogy to Eq. (7.18), Eqs. (7.34) for the line half width.

Interaction results are obtainable for the case of two molecules, however, as for example, Eqs. (7.29). Margenau and Watson used this binary interaction within the framework of the Statistical Theory to obtain Eq. (7.32) for the half width. This result should be a reasonable one for those situations in which the Statistical Theory may be expected to hold and for pressure sufficiently low that we need not consider the simultaneous interaction of more than two molecules.

The fourth broadening theory which was advanced was nothing more nor less than the application of the Michelson-Lorentz theory of Interruption broadening to the case of self broadening. Here a parameter — the optical collision diameter — is conveniently present which, if it is taken a good bit larger than in the case of foreign gas broadening, does yield results. If we wish to calculate this parameter under the assumptions utilized in obtaining Eq. (7.57) we could still adjust the final result by adjusting the phase change which defines a collision. Weisskopf mentions the fact that in some cases the theory only yields a $\rho$ which is of the order of magnitude of the correct result and in other cases not even this accuracy is attained. These other cases can, of course, be explained as "due to other causes."

### 7.9. QUALITATIVE CONSIDERATION OF THE ENERGY TRANSFER THEORY

Some four years after the publication of Weisskopf's theory Furssow and Wlassow[47] entered the field with what did amount to a new approach. Their entry was marked by the intriguing statement that the

Weisskopf theory — and the Lenz theory in passing — was completely incorrect.* Although one obvious reason for their statement may have been to pave the way for the introduction of their theory, it would appear reasonable for us to briefly consider the reasons which they advanced for this conclusion.

For greatest accuracy of consideration let us quote the Furssow and Wlassow statement verbatim before attempting to consider their reasoning.

"To be sure Weisskopf's considerations of the collisions between the like atoms is not entirely correct. Weisskopf without foundation applies the correct concept of the mechanism of the collision damping in the case of non-extinguishing atoms of different types to the case of like atoms. As is known the broadening of the lines through collisions result not only when the wave train emitted by the atom is propagated after the collision (extinguishing gases) but also at the time when at the collision a change of the vibration phase of the excited atom sets in (non-extinguishing gases). In order to compute the phase shift during the collision one must take the change of the frequency $\Delta\omega$† of the emitting atom which occurs through the interaction with foreign atoms and integrate over the collision time.† If one makes this integral equal to one then the magnitude of the optical collision diameter can be evaluated. The collisions of the like atoms Weisskopf takes instead of $\Delta\omega$ arbitrarily the difference between the frequency of one of the normal vibrations of a system of two dipole linked like linear oscillators and the frequency of the isolated atom. It is clear that this computation is based on a misunderstanding. $\Delta\omega$ is in terms of its nature the change of the frequency of the emitting atom, the light of which is analyzed according to Fourier. That however which Weisskopf substitutes instead of it has nothing at all to do with the matter because of the degeneracy . . . the concept that in the collision of two like atoms one of which is excited and the other of which is unexcited the vibration phase of the excited atom is changed does not at all correspond to reality."[47]

It might be remarked first that the $\Delta\omega$ which they believe to have been improperly chosen seems to be the very one whose choice they advocate for the following reason " . . . take the change of the frequency $\Delta\omega$ . . . and integrate over the collision time."[47] Now it is true that integration is not extended over these limits in Eq. (7.54a), but let us recall that this latter equation is an approximation which has its roots in the more nearly correct Eq. (6.6). Further, the remarks which they make about coupled oscillators seems less applicable to Weisskopf than to almost any other resonance author. If they base their argument on the "degeneracy" — they do not define this degeneracy but we can assume that it is that degeneracy arising from the indistinguishability of the atoms of our ensemble — then the question of which approach is more nearly correct has to be answered, and no one seems to have done this to date, at least not to the satisfaction of more than a few. Surely though the adjustable-parameter-dependent Weisskopf theory has not been so devastated by the above quoted argument that it cannot be considered as remaining a reasonable approximation.

The Furssow and Wlassow theory** really has its basis in a conception advanced by Kallmann and London[83] in 1929 to the effect that like atoms may simply exchange energy between each other without accompanying radiation. Even a cursory consideration of this conception gives an inkling of an application to the theory of self-broadening. We may examine it from either a quantum or a classical viewpoint.

First the classical viewpoint. To begin with we consider our molecules as classical oscillators, and again we have the dipole interaction between two like oscillators, one of which is excited and the other of

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* Houston took mild exception to this statement to the effect that " . . . the criticism of Weisskopf's work contained in this paper does not appear to be justified . . ."[72] but did not reply to the Furssow and Wlassow criticism specifically.

† Underlining added.

** Although the physical theory here is different, we shall see that it leads to precisely the mathematical results of Secs. 7.3 and 7.5.

which is unexcited. As a result of this interaction the amplitude of oscillation of the excited molecule decreases while that of the unexcited molecule increases, that is, an energy transfer occurs. This is effectively the same as damping the oscillations of the excited molecule, and, as in the case of the Lorentz damping* will result in a broadening of the spectral line. Let us now consider qualitatively the quantum mechanical explanation of this effect.

Energy is assumed to be transferred as a result again of the dipole interaction from an excited to an unexcited molecule of the same kind. Whatever the lifetime of the excited state would be under conditions of no transfer this lifetime will be greatly shortened by a high probability of transfer before radiation. Now we may recall that one form of the Heisenberg uncertainty principle states that $\Delta E \Delta t > h$. Thus, if, as is the case in the ground state, the state lifetime is infinite, the ground state will be infinitely well defined or virtually infinitely narrow. As soon as we consider a state with a finite lifetime, however, the situation changes. A certain lifetime $\Delta t$ will give us a certain indefiniteness $\Delta E$ in the state energy, or a certain level width. This level width in turn will mean that a spectral line arising from the combination of this level with another will be broadened as a consequence. Thus, when we increase our state lifetime by this energy transfer, quantum mechanics decrees that we indirectly broaden our spectral line by widening the energy level.

These then are the classical and quantum forms of the theory as advanced by Furssow and Wlassow. It now remains only to rewrite our qualitative conjectures after a quantitative fashion. Let us consider the classical approach first.

## 7.10. THE CLASSICAL ENERGY TRANSFER (LOW PRESSURE)

To begin with it is of course necessary to make a few simple assumptions regarding our system. In this consideration we are assuming our molecule to be a classical harmonic oscillator. Now we shall consider that the electronic transition which gives rise to our broadened spectral line proceeds to the ground state. We will assume that only one valence electron is responsible for the spectral line under consideration. Finally let us suppose that the excited molecule, of which our system contains one for our purposes here, moves in the neighborhood of the remainder of the unexcited molecules. The excited molecule we then consider as moving rectilinearly with velocity $v$. We might possibly bring up the same type of objection to the utilization of a linear velocity here as was brought up by Jablonski in objection to Weisskopf's utilization of a linear velocity in a central force problem. However this is probably minor at this stage.†

In considering our interaction which leads to the self broadening of the line, we shall assume this interaction to take place between our emitter and one of the unexcited broadening molecules. It has already been assumed that the broadening molecules are stationary so we shall place our broadener at the origin of the inertial reference frame. The coordinates of the valence electron of this unexcited molecule let us designate as $x_1y_1z_1$. We next establish a moving reference frame at the excited molecule. The coordinates of the valence electron are taken to be $x_2y_2z_2$ which coordinates are, of course, referred to the moving frame. Finally, let us designate by $R$ the separation of the two reference frames.

As has been mentioned earlier, it is here desired to use as the potential of the interaction the electric dipole potential. Thus, we are essentially faced with the same task with which we were presented in deriving Eq. (5.1). We make the same assumptions, that is, we first assume that $R$ is very large compared to the

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* Cf. *supra*, Chap. 1.

† Most authors appear to consider it minor at any stage, although this is not conclusive.

size of the molecules and hence compared to separation of the electron from the nucleus. Now we assume that the moving reference frame is so oriented with respect to the inertial frame that one axis moves parallel to the corresponding axis in the inertial frame and the other corresponding axes remain parallel to each other. Now let us further suppose that the angles made by the radius vector $R$ with the coordinate axes are $\alpha$, $\beta$, $\gamma$. Under these assumptions the Coulomb interaction may be expanded in terms of $\alpha$, $\beta$, $\gamma$.* The first term in this expansion will, as we have seen, be the electric dipole potential, which potential we shall assume to be responsible for the interaction between the excited and unexcited molecules. The electric dipole potential is given by:

$$\begin{aligned} V = \frac{e^2}{R^3}\big[&x_1x_2(1 - 3\cos^2\alpha) + y_1y_2(1 - 3\cos^2\beta) + z_1z_2(1 - 3\cos^2\gamma) - 3(x_1y_1\cos\alpha\cos\beta \\ &+ x_1z_2\cos\alpha\cos\gamma + y_1x_2\cos\beta\cos\alpha + y_1z_2\cos\beta\cos\gamma \\ &+ z_1x_2\cos\gamma\cos\alpha + z_1y_2\cos\gamma\cos\beta)\big] \end{aligned} \tag{7.58}$$

If our molecule was a one dimensional harmonic oscillator which was undergoing no interaction with any other oscillators Newton's equation of motion would be $\ddot{x} + \omega_0^2x = 0$, assuming of course that motion is along the $x$-axis. Here $\omega_0$ is the natural frequency of the molecular oscillator. Now, however, we must modify this equation to include the interaction with the second oscillator and the effects of three dimensional oscillation. The modification to include the electric dipole interaction may be taken directly from Eq. (7.58) to yield the following system of equations:

$$\begin{aligned} &\ddot{x}_1 + \omega_0^2x_1 + \Lambda\left[(1 - 3\cos^2\alpha)x_2 - 3\cos\alpha\cos\beta\, y_2 - 3\cos\alpha\cos\gamma\, z_2\right] = 0 \\ &\ddot{y}_1 + \omega_0^2y_1 + \Lambda\left[(1 - 3\cos^2\beta)y_2 - 3\cos\beta\cos\gamma\, z_2 - 3\cos\beta\cos\alpha\, x_2\right] = 0 \\ &\ddot{z}_1 + \omega_0^2z_1 + \Lambda\left[(1 - 3\cos^2\gamma)z_2 - 3\cos\gamma\cos\alpha\, x_2 - 3\cos\gamma\cos\beta\, y_2\right] = 0 \\ &\ddot{x}_2 + \omega_0^2x_2 + \Lambda\left[(1 - 3\cos^2\alpha)x_1 - 3\cos\alpha\cos\beta\, y_1 - 3\cos\alpha\cos\gamma\, z_1\right] = 0 \\ &\ddot{y}_2 + \omega_0^2y_2 + \Lambda\left[(1 - 3\cos^2\beta)y_1 - 3\cos\beta\cos\gamma\, z_1 - 3\cos\beta\cos\alpha\, x_1\right] = 0 \\ &\ddot{z}_2 + \omega_0^2z_2 + \Lambda\left[(1 - 3\cos^2\gamma)z_1 - 3\cos\gamma\cos\alpha\, x_1 - 3\cos\gamma\cos\beta\, y_1\right] = 0 \end{aligned} \tag{7.59}$$

where:

$$\Lambda = \frac{e^2}{m}\frac{1}{R^3}$$

Furssow and Wlasson solved the system of equations given by Eq. (7.59) by using a method of successive approximations. First, let us assume that the bracketed terms in this equational system are all zero. The solution of the system of equations resulting from this approximation, we will consider our zeroth-order solution. Initially, the unexcited molecule whose electronic coordinates are $x_1y_1z_1$ is undergoing no electronic vibrations. For simplicity of consideration, we shall assume that the excited molecule is carrying out vibrations along its $z$-axis. When these approximations are taken into account the zeroth-order solution to the problem is as follows:

$$x_1^{(0)} = y_1^{(0)} = z_1^{(0)} = x_2^{(0)} = y_2^{(0)} = 0 \tag{7.60a}$$

$$z_2^{(0)} = A\cos\omega_0t \tag{7.60b}$$

We may now substitute the values for $x_1, y_1, \ldots, z_2$ back into Eq. (7.59). The solution of the resulting system of equations yields the first approximate solution.

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* Cf. *supra*, Eq. (5.1).

Let us consider briefly one example of the method used in obtaining this first approximate solution. To begin with after we have substituted our zeroth-order approximation Eqs. (7.59), we will obtain equations of the type:

$$\ddot{\eta} + \omega_0{}^2\eta = N(t) \quad . \tag{7.61a}$$

The solution to Eq. (7.61a) under the assumption that $\eta(0) = \dot{\eta}(0) = 0$ is the following:*

$$\eta(t) = \frac{1}{\omega_0} \int_0^t N(t) \sin \omega_0(t - \tau) d\tau \tag{7.61b}$$

Now let $N(t) = \alpha(t) \cos \omega_0 t$. This $N(t)$, in general, represents the function which will arise out of the bracketed terms in Eq. (7.59). $\omega_0$ is, of course, of the order of magnitude of the frequency of the emitted radiation. $\alpha(t)$ on the other hand is a function of the angles between the radius vector and the coordinate systems, and, as a result of this, its time change will depend on the heat motion of the molecules. Thus $\alpha(t)$ will vary quite slowly in comparison to $\cos \omega_0 t$. Now let us substitute the expression for $N(t)$ into Eq. (7.61b) and expand the resulting cossin integrand to obtain the following:

$$\eta(t) = \frac{1}{2\omega_0} \left\{ \sin \omega_0 t \int_0^t \alpha(t)\,(1 + \cos 2\omega_0\tau) d\tau \; - \; \cos \omega_0 t \int_0^t \alpha\,(t) \sin 2\omega_0\tau \; d\tau \right\} \tag{7.62a}$$

If we let $T = 2\pi/\omega_0$, that is, $T$ identical to the period of the electronic oscillation, Eq, (7.62a) becomes:

$$\eta(t) = \frac{1}{2\omega_0} \sum_k \left\{ \sin \omega_0 t \, \alpha(\tau_k) \left[ \int_{kT}^{(k+1)T} d\tau + \int_{kT}^{(k+1)T} \cos 2\omega_0\tau \; d\tau \right] - \cos \omega_0 t \, \alpha(\tau\omega_k{}') \int_{kT}^{(k+1)T} \sin 2\omega_0 \, \tau \; d\tau \right\} \tag{7.62b}$$

We have taken $\alpha(\tau_k)$ outside the integral sign due to the fact that it varies so slowly during one period of electronic oscillation. The summation over $k$ suffices to give us any overall time period which we desire. We may note that the integral of the cosine and the integral of the sine over a period vanishes. Thus Eq. (7.62b) becomes:

$$\eta(t) = \frac{1}{2\omega_0} \sin \omega_0 t \sum_k \alpha(\tau_k{}')\, \Delta\tau_k = \frac{1}{2\omega_0} \int_0^t \alpha(\tau)\, d\tau \sin \omega_0 t \tag{7.63}$$

Eq. (7.63) furnishes the general form for the first approximate solution to the equational system given by Eq. (7.59) as modified by the zeroth-order solution. Eq. (7.63) yields, for the specific cases under consideration, the following solutions:

$$\begin{aligned}
x_1{}^{(1)} &= \frac{3A}{2\omega_0} \int^t \Lambda \cos \alpha \cos \gamma \; dt \sin \omega_0 t \\
y_1{}^{(1)} &= \frac{3A}{2\omega_0} \int^t \Lambda \cos \beta \cos \gamma \; dt \sin \omega_0 t \\
z_1{}^{(1)} &= - \frac{A}{2\omega_0} \int^t \Lambda(1 - 3 \cos^2 \gamma) \; dt \sin \omega_0 t \\
x_2{}^{(1)} &= y_2{}^{(1)} = 0 \, ; \; z_2{}^{(1)} = A \cos \omega_0 t
\end{aligned} \tag{7.64}$$

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* See page 282 of Reference 205a.

Eqs. (7.64) are very enlightening in that they serve to show the manner in which the energy is transferred from the excited molecule to an unexcited molecule during the course of an optical collision. We see that $z_2$ has not been changed by the collision. In addition we see how vibrations along all three axes in the system of the initially unexcited molecule have been excited.

Furssow and Wlassow carried forward the problem to higher orders of approximation, and they reported generally on the results which they had attained. According to their statement, they had found that the second-order approximation yielded no changes in the vibrational amplitudes $x_1y_1z_1$. They found that the third-order approximate solution did yield a small change in the vibrational amplitudes for the initially unexcited molecule. In like manner the fifth-order approximation and higher order odd approximations yielded a rapidly converging series of corrections to the amplitude. Since this series did converge rapidly they felt that Eqs. (7.64) should suffice to describe the energy transfer as a result of an optical collision at large separation. We must now introduce, after the manner of Furssow and Wlassow, a few additional quantities which will prove useful in the continuation of the calculation. First of all, we may recall that we have considered the initially excited molecule as moving rectilinearly among an ensemble of stationary, initially unexcited molecules. We again assume an interaction between one unexcited molecule and our excited molecule. Let us take the vector $\underline{\rho}$ as the perpendicular from the unexcited molecule to the velocity vector of the excited molecule. Let us designate by $\alpha_1\beta_1\gamma_1$ the angles which the velocity vector v makes with the coordinate axes. By the symbols $\alpha_2\beta_2\gamma_2$ we will denote the angles which the vector $\underline{\rho}$ makes with the coordinate axes. No ambiguity is introduced here by simply referring to coordinate axes as we may recall that the frame of the excited molecule remains parallel to the frame of the unexcited molecule.

Let us assume that the optical collision, which serves to transfer energy from the excited to the unexcited molecule, lasts a time interval $\tau$. If this is the case, and if we assume the collision to begin at time $t = 0$, then the collision must be initiated at a distance $-\dfrac{v\tau}{2}$ from $\underline{\rho}$.

Then after a collision of duration $\tau$, the amplitude, for example, we may obtain from Eq. (7.64):

$$X_1^{(1)} = \frac{3A}{2\omega_0} \int_0^\tau \Lambda \cos\alpha \cos\gamma \, dt \tag{7.65}$$

It is apparent as we have mentioned previously that $\alpha\beta\gamma$ are time dependent through the heat motion of the atoms. We would like then to find some expression in terms of time for these three angles. Straightforward geometrical considerations yield the following expressions for these three angle functions:

$$\begin{aligned}
\cos\alpha &= \rho\,\frac{\cos\alpha_2 + v(t - \frac{1}{2}\tau)\cos\alpha_1}{R} \\
\cos\beta &= \rho\,\frac{\cos\beta_2 + v(t - \frac{1}{2}\tau)\cos\beta_1}{R} \\
\cos\gamma &= \rho\,\frac{\cos\gamma_2 + v(t - \frac{1}{2}\tau)\cos\gamma_1}{R}
\end{aligned} \tag{7.66}$$

$$R^2 = \rho^2 + v^2(t - \tfrac{1}{2}\tau)^2$$

The relations given by Eq. (7.66) are quite obvious ones among the three previously defined vectors **R**, **v**, and $\underline{\rho}$.

We may substitute Eq. (7.66) into Eq. (7.65). When the variable $t' = t - \frac{1}{2}\tau$ is substituted for $t$ in the resulting expression we obtain:

$$X_1^{(1)} = \frac{3A}{2\omega_0}\frac{e^2}{m}\int_{-\tau/2}^{+\tau/2}\frac{(\rho\cos\alpha_2 + vt'\cos\alpha_1)(\rho\cos\gamma_2 + vt'\cos\gamma_1)}{\sqrt{(\rho^2 + v^2t'^2)^5}}\,dt' \tag{7.67}$$

It is apparent that we could also obtain analogous expressions for $Y_1^{(1)}$ and $Z_1^{(1)}$. We may make a simplification for the purpose of evaluating the integral in Eq. (7.67) by letting $\tau$ go to infinity and thus extending the limits on the integral to $-\infty$ and $+\infty$. Again this may be justified, as has been done in similar cases, in that only that portion of time immediately before and after the time of optical collision is of any import. Thus, the extension of the limits to minus and plus infinity serves merely to encompass regions which contribute nothing to the integral in question.

We may, by elementary means, evaluate the integrals of the form Eq. (7.67):

$$\begin{aligned}
X_1^{(1)} &= \frac{e^2}{m\omega_0}\,\frac{A}{\rho^2 v}\,(2\cos\alpha_2\cos\gamma_2 + \cos\alpha_1\cos\gamma_1)\\
Y_1^{(1)} &= \frac{e^2}{m\omega_0}\,\frac{A}{\rho^2 v}\,(2\cos\beta_2\cos\gamma_2 + \cos\beta_1\cos\gamma_1)\\
Z_1^{(1)} &= \frac{e^2}{m\omega_0}\,\frac{A}{\rho^2 v}\,(2\cos\gamma_2 + \cos^2\gamma_1 - 1)
\end{aligned} \tag{7.68}$$

We are now desirous of obtaining the amount of energy which is transferred during the collision from the initially excited molecule to the initially unexcited one. In doing so, let us first recall that the energy of a classical oscillator is given by $E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$ where we have here assumed a linear harmonic oscillator which is vibrating in the $x$-direction. Since $\dot{x}$ is given by $\omega_0 A\cos\omega_0 t$ and $k$ is given by $m\omega_0^2$, $E$ becomes $\frac{1}{2}m\omega_0^2A^2\cos\omega_0 t + \frac{1}{2}m\omega_0^2A^2\sin\omega_0 t$. Thus, the energy is $\frac{1}{2}m\omega_0^2A^2$ or the square of the vibrational amplitude multiplied by $\frac{1}{2}m\omega_0^2$. Hence, in the present case the energy $E$ which has been transferred to the initially unexcited molecule will be given by the sum of the squares of the amplitude components as given by Eq. (7.68) multiplied by $\frac{1}{2}m\omega_0^2$. We then obtain for the transferred energy:

$$\epsilon = \frac{e^4}{m^2\omega_0^2}\,\frac{1}{\rho^4v^2}\,\sin^2\gamma_1\,E \tag{7.69}$$

where $E$, the initial energy of the excited molecule, is, of course, $\frac{1}{2}\omega_0^2A^2$.

Eq. (7.69) is predicated on the first approximate solutions as given by Eq. (7.64) to Eq. (7.59). The validity of these Eqs. (7.64) is assumed only for large transit distances. Furssow and Wlassow defined the minimum distance of closest approach — transit distance — as that distance at which the transferred energy is equal to the energy at time zero of the initially excited oscillator, that is, $\epsilon = E$. Thus if $\rho_0$ is taken as the minimum transit distance Eq. (7.69) leads us to the following criteria for large distances:

$$\frac{1}{\rho_0^2 v} = \frac{m\omega_0}{e^2}$$

In Eq. (7.70a) sin $\gamma_1$ has been replaced by its maximum value.

We have thus determined the energy which will be transferred during an optical collision between an initially unexcited molecule and an initially excited one. Now in order to determine the total energy which our initially excited molecule will lose in the course of time it will be necessary to ascertain the total loss of energy to all the molecules in the neighborhood. Let us assume that our unexcited molecules are uniformly distributed, there being $N$ of them per unit of volume. Let us consider a layer of thickness $\Delta s$ lying perpendicular to the direction of motion of the excited molecule. Then during the time when the excited molecule is in this layer of thickness $\Delta s$ those molecules will be capable of obtaining energy from it which lie at distances of $\rho_0$ or at greater distances. Thus, the increment of energy loss by the excited molecule during its passage through this layer will be given by:

$$dE = -2\pi N\Delta s \int_{\rho_0}^{\infty} \epsilon\rho d\rho = -\pi N\Delta s \frac{e^4}{m^2\omega_0^2}\sin^2\gamma_1\frac{1}{\rho_0^2v^2} E \tag{7.71a}$$

Now $\Delta s$ may also be written as $vdt$. When this is done and when the value for $1/\rho_0^2v$ is substituted from Eq. (7.70):

$$dE = -\pi N \frac{e^2}{m\omega_0} \sin^2 \gamma_1 \, Edt \tag{7.71b}$$

From Eq. (7.71b) Furssow and Wlassow obtained:

$$E = E_0e^{-\Upsilon_0't} \tag{7.71c}$$

where:

$$\Upsilon_0' = \frac{2\pi}{3}\frac{Ne^2}{m\omega_0}$$

In obtaining Eq. (7.71c) Furssow and Wlassow averaged Eq. (7.71c) over $\gamma_1$, and integrated the separable differential equation which resulted. In a slightly more refined treatment in which they assumed motion on the part of the initially unexcited molecules and where averaging was carried out over all orientations for this motion they obtained instead of the $\Upsilon_0'$ given above:

$$\Upsilon = \frac{\pi}{2}\frac{e^2}{m\omega_0} N(1 + \tfrac{1}{2}\sin^2\alpha)$$

Here $\alpha$ is the angle between the electric moment and the direction of motion of the emitter.

We have thus attained in Eq. (7.71c) an expression for the attenuation of the energy of the initially excited molecule with time. This is, of course, not the desired objective. We are desirous of obtaining the broadening of the emitted spectral line as a result of this energy attenuation. In order to arrive at this we shall consider the analogous case of damping by some other means such as a radiation damping of the molecular oscillations.

First consider the equation for a molecular oscillator of natural frequency $\omega_0$ and subjected to a damping of damping constant $\gamma$:

$$m\ddot{x} + m\omega_0^2x + m\gamma\dot{x} = 0 \tag{7.72}$$

For the case $\gamma \ll \omega_0$ — which we shall find to be an excellent approximation — the solution of Eq. (7.72) can be shown to be:

$$x = x_0e^{-\gamma t/2}e^{i\omega t} \tag{7.73}$$

It may be seen, as we have specifically mentioned earlier,* that the energy of the oscillator whose amplitude is governed by Eq. (7.73) is $E_0 e^{-\gamma t}$. This $\gamma$ corresponds to the $\Upsilon_0'$ in Eq. (7.71c). Here we know that the electric vector of the radiation emitted by our molecular oscillator will also contain the exponential of Eq. (7.73).† The electric vector of the radiation field will be of the form:

$$\mathbf{E} = \mathbf{E}_0 \, e^{-\gamma t/2} \, e^{i\omega_0 t}$$

In the usual manner the electric vector may be expanded in a Fourier integral in order to obtain the amplitude of this vector as a function of frequency:

$$E(\nu) = \frac{1}{2\pi} \, \frac{1}{i(\omega - \omega_0) - \gamma/2}$$

We may thus obtain the intensity of the emitted spectral line as a function of frequency by simply taking the absolute square of the amplitude of the electric vector:

$$I(\nu) \doteq |E(\nu)|^2 \propto \text{const.} \, \frac{\gamma/2}{(\omega - \omega_0)^2 + (\gamma/2)^2} \tag{7.74}$$

It can then be seen from the familiar Eq. (7.74) that $\gamma$ or $\Upsilon$ is the half-width of the emitted spectral line. Thus, from Eq. (7.71c) the half-width of the emitted spectral line is found to be:

$$\delta_r' = \frac{2\pi}{3} \, \frac{e^2}{m\omega_0} \, N \tag{7.75}$$

It is then apparent that the effect of this energy transfer at large transit distances is a damping of the molecular oscillations resulting in a broadening of the spectral line whose half-width is given by Eq. (7.75). Finally the half-width $\delta_r'$ should be multiplied by the oscillator strength of the transition under consideration.

We thus have treated collisions at transit distances of greater than $\rho_0$ as defined by Eq. (7.70). Now with Furssow and Wlassow we may essentially define $\rho_0$ in analogy to the optical collision diameter of Weisskopf. There the optical collisions, which have already been treated, resulted in only a change in the amplitude of the electronic oscillations, Furssow and Wlassow considered collisions at less than this optical collision diameter as changing not only the amplitude but also the orientation of the electronic oscillation. For these latter cases they simply took the half-width as given by the Lorentz-Lenz-Weisskopf-etc. collision theory:**

$$\delta_s' = \pi \rho_0^2 N \langle v \rangle = 2\pi \, \frac{e^2}{m\omega_0} \, N \tag{7.76}$$

where again $\delta_s'$ is to be multiplied by the oscillator strength for the collision.

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* See *supra*, Eq. (7.69) and preceding.

† Cf. *supra*, Sec. 1.8.

** All of which would appear rather paradoxical.

Finally the line broadening as a result of near and distant collisions may be assumed as the algebraic sum of the widths due to the two types. Thus, we eventually arrive at the line half-widths as obtained from the classical energy transfer theory:

$$\delta = f(\delta_r' + \delta_s') = \frac{8\pi}{3}\frac{e^2}{m\omega_0}\ Nf \qquad (7.77)^*$$

A comparison of Eq. (7.77) with Eq. (7.57) shows that the Furssow-Wlassow theory yields line widths 4/3 times as great as the Weisskopf theory.

The manner in which the dipole interaction between two like molecules causes a transfer of the oscillatory energy from the initially excited molecules to the remaining initially unexcited molecules has been shown. This energy transfer then acts as a damping force on the oscillatory motion of the molecule and, as a result, the emitted radiation is broadened into a spectral line of finite width. We shall see that a quantum consideration under certain specific assumptions leads to approximately the same results.

## 7.11. QUANTUM TREATMENT OF LOW PRESSURE SELF-BROADENING

We have sketched qualitatively the quantum mechanical theory of resonance broadening by energy transfer, and our first task in a quantitative consideration will be to ascertain the time change of eigenfunctions — probability amplitudes — of the excited molecule due to this energy transfer.

Again the system is initially taken as two like molecules one of which is excited and one of which is unexcited. The motion of the molecule will be considered classically† as is normally done in problems of this kind* with quite reasonable justification. The potential of interaction between the two atoms is still the dipole potential of Eq. (7.58). The symbols such as $\underline{\rho}$, $\alpha_1$, etc. which were utilized in the classical consideration will again appear with the same connotation.

Since specific assumptions regarding the states of the two molecules must be made, the simplest ones possible are utilized, namely, the unexcited molecule is assumed to be initially in a ground state where $\psi_{lmn}(1) = \psi_{n00}(1)$, and the excited molecule is assumed in a $p$ state, with eigenfunction $a\psi_{nn0}(2) + c\psi_{n00}(2)$. This eigenfunction assumes that the emitted radiation is polarized in the $z$ direction since $\Delta m = 0$ — the only transition possible from this eigenfunction — corresponds to such a polarization. We might look ahead a bit at this point by a consideration of the eigenfunction of the excited molecule. The probability that the emitter is in the state $m10$ at time $t$ is given by $|a(t)|^2$. Thus the behavior of $a(t)$ will tell us the probability that the emitter will transfer its energy to the initially unexcited molecule in the course of time. Qualitatively at least it is apparent that this determines the state lifetime change and the resulting line broadening.

In the considerations which led to Eq. (7.20) no spatial degeneracy was considered so that only a two-fold degeneracy resulted for the system. When we consider the three values which $m$ may assume when either of our molecules is in the first excited state, a six fold degeneracy for the first excited state

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* The Jablonski theory provides the only exception.

† This appears intuitively justifiable, but for a mathematical justification one may consult Reference 127.

of the system results. The ground state of the system remains, of course, non-degenerate. On the basis of these considerations we choose as eigenfunctions to describe the system during the time of transit:

$$\psi(1,2,t) = \{a_1(t)\psi_{n00}(1)\psi_{m10}(2) + a_2(t)\psi_{n00}(1)\psi_{m11}(2) + a_3(t)\psi_{n00}(1)\psi_{m1-1}(2) + b_1(t)\psi_{m10}(1)\psi_{n00}(2)$$
$$+ b_2(t)\psi_{m11}(1)\psi_{n00}(2) + b_3(t)\psi_{m1-1}(1)\psi_{n00}(2)\}e^{-i\frac{E_n+E_m}{\hbar}t} + c_1(t)\psi_{n00}(1)\psi_{n00}(2)e^{-i2\frac{E_n}{\hbar}t} \tag{7.78}$$

The Schrodinger equation for our system — neglecting the radiation field — is:

$$[H(1) + H(2) + V(1,2,t)]\psi(1,2,t) = i\hbar\frac{\partial}{\partial t}\psi(1,2,t) \tag{7.79a}$$

In Eq. (7.79a) $H(1)$ is the unperturbed Hamiltonian for the initially unexcited molecule; $H(2)$ is the Hamiltonian for the initially excited molecule, and $V(1,2,t)$ is the perturbing Hamiltonian introduced by the dipole interaction as given by Eq. (7.58). Let us now substitute Eq. (7.78) into Eq. (7.79a) to obtain:

$$ih\sum_{i=1}^{3}\dot{a}_i\,\psi_i + i\hbar\sum_{i=1}^{3}\dot{b}_i\psi_i + i\hbar\dot{c}_1\,\psi_{n00}(1)\,\psi_{n00}(2)\,e^{i2\frac{E_n}{\hbar}t} + \sum_{i=1}^{3}a_iE_l\psi_i$$
$$+ \sum_{i=1}^{3}b_iE_l\psi_i + 2c_1E_n\psi_{n00}(1)\,\psi_{n00}(2) = \sum_{i=1}^{3}a_i[H(1) + H(2)]\,\psi_i + \sum_{i=1}^{3}b_i[H(1) + H(2)]\,\psi_i$$
$$+ c_1[H(1) + H(2)]\,\psi_{n00}(1)\,\psi_{n00}(2) + V(1,2,t)\,\psi(1,2,t) \tag{7.79b}$$

In Eq. (7.79b) $E_l = E_n + E_m$, and $\psi_i$, represents the $\psi_{nlm}(1)\,\psi_{nlm}(2)$ going with the appropriate $a_i$ or $b_i$. Let us find $\dot{a}_1$ as an example.

Eq. (7.79b) is first multiplied through on the left by $\overline{\psi_{n00}(1)\psi_{m10}(2)}$ and the resulting expression is integrated over all space. The result is:

$$i\hbar\dot{a}_1 + a_1E_l = a_1E_n + a_1E_m + \int\overline{\psi_{n00}(1)\,\psi_{m10}(2)}\,V(1,2,t)\,\psi(1,2,t)\,d\tau \tag{7.80}$$

The results obtained here are entirely due to the orthnormality of the unperturbed eigenfunctions of the two molecules. In the integral on the right all terms containing $\int\overline{\psi_{n00}(1)}\,V\psi_{n00}d\tau$ will disappear since $V(1,2,t)$ averaged over the spherically symmetrical ground state is zero.* As a consequence, if we adopt the convention:

$$V^{n00;m10}_{m10;n00} = \int\overline{\psi_{n00}(1)\,\psi_{m10}(2)}\,V(1,2,t)\,\psi_{m10}(1)\,\psi_{n00}(2)\,d\tau \tag{7.81}$$

we obtain for $a$:

$$i\hbar\dot{a}_1 = V^{n00;m10}_{m10;n00}b_1 + V^{n00;m10}_{m11;n00}b_2 + V^{n00;m10}_{m1-1;n00}b_3 \tag{7.82}$$

In this manner we may obtain the equations for the time rate of change of the coefficients in Eq. (7.78) as:

$$\begin{aligned}
i\hbar\dot{a}_1 &= V^{n00;m10}_{m10;n00}\,b_1 + V^{n00;m10}_{m11;n00}\,b_2 + V^{n00;m10}_{m1-1;n00}\,b_3\\
i\hbar\dot{a}_2 &= V^{n00;m11}_{m10;n00}\,b_1 + V^{n00;m11}_{m11;n00}\,b_2 + V^{n00;m11}_{m1-1;n00}\,b_3\\
i\hbar\dot{a}_3 &= V^{n00;m1-1}_{m10;n00}\,b_1 + V^{n00;m1-1}_{m11;n00}\,b_2 + V^{n00;m1-1}_{m1-1;n00}\,b_3\\
i\hbar\dot{b}_1 &= V^{m10;n00}_{n00;m10}\,a_1 + V^{m10;n00}_{n00;m11}\,a_2 + V^{m10;n00}_{n00;m1-1}\,a_3\\
i\hbar\dot{b}_2 &= V^{m11;n00}_{n00;m10}\,a_1 + V^{m11;n00}_{n00;m11}\,a_2 + V^{m11;n00}_{n00;m1-1}\,a_3\\
i\hbar\dot{b}_3 &= V^{m1-1;n00}_{n00;m10}\,a_1 + V^{m1-1;n00}_{n00;m11}\,a_2 + V^{m1-1;n00}_{n00;m1-1}\,a_3\\
i\hbar\dot{c}_1 &= 0
\end{aligned} \tag{7.83}$$

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* Cf. *supra*, Eq. (5.1).

It is reasonably obvious that the selection of two higher and more degenerate states would have complicated the problem a bit.

Now it may again be assumed that the interaction between the two molecules begins at time $t = 0$ when the emitter is a distance $\frac{v\tau}{2}$ from $\rho$. On this basis we may solve the quantum mechanical problem by a series of approximations.

We have assumed that previous to the introduction of the dipole interaction the upper state is a $p$ state with $m = 0$. Thus at time $t = 0$ there is a finite probability of $\psi_{n00}(1)\psi_{m10}(2)$ or $\psi_{n00}(1)\psi_{n00}(2)$ — there will always be a finite probability for the existence of the ground state — but no probability for the existence of any other state. These conditions lead us to the zero order solution:

$$\begin{aligned} &a_1(0) = a\,; \quad a_2(0) = a_3(0) = 0 \\ &b_1(0) = b_2(0) = b_3(0) = 0\,; \quad c_1(0) = c \end{aligned} \tag{7.84}$$

For the first approximation it may be assumed that $a_1$ remains a constant during time $\tau$. This would mean that no probability for $\psi_{m11}(2)$ or $\psi_{m1-1}(2)$ exists during this interval. This yields:

$$\begin{aligned} &a_1 = a\,; \quad a_2 = a_3 = 0 \\ &b_1 = \frac{a}{i\hbar}\int_0^\tau V^{m10;\,n00}_{n00;\,m10}\,dt\,; \quad b_2 = \frac{a}{i\hbar}\int_0^\tau V^{m11;\,n00}_{n00;\,m10}\,dt \\ &b_3 = \frac{a}{i\hbar}\int_0^\tau V^{m1-1;\,n00}_{n00;\,m10}\,dt \end{aligned} \tag{7.85}$$

In order to determine the matrix elements of $V$, it is apparent from Eq. (7.58) that the matrix elements of $x$, $y$, and $z$ must first be determined. Hydrogen-like wave functions of the form of Eq. (5.7) are utilized for this purpose. As an example:

$$\begin{aligned} (n00\,|x|\,m11) &= \int \psi_{n00}\,x\,\psi_{m11}\,d\tau = \frac{\sqrt{6}}{8\pi}\int_0^\infty\int_0^{2\pi}\int_0^\pi [R_{n0}(r)]\,[r\sin\vartheta\cos\varphi] \\ &\cdot [R_{m1}(r)\sin\vartheta\, e^{i\varphi}]\,r^2\sin\vartheta\,d\vartheta\,d\varphi\,dr = \frac{1}{2}\sqrt{\frac{2}{3}}\,r_{nm} = (m11\,|x|\,n00) \end{aligned}$$

where $r_{nm}$ is the radial matrix element $\int_0^\infty r^3\,R_{n0}(r)R_{m1}(r)\,dr$.

In like manner the non-vanishing matrix elements may be found as:

$$\begin{aligned} (n00\,|x|\,m11) &= (m11\,|x|\,n00) = \frac{1}{2}\sqrt{\frac{2}{3}}\,r_{nm} \\ (n00\,|x|\,m1-1) &= (m1-1\,|x|\,n00) = -\frac{1}{2}\sqrt{\frac{2}{3}}\,r_{nm} \\ (n00\,|y|\,m11) &= (m11\,|y|\,n00) = \frac{i}{2}\sqrt{\frac{2}{3}}\,r_{nm} \\ (n00\,|y|\,m1-1) &= (m1-1\,|y|\,n00) = -\frac{i}{2}\sqrt{\frac{2}{3}}\,r_{nm} \\ (n00\,|z|\,m10) &= (m10\,|z|\,n00) = \frac{1}{\sqrt{3}}\,r_{nm} \end{aligned} \tag{7.86}$$

In finding a matrix element of $V$ we carry the angle functions as constants — it may be recalled that these angle functions depend on the heat motion of the molecules. Thus a matrix element of $V$ is simply some combination of the matrix elements of $x_1, y_1, \ldots z_2$. Now, for example, in the case of $V^{m10;\,n00}_{n00;\,m10}$ the matrix element of all the terms in $V$ except $z_1z_2(1 - 3\cos^2\gamma)$ vanish. As a result:

$$V^{m10;\,n00}_{n00;\,m10} = \frac{e^2}{R^3}\,(n00\,|z|\,m10)^2\,(1 - 3\cos^2\gamma)$$

Finally then Eq. (7.85) becomes:

$$b_1 = \frac{a}{i\hbar}\,e^2(n00\,|z|\,m10)^2 \int_0^\tau \frac{(1 - 3\cos^2\gamma)}{R^3}\,dt$$

$$b_2 = \bar{b}_3 = -\frac{a}{i\hbar}\,\frac{3\sqrt{2}}{2}\,e^2(n00\,|z|\,m10)^2 \int_0^\tau \frac{\cos\gamma(\cos\alpha - i\cos\beta)}{R^3}\,dt \tag{7.87}$$

Again, as in the classical case, we allow $\tau$ (the collision time) to approach infinity and integrate Eq. (7.87) to obtain:

$$\begin{aligned} b_1 &= \frac{a}{i\hbar}\,2e^2(n00\,|z|\,m10)^2\,\frac{1}{v\rho^2}\,(1 - \cos^2\gamma_1 - 2\cos^2\gamma_2) \\ b_2 = \bar{b}_3 &= -\frac{a}{i\hbar}\sqrt{2}\,e^2(n00\,|z|\,m10)^2\,\frac{1}{v\rho^2}\,[\cos\gamma_1\,(\cos\alpha_1 - i\cos\beta_1) + 2\cos\gamma_2(\cos\alpha_2 - i\cos\beta_2)] \end{aligned} \tag{7.88}$$

where Eq. (7.66) has been utilized for the $\alpha\beta\gamma$. From Eq. (7.88) it is apparent that the probability for excitation of the initially unexcited molecule is:

$$|b_1|^2 + |b_2|^2 + |b_3|^2 = a^2\,\frac{4e^4}{\hbar^2\rho^4v^2}\,\sin^2\gamma_1(n00\,|z|\,m10)^4 \tag{7.89}$$

We may now carry out a second approximation to find $a_1$, still under the assumption $a_2 = a_3 = 0$:

$$|a_1|^2 + |b_1|^2 + |b_2|^2 + |b_3|^2 + |c_1|^2 = |a|^2 + |c|^2 \tag{7.90}$$

and, if we suppose $|c_1|^2 = |c|^2$, the change in $|a|^2$ may be determined from Eq. (7.90) as:

$$\begin{aligned} \Delta\,|a|^2 &= |a_1|^2 - |a|^2 = -\,(|b_1|^2 + |b_2|^2 + |b_3|^2) \\ &= -\,|a|^2\,\frac{4e^4}{\hbar^2\rho^4v^2}\,\sin^2\gamma_1(n00\,|z|\,m10)^4 \\ &= -\,|a|^2\,\frac{e^4}{m^2\omega_{nm}{}^2}\,f_{nm}{}^2\,\frac{1}{\rho^4v^2}\,\sin^2\gamma_1 \end{aligned} \tag{7.91}$$

where $f_{nm} = \dfrac{2m\omega_{nm}}{\hbar}(n00\,|z|\,m10)^2$, the oscillator strength of the $mn$ transition.

The similarity of Eqs. (7.91) and (7.69) is quite apparent, especially when the $E - |a|^2$ analogy is considered.

We earlier set the condition $\epsilon = E$ for determining $\rho_0$.* Similarly, we now establish the criteria for $\rho_0$ as $\Delta\ |a|^2 = |a|^2$, that is, the change in the probability of finding the system in the state $\psi_{n00}(1)\psi_{m10}(2)$ is equal to the probability of finding the system in this state. From Eq. (7.91) $\rho_0$ may then be defined as:

$$\rho_0 = \sqrt{\frac{e^2}{m\omega_{mn}} f_{nm} \frac{1}{v}} \tag{7.92}$$

where $\sin \gamma_1$ has again been given its maximum value.

To this point in the quantum mechanical development of their theory Furssow and Wlassow proceeded in a rather straightforward manner, but their subsequent machinations should at least be critically considered. We might recall that when we viewed resonance broadening as a case of identical particle degeneracy the two molecular problem was solvable, but the $N$-atomic case had no apparent solution. What Furssow and Wlassow did was extend the results of the two molecular case to that of many molecules, and if this procedure is not justifiable in the degeneracy picture, it should not be any more justifiable in the energy exchange picture. We must, therefore, agree and keep in mind the fact that this is simply an approximation, no matter how good a one.

If there are $N$ molecules per unit of volume of our gas then surely $2\pi\rho d\rho vN$ of them appear per units of time lying a distance between $\rho$ and $\rho + d\rho$ from the emitter. Furssow and Wlassow asserted this to mean that the total change of the probability per unit of time is:

$$\frac{d}{dt}\,|a|^2 = -\,|a|^2\,\frac{e^4}{m^2\omega_{nm}}\,f_{nm}{}^2\,\frac{1}{v^2}\,\sin^2\gamma_1\int\limits_{\rho_0}^{\infty}\frac{2\pi\rho\,d\rho}{\rho^4}\,vN = -\,\pi\,|a|^2\,\frac{e^2}{m\omega_{mn}}\,f_{nm}\,N\sin^2\gamma_1 \tag{7.93}$$

If Eq. (7.93) is averaged over $\gamma_1$, and the resulting equation solved for $|a|^2$, the quantum mechanical analog of Eq. (7.71c) is obtained:

$$|a|^2 = |a_0|^2\,e^{-\Upsilon_0 t} \tag{7.94}$$

where:

$$\Upsilon_0 = \frac{2\pi}{3}\,\frac{e^2}{m\omega_{nm}}\,f_{nm}\,N$$

Thus the state lifetime has been decreased by the energy exchange as predicted, and this decrease is dependent on the gas density.

Now let us write down the Hamiltonian for the system, excited molecule plus field:†

$$H = H_a + H_f + H_{af} \tag{7.95a}$$

In Eq. (7.95a) $H_a$ is the Hamiltonian for the molecule alone; $H_f$ is the Hamiltonian of the field, and $H_{af}$ is the Hamiltonian of the field-molecule interaction. Eq. (7.95a) may be written as

$$H = H_0 + H_{af} = H_0 + V \tag{7.95b}$$

and the Schrodinger equation as:

$$i\hbar\frac{\partial\psi}{\partial t} = (H_0 + V)\psi \tag{7.95c}$$

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* See *supra*, Eq. (7.70) and preceding.

† See *supra*, Eq. (3.51).

When we assume that $\psi = \sum\limits_r a_r \psi_r$ where the $\psi_r$ are the eigenfunctions of the unperturbed system, we may utilize the method by which we arrived at Eq. (7.82) to find the $a_r$. Let us recall that the symbol $r$ is a quantum conglomerate of the form $nN_1N_2 \ldots$. where, to begin with, $n$ specifies the state of the molecule in the system and the $N_i$ specify the states of the $i$-th radiation oscillator.*

The analog of Eq. (7.82) is then:

$$i\hbar \dot{a}_{n'N_1'N_2'\ldots} = \sum_{nN_1N_2\ldots} H^{n'N_1'N_2'\ldots}_{nN_1N_2\ldots} \, a_{nN_1N_2\ldots} \, e^{i\frac{E_{n'N_1'N_2\ldots} - E_{nN_1N_2\ldots}}{\hbar}t} \tag{7.96a}$$

where, of course, the $|a_i|^2$ still have a probability interpretation.

It is reasonable to assume here that at time $t = 0$ the molecule is in the excited state, and there are no photons in the field. This would mean that $a_{m00\ldots0_s0\ldots}(0) = 1$ while all other $a_{nN_1N_2\ldots}(0) = 0$. At some later time the molecule will be in the ground state and there will be a quantum of type $s$ in the field where $\nu_s$ is the frequency of this quantum, and $\nu_{nm}$ is the frequency of the molecular transition $mn$. Under the assumption that all amplitudes do remain zero except $a_{m00\ldots0_s0\ldots}(t)$ during the time involved in this transition we obtain:

$$i\hbar \dot{a}_{n00\ldots0_s0\ldots}(t) = H^{n00\ldots1_s0\ldots}_{m00\ldots0_s0\ldots} \, a_{m00\ldots}(t) \, e^{i(\omega_{mn}-\omega_s)t} \tag{7.96b}$$

Since $\omega_s$ is the frequency of the photon which is present in the field after the transition of frequency $\omega_{mn}$ has taken place, $\omega_s$ is of the order of $\omega_{mn}$.

It is clear that the probability amplitude $a_{m00\ldots}(t)$ will be the same as the probability amplitude of the initially excited molecule in the state designated by the quantum number $m$. In addition we may find $a(t)$ from Eq. (7.94):

$$a_{m00\ldots}(t) = a(t) = e^{-\frac{\Upsilon_0}{2}t} \tag{7.96c}$$

When this expression is substituted into Eq. (7.96b) and the resulting equation is integrated over time 0 to $t$ we will obtain:

$$a_{n00\ldots1_s0\ldots}(t) = H^{n00\ldots1_s0\ldots}_{m00\ldots0_s0\ldots} \frac{e^{i(\omega_s-\omega_{mn})t-\frac{\Upsilon_0}{2}t} - 1}{-h\left[\omega_s - \omega_{nm} + i\left(\frac{\Upsilon_0}{2}\right)\right]} \tag{7.97}$$

After a time $t \to \infty$ the initially excited molecule will surely have undergone the transition to the ground state. Now the intensity of a frequency $\omega$ after this time will certainly be proportional to the probability of a photon of this frequency being present in the radiation field. These considerations lead to the following expression for the intensity distribution:

$$I(\omega) = \text{const}\, |a_{n00\ldots1_s0\ldots}(\infty)|^2 = \frac{\text{const}}{(\omega - \omega_{mn})^2 + \left(\frac{\Upsilon_0}{2}\right)^2} \tag{7.98}$$

From Eq. (7.98) it is apparent that our half-width is given by the following:

$$\delta_r = \Upsilon_0 = \frac{2\pi}{3} \frac{e^2}{m\omega_{mn}} f_{mn} N \tag{7.99}$$

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* Cf. *supra*, Eq. (3.60) and preceding.

It can be seen that Eq. (7.99) yields the same results for the half-width as Eq. (7.75) which latter equation was found for the case of distant collisions.

For the case of near collisions let us utilize the Heisenberg uncertainty principle in the form:

$$\Delta E \Delta t = \hbar$$

where we shall now assume $\Delta E$ to be the width of the state and $\Delta t$ to be the mean lifetime of the state.

Let us suppose that the life of a state is terminated by a collision so that $\Delta t = \tau$ where $\tau$ is the mean time between collisions. This means that the width of the state will now be:

$$\Delta E = \frac{\hbar}{\Delta t} = \frac{\hbar}{\tau} = 2\hbar\pi \frac{e^2}{m\omega_0} f_{nm} N$$

from Eq. (7.53).

Or:

$$\delta_s = \Delta\omega = \frac{\Delta E}{\hbar} = 2\pi \frac{e^2}{m\omega_0} f_{nm} N \tag{7.94b}$$

Finally we obtain for the half width:

$$\delta = \delta_r + \delta_s = \frac{8}{3}\pi \frac{e^2}{m\omega_0} f_{nm} N \tag{7.94c}$$

In the main Furssow and Wlassow considered their results to hold only in the case of low gas densities. It may be recalled we have questioned the Furssow-Wlassow procedure in which they work out the broadening effect of one like molecule and then simply extend these results to the case of $N$ similar molecules. Furssow and Wlassow felt that their results were only applicable to low gas densities. In a later paper on the subject they investigated the self-broadening of a spectral line in the case of high gas densities. They found it necessary to use a slightly different although comparable method of approach. We shall discuss this in greater detail at a later point.

We have considered several theories, the reason for the existence of which is the explanation of the self-broadening of spectral lines. In the time honored tradition Houston[72] now entered the field to show that theories of (a) Furssow and Wlassow, (b) Weisskopf, and (c) Jablonski and Margenau* were essentially equivalent. "A complete analysis, however, shows that they are merely three approximations to the exact quantum mechanical treatment."[72]

### 7.12. EQUIVALENCE OF STATISTICAL, INTERRUPTION AND ENERGY EXCHANGE THEORIES

We begin, with Houston, by making the assumption which was previously utilized by Furssow and Wlassow, that is, that our pressure is low enough to make a collision between one excited and one unexcited molecule a good approximation. The method of setting up and solving the problem which was utilized by Houston is essentially the one of Furssow and Wlassow,† but, since it is a slightly more comprehensive application to resonance broadening let us rapidly carry out the formulation.

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* See *supra*, Chap. 5.

† Cf. also *supra*, Sec. 4.22.

We begin by considering two electronic states, let us say, the ground and first excited states. In addition a continuum of translational states is contemplated. We then obtain for the electronic eigenfunctions of our system of two atoms:

$$\begin{aligned} U_a &= u_0(1)u_1(2) \\ U_b &= u_0(2)u_1(1) \\ U_0 &= u_0(1)u_0(2) \end{aligned} \tag{7.100}$$

where $u_0$ specifies the ground state and $u_1$ the excited state. The radiation field may be described by the function $F_0$, when there are no quanta in the field. The field may be described by $F_\nu$, when there is a quantum of energy $h\nu$ in the field. Finally if we let $v_1(R,t)$ be the function of the nuclear motion before the collision and $v_0(R,t)$ be the function of this motion after the collision, we will obtain as the eigenfunctions of the three states which are of import here:

$$\begin{aligned} \psi_a &= U_a v_1(R,t)F_0 \exp\left[-\,(i/\hbar)E_1 t\right] \\ \psi_b &= U_b v_1(R,t)F_0 \exp\left[-\,(i/\hbar)E_1 t\right] \\ \psi_0 &= U_0 v_0(R,t)F_\nu \exp\left[-\,(i/\hbar)(E_0 + h\nu)t\right] \end{aligned} \tag{7.101}$$

The Hamiltonian of our system will be:

$$H = H_a + H_f + V(R) + S \tag{7.102}$$

where $H_a$ is the Hamiltonian of the unperturbed atoms, $H_f$ is the Hamiltonian of the unperturbed radiation field, $V(R)$ the Hamiltonian of the dipole interaction between the two atoms, and $S$ the Hamiltonian of the interaction between the atoms and the radiation field.

The solution to the Schrodinger equation which results from the Hamiltonian of Eq. (7.102) is surely:

$$\Psi = a\psi_a + b\psi_b + c\psi_0 \tag{7.103}$$

In the same manner in which we obtained Eq. (7.83) we may now obtain:

$$\begin{aligned} \dot{a} &= -\frac{i}{\hbar}(a\,|V|\,b)b - \frac{i}{\hbar}(a\,|S|\,c)c \exp\left[\frac{i}{\hbar}(E_1 - E_0 - h\nu)t\right] \\ \dot{b} &= -\frac{i}{\hbar}(b\,|V|\,a)a - \frac{i}{\hbar}(b\,|S|\,c)c \exp\left[\frac{i}{\hbar}(E_1 - E_0 - h\nu)t\right] \\ \dot{c} &= -\frac{i}{\hbar}(c\,|S|\,a)a \exp\left[-\frac{i}{\hbar}(E_1 - E_0 - h\nu)t\right] - \frac{i}{\hbar}(c\,|S|\,b)b \exp\left[-\frac{i}{\hbar}(E_1 - E_0 - h\nu)t\right] \end{aligned} \tag{7.104}$$

We are here interested in the matrix elements of $V$ but not in those of $S$. The reason for this is apparent when we consider that the matrix elements of $S$ are to those of $V$ as the natural width of the line is to the self-broadened width. On this basis Houston neglected the matrix elements of $S$. A solution to Eq. (7.104) is surely:

$$\begin{aligned} a &= A \exp\left[-\frac{i}{\hbar}\int(a\,|V|\,b)dt\right] + B \exp\left[\frac{i}{\hbar}\int(a\,|V|\,b)dt\right] \\ b &= A \exp\left[-\frac{i}{\hbar}\int(a\,|V|\,b)dt\right] - B \exp\left[\frac{i}{\hbar}\int(a\,|V|\,b)dt\right] \end{aligned} \tag{7.105}$$

where $|A|^2 + |B|^2 = 1/2.$

Again we consider molecule 1 as initially excited and molecule 2 as initially unexcited. This means that $a(0) = 0$ and $b(0) = 1$. These initials condition yield:

$$a = -i \sin \frac{1}{\hbar} \int_{t_0}^{t} (a\,|V|\,b)dt$$

$$b = \cos \frac{1}{\hbar} \int_{t_0}^{t} (a\,|V|\,b)dt \qquad (7.106)$$

We are treating the nuclear motion classically, and as a result the molecular separation will have a precise value. As in Eq. (7.29b) we obtain:

$$(a\,|V|\,b) = \frac{\alpha}{R^3} = \frac{\alpha}{(\rho^2 + v^2t^2)^{3/2}} \qquad (7.107)$$

where $\alpha$ is a constant, and $\rho$ is the distance of closest approach.

Let us substitute Eq. (7.105) into the equation for $c$ in Eq. (7.104). We will obtain then for $c$ functions of the form $\exp\left\{-\frac{1}{\hbar}\left[\int (a\,|V|\,b)dt + (E_1 - E_0)t\right] + i\omega t\right\}$. Now $c$ is the probability amplitude for the existence of a photon of frequency $\nu$ in the field. Thus it is necessary for us to show the equivalence of $c$ with $J(\omega)$ in Eq. (6.5a) in order to show the equivalence of this theory, which is essentially the Furssow and Wlassow theory, with the theory of Weisskopf. From Eq. (7.107) it is apparent that the integral of the matrix element corresponds to Eq. (7.54) of the Weisskopf theory. Thus, the integral of $\omega_0(\tau)d\tau$ appearing in Eq. (6.5a) corresponds to the bracketed expression in the exponential which appears in the expressions for $c$. Finally the $\omega$ appearing in the expression for $c$ is the frequency of the photon in the field corresponding to the $\omega$ in Eq. (6.5a). Thus, the correspondence between the Furssow and Wlassow theory and the Weisskopf theory is demonstrated. The demonstration of this equivalence then leads us directly to an equivalence between the Jablonski theory or the Margenau theory and the Furssow and Wlassow theory.*

In this same paper Houston used the Furssow and Wlassow method of attack to show that all members of a Russell Saunders multiplet are broadened to the same extent in the case of a resonance broadening.† He compares his results to the experimental work of Hughes and Lloyd.[73] These authors had experimentally demonstrated the equality of the broadening of the two members of the first doublet of the principal series of potassium. In addition they had found the predicted dependence of the half-width on $N$. Unfortunately, Houston's theoretical calculation of the half-width of the members of this doublet varied by a factor of five from the observations of Hughes and Lloyd. Houston felt that this discrepancy lay in the uncertainty as to the vapor pressure of the potassium as a function of temperature. We shall see that Furssow and Wlassow offered a quite different and more basic reason for this discrepancy.

We have noted that the earlier Furssow and Wlassow theory[47] was not applicable to the case of high like-gas pressure due to the method of approach utilized by these authors in attacking the problem. In a

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* See *supra*, Sec. 6.4.

† The preponderant weight of subsequent experimental data indicates this to be incorrect.

later paper on the subject these two authors attacked the case of resonance broadening for high like gas pressure.[48] Schulz and Rompe[158, 159] had applied the Furssow-Wlassow theory to the broadening of spectral lines, but the writers of the theory felt that theirs was a misapplication. The basis for this viewpoint is of itself interesting and leads to the refined Furssow-Wlassow method.

## 7.13. HIGH PRESSURE QUANTUM RESONANCE BROADENING

The theory was really predicated on a collision between two particles. Now if, as in the Schulz and Rompe experiments, we take $\omega_0 = 1.02 \times 10^{16}$ sec.$^{-1}$, $f = 1.3$, $T = 6000°$, we will obtain a $\rho$ of approximately $5.35 \times 10^{-7}$. Then with the pressure used by Schulz and Rompe $N \doteq 2.57 \times 10^{19}$ cm.$^{-3}$. This means that in the "sphere of action" we will have $\frac{4}{3}\pi\rho^3 N \doteq 17$ molecules. This in turn means that in the sphere of action as defined by the optical collision diameter at any time there will be approximately 17 particles. Thus, the approximation of a two particle collision is hardly reasonable.

A modification of the first theory is certainly called for, and, in this paper, Furssow and Wlassow[48] set out to calculate the broadening of the resonance level for this higher pressure case.

Let us begin by supposing the gas density sufficiently high that we can expect a large number $n$ of molecules within the sphere of action. If we allow this system of $n + 1$ molecules to possess two levels, the resonance level and the ground state, the possible eigenfunctions to describe the system in the upper state will be:

$$\begin{aligned} \psi_a &= u_1(0)u_0(1) \ldots u_0(n) \\ \psi_{b_1} &= u_0(0)u_1(1) \ldots u_0(n) \\ &\vdots \qquad\qquad \vdots \\ \psi_{b_n} &= u_0(0)u_0(1) \ldots u_1(n) \end{aligned} \tag{7.108}$$

where we have assumed molecule 0 to be the initially excited atom.

The Hamiltonian of the dipole interaction will be:

$$U = \sum_{k \neq k'}\sum V(k,k') = \sum_{k=1}^{n} V(0,k) + \sum\sum V(k,k') \tag{7.109}$$

The solution to the Schrodinger equations which results from this interaction Hamiltonian is surely:

$$\Psi = a\psi_a + \sum_{k=1}^{n} b_k\psi_{b_k} \tag{7.110}$$

Using methods which have certainly become familiar we find:

$$\begin{aligned} i\hbar\dot{a} &= \sum_{k=1}^{n} (a\,|U|\,b_k)b_k \\ i\hbar\dot{b}_k &= (b_k\,|U|\,a)a + \sum_{k'} (b_k\,|U|\,b_{k'})b_k \end{aligned} \tag{7.111}$$

Again under the initial conditions stipulating that molecule 0 is initially excited we obtain $a(t) = a(0) = 1$ and $b(0) = 0$. Subsequent to the time $t = 0$ we can expect the transfer of energy from the initially excited to the unexcited molecules to proceed as governed by the matrix element $(a|U|\,b_{k'})$. In addition Eq. (7.111) tells us that there will be a secondary transfer of energy among the initially unexcited molecules as governed by the matrix element $(b_k\,|U|\,b_{k'})$. "Generally speaking one can characterize the whole process as a process of diffusion of the excitation energy from the atom initially excited."[48] We now introduce the approximation that the secondary energy transfer process as governed by $(b_k\,|U|\,b_{k'})$ can be disregarded. This allows us to rewrite Eq. (7.111) as:

$$ih\dot{a} = \sum_{k=1}^{n} (a\,|U|\,b_k)b_k \tag{7.112a}$$

$$ih\dot{b}_k = (b_k\,|U|\,a)a \tag{7.112b}$$

We next introduce an additional approximation to the effect that $U$ is not time dependent. This is nothing more nor less than saying that the thermal motion of the molecules is so small as to be considered negligible during the energy transfer process. As we shall see, at high pressure for the resonance level this is a reasonable approximation. Now let us take the time derivative of Eq. (7.112a) and substitute for $b_k$ from Eq. (7.112b) in the resulting equation. This yields:

$$-\hbar^2\ddot{a} = a\sum_{k=1}^{n} (a\,|U|\,b_k)^2 \tag{7.112}$$

If we now ignore the angular dependence of the dipole interaction, there results:

$$\ddot{a} + p^2 a = 0 \tag{7.114a}$$

$$p^2 = \sum_{k=1}^{n} \frac{\alpha}{R_k^6}\,; \quad \alpha = \frac{e^4 f^2}{4m^2\omega_0^2} \tag{7.114b}$$

A solution of Eq. (7.114a) which satisfies the initial condition $a(0) = 0$ is:

$$a = \cos pt \tag{7.115}$$

If we again assume that the condition $a = 0$ — that is, the energy has been transferred from the initially excited molecule — determines the collision time, $\tau$, then from Eq. (7.115) there results:

$$\tau = \frac{\pi}{2p} \tag{7.116}$$

We wish to develop $a$ in a Fourier integral. We have only obtained an approximation for $a$, and another approximation which should be almost as good is the step function:

$$a = 1 \quad \text{for} \quad 0 \leqslant t \leqslant \tau$$

$$a = 0 \quad \text{for} \quad 0 < t > \tau \tag{7.117}$$

In a quite straightforward manner we may write down the Fourier integral for $a$ as:

$$a = \int_{-\infty}^{+\infty} g(\omega)e^{i\omega t}d\omega \tag{7.118a}$$

$$g(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} ae^{-i\omega t}d\omega = \frac{1}{2\pi}\int_{0}^{\tau} 1 \cdot e^{-i\omega t}\, d\omega = \frac{1}{2\pi}\,\frac{1 - e^{-i\omega t}}{i\omega} \tag{7.118b}$$

The distribution of the energy in the level will surely be given by the absolute square of the Fourier amplitude $g(\omega)$:

$$|g(\omega)|^2 = \frac{1}{2\pi^2}\,\frac{1 - \cos \omega t}{\omega^2} \tag{7.119}$$

Eq. (7.119) gives us the desired result for a specific collision time $\tau$. It would now appear reasonable to average this expression over all collision times in order to obtain the observed distribution in the level. Let us suppose that $w(\tau)d\tau$ is the probability that the collision time lies between $\tau$ and $\tau + d\tau$. Then for $J(\omega)$ we obtain:

$$J(\omega) = \int_{0}^{\infty} |g(\omega)|^2\, w(\tau)d\tau \tag{7.120}$$

Let us utilize the expression:

$$\nu = \frac{\pi^2}{4\tau^2} = p^2 \tag{7.121}$$

for a change in variable in Eq. (7.122) as follows:

$$w(\tau)d\tau = \frac{\pi w(\pi/2\sqrt{\nu}\,)}{4\sqrt{\nu^3}}\,d\nu = -\, I'(\nu)d\nu \tag{7.122}$$

In order to find $I'(\nu)d\nu$ we may proceed in the following manner. Let us establish a configuration space of $3n$ dimensions whose volume is $\Gamma = v^n$ where $v$ is the volume of our gas. Now if we temporarily disregard the intermolecular forces, we can expect equal probability for the occupation of any portion of this space. This means that the following relation will hold:

$$I'(\nu)d\nu = \frac{\Delta\Gamma}{\Gamma} \tag{7.123}$$

where $\Delta\Gamma$ represents that portion of configuration space for which our $\nu$ lies between $\nu$ and $\nu + d\nu$. This value of $\nu$ will, of course, depend on the distribution of the $R_k$ in Eq. (7.114b). Thus:

$$\Delta\Gamma = (4\pi)^n \int \ldots \int R_1^2R_2^2 \ldots R_n^2\, dR_1dR_2 \ldots dR_n \tag{7.124}$$

The analogy to Margenau's Eq. (5.23a) is apparent. Our solution then is given by Eq. (5.41) as:

$$I'(\nu) = \frac{2}{3}\,\pi N\sqrt{\alpha}\,\frac{e^{-\frac{4\pi^3\alpha N^2}{9\nu}}}{\sqrt{\nu^3}} \tag{7.125}$$

We may now transform back to our variable $\tau$ by utilizing Eq. (7.122). We obtain:

$$w(\tau) = \frac{2\Upsilon}{\sqrt{\pi}} e^{-\Upsilon^2\tau^2} \tag{7.126}$$

$$\Upsilon = \frac{4}{3} N\sqrt{\pi\alpha} = \frac{2}{3}\sqrt{\pi}\frac{fe^2}{m\omega_0} N \tag{7.127}$$

Eqs. (7.116) and (7.126) may now be substituted into Eq. (7.120) and the results integrated to obtain:

$$I(\omega) = \frac{1}{2\pi^2}\frac{1 - e^{-(\omega/2\Upsilon)^2}}{\omega^2} \tag{7.128}$$

as the distribution of energies in the resonance level. For the breadth we obtain:

$$\delta = 2.54\Upsilon = 3\frac{fe^2}{m\omega_0} N \tag{7.129}$$

It is Eq. (7.129) which Furssow and Wlassow used to determine the resonance level width for comparison with experiment. In order to find the spectral line width, it would appear reasonable to assume that we must needs have a knowledge of not only the resonance level width but also the width of the level from which the radiating transition originates.* The phrase "from which" leads us to the next consideration.

Furssow and Wlassow felt in their second paper (they experienced no such qualms in their first) that their results should only be applied to transitions proceeding from upper levels to the resonance level, that is, these results should not be applied to the transition from the resonance level to the ground state. A short consideration renders this assertion quite plausible.

Let us suppose that the initially excited molecule undergoes a transition from the resonance level to the ground state with the accompanying emission of radiation. This emitted radiation may be absorbed by one of the unexcited molecules where absorption would not be possible were this radiation the result of a transition to some level above the ground state. This process, which should not be confused with the transfer of energy without accompanying radiation has certainly not been considered in the theory, and, since it can be expected to have some effect on the line broadening, this theory cannot be expected to hold in such cases. These authors felt that the failure of Houston's[72] results to agree with those of Hughes and Lloyd[73] could be traced to this cause.

The justification for the assumption of fixed atoms, that is, $\frac{d}{dt}(a\,|U|\,b_k) = 0$, which led to Eq. (7.113) appears worthy of note here. Let us consider the Rompe and Schulz case.[158] The pressure is 80 atmospheres and $T = 2800°$. The experimental width was found to be $\delta = 7 \times 10^{12}$ sec. $^{-1}$ so that the mean life of the resonance level is $\tau = 1/\delta = 1.4 \times 10^{-13}$ sec. The mean relative velocity is $v = 1.3 \times 10^5$ cm./sec., which leads us to the conclusion that during the mean level life we may expect our atoms to move a distance $v\tau = 1.8 \times 10^{-8}$ cm., or the order of their own diameter. Thus, the approximation appears a reasonable one.

Finally let us consider the agreement which Furssow and Wlassow's high pressure theory gives with the results of Schulz and Rompe.

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* The complexity if not impossibility of computing the width of a higher level may be inferred from the preceding work.

| $T$ (°$K$) | Pressure (atmos.) | $N \times 10^{-19}$ (cm.$^{-3}$) | $\delta_{\text{Theor}} \times 10^{-12}$ | $\delta_{\text{exp}} \times 10^{-12}$ |
|---|---|---|---|---|
| 7800 | 20 | 1.83 | 1.83 | 2.64 |
| 6000 | 21 | 2.57 | 2.55 | 3.01 |
| 7800 | 80 | 7.56 | 7.32 | 6.98 |

Table (7.1). Widths of the resonance level of Mercury. (After Furssow and Wlassow[48])

## 7.14. COMPARISON OF SOME EXPERIMENTAL RESULTS

Furssow and Wlassow explain the worst discrepancy in Table (7.1) by the assertion that Schulz and Rompe probably did not measure their temperature correctly, but more important than this, let us pause for a moment to consider just exactly what numbers we are comparing. Let us specifically consider the second row of Table (7.1). The experimental results are from the first Schulz and Rompe paper.[48]

Now Furssow and Wlassow claim that $2.55 \times 10^{-12}$ sec.$^{-1}$ is the width of the resonance level of $Hg$ which happens to be a $^3P_1$ state. In order to find this width by Eq. (7.115), Eq. (7.113) requires that we utilize the wave length of the resonance line which, for $Hg$, is 2537$A$ (2536.52$A$). In addition we need the $f$ value from the resonance transition ($^3P_1 \rightarrow {}^1S_0$) and Furssow and Wlassow used the value 0.025 from Schulz and Rompe. These values when put into Eq. (7.115) do indeed yield $2.55 \times 10^{-12}$ sec.$^{-1}$, but is $3.01 \times 10^{-12}$ sec.$^{-1}$ the level width from experiment? Let us consider the Schulz and Rompe results more closely.

We consider Fig. (7.2). The solid line in the figure is an example of one type of trace — the type which will concern us — which these two authors obtained. The circles represent the application of a dispersion distribution to the trace. Now $3.01 \times 10^{-12}$ sec.$^{-1}$ is half the line width at half height of this dispersion distribution for the $Hg$ spectral line at 10140$A$ corresponding to a transition from the $^1S_0$ (seventh shell) to the $^1P_1$ (sixth).

We might finally note that Schulz and Rompe obtained a symmetrical distribution for the $Hg$ lines in several cases, thus agreeing with the earlier theory, but in others a Margenau shape occurred. We have very little basis for comparison here, however, since the theory was worked out initially for the resonance line only and subsequently just for the resonance level.

Let us now compare the equations of Weisskopf,[193] Margenau and Watson,[200] and Furssow and Wlassow[47] with the results of some later experimental work — we shall not compare Houston's since comparison only serves to show that the members of a Russell-Saunders multiplet are almost never broadened by the same amount.

To begin with the three equations for the half width are:

Weisskopf: $$\delta = \frac{e^2}{m\omega_0} f_{nm} N \tag{7.57}$$

Margenau and Watson: $$\delta = \frac{\pi}{3}\frac{e^2}{m\omega_0} f_{nm} N \tag{7.32}$$

Furssow and Wlassow: $$\delta = \frac{4}{3}\frac{e^2}{m\omega_0} f_{nm} N \tag{7.77}$$

in frequency units $\nu$.

In 1940 Shang-Yi[171] conducted a study of the resonance doublet of rubidium ($^2P_{3/2} \rightarrow {}^2S_{1/2}$) and ($^2P_{1/2} \rightarrow {}^2S_{1/2}$). We might preface our remarks by noting that the results obtained by Shang-Yi do not provide much of a justification for the resonance theories so far obtained.

Firstly, symmetrical lines were obtained only for pressures up to 1 mm. Above this pressure asymetries appeared in the lines. Furssow and Wlassow do not claim application for their high pressure theory to resonance lines. Other than this fact all theories so far — save that of Jablonski — yield symmetrical intensity distributions. We might then take this as an indication for the pressure at which the low pressure Furssow and Wlassow theory fails.

Insofar as the half width is concerned we can hardly consider widths of the asymmetrical lines, at least not with much confidence, since a dispersion type line shape was utilized by Shang-Yi to compute the half-width from the experimental data. Thus, the usable data consists of half-width measurements for the two lines at five pressures ranging from $1.87 \times 10^{-3}$ mm. to $9.83 \times 10^{-1}$ mm. For the pressure considered does not seem to be exactly "... proportional to $N$ as predicted by the theory ..."[171] since it varies, for example, from $0.72 \times 10^{-7} \times 10^{-7}/N$ at $1.87 \times 10^{-6}$ mm. for the $^2P_{3/2} \rightarrow {}^2S_{1/2}$ line, although this can perhaps be attributed to "experimental error." At any rate the mean values for the two lines are:

$$\delta\ (^2P_{3/2})/N = 1.22 \times 10^{-7}$$

$$\delta\ (^2P_{1/2})/N = 0.77 \times 10^{-7}$$

Table (7.2) provides a comparison of these experimental values with three of the theories propounded

| | Exp. | Weisskopf | Margenau and Watson | Furssow and Wlassow |
|---|---|---|---|---|
| $\delta \times 10^7/N$ ($^2P_{3/2} \rightarrow {}^2S_{1/2}$) | 1 22 | .70 | .73 | .93 |
| $\delta \times 10^7/N$ ($^2P_{1/2} \rightarrow {}^2S_{1/2}$) | .77 | .33 | .35 | .44 |

Table (7.2). Comparison of Shang-Yi results[171] for the broadening of the rubidium resonance lines with the theory. $f(^2P_{3/2}) = 2/3$. $f(^2P_{1/2}) = 1/3$.

The table would appear to be self-explanatory. At about this time Watanabe[189] carried out measurements on the broadening of the $NaD$ lines. Of what he termed "most reliable" there are ten values of the width for various pressures ranging from $1.22 \times 10^{-2}$ mm. to 5.96 mm. which are compared with the theoretical predictions in Table (7.3).*

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* It should be mentioned too that Watanabe very nearly obtains $\delta/N$ a constant.

Watanabe's highest recorded pressure was 72.3 mm., and it is of interest to note that he obtained no " . . . definite evidence of van der Waals force . . . at the higher pressures; likewise no appreciable shifts or asymmetries."[189]

| | Exp. | Weisskopf | Margenau and Watson | Furssow and Wlassow |
|---|---|---|---|---|
| $\delta \times 10^7/N$ $D_1$ | .75 | .26 | .27 | .35 |
| $\delta \times 10^7/N$ $D_2$ | .84 | .53 | .56 | .70 |

Table (7.3). Comparison of Watanabe's results[189] for the broadening of the *Na-D* lines with theory. $f_1 = 1/3$. $f_2 = 2/3$.

A discrepancy which was unfortunately to occur in Gregory's work can, it is believed, be traced to his use of Watanabe's Eq. (5):

$$\Delta\nu_{1/2} = k\left(\frac{e^2 f}{m\nu_0\pi}\right) N \text{ sec.}^{-1} \tag{7.130}$$

for the computation of his theoretical half-widths. Watanabe let $k = 1/4, 1/2$, and $2/3$ to yield Eqs. (7.57), (7.32), and (7.77), respectively.

As we may have observed the experiments have certainly "yielded results which were not in complete accord with the various theories . . ." all of which led Gregory[54] to an experimental investigation of the resonance lines of the alkali *Cs*.

Insofar as line shape is concerned, Gregory obtained a symmetrical line for pressures below one mm and an asymmetrical line for higher pressures. Attempts to " . . . fit the contours to the '$-$ 3/2' type of curve . . ." proved fruitless. He measured the width at densities varying from $13.43 \times 10^{13}$ cm.$^{-3}$ ($p_{\text{mm}} = 5.75 \times 10^{-3}$ mm.) to $4.09 \times 10^{-3}$ ($p_{\text{mm}} = 2.47$ mm.). For the first member of the doublet ($^2P_{3/2} \rightarrow {}^2S_{1/2}$) an average value for $\delta/N$ was obtained as $1.45 \times 10^{-7}$ sec.$^{-1}$. For the second member an average value of $.84 \times 10^{-7}$ sec.$^{-1}$ was obtained. In order to obtain these results from the experimental data Gregory assumed a dispersion distribution. In this case the value of $\delta/N$ was very nearly a constant for the various densities.

Table (7.4) gives a comparison of Gregory's experimental result with the theory.*

| | Experimental | Weisskopf | Margenau and Watson | Furssow and Wlassow |
|---|---|---|---|---|
| $\delta \times 10^7/N$ $(^2P_{3/2} \rightarrow {}^2S_{1/2})$ | 1.45 | .76 | .80 | 1.01 |
| $\delta \times 10^7/N$ $(^2P_{1/2} \rightarrow {}^2S_{1/2})$ | .84 | .38 | .40 | .51 |

Table (7.4). Gregory's results[54] for the resonance lines of Cs together with that predicted by theory. $f_{3/2} = .66$. $f_{1/2} = .32$.

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* With the exception of the Margenau and Watson width Gregory did not obtain the theoretical widths given here. This is because he used Eq. (7.130) for the three theories.

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* With the exception of the Margenau and Watson width Gregory did not obtain the theoretical widths given here. This is because he used Eq. (7.130) for the three theories.

Other than demonstrating the fact that none of the theories propounded in explanation of the resonance broadening phenomenon is precisely correct these experimental results indicate that the combined resonance and, say, van der Waals forces should be investigated. Such an investigation might provide the explanation of the observed line shape variations with radiating transition as well as with pressure.*

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*We have not included certain of the resonance theories which may be taken as special cases of the more general theories. The Foley theory (*see supra*, Eq. (6.143)) provides an example of such a situation, and the specific case of resonance broadening follows quite straightforwardly from the general case.

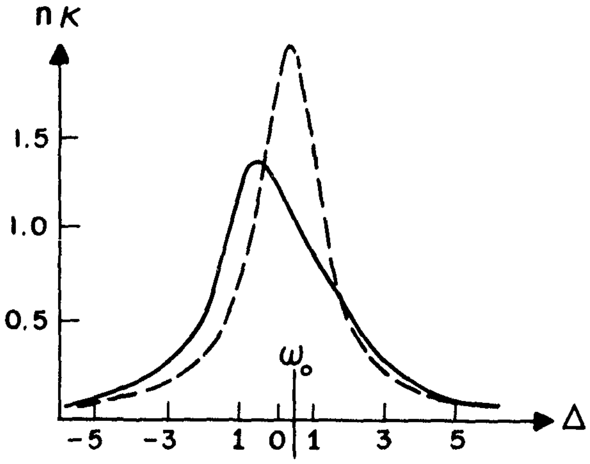

Fig. (7.1). Line shape according to the more sophisticated Weisskopf theory. (After Weisskopf.[193a])

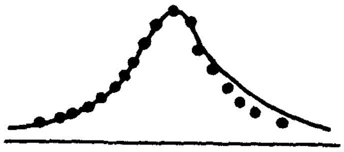

Fig. (7.2). The Schulz and Rompe treatment of an experimental trace (solid line) in order to obtain a half width. (After Schulz and Rompe.[158])

# CHAPTER 8

# MOLECULAR BROADENING

We shall now restrict ourselves to consideration of polyatomic molecules, and we trouble to do so since special phenomena are attached to this type molecule. Both monatomic and polyatomic molecules are, of course, possessed of electronic structure so that it would appear obvious that we should look to the rotations and vibrations of these latter molecules, as given, for example, by Eq. (2.38) in zeroth-order for the explanation of these special phenomena. This is assuredly an à posteriori judgement here, but it certainly could have been à priori synthetical one.*

Before launching ourselves into the development of molecular† broadening theory let us first introduce two apparently irrelevant facts which will later prove of value.

## 8.1. COMPARATIVE ENERGIES AND MATRIX ELEMENTS

Monatomic as well as polyatomic molecules emit electronic spectra as we have noted, and in addition, polyatomic molecules may emit vibrational and rotational spectra. Now we may say, as a rule of thumb, of the three types of radiation that the electronic radiation is of the order of one hundred units of energy, the vibrational of the order of ten, and the rotational of the order of one. As is generally the case with rules of thumb, this statement is usually false, but it nevertheless can be utilized as a guide in some of our later considerations.

As our second introductory item, let us consider the matrix element governing the absorption of electric dipole radiation. As we are well aware, the matrix element of the electric dipole moment between two states tells us the allowability or otherwise of our molecule undergoing a transition between the two states in question, with the accompanying absorption of electric dipole radiation. This is surely reasonable since this matrix element simply shows the manner in which the two states combine under the influence of this radiation. Now in expressing the electric dipole moment of the molecule, it is convenient as well as informative to expand this moment in terms of the normal vibrational coordinates of the molecule as obtained from Eq. (2.15). The first term in this expansion will be the permanent electric dipole moment, that is, the moment which the molecule possesses when it is undergoing no internal vibration. If, say, the molecule is undergoing a vibration described by the normal coordinate $q_a$, the subsequent terms will be functions of the $q_a$. Then two possible situations present themselves: (1) the vibrational matrix element or (2) the pure rotational matrix element only is present. We wish to consider the second of these possibilities. Here only the first term in the expansion of the dipole moment, the permanent moment, is present. Thus, unless the molecule possesses a permanent moment, the rotational matrix element will disappear and no radiation absorbing transition will be possible.

## 8.2. EARLY WORK ON BROADENING OF ROTATION-VIBRATION LINES

We might begin by remarking that the three main types of foreign gas broadening as developed in Chapters 4 through 6 could be applied in general to the present molecular case of rotation and rotation-

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* And, that is the ding an sich of that.

† In this chapter we shall understand "molecule" to refer to polyatomic molecule.

vibration lines. Indeed in an early work Kussmann[96] did just this, that is, he investigated the broadening of HCl rotation lines and checked the experimental results against the predictions of Holtzmark's Stark theory and Lorentz' Interruption theory. He concluded that the Lorentz theory agreed best and the subsequent work of Lasareff[97] and Grasse[53] on rotation-vibration lines appeared to bear this out. Thus, to this point, those interested in the broadening of rotation and rotation-vibration lines had found no reason for treating this type line any differently from electronic lines. The intimation that some different approach to the broadening of the former was in order appears to have arisen first in the work of Herzberg and Spinks.[62]. These investigators found a decrease of the line width with higher values of the rotational quantum number $J$ in the near infrared spectra of HCN. This discovery would surely indicate that rotation-vibration spectra should be treated differently than electronic spectra, but this clear indication was rather clouded when the work of Cornell and Watson[23] and Herzberg, Spinks, and Watson[63] failed to verify this variation with $J$ The hint had been given however, and it was certainly apparent that the possibility of $J$ width dependence and other unique molecular phenomena should be theoretically investigated.

## 8.3. INTERACTIONS BETWEEN ROTATING DIPOLES (DIRECTIONAL EFFECT)

We shall now consider as an introduction to our first broadening investigation, the interaction between two rotators, one or both of which may possess an electric dipole moment.*

First, let us carry out a rather obvious modification of Eq. (5.1) to obtain:

$$V = -\frac{1}{R^3}\sum_{ij} e_i e_j (2z_i z_j - x_i x_j - y_i y_j) \tag{8.1}$$

In Eq. (8.1) we have denoted the system of charges and the coordinates of those charges belonging to one of the rotators by $i$, and the charges and coordinates belonging to the other by $j$. Here also we have allowed the interrotator axis to be the common axis of the two systems, and $R$ now specifies the (large) separation of the two rotators.

Now let us specify the dipole moments of the rotators by $\mu_1$ and $\mu_2$ and introduce spherical polar coordinates for the two systems. In this case then, there results:

$$V = \frac{\mu_1 \mu_2}{R_3}[\sin\vartheta_1 \cos\varphi_1 \sin\vartheta_2 \cos\varphi_2 + \sin\vartheta_1 \sin\varphi_1 \sin\vartheta_2 \sin\varphi_2 - 2\cos\vartheta_1 \cos\vartheta_2] \tag{8.2}$$

The conditions here must conform to those leading up to Eq. (5.4), that is, we assume the separation of the rotators to be large enough so that no charge overlap or exchange need be considered. Thus the perturbation resulting from the action of these two dipoles is given by Eq. (5.4). Before writing this result down, however, let us recall that we have already determined the eigenvalues of the rotators in question as:

$$E_{JM} = \frac{\hbar^2}{2I} J(J+1) \equiv E_J \tag{2.37a}$$

where $J$ is the total angular momentum quantum number and $M$ the magnetic quantum number.

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* See references 68 and 177.

If we now designate initial states by a double prime, final states by a prime and indicate the two rotators by the subscripts one and two, we may write Eq. (5.4) for the present case as:

$$E^{(2)} = \sum_{\substack{J_1 J_2' \\ M_1'M_2'}} \frac{|\,(J_1''M_1''J_2''M_2''\mid V\mid J_1'M_1'J_2'M_2')\,|^2}{E_{J_1''} - E_{J_1'} + E_{J_2''} - E_{J_2'}} \tag{8.3}$$

where $V$ is given by Eq. (8.2).

Since no magnetic field, in which the magnetic quantum numbers may interest themselves, is present, we simply average $E^{(2)}$ over these quantum numbers. Equal probability for them is assumed and there results:

$$<E^{(2)}> = \frac{1}{(2J_1''+1)\,(2J_2''+1)} \sum_{M_1''M_2''} E^{(2)} \tag{8.4}$$

since each $J_i''$ level is $(2J_i''+1)$-fold degenerate.

From Eq. (2.35a) the eigenfunctions for our rotator system will be:

$$\psi(1,2) = \psi_{J_1M_1}\psi_{J_2M_2} = Ne^{\pm iM_1\varphi_1}P_{J_1}^{M_1}(\cos\vartheta)e^{\pm iM_2\varphi_2}P_{J_2}^{M_2}\,(\cos\vartheta_2) \tag{8.5}$$

where the $P_{J_i}^{M_i}$ are associated Legendre functions.

In Eq. (8.3) we shall need matrix elements of $\cos\vartheta$, $\sin\vartheta\cos\varphi$, and $\sin\vartheta\sin\varphi$. In order to determine these matrix elements let us introduce three recursion formulas relating the associated Legendre functions as:

$$(1-z^2)^{1/2}\,P_J^{|M|-1}(z) = \frac{1}{(2J+1)}P_{J+1}^{|M|}(z) - \frac{1}{(2J+1)}P_{J-1}^{|M|}(z) \tag{8.6a}$$

$$(1-z^2)^{1/2}P_J^{|M|+1}(z) = \frac{(J+|M|)(J+|M|+1)}{(2J+1)}P_{J-1}^{|M|}(z) - \frac{(J-|M|)\,(J-|M|+1)}{(2J+1)}P_{J+1}^{|M|}(z) \tag{8.6b}$$

$$z\,P_J^{|M|}(z) = \frac{(J+|M|)}{(2J+1)}\,P_{J-1}^{|M|}(z) + \frac{(J-|M|+1)}{(2J+1)}\,P_{J+1}^{|M|}(z) \tag{8.6c}$$

where $z = \cos\vartheta$.

For future reference, let us note that:

$$\int_{-1}^{+1} P_{J''}^{|M''|}(z)P_{J'}^{|M''|}(z)dz = \begin{cases} 0 & \text{for } J'' \neq J' \\ \dfrac{2}{(2J''+1)}\,\dfrac{(J''+|M''|)!}{(J''-|M''|)!} & \text{for } J'' = J' \end{cases} \tag{8.7a}$$

by means of which we may obtain the normalization factor for $\Theta_{JM}(\vartheta)$ as:

$$\Theta_{JM}(\vartheta) = \left[\frac{(2J+1)}{2}\,\frac{(J-|M|)!}{(J+|M|)!}\right]^{1/2} P_J^{|M|}\,(\cos\vartheta) = NP_J^{|M|}\,(\cos\vartheta) \tag{8.7b}$$

Let us evaluate a portion of the matrix element of sin $\vartheta$ sin $\varphi$ as an example.

$$(J''M'' \mid \sin\vartheta \sin\varphi \mid J'M') = \frac{N''N'}{2\pi} \int_{-1}^{+1}\int_{0}^{2\pi} e^{iM''\varphi}\, P_{J''}^{|M''|} \sin\vartheta \sin\varphi\, e^{-iM'\varphi}\, P_{J'}^{|M'|}\, d\varphi dz$$

$$= \frac{N''N'}{2\pi} \int_{-1}^{+1}\int_{0}^{2\pi} e^{iM''\varphi}\, e^{-iM'\varphi} \left(\frac{e^{i\varphi} - e^{-i\varphi}}{2i}\right) P_{J''}^{|M''|}\, P_{J'}^{|M'|}\, (1 - z^2)^{1/2}\, d\varphi dz \tag{8.8a}$$

The integration over $\varphi$ in Eq. (8.8a) goes to zero due to the periodicity of $\varphi$ unless $M' = M'' \pm 1$. We carry out the integration over $\varphi$ for the case $M' = M'' + 1$ ($\Delta M = +1$) to obtain:

$$\frac{N''N'}{2i} \int_{-1}^{+1} P_{J''}^{|M''|}\, P_{J'}^{|M''|+1}\, (1 - z^2)^{1/2}\, dz \tag{8.8b}$$

Now for $M \geqslant 0$ it follows that $| M + 1 | = | M | + 1$ and for $M < 0$, $| M + 1 | = | M | - 1$. First the case $M \geqslant 0$ may be considered and Eq. (8.6b) utilized to obtain:

$$\frac{N''N'}{2i} \int_{-1}^{+1} P_{J''}^{|M''|}\, P_{J'}^{|M''|+1}\, (1 - z^2)^{1/2}\, dz = \frac{N'N''}{2i}\, \frac{(J' + | M'' |)\,(J' + | M'' | + 1)}{(2J' + 1)} \int_{-1}^{+1} P_{J''}^{|M''|}\, P_{J'-1}^{|M''|}\, dz$$

$$- \frac{N'N''}{2i}\, \frac{(J' - | M'' |)\,(J' - | M'' | + 1)}{(2J' + 1)} \int_{-1}^{+1} P_{J''}^{|M''|}\, P_{J'+1}^{|M''|}\, dz \tag{8.8c}$$

Where Eq. (8.8a) told us that $M$ may only change by $\pm 1$, Eq. (8.8c) tells us that $J$ may only change by $+1$. The $J$ change is here governed by the orthogonality of the associated Legendre functions. Let us further limit ourselves to the first integral in Eq. (8.8c) which only fails to disappear for $J' = J'' + 1$ We are then considering the case $\Delta M = +1$, $\Delta J = +1$, $\Delta M \geqslant 0$.

$$\frac{N'N''}{2i}\, \frac{(J' + | M'' |)\,(J' + | M'' | + 1)}{(2J' + 1)} \int_{-1}^{+1} P_{J''}{}^{|M''|}\, P_{J'-1}{}^{|M''|}\, dz$$

$$= \frac{1}{2i} \left[\frac{(2J'' + 1)\,(2J'' + 3)\,(J'' - | M'' |)\,!\,(J'' - | M'' | + 2)\,!}{4(J'' + | M'' |)\,!\,(J'' + | M'' |)\,!}\right]^{1/2}$$

$$\cdot \left[\frac{2}{(2J'' + 1)}\, \frac{(J'' + | M'' |)\,!}{(J'' - | M'' |)\,!}\right] \left[\frac{1}{(2J''+3)}\right]$$

$$= \frac{1}{2i} \left[\frac{(J'' + M'' + 1)\,(J'' + M'' + 2)}{(2J'' + 1)\,(2J'' + 3)}\right]^{1/2} \tag{8.9a}$$

If we now go back and consider Eq. (8.8b) for $M < 0$, we again obtain Eq. (8.9a). Thus:

$$(J''M'' \mid \sin\vartheta \sin\varphi \mid J' + 1, M'' + 1) = \frac{1}{2i}\left[\frac{(J'' + M'' + 1)\,(J'' + M'' + 2)}{(2J'' + 1)\,(2J'' + 3)}\right]^{1/2} \qquad (8.9b)$$

In an entirely analogous manner we may obtain all allowed matrix elements of $\cos\vartheta$, $\sin\vartheta\cos\varphi$, and $\sin\vartheta\sin\varphi$ using Eqs. (8.6). We finally obtain for the desired matrix elements:

$$(J''M'' \mid \sin\vartheta\cos\varphi \mid J'M') = \frac{1}{2} A\,(+)\,\delta\,(M', M'' + 1) - \frac{1}{2} A\,(-)\,\delta\,(M', M'' - 1) \qquad (8.10a)$$

$$(J''M'' \mid \sin\vartheta\sin\varphi \mid J'M') = \frac{1}{2i} A\,(+)\,\delta\,(M', M'' + 1) + \frac{1}{2i} A\,(-)\,\delta\,(M', M'' - 1) \qquad (8.10b)$$

$$(J''M'' \mid \cos\vartheta \mid J'M') = B\,\delta\,(M', M'') \qquad (8.10c)$$

where:

$$A(\pm) = \left[\frac{(J''\pm M''+2)\,(J''\pm M''+1)}{(2J''+1)\,(2J''+3)}\right]^{1/2} \delta(J',J''+1) - \left[\frac{(J''\mp M''-1)\,(J''\mp M'')}{(2J''+1)\,(2J''-1)}\right]^{1/2} \delta(J',J''-1) \qquad (8.10d)$$

$$B = \left[\frac{(J''+M''+1)\,(J''-M''+1)}{(2J''+1)\,(2J''+3)}\right]^{1/2} \delta(J',J''+1) + \left[\frac{(J''+M'')\,(J''-M'')}{(2J''+1)\,(2J''-1)}\right]^{1/2} \delta(J',J'' - 1) \qquad (8.10e)$$

Now in order to find the matrix elements of $V$ we merely add products of Eqs. (8.10) as indicated by Eq. (8.2). We need not write down this intermediate result. What we finally desire, although it may not still appear so, are the squares of the matrix elements of $V$. When we square the matrix elements of $V$, a consideration of Eq. (8.2) tells us that we will obtain cross product terms of the form:

$$(J_1''M_1'' \mid \sin\vartheta_1 \cos\varphi_1 \mid J_1'M_1')\,(J_1''M_1'' \mid \sin\vartheta_1 \sin\varphi_1 \mid J_1'\,M_1')$$

All terms of this form will disappear when the summation over $M_1'$ and $M_2'$ indicated in Eq. (8.3) and the averaging over $M_1''$ and $M_2''$ indicated in Eq. (8.4) are carried out.* Thus $|(J_1''M_1''J_2''M_2''|V|J_1'M_1'J_2'M_2')|$ contains three terms of the form:

$$(J_1''M_1'' \mid \sin\vartheta_1 \cos\varphi_1 \mid J_1'M_1')^2\,(J_2''M_2'' \mid \sin\vartheta_2 \cos\varphi_2 \mid J_2'M_2')^2$$

according to Eq. (8.2).

Next we carry out the summation over $M_1'$ as indicated by Eq. (8.3):

$$\sum_{M'} (J''M'' \mid \sin\vartheta\cos\varphi \mid J'M')^2 = \sum_{M'} (J''M'' \mid \sin\vartheta\sin\varphi \mid J'M')^2 = \frac{1}{4}[A^2\,(+) + A^2\,(-)]^2 \qquad (8.11a)$$

$$\sum_{M'} (J''M'' \mid \cos\vartheta \mid J'M')^2 = B^2 \qquad (8.11b)$$

according to Eqs. (8.10).

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* This may be verified by utilizing Eqs. (8.10).

We may quite easily show that:

$$<M^2> = \frac{1}{2J+1} \sum_{-J}^{+J} M^2 = \frac{1}{3} J(J+1)$$

by the use of which in conjunction with Eqs. (8.10) there results:

$$<A^2> = \frac{1}{(2J+1)} \sum_{M} A^2 = \frac{2}{3(2J+1)} [(J+1)\,\delta\,(J,'J''+1) + J\delta\,(J,'J''-1)] \tag{8.12a}$$

$$<B^2> = \frac{1}{2} <A^2> \tag{8.12b}$$

Very straight forward substitution indeed of Eqs. (8.12) into (8.11) and utilization of the results yields:

$$\sum_{\substack{M_1''M_2'' \\ M_1'\,M_2'}} |(J_1''M_1''J_2''M_2''|V|J_1'M_1'J_2'M_2')|^2 = \frac{2}{3}\frac{\mu_1\mu_2}{R^6}\frac{1}{(2J_1''+1)(2J_2''+1)}$$

$$\cdot [(J_1''+1)\,\delta\,(J_1',J_1''+1) + J_1''\,\delta\,(J_1',J_1''-1)][(J_2''+1)\,\delta\,(J_2',J_2''+1)+J_2''\,\delta\,(J_2',J_2''-1)] \tag{8.13a}$$

In order to obtain Eq. (8.4) we simply need to substitute the energy eigenvalues from Eq. (2.37a) and carry out the summation over $J_i'$, the upper rotational states:

$$<E^{(2)}> = -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{R^6}\frac{1}{(2J_1+1)(2J_2+1)}\left\{\frac{(J_1+1)(J_2+1)}{2(J_1+1)A_1+2(J_2+1)A_2} + \frac{(J_1+1)J_2}{2(J_1+1)A_1-2J_2A_2}\right.$$

$$\left. + \frac{J_1(J_2+1)}{2J_1A_1+2(J_2+1)A_2} - \frac{J_1J_2}{2J_1A_1+2J_2A_2}\right\} \tag{8.13b}$$

$$= -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{R^6}\frac{1}{(2J_1+1)(2J_2+1)}\left\{\left[\frac{2A_1}{J_2+1}+\frac{2A_2}{J_1+1}\right]^{-1} + \left[\frac{2A_1}{J_2}-\frac{2A_2}{J_1+1}\right]^{-1}\right.$$

$$\left. - \left[\frac{2A_1}{J_2+1}-\frac{2A_2}{J_1}\right]^{-1} - \left[\frac{2A_1}{J_2}+\frac{2A_2}{J_1}\right]^{-1}\right\} \tag{8.14}$$

where the primes have been dropped, and it is now understood that the $J_i$ refer to the lower state.

If the two molecules are identical so that $A_1 = A_2$ and $\mu_1 = \mu_2$ Eq. (8.14) becomes:

$$<E^{(2)}> = \frac{2}{3}\frac{\mu^4 I}{\hbar^2 R^6}\frac{J_1(J_1+1)+J_2(J_2+1)}{(J_1+J_2)(J_1+J_2+2)(J_1-J_2-1)(J_1-J_2+1)} \tag{8.15}$$

In order to consider the special case of the broadener in the ground state, let us refer to Section 5.3. To begin with a comparison of Eq. (2.35a) (the rigid rotator eigenfunction) and Eq. (5.7) (the hydrogen-like wave function) tells us that they differ only in the radial wave function $R_{nl}(r)$ of the latter. Thus, with the neglect of the matrix elements of $r$, the results of Section 5.3 should be equally applicable here. Let us then rewrite Eq. (5.6) with the help of Eqs. (6.6) as:

$$\begin{aligned}\sum_{m\,\beta} |V_{10,\alpha\beta}|^2 &= \frac{e^4}{r^6}[y_{1\alpha}^2(1) + z_{1\alpha}^2(1) + 4x_{1\alpha}^2(1)]\frac{1}{3}r_{0\beta}^2(2)\,\delta_{l_\beta 1} \\ &= \frac{e^4}{r^6}[y_{1\alpha}(1) + z_{1\alpha}(1) - 2x_{1\alpha}(1)]^2\frac{1}{3}r_{0\beta}^2(2)\,\delta_{l_\beta 1} \\ &= |(1|r|\alpha)|^2\,|(0|V|\beta)|^2 \qquad (8.16)\end{aligned}$$

Now for our present case we may apply Eq. (8.16) by, say, taking a rigid rotator in the ground state as the perturber and another rigid rotator — not necessarily in the ground state — as the absorber. For this case, we would obtain from Eqs. (8.13) and (8.16):

$$<E^{(2)}> = -\frac{2}{3}\frac{\mu_1^2}{R^6}\frac{1}{2J_2''+1}\left\{\Sigma'|(00|er|J_1'M_1')|^2\left(\frac{J_2''+1}{E_{J_1}-E_0-2(J_2''+1)B}+\frac{J_2''}{E_{J_1}-E_0+2J_2''B}\right)\right\} \qquad (8.17)$$

In passing, let us note a corresponding expression for the dipole-dipole interaction of two symmetric top molecules* possessed of dipoles as given by Carroll[16]:

$$\begin{aligned}<E^{(2)}> = -\frac{2}{3}\frac{\mu^4}{R^6}\frac{I_A}{h^2}\Bigg\{&\frac{(J_1+1)^2-K_1^2}{(J_1+1)(2J_1+1)}\left[\frac{(J_2+1)^2-K_2^2}{(J_2+1)(2J_2+1)(J_1+J_2+2)}+\frac{K_2^2}{J_2(J_2+1)(J_1+1)}\right. \\ &\left.+\frac{J_2^2-K_2^2}{J_2(2J_2+1)(J_1-J_2+1)}\right]+\frac{K_1^2K_2^2}{J_1(J_1+1)J_2^2(J_2+1)^2}+\frac{J_1^2-K_1^2}{J_1(2J_1+1)} \\ &\cdot\left[\frac{(J_2+1)^2-K_2^2}{(J_2+1)(2J_2+1)(J_2-J_1+1)}-\frac{K_2^2}{J_1J_2(J_2+1)}-\frac{J_2^2-K_2^2}{J_2(2J_2+1)(J_1+J_2)}\right]\Bigg\} \qquad (8.18)\end{aligned}$$

### 8.4. ROTATIONAL RESONANCE AND THE CASE $J_1 = J_2 = 0$

A consideration of Eq. (8.15) tells us that a rotational resonance condition sets in for identical rotators for $|J_1 - J_2| = 1$. Although the result is that the equation does not hold for this case, it certainly does indicate that strong interactions can be expected for, say, $|J_1 - J_2| < 2$ or 3. Further Eq. (8.14) indicates for dissimilar dipoles that an accidental rotational resonance condition comes about when $J_2A_2 = (J_1 + 1)A_1$ or $(J_2 + 1)A_2 = J_1A_1$. Actually these cases should be treated as for two indistinguishable particles,† where we are unable to state which of the two is excited, but only that the system of two contains one excited and one unexcited molecule. Margenau[115] considers this case as follows:

If we have the quantum numbers involved related by $J_1 = J - 1$ and $J_2A_2 = (J_1 + 1)A_1$ the same energy results as for the case $J_1 = J$ and $(J_2 + 1)A_2 = J_1A_1$, namely, $J^2(A_1 + A_2)A_1/A_2$ — note that for identical rotators we simply let $A_1 = A_2$ which does not much affect our results. Now each state is twofold degenerate due to this effect, so we now average over this degeneracy as we have previously averaged over

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* The eigenfunctions and the energy eigenvalues for the symmetric top rotator have been given by Eq. (2.35b) and (2.37b) respectively.

† This leads us to an interaction dependence as $1/R^3$. See *supra*, Chap. 7.

the spatial degeneracy (given by $M$). As a result of this averaging process the singular terms cancel each other out since they have opposite signs for the two cases and we obtain:

$$< E^{(2)} > = -\frac{1}{6}\frac{\mu^4}{\hbar^2}\frac{I}{R^6}\frac{4J^4 - J^2 + 1}{(4J^2 - 1)^2} \tag{8.19}$$

in place of Eq. (8.15).

Let us bring out a rather obvious but nonetheless important facet of Eq. (8.15). A perusal of the numerator of this equation tells us that for $| J_1 - J_2 | \geqslant 2$ the force averaged over all $M$ between two similar dipoles is repulsive, while for other values of $| J_1 - J_2 |$ this average force is attractive. In essence, we must bar $| J_1 - J_2 | = 1$ so that the forces are attractive only for $J_1 = J_2$.

In actuality the resonance situation which exists here would lead one to ask whether under these conditions there may not be a first order contribution to the energy. The answer, of course, is that there is. We may recall that the manner of the earlier disappearance of the first order contribution was contingent on the summation over the spatial degeneracy parameter $M$. With a two rotator system we now have an additional degeneracy since the system has the same energy for $(J_1, J_2 + 1)$ and $(J_1 + 1, J_2)$ where $J_1 = J_2$.

As usual the problem in degenerate perturbation theory requires a solution of:

$$| V_{ij} - E^{(1)} \delta_{ij} | = 0 \tag{8.20}$$

and we may quite conveniently divide the $V_j$ into four types:

$$(J_1''M_1'', J_2'' + 1, M_2'' \mid V \mid J_1''M_1', J_2'' + 1, M_2') \tag{8.21a}$$

$$(J_1'' + 1, M_1''J_2''M_2'' \mid V \mid J_1'' + 1, M_1'J_2''M_2') \tag{8.21b}$$

$$(J_1''M_1'', J_2'' + 1, M_2'' \mid V \mid J_1'' + 1, M_1'J_2''M_2') \tag{8.21c}$$

$$(J_1'' + 1, M_1''J_2''M_2'' \mid V \mid J_1''M_1', J_2'' + 1, M_2') \tag{8.21d}$$

where in all cases $J_1 = J_2$.

The matrix elements given by Eqs. (8.21a) and (8.21b) are the type with which we have previously dealt, and these may be expected to vanish. In addition, all $V_{ii}$ vanish.

In the manner of Section 8.3 we may then obtain for the remaining elements:

$$\begin{aligned}(J_1''M_1'', J_2'' + 1, M_2'' \mid V \mid J_1'' + 1, M_1'J_2''M_2') &= \frac{\mu^2}{R^3}\frac{1}{(2J + 1)(2J + 3)}\\ \cdot \{ -2\,[(J + M_1'' + 1)(J - M_1'' + 1)(J + M_2'' + 1)(J - M_2'' + 1)]^{1/2}\,&\delta(M_1''M_1')\,\delta(M_2''M_2')\\ + \tfrac{1}{2}\,[(J - M_1'' + 2)(J - M_1'' + 1)(J - M_2'')(J - M_2'' + 1)]^{1/2}\,&\delta(M_1', M_1'' - 1)\,\delta(M_2', M_2'' + 1)\\ + \tfrac{1}{2}\,[(J + M_1'' + 2)(J + M_1'' + 1)(J + M_2'')(J + M_2'' + 1)]^{1/2}\,&\delta(M_1,'M_1'' + 1)\,\delta(M_2'M_2'' - 1)\}\end{aligned} \tag{8.22}$$

After a fashion, which we shall detail,[*] the fact that $V_{ii} = 0$ requires that the mean value of $E$ be zero,

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[*] See *infra*, Sec. 8.10.

and the root mean square value of $E$ may be found as:

$$[< E^{(1)2} >]^{1/2} = \left(\frac{2}{3}\right)^{1/2} \frac{J+1}{[(2J+1)\,(2J+3)]^{1/2}} \frac{\mu^2}{R^3} \tag{8.23}$$

Margenau[115] has considered the special resonance case $J_1 = 0$, $J_2 = 1$. Leaving out the fixed $J_i$ from the matrix element symbol and noting that $M_1'' = M_2' = 0$ leads to:

$$(0M_2'' \mid V \mid M_1'0) = \frac{1}{3}\frac{\mu^2}{R^3}[-2\,\delta\,(M_2''0)\,\delta\,(M_1'0) + \delta\,(M_2'', -1)\,\delta\,(M_1', -1)$$

$$+ \delta\,(M_2''1)\,\delta\,(M_1''1)] \tag{8.24}$$

from Eq. (8.22).

Eq. (8.24) yields the secular determinant:

$$\begin{vmatrix} -E^{(1)} & 1/3a & 0 & 0 & 0 & 0 \\ 1/3a & -E^{(1)} & 0 & 0 & 0 & 0 \\ 0 & 0 & -E^{(1)} & -2/3a & 0 & 0 \\ 0 & 0 & -2/3a & -E^{(1)} & 0 & 0 \\ 0 & 0 & 0 & 0 & -E^{(1)} & 1/3a \\ 0 & 0 & 0 & 0 & 1/3a & -E^{(1)} \end{vmatrix} = 0$$

of solution:

$$E^{(1)} = \pm\,\frac{1}{3}\frac{\mu^2}{R^3},\ \pm\,\frac{2}{3}\frac{\mu^2}{R^3} \tag{8.25}$$

In some instances, the perturbations may become of the order of magnitude of the unperturbed energies or of the differences of these unperturbed energies. In such cases, ordinary perturbation methods fail and some other approach such as the Variation Method is called for.

Let us suppose we are, for some reason or other, possessed of the Hamiltonian $H$. We now choose a so-called variation function $\varphi$ — it is only required that $\varphi$ behave more or less as a wave function should — and we maintain that, if $E_0$ is the lowest energy eigenvalue of $H$, the following is true.*

$$E_0 \leqslant \int \varphi H \varphi d\tau = E \tag{8.26}$$

where $\varphi$ has been supposed real, so that $\bar{\varphi} = \varphi$.

Now let us be a bit more specific and suppose $H$ to be $H_0 + V$, where $V$ is our familiar interaction. Next we expand the variation function in terms of the unperturbed eigenfunctions of our system:

$$\varphi = \sum_i a_i \psi_i \tag{8.27}$$

and we recall that $|\, a_j \,|^2$ will be the probability that the system is in the state $\psi_j$.

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* This follows directly from (1) the Schrodinger equation $H\psi_n = E_n\psi_n \longleftrightarrow \int \psi_n H \psi_n d\tau = E_{nj}$; (2) $\psi_n = \Sigma a_{ni}\varphi_i$ and (3) $E_0 < E_1 < \ldots < E_n < \ldots$

Since the right side of Eq. (8.26) is always greater than the desired value $E_0$, minimization of this integral is called for. This may be accomplished as follows:

$$E = \frac{\int \varphi H \varphi d\tau}{\int \varphi \varphi d\tau} = \frac{\sum\limits_{ij} c_i c_j H_{ij}}{\sum\limits_{ij} c_i c_j \delta_{ij}} \tag{8.28}$$

where:

$$H_{ij} = \int \psi_i H \psi_j d\tau \text{ and } \delta_{ij} = \int \psi_i \psi_j d\tau$$

or:

$$E \sum_{ij} c_i c_j \delta_{ij} = \sum_{ij} c_i c_j H_{ij} \tag{8.29}$$

It should be quite apparent that the only entities in Eq. (8.29) which may be adjusted to minimize $E$ are the $c_k$. We proceed to differentiate with respect to each $c_k$:

$$\frac{\partial E}{\partial c_k} \sum_{ij} c_i c_j \delta_{ij} + E \frac{\partial}{\partial c_k} (\sum_{ij} c_i c_j \delta_{ij}) = \frac{\partial}{\partial c_k} (\sum_{ij} c_i c_j H_{ij}) \tag{8.30}$$

and in order for a minimum to be attained, it appears necessary that $\frac{\partial E}{\partial c_k} = 0$ for each $c_k$. All of which leads to:

$$\sum_i c_i (H_{ik} - \delta_{ik} E) = 0 \text{ for } k = 1,2, \ldots \tag{8.31}$$

which set of equations in turn yields the secular determinant:

$$| H_{ik} - \delta_{ik} E | = 0 \tag{8.32}$$

It is also true that:

$$H_{ik} = E_{ik}{}^0 \delta_{ik} + V_{ik} \longleftrightarrow |V_{ik} + (E_i{}^0 - E)\delta_{ik}| = 0 \tag{8.33}$$

by definition.

Margenau[115] utilized this variational perturbation method to treat the resonance case $J_1 = J_2 = 0$. As our variation function we take:

$$\psi = c_0 \psi_1 + c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 \tag{8.34}$$

where $\psi_0 = \psi_{J_1 M_1}(1) \psi_{J_2 M_2}(2) = \psi_{00}(1) \psi_{00}(2)$ is the ground state function and the remaining $\psi_i$ are those eigenfunctions with which this ground state function may combine under the influence of $V$. Of course:

$$\psi_1 = \psi_{10}(1) \psi_{10}(2); \qquad \psi_2 = \psi_{1-1}(1) \psi_{11}(2) \tag{8.35}$$

$$\psi_3 = \psi_{11}(1) \psi_{1-1}(2)$$

The $E_1{}^0$ required in Eq. (8.33) may be obtained from Eq. (2.37a) as:

$$E_0{}^0 = 0; E_1{}^0 = E_2{}^0 = E_3{}^0 = 2\epsilon = \frac{2\hbar^2}{I} \tag{8.36}$$

From Eqs. (8.10) we may obtain:

$$V_{01} = -\frac{2}{3} a; \quad V_{02} = V_{03} = -\frac{1}{3} a; \quad V_{ik} = V_{ki} \tag{8.37}$$

where $a = \frac{\mu^2}{R^3}$.

As a consequence Eq. (8.33) takes the form.

$$\begin{vmatrix} -E^{(1)} & -2/3a & -1/3a & -1/3a \\ -2/3a & 2\epsilon - E^{(1)} & 0 & 0 \\ -1/3a & 0 & 2\epsilon - E^{(1)} & 0 \\ -1/3a & 0 & 0 & 2\epsilon - E^{(1)} \end{vmatrix} = 0 \qquad (8.38)$$

whose solution is:

$$E^{(1)} = \frac{h^2}{I}\left[1 - \left(1 + \frac{2\mu^4 I^2}{3h^4 R^6}\right)^{1/2}\right] \qquad (8.39)$$

Eq. (8.39) tells us the first order interaction energy for two like dipole linear rotators for the case $J_1 = J_2 = 0$. For large $R$, the radical in this equation may be expanded with the result:

$$E^{(1)} \doteq -\frac{\mu^4 I}{3h^2 R^6} \qquad (8.40)$$

and for small $R$ Eq. (8.39) becomes:

$$E^{(1)} \doteq -\left(\frac{2}{3}\right)^{1/2} \frac{\mu^2}{R^3} \qquad (8.41)$$

One can hardly help but note the comparison between Eq. (8.21b) and the equation for the classical potential, $-\frac{2\mu^2}{R^3}$, of two dipoles aligned along $R$. The interaction law change from $R^{-6}$ to $R^{-3}$ is also rather striking.

Let us now sketch a resonance development of London[105] in just enough detail so that the results which we shall later utilize will be somewhat intelligible. This author used what we might as well call an order-of-magnitude technique to arrive at the secular determinant:

$$| V_{\Upsilon_i \Upsilon_j} + (E_{\Upsilon_i}{}^{(0)} - E_{\Upsilon_k}{}^{(0)} - E_k{}^{(1)})\, \delta_{\Upsilon_i \Upsilon_j} | = 0 \qquad (8.42)$$

We shall be able to define the new symbols $E_{\Upsilon_i}{}^{(0)}$ and $E_{\Upsilon_k}{}^{(0)}$ after another step in the development.

London considered only the eigenfunction $\psi_{J_1}^{M_1}\, \psi_{J_2}^{M_2}$ and the thirteen eigenfunctions with which this eigenfunction may combine, as always, under the influence of $V$. The possible combinations are governed by the selection rules $\Delta J_1 = \pm 1$, $\Delta J_2 = \pm 1$, $\Delta M_1 = -\Delta M_2 = \pm 1, 0$. He did not consider the twelve functions with which each of these twelve functions could combine, etc., etc., and as a consequence as Margenau noted his " . . . expression does not yield the correct positions of the roots of the complete secular equation, but may allow in many cases a useful approximation, for it has the same 'root mean square' as the true solution."[115]

Under these restrictions then, we shall utilize the eigenfunctions:

$$u_0 = \psi_{J_1}^{M_1}\,\psi_{J_2}^{M_2}$$

$$\left.\begin{aligned} u_1 &= \psi_{J_1+1}^{M_1}\,\psi_{J_2+1}^{M_2} \\ u_2 &= \psi_{J_1+1}^{M_1+1}\,\psi_{J_2+1}^{M_2-1} \\ u_3 &= \psi_{J_1+1}^{M_1-1}\,\psi_{J_2+1}^{M_2+1} \end{aligned}\right\}\ \Upsilon_1 \qquad \left.\begin{aligned} u_7 &= \psi_{J_1+1}^{M_1}\,\psi_{J_2-1}^{M_2} \\ u_8 &= \psi_{J_1+1}^{M_1+1}\,\psi_{J_2-1}^{M_2-1} \\ u_9 &= \psi_{J_1+1}^{M_1-1}\,\psi_{J_2-1}^{M_2+1} \end{aligned}\right\}\ \Upsilon_7$$

$$\left.\begin{aligned} u_4 &= \psi_{J_1-1}^{M_1}\,\psi_{J_2-1}^{M_2} \\ u_5 &= \psi_{J_1-1}^{M_1+1}\,\psi_{J_2-1}^{M_2-1} \\ u_6 &= \psi_{J_1-1}^{M_1-1}\,\psi_{J_2-1}^{M_2+1} \end{aligned}\right\}\ \Upsilon_4 \qquad \left.\begin{aligned} u_{10} &= \psi_{J_1-1}^{M_1}\,\psi_{J_2+1}^{M_2} \\ u_{11} &= \psi_{J_1-1}^{M_1+1}\,\psi_{J_2+1}^{M_2-1} \\ u_{12} &= \psi_{J_1-1}^{M_1-1}\,\psi_{J_2+1}^{M_2+1} \end{aligned}\right\}\ \Upsilon_{10} \tag{8.43}$$

from which we may define $E_{\Upsilon_i}{}^{(0)}$ and $E_{\Upsilon_k}{}^{(0)}$.

$E_{\Upsilon_k}{}^{(0)}$ is in all cases the zeroth-order energy going with $u_0$ as given by Eq. (2.37a). $E_{\Upsilon_i}{}^{(0)}$ are the zeroth-order energies going with $u_1, u_2, \ldots, u_{12}$ as again given by Eq. (2.37a). We may note that the energies associated with $u_1, u_2, u_3$, are the same; as are those associated with $u_4, u_5, u_6$, and so forth. Thus:

$$\begin{aligned} E_1 &= E_{\Upsilon_1}{}^{(0)} - E_{\Upsilon_0}{}^{(0)} = (J_1 + J_2 + 2)\frac{\hbar^2}{I} \\ E_2 &= E_{\Upsilon_4}{}^{(0)} - E_{\Upsilon_0}{}^{(0)} = -(J_1 + J_2)\frac{\hbar^2}{I} \\ E_3 &= E_{\Upsilon_7}{}^{(0)} - E_{\Upsilon_0}{}^{(0)} = (J_1 - J_2 + 1)\frac{\hbar^2}{I} \\ E_4 &= E_{\Upsilon_{10}}{}^{(0)} - E_{\Upsilon_0}{}^{(0)} = (J_2 - J_1 + 1)\frac{\hbar^2}{I} \end{aligned} \tag{8.44}$$

A secular determinant of precisely the form Eq. (8.44) wherein the $2\epsilon$ are now replaced by the $E_i$ from Eq. (8.42) results. In addition, we let $V_{0i} = V_i$, and from this secular determinant, the equation:

$$R^6E^{(1)} = \frac{a_1{}^2}{E^{(1)} - E_1} + \frac{a_2{}^2}{E^{(1)} - E_2} + \frac{a_3{}^2}{E^{(1)} - E_3} + \frac{a_4{}^2}{E^{(1)} - E_4} \tag{8.45}$$

follows, where:

$$\frac{a_i{}^2}{R^6} = V_{3i}{}^2 + V_{3i-1}{}^2 + V_{3i-2}{}^2 \tag{8.46}$$

For the resonance case ($J_1 > 0$, $J_2 > 0$, $J_1 = J_2 + 1$) Eq. (8.45) becomes:

$$R^6E^{(1)} = \frac{a_1{}^2}{E^{(1)} - E_1} + \frac{a_2{}^2}{E^{(1)} - E_2} + \frac{a_3{}^2}{E^{(1)} - E_3} + \frac{a_4{}^2}{E^{(1)}} \tag{8.47}$$

For large $R$ and $|E^{(0)}| \ll |E_i|$:

$$R^6 (E^{(1)})^2 + \left(\frac{a_1^2}{E_1} + \frac{a_2^2}{E_2} + \frac{a_3^2}{E_3}\right)E^{(1)} - a_4^2 = 0$$

whose solution is:

$$E^{(1)} = \frac{1}{2R^6}\left[-\left(\frac{a_1^2}{E_1} + \frac{a_2^2}{E_2} + \frac{a_3^2}{E_3}\right) \pm \sqrt{\left(\frac{a_1^2}{E_1} + \frac{a_2^2}{E_2} + \frac{a_3^2}{E_3}\right)^2 + 4a_4^2R^6}\right]$$

$$= -\frac{1}{2}\left(\frac{a_1^2}{E_1} + \frac{a_2^2}{E_2} + \frac{a_3^2}{E_3}\right)\frac{1}{R^6} \pm \frac{a_4}{R^3} \tag{8.48}$$

Eq. (8.48) gives the first-order perturbation energy for the rotational resonance case. We note the comparison with Eq. (8.25).

## 8.5. INTERACTION BETWEEN A DEFORMABLE AND A RIGID DIPOLE (INDUCTION EFFECT)*

Let us next consider the interaction between two molecular models, one a rigid dipole rotator and the other a deformable dipole. Now by deformable, we mean that the latter dipole may undergo distorting vibrations resulting in its possession of vibrational energy levels and to it also we attribute electronic energy levels. In this case, we may carry through the treatment in exactly the manner of Sec. 8.3 as far as Eq. (8.13). To this point in the development, the new physical conditions introduce no changes. In Eq. (8.13) the subscript 1 now indicates the deformable dipole while the subscript 2 represents the rigid dipole. From this point, it is the summation over $J_1'$ and $J_2'$, as indicated in Eq. (8.3), which must be modified.

The summation over $J_2'$ remains unchanged since the rigid dipole possesses only rotational energy, but now we must not only sum over the upper rotational states of dipole 2 (for the ground electronic vibration state) but also over all upper electronic-vibration-rotation states. The grand sum which results may be broken up into two sums, (1) the sum over all $J_1'$ for the electronic-vibration ground state and (2) the sum over the remaining upper states for the deformable dipole. Both of these sums are to be combined, of course, with the sum over the rotational levels of the rigid dipole. Subsum (1) corresponds precisely with Eq. (8.14).† Subsum (2), on the other hand takes the form:

$$<E^{(2)}> = \frac{2}{3}\frac{\mu_2^2}{R^6}\sum_{K_1J_2'}\frac{|(0|e\mathbf{r}_1|k_1)|^2\,[(J_2''+1)\,\delta\,(J_2',J_2''+1) + J_2''\,\delta\,(J_2',J_2'-1)]}{[E_0 - E_{K_1} + E_{J_2''} - E_{J_2'}]\,(2J_2''+1)} \tag{8.49}$$

where now $K_1$ is a quantum number aggregate representing the upper state electronic and vibrational quantum numbers.

## 8.6. INTERACTION BETWEEN A DEFORMABLE ROTATOR AND AN ISOTROPIC HARMONIC OSCILLATOR

We now take as our absorber an isotropic, three dimensional, harmonic oscillator and as our perturber a deformable rotator in the ground state. The eigenfunction describing such an oscillator has been given

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* Cf. references 157, 177, 179, and 180.

† Except that now $\mu_1$ will be a function of the electronic vibration level involved.

by Eq. (2.30c) in spherical polar coordinates. Although this form of the eigenfunction is the most descriptive, we shall find that it will be more convenient here to use the rectangular coordinate form, namely:

$$\psi(v_1v_2v_3) = \prod_{i=1}^{3} H_{v_i}\,(\beta^{1/2}x_i)\,\exp\left[-\beta/2\;x_i^2\right] \tag{8.50}$$

where $\beta = \dfrac{m\omega}{\hbar}$ .

In order to simplify our considerations, let us suppose that $v_1'' = v_2'' = v_3''$. Eq. (8.15) may be utilized in order to write Eq. (8.3) as:*

$$E^{(2)} = \sum_{v'\Lambda} \frac{|\,(v_1''v_2''v_3''\,|\,V\,|\,v_1'v_2'v_3')\,|^2\,|\,(0\,|\,er\,|\,\Lambda)\,|^2}{E_{v'} - E_{v''} + E_\Lambda - E_0} \tag{8.51}$$

where $V$ is given by $V = \dfrac{e}{R^3}\,[2z - x - y]$.

Using the recursion formula for Hermite polynomials

$$\xi H_n\,(\xi) = \tfrac{1}{2}\,H_{n+1}\,(\xi) + 2n\,H_{n-1}\,(\xi)$$

we may show that, for the harmonic oscillator:

$$x_{v''v'} = y_{v''v'} = z_{v''v'} = \begin{cases} \sqrt{\dfrac{v''+1}{2\beta}} & \text{for } v' = v'' + 1 \\ \sqrt{\dfrac{v''}{2\beta}} & \text{for } v' = v'' - 1 \\ 0 & \text{for } v' \neq v'' \pm 1 \end{cases} \tag{8.52}$$

Quite obviously then, the three vibrational quantum numbers in the eigenfunction of Eq. (8.50) may only individually change by ± 1. The states with which $\psi(v_1''v_2''v_3'')$ may combine under the influence of $V$ are listed in Table (8.1). The matrix elements $V_{v''v'}$ resulting from these combinations together with the corresponding values of $E_{v'} - E_{v''}$† are also given in the table.

| $\psi(v_1'v_2'v_3')$ | $E_{v'} - E_{v''}$ | $-\dfrac{R^3}{e}\,V_{v''v'}$ |
|---|---|---|
| $\psi(v_1'' + 1, v_2'', v_3'')$ | $h\nu$ | $-\,(2\beta)^{-1/2}(v_1 + 1)^{1/2}$ |
| $\psi(v_1'', v_2'' + 1, v_3'')$ | $h\nu$ | $-\,(2\beta)^{-1/2}(v_2 + 1)^{1/2}$ |
| $\psi(v_1'', v_2'', v_3'' + 1)$ | $h\nu$ | $2(2\beta)^{-1/2}(v_3 + 1)^{1/2}$ |
| $\psi(v_1'' - 1, v_2'', v_3'')$ | $-\,h\nu$ | $-\,(2\beta)^{-1/2}(v_1)^{1/2}$ |
| $\psi(v_1'', v_2'' - 1, v_3'')$ | $-\,h\nu$ | $-\,(2\beta)^{-1/2}(v_2)^{1/2}$ |
| $\psi(v_1'', v_2'', v_3'' - 1)$ | $-\,h\nu$ | $2(2\beta)^{-1/2}(v_3)^{1/2}$ |

Table 8.1

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* Eq. (2.30c) tells us that the special case (rigid rotator) considered in obtaining Eq. (8.16) could be extended to the rotator-vibrator, or to the rotator-vibrator possessing also a hydrogen like electronic eigenfunction, etc.

† See *supra*, Eq. (2.33a) for the oscillator energies.

Let us note the threefold degeneracy* that exists in the final states of the same energy in Table (8.1)—at least for our purposes here. This will require our dividing by three when taking the sum indicated in Eq. (8.51).

We may now utilize the results of Table (8.1) in Eq. (8.51) to obtain:

$$<E^{(2)}> = \frac{1}{3}\frac{e^2}{R^6}\frac{\hbar}{2m\omega}\sum_{\Lambda}\left\{\frac{v_1 + 1 + v_2 + 1 + 4(v_3 + 1)}{E_\Lambda - E_0 + h\nu} + \frac{v_1 + v_2 + 4v_3}{E_\Lambda - E_0 - h\nu}\right\} \mid (0 \mid V \mid \Lambda) \mid^2$$

$$= \frac{e^2}{R^6}\frac{\hbar\omega}{m\omega^2}\sum_{\Lambda}\left\{\frac{v + 1}{E_\Lambda - E_0 + h\nu} + \frac{v}{E_\Lambda - E_0 + h\nu}\right\} \mid (0 \mid er \mid \Lambda) \mid^2 \tag{8.53a}$$

since $v_1'' = v_2'' = v_3''$.

If $E_\Lambda - E_0$ is large compared to $h\nu$ Eq. (8.53a) may be rewritten as:

$$<E^{(2)}> \doteq \frac{e^2}{R^6}\frac{\hbar\omega(2v + 1)}{m\omega^2}\sum_{\Lambda}\frac{\mid (0 \mid er \mid \Lambda) \mid^2}{E_\Lambda - E_0}$$

$$= 2\frac{e^2}{R^6}\frac{E_v}{m\omega^2}\sum_{\Lambda}\frac{\mid (0 \mid er \mid \Lambda) \mid^2}{E_\Lambda - E_0} \tag{8.53b}$$

where $E_v = \hbar\omega(v + \frac{1}{2})$ according to Eq. (2.33a).

This is, of course, the dipole-dipole interaction only. Utilizing the same principles which have arisen in this section, Margenau[116] obtained for the interaction between two threefold harmonic oscillators in the ground state, the following:

$$E^{(2)} = -\frac{3}{4}\frac{\alpha^2 h\nu}{R^6} - \frac{15}{4}\frac{\alpha^3(h\nu)^2}{e^2R^8} - \frac{315}{32}\frac{\alpha^4(h\nu)^3}{e^4R^{10}} \tag{8.54}$$

where $\alpha$ is the polarizability of either oscillator. The first term represents the dipole-dipole interaction, the second the dipole-quadrapole, and the third the quadrapole-quadrapole.

## 8.7. BROADENING BY MOLECULES WITH NO PERMANENT POLES (DISPERSION EFFECT)

Margenau[115] initiated the first attack on the Theory of Molecular Broadening in 1936. Of the many possible special cases of this phenomenon which could have been considered, he chose to investigate the case of broadening by foreign gases which possess no permanent poles since Watson and Hull[191] had previously obtained experimental data on this case.

Watson and Hull had investigated the broadening of AlH by $H_2$, BeO by $O_2$, CN by $N_2$, and MgH by $H_2$.† These authors discussed the first two of these combinations in detail although we shall neglect their BeO by $O_2$ results. We shall neglect these latter results since instead of yielding the phenomenon with which we shall be concerned, they simply require explanation (justified though it may be) as to why we do not obtain what we are looking for. It does not appear very straightforward to base our theoretical considerations on experimental results which we would have obtained had the situation been different.

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* Actually each level is $\frac{1}{2}(v + 1)\ (v + 2)$ -fold degenerate in general.

† We may recall, that in general, homonuclear diatomic molecules ($H_2$, etc.) are possessed of no permanent or vibration induced electric dipole moments.

The AlH lines broadened by $H_2$ in the band at 4260A were studied for values of $J < 22$ and ranging from $Q$ (6) to $J(22)$. Pressures of 5.7, 10.7 and 14.7 atmospheres were utilized. To begin with no $J$ dependence in line width was observed. A line shift of 0.051 cm.$^{-1}$ ± 50% per atmosphere $H_2$ pressure and a linear line width increase of 0.24 ± 0.03 cm.$^{-1}$ per atmosphere were obtained. A comparison of these results with those for the electronic resonance lines of Hg and Na shows a sufficient correspondence to indicate that, for the type of broadening under consideration, the rotation-vibration lines may be expected to be broadened and shifted by about the same amount as the electronic lines. All of which led Margenau to the investigation to which we now direct our attention.

Let us label the states of an absorber by $K$ with the state in which we now find this absorber being designated $k$. The broadener states we label $\Lambda$ with the lowest state 0. Now from Eq. (8.16) we may obtain the perturbation on the energy of the absorber averaged over all orientations of the absorber as:

$$<E^{(2)}> = -\frac{2}{3R^6}\sum_{\Lambda\kappa}{}' \frac{|(er)_{0\Lambda}|^2\,|(V)_{k\kappa}|^2}{E_\Lambda - E_0 + E_\kappa - E_k} \qquad (8.55)$$

We have stipulated that $E_0$ is the lowest energy of the perturber. This means that $E_\Lambda - E_0$ will always be positive. In addition we have not allowed this perturber a permanent dipole moment. This means, according to our considerations of Section 1, that no pure rotational transitions, which amount to the lowest energy transitions, are possible. Thus, according to our rule of thumb of Section 1 the 10 volt vibrational transitions are the lowest energy allowed.

On the other hand, $E_\kappa - E_k$ may be positive or negative. This means that $<E^{(2)}>$ may be greater than or less than zero so that the spectral line may exhibit either a violet or a red asymmetry.

Now where we simply have dealt with a set of relatively widely spaced electronic levels in our monatomic considerations, we now deal with a modification of this situation. We still have the set of electronic levels, but on each of these is superposed a set of more closely spaced vibrational levels, and, in turn, on each of these vibrational levels is superposed a set of still more closely spaced rotational levels. When we are considering the visible and ultra-violet portion of the spectrum (but certainly not when we are considering the infrared) we may, as an approximation, consider only the electronic contributions to $E_k - E_k$ — they surely constitute the largest ones — and merely let the rotation-vibration levels superposed upon them amount to degeneracies accounted for by a summation in Eq. (8.55). It follows that the result will closely correspond to that for monatomic molecules. To be sure, this could only be expected to give us results for electronic band spectra, but it does tend to indicate that we should not expect too heavy a broadening or shift dependence on rotational or vibrational quantum numbers under the present physical conditions.

In order to consider the possible effect of molecular rotation let us approximate our absorber by a rigid rotator of dipole moment $\mu$. Then Eq. (8.2) takes the form Eq. (8.17):

$$<E_{J^{(2)}}> = -\frac{2}{3}\frac{\mu^2}{R^6}\frac{1}{2J+1}\left\{\sum_{\Lambda}{}' \,|(er)_{0\Lambda}|^2\left(\frac{J+1}{E_\Lambda - E_0 - 2(J+1)B} + \frac{J}{E_\Lambda - E_0 + 2JB}\right)\right\} \qquad (8.17)$$

where, as usual, $B = h^2/8\pi^2 I$.

Now $I$ is usually of the order of $10^{-40}$, and, with $h$ of the order of $10^{-27}$ we see that $B$ will be small compared to $E_\Lambda - E_0$ when the perturber has no permanent dipole. When $B$ is neglected Eq. (8.5a) becomes:

$$< E^{(2)} > = -\frac{2}{3}\frac{\mu^2}{R^6}\sum_{\Lambda}{}'\frac{|(er)_{0\Lambda}|^2}{E_\Lambda - E_0} = -\frac{\alpha\mu^2}{R^6} \qquad (8.56a)$$

If the dipole moment $\mu \doteq 10^{-18}$ the perturbation given by Eq. (8.5b) is about 1/20 of that for the electronic case. Now let us write Eq. (8.17) as:

$$<E_J^{(2)}> = -\frac{2}{3}\frac{\mu^2}{R^6}\frac{1}{(2J+1)}\sum_{\Lambda}{}' \, |(er)_{0\Lambda}|^2 \left[\frac{J+1}{(E_\Lambda - E_0)\left[1 - \frac{2(J+1)B}{E_\Lambda - E_0}\right]} + \frac{J}{(E_\Lambda - E_0)\left[1 + \frac{2JB}{E_\Lambda - E_0}\right]}\right]$$

$$= -\frac{\alpha\mu^2}{R^6}\frac{1}{(2J+1)}\left[(J+1)\left\{1 + \frac{2(J+1)B}{E_\Lambda - E_0} + \frac{4(J+1)^2B^2}{(E_\Lambda - E_0)^2} + \dots\right\} + J\left\{1 - \frac{2JB}{E_\Lambda - E_0} + \frac{4J^2B^2}{(E_\Lambda - E_0)^2} + \dots\right\}\right]$$

$$= -\frac{\alpha\mu^2}{R^6}\left[1 + \frac{2B}{(E_\Lambda - E_0)} + \frac{4(J^2 + J + 1)B^2}{(E_\Lambda - E_0)^2} + \dots\right] \qquad (8.56b)$$

It is apparent from Eq. (8.56b) that the portion of $<E_J^{(2)}>$ which depends on $J$ is very small due to the appearance of $B^2$ in the numerator and $(E_\Lambda - E_0)^2$ in the denominator involved.

Margenau carried out his considerations of the effect of molecular vibrations in an analogous manner. In this case we obtain from Eq. (8.53b):

$$<E_v^{(2)}> = 3\,\frac{e^2E_v}{m\omega^2R^6}\,\alpha \qquad (8.57)^*$$

From Eq. (8.57) we may note that a more marked dependence on the vibrational quantum number is exhibited than on the rotational quantum number as given by Eq. (8.17). On the other hand the perturbation given by Eq. (8.17) is about five times that given by Eq. (8.57).

On the basis of these investigations, then Margenau concluded that "within obtainable experimental accuracy" all rotation-vibration lines associated with the same electronic transition should show broadening and shift of about the same degree when the broadening agent is a non-polar molecule. In addition these lines should be affected by foreign perturbers almost in the manner of the corresponding monatomic lines under similar circumstances.

As Watson[190] has noted "dispersion forces" — the type considered — also appear to predominate in the self-broadening of non-polar molecular lines. Were the normal resonance forces between like monatomic molecules present, we would not normally expect this to be the case, but the closely spaced rotational levels of the polyatomic molecule render this predominance reasonable. As we have noted, the rotational levels specified by, say, just $J$ are comparatively closely spaced energywise. As a consequence a Maxwell-Boltzmann temperature distribution of molecules over these levels will not lead to the preferential population of the monatomic case, and they will be more equally divided among many levels. On the other hand the allowed $J$ change in transition is generally limited to ±1 or 0 so that the probability of energy exchange with the resultant degeneracy is severely restricted. In toto, then, this resonance effect would not appear to be primarily responsible for self-broadening, and we may safely look to these dispersion forces as broadening agents for non-polar molecules. This conclusion had been verified for the case of methane by Childs,[19] Dennison and Ingram,[29] and Vedder and Mecke,[183] for atmospheric pressure and above, and for the case of acetylene by Hedfield and Mecke,[58] Herzberg and Spinks,[61] Lochte-Holtgreven and Eastwood,[104] and McKellar and Bradley[125] for atmospheric pressure.

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* Margenau obtained $\frac{e^2E_v}{m\omega^2R^6}\alpha$.

We have broadened molecular lines by non-polar molecules, and it would now appear a logical next step to broaden these lines by polar molecules. Let us then consider first the work of Margenau and Watson on this phenomenon.

## 8.8. BROADENING BY LINEAR DIPOLE MOLECULES

Before turning to the qualitative considerations of Margenau and Watson[122] in this regard, we consider briefly an earlier work of London[105] in which this author contributed much toward the systematizing of inter-molecular forces.

In what might be considered the natural course of events we have encountered the "Directional Effect" of Keesom,[86] the "Static Induction Effect" of Debye, and the "Dispersion Effect" of London in Sections 8.3, 8.5, and 8.7 respectively. London, on the other hand, began his considerations by the introduction of these effects. He started from Eq. (5.4) and considered the contribution of this equation to consist of a sum of terms of the form:

$$E_{kl}^{(2)} = E_{kl}^{(rr)} + E_{kl}^{(rg)} + E_{kl}^{(gr)} + E_{kl}^{(gg)}$$

In this equation $E_{kl}^{(rr)}$ is associated with small "jumps" or quantum number changes on the part of both interacting molecules. $E_{kl}^{(rg)}$ and $E_{kl}^{(gr)}$ arise due to a small jump by one molecule and a large jump by the other, and, finally, $E_{kl}^{(gg)}$ results from large jumps by both.

$E_{kl}^{(gg)}$ corresponds to the Dispersion Effect and is present to a greater or lesser extent for all molecules. The contribution is due to the "kurzperiodischen Storungen" arising from the motion of the inner electrons. The potential arising from this is of the form $-1/R^6$, $-1/R^8$ and higher inverse powers of $R$.

$E^{(rr)}$ is the contribution of the Directional Effect of Section 8.3 and arises from the interactions of the dipoles (or quadrapoles) at various relative orientations. We have seen the manner in which this effect depends on $\pm\ 1/R^6$ for dipoles at large distances and $-\ 1/R^3$ for the lowest state or, in the case of the suppression of degeneracy, in the metastable state at short distances (Sec. 8.4). For quadrapoles, a corresponding $\pm\ 1/R^{10}$ and $-\ 1/R^5$ dependence results.

$E^{(gr)}$ and $E^{(rg)}$ result from the Static Induction Effect, and, as we have noted, depend on $-\ 1/R^6$ or $-1/R^8$ for dipoles or quadrapoles respectively. London describes this effect as "due to the charge distribution of the entire molecules."

It is to one of these three effects than that Margenau and Watson[122] looked for an explanation of the broadening in linear dipole molecules such as HCN possessed of relatively large ($>10^{-18}$) dipole moments. They believed the principal cause of broadening to be the directional effect and we might enumerate the spectral prognostications toward which such an assumption leads.

To begin with we must hypothesize the unpolarizable (rigid) dipoles of Section (8.3) and we recall from Sections (8.3) and (8.4) that (1) the intermolecular forces are relatively weak except when the near resonance condition, $|\ J_1\ -\ J_2\ |\ <\ 2$ or 3, sets in and (2) the lowest rotational state is most strongly influenced by other molecules in the lowest or neighboring states.*

The lower state $J_1''$ we take as other than the lowest rotational state so that we can concern ourselves with (1). As has been mentioned, the rotational levels lie sufficiently close together so that a thermal distribution over them may be expected. Suppose $J_1''$ to designate a level near the maximum of this thermal distribution. Then a much greater number of perturbers can be expected to fulfill the condition

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* Cf., for example, *supra*, Eqs. (8.21).

$| J_1'' - J_2'' | < 2$ or 3 than would be the case were the $J_1''$ level to be found toward the wings of this thermal distribution. Since the upper level will also enter into the line broadening one cannot say more as yet than that those most intense lines arising from $J$ levels near the maximum of the thermal distribution should be broadened more than the remainder of the lines of the band.

In regard to (2) this indicates that a greater broadening of the line arising from the lowest rotational level is to be expected, but only under certain conditions. At normal temperatures, the thermal distribution should not populate levels lying near $J_1'' = 0$ very highly so that the effect may not be very pronounced. As the temperature is lowered, however, these low level populations will increase and we should expect to see an increase in the broadening of the line with $J_1'' = 0$ over neighboring spectral lines. It might be noted also that due to "greater flexibility downward" a violet asymmetry in this line may be expected.

We now devote ourselves to Margenau and Warren's more quantitative consideration of the broadening effected by dipole interactions.

## 8.9. INTERACTIONS BETWEEN SYMMETRICAL TOP DIPOLE MOLECULES

For our two interacting molecules we choose two identical symmetrical rotators each possessed of a permanent electric dipole moment $\mu$ oriented along the molecular figure axis. The interaction potential between the two rotators is again given by Eq. (8.2) where now $\mu_1 = \mu_2 = \mu$. The eigenfunctions for this system are given, according to Eq. (2.35b), by:

$$\psi_{J_1K_1M_1J_2K_2M_2} = N(J_1K_1M_1)N(J_2K_2M_2)\ \Theta_{J_1K_1M_1}(\vartheta_1)\ \Theta_{J_2K_2M_2}(\vartheta_2)e^{i(M_1\varphi_1+M_2\varphi_2+K_1\chi_1+K_2\chi_2)} \qquad (8.58)$$

for sufficient separation $R$. Eq. (8.2) tells us that $V$ is not dependent on the Eulerian angle $\chi$ so that $K_1'' = K_1'$ and $K_2'' = K_2'$ under the aegis of $V$, and the matrix of $V$ is diagonal in $K_1$ and $K_2$ as a consequence.

Now in obtaining the matrix elements of $V$, the integrations over $\varphi_i$ and $\chi_i$ may be carried out immediately to yield:

$$\begin{aligned}
&(J_1''K_1''M_1''J_2''K_2''M_2'' \mid V \mid J_1''K_1''M_1'J_2''K_2''M_2') \\
&= -\frac{\mu^2}{R^3} N_{M_1''} N_{M_2''} N_{M_1'} N_{M_2'} \{32\pi^4 I_1(J_1''K_1''M_1'')\ I_1(J_2''K_2''M_2'')\ \delta(M_1'M_1'')\ \delta(M_2'M_2'') \\
&\quad -8\pi^4 I_2(J_1''K_1''M_1'')\ I_3(J_2''K_2''M_2'')\ \delta(M_1',M_1''-1)\ \delta(M_2',M_2''+1) \\
&\quad -8\pi^4 I_3(J_1''K_1''M_1'')\ I_2(J_2''K_2''M_2'')\ \delta(M_1',M_1''+1)\ \delta(M_2',M_2''-1)\}
\end{aligned} \qquad (8.59a)$$

where:

$$I_1(J''K''M'') = \int_0^\pi \cos\vartheta\,\Theta^2_{J''K''M''} \sin\vartheta\, d\vartheta = 2\int_0^1 (1-2x)\,\Theta^2_{J''K''M''}(x)dx \qquad (8.59b)$$

$$I_2(J''K''M'') = \int_0^\pi \sin\vartheta\,\Theta_{J''K''M''}\Theta_{J''K'',M''-1} \sin\vartheta\, d\vartheta = 4\int_0^1 x^{1/2}(1-x)^{1/2}\,\Theta_{J''K''M''}(x)\Theta_{J''K'',M''-1}(x)dx \qquad (8.59c)$$

$$I_3(J''K''M'') = \int_0^\pi \sin\vartheta\,\Theta_{J''K''M''}\Theta_{J''K'',M''+1} \sin\vartheta\, d\vartheta = I_2(J''K'',M''+1) \qquad (8.59d)$$

and

$I_1$ has been evaluated by Reiche and Rademacher[150, 151] — among others — and is given by:

$$N^2(M'')I_1(J''K''M'') = \frac{K''M''}{4\pi^2 J''(J''+1)} \qquad (8.60a)$$

Margenau and Warren calculated $I_2$ by the reduction method of Reiche and Rademacher with the result:

$$N(M'')N(M''-1)\,I_2(J''K''M'') = \frac{\pm K''\,[(J''-M''+1)\,(J''+M'')]^{1/2}}{4\pi^2 J''(J''+1)} \tag{8.60b}$$

where the minus sign is to be taken if the numerically greater of $K$ or $M$ is positive while for the opposite case or if $K = -M$ the positive sign is to be taken.

Eqs. (8.50) may now be substituted into Eq. (8.59a) to obtain the result:

$$(M_1''M_2''\mid V\mid M_1'M_2') = \frac{\mu^2}{R^3}\,\frac{K_1K_2}{J_1(J_1+1)\,J_2(J_2+1)}\,\big\{-2M_1''M_2''\,\delta\,(M_1'M_1'')\,\delta\,(M_2'M_2'')$$

$$\pm\tfrac{1}{2}[(J_1-M_1''+1)\,(J_1+M_1'')\,(J_2-M_2'')\,(J_2+M_2''+1)]^{1/2}\,\delta\,(M_1',M_1''-1)\,\delta\,(M_2',M_2''+1)$$

$$\pm\tfrac{1}{2}[(J_1+M_1''-1)\,(J_1-M_1'')\,(J_2-M_2''+1)\,(J_2+M_2'')]^{1/2}\,\delta\,(M_1',M_1''+1)\,\delta\,(M_2',M_2''-1)\big\} \tag{8.61}$$

From Eq. (8.61) it is apparent that we are dealing with a somewhat different situation than had previously arisen in our molecular model considerations in that the matrix elements of $V = H'$ over the ***system*** do not disappear. As a consequence the first-order perturbation energy does not disappear. In addition, the problem is one of degenerate perturbation theory in which the degeneracy in $M$ is partially removed in first order.* Our next step is then the solution of the secular determinant $\mid V_{ij} - E^{(1)}\,\delta_{ij}\mid = 0$ of the form Table (7.3). Since $J$ and $K$ are fixed and since $M$ takes on all values from $-J$ to $+J$, this determinant will possess $(2J_1 + 1)\,(2J_2 + 1)$ rows and columns. This determinant is given in Table (8.2).

| $M_1''$<br>$M_2''$<br>$M_1'.\,M_2'$ | $(-J_1)$<br>$(-J_2)$ | $(-J_1)$<br>$(-J_2+1)$ | $(-J_1+1)$<br>$(-J_2)$ | $(-J_1)$<br>$(-J_2+2)$ | $(-J_1+1)$<br>$(-J_2+1)$ | $(-J_1+2)$<br>$(-J_2)$ | .....<br>..... | $(J_1-2)$<br>$(J_2)$ | $(J_1-1)$<br>$(J_2-1)$ | $(J_1)$<br>$(J_2-2)$ | $(J_1-1)$<br>$(J_2)$ | $(J_1)$<br>$(J_2-1)$ | $(J_1)$<br>$(J_2)$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(-J_1)\,(-J_2)$ | $E-H$ | | | | | | | | | | | | | |
| $(-J_1)(-J_2+1)$ | | $E-H$ | $-H$ | | | | | | | | | | | |
| $(-J_1+1)(-J_2)$ | | $-H$ | $E-H$ | | | | | | | | | | | |
| $(-J_1)(-J_2+2)$ | | | | $E-H$ | $-H$ | 0 | | | | | | | | |
| $(-J_1+1)(-J_2+1)$ | | | | $-H$ | $E-H$ | $-H$ | | | | | | | | |
| $(-J_1+2)(-J_2)$ | | | | 0 | $-H$ | $E-H$ | | | | | | | | |
| . | | | | | | | Increasing sized | | | | | | | |
| . | | | | | | | blocks symmetric | | | | | | | $=0$ |
| . | | | | | | | about the secondary diagonal | | | | | | | |
| $(J_1-2)(J_2)$ | | | | | | | | $E-H$ | $-H$ | 0 | | | | |
| $(J_1-1)(J_2-1)$ | | | | | | | | $-H$ | $E-H$ | $-H$ | | | | |
| $(J_1)(J_2-2)$ | | | | | | | | 0 | $-H$ | $E-H$ | | | | |
| $(J_1-1)(J_2)$ | | | | | | | | | | | $E-H$ | $-H$ | | |
| $(J_1)(J_2-1)$ | | | | | | | | | | | $-H$ | $E-H$ | | |
| $(J_1)(J_2)$ | | | | | | | | | | | | | $E-H$ | |

Table 8.2. The secular determinant $\mid E\delta_{ij}-H_{ij}'\mid = 0$ for $V = H'$ as given by Eq. (8.61). The blocks increase to a maximum size of $(2J_2 + 1)$ by $(2J_2 + 1)$ for the $(2J_2 + 1)$-st block for $J_1 > J_2$.

---

* We note no dependence of the unperturbed energies as given by Eq. (2.37b) on $M$ while the energy dependence in first order may be seen from Eqs. (4.147) and (8.61).

A consideration of Table (8.2) tells us that the determinant has broken into blocks, with identical blocks symmetrical about the secondary diagonal. This immediately tells us that every root of this determinant will be a double root.

A little consideration of the situation indicates that a general equation describing the level splitting due to this interaction is not to be found, but an idea as to the maximum splitting may be obtained, and the example of a special case may be presented.

We may write down from Eq. (8.61) the double root which lies at either end of the principal diagonal and where $J_1 = M_1$ and $J_2 = M_2$.

$$E^{(1)} = -\frac{2\mu^2}{R^3} \frac{K_1 K_2}{(J_1 + 1)(J_2 + 1)} \tag{8.62}$$

If we recall the linear Stark effect,

$$E^{(1)} = \mu E \frac{KM}{J(J+1)} \tag{8.63a}$$

it is interesting to note the close resemblance which its maximum $(J = M)$,

$$E^{(1)} = \mu E \frac{K}{J+1} \tag{8.63b}$$

bears to our result Eq. (8.62).

Fig. (8.1) illustrates the level splitting with the rotator separation $R$ and the magnetic quantum number $M$ for the special case $J_1 = K_1 = 2, J_2' = K_2' = 1$ for the upper state and $J_1'' = K_1'' = 1, J_2'' = K_2'' = 1$ for the lower state.

Let us finally remark that since $K = 0$ for a spherical top rotator, the matrix elements of $V$ in Eq. (8.61) would all be zero so that the effect considered would not take place.

Insofar as second order effects are concerned, we certainly are aware that they will depend on the inverse sixth power of the molecular separation. In addition Margenau and Warren felt that for finding those regions in which the first order perturbations predominate, London's second order results for diatomic molecules should be sufficient. Under these assumptions a limiting range of about 7A for the predominance of the forces which we have considered was imposed by these authors.

## 8.10. THE BROADENING AND SHIFT DUE TO THE SYMMETRICAL TOP DIPOLE INTERACTION

The secular determinant of Table (8.2) will have $(2J_1 + 1)(2J_2 + 1)$ roots which we may designate by $\epsilon_1, \epsilon_2, \ldots$, and, for convenience, let these roots be given in units of:

$$\frac{\mu^2}{R^3} \frac{K_1 K_2}{J_1(J_1+1)J_2(J_2+1)}$$

the "coefficient" in Eq. (8.61). The secular determinant leads to the secular equation possessed of these roots so we may write,

$$| V_{ij} - \epsilon\delta_{ij} | = \prod_i (\epsilon - \epsilon_i) = \epsilon^n - a\epsilon^{n-1} + b\epsilon^{n-2} - \ldots + x = 0 \tag{8.64}$$

and let us recall the relations which exist among the roots and coefficients of a polynomial and which were discussed in connection with Eq. (7.9). These relations first lead us to:

$$a = \sum_i \epsilon_i = \sum_i V_{ii} \tag{8.65a}$$

Eq. (8.65a) may be evaluated specifically using Eq. (8.61) as:

$$a = \sum_{M_1=-J_1}^{J_1} \sum_{M_2=-J_2}^{J_2} 2M_1M_2 = 0 \tag{8.65b}$$

Thus, the weighted mean of the energy perturbation is zero which in turn means that we would expect no shift of the spectral line, a situation which also arises in connection with the $R^{-3}$ interaction in atomic resonance broadening.

As a measure of the broadening of the line due to this interaction, let us now find the root mean square spread of the perturbed energy levels. The coefficient $b$ is given by:

$$\begin{aligned} b &= \sum_{i>j} (V_{ii}\,V_{jj} - V_{ij}^2) \\ &= \tfrac{1}{2} \sum_i \sum_j V_{ii}\,V_{jj} - \tfrac{1}{2} \sum_i V_{ii}^2 - \sum_{i>j} V_{ij}^2 \end{aligned} \tag{8.66a}$$

or by:

$$b = \sum_{i>j}\sum \epsilon_i\epsilon_j = \tfrac{1}{2} \sum_i \epsilon_i \sum_j \epsilon_j - \tfrac{1}{2} \sum_i \epsilon_i^2 = -\tfrac{1}{2} \sum_i \epsilon_i^2 \tag{8.66b}$$

by virtue of Eq. (8.65). The substitution for the $V_{ij}$ in Eq. (8.66a) from Eq. (8.61) results in:

$$\begin{aligned} b &= 2 \sum_{M_1''M_1'} \sum_{M_2''M_2'} M_1''M_2''M_1'M_2' - 2 \sum_{M_1''M_2''} M_1''^2M_2''^2 \\ &- \tfrac{1}{4} \sum_{M_1''M_2''} (J_1^2 - M_1''^2 + J_1 + M_1'')\,(J_2''^2 - M_2''^2 + J_2 - M_2'') = 0 - \tfrac{2}{9}\, J_1(J_1+1)\,(2J_1+1)\,J_2(J_2+1)\,(2J_2+1) \\ &- \tfrac{1}{4}\left[(J_1^2 + J_1)\,(2J_1 + 1) - \tfrac{1}{3}\, J_1(J_1 + 1)\,(2J_1 + 1)\right]\left[(J_2^2 + J_2)\,(2J_2 + 1)\right. \\ &\left. - \tfrac{1}{3}\, J_2\,(J_2 + 1)\,(2J_2 + 1)\right] = -\tfrac{1}{3}\, J_1(J_1 + 1)\,(2J_1 + 1)\,J_2(J_2 + 1)\,(2J_2 + 1) \end{aligned} \tag{8.67}$$

Eqs. (8.66b) and (8.67) lead to the result:

$$<\epsilon_i^2>^{1/2} = \left[\frac{2}{3}\, J_1(J_1 + 1)\, J_2(J_2 + 1)\right]^{1/2} \tag{8.68a}$$

which in more normal energy units is:

$$<(E^{(1)})^2>^{1/2} = \left(\frac{2}{3}\right)^{1/2} \frac{\mu^2}{R^3} \frac{K_1K_2}{\left[J_1(J_1 + 1)\, J_2(J_2 + 1)\right]^{1/2}} \tag{8.68b}$$

In Chapter 7 it was shown that when a resonance interaction, resulting from a potential of the form

$$E^{(1)} = \pm B/R^3$$

occurs, the statistical theory decrees an approximate half-width.

$$\delta \doteq \frac{4}{3} \pi^2 \frac{B}{h} N$$

Margenau and Warren make the point that while it would be "indefensible to identify the splitting pattern . . . (Sec. 8) . . . with *any* pattern having the same standard deviation . . . "[120] a reasonable approximation to the half width arising from these considerations may surely be expected if we equate $B$ to

$$\left(\frac{2}{3}\right)^{1/2} \mu^2 \frac{|K_1K_2|}{[J_1(J_1+1)\,J_2(J_2+1)]^{1/2}}$$

There then results:

$$\delta \doteq \frac{\pi^2\mu^2\,|K_1K_2|\,N}{h[J_1(J_1+1)\,J_2(J_2+1)]^{1/2}} \tag{8.69}$$

It is true, of course, that we have here found the level width while we are really desirous of the spectral line width. The level here $(J_1K_1J_2K_2)$ would have to be considered in conjunction with another possible level $(J_1 \pm 1, 0;\ K_1 \pm 1, 0;\ J_2\ K_2)$. One may perhaps consider the $K_1$ and $J_1$ appearing in Eq. (8.69) as the mean of the quantum numbers for the two states.

We might conclude by noting that the effect as given by Eq. (8.69) is around 20 times as weak as the self-broadening effect in monatomic resonance lines.

The results of this theory were born out order of magnitudewise by Cornell's results.[22] In this author's investigations of $NH_3$ (a symmetric rotator possessed of a dipole) he obtained average widths of 1.45 cm.$^{-1}$ for the 7920A band and 0.81 cm.$^{-1}$ for the 10230A. Taking the weighted mean of $|K_1K_2|\,[J_1(J_1+1)\cdot J_2(J_2+1)]^{-1/2}$ as 1/2 the theory yields $\delta = \frac{1}{2}\pi^2\frac{\mu^2}{h}N = 1.5$ cm.$^{-1}$ for a pressure of one atmosphere.

### 8.11. BROADENING BY THE LINEAR DIPOLE MOLECULE HCN

The first attempt at a rigorous theoretical interpretation of the self broadening of the absorption lines of a linear dipole molecule was carried out by Lindholm[100] for the $HCN$ molecule. This investigator found that, as he put it, the Directional Effect ($\sim R^{-6}$) alone,* was not sufficient to account for the strong, $J$-dependent broadening observed, so that he considered also the Resonance Effect ($\sim R^{-3}$) in conjunction with the former. As we have remarked† what Lindholm called the rotational Resonance Effect is in actuality a special case of the Directional Effect. Let us keep this fact in mind, but for convenience of consideration we shall use the Lindholm nomenclature for the two interaction relations ($R^{-3}$ and $R^{-6}$) in this section.

In essence Lindholm uses the energy perturbations due to the Directional and Resonance Effects within the framework of the Weisskopf theory of Interruption Broadening to determine the broadening of the $HCN$ lines in a manner which we now consider.

According to Eq. (7.53) the half width of the lines will be given by:

$$\delta = \rho^2 \langle v \rangle N$$

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* See *supra*, Sec. 8.8.

† See *supra*, Sec. 8.8.

for a homogeneous gas. For a heterogeneous gas containing $N_1$ molecules with optical collision diameters $\rho_1$, $N_2$ with diameters $\rho_2$, etc.

$$\delta = <v>\sum_i N_i\rho_i^2 \tag{8.70}$$

if all molecules are of the same mass, thus allowing a common $<v>$*. Let us next consider the necessity for introducing Eq. (7.70).

From Lindholm's experimental results, it is quite apparent that a marked dependence on $J$ is present in the line width. In the Weisskopf theory, this can only come about through some variation in $N$ and $\rho$ with $J_1$ (the absorber $J$ value) and $J_2$ (the perturber $J$ value). Thus, we hypothesize a dependence of $\rho$ on $J_1$ and $J_2$ which a little consideration immediately bears out. To begin with a frequency perturbation $\Delta\nu = b/R^6$ (which is brought about by the Directional Effect $|J_1 - J_2| \neq 1$) leads to an optical collision diameter:

$$\rho = \left(\frac{3\pi^2}{4}\frac{b}{<v>}\right)^{1/5} \tag{6.9'}$$

On the other hand, a frequency perturbation $\Delta\nu = \pm B/R^3$ (which may arise from the Resonance Effect $|J_1 - J_2| = 1$) occasions an optical collision diameter:

$$\rho = \left(\frac{4\pi B}{<v>}\right)^{1/2} \tag{7.54b'}$$

This then is at least a part of the general manner in which $\rho$ may depend on $J_1$ and $J_2$, and let us now specificize this into usefulness. Lindholm dealt only with the $P$-Branches ($\Delta J = -1$) of the two *HCN* bands which he considered. Insofar as the vibrational quantum numbers involved are concerned $v_1'' = v_2'' = 0$. We now let:

$$\Delta = J_2'' - J_1'' \tag{8.71a}$$

so that:

$$J_2'' - J_1' = J_2'' - (J_1'' - 1) = \Delta + 1 \tag{8.71b}$$

for the upper state since we consider only the $P$-Branch. $\Delta$ is now a convenient parameter for the determination of the type effect to be considered. (1) For $\Delta = \pm 1$ we obtain the Resonance Effect in the ground state and the Directional Effect in the upper State. (2) For $\Delta = 0, -2$ there results the Directional Effect in the ground state and the Resonance Effect in the upper state. (3) Finally for all other $\Delta$ the Directional Effect occurs in both states. The case of small $J$† was not considered by Lindholm. The optical collision diameters for these three cases may now be determined from Eqs. (6.9′) and (7.54b′)

Case (1):

$$\text{Frequency perturbation:}\quad \Delta\nu = \frac{b}{R^6} \pm \frac{B}{R^3} \tag{8.72a}$$

$$\int 2\pi\,\Delta\nu dt = \left|\frac{3\pi^2 b}{4<v>}\frac{1}{\rho^5} \pm \frac{4\pi B}{<v>}\frac{1}{\rho^2}\right| = 1 \tag{8.72b}$$

Case (2):

Same as Case (1).

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* Lindholm defines $<v>$ as the mean relative velocity.

† See *supra*, Sec. 8.4.

Case (3):

Frequency perturbation: $\Delta\nu = b/R^6$ (8.73a)

$$\rho = \sqrt[5]{\frac{3\pi^2}{4}\frac{b}{<v>}} \tag{8.73b}$$

In Cases (1) and (2) $\rho$ may be found as roots of Eq. (8.72b), in particular there will be roots $\rho_+$ for the repulsive case (positive sign) and $\rho_-$ for the attractive case (negative sign). In all cases of multiple roots $\rho$ the highest valued root will be taken as significant. Further we shall suppose there to be equal amounts of resonance repulsion and attraction so that for $\rho^2$ from Eq. (8.72b) we shall write $\frac{\rho_+^2 + \rho_-^2}{2}$. Now the $\rho$ values furnished by the three possible sets of physical conditions may be substituted into Eq. (8.70) with the result:

$$\delta = 2.2\,(<v>)^{3/5} \sum_i b_i^{3/5} N_i + <v> \sum_j N_j \frac{\rho_{+j}^2 + \rho_{-j}^2}{2} \tag{8.74}$$

Let us first consider the Directional Effect contributions. The energy perturbation of a level for this case has been given by Eq. (8.15). Lindholm approximated this equation by the expression:

$$E^{(2)}_{J_1 J_2} = \frac{1}{R^6}\,\frac{\mu^4 I}{3\hbar^2(\Delta^2 - 1)} \tag{8.75}$$

which he noted is asymptotic for large $J$, exact for $J_1 = J_2$, 86% of the correct value for $J_1 = 1, J_2 = 3$, and 92% of the correct value for $J_1 = 2, J_2 = 4$.

We are desirous of obtaining $b$ for Eq. (8.74) from Eq. (8.75). $b$ will be given by:

$$b = \frac{R^6}{h}\left[E^{(2)}_{J_1' J_2'} - E^{(2)}_{J_1'' J_2''}\right] = \frac{4\pi^2\mu^4 I}{3\hbar^3}\left[\frac{1}{(\Delta + 1)^2 - 1} - \frac{1}{\Delta^2 - 1}\right] \tag{8.76}$$

according to Eqs. (8.71).

In order to find $N_i$ a Maxwell-Boltzmann distribution of the molecules over the rotational levels is assumed. The rotational energy of these linear molecules is:

$$E_J = hcBJ(J + 1)$$

where: $B = \frac{h}{8\pi^2 Ic}$

so that the level population will contain the term $e^{-\frac{hcBJ(J+1)}{kT}} = e^{-E/kT}$. In addition each rotational level is $(2J + 1)$-fold spatially degenerate as determined by $M$. Thus, if there are $N$ molecules per cubic centimeter, the number in the rotational state described by $J_i$ will be:

$$N\begin{pmatrix}\%\ \text{molecules} \\ \text{in } J_i\end{pmatrix} = N\left(\frac{(2J_i + 1)\, e^{-\frac{hcBJ_i(J_i+1)}{kT}}}{\sum_{J=0}^{\infty}(2J+1)\, e^{-\frac{hcBJ(J+1)}{kT}}}\right) = N\frac{w_i}{\sum_{J=0}^{\infty} w_J} \tag{8.77}$$

Eqs. (8.76) and (8.77) may now be substituted into the first term of Eq. (8.74) with the result:

$$\delta_D = 2.2(<v>)^{3/5}\left(\frac{4\mu^4\pi^2 I}{3h^3}\right)^{2/5} \frac{N}{\sum\limits_{J_2=0}^{\infty} w_{J_2}} \sum_{J_2=0}^{\infty} w_{J_2}\left[\frac{1}{(\Delta+1)^2-1} - \frac{1}{\Delta^2-1}\right]^{2/5} \tag{8.78}$$

where the prime on the summation sign decrees the dropping of those $J_2$ values for which $\Delta = \pm 1, 0, -2$ (Resonance Effect).

Lindholm utilized the values $\mu = 2.65 \text{ x } 10,^{-18}$ $<v> = 67560, N = 1.937 \text{ x } 10^{19}$ and $I = 18.70 \text{ x} 10^{-40}$. For these values of the constants, the first twenty or thirty terms in the sum must be considered. For $J_2$ values greater than this, the exponential factor in Eq. (8.77) leads to sum contributions small enough to be neglected.

Now our attention may be devoted to the resonance contributions to Eq. (8.74). Lindholm utilized a mildly modified version of the London development leading to Eq. (8.48). London's molecular model, if you will, consisted of a rigid rotator. Lindholm's modifications amounted to a model change to a rotating-vibrating molecule. As we have seen in Chapter 2, this means that the eigenfunctions will now be of the form:

$$\psi_{vJM} = \psi_v \psi_{JM} \tag{8.79}$$

Interactions will arise between rotation and vibration, but the only one with which we shall be required to concern ourselves is the change in the moment of inertia with vibrational state. An example of this has already been given by Eqs. (2.40).[*] The rotational energies will now be:

$$E_J = B_v hcJ(J+1) \tag{8.80}$$

We shall return to these considerations at a later point, but let us first consider the case of both molecules in the ground state with $\Delta = \pm 1$. For the vibrational quantum numbers, the same Eq. (8.48) is valid as it stands. London had calculated the matrix elements requisite for the evaluation of $a_1$, $a_2$, and $a_3$ and had obtained the

$$-\tfrac{1}{2}\left(\frac{a_1^2}{E_1} + \frac{a_2^2}{E_2} + \frac{a_3^2}{E_3}\right) \doteq -\frac{1}{R^6}\,\frac{\pi^2\mu^4 A}{6h^2} \tag{8.81a}$$

Lindholm proceeded to evaluate $a_4$ as follows: From Eq. (8.46):

$$\frac{a_4^2}{R^6} = V_{12}^2 + V_{11}^2 + V_{10}^2$$

He obtained the $V_i$ after the usual fashion from which there resulted:

$$a_4 = \frac{\mu^2}{2(2J+1)(2J+3)}\sqrt{\begin{matrix}(J+M_1)(J+M_1+1)(J+M_2+2)+(J-M_1)(J-M_1+1)(J-M_2+1)(J-M_2+2)\\ +16\left[(J+1)^2-M_1^2\right]\left[(J+1)^2-M_2^2\right]\end{matrix}} \tag{8.82}$$

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[*] The last three terms of Eq. (2.40a) are concerned with the effects of centrifugal stretching due to rotation and this effect we neglect. The fact that this equation refers to a symmetrical top should cause no concern.

Next $a_4$ must needs be averaged over all orientations of both molecules as determined by $M_1$ and $M_2$ where $(J+1) \geqslant M \geqslant -(J+1)$ and $J \geqslant M_2 \geqslant -J$ as decreed by the resonance condition. For the mean square value of $a_4$ he obtained, as was to be expected, Eq. (8.23):

$$<a_4^2> = \frac{2}{3}\mu_4 \frac{(J+1)^2}{(2J+1)(2J+3)} = \frac{\mu^4(2J+2)^2}{6(2J+1)(2J+3)} \tag{8.23}$$

Eq. (8.23) would appear almost completely independent of $J$ for large $J$. (1) Lindholm supposed that this would also be the case for $<a_4>$. (2) For sufficiently large $J$ it is a reasonable approximation to replace $\sum\limits_{M_1=-(J+1)}^{J+1}$ and $\sum\limits_{M_2=-J}^{J}$ by $\int_{-J}^{J} dM_1$, and $\int_{-J}^{J} dM_2$ respectively. (3) Only the highest order of magnitude terms under the radical in Eq. (8.82) are to be retained. Utilizing these three approximations Eq. (8.82) may be employed and we may let $M_1 = xJ, M_2 = yJ$ to obtain:

$$<a_4> = \frac{\mu^2}{32}\int_{-1}^{+1}\int_{-1}^{+1} dxdy\ \sqrt{18 + (18x^2y^2 + 18xy - 14x^2 - 14y^2)} \doteq \frac{\mu^2}{2.52} \tag{8.81b}$$

after series expansion of the integrand and integration of the first five terms.

For small $J$ direct calculation using Eq. (8.82)

$$J = 0 \rightarrow <a_4> = \frac{\mu^2}{2.25} \quad ; \quad J = 1 \rightarrow <a_4> = \frac{\mu^2}{2.48}$$

indicates a rapid convergence toward Eq. (8.81b). Let us then substitute Eqs. (8.81) into Eq. (8.48) with the result:

$$E^{(1)} = -\frac{\pi^2\mu^4 I}{6h^2}\frac{1}{R^6} \pm \frac{\mu^2}{2.52}\frac{1}{R^3} \tag{8.83}$$

Eq. (8.83) then gives the *first-order* interaction energy for this resonance condition, in the lower state (Case 1). Eqs. (8.72) must now be solved for $\rho$. In Eq. (8.72b) $B$ is simply given by the coefficient of $R^{-3}$ in Eq. (8.83) $b$ is a slightly different case, however. Since in the upper state, we have the Directional Effect taking place $b_{\text{upper}}$ will be given by the coefficient of $R^{-6}$ in Eq. (8.75). On the other hand, the Resonance Effect of the lower state furnishes $b_{\text{lower}}$ which is the coefficient of the $R^{-6}$ term in Eq. (8.83) Finally:

$$b = b_{\text{upper}} - b_{\text{lower}} \tag{8.84}$$

The values of $B$ and $b$ thus obtained may now be used in Eq. (8.72b) to yield the $\rho$ values listed in Table (8.3)

| $\Delta$ | $\rho$ from Eq. (8.58$b'$) | $\rho+$ | $\rho-$ |
|---|---|---|---|
| +1 | $2.82 \times 10^{-7}$ | $2.96 \times 10^{-7}$ | $2.58 \times 10^{-7}$ |
| −1 | $2.82 \times 10^{-7}$ | $3.06 \times 10^{-7}$ | $1.59 \times 10^{-7}$ |

Table (8.3) $\rho+$ and $\rho-$ for Case (1), resonance in lower state and directional effect in upper state. Also $\rho$ for resonance alone in the lower state. (After Lindholm[100]).

From Table (8.3) the more powerful influence of the Directional Effect for $\Delta = -1$ is apparent. Substitution from this table into Eq. (8.74) yields:

$$\delta_R = \langle v \rangle \frac{N}{\sum\limits_{J'=0}^{\infty} w_{J'}} [w_{J+1} \, 7.71 \times 10^{-14} + w_{J-1} \, 5.95 \times 10^{-14}] \tag{8.85}$$

where again the $w_J$ are defined by Eq. (8.77).

Finally Case (2) remains to be investigated and we now utilize the molecular model of Eqs. (8.79) and (8.80). In correspondence with the $u_0$ of Eq. (8.43) let us take:

$$u_0' = \psi_{J+1}^{M_1} \psi_v(1) \psi_J^{M_2} \psi_{v'}(2)$$

and now there will be twenty-four additional eigenfunctions of this form which may combine with this one — we assume that $v$ is the ground vibrational state and $v'$ some resonating upper vibrational state.

In considering the matrix elements of $V$, we first note that, in Eq. (8.2), the $\mu_i$ will be functions of the vibrational coordinates. Corresponding to each of London's matrix elements $V_i = V_{0i}$ there are now two matrix elements. As an example, to $V_1$ there correspond:

$$V_{01}' = V_1' = \int \psi_{J+1}^{M_1} \psi_v(1) \psi_J^{M_2} \psi_{v'} V \psi_{J+2}^{M_1} \psi_J(1) \psi_{J+1}^{M_2} \psi_{v'}(2) d\tau \tag{8.86a}$$

$$V_1'' = \int \psi_{J+1}^{M_1} \psi_v(1) \psi_J^{M_2} \psi_{v'}(2) V \psi_{J+2}^{M_1} \psi_{v'}(1) \psi_{J+1}^{M_2} \psi_{v'}(2) d\tau \tag{8.86b}$$

Let us look at Eqs. (8.86) rather carefully since some important physical phenomena are inferred by them. The rotational resonance condition $| J_1 - J_2 | = 1$ is fulfilled by all four two-molecule eigenfunctions. In Eq. (8.86a) the individual vibrational quantum numbers remains the same for both system state functions appearing in the matrix element. Eq. (8.86b) presents a different case, however. In this matrix element, the vibrational quantum number for molecule one changes from $v$ to $v'$ under the aegis of $V$ while the vibrational quantum number for molecule two changes from $v'$ to $v$. Thus, one or more quanta of vibrational energy are *exchanged* in this process, and resonance in the sense of Chapter 7 sets in. It seems important to clearly differentiate between this exchange type resonance and the rotational type of Eq. (8.15). Perhaps this type differentiation is not too satisfactory for $| J_1 - J_2 | = 1$ also implies an exchange in that the two molecules may exchange one quantum of rotational energy between themselves. The semantics of the situation should hardly trouble us, however, if we have a clear picture of the physical phenomena involved. In order to determine one of the reasons for neglecting exchange resonance, the vibrational portions of Eqs. (8.86) may be written as:

$$V_{v1}' = \int \psi_v(1) \mu_1 \psi_v(1) d\tau \int \psi_{v'}(2) \mu_2 \psi_{v'}(2) d\tau = \mu^2 \tag{8.87a}$$

$$V_{v1}'' = \int \psi_v(1) \mu_1 \psi_{v'}(1) d\tau \int \psi_v(2) \mu_2 \psi_{v'}(2) d\tau \tag{8.87b}$$

Eq. (8.87a) tells us that $V_i' = V_i$, London's matrix elements. Eq. (8.87b) is nothing more nor less than the square (the molecules are identical) of the matrix element of the electric dipole moment for the vibrational transition $v \rightarrow v$ In other words, it is proportional to the intensity of the rotation-vibration band involved. For the bands which Lindholm considered, the intensity is very low which means that Eq. (8.87b) will be small. This in turn will cause Eq. (8.86b) to be small which allows us to neglect the exchange resonance. Another consideration leads to the weakness of exchange resonance. The dispersion *f*-value oscillator strength, or what have you, enters this resonance broadening as we have seen in Chapter 7. In this case, we apply the "Principle of Spectroscopic Stability" in reverse and portion out pieces of the dispersion *f*-value* for a monatomic transition to myriads of rotation vibration levels. The net result of all this is a further decrease in the exchange resonance effect which we now proceed to neglect. This means that we are again only concerned with twelve matrix elements of the form Eq. (8.86a).

The perturber — we may distinguish it since we neglect exchange resonance — will hereinafter be in the ground vibrational state and the absorber in an upper vibrational state for our considerations of Case (2): $\Delta = 0, -2$. If molecule one is the absorber and two the perturber, then:

$$\begin{aligned} E(1) &= B'hcJ'(J'+1) \\ E(2) &= B''hcJ''(J''+1) \end{aligned} \tag{8.88}$$

according to Eq. (8.80) where $B'$ is the value of rotational "constant" in the upper state and $B''$ its value in the lower state.

The eigenfunction which we select to correspond to $u_0$ of Eq. (8.43) is:

$$u_0' = \psi_{Jv'}^{M_1}\,\psi_{J+1,v}^{M_2} \tag{8.89}$$

The twelve eigenfunctions with which $u_0'$ may combine are then analogous to the twelve functions of Eq. (8.43), for example:

$$u_1' = \psi_{J+1,v}^{M_1}\,\psi_{J+2,v}^{M_2} \quad , \quad \text{etc.}$$

Having obtained the requisite eigenfunctions, we may write down the equivalent of Eq. (8.44) using Eq. (8.88)

$$\begin{aligned} E_1' &= 2hc(B'+B'')\,(J+1) + 2B''hc \\ E_2' &= -2hc(B'+B'')\,J - 3B''hc \\ E_3' &= -2hc(B'+B'')J + B''hc \\ E_4' &= 2hc(B'-B'')(J+1) \end{aligned} \tag{8.90}$$

Now $|\,B' - B''\,| \ll B', B''$, since the variation of rotational constant with vibrational quantum number should not be too great. Thus, although $|\,E_1'\,|, |\,E_2'\,|, |\,E_3'\,| \gg |\,E^{(1)}\,|$, this inequality does not hold between $E^{(1)}$ and $E_4'$. As a consequence, $E^{(1)}$ may be dropped from the first three denominators on the right of Eq. (8.45) but not from the fourth so that for Case (2) we obtain:

$$R^6\,E^{(1)} = -\left(\frac{a_1^2}{E_1'} + \frac{a_2^2}{E_2'} + \frac{a_3^2}{E_3'}\right) + \frac{a_4^2}{E^{(1)} - E_4'} \tag{8.91}$$

where $a_i$ is again given by Eq. (8.46).

The value of the first term on the right is available from Eq. (9.50a) $< a_4^2 >$ may be taken as $\mu^4/6$ from Eq. (8.23) with the result:

$$6R^6(E^{(1)})^2 - E^{(1)}\left(6R^6E_4 - \frac{6\pi^2\mu^4 I}{3h^2}\right) - \left(\frac{6\pi^2\mu^4 I E_4}{3h^2} + \mu^4\right) = 0$$

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* "Do you really eat babies, Mr. Swift?" "No, nor do I portion out pieces of dispersion *f*-values."

of solution:

$$E^{(1)} = \tfrac{1}{2}\left\{E_4 - \frac{\pi^2\mu^4 I}{3h^2R^6} \pm \sqrt{E_4^2 + \frac{2E_4\pi^2\mu^4 I}{3h^2R^6} + \frac{4\mu^4}{6R^6}}\right\} \tag{8.92}$$

in which the term in $R^{-12}$ under the radical has been dropped.

The second term within the curly braces in Eq. (8.92) gives us $b_{\text{upper}}$. $b_{\text{lower}}$ is again obtained from Eq. (8.75).

From which:

$$\frac{3\pi^2 b}{4} = \frac{3\pi^2}{4}\left(b_{\text{upper}} - b_{\text{lower}}\right) = \frac{7}{8}\,\frac{\pi^4\mu^4 I}{h^3} \tag{8.93}$$

It is again necessary to solve Eq. (8.72b) for $\rho$. If we let $E_1^{(1)}$ be $E^{(1)}$ with the $b_{\text{upper}}$ contribution deleted, $\frac{4\pi B}{<v>}\,\frac{1}{\rho^2}$ may be replaced in Eq. (8.72b) by $\frac{2\pi}{h}\int E_1^{(1)}\,dt$ so that this equation becomes:

$$\left|\frac{7\pi^4\mu^4 I}{8h^3<v>}\,\frac{1}{\rho^6} + 2\pi\int_{-\infty}^{+\infty}\left[\sqrt{\frac{E_4^2}{4h^2} + \frac{E_4\pi^2\mu^4 I}{6h^4\rho^6} + \frac{\mu^4}{6h^2\rho^6}} + \frac{E_4}{2h}\right]dt\right| = 1 \tag{8.94}$$

In his first paper on the subject[100] Lindhom concluded that $B$ contributed little to the optical collision diameter* so that he neglected the resonance contribution in this case. This small contribution would indicate that a sharp resonance is required for effect. This sharpness is reduced by the variation of the rotational constant for the two states since this variation will in turn cause a variation in the rotational level separations for the two vibrational states.

Lindholm then obtained the Case (2) contribution as the additional Directional Effect contribution:

$$\delta_D = <v>\;\frac{N}{\sum\limits_{J'=0}^{\infty} w_{J'}}\left[w_J\, 4.78 \times 10^{-14} + w_{J-2}\, 3.43 \times 10^{-14}\right] \tag{8.95}$$

with the $w_J$ defined as before.

The total half-width is now the sum of Eqs. (8.78), (8.92), and (8.85). Fig. (8.2) gives the Directional and Resonance Effect contributions as well as the sum of the Directional Effect plus the Resonance Effect. Fig. (8.3) gives the individual Directional Effect contributions as well as the sum of the total Directional Effect and Resonance Effect. Figs. (8.4), (8.5), and (8.6) simply give the total predicted widths in comparison with Lindholm's observed widths.

In a later paper[101] Lindholm concluded that his approximation Eq. (8.95), was not sufficient and that Eq. (8.94) should be utilized for a numerical calculation of $\rho$ for each $J$ value. This has the effect of raising the plot of Eq. (8.95) in Fig. (8.2) 0.06 cm.$^{-1}$ for $J = 2$, 0.12 cm.$^{-1}$ for $J = 5$, 0.11 cm.$^{-1}$ for $J = 10$, 0.05 cm.$^{-1}$ for $J = 16$, and 0.02 cm.$^{-1}$ for $J = 20$.

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* See *supra*, Eq. (8.72b).

## 8.12. BROADENING IN THE DIATOMIC DIPOLE MOLECULE HCl

Lindholm also carried out an investigation similar to that of HCN for the HCl molecule.[101] This molecule together with HCN provide two of the rare examples of simple linear molecules possessed of large dipole moments. This fact led to Lindholm's choice of it as an object of his considerations.

The vibrational transition involved was 0 → 4 resulting in the band at 9152A. In this case he considered both the $P$ and the $R$ branches in contradistinction to the HCN investigation.

We begin by considering case (3) of Sec. 11, the Directional Effect in both upper and lower states. In arriving at Eq. (8.76) for this case for HCN the constancy of the moment of inertia in the two vibrational states was inferred. Since this would be a much worse approximation for a diatomic molecule, the use of Eq. (8.75) for the HCl energy perturbation with the perturber in the lower vibrational state and the absorber in the upper vibrational state is ruled out. Eq. (8.75) may still be used, however, when both perturber and absorber are in the lower state. Margenau's Eq. (8.14) may be used for the interaction energy with the absorber in the upper state. We again let the subscripts one and two denote the absorber and the perturber respectively and $I_0$ and $I_4$ the moments of inertia in the ground vibrational state and in the vibrational state having $v = 4$ respectively. Eqs. (8.14) and (8.75) are used to obtain $b$ from an equation of the form Eq. (8.76); $\rho$ is subsequently found from Eq. (8.73b) and the result for the $P$-Branch follows* from Eq. (8.74):

$$\delta_D = 2.2(<v>)^{3/5}\left(\frac{8\pi^2\mu^4 I_0}{3h^2}\right)^{2/5} \frac{N}{\sum\limits_{J_2=0}^{\infty} w_{J_2}} \sum_{J_2=0}^{\infty}{}' w_{J_2}\left[\frac{1}{(2J_1-1)\,(2J_1+1)}\left\{\left(\frac{1}{J_1}+\frac{I_0/I_4}{J_2+1}\right)^{-1}\right.\right.$$
$$\left.\left.+\left(\frac{1}{J_1-1}-\frac{I_0/I_4}{J_2+1}\right)^{-1}-\left(\frac{1}{J_1}-\frac{I_0/I_4}{J_2}\right)^{-1}-\left(\frac{1}{J_1-1}+\frac{I_0/I_4}{J_2}\right)^{-1}\right\}+\frac{1}{2(\Delta^2-1)}\right]^{2/5} \tag{8.96}$$

in which all symbols are defined as in Sec. 11.

One may obtain a quite similar expression for the $R$-Branch ($\Delta J = +1$). In addition to Eq. (8.96) Lindholm imposed the restriction on $\delta_D$ that $\rho \geqslant 0.30 \times 10^{-7}$ cm., the Landolt-Bornstein value of the gas kinetic diameter. The resulting line widths with $J$-value for the Directional Effect alone (Case (3)) are given in Fig. (8.7).

Case (1) of Section 11 may now be considered. One again obtains Eq. (8.84) for the Resonance Effect in the lower state. The treatment of the Directional Effect in the upper state of the absorber differs now from Sec. 11 in that we again use Eq. (8.14) to determine $b_{\text{upper}}$ of Eq. (8.84). Having found $b_{\text{upper}}$, Eqs. (8.83) and (8.84) may be used as in Sec. 11 to arrive at two equations (one for the $P$-Branch and one for the $R$-Branch) similar to Eq. (8.85). The resulting $\delta_R$ vs. $J$ curves for Case (1) appear in Fig. (8.7).

Finally Eq. (8.94) (and a similar equation for the $R$-Branch) was utilized by Lindholm in the treatment of Case (2). By numerical solution of these two equations for $\rho$ for each value of $J$ in the $P$ and $R$-Branches and subsequent utilization of them in an equation of the form Eq. (8.70) (with the $N_i$ given by Eq. (8.77)) this author obtained the Case (2) contributions as given by Fig. (8.7).

Fig. (8.7) gives also the sum of the three contributions to the line width as well as Lindholm's experimental results for the HCl widths considered. Although the agreement between theory and experiment appears confirmatory, Lindholm investigated the possible contributions of the Dispersion and Induction Effects as being responsible, rather than experimental error, for the disagreement observed. In general he

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* Cf. *supra*, Eq. (8.78).

concluded that the effect of these two phenomena was negligible except possibly for $J = 0$, thus explaining the $R(1)$ discrepancy apparent in the figure.

The pure rotation line widths may also be calculated for HCl. All absorbing transitions in this case arise from $\Delta J = +1$, and no change in the moment of inertia with rotational state occurs. For the Directional Effect then, we obtain Eq. (8.78) with the bracketed expression replaced by:

$$\left[\frac{1}{(\Delta - 1)^2 - 1} - \frac{1}{\Delta^2 - 1}\right] \tag{8.97}$$

Since there is no change in the moment of inertia with rotational state, we may here obtain sharp resonance both for the upper and lower of a pair of states. Thus one would obtain in place of Eqs. (8.85) and (8.95):

$$\delta_R = <v> \frac{N}{\sum\limits_{J_2=0}^{\infty} w_{J_2}} [1.364 \times 10^{-14}(w_{J_1-1} + w_{J_1+2}) + 1.357 \times 10^{-14}(w_{J_1} + w_{J_1+1})] \tag{8.98}$$

## 8.13. BROADENING OF LINEAR DIPOLE MOLECULES ACCORDING TO FOLEY

Foley[37] considered the broadening of the rotation-vibration lines utilizing his Eqs. (6.143) and (6.144) for the half-width and shift respectively.

For an inverse third power dependence of the interaction energy on the molecular separation, for example, $p = 3$ in Eq. (6.143) and this equation becomes:

$$\delta = 8\pi N \sum_k \frac{\gamma_k}{2} \int_0^{\infty} \frac{d\alpha \sin^2 \alpha}{\alpha^2} = 4\pi N \sum_k \gamma_k \frac{\pi}{2} = 4\pi^2 N <\beta> \tag{8.99}$$

where we may recall that $\gamma$ arises from $\Delta\nu = \hbar\gamma/r^3$ while $\beta$ arises from $\Delta\nu = \hbar\beta/r^3$.

Now Foley used Eq. (8.23) — the root mean square value of the Rotational Resonance interaction — as $<\beta>$ in Eq. (8.99) to obtain the half-width due to this effect. One might question this procedure, however, since Foley's definition of $\gamma^*$ is the difference between two $\beta$'s defining interactions for two states. At any rate, the resonance half-widths obtained in this manner are listed in Table (8.4).

Foley utilized Eq. (6.143) with $p = 6$ for the case of the Directional Effect, and for this case the interaction constants were obtained by him from Eq. (8.15). The results of his calculations for HCN and HCl are given in Table (8.4).

Fig. (8.18) gives a comparison between the $\delta$ vs. $J$ curve for Foley as well as Lindholm. It would appear that Lindholm's curve more closely approximates the experimental results than Foley's which Anderson[8] attributed to possible errors in Foley's calculations. Actually there is no reason for much variation in these two sets of results. If Foley was desirous of working within the framework of his theory rather than Weisskopf's there appears to be no particular reason for his not using Lindholm's careful method of doing so. Had he so done it seems reasonable to suppose that the result would have been to raise Lindholm's curves of Fig. (8.18) (for $p$ equals three or six in Eq. (6.47) Foley's half-widths exceed Weisskopf's by factors of 1.57 and 1.21 respectively) perhaps to better agreement with experimental data rather than to distort these curves.

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[*] Cf. supra, Eq. (6.139).

| | HCl | | | | HCN | |
|---|---|---|---|---|---|---|
| $l$ | $\delta$ cm.$^{-1}$ | $l$ | $\delta$ sec. order | Resonance | Total | Shift |
| 0 | 0.39 | 0 | 0.32 | 0.54 | 0.86 | +0.12 |
| 1 | 0.60 | 1 | 0.39 | 0.92 | 1.31 | +0.14 |
| 2 | 0.72 | 2 | 0.44 | 1.33 | 1.87 | +0.14 |
| 3 | 0.70 | 3 | 0.48 | 1.69 | 2.17 | +0.14 |
| 4 | 0.58 | 4 | 0.50 | 1.98 | 2.48 | +0.13 |
| 5 | 0.42 | 5 | 0.53 | 2.20 | 2.73 | +0.12 |
| 6 | 0.27 | 6 | 0.54 | 2.35 | 2.89 | +0.10 |
| 7 | 0.158 | 7 | 0.54 | 2.41 | 2.95 | +0.065 |
| 8 | 0.80 | 8 | 0.55 | 2.41 | 2.96 | +0.040 |
| 9 | 0.038 | 9 | 0.56 | 2.34 | 2.90 | +0.010 |
| 10 | 0.016 | 10 | 0.55 | 2.24 | 2.79 | −0.018 |
| | | 11 | 0.54 | 2.06 | 2.60 | −0.043 |
| | | 12 | 0.53 | 1.87 | 2.40 | −0.067 |
| | | 13 | 0.51 | 1.67 | 2.17 | −0.082 |
| | | 14 | 0.50 | 1.46 | 1.96 | −0.10 |
| | | 15 | 0.48 | 1.25 | 1.73 | −0.11 |
| | | 16 | 0.44 | 1.05 | 1.49 | −0.11 |
| | | 17 | 0.42 | 0.87 | 1.29 | −0.12 |
| | | 18 | 0.38 | 0.71 | 1.09 | −0.11 |
| | | 19 | 0.36 | 0.56 | 0.92 | −0.11 |
| | | 20 | 0.32 | 0.44 | 0.76 | −0.10 |
| | | 21 | 0.30 | 0.34 | 0.64 | −0.10 |
| | | 22 | 0.26 | 0.26 | 0.52 | −0.088 |

Table (8.4). (After Foley[37])

## 8.14. AN APPLICATION OF SYMMETRICAL TOP DIPOLE BROADENING. AMMONIA

The development of microwave spectroscopic techniques in recent years has naturally led to a quickened interest on the part of many investigators in pure rotational spectra and the line broadening particular to this spectra. In this and the next several sections we shall consider some of the theories which have been advanced recently aimed directly at microwave broadening effects or at microwave and infrared effects.

In Appendix (VI) the manner in which absorbing transitions may take place between the two members of an inversion doubled vibrational level has been indicated. Taking, for example, the ground vibrational state and the possible inversion transition within this state, the variation of the inversion doublet separation with $J$ and $K$ will be responsible for the occurrence of many spectral lines as a result of this transition.

Bleaney and Penrose[9] have furnished the microwave field with some excellent results on the widths of these ammonia inversion lines. Some of the results of their experiments are contained in Fig. (8.9). Bleaney[7] used an interruption type approach to this broadening under the assumption that the disturbing ammonia molecule causes a certain perturbation of the absorbing ammonia molecule due to the field of its dipole. A collision is declared as having occurred at a certain separation or interaction energy, and, under an application of the normal interruption theory, Bleaney determines the half-widths as proportional to $3\sqrt{K^2/J^2 + J}$. Although a cursorily satisfactory agreement between theory and experiment was thus obtained, Margenau[117] has made a telling point which casts more than a little doubt on the meaningfulness of this agreement.

In order that this interruption approach succeed in explaining the broadening, it was found that an interaction energy (corresponding to a minimum collision-defining separation) of around twice the inversion doublet level separation be used. "If this were to be taken literally it would imply that the molecule could go on absorbing even when the perturbation is larger than its natural frequency or indeed when the natural frequency is negative. In suggesting this the impact theory rather defeats itself."[117] This is not only a telling but also a restrained comment on the situation.

Margenau thus decided to use the interaction between two symmetric dipole rotators* in conjunction with his Statistical theory to account for this broadening. His results were in good, if not spectacular, agreement with those of experiment, but, equally important, they were based on tenable theoretical considerations.

To begin with, the interaction energy has already been found as:

$$V(J_1K_1J_2K_2\Lambda) = \frac{\mu^2}{R^3}\,\frac{K_1K_2}{J_1(J_1+1)J_2(J_2+1)}\,\epsilon_\Lambda \tag{8.100}$$

where $\epsilon_\Lambda$ is the expression (in $M_1$ and $M_2$) in curly braces in Eq. (8.61). Here $\Lambda$, and hence $\epsilon_\Lambda$, may take on $(2J_1 + 1)(2J_2 + 1)$ values corresponding to the number of values available to $M_1$ and $M_2$.

Eq. (8.65b) has already told us that an interaction of the form Eq. (8.100) will result in no spectral line shift so we turn our attention solely to the widths.

If the doublet transition "normally" results in the absorption of radiation of frequency $\nu_0$, then at separation $R$ between two ammonia molecules, the absorber would absorb radiation of frequency:

$$\nu = \nu_0 + \frac{1}{h}\,(V' - V'') = \nu_0 + \frac{B_{\Lambda\mu}}{R^3} \tag{8.101a}$$

where, from Eq. (9.69):

$$B_{\Lambda\mu} = \frac{\mu^2}{h}\,\frac{K_1K_2}{J_1(J_1+1)J_2(J_2+1)}\,(\epsilon_\Lambda - \epsilon_\mu) = b(\epsilon_\Lambda - \epsilon_\mu) \tag{8.101b}$$

Perhaps it should be emphasized again that in the transition from one member of the inversion doubled vibrational level to the other $J_1K_1J_2K_2$ do *not* change their values although the dipole changes its orientation causing $M_i$ to change. If this were not the case Eq. (9.70b) would obviously not be justified. Margenau ignored the selection rules on the basis of the large number of possibilities for $J_1$ and $J_2$ for all but small $J_1$ and $J_2$. For this reason $\Lambda_\mu$ is replaced by $\sigma$ where $\sigma$ takes on all values from one to $n=[(2J_1+1)\,(2J_2+1)].^{1/2}$

We are now in a position, after assuming binary encounters and the resulting low pressure,† to carry out the probability calculation leading to a statistical line shape.

We now divide space into private cells of volume $1/N$, and to each of these we assign a perturber. Next, $n$ of these cells are taken, one for each value of $(1 \leqslant \sigma \leqslant n)$. In the $\sigma$-th cell:

$$\nu = \nu_0 + \frac{B_\sigma}{R^3} = \nu_0 + f \tag{8.102}$$

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* See *supra*, Sec. 9.

† Bleaney and Penrose used quite low pressures so that this should be a reasonable approximation.

according to Eq. (8.101a) at separation $R$. We presume the cells to be spherical, and the probability that the frequency lies near $f$ (the portion of the $\sigma$-th space contributing this frequency being a spherical shell of radius $R$) is:

$$I_\sigma(f)df \propto \frac{4\pi}{3}\left(\frac{d}{df}R^3\right)_\sigma df \tag{8.103}$$

Let us take $f > 0$ which means that one half the $n$ cells will contribute to the probability since Eq. (8.101b) is symmetrical as indicated by the zero value for its mean. In order to obtain the intensity at a frequency separation $f$ from the line center it is now merely necessary to sum Eq. (8.103) over all $n/2$ values of $\sigma$ (for $f > 0$) with the result:

$$I(f) = \left|\frac{N}{n}\sum_{\sigma}^{n/2}\frac{4}{3}\pi\left(\frac{dR^3}{df}\right)_\sigma\right| = \frac{4\pi}{3}\frac{N}{n}\left|\sum_{\sigma}^{n/2}\frac{d}{df}\left(\frac{B_\sigma}{f}\right)\right| \tag{8.104}$$

where $N/n$, the normalizing factor, is simply the reciprocal of the volume contained in the $n$ cells.

Again utilizing the symmetry of the $B_\sigma$ arising from the disappearance of the mean value

$$\frac{d}{df}\sum_{\sigma}^{n/2}\frac{|B_\sigma|}{f} = \tfrac{1}{2}\frac{d}{df}\sum_{\sigma}^{n}\frac{|B_\sigma|}{f}$$

so that Eq. (8.104) becomes:

$$I(f) = \frac{2\pi}{3}\frac{N}{f^2}\frac{\sum_\sigma |B_\sigma|}{n} \tag{8.105}$$

In normalizing $I_f$, the limits of integration are $B_\sigma/R^3_{\max}$ ($R^3_{\max} = 3\pi N/4$) and infinity, where the lower limit is different in each term of the sum in Eq. (8.105). Eq. (8.105) gives the positive wing ($f > 0$) of the distribution which, however, is mirrored in the negative wing ($f < 0$). Consequently the normalization integral $I(f)$ must be equal to one half.

On the basis of the large value of $n$, Margenau assumed a Gaussian distribution* of the $B_\sigma$. By virtue of this Gaussian assumption we may equate the mean of the absolute values to the standard deviation or root mean square value of the deviation from average times $\sqrt{\frac{2}{\pi}}$.

$$\frac{1}{n}\sum_{\sigma}|B_\sigma| = \sqrt{\frac{2}{\pi}}\left[\frac{1}{n}\sum_{\sigma}(B_\sigma - B)^2\right]^{1/2} = \sqrt{\frac{2}{\pi}}\left[\frac{1}{n}\sum_{\sigma}B_\sigma^2\right]^{1/2} \tag{8.106a}$$

and from Eq. (8.101):

$$\sum_{\sigma} B_\sigma^2 = b^2\sum_{\Lambda\mu}(\epsilon_\Lambda - \epsilon_\mu)^2 = 2b^2n^{1/2}\sum_{\Lambda}\epsilon_\Lambda^2 = 2b^2n <\epsilon^2> \tag{8.107b}$$

where $<\epsilon^2>$ is the mean square energy and has been given by Eq. (8.68a).

Eq. (8.106b) may now be substituted into Eq. (8.106a) and the result in turn substituted into Eq. (8.105) to yield:

$$I(f) = \frac{4}{3}\left(\frac{2\pi}{3}\right)^{1/2}\frac{\mu^2}{h}\frac{K_1K_2}{[J_1(J_1+1)J_2(J_2+1)]^{1/2}}\frac{N}{f^2} \tag{8.107}$$

which quite obviously holds only in the line wing.

---

* This should not be supposed to imply a Gaussian distribution of intensities in the spectral line.

If we assume a dispersion distribution, one obtains for large $f = \nu - \nu_0$:

$$I(f) \rightarrow \frac{1}{\pi} \frac{\delta}{(\nu - \nu_0)^2}$$

so that:

$$\delta = 2\left(\frac{2\pi}{3}\right)^{3/2} \frac{\mu^2}{h} N \frac{K_1K_2}{[J_1(J_1 + 1)J_2(J_2 + 1)]^{1/2}} \tag{8.108a}$$

Finally the average value of the involved combination of perturber quantum numbers over a Maxwell-Boltzmann distribution* is taken:

$$<K_2J_2(J_2 + 1)> = \frac{\sum\limits_{J_2K_2} [K_2(J_2^2 + J_2)]\, g(J_2K_2)e^{-W(J_2K_2)/kT}}{\sum\limits_{J_2K_2} g(J_2K_2)e^{-W(J_2K_2)/kT}} \tag{8.109}$$

In Eq. (8.109) the $W(J_2K_2)$ are the symmetric rotator energies as given by Eq. (2.37b). The $g(J_2K_2)$ are the statistical weights of the levels. Smith[172] has carried out the calculation indicated by Eq. (8.109) to obtain 0.54 for $T = 20°C$. For ammonia $\mu = 1.44 \times 10^{-18}$ e.s.u. On this basis Margenau obtained the result:

$$\frac{\delta}{p} = 1.13 \times 10^{-3} \frac{K_1}{[J_1(J_1 + 1)]^{1/2}}\ cm^{-1}(mmHg)^{-1} \ @\ 20°C. \tag{8.110}$$

and the straight line in Fig. (8.9) yields the results of applying this equation.

This then is Margenau's low pressure (and the theory has not here developed for any but low pressures) result for ammonia inversion lines, and its success for this case is manifestly apparent from Fig. (8.11). Some of the modifications which higher pressures invoke will become apparent in Margenau's more refined treatment of interactions between potential hill molecules which we consider next.

## 8.15. INTERACTIONS BETWEEN LINEAR VIBRATORS WITH MIRROR POTENTIALS

The shift to the red with increase of pressure of the $NH_3$ inversion line, which had recently been observed,[8, 172] provoked the Margenau investigation[118] of the phenomenon which we shall consider in this and the two succeeding sections. First let us note that in applying the term "linear" to $NH_3$ (or other mirror potential molecules) we simply wish to imply that the mirror potential of the molecule is a function only of the separation of the $N$ atom from the $H$ plane.

In considering this problem we again take the eigenfunctions for the two doublet members of a vibrational level as:

$$\psi_1 = [2(1 - \Upsilon)]^{-1/2} (\psi_- - \psi_+) \tag{8.111a}$$

$$\psi_2 = [2(1 + \Upsilon)]^{-1/2} (\psi_- + \psi_+) \tag{8.111b}$$

where again $E_1 > E_2$.

Now two interacting molecules of this type are to be considered.

Margenau chooses to treat the case in which the dipoles of the two molecules are aligned along the same axis. If we let $x_i$ be the separation of the mean positive charge from the center of mass of a molecule, the resulting interaction between the two molecules under these circumstances is:

$$U = -2e^2 \frac{x_1x_2}{R^3} \tag{8.112}$$

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* See *supra*, Eq. (8.77).

If $H(1)$ and $H(2)$ are the unperturbed Hamiltonians for the two molecules and $U(1, 2)$ the Hamiltonian of the interaction, then the present problem may be approached by minimizing

$$H(1,2) = H(1) + H(2) + U(1,2) \tag{8.113}$$

after the fashion of Sec. 8.4. Eq. (8.27) for the present case is:

$$\begin{aligned} \varphi &= A\psi_1(1)\psi_1(2) + B\psi_2(1)\psi_2(2) + C\psi_1(1)\psi_2(2) + D\psi_2(1)\psi_1(2) \\ &= A\psi_A + B\psi_B + C\psi_C + D\psi_D \end{aligned} \tag{8.114}$$

All diagonal elements of $U$ vanish, which can be made easily apparent. As we have noted an integrand must be symmetric. Now a linear combination of position coordinates is antisymmetric. Thus, $\psi_2$ is symmetric so $x\psi_2$ is antisymmetric and $\psi_2 x\psi_2$ is antisymmetric. $\psi_1$ is antisymmetric so $x\psi_1$ is symmetric and $\psi_1 x\psi_1$ is antisymmetric. Thus, the integrals involved in the diagonal elements of $U$ disappear. As a consequence the only allowed elements of $U$ are:

$$U_{AB} = U_{CD} = -\frac{2e^2}{R^3}x_{12}^2 \tag{8.115a}$$

where:

$$x_{12} = \int \psi_1 x \psi_2 dx = -\frac{\bar{x}}{(1 - T^2)^{1/2}} \tag{8.115b}$$

and

$$\bar{x} = \int x\psi_+^2 dx = -\int x\psi_-^2 dx \tag{8.115c}$$

Thus, the nonvanishing matrix elements of $H(1,2)$ are:

$$\begin{aligned} H_{AA} = 2E_1;\ H_{BB} = 2E_2;\ H_{CC} = H_{DD} = E_1 + E_2 \\ H_{AB} = H_{CD} = U_{AB} \end{aligned} \tag{8.116}$$

Eq. (3.116) leads immediately to the secular determinant:

$$\begin{vmatrix} 2E_1 - E & y & 0 & 0 \\ y & 2E_2 - E & 0 & 0 \\ 0 & 0 & E_1 + E_2 - E & y \\ 0 & 0 & y & E_1 + E_2 - E \end{vmatrix} = 0 \tag{8.117}$$

in which we have replaced the $U_{ij}$ by $y$.

As is apparent from Eq. (8.117) the determinant has been split into two, two by two blocks, each of which has two solutions. One simply solves for the $E^{(i)}$ and subsequently obtains the constants $A$ through $D$ in Eq. (8.114) from equations of the form Eq. (8.31). After this fashion one obtains as first order energies and eigengunctions:

$$\begin{aligned} E^{(1)} &= 2E_1 + R(E_1 - E_2) \\ \Phi^{(1)} &= (1 + S^2)^{-1/2}[\psi_1(1)\psi_1(2) + S\psi_2(1)\psi_2(2)] \end{aligned} \tag{8.118a}$$

$$\begin{aligned} E^{(3)} &= 2E_2 - R(E_1 - E_2) \\ \Phi^{(3)} &= (1 + S^{-2})^{-1/2}[\psi_1(1)\psi_1(2) - S^{-1}\psi_2(1)\psi_2(2)] \end{aligned} \tag{8.118b}$$

$$\begin{aligned} E^{(2)} &= E_1 + E_2 + y \\ \Phi^{(2)} &= \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)] \end{aligned} \tag{8.118c}$$

$$\begin{aligned} E^{(4)} &= E_1 + E_2 - y \\ \Phi^{(4)} &= \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)] \end{aligned} \tag{8.118d}$$

$$R = \left[1 + \left(\frac{y}{E_1 - E_2}\right)^2\right]^{1/2} - 1$$

$$S = \frac{E_1 - E_2}{y} R \tag{8.118e}$$

A cursory consideration of Eq. (8.118d) is sufficient to show that the eigenfunction in this equation is the only one which is antisymmetric (changes sign) on exchange of the coordinates one and two. As a consequence $\Phi^{(4)}$ cannot combine with any of the other eigenfunctions, and may be neglected.

Now $\Phi^{(1)}$ and $\Phi^{(3)}$ are symmetric with respect to a reflection of their coordinates through the origin (even parity). On the other hand, $\Phi^{(2)}$ is antisymmetric (odd parity). The matrix elements of $X = x_1 + x_2\Lambda$, the electric dipole moment (odd parity), determine the intensities of possible transitions among the states whose energies and eigenfunctions we have ascertained. Since $X$ is antisymmetric, it may only combine with a symmetric and an antisymmetric pair of eigenfunctions. This means that under the influence of $X$, $\Phi^{(1)}$ and $\Phi^{(2)}$ as well as $\Phi^{(3)}$ and $\Phi^{(2)}$ may combine, but $\Phi^{(1)}$ and $\Phi^{(3)}$ may not. If we let $\Delta_i$ and $w_i$ respectively be the energy difference and probability of such a combination, there results, from Eqs. (8.118):

$$\Delta_I = E^{(1)} - E^{(2)} = (E_1 - E_2)\left[(1 + \Lambda^2)^{1/2} + \Lambda\right] \tag{8.119a}$$

$$\Delta_{II} = E^{(2)} - E^{(3)} = (E_1 - E_2)\left[(1 + \Lambda^2)^{1/2} - \Lambda\right] \tag{8.119b}$$

$$\Lambda = \frac{|y|}{E_1 - E_2} = \frac{2\mu_2}{(1 - \Upsilon^2)R^3}\,\frac{1}{(E_1 - E_2)} \tag{8.119c}$$

$$w_1 \doteq \left|\int \Phi^{(1)} X\, \Phi^{(2)}\, dx\right|^2 = 2\,\frac{(S+1)^2}{S^2+1}\; x_{12}^2 \tag{8.119d}$$

$$w_2 \doteq \left|\int \Phi^{(2)} X\, \Phi^{(3)}\, dx\right|^2 = 2\,\frac{(S-1)^2}{S^2+1}\; x_{12}^2 \tag{8.119e}$$

wherein all symbols have previously been explained.

The results of Eqs. (8.119) are rather self-evident, and appear in Fig. (8.12). The frequencies appearing in this figure are given in units of the inversion doublet separation. From this figure also the manner in which the line splitting increases with decreasing particle separation is apparent. The decrease in the intensity with decreasing separation for the higher frequency is also notable. From these considerations, however, one would expect that with increasing pressure the inversion line frequency should decrease as indeed it does. One further point might be made to the effect that the line width could hardly be expected to vary with the pressure, as Margenau has noted, under the conditions prevalent here — two frequencies varying differently with pressure.

### 8.16. ROTATING LINEAR DIPOLES WITH MIRROR POTENTIALS

We now allow our dipoles to rotate as symmetric tops in addition to the behavior which we prescribed in the last section as a next approximation to the actual molecular phenomenon. It appears apparent that our Hamiltonian will now take the form:

$$H = H_0 + Q = H_r(1) + H_r(2) + H_v(1) + H_v(2) + Uf(\vartheta,\varphi) \tag{8.120}$$

where $H_r$ is the Hamiltonian of a symmetric top rotator; $H_v$ is the $H(i)$ of Eq. (8.113) and $2f(\vartheta,\varphi)$ is the bracketed expression of Eq. (8.2).

As our unperturbed eigenfunctions let us choose:

$$\Phi_N\,(x_1x_2)\;\psi_{J_1K_1M_1}(\vartheta_1\varphi_1\chi_1)\;\psi_{J_2K_2M_2}\,(\vartheta_2\varphi_2\chi_2) \tag{8.121a}$$

where the $\psi_{JKM}$ are given by Eq. (2.35b). Section 16 indicates that a good choice for $\Phi_N$ will be:

$$\begin{aligned} \Phi_1 &= \psi_1(1)\psi_1(2) \\ \Phi_2 &= \sqrt{\tfrac{1}{2}}\,[\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)] \\ \Phi_3 &= \psi_2(1)\psi_2(2) \end{aligned} \tag{8.121b}$$

There is no question but that $H_0$ is diagonal with respect to Eqs. (8.121) since the eigenfunctions of this latter equation are the eigenfunctions of the Hamiltonian operator $H_0$. The eigenvalues of this operator we know to be:

$$(NJ_1K_1M_1J_2K_2M_2|H_0|\,NJ_1K_1M_1J_2K_2M_2) = E_N + E_{J_1K_1} + E_{J_2K_2} \tag{8.122}$$

in which the $E_N$ are given by the diagonal elements in Eq. (8.116), and the $E_{JK}$ are given by Eq. (2.37b).

$Q$, on the other hand, is not diagonal and its matrix elements are given by:

$$\begin{aligned} (N''J_1K_1M_1''J_2K_2M_2''\,|\,Q\,|\,N'J_1K_1M_1'J_2K_2M_2') &= (N''\,|\,U\,|\,N')(J_1K_1M_1''J_2K_2M_2''\,|f|\,J_1K_1M_1'J_2K_2M_2') \\ &= (N''\,|\,U\,|\,N')\,(M_1''M_2''\,|\,f\,|\,M_1'M_2') \end{aligned} \tag{8.123}$$

In Eq. (8.123) the matrix elements of $f$ which are involved with changes in the quantum numbers $J$ and $K$ are neglected. This ignoration entails a good approximation since the levels having different $J$ and $K$ are so greatly separated in comparison to the separation of the two members of an inversion doublet that they may be neglected. Neglecting $M$, the spatial degeneracy parameter, and its possible change would be something else again.

Eqs. (8.112), (8.115), and (8.121b) may now be used directly to obtain:

$$||\,U\,|| = ||\,(N''\,|\,U\,|\,N')\,|| = -\,\frac{2e^2}{R^3}\,x_{12}^2\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \tag{8.124}$$

In addition Eq. (8.122) may be written as:

$$||\,T\,|| = \begin{pmatrix} E_r + 2E_1 & 0 & 0 \\ 0 & E_r + E_1 + E_2 & 0 \\ 0 & 0 & E_r + 2E_2 \end{pmatrix} \tag{8.125}$$

Then from Eqs. (8.120) and (8.122) through (8.125):

$$H = ||\,T\,||\;||\,(M_1''M_2''\,|\,1\,|\,M_1'M_2')\,|| + ||\,U\,||\;||\,(M_1''M_2''\,|f|\,M_1'M_2')\,|| \tag{8.126}$$

A quite standard and well known procedure exists* for diagonalizing $||\,(M_1''M_2''\,|\,f\,|\,M_1'M_2')\,||$ while leaving $||\,(M_1''M_2''\,|\,1\,|\,M_1'M_2')\,||$ a unit matrix. This procedure is carried out to obtain a matrix for $H$ which consists of three by three blocks along the principal diagonal of the form:

$$||\,T + f_iU\,|| = \begin{pmatrix} E_r + 2E_1 & 0 & f_iy \\ 0 & E_r + E_1 + E_2 + f_iy & 0 \\ f_iy & 0 & E_r + 2E_2 \end{pmatrix} \tag{8.127}$$

whose eigenvalues must be determined.

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* For example the procedure is carried out every time one determines the normal modes of a harmonic oscillator.

In order to accomplish this Margenau let $\epsilon = E - (E_1 + E_2) - E_r$, that is, he let $\epsilon$ be the difference between the perturbed energy $E$ and the intermediate of the three unperturbed levels (see for example Eq. (8.125)). Solutions are then required of:

$$\begin{pmatrix} E_1 - E_2 - \epsilon & 0 & f_i y \\ 0 & f_i y - \epsilon & 0 \\ f_i y & 0 & -(E_1 - E_2) - \epsilon \end{pmatrix} = 0 \qquad (8.128)$$

which turn out to be

$$\epsilon_i^{(1)} = [(E_1 - E_2)^2 + f_i^2 y^2]^{1/2} = (E_1 - E_2)(R_i + 1) \qquad (8.129a)$$

$$\epsilon_i^{(2)} = f_i y \qquad (8.129b)$$

$$\epsilon_i^{(3)} = -[(E_1 - E_2)^2 + f_i^2 y^2]^{1/2} = -(E_1 - E_2)(R_i + 1) \qquad (8.129c)$$

where we now define $R_i$ as: $R_i = \left[1 + \left(\frac{f_i y}{E_1 - E_2}\right)^2\right]^{1/2} - 1$

We may note the agreement between Eqs. (8.118) and (8.129) when $E_r$ is neglected. Let us consider just how the problem stands at this point.

The matrix of $f$ in Eq. (8.126) contains $(2J_1 + 1)(2J_2 + 1)$ rows and columns since this is the possible number of values of $M_1$ and $M_2$. This in turn means that there will be this number of diagonal elements. Note that in Eq. (8.126) each element of the matrix of $f$ is multiplied by the three by three matrix $\| U \|$ and similarly for the unit matrix. In the diagonalized version of Eq. (8.126) there will be $(2J_1 + 1)(2J_2 + 1)$ matrices of the form Eq. (8.128) along the principal diagonal leading to $3(2J_1 + 1)(2J_2 + 1)$ roots of the form Eq. (8.129). This means quite simply that due to the interaction considered in this section each inversion doublet will be split into $3(2J_1 + 1)(2J_2 + 1)$ energy levels.

The symmetries of the eigenfunctions associated with Eqs. (8.129) are the same as those associated with the corresponding eigenvalues of Eqs. (8.28). Thus the corresponding states may combine here. In place of the two spectral lines resulting from the considerations of Sec. 16 we now have $(2J_1 + 1)(2J_2 + 1)$ lines of increased frequency and a like number of lines of diminished frequency. If $\Lambda$ is replaced by $f_i\Lambda$ in Eqs. (8.119), thus redefining also $S$, the transition probabilities for the present case result. As may be noted from Eq. (8.2) $f_i$ is never greater than unity so that in general we may expect the level shift indicated by Eqs. (8.129) to be somewhat less, on the whole, than the shift of the previous section.

We shall return to a consideration of the results of this section after a brief study of multiple encounters, but now let us merely mention an earlier point which this section bears out before turning our attention to a three molecule interaction.

In Eqs. (8.129a) and (8.129c) $\epsilon$ has a dependence on quadratic $f_i y$ while in Eq. (8.129b) a linear relationship exists. Then for the case $f_i y \ll 1$ we may consider the upper and lower levels, as given by the first and third of Eqs. (8.129), as fixed while the intermediate level shifts its position in linear relation to $f_i y$. This in turn means that the two inversion frequencies change in value as $\pm f_i y$, and we may recall that this result was forecast in Sec. 15 for the case of low pressure. The more accurate low pressure treatment of this section tends then to bear out this earlier result.

## 8.17. THREE MOLECULE INTERACTIONS AND THE $NH_3$ INVERSION LINE SHIFT

In order to determine whether a consideration of many molecule interactions tends to change the theoretical prognostications in the preceding sections, Margenau investigated the case of the interaction between three very symmetrically arranged linear vibrators possessed of mirror potentials. The simplest configuration of three such models is a placement of them at the vertices of an equilateral triangle with the axes of their dipoles aligned parallel to the opposing faces of this triangle. This was done; no rotation was allowed, and the resulting interaction effect on the energy levels was determined after the fashion of Sec. 16. Let us sketch this solution very briefly.

Eq. (8.112) becomes:

$$U = -\frac{5}{4}\frac{e^2}{R^3}(x_1x_2 + x_1x_3 + x_2x_3) \tag{8.130}$$

and the symmetric eigenfunctions corresponding to those in Eq. (8.114)

$$\begin{aligned}
\psi_A &= \psi_1(1)\psi_1(2)\psi_1(3) \equiv 111 & E_A &= 3E_1 \\
\psi_B &= 112 + 121 + 211 & E_B &= 2E_1 + E_2 \\
\psi_C &= 122 + 212 + 221 & E_C &= E_1 + 2E_2 \\
\psi_D &= 222 & E_D &= 3E_2
\end{aligned} \tag{8.131}$$

which lead to:

$$\| U \| = \begin{pmatrix} 0 & 0 & 32 & 0 \\ 0 & 62 & 0 & 32 \\ 32 & 0 & 62 & 0 \\ 0 & 32 & 0 & 0 \end{pmatrix} \tag{8.132}$$

where: $z = -\dfrac{5}{4(1 - \Upsilon^2)}\dfrac{\mu^2}{R^3}$

The determinantal analogy to Eq. (8.119)

$$\begin{vmatrix} 3E_1 - E & 0 & 32 & 0 \\ 0 & 2E_1 + E_2 + 2z - E & 0 & z \\ z & 0 & E_1 + 2E_2 + 2z - E & 0 \\ 0 & 32 & 0 & 3E_2 - E \end{vmatrix} = 0 \tag{8.133}$$

of solution:

$$E^{(1)} = 3E_1 + \eta_1(E - E_2) \ ; \ \Phi^{(1)} = \left(1 + \frac{\eta_1^2}{3\Lambda^2}\right)^{-1/2}\left[\psi_A + \frac{\eta_1}{3\Lambda}\psi_C\right] \tag{8.134a}$$

$$E^{(2)} = 3E_2 + \eta_2(E_1 - E_2) \ ; \ \Phi^{(2)} = \left(1 + \frac{\eta_2^2}{3\Lambda^2}\right)^{-1/2}\left[\frac{\eta_2}{3\Lambda}\psi_B + \psi_D\right] \tag{8.134b}$$

$$E^{(3)} = 3E_1 + \eta_3(E_1 - E_2) \ ; \ \Phi^{(3)} = \left(1 + \frac{\eta_3^2}{3\Lambda^2}\right)^{-1/2}\left[\psi_A + \frac{\eta_3}{3\Lambda}\psi_C\right] \tag{8.134c}$$

$$E^{(4)} = 3E_2 + \eta_4(E_1 - E_2) \ ; \ \Phi^{(4)} = \left(1 + \frac{\eta_4^2}{3\Lambda^2}\right)^{-1/2}\left[\frac{\eta_4}{3\Lambda}\psi_B + \psi_D\right] \tag{8.134d}$$

where: $\Lambda = \dfrac{z}{E_1 - E_2}$ ; $\eta_1 = [(1-\Lambda)^2 + 3\Lambda^2]^{1/2} - (1-\Lambda)$ ; $\eta_2 = [(1+\Lambda)^2 + 3\Lambda^2]^{1/2} + (1+\Lambda)$

$\eta_3 = -[(1-\Lambda)^2 + 3\Lambda^2]^{1/2} - (1-\Lambda)$ ; $\eta_4 = -[(1+\Lambda)^2 + 3\Lambda^2]^{1/2} + (1+\Lambda)$

The allowed matrix elements of $X \equiv x_1 + x_2 + x_3$ together with the corresponding energy differences are:

$$X_{12}^2 = \frac{(\Lambda\eta_1 + \Lambda\eta_2 + \frac{2}{3}\eta_1\eta_2)^2}{(\Lambda^2 + \frac{1}{3}\eta_1^2)(\Lambda^2 + \frac{1}{3}\eta_2^2)}\bar{x}^2 \; ; \; \Delta_{12} = (3 + \eta_1 - \eta_2)(E_1 - E_2) \tag{8.135a}$$

$$X_{14}^2 = \frac{(\Lambda\eta_1 + \Lambda\eta_4 + \frac{2}{3}\eta_1\eta_4)^2}{(\Lambda^2 + \frac{1}{3}\eta_1^2)(\Lambda^2 + \frac{1}{3}\eta_4)^2}\bar{x}^2 \; ; \; \Delta_{14} = (3 + \eta_1 - \eta_4)(E_1 - E_2) \tag{8.135b}$$

$$X_{23}^2 = \frac{(\Lambda\eta_2 + \Lambda\eta_3 + \frac{2}{3}\eta_2\eta_3)^2}{(\Lambda^2 + \frac{1}{3}\eta_2^2)(\Lambda^2 + \frac{1}{3}\eta_3^2)}\bar{x}^2 \; ; \; \Delta_{23} = (-3 + \eta_2 - \eta_3)(E_1 - E_2) \tag{8.135c}$$

$$X_{34}^2 = \frac{(\Lambda\eta_3 + \Lambda\eta_4 + \frac{2}{3}\eta_3\eta_4)^2}{(\Lambda^2 + \frac{1}{3}\eta_3^2)(\Lambda^2 + \frac{1}{3}\eta_4^2)}\bar{x}^2 \; ; \; \Delta_{34} = (3 + \eta_3 - \eta_4)(E_1 - E_2) \tag{8.135d}$$

The results of Eqs. (8.135) are plotted in Fig. (8.13). Since the transition probability $X_{14}^2$ is very small it has not been indicated on these plots, and, correspondingly $\Delta_{14}$ has been neglected. As was to be expected the inversion frequency has now been split into four components. Of the three we are here considering, it is to be noted that as in the two particle collision case the component of decreasing energy is also the component of increasing intensity while the reverse now holds for both the components of increasing energy. A comparison of Figs. (8.12) and (8.13) serves to illustrate a notable difference between the two and three particle cases. The dominant (intensitywise) frequency decreases much more rapidly with $\Lambda$ in the three molecule case than it does in the two molecule case. This "fact" leads Margenau to an interesting conclusion.

As we have seen the larger number of interacting particles has led to a greater frequency perturbation. Through Eq. (8.129) the effect of rotation is to decrease this spread. Compensating effects appear to be in the wind, and the results of Sec. 16 are at least suggested as valid under these conditions.

Under the assumption that the resonance frequency could be approximated by the mean frequency, as given by $h\bar{\nu} = w_I\Delta_I + w_{II}\Delta_{II}$, and that $\Lambda \ll 1$, Margenau obtained for the shifted frequency:

$$\bar{\nu} \doteq \nu_0(1 - \Lambda^2) \tag{8.136a}$$

Since:

$$\Lambda = \frac{2\mu^2}{(E_1 - E_2)R^3} \doteq \frac{2\mu^2 N}{E_1 - E_2} \doteq 0.6p$$

where $p$ is the ammonia pressure in atmospheres, $E_1 - E_2 \doteq 0.8$ cm.$^{-1}$, $\mu = 1.44 \times 10^{-18}$ and the temperature is taken as 0°C, Eq. (8.136a) becomes:

$$\bar{\nu} \doteq \nu_0(1 - 0.36p^2) \tag{8.136b}$$

This can only be expected to hold at low pressures since (1) it has been obtained under the assumption of a binary collision or a two particle interaction and (2) the factor $\Lambda$ has been assumed as small. The "dominant" frequency may also be written approximately for low pressures from the binary theory as:

$$\nu_{II} = \nu_0(1 - 0.6p) \tag{8.136c}$$

and this may be compared with the experimental results.

From Fig. (8.12) the result is 0.44 cm.$^{-1}$ and from the experimental data[60] 0.5 cm.$^{-1}$ for the dominant frequency at one atmosphere. It would appear from this agreement then that this approximation and the theory from which it arose is good up to pressures of this order. As Margenau has demonstrated it definitely fails for ammonia above this pressure, however.

Thus, in this and the preceding two sections we have considered Margenau's method of approach in successfully accounting for the shift of the inversion line at low pressures through the assumption of binary interactions. We have also noted the much more rapid decrease of the energy of the "dominant" frequency* with $\Lambda$ for the three particle case than for the two particle case.† The actual failure of the two particle theory for higher pressures stems from an inability on the part of this theory to cause a rapid enough decrease of this frequency with $\Lambda$. Thus, it would appear that the many particle interactions are at least pointing in the direction of the required correction for higher pressures.

## 8.18. ANDERSON'S LINE BROADENING THEORY

What Mizushima has described as an elaborate approach was utilized by Anderson[3] in what we may, with some justification, term another Interruption Broadening consideration. Our consideration of his theory will perhaps be somewhat sketchy in comparison to certain of our other studies.**

Anderson begins by making what he calls the "assumption of a classical path." We might interject here that we have inferred the translational motion of the molecules as classical — the meaning of the above phrase — except in our consideration of the Jablonski theory. He then arrives at the equation for the intensity:

$$I(\omega) = \text{const}\ \omega^4 Tr \,||\, \rho_0 \int_{-\infty}^{+\infty} dt e^{i\omega t}\mu_z(t) \int dt' e^{i\omega t'}\, \mu_z(t') \,|| \tag{8.137}$$

which has a somewhat familiar appearance. In essence a rather hugger mugger†† quantum mechanical solution of this equation for the line shape, line width, and line shift under certain rather standard interruption assumptions constitute the residue of the theory. We shall be a little less sketchy than this, however.

First the matter of obtaining Eq. (8.137) must needs be considered and we shall only do so in a qualitative manner which tends to justify the result. Anderson, in his dissertation, has used the quantum radiation theory to obtain this equation, and Margenau and Bloom[12] have, in quite a sophisticated manner, obtained an equation of the form Eq. (8.137) which contains two terms, one for the true absorption and the second for the induced emission. Let us merely indicate how this equation might arise.

We begin with the classical intensity distribution based on the Fourier analysis of the varying dipole moment of a molecule:

$$\omega^4 \left| \int_{-\infty}^{+\infty} \mu_z(t) e^{i\omega t} dt \right|^2 \tag{8.138}$$

which we suppose averaged over all states. Based on an appeal to correspondences we now replace the observables in Eq. (8.138), namely, $\mu_z(t)$, by the analogous quantum operator. In order to find an average we utilize the density matrix as indicated by Eq. (6.162) to obtain Eq. (6.117). Objections to this method can, of course, be raised (commutability of $\mu_z(t')$ and $\mu_z(t)$ for example) with complete justification, but we accept Eq. (8.137) since we agree that a rigorous derivation of it exists.

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* See Fig. (8.13).

† See Fig. (8.12).

** A thorough coverage of the Anderson theory has been carried out quite recently by Tsao and Curnutte.[18]

†† The degree of hugger muggery here is directly related to the brevity of the article in question.

Before continuing let us discuss time development operators, unitary transformations and such, briefly, of course.

Suppose there to be a Hamiltonian of the form $H_0 + H_1$ where the $H_0$ is the unperturbed Hamiltonian of a two particle system and the $H_1$ that for the particle interaction. We further assume that we have diagonalized the matrix of $H_0$ and obtained this operator's eigenfunctions as $\psi_n(0)$. Under the aegis of $H$ we develop from these eigenfunctions the eigenfunctions $\psi_n(t)$ as follows:

$$\psi_n(t) = U\psi_n(0) \tag{8.139}$$

where $U$ is the so-called "time development operator." This operator is of the form $e^{(i/\hbar)Ht}$ for $H \neq H(t)$ and of the form $e^{-i/\hbar \int_0 H(t')dt'}$ for $H = H(t)$ where $H(t_1)$ commutes with $H(t_2)$, that is:

$$H(t_1)H(t_2) = H(t_2)H(t_1)$$

for any $t_1$ and $t_2$. The substitution of this latter operator into $\left(i\hbar\frac{\partial}{\partial t} - H(t)\right) = 0$ tends to verify this immediately.

Let us suppose we have a matrix relation as follows:

$$\underline{\mu}(t) = \mathbf{U}^{-1}\underline{\mu}_0\mathbf{U} \tag{8.140}$$

Then we have carried out a similarity transformation, and a factor concerning this transformation for which we shall have some little use is the invariance of the trace under such a transformation. In Eq. (8.140)$\mathbf{U}^{-1}$ is the inverse matrix* such that $\mathbf{U}^{-1}\mathbf{U} = 1$. We shall be primarily interested in unitary matrices which are defined by the relation $\mathbf{U}^{-1} = \mathbf{U}^\dagger$ where $\mathbf{U}^\dagger$ is the adjoint matrix.** If the matrix $\mathbf{U}$ in Eq. (8.140) is unitary then the transformation of Eq. (8.140) is unitary.

It so happens that Eq. (8.140) not only served to illustrate some facts about matrices but also is a relation among the time development matrix (*TDM*), the moment matrix $\underline{\mu}(t)$, and the matrix, $\underline{\mu}_0$, of $\underline{\mu}(t)$ at $t = 0$. Although we shall not dwell on this relation one may surely intuitively grasp the manner in which the *TDM* shapes the behavior with time of the moment matrix from the value of that matrix at time zero.

A modified *TDM* may now be defined such that:

$$\mathbf{T} = \mathbf{U}_0^{-1}\mathbf{U} \longleftrightarrow \mathbf{U} = \mathbf{U}_0\mathbf{T} \tag{8.141a}$$

where:

$$\mathbf{U}_0 = \exp\left[-\frac{\mathbf{i}}{\hbar}\mathbf{H}_0\mathbf{t}\right] \tag{8.141b}$$

When Eqs. (8.141) are substituted into $(i\hbar\frac{\partial}{\partial t} - H) = 0$ the result is:

$$i\hbar(\dot{\mathbf{U}}_0\mathbf{T} + \mathbf{U}_0\dot{\mathbf{T}}) = (\mathbf{H}_0 + \mathbf{H}_1)\mathbf{U}_0\mathbf{T} \longleftrightarrow i\hbar\mathbf{U}_0\dot{\mathbf{T}} = \mathbf{H}_1\mathbf{U}_0\mathbf{T} \longleftrightarrow i\hbar\dot{\mathbf{T}} = (\mathbf{U}_0^{-1}\mathbf{H}_1\mathbf{U}_0)\mathbf{T} \tag{8.142a}$$

and when they are substituted into Eq. (8.140) one finds:

$$\underline{\mu}(t) = \mathbf{T}^{-1}\exp\left(\frac{i}{\hbar}H_0t\right)\underline{\mu}_0\exp\left(-\frac{i}{\hbar}H_0t\right)\mathbf{T} \tag{8.142b}$$

---

* We shall cease to use the symbol || || as designating a matrix and simply use boldfaced type from this point on.

** We here refer to the complex conjugate transpose ($a_{ij} = \bar{a}_{ji}$) which is sometimes termed the "associate matrix."

a typical matrix element of which is:

$$(m \mid \mu(t) \mid n) = \sum_{ijkl} (m \mid T^{-1} \mid i) \left( i \middle| \exp\left(\frac{i}{\hbar} H_0 t\right) \middle| k \right) (k \mid \mu_0 \mid j) \left( j \mid \exp\left(-\frac{i}{\hbar} H_0 t\right) \mid l \right) (l \mid T \mid n)$$

$$= \sum_{kl} (m \mid T^{-1} \mid k) \exp(-i\omega_{kl} t) (k \mid \mu_0 \mid l)(l \mid T \mid n) \tag{8.142c*}$$

where all but the diagonal elements of $U_0$ have disappeared due to the diagonal quality of this matrix and where $\hbar\omega_{kl} = (E_l - E_k)$.

We directly substitute Eq. (8.142c) into Eq. (8.137) as a typical matrix element of $\mu(t)$. What we desire is the element of the product matrix of $\mu(t)$ and the density matrix. We take the proper element and then sum over the diagonal elements of this product matrix in order to obtain the desired trace. Finally then:

$$I(\omega) = \text{const} \cdot \omega^4 \sum_{abcdefg} (a \mid \rho_0 \mid b) \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dt' e^{i\omega(t-t')} (b \mid T^{-1}(t) \mid c)(c \mid \mu_0 \mid d) \exp(i\omega_{cd} t)$$

$$\cdot (d \mid T(t) \mid e)(e \mid T^{-1}(t') \mid f)(f \mid \mu_0 \mid g) \exp(-i\omega_{fg} t')(g \mid T(t') \mid a) \tag{8.143}$$

We might stop to remember at this point that all the operations which have been carried out so far and all those which will follow are simply for the purpose of transforming Eq. (8.137) into some form which will tell us explicitly the shift, the shape and the width of the spectrum line which we are to expect.

We now modify Eq. (8.143) by substituting a relation of the form Eq. (8.140) for the density matrix at $t = 0$, $\underline{\rho}_0 = \mathrm{T}^{-1}\underline{\rho}\mathrm{T}$ and then, substituting the new time development matrix,

$$\mathrm{T}(t \rightarrow t') = \mathrm{T}(t')\mathrm{T}^{-1}(t)$$

we obtain a function of the form $Tr(\mathrm{T}^{-1}\mathrm{Z}\ \mathrm{T})$ which since we know the trace to be invariant under a similarity transformation is equivalent to $Tr\mathrm{Z}$. Thus, there finally results:

$$I(\omega) = \text{const} \cdot \omega^4 \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} dt' e^{i\omega(t-t')} \sum_{abcde} (a \mid \rho(t) \mid b)(b \mid \mu_0 \mid c) \exp(-i\omega_{bc} t)$$

$$\cdot (c \mid T^{-1}(t \rightarrow t') \mid d)(d \mid \mu_0 \mid e) \exp(-i\omega_{de} t')(e \mid T(t \rightarrow t') \mid a) \tag{8.144}$$

By using the substitution $t' = t + \tau$ Eq. (8.144) may be reexpressed in "Correlation Function Form"† as:

$$I(\omega) = \omega^4 \text{ const} \sum_{de} \int_{-\infty}^{+\infty} d\tau \exp[i(\omega - \omega_{de})\tau]\, \varphi_{de}(\tau) \tag{8.145a}$$

$$\varphi_{de}(\tau) = \int_{-\infty}^{+\infty} dt \sum_{abc} \exp[-i(\omega_{bc} + \omega_{de})t]\, (a \mid \rho(t) \mid b)(b \mid \mu_0 \mid c)(c \mid T^{-1}(t) \mid d)(d \mid \mu_0 \mid e)(e \mid T(t) \mid a) \tag{8.145b}$$

Up to this point no restrictions on the theory in the form of modifying approximations have been made, but at this point Anderson found it necessary to introduce the condition which changes the subsequent treatment into an Interruption type treatment. The assumption to be made is that the time between colli-

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* If $a_{ij}$ is an element of A, etc., we may recall the labelling rule for the multiplication of matrices: $(\mathrm{ABCD})_{nm} = \sum_{jkl} a_{nj} b_{jk} c_{kl} d_{lm}$, and so on for the element in the product matrix for larger products.

† See *supra*, Chap. 6.

sions is much greater than the time of collision. This assumption when applied to a consideration of the matrix elements of $(\mathrm{U}_0^{-1}\,\mathbf{H}_1\mathrm{U}_0)$ leads one to the conclusion that these matrix elements and hence Eq. (8.145b) disappear unless:

$$\omega_{bc} + \omega_{de} = 0 \tag{8.146}$$

and the two frequencies appear to be resonating.

Eq. (8.146), of course, has the advantage of greatly simplifying Eq. (8.145b) by removing the exponentials in question from it. Anderson noted that Eq. (8.145b) had the look of a time average. Let us now investigate the consequences of this conclusion.

To begin with we specify the density matrix by a typical matrix element as:

$$(n \mid \rho_B \mid m)\delta_{nm}g_n \exp\left(-E_n/kT\right) / \sum_n g_n \exp\left(-E_n/kT\right) \tag{8.147}$$

This would appear to be the reasonable time to introduce the degenerate indices as well as the explicit fact that there are two molecules present both of whose states must be considered. Although the electric dipole moment could refer also to molecule 2 (the perturber) we suppose that it does not so that this operator is diagonal in the states of the perturber. We then (1) replace the integral in Eq. (8.145b) by an average (2) replace $\rho(t)$ by its specific value (3) introduce degenerate indices and (4) recognize the existence of perturber and emitter to obtain from Eqs. (8.145):

$$I = \sum_{if} \int_{-\infty}^{+\infty} d\tau \exp\left[i(\omega_{if} - \omega)\tau\right] \frac{1}{g_i} \left(J_i \mid \rho_B \mid J_i\right)\varphi_{if}(\tau) \tag{8.148a}$$

$$\varphi_{if}(\tau) = \sum_{J_2} \frac{1}{g_2} \left(J_2 \mid \rho_B \mid J_2\right) \sum_{J_2'} \sum_{\substack{M_iM_i'M_fM_f' \\ M_2M_2'}} (J_iM_i \mid \mu_z \mid J_fM_f) < (J_fM_fJ_2M_2 \mid T^{-1}(\tau) \mid J_fM_f'J_2'M_2')$$

$$\cdot\, (J_fM_f' \mid \mu_z \mid J_iM_i')(J_iM_i'J_2'M_2' \mid T(\tau) \mid J_iM_iJ_2M_2) >_{\text{over } t} \tag{8.148b}$$

It is certainly reasonable to suppose that the collisions which the emitter undergoes occur isotropically insofar as collision direction is concerned. As a consequence the average of $\mathbf{T}^{-1}\underline{\mu}_z\,\mathbf{T}$ will be independent of the actual placement of the $z$-axis. We are thus free to conclude that for a rotation of the reference frame specified by:

$$\underline{\mu}_z = \underline{\alpha}_1\underline{\mu}_x' + \underline{\alpha}_2\underline{\mu}_y' + \underline{\alpha}_3\underline{\mu}_z' \tag{8.149a}$$

the average transforms as:

$$<\mathrm{T}^{-1}\underline{\mu}_z\mathrm{T}> \; = \underline{\alpha}_1<\mathrm{T}^{-1}\underline{\mu}_x'\mathrm{T}> + \underline{\alpha}_2<\mathrm{T}^{-1}\underline{\mu}_y'\mathrm{T}> + \underline{\alpha}_3<\mathrm{T}^{-1}\underline{\mu}_z\mathrm{T}> \tag{8.149b}$$

so that this average transforms as a vector according to Eq. (3.1). We shall not demonstrate it, but it is known[205] that the matrix elements of this averaged matrix, due to its vector component behavior, are determined by the transformation property so that we may write:

$$(J_fM_fJ_2M_2 \mid <T^{-1}\mu_zT> \mid J_iM_iJ_2'M_2') = (J_fM_f \mid \mu_z \mid J_iM_i)\, \delta_{J_2J_2'}\, \delta_{M_2M_2'}\, F(\tau) \tag{8.150}$$

The substitution of Eq. (8.150) into Eq. (8.148b) results in:

$$\varphi(\tau) = \sum_{M_iM_f} | (J_iM_i \mid \mu_z \mid J_fM_f) |^2 F(\tau) = Tr\,[\mu_z{}^{if}\mu_z{}^{fi}]\, F(\tau) \tag{8.151}$$

since the square arises by matrix multiplication definition; the summation over $M_2$ cancels the $g_2$ in the numerator of Eq. (8.148b) and:

$$\sum_{J_2} (J_2 \mid \rho \mid J_2) = 1$$

The next step in the solution amounts to determining $F(\tau)$ from a differential equation for this quantity which may be obtained. Then from an equation of the form Eq. (6.138) (which we may recall also arose from a "Correlation Function" type process) expression for the shift and shape may be obtained.

We now let:

$$\mathbf{T}(\tau \rightarrow \tau + d\tau) = \mathbf{T}(\tau + d\tau)\mathbf{T}^{-1}(\tau) \tag{8.152}$$

and note that, since the collisions are random, the events occurring in the time intervals $\tau$ and $d\tau$ are independent and consequently the *TDM*'s for these two periods commute. We make the substitution as indicated by Eq. (8.152), and then utilize Eq. (8.151) to carry through a series of steps quite similar to those which we have already carried out to finally obtain:

$$\varphi(\tau + d\tau) = \sum_{J_2} \frac{(J_2 \mid \rho \mid J_2)}{g_{J_2}} \sum_{J_2'} Tr\!<\!\mu_z{}^{if}\, [T^{-1}]^{f2,ff'2'} \mu_z{}^{fi}\, [T]^{ii'2',i2}\!>\! F(\tau) \tag{8.153}$$

where:

$$[T]^{f2,ff'2'} = (J_fM_fJ_2M_2 \mid T \mid J_fM_f'J_2'M_2') \tag{8.154}$$

We now suppose that different types (this means collisions of different optical collision diameter and direction) of collisions are designated by different values of $\sigma$. Now the probability that a collision will occur during the time interval $d\tau$ and lie in the type range $d\sigma$ is given:

$$p(d\sigma \text{ in } d\tau) = Nvd\sigma d\tau \tag{8.155}$$

Next $d\varphi(\tau)$ is averaged over these collisions as:

$$d\varphi(\tau) = d\tau Nv \int d\sigma\, [\varphi(\tau + d\tau) - \varphi(\tau)] \tag{8.156}$$

A substitution may be made for $d\varphi(\tau)$ from Eq. (8.151) for $\varphi(\tau)$, and from Eq. (8.153a) for $\varphi(\tau + d\tau)$. These substitutions result in the differential equation for $F(\tau)$:

$$\frac{d}{d\tau} F(\tau) = -Nv\sigma F(\tau) \tag{8.157a}$$

where:

$$\sigma = \int d\sigma \left[ 1 - \frac{\displaystyle\sum_{J_2} \frac{(J_2 \mid \rho \mid J_2)}{g_{J_2}} \sum_{J_2'} Tr\,[\mu_z{}^{if} \{ T^{-1}(d\sigma) \}^{f2,ff'2'} \mu_z{}^{fi} \{ T(d\sigma) \}^{ii'2,i2}]}{Tr\,[\mu_z{}^{if}\, \mu_z{}^{fi}]} \right] \tag{8.157b}$$

or, with

$$1 = \sum_{J_2} (J_2 \mid \rho \mid J_2):\ \sigma = \sum_{J_2} (J_2 \mid \rho \mid J_2)\sigma_{J_2} \tag{8.157c}$$

where:

$$\sigma_{J_2} = \int d\sigma \left[ 1 - \frac{\sum_{J_2'} Tr\left[\mu_z^{if}\left\{T^{-1}(d\sigma)\right\}^{f2,ff'2'} \mu_z^{fi}\left\{T(d\sigma)\right\}^{ii'2',i2}\right]}{g_{J_2} Tr\left[\mu_z^{if}\mu_z^{fi}\right]} \right] \tag{8.157d}$$

The solution of Eq. (8.157a) is:

$$F(\tau) = e^{-Nv\sigma\tau} \tag{8.158a}$$

where:

$$\sigma = \sigma_r + i\sigma_i \tag{8.158b}$$

In order to obtain the intensity distribution in the broadened spectral line we substitute Eqs. (8.158a) and (8.151) into Eq. (8.148a). Integration subsequently yields:

$$I(\omega) = \sum_{J_iJ_f} \frac{(J_i \mid \rho \mid J_i)}{g_{J_i}} \sum_{M_iM_f} \mid (J_iM_i \mid \mu_z \mid J_fM_f) \mid^2 \frac{Nv\sigma_r}{(\omega - \omega_{fi} + Nv\sigma_i)^2 + (Nv\sigma_r)^2} \tag{8.159}$$

From Eq. (8.159) we may immediately obtain the line half-width and shift as:

$$\delta = \frac{Nv}{\pi c}\sigma_r \text{ cm.}^{-1} \tag{8.160a}$$

$$D = -\frac{Nv}{2\pi c}\sigma_i \text{ cm.}^{-1} \tag{8.160b}$$

It would now appear that were $\sigma$ in a form which was amenable to calculation the problem would be essentially solved, and indeed this remains the major step to solution.

By a series of manipulations involving vector addition coefficients and certain relations among them* the traces in Eq. (8.157d) may be evaluated. Choosing the axis of quantization (simply the axis along which the spatial degeneracy parameter $M$ has meaning) so that it coincides with the $z$-axis allows the expression of the trace in the denominator of Eq. (8.157d) in terms of these vector addition coefficients and the subsequent evaluation of this trace.

In evaluating the trace in the numerator a few preliminary considerations are requisite. This trace contains the matrix $T$ — and its inverse, of course — so that for a given optical collision diameter $\rho$ this trace must needs be averaged over all directions.† Now the trace is independent of the axis of quantization, however, so that the axis of quantization may be taken along the optical collision diameter and the trace subsequently averaged over all directions, of this axis which we have specified as along the $z$-axis. The averaged trace in question may be calculated with the result that Eq. (8.157d) takes the form:

$$\sigma_{J_2} = \int_0^\infty 2\pi\rho d\rho\, S(\rho) \tag{8.161a}$$

$$S(\rho) = 1 - \sum_{\substack{M_iM_i'M_f\\ M_f'M_2M_2'\\ M}} \sum_{J_2'} \frac{(J_f1M_fM \mid J_f1J_iM_i)\,(J_f1M_f'M \mid J_f1J_iM_i')}{(2J_i+1)\,(2J_2+1)} \cdot$$

$$\cdot\, (J_fM_fJ_2M_2 \mid T^{-1}(\rho) \mid J_fM_f'J_2'M_2')(J_iM_i'J_2'M_2') \mid T(\rho) \mid J_iM_iJ_2M_2) \tag{8.161b}$$

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* These coefficients are described in detail in Chapter III of Reference 205 and it would not appear of any value for us to go into the detail required for their discussion here.

† Jablonski would undoubtedly object to this inferred (but unstated) assumption of rectilinear motion.

where the first two symbols on the right of Eq. (8.161b) are vector addition coefficients. The differential $d\sigma$ which indicates a certain range of optical collision diameter and optical collision diameter direction has been replaced by $2\pi\rho d\rho$ since $S(\rho)$ has already been averaged over various collision directions.

The next step in carrying out a calculation of $\sigma$ is the computation of T, and a successive approximation procedure has been used where, to begin with:

$$\mathbf{T} = \mathbf{T}_0 + \mathbf{T}_1 + \mathbf{T}_2 \ldots ; \quad \mathbf{T}_0 = 1 \tag{8.162a}$$

so that, from Eq. (8.140a):

$$\mathbf{T}_1(t) = -\frac{i}{\hbar} \int_{-\infty}^{t} (\mathbf{U}_0^{-1}\, \mathbf{H}_c(t) \mathbf{U}_0)\, dt \tag{8.162b}$$

$$\mathbf{T}_2(t) = -\frac{1}{\hbar^2} \int_{-\infty}^{t} (\mathbf{U}_0^{-1}\mathbf{H}_c(t')\mathbf{U}_0) dt' \int_{-\infty}^{t'} (\mathbf{U}_0^{-1}\mathbf{H}_c(t'')\mathbf{U}_0) dt'' \tag{8.162c}$$

As we have mentioned in connection with Eq. (8.139), if $H_c$ commutes with itself at different times then

$$\mathbf{T}(t) = \exp\left[ -\frac{i}{\hbar} \int_{-\infty}^{t} (\mathbf{U}_0^{-1}\mathbf{H}_c(t)\mathbf{U}_0) dt \right] \tag{8.163}$$

and Eqs. (8.162) would simply be the power series expansion for the exponential in Eq. (8.163). It so happens that $\mathbf{H}_c$ does not so commute, but Anderson has carried out calculations which tend to indicate that the assumption of this commutation proves a good approximation. As a consequence then, if we take only the first three terms in the expansion of Eq. (8.163) there results for **T**:

$$\mathbf{T}(\rho) \doteq \mathbf{T}_0 + \mathbf{T}_1 + \mathbf{T}_2$$

$$\mathbf{T}_0 = 1; \qquad \mathbf{T}_1 = -i\mathbf{P}; \qquad \mathbf{T}_2 = \tfrac{1}{2}\mathbf{P}^2 \tag{8.164a}$$

where:

$$\mathbf{P} = \frac{1}{\hbar} \int_{-\infty}^{+\infty} (\mathbf{U}_0^{-1}\mathbf{H}_c\mathbf{U}_0) dt \tag{8.164b}$$

An approximation type solution for $S(\rho)$ may now be carried out:

$$S = S_0 + S_1 + S_2 + \ldots . \tag{8.165a}$$

where the successive approximations to $S$ arise from successive powers of the **P** matrix (Eq. (6.164)) in Eq. (8.161b). $\mathbf{T}_0 = \mathbf{P}^0$ yields:

$$S_0(\rho) = 0 \tag{8.165b}$$

In the first-order approximation to $S(\rho)\mathbf{T}_0^{-1}$, $\mathbf{T}_1$ and $\mathbf{T}_0$, $\mathbf{T}_1^{-1}$ both contribute to the result:

$$S_1(\rho) = i\left[ \sum_{M_iM_2} \frac{(J_iM_iJ_2M_2 \mid P \mid J_iM_iJ_2M_2)}{(2J_i+1)\,(2J_2+1)} - \sum_{M_fM_2} \frac{(J_fM_fJ_2M_2 \mid P \mid J_fM_fJ_2M_2)}{(2J_f+1)\,(2J_2+1)} \right] \tag{8.165c}$$

For the second order approximation the possibilities $T_0^{-1}$, $T_2$ and $T_0, T_2^{-1}$ yield:

$$S_2(\rho)_{\text{outer}} = \tfrac{1}{2}\left[\sum_{M_iM_2} \frac{(J_iM_iJ_2M_2 \mid P^2 \mid J_iM_iJ_2M_2)}{(2J_i+1)\,(2J_2+1)} + \sum_{M_fM_2} \frac{(J_fM_fJ_2M_2 \mid P^2 \mid J_fM_fJ_2M_2)}{(2J_f+1)\,(2J_2+1)}\right] \tag{8.165d}$$

while $T_1^{-1}$, $T_1$ result in:

$$S_2(\rho)_{\text{middle}} = \sum_{\substack{M_iM_i'M_f\\ M_f'M_2M_2'\\ M}} \sum_{J_2'} \frac{(J_f1M_fM \mid J_f1J_2M_2)(J_f1M_f'M \mid J_f1J_iM_i')}{(2J_i+1)\,(2J_2+1)} (J_fM_fJ_2M_2 \mid P \mid J_fM_f'J_2'M_2')$$
$$\cdot\ (J_iM_i'J_2'M_2' \mid P \mid J_iM_iJ_2M_2) \tag{8.165e}$$

so that:

$$S_2(\rho) = S_2(\rho)_{\text{outer}} + S_2(\rho)_{\text{middle}} \tag{8.165f}$$

In Eqs. (8.165) we note that a summation over $J_2'$ not occurring in Anderson's Eqs. (54) is present. This is due to the fact that Anderson had assumed $T$ as diagonal in $J_2$. This is certainly true if (a) $T$ causes no transitions among the nondegenerate states of the perturber or (b) changes in the quantum numbers of the perturber may only occur simultaneously with changes in that of the emitter. This latter corresponds to the resonance effect, of course. Under these assumptions we may drop this summation.

Let us also notice that $S_1(\rho)$ contributes only toward line shift while the $S_2(\rho)$ contributes only to line breadth, not that these facts should prove startling.

The theory in general form is now complete and stands ready to be applied, but before we go into Anderson's applications of it to actual cases, let us consider some necessary restrictions to it, a summarization of its development, and the approximations contained within it.

As has been the case with the varied and sundry theories which we have considered, the theory breaks down for small values of $\rho$. This transpires in the following manner. $H_c$ in Eq. (8.164b) depends — for the dipole-dipole interaction which is the only one which Anderson considered* — on $r^{-3}$ in first order and $r^{-6}$ in second order. This means that for sufficiently small $r$, $P$ will become as large as you like. The expansion of $S$ in terms of $P$, Eq. (8.165a), is only valid, however, for small $P$. Thus does the theory, through $S$, break down for small $\rho$. Anderson treats this in a manner which we may now detail.

To begin with Anderson assumed that for very small values of $\rho$ the collisions are so strong that they terminate the radiation by causing the molecule to proceed to some different nondegenerate state or when the molecule remains in the same state they result in an arbitrary phase shift that averages to zero. In either case then Eq. (8.161b) contains only the first term unity, so that while $S_2(\rho)$ is given by Eq. (8.165f) for values of $\rho$ greater than $\rho_1$ where $S_2(\rho_1) = 1$, it is simply given by one for lesser values of $\rho$.

Anderson also tried two other approximations for $S(\rho)$, namely:

$$S_{f1}(\rho) = 1 - \cos\,(2S_2(\rho))^{1/2}$$

and

$$S_{f3}(\rho) = 1 - \exp\,(-2S_2(\rho))$$

These three possibilities for $S_2$ are illustrated in Fig. (8.14), and we might note here that Anderson found the best agreement with experiment to arise from $S_{f2}$.

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* Tsao and Curnutte[182] have also considered dipole-quadrapole and quadrapole-quadrapole interaction within the framework of the Anderson theory.

Let us obtain Anderson's "region of resonance parameter" $k$. Now if $H_c = Kr^{-3}$ or $Kr^{-6}$ and (the rectilinear assumption) $r^2 = \rho^2 + v^2t^2$

$$(a\,|\,P\,|\,b) = \int_{-\infty}^{+\infty} dt \exp(i\omega_{ab}t)\,(a\,|\,H_1(t)\,|\,b) = K \int dt \exp(i\omega_{ab}t)\,(\rho^2 + v^2t^2)^{-3/2 \text{ or } -3}$$

$$= \frac{k}{\rho^2 v \text{ or } \rho^5 v} \int dx\, e^{ikx}\,(Hx^2)^{-3 \text{ or } -3/2} \tag{8.166a}$$

where:

$$x = \frac{vt}{\rho}\ ;\ k = \frac{\rho\omega_{ab}}{v} \tag{8.166b}$$

The parameter $k$ tells us whether the molecules have undergone fast collisions and/or whether the $\omega_{ab}$ perhaps refers to degenerate levels. Either of the two integrals appearing in Eq. (8.166b) has about the same value for values of $k$ up to about one as it has for $k$ zero. Within this region then ($0 < k < 1$) transitions will occur between the states $a$ and $b$ as though these two states were resonant (or degenerate). Anderson explains this by an appeal to the uncertainty principle. For $k < 1$ the velocity may be supposed sufficiently high that, with $\Delta t$ the time of collision, there will be an uncertainty in energy (from $\Delta E \Delta t > h$) such that $\omega_{ab}$ acts as though it were negligible, this in turn means that the two states in question act as if they were resonant.

Let us now rapidly review the major facets of the Anderson theory. We began with the expression Eq. (8.137) for the intensity distribution in the broadened line which we only approximately justified but which has been justified in some detail by Anderson as well as later authors.[12] We then obtained from the time development matrix defined by Eq. (8.139) a modified time development matrix, which proves mathematically more convenient, as given by Eq. (8.141a). A few straightforward, mathematical manipulations were carried out to obtain Eq. (8.145b) at which point one of the oft used approximations of the Interruption theory was introduced, namely, (A) THE DURATION OF THE COLLISION IS VERY SHORT COMPARED TO THE INTERVAL BETWEEN COLLISIONS. By this time the intensity integral had been written in Correlation Function Form. The Maxwell-Boltzmann form of the density matrix was introduced and the approximations of (B) BINARY COLLISIONS was introduced. This led to Eqs. (8.148). The fact that collisions may certainly be expected to occur isotropically allows us to obtain relations of the form Eq. (8.150) which yield further simplifications. Additional manipulations yield Eqs. (8.157) and (8.158) for the quantity $F(\tau)$, which, when obtained, may be utilized in Eq. (8.148a) to obtain Eqs. (8.159) and (8.160) for the line shape, width, and shift. We may note here the decrease of the intensity with the inverse square of the frequency separation from line center which is certainly not generally correct.

In evaluating $\sigma$ an expansion for $T$ was utilized. This required the approximation of a (C) MINIMUM DISTANCE OF APPROACH OF THE COLLIDING PARTICLES.

At any rate, $\sigma$ was obtained in terms of $S(\rho)$, an expansion whose third term, $S_2$, as given by Eq. (8.165) contributes only to the line width and whose second term, $S_1$, as given by Eqs. (8.165), contributes only to the line shift. Thus, when one has computed $P$ from Eq. (8.164b) and subsequently $S_1$ and $S_2$ from Eqs. (8.165) the shift and shape may be computed from Eq. (8.161a) and (8.157c). Also included in the development was the approximation of (D) A CLASSICAL PATH. Let us touch on these four approximations briefly.

Insofar as (A) is concerned only Lindholm and Lenz of the Interruption writers had failed to include this, and we might recall that Lindholm showed his ability to obtain Lenz's result without considering the time of collision. His more refined treatment did very definitely include it, and, it might be added, he obtained more "variety" in his line shape equations as a consequence. Approximation (B) is also a rather common one, but we have noted in Sec. 18 the manner in which in the statistical theory the progression toward larger numbers of interacting particles in the theory seems to point toward better agreement with theory. Approximation (C) has been used without any exceptions that come to mind. Approximation (D) has been used in all cases except in the work of Jablonski.

Let us now give Anderson's specific treatment of the ammonia inversion line as an example of the application of the theory.

### 8.19. SOME APPLICATIONS OF ANDERSON'S THEORY

A brief consideration of Anderson's calculations with regard to ammonia will not only serve to illustrate the application of his theory, but will also tend to indicate its agreement with experiment so we now consider this application.

We will consider the self broadening of the inversion line which we have already considered according to Margenau's statistical theory method. This appears to be a very popular transition. To begin with $S_2(\rho)_{\text{middle}}$, the " 'difficult' term" vanishes in this problem.

We consider the inversion doubled levels of the symmetric top under the interaction potential:

$$H = \left[ \underline{\mu}_1 \cdot \underline{\mu}_2 - 3\, \frac{(\underline{\mu}_1 \cdot \mathbf{r})\, (\underline{\mu}_2 \cdot \mathbf{r})}{r^2} \right] r^{-3} \tag{8.167}$$

the familiar dipole-dipole interaction. The polar axis of coordinates is taken as the optical collision diameter to which the polar coordinates $\vartheta_1$, $\vartheta_2$, $\varphi_1$ and $\varphi_2$ are referred. We designate $\tan^{-1}((vt)/(\rho))$ as the angle $\psi$. Eq. (8.167) may now be expressed in terms of these angular coordinates, and certain of the matrix elements of the symmetric top provide the matrix elements of the resulting equation.

There are now essentially two types of interaction matrix elements involved in the expression for $P$, Eq. (8.164b), namely, (1) the first order Stark effect where collisions between molecules having the same $J$ values are considered and (2) the case of rotational resonance where the $J$ values for the colliding molecules differ by ±1.

Now let us evaluate $k$, the resonance region parameter. To begin with we suppose that both molecules are either in the plus inversion state or the minus. Then for both of them to undergo a transition to the other inversion state, an energy change of about 1.6 cm.$^{-1}$ is called for. The mean velocity here is about $8 \times 10^4$ so that according to Eq. (8.166b)

$$k = \frac{\rho}{v} = \frac{\rho(A) \times 10^{-8} \times 3 \times 1.6 \times 10^{18} \times 2}{8 \times 104} = \rho(A) \times 0.035$$

which we shall subsequently make use of.

Next we wish to evaluate $P$ as given by Eq. (8.164b) or (8.166a). If one molecule is in a plus inversion state and the other in a minus we can have true resonance and neglect the exponential time factor. If the optical collision diameter is less than $15A$ according to the above $k$ calculation the pseudo resonance situation will arise and we may still neglect the exponential factor. As a consequence of this situation $H_c$ may be integrated before the matrix elements of it are taken to obtain $P$. If we let:

$$r^2 = \rho^2 + v^2t^2 \text{ so that: } \cos\psi = \rho/r \ ; \ \sin\psi = vt/r$$

we may obtain:

$$\int_{-\infty}^{+\infty} \frac{H_1 dt}{\hbar} = \frac{2\mu^2}{\rho^2 v \hbar} \left[-\cos\vartheta_1 \cos\vartheta_2 - \sin\vartheta_1 \sin\vartheta_2 \sin\varphi_1 \sin\varphi_2\right] \tag{8.168}$$

The $S_2$ sums may now be computed according to Eq. (8.168) with the result:

$$S_2(J_2K_2) = \frac{8}{9} \frac{\mu^4}{\rho^4 v^2 \hbar^2} \frac{K_1^2 K_2^2}{J_1(J_1+1)\, J_2(J_2+1)} \tag{8.169a}$$

for the case $J_1 = J_2$, and:

$$S_2(J_1 - 1, K_2) = \frac{8}{9} \frac{\mu^4}{\rho^4 v^2 \hbar^2} \frac{(J_1^2 - K_1^2)\,(J_1^2 - K_2^2)}{J_1^2(2J_1+1)\,(2J_1-1)} \tag{8.169b}$$

$$S_2(J_1 + 1, K_2) = \frac{8}{9} \frac{\mu^4}{\rho^4 v^2 \hbar^2} \frac{[(J_1+1)^2 - K_1^2]\,[(J_1+1)^2 - K_2^2]}{(J_1+1)^2\,(2J_1+1)\,(2J_1+3)} \tag{8.169c}$$

for the case $J_2 = J_1 \pm 1$.

We are evaluating Eq. (8.165d) which we now consider. Now neither in this consideration of ammonia nor in subsequent considerations of HCN and HCl does Anderson consider the Alignment Forces* since, according to this author, "... the sums required become quite difficult for the second-order alignment forces."[3]

If the abbreviation:

$$S(J_2, K_2) = A^2/\rho^4 \tag{8.170}$$

is used, there results for the three approximate forms of $S$:

$$\#1. \quad \sigma_1(J_2,K_2) = \rho_3(J_2,K_2)\, 2\pi\, (1.11A) \tag{8.171a}$$

$$\#2. \quad \sigma_2(J_2,K_2) = \rho_3(J_2,K_2)\, 2\pi A \tag{8.171b}$$

$$\#3. \quad \sigma_3(J_2,K_2) = \rho_3(J_2, K_2)\, 2\pi\, (0.885A) \tag{8.171c}$$

in the evaluation of which from Eq. (8.161a) the method of Jensen† was used.

Finally one obtains:

$$\sigma = \sum_{J_2K_2} \sigma\, (J_2K_2) \tag{8.172a}$$

$$\delta = \frac{nv}{\pi c}\, \sigma \text{ cm.}^{-1} \tag{8.172b}$$

from Eqs. (8.157c) and (8.160a) respectively.

Anderson presented two types of comparison with experiment, both of which are rather impressive in this case. The first type is a comparison of the absolute width of the line as measured and as computed with

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* See *supra*, Sec. 3.

† See *supra*, Chap. 6.

this theory. The line used was the inversion line having rotational quantum numbers $J_1 = 3$ and $K_1 = 3$ for which there should be negligible rotational resonance so that Eqs. (8.169b) and (8.169c) may be neglected. Under these conditions the results of Table (8.5) are obtained where the experimental data is that of Bleaney and Penrose.[203]

| | Theory | | | Experiment |
|---|---|---|---|---|
| Approx. | #1 | #2 | #3 | |
| $\frac{1}{2}\delta$ | 0.86 | 0.77 | 0.68 cm. $^{-1}$ atm.$^{-1}$ | 0.74 |

Table (8.5) A comparison of an absolute width by the Anderson theory with experiment. (After Anderson.[3])

Finally a comparison of the relative line breadths with experiment[10, 11] is made in which the theoretical value for $J = 33$ is made to agree with the experimental for normalization purposes. The results are given in Table (8.6).

| $J$ | $K$ | Theory | Experiment |
|---|---|---|---|
| 2 | 1 | 2.6 | 2.6 |
| 3 | 1 | 2.3 | 2.4 |
| 3 | 2 | 3.3 | 3.2 |
| 3 | 3 | 4.5 | 4.5 |
| 4 | 4 | 4.6 | 4.5 |
| 5 | 1 | 1.8 | 1.8 |
| 5 | 2 | 2.5 | 2.6 |
| 5 | 3 | 3.3 | 3.3 |
| 5 | 5 | 4.8 | 4.7 |
| 6 | 3 | 2.8 | 3.1 |
| 6 | 4 | 3.5 | 3.6 |
| 6 | 6 | 4.8 | 4.7 |
| 7 | 5 | 3.7 | 4.1 |
| 7 | 6 | 4.3 | 3.9 |
| 8 | 7 | 4.3 | 4.1 |
| 10 | 9 | 4.5 | 4.2 |
| 11 | 9 | 4.1 | 2.9 |

Table (8.6). Comparison of the relative widths. Data were in cm.$^{-1}$ × $10^{-4}$ at 0.5mm. Hg. (After Anderson.[3])

Anderson also considered the self-broadening of HCN and HCl and the foreign gas broadening by several molecules. The HCN results are given in Fig. (8.14) in comparison with those earlier results of Lindholm and Foley. He reported his agreement as fair in the case of HCl which to the author in question meant 30%. Insofar as his foreign gas broadening results are concerned we shall let the author describe them* "We do not present this evaluation because the results, in general, do not have any relation to experimental results."[3]

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* We recall that here Anderson has utilized only the dipole-dipole interaction. In a later consideration of the broadening of ammonia by foreign gases[182] he included also the interaction between the quadrapole moment of ammonia and the induced dipole moment of the broadening atoms with a resulting agreement which was quite good.

This then is the agreement of the Anderson theory with the experimental results, certainly quite impressive for ammonia. It is not quite as impressive for HCN since the author found it necessary to simply borrow Lindholm's results for the Alignment Forces due to the difficulty involved in evaluation according to his theory even though his final results were quite good. For HCl and foreign gas broadening the impressivity continues to decrease.

"Elegance" (in several connotations) is present in this theory in abundance, but "simplicity" would certainly appear to be lacking, and it appears that the theory may be rather restricted thereby. One disappointing feature of this theory is the rigid requirement of an inverse dependence of the intensity on the inverse square of the frequency separation from line center. This is certainly not true in all cases, not even for polyatomic molecules.

## 8.20. ANOTHER ADIABATIC THEORY

We shall now conclude this chapter with a brief consideration of an adiabatic theory due to Mizushima.[131] Commencing with the Hamiltonian

$$H_1 + H_2 + H_{1,2} + H_r$$

with which we are quite familiar, Mizushima eliminates the nonadiabaticity from the state growth equation:

$$ih \frac{\partial}{\partial t} a_j = \sum_i \left(H - i\hbar \frac{\partial}{\partial t}\right)_{ji} a_i$$

by eliminating the partial time derivative on the right hand side of this equation. Subsequently a series of unitary transformations yields, for the author, the "generalized fourier integral formula." By assuming $T^*$ — the matrix diagonalizing $H_1 + H_2 + H_{1,2}$ — Mizushima obtained an expression which when integrated yields the Weisskopf result.

We have already noted in connection with Foley's theory* that Mizushima disagreed with the Foley procedure and finally obtained instead of the Foley result:

$$I(\nu) = \frac{c}{\pi} \frac{\delta}{(\nu - \nu_0 - \Delta)^2 + \delta^2} \tag{6.137a'}$$

$$\delta = \int F(\rho)\,(1 - \cos \alpha_\rho) d\rho/2\pi \tag{6.137b'}$$

$$\Delta = \int F(\rho) \sin \alpha_\rho d\rho/2\pi \tag{6.137c'}$$

$$\alpha = \int \frac{\Delta p}{h}\, dt \tag{8.173}$$

The number of collisions with collision diameters between $\rho$ and $\rho + d\rho$ per unit time is given by:

$$F(s)ds = 8\sqrt{\pi} \left(\frac{m}{2kT}\right)^{3/2} \exp\,(-mv^2/2kT) v^3 dv \rho d\rho\; GN \tag{8.174}$$

Let us consider this expression at sufficient length for justification. To begin with the factors preceding $dv$ constitute nothing more nor less than the Maxwell-Boltzmann probability expression for the velocity having value between $v$ and $v + dv$. The term $\rho d\rho$ is the probability for the occurrence of the optical collision diameter between a $\rho$ and $\rho + d\rho$, a simple enough expression since we assume random probability. Finally

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* See *supra*, Chap. 6.

the expression $G$ for the probability for the occurrence of a given rotational state will be given by a weighted Maxwell-Boltzmann function of the form, say, Eq. (8.77).

The materials are now at hand for an evaluation of the shift and shape according to this theory. Mizushima carries out this evaluation for (a) a well type potential and (b) an inverse power potential. For the well type:

$$\Delta p = \gamma \text{ for } r < a \text{ ; } \Delta p = 0 \text{ for } r > a \tag{8.175}$$

so that:

$$\alpha = 2(a^2 - p^2)^{1/2}\, \gamma / v\hbar \tag{8.176}$$

Eqs. (6.137) give then:

$$\delta = \tfrac{1}{2}a^2 <v> N - \frac{4}{\sqrt{\pi}}\, \hbar^2 \left(\frac{m}{4kT}\right)^{3/2} \int_0^\infty \varphi^{-\infty} \exp\left(-\frac{m}{4kT\varphi^2}\right)$$

$$\cdot \left\{ \left(\frac{a\varphi}{2\gamma\hbar}\right) \sin\left(\frac{2\gamma a\varphi}{\hbar}\right) + \frac{\left[\cos\left(\frac{2\gamma a\varphi}{\hbar}\right) - 1\right]}{4\gamma^2} \right\} d\varphi \tag{8.177}$$

$$\Delta = \frac{4}{\sqrt{\pi}}\, \hbar^2 \left(\frac{m}{4kT}\right)^{3/2} \int_0^\infty \varphi^{-\infty} \exp\left(-\frac{m}{4kT\varphi^2}\right)$$

$$\cdot \left\{ \frac{\sin\left(\frac{2\gamma a\varphi}{\hbar}\right)}{4\gamma^2} - \frac{a\varphi}{2\gamma\hbar} \cos\left(\frac{2\gamma a\varphi}{\hbar}\right) \right\} d\varphi \tag{8.178}$$

For the case $\gamma = \infty$ :

$$\delta = \tfrac{1}{2}a^2 <v> N \text{ and } \Delta = 0 \tag{8.179}$$

For the inverse power potential:

$$\Delta p = \frac{\hbar \Delta\mu}{r^n} \tag{8.180}$$

so that:

$$\alpha = \int_{-\infty}^{+\infty} \frac{\Delta\mu}{(\rho^2 + v^2 t^2)^{n/2}}\, dt$$

$$= \frac{\Delta\mu}{v\rho^{n-1}}\, \pi\, \frac{\Gamma(n-1)2^{2-n}}{[\Gamma\,(n/2)]^2} \tag{8.181}$$

Eqs. (8.174) and (8.181) subsequently lead to:

$$\delta = \frac{\pi^{(s-n)/(2n-2)}}{2} \left(\frac{kT}{2m}\right)^{(3-n)/(2n-2)} \Gamma\left(\frac{2n-3}{n-1}\right) \Gamma\left(\frac{n-3}{n-1}\right)$$

$$\cdot \left[\frac{\Gamma(n-1)}{\{\Gamma\,(n/2)\}^2}\right]^{2/n-1} \sin\left\{\pi \frac{n-3}{2n-2}\right\} < |\,\Delta\mu\,|^{2/n-1} > N. \tag{8.182}$$

$$\Delta = \tan\left(\frac{\pi}{n-1}\right) \delta \left\langle \frac{\Delta\mu}{|\,\Delta\mu\,|} \right\rangle \tag{8.183}$$

Eq. (8.182) leads to the following specializations for three of the most important interactions:

$$\delta = \frac{\pi}{2} < | \Delta\mu | > N \quad \text{for} \quad n = 3 \tag{8.184a}$$

$$\delta = \frac{2}{\sqrt{3}} \Gamma\left(\frac{7}{4}\right)\left(\frac{kT}{M}\right)^{1/4} < | \Delta\mu |^{1/2} > N \quad \text{for} \quad n = 5 \tag{8.184b}$$

$$\delta = \frac{1}{2\pi^{1/10}}\left(\frac{kT}{M}\right)^{3/10} \Gamma\left(\frac{9}{5}\right) \Gamma\left(\frac{3}{5}\right) \left\{\frac{12}{\Gamma(3)}\right\}^{2/5} \sin\left(\frac{3\pi}{10}\right) < | \Delta\mu |^{2/5} > N \quad \text{for} \quad n = 6 \tag{8.184c}$$

If the sign of $\Delta\mu$ is common to all collisions we will obtain Foley's Eq. (6.145) for the ratio between shift and width from the present theory. The converse of this can be seen, for example, for the case in which the average value of this quantity is zero and no shift results.

In applying the equations obtained above for the shift and width of the spectral line according to this adiabatic theory, the task, of course, becomes one of evaluating the matrix elements of the intermolecular interaction in order to obtain the values of $\Delta\mu$ which must be used in these evaluations.

(A) ADIABATICITY and (B) WEAK INTERACTIONS were perhaps the most important assumptions of this section. No binary assumption has been made as yet for example but it would probably have to be made during the interaction matrix elements evaluation.

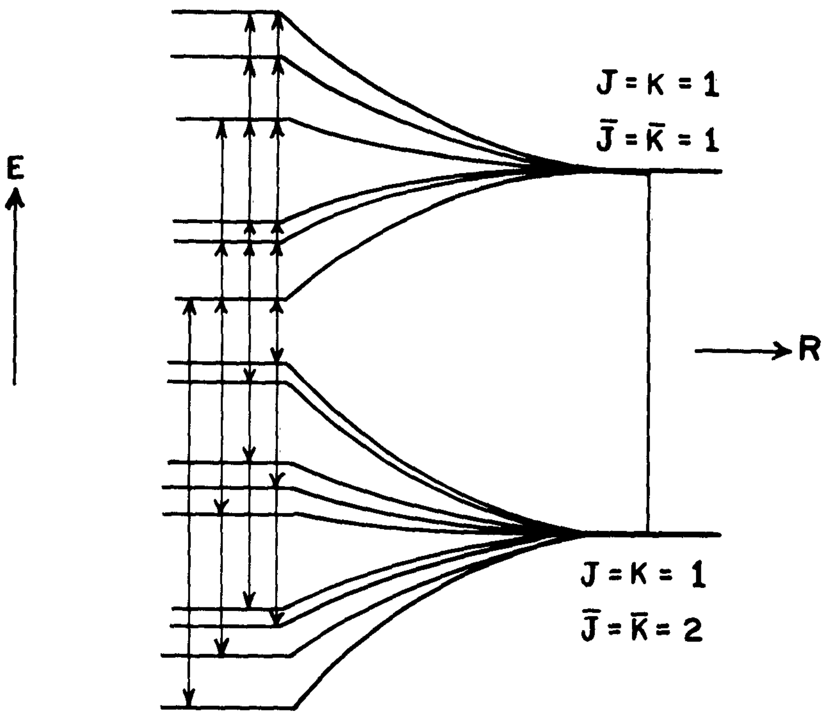

Fig. (8.1). Level splitting with molecular separation for the symmetric dipole interation. (After Margenau and Warren.[120])

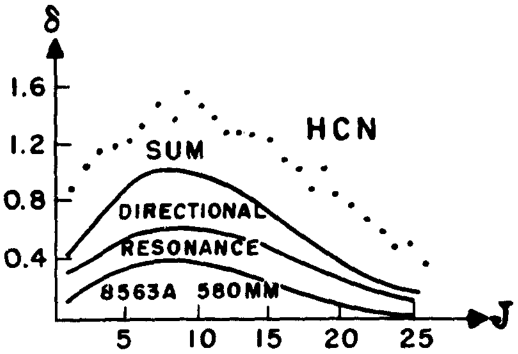

Fig. (8.2). Half width as a function of J. The solid lines represent theoretical contributions as indicated. (After Lindholm.[100])

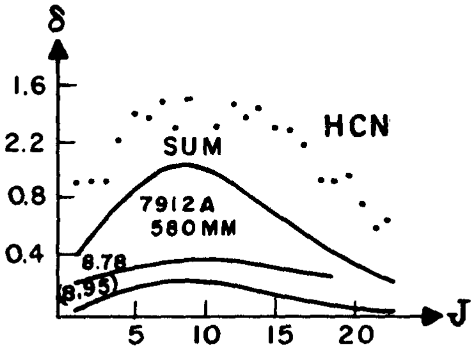

Fig. (8.3). The individual Directional Effect contributions are indicated. (After Lindholm.[100])

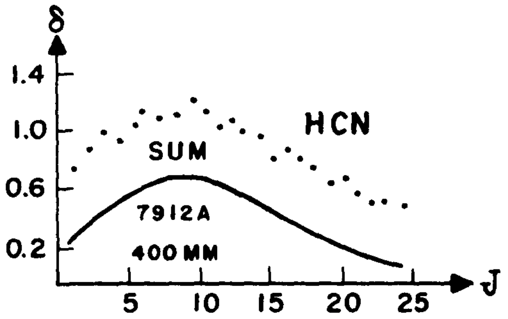

Fig. (8.4). The points are experimental results for the band and pressure indicated. (After Lindholm.[100])

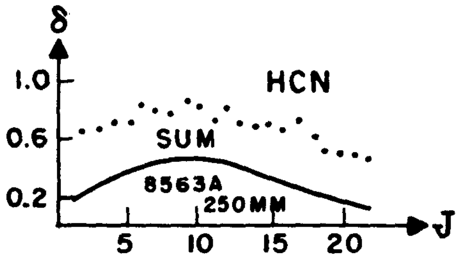

Fig. (8.5). (After Lindholm.[100])

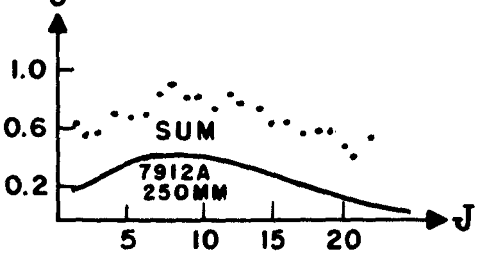

Fig. (8.6). (After Lindholm.[100])

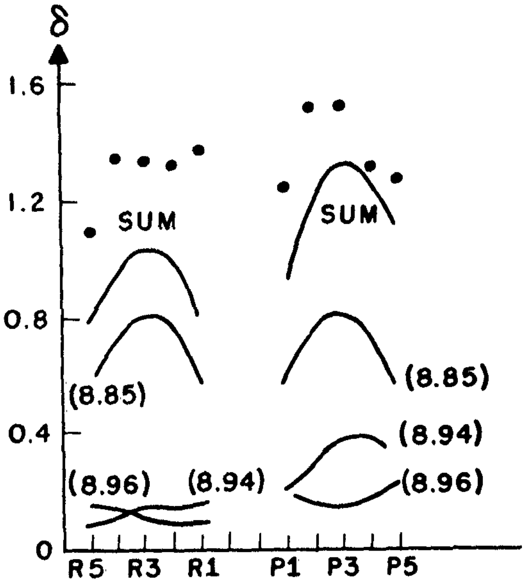

Fig. (8.7). The broadening of HCl as a function of J. Theoretical contributions arise from equations as indicated. (After Lindholm.[101])

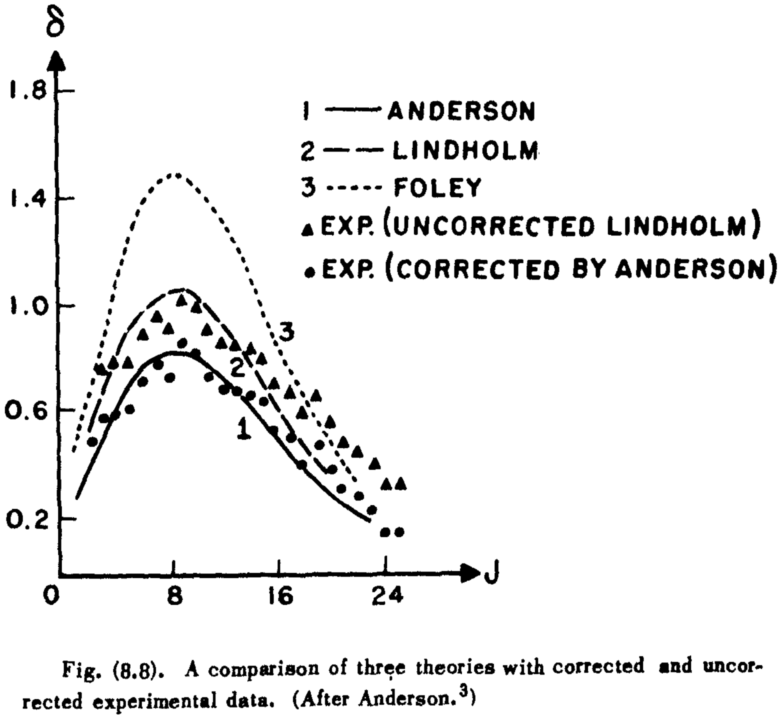

Fig. (8.8). A comparison of three theories with corrected and uncorrected experimental data. (After Anderson.[3])

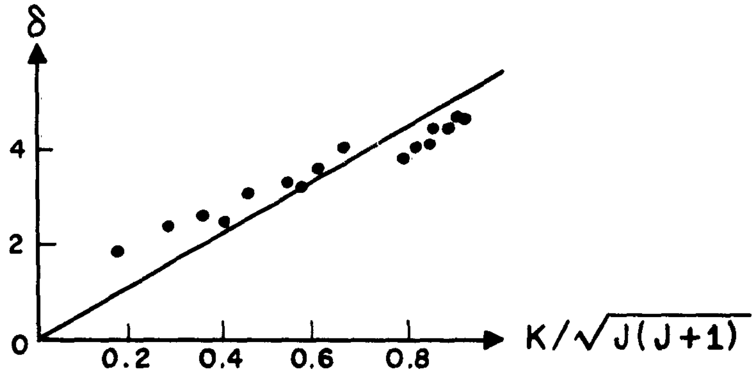

Fig. (8.9). Half widths of the ammonia inversion line. The experimental results are indicated by points. (After Margenau.[117])

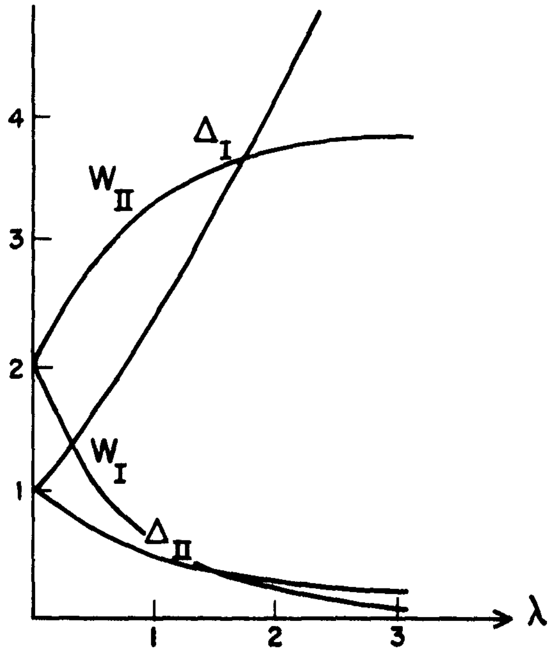

Fig. (8.10). The intensities and shifts of the $NH_3$ line split and shifted by the interaction of two linear vibrators with mirror potentials. (After Margenau.[118])

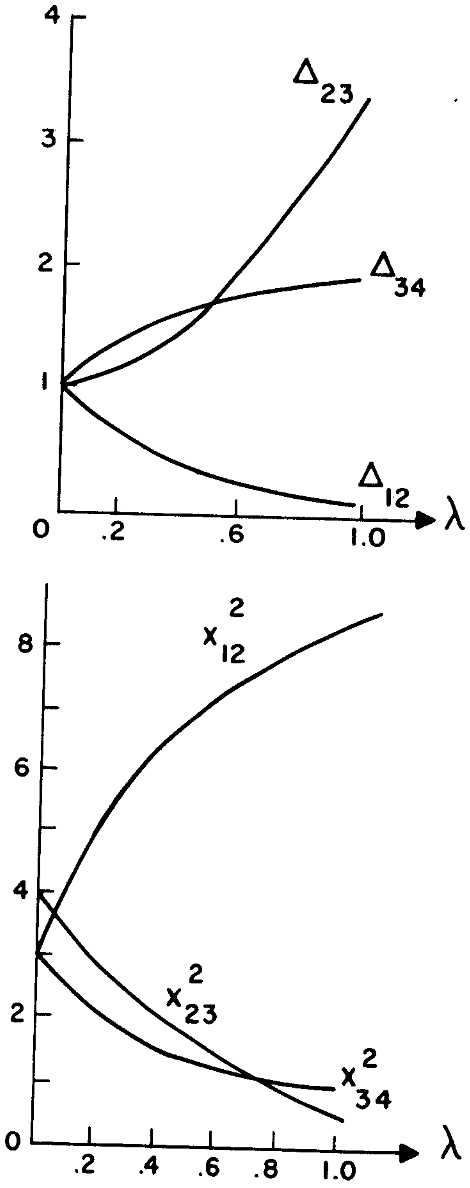

Fig. (8.11). The effect of the interaction between three linear vibrators with mirror potentials. (After Margenau.[118])

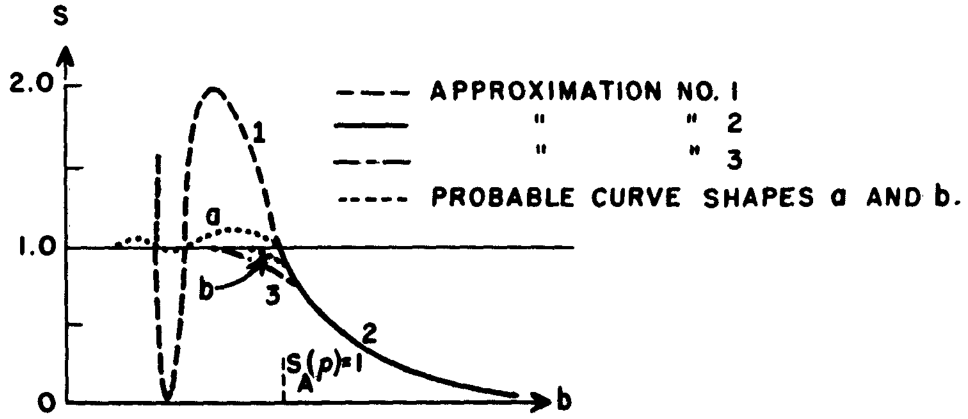

Fig. (8.12). Approximations to S($\rho$) in Anderson's Theory. (After Anderson.$^3$)

# CHAPTER 9.

# THE BROADENING AND SHIFT OF THE HIGH SERIES MEMBERS

The foreign gas broadening theories which we have considered previously have all been amenable to a more or less tenuous association with the labels Interruption or Statistical. Although we have devoted a separate chapter to it, this association also holds for the Stark theory. The theory which we are now to consider might, by rather stretching a point, be labeled pseudo-Statistical, but, since the general principles of it are sufficiently unique, let us not attempt to so classify it. In all the theories considered we have been able to suppose the molecule, whose spectral lines were being broadened, as an entity of itself which was affected from without by one or a combination of broadening molecules. The theory which we are about to examine proves quite different from this, however.

## 9.1. A QUALITATIVE EXPLANATION OF THE HIGH SERIES SHIFT

The indication that the higher series members should be treated any differently from any other spectral lines was quite clearly given in the results which were obtained by Amaldi and Segre[1,2] for the shift and broadening of the spectral lines of the two alkali atoms, sodium and potassium, by $H_2$, $N_2$, $He$ and $A$.

Let us recall that when we speak of the higher series members we refer to spectral lines which arise from transitions from photoelectron states of high principal quantum number $n$. In the conceptual language of the Bohr theory this means that the orbit of the photoelectron is at a great distance from the atomic nucleus, in fact, for principal quantum number 30 the radius of the Bohr orbit is around 500A. The size of this orbit — or any other high $n$ orbit — is the basis which Fermi used for the theory by means of which he sought to explain the anomalies which Amaldi and Segre found in their high series spectra, namely: (1) The spectral line shift increases as the series member increases, that is, the shift increases for upper states with higher $n$. (2) As the order of the upper state continues to increase the line shift appears to converge toward a value which is approximately proportional to the pressure. (3) The magnitude of the shift was found to be the same for the spectral lines of sodium and potassium. (4) The amount and direction (violet or red) appear to depend on the nature of the foreign broadening gas. Qualitatively Fermi explained these results, or some of them, as follows:

To begin with only those electron orbits will be treated which are of sufficient radius to include within the spheres corresponding to them several thousand foreign gas atoms. It is precisely this orbit size which forms the basis for the present treatment. In the case $n = 30$ of the last paragraph there are, at atmospheric pressure, 30,000 atoms within the orbit.* In addition the velocity of the electron at these distances from its nucleus is low. The picture that then presents itself, and which is all important to the theory, is that of the photoelectron moving slowly through the atoms of the foreign gas. From this picture Fermi evolved two co-acting methods by which the lines are broadened.

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* Quite often nannies and kids are pastured separately for reasons which need not concern us. In the evening when the kids and their maternal ancestors are again placed in the same corral it is most impressive to watch a nanny rapidly and unerringly pick her offspring from among hundreds of other and apparently identical kids while refusing to be cozened by the younger members of other families. Although impressive, we must admit that this cannot hold a candle to the selectivity of the electron and nucleus to which we refer.

(a) The Polarization Effect. As we are well aware the electrons in an atom may be considered as arranged in shells around the nucleus with a sufficient number of shells filled so that the positive charge of the nucleus is screened or counteracted in such a manner that no electric field will arise due to the nuclear charge. Now when we move the photoelectron out to such a distance that one or more atoms are either at the same or lesser distance from the nucleus, the shielding effect of this electron will be absent insofar as these atoms are concerned. As a consequence these atoms will be under the influence of a field of an ion of charge $e$. We shall assume that they are not possessed of a permanent dipole, but an interaction between the dipole induced on these atoms and the electric field will occur. The energy of this interaction can only arise from one place, and that is the emitting atom. The result is that the energies of the energy levels of the atom are lowered by the amount contributed to this interaction. In toto then the emitted spectral line is shifted to the red as a result of the Polarization Effect.

(b) The Potential Valley Effect. We have considered an interaction between the partially unscreened nucleus and the broadeners, and now we consider the interaction between the photoelectron and the broadeners. Fermi considered the broadeners as effectively scattering potential valleys along the flight path of the photoelectron. These valleys would not be large in extent, however, since the atoms causing them are neutral. Quite obviously these valleys will have some effect on the energies of the electron, and we shall see that (1) the line shift resulting may be either to the red or the violet and (2) the magnitude is always greater than that of the Polarization Effect.

## 9.2. THE POLARIZATION EFFECT

Let us first consider one of the many foreign gas atoms contained within the orbit of the photoelectron and hence acted on by the field of a charge $e$. If the separation of this atom from the center of the emitting atom is $r_i$, then the field in which this atom finds itself is $\frac{e}{r_i^2}$.

We now make our first assumption, namely, (A) THE BROADENERS POSSESS NO PERMANENT DIPOLES. If, as usual, we take the polarizability as $\alpha$, then the interaction energy will be given by $-\frac{1}{2}\alpha E^2 = -\frac{1}{2}\alpha e^2 \frac{1}{r_i^4}$ so that the total energy shift resulting may be found by summing over all atoms within the orbit as:

$$\Delta E = -\frac{\alpha e^2}{2}\sum_i \frac{1}{r_i^4} \tag{9.1}$$

Very little error is introduced by extending this sum over all perturbers (this arises from the rapid convergence of $r_i^4$) so we do precisely this.

Now the spectral line may be supposed shifted by the same amount as the upper level since we may imagine this effect as not present for the lower level involved in the transition. The shift of the line intensity maximum due to the effect under consideration may then be taken as the energy perturbation resulting from the most probable perturber configuration. This most probable configuration is a uniform distribution of the perturbers, with the nearest one a distance $\frac{4}{3}\pi R_1^3 = \frac{1}{N}$, where now the volumes of the individual perturbers of size $1/N$ are distributed in spherical shells. In order to find the value of the summation over $r_i$ then we simply replace the summation in Eq. (9.1) by an integration of lower limit $r_1$ with the result:

$$\sum_i \frac{1}{r_i^4} = 4\pi N \int_{R_1}^{\infty} \frac{r^2 dr}{r^4} = \frac{4\pi N}{R_1} \tag{9.2}$$

Eq. (9.2) may now be substituted into Eq. (9.1) to obtain:

$$\Delta E = -10\, e^2 \alpha N^{4/3} \text{ ergs} = -2.8 \times 10^n(\epsilon - 1)\, N^{1/2} \text{ sec}^{-1} = +.00093(\epsilon - 1)N^{1/3} \text{ cm}^{-1} \tag{9.3}$$

according to Eq. (7.41b) under the standard assumption $\epsilon \doteq 1$. The symbol $\epsilon$ represents the dielectric constant of the foreign gas.

Eq. (9.3) yields a shift of about a reciprocal centimeter for a foreign gas pressure of one atmosphere.

## 9.3. THE POTENTIAL VALLEY EFFECT

In taking up this second effect let us first introduce the assumption (B) THE MOLECULES ARE MONATOMIC. This will tend to restrict the theory, but it will be important in the proof.

We wish to set up the Schrodinger equation for the photoelectron. First then we are in need of a potential function which conveniently presents itself as a sum of the potential due to the remainder of the emitter (excluding the photoelectron) $U$, and the potential due to all broadeners present, $\sum_i V_i$. Now the de Broglie wavelength* of our earlier example — the atom with an $n$ of 30 — is in the neighborhood of 100A. The perturbing atoms' potential $V_i$ will be of limited extent — and spherical symmetry — since the atoms are neutral, however, so that the de Broglie wavelength will be large compared to the spatial extent of the $V_i$.

Our Schrodinger equation will then be:

$$\nabla^2\psi + \frac{2m}{h^2}\,[E - U - \sum_i V_i]\,\psi = 0 \tag{9.4}$$

Next a function, $<\psi>$, is defined which is the space average of the eigenfunction of Eq. (9.4) in a domain of small extent compared to the de Broglie wavelength but sufficiently large to contain a goodly number of perturbers. The potential $U$ will surely be about constant in such a region, and we shall so consider it. The function which we have defined satisfies the equation:

$$\nabla^2<\psi> + \frac{2m}{\hbar^2}\,[E - U]<\psi> - \frac{2m}{\hbar^2}<\sum_i V_i\psi> = 0 \tag{9.5}$$

We are now faced with the problem of computing $<\sum_i V_i\psi>$ which may be accomplished in the following approximate manner.

Since the remainder of the atom is some hundreds of angstroms away, we may expect $E - U$ to be sufficiently small so that it may be neglected in comparison to $V_i$ in a small region about the $i$-th perturber. In addition we have supposed our broadeners in a spherically symmetric state so that the potential will be simply a function of $r$, measured, of course, from the perturber center. Consequently $V_i = V_i(r)$, and the Schrodinger equation takes the approximate form:

$$\nabla^2\psi = \frac{2m}{\hbar^2}\,V_i\,\psi \tag{9.6a}$$

When we set $\psi = u(r)/r$, this becomes:

$$u'' = \frac{2m}{\hbar^2}V_i\,u \tag{9.6b}$$

In that part of space sufficiently far removed from the perturber, $\psi$ will tend toward the average value $<\psi>$ which we have already defined. On the other hand the solution to Eq. (9.6b) at a position far from the potential valley of the perturber is:

$$u = c_1 + c_2 r \tag{9.7a}$$

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* It may be remembered that the de Broglie wavelength of a particle is related to the linear momentum of the particle by the relation: $h/\lambda = p$.

Since $\psi$ is tending toward $<\psi>$ at great distance, $c_2$ is given by $<\psi>$ since $u(r) = r\psi$. There can be no objection to replacing the constant $c_1$ by the constant $a<\psi>$, so that Eq. (9.7) becomes:

$$u = (a + r)<\psi> \tag{9.7b}$$

and the significance of $a$ is apparent from Fig. (9.1).

We now integrate Eqs. (9.6) with the result:

$$\frac{2m}{\hbar^2}\int V\psi d\tau = 4\pi\frac{2m}{\hbar^2}\int Vurdr = 4\pi\int u''rdr$$

$$= 4\pi \left| u'r - u \right|_0^r = -4\pi a<\psi> \tag{9.8}$$

where the final evaluation is obtained directly from Eq. (9.7b).

Eq. (9.8) leads directly to:

$$\frac{2m}{\hbar^2}<\sum_i V_i\,\psi> = -4\pi aN<\psi> \tag{9.9}$$

Eq. (9.9) may now be substituted into Eq. (9.5) to obtain:

$$\nabla^2<\psi> + \frac{2m}{\hbar^2}\left[E_0 - U\right]<\psi> = 0 \tag{9.10}$$

where:

$$E_0 = E + \frac{h^2aN}{2\pi m} \tag{9.11}$$

Eq. (9.10) is the Schrodinger equation for the emitting atom — considered as central core plus photoelectron — when the perturbing foreign gas atoms are not present. Thus, $E_0$ will take on the various values of the unperturbed atom energies. Since $E$ is the energy of the perturbed atom, it will, according to Eq. (9.11), differ from the unperturbed energy by amount:

$$\Delta E = -\frac{h^2aN}{2\pi m} \tag{9.12}$$

It is apparent from Eq. (9.12) that the direction of level and line shift will depend on the sign of the quantity $a$. The problem is essentially solved then if some further information about the constant $a$ can be obtained. Fermi was able to obtain an approximate value for the magnitude of this factor — not the sign — by beginning with Wentzel's expression[194] for the collisional cross section for very slow electrons on the foreign gas atoms:

$$\sigma = \frac{h^2}{\pi p^2}\sin^2\Upsilon_0 \tag{9.13}$$

where $p$ is the electronic linear momentum, and $\Upsilon_0$ is the phase change occurring in the matter waves associated with the electron due to the perturber valley. Since the sign is equal to its argument for very small $p$:

$$\Upsilon = \frac{p}{h}\sqrt{\pi\sigma} \tag{9.14}$$

We may obtain an alternate expression for the phase change by a study of Fig. (9.1). A consideration of this figure is sufficient to tell us that the matter wave of the electron has suffered a phase change of $a$ $\lambda$ wavelengths after having undergone the influence of one of the potential valleys. It follows then that:

$$a/\lambda = \frac{\Upsilon}{2\pi} \tag{9.15}$$

We substitute Eq. (9.15) into Eq. (9.14) to obtain:

$$\sigma = 4\pi a^2 \tag{9.16}$$

which may be utilized for the magnitude of $a$ in Eq. (9.12), but, as we have noted earlier, which tells us nothing about the sign, and hence nothing about the direction of the shift.

Finally, Fermi added the effect of Sec. 2 as given by Eq. (9.3) to Eq. (9.12) to obtain, as the overall shift due to the interactions of this and the preceding sections:

$$\Delta = -2.8 \text{ x } 10^7(\epsilon - 1)N^{1/3} \pm 0.33\sigma^{1/2}N \tag{9.17}$$

Eq. (9.17) is valid then for (C) FOR PRESSURES HIGH ENOUGH SO THAT SEVERAL ATOMS WILL BE FOUND IN A CUBE OF SIDE THE DE BROGLIE WAVELENGTH OF THE ELECTRON AND LOW ENOUGH SO THEIR SEPARATION IS MUCH GREATER THAN THEIR RADIUS OR THE RADIUS OF THE COLLISIONAL CROSS SECTION. On this basis Fermi set the minimum pressure at about one atmosphere.

Fermi considered the broadening of the high series members very briefly, although it is directly apparent that the same phenomena will lead to broadening as led to shift. By a rather qualitative line of reasoning he gave as the width due to the Polarization Effect Eq. (9.3). It might also be of some interest to obtain his result for the highest order line appearing. The premise here is that in order for a line to be distinct the free path of the photoelectron must be sufficiently long that said electron is given the opportunity of completing several circuits of its orbit. If $\sigma$ is the collisional cross section for the electron on the foreign gas atoms, we will readily concede that the free path is given by:

$$l = 1/\sigma N \tag{9.18}$$

and the orbit circumference may be approximated by:

$$4r_0n^2 \tag{9.19}$$

where $r_0$ is the radius of the first Bohr orbit.

Then our condition for distinctness of lines leads to the relation:

$$4r_0n^2 < \frac{1}{\sigma N}$$

from which we conclude that the highest principal quantum number specifying the upper state of a spectral line is given by:

$$n_0 = \frac{1}{2\sqrt{r_0\sigma N}} \tag{9.20}$$

As Fermi noted, however, one may not be able to observe quite this high order a line since other causes of broadening will further affect the line distinctness.

### 9.4. AXIALLY SYMMETRIC BROADENERS AND THE SHIFT DIRECTION

Reinsberg next considered the high series shift problem[152] under the same basic assumptions as Fermi had first stated. Insofar as the actual treatment which he gave the problem was concerned, his work was about the equivalent of Fermi's for the spherically symmetric broadeners. This, of course, resulted in his obtaining Fermi's earlier results for this case with one magnitudewise minor but otherwise important difference which we shall note in due course.

From Eqs. (9.5) and (9.6) Reinsberg obtained instead of Eq. (9.6):

$$\nabla^2\psi + \frac{2m}{\hbar^2}\,[E - \dot{V}_i]\,\psi = 0 \tag{9.20a}$$

$$\nabla^2\langle\psi\rangle + \frac{2m}{\hbar^2}E\langle\psi\rangle - \frac{2m}{\hbar^2}\langle V_i\psi\rangle = 0 \tag{9.20b}$$

where all symbols continue to have the meaning previously ascribed to them.

The undisturbed solution of:

$$\nabla^2\psi^0 + \frac{2m}{\hbar^2}E\psi^0 = 0 \tag{9.21}$$

will also be useful. For the same reasons leading to the choice in Eqs. (9.6) a first approximation to $\psi$ and $\psi^0$ may be taken as $u(r)/r$ and $u^0(r)/r$ respectively. There then results for Eq. (9.20a) and (9.21):

$$u'' + \frac{2m}{\hbar^2}(E - V_i)u = 0 \tag{9.22a}$$

$$u^{0''} + \frac{2m}{\hbar^2}Eu^0 = 0 \tag{9.22b}$$

Clearly, the solution to Eq. (9.22b) is:

$$u^0 = A \sin \frac{\sqrt{2mE}}{\hbar} r \tag{9.23}$$

Now for very large $r$, $V_i(r)$ goes to zero, and, since this potential constitutes the only difference between Eqs. (9.22), the solutions to these two equations may surely only differ by an amplitude factor and a phase factor. Thus, there results from Eq. (9.23):

$$u = \alpha_0 A \sin\left(\frac{\sqrt{2mE}}{\hbar} r + \Upsilon_0\right) \tag{9.24a}$$

or, since $\sin(a + b) = \cos a \cdot \cos b\,(\tan a + \tan b)$ and $p$ is presumed very small, Eq. (9.24a) may be approximated as:

$$u = \alpha_0 A \frac{\sqrt{2mE}}{\hbar} \cos \Upsilon_0 \left[ r + \frac{\hbar}{\sqrt{2mE}} \tan \Upsilon_0 \right] \tag{9.24b}$$

since in this case $\cos a = 1$ and $\tan a = \sin a = a$ for $a$ quite small.

Now in place of Eq. (9.7b) we obtain, after a solution exactly coinciding to Eqs. (9.6):

$$u = \left(\frac{\hbar}{\sqrt{2mE}} \tan \Upsilon_0 + r\right) <\psi> \tag{9.25}$$

A comparison of Eq. (9.25) with Eq. (9.7b) tells us the most important relation to be obtained here:

$$a = \frac{\hbar}{\sqrt{2mE}} \tan \Upsilon_0 \tag{9.26}$$

The reason for the importance of this expression as opposed to an analogous expression obtained from Eqs. (9.13) and (9.16) is that here a possibility exists for obtaining different signs for $a$ for different values of the phase shift $\Upsilon_0$. One further point should be made. The equation obtained for $a$ from Eqs. (9.13) and (9.16) must be expected to agree with Eq. (9.26), and let us remark that they will so agree for small linear momentum (slow electrons). $\Upsilon_0$ can be expected to differ but little from some integral multiple of $\pi$. In consequence the sine and tangent are about equal.

Reinsberg treated the case of the axially symmetric broadener by setting the problem up in ellipsoidal coordinates and solving the resulting Schrodinger equation by a method quite similar to that which we have used in this and the previous section for the spherically symmetric perturber. The shift is found to be that of the spherically symmetric molecule, namely, Eq. (9.12) with $a$ given by Eq. (9.26). Now the matter of shift direction may more conveniently be considered for application to either type broadener.

The particular phenomenon of slow electron deflection by the noble gases had been investigated in considerable detail by Ramsauer.* Faxen and Holtsmark[35] had treated the situation theoretically from the quantum mechanical point of view, and, finally, Holtsmark[69, 70] and Heuneberg[64] had furnished the results of which we shall make specific use.

Firstly Heuneberg had shown that for medium and high velocities the phase constant increases monotonically with decreasing electron velocities. Holtsmark carried his considerations of the problem to much lower velocities and determined that the phase shift must needs proceed to multiples of $\pi$ unless, as may possibly occur, $\Upsilon_0$ has already attained the limiting value for infinitely small velocities for some small value of the electronic energy. This means that the phase shift has a maximum and the Ramsauer cross section has a maximum as indicated by Fig. (9.2). Now for this case, since in this limiting case $\Upsilon_0$ approaches some multiple of $\pi$, the phase change becomes equal to $k\pi + \beta$ where $0 \leqslant \beta \leqslant \frac{\pi}{2}$. This means that tan $\Upsilon_0$ occurring in Eq. (9.26) must be positive so that $a$ is positive, and the line shift as given by Eq. (9.11) is to the red.

Thus, **IF THE RAMSAUER CROSS SECTION FOR THE BROADENING GAS FOR LOW ELECTRON VELOCITIES HAS A MINIMUM THE SPECTRAL LINE IS SHIFTED TOWARD THE RED AND IF THIS CROSS SECTION HAS NO MINIMUM THE LINE IS SHIFTED TOWARD THE VIOLET.**

*A* and *Xe* have minimums while *He* and *Ne* do not, so that one would expect from the theory that the shift direction would be red for the two former and violet for the two latter. This has been found to be indeed the case.[2, 42, 46]

*Hg* has been experimentally determined as displaced to the red which to a cursory inspection might indicate a minimum. If, however, the Polarization Effect† is large enough, the Potential Valley Effect of this and the last section might not be large enough to overcome it so that even though the aggregate shift is toward the red, the Valley shift might be toward the violet. This is Reinsberg's assumption in this case at any rate.

Reinsberg calculated the magnitudes of some shifts with quite good results. In doing so he took the values of the phase shift from the work of Faxen and Holtsmark.[35]

## 9.5. THE LIMITING BREADTHS OF THE HIGH SERIES LINES

As our last consideration of this specialized effect, we shall consider Reinsberg's treatment[153] of the breadth of the spectral lines in the limiting case of very high principal quantum number. Let us first remark the results of Fuchtbauer on the breadths of spectral lines as a function of principal quantum number.[44] Quite concisely, Fig. (9.3) gives the manner in which, as an example, the $(1s - np)$ *Na* line broadened by *A* varies with principal quantum number, $n$. It is very apparent from this figure that, for sufficiently high $n$, the line width approaches a limiting value. It is this limiting line width which Reinsberg attempted to obtain.

In carrying through this calculation the general method will be an incorporation of the interaction forces of Secs. 2 and 3 into the framework of the Lorentz collision theory through the medium of the collision cross section.

To begin with then the level** width is given by:

$$\delta = \frac{1}{\pi\tau} = \frac{2T_0N_0}{\pi}\sqrt{\frac{2k}{\pi}}\,\frac{p\sigma}{\sqrt{mT}} \tag{9.27}$$

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* References 142, 143, and 144.

† See *supra*, Sec. 9.2.

** Reinsberg simply used the Lorentz result for the levels giving rise to a line rather than for the line itself.

where now $T_0$ and $N_0$ are a temperature of 273.3°K and the number of atoms per unit of volume respectively. $\sigma$ is the cross section through which the special effects of this chapter will enter.

Now we begin the problem by choosing as the absorber the hydrogen atom. Next the Bohr assumption is utilized to the effect that we take as the radius of an orbit corresponding to principal quantum number $n$ the value $r_0 n^2$. As a consequence, when we suppose the electron to be a unit of charge uniformly smeared out* through the sphere corresponding to this orbit, the constant electron density (or charge density) is:

$$d = \frac{3}{4\pi r_0^3 n^6} \tag{9.28}$$

Now Eqs. (9.12) and (9.26) tell us that *one* noble gas atom in interaction with one electron has the interaction energy:

$$E_1 = \frac{h^2 \tan \Upsilon_0}{4m\pi^2\sqrt{2mE'}} \tag{9.29}$$

so that this atom will now be affected by a potential:

$$E_1 d \tag{9.30}$$

as given by Eqs. (9.28) and (9.29).

Eq. (9.30) gives the main contribution to the potential curve shown in Fig. (9.4) between the points $r_1$ and $r_2$. For convenience one might consider it as the only contribution in this region to a fair approximation. Thus, the Potential Valley Effect builds the potential curve in this portion of space.

To build the remainder of the potential curve we utilize, as one might suspect, the Polarization Effect so that the interior portion of the curve is given by the equation:

$$\frac{\alpha e^2}{2r^4} \tag{9.31}$$

Broadeners of thermal $E = 3/2kT$ are now to be considered, and one of two rather obvious situations may arise, either $E < V_0$ or $E > V_0$. Although these "things" which the energy may do are rather obvious, they lead to some rather important consequences.

First the case $E < V_0$. In this case the foreign gas atom cannot climb the wall at $r_2$, and, as a result, all within a sphere of this radius is forbidden to it. This means that the collision cross section for such an atom is:

$$\pi r_2^2 = \pi r_0^2 n^4 \tag{9.32}$$

It also hardly needs remarking that this will form a lower limit on cross sections for atoms of higher energies. We shall return to a consideration of the more complex problem of cross sections for these higher energies after a few preliminary remarks.

Through Eq. (9.27) the level widths are directly proportional to the cross sections with which we have been concerning ourselves. Now Reinsberg supposed that the width of the $np$ level might simply be added to the width of the $1s$ (only transitions $(1s - np)$ are being considered) level in order to obtain the width of spectral line. Further the $1s$ level width is negligible compared to the width of the other combining levels so that the course of the level width with principal quantum number may be inferred directly from Fig. (9.5). Another interesting point is illustrated by Fig. (9.5). This figure shows the displacement of the curve of the level widths with temperature. This latter effect may be directly traced to the increase of the cross section

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* This may better be considered as smeared out location probability and hence timewise charge smearing.

(and consequently the level width) with a decrease in temperature (accompanied, of course, by a decrease in energy) according to Eq. (9.32).

It now appears that the obtention of the cross section for $E > V_0$ will mean that the problem as set up has been solved. The solution is furnished us by the work of Massey and Mohr.[124] These two authors[123, 124], in quantizing the earlier work of Chapman[17, 18] on free paths and various transport phenomena, obtained the expression for the cross section which will prove applicable to the present situation.

We begin by defining the quantity $I(\vartheta) \sin \vartheta d\vartheta$ as the probability that a particle will be scattered on collision through an angle between $\vartheta$ and $\vartheta + d\vartheta$. From this definition, it follows logically that we may find the collision cross section — the total probability that the particle will be scattered in any direction whatsoever — as:

$$\sigma = 2\pi \int I(\vartheta) \sin \vartheta \, d\vartheta \tag{9.33}$$

Quite evidently then the determination of the collision cross section demands the prior determination of $I(\vartheta)$. This we proceed to do.

We initially assume that a solution of the equation

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V(r)] \psi = 0 \tag{9.34}$$

at some distance from the scattering atom, the absorber, is desired. It will be of the form:

$$e^{ikz} + \frac{1}{r} e^{ikr} f(\vartheta) \text{ where: } k^2 = \frac{2mE}{\hbar^2} \tag{9.35}$$

where the first term represents the incident particle in the form of a plane wave and the second term represents the scattered particle. Since the solution $P_n(\cos \vartheta) f_n(r)$ is a quite satisfactory one, the solution

$$\sum_n A_n P_n (\cos \vartheta) f_n(r) \tag{9.36}$$

is equally so. From this equation one may, by integration and requiring that the asymptotic form of $f_n(r)$ be:

$$f_n(r) \to \frac{1}{kr} \sin \left( kr - \frac{n\pi}{2} \right) \tag{9.37}$$

determine the $A_n$ so that:

$$e^{ikz} = \sum_n (2n + 1) i^n P_n (\cos \vartheta) f_n(r) \tag{9.38}$$

We take the solution, Eq. (5.55), where, we may recall, the $rL_n(r)$ is the solution to Eq. (5.56a). Now Eq. (9.38) is subtracted from Eq. (5.55) with the intention of obtaining the expression for the scattered wave in this fashion:

$$A_n L_n(r) - (2n + 1) i^n f_n(r) \doteq C_n r^{-1} e^{ikr} \tag{9.39}$$

When the asymptotic expressions for the $f_n(r)$ from Eq. (9.37) and $L_n(r)$ from Eq. (5.59) are utilized, there results:

$$\frac{e^{ik\rho}}{2ikr} [A_n e^{i\Upsilon_n} - (2n + 1) i^n] - \frac{e^{ik\rho}}{2ikr} [A_n e^{-i\Upsilon_n} - (2n + 1) i^n] \text{ where: } k\rho = kr - \frac{n\pi}{2} \tag{9.40}$$

It is apparent from Eq. (9.35) that, since this is to be the expression for the scattered wave, $A_n$ must be given by:

$$A_n = (2n + 1) i^n e^{i\Upsilon_n} \tag{9.41}$$

Thus, the wave function representing the incident and the scattered wave is:

$$\psi = \sum_n (2n + 1) i^n e^{i\Upsilon_n} L_n(r) P_n (\cos \vartheta) \tag{9.42}$$

of asymptotic form:

$$r^{-1}e^{ikr}f\,(\vartheta)$$

so that:

$$f(\vartheta) = \frac{1}{2ik} \sum_n (2n + 1) \left[e^{2i\Upsilon_n} - 1\right] P\,(\cos\vartheta) \tag{9.43}$$

This equation is precisely the one for which we have been looking since by quantum mechanical definition the absolute square of $f(\vartheta)$ multiplied by the angular volume element gives us the probability that the particle will be in the angular volume element. Thus, from Eq. (9.43):

$$I(\vartheta) = \frac{1}{4k^2} \sum_n \left| (2n + 1) \left[e^{2i\Upsilon_n} - 1\right] P_n\,(\cos\vartheta) \right|^2 \tag{9.44}$$

The substitution of this expression into Eq. (9.33) leads to:

$$\sigma = \frac{4\pi}{k^2} \sum_n (2n + 1) \sin^2 \Upsilon_n \tag{9.45}$$

Eq. (9.45) is the one which Massey and Mohr treated under the assumption of a potential of the form $Cr^{-s}$, exactly the type with which we are concerned. Beginning with Jeffery's form[81] for the phase shifts in Eq. (9.45), these authors carried out an asymptotic solution for large $n$ to obtain:

$$\sigma = \pi \frac{2s - 3}{s - 2} \left[\frac{(s - 3)!!}{(s - 2)!!} \frac{\pi}{2}\right]^{2/s-1} \left(\frac{C}{p}\right)^{2/s-1} \tag{9.46}$$

Eq. (9.31) tells us that $s = 4$ and $C = 1/2\ \alpha e^2$, and, when we recall that $\alpha = \dfrac{\epsilon - 1}{4\pi N_0}$:

$$\sigma = \frac{5}{2} \pi^3 \left(\frac{e^2}{4h}\right)^{2/3} \left(\frac{\epsilon - 1}{4\pi N_0}\right)^{2/3} \left(\frac{1}{2\pi k}\right)^{1/3} \left(\frac{m}{T}\right)^{1/3} \tag{9.47}$$

The limiting value for the line width may then be found by substituting Eq. (9.47) into Eq. (9.27):

$$\delta_\infty = \frac{5}{2} \frac{T_0}{c} \left(\frac{N_0\pi}{2}\right)^{1/3} \left(\frac{e^2}{4h}\right)^{2/3} (2\pi k)^{1/6} (\epsilon - 1)^{2/3} p\ (mT^5)^{-1/6} \tag{9.48}$$

To this width is added, for the line width, the width due to the Valley Effect. A comparison of the widths calculated in this manner with those observed by Fuchtbauer and Schulz[44] is given in Table (9.1). Although the agreement is not of the best, one should remember that the consideration has been a bit rough, and, perhaps more important, only this particular type effect has been considered while the broadening of the lower level has been neglected.

| | $p$ | $T$ | $(\epsilon - 1)10^6$ | $\delta_\infty$ | $\delta_1$ | $\delta_1 + \delta_\infty$ | $\delta_{\text{exp}}$ |
|---|---|---|---|---|---|---|---|
| Na/A | 2.26 | 762.0 | 57.4 | 3.77 | 0.08 | 3.85 | 3.59 |
| K/A | 4.00 | 754.3 | 57.4 | 6.39 | 0.15 | 6.44 | 6.25 |
| Na/He | 8.30 | 805.8 | 6.85 | 4.07 | 9.53 | 4.64 | 5.44 |
| Na/Ne | 8.06 | 743.5 | 13.30 | 5.44 | 0.31 | 5.75 | 4.18 |
| Cs/Kr | 1.11 | 567.0 | 83.47 | 2.45 | 0.04 | 2.49 | 3.73 |
| Cs/Xe | 1.97 | 568.3 | 136.00 | 5.81 | 0.06 | 5.87 | 8.30 |
| Na/$H_2$ | 1.48 | 792.6 | 26.40 | 2.16 | 0.12 | 2.18 | 3.24 |
| Na/$H_2$ | 1.48 | 755.8 | 54.70 | 2.58 | 0.06 | 2.64 | 3.27 |

Table 9.1. (After Reinsberg.[153])

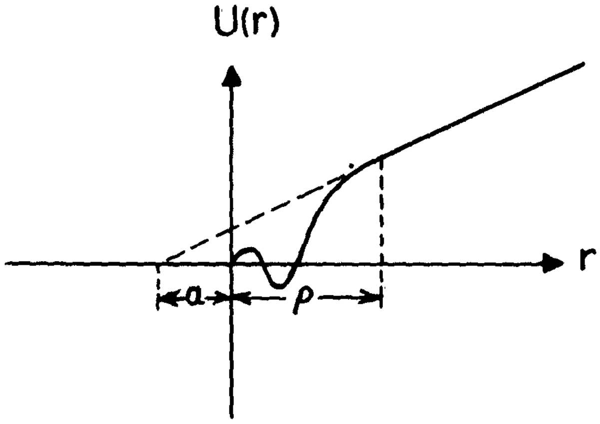

Fig. (9.1). A plot of Eq. (9.7b). (After Fermi.[36])

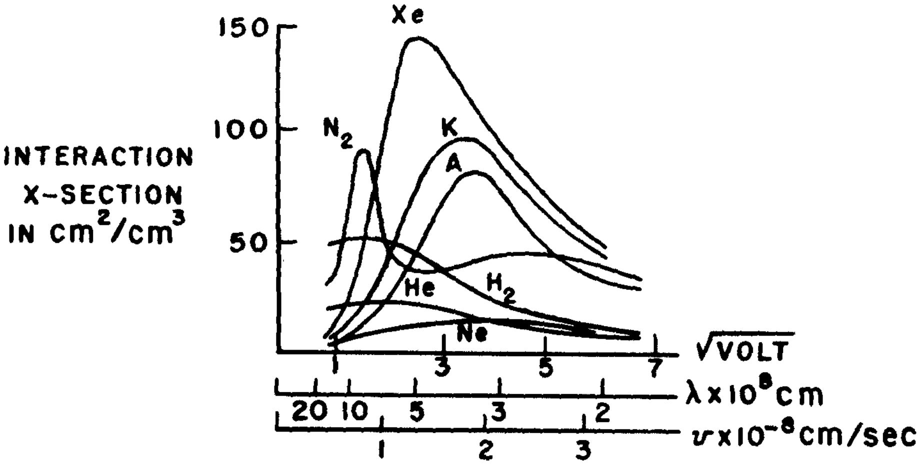

Fig. (9.2). Ramsauer cross sections for slow electrons. T = 0°C. p = 1 mm. (After Faxen and Holtsmark.[35])

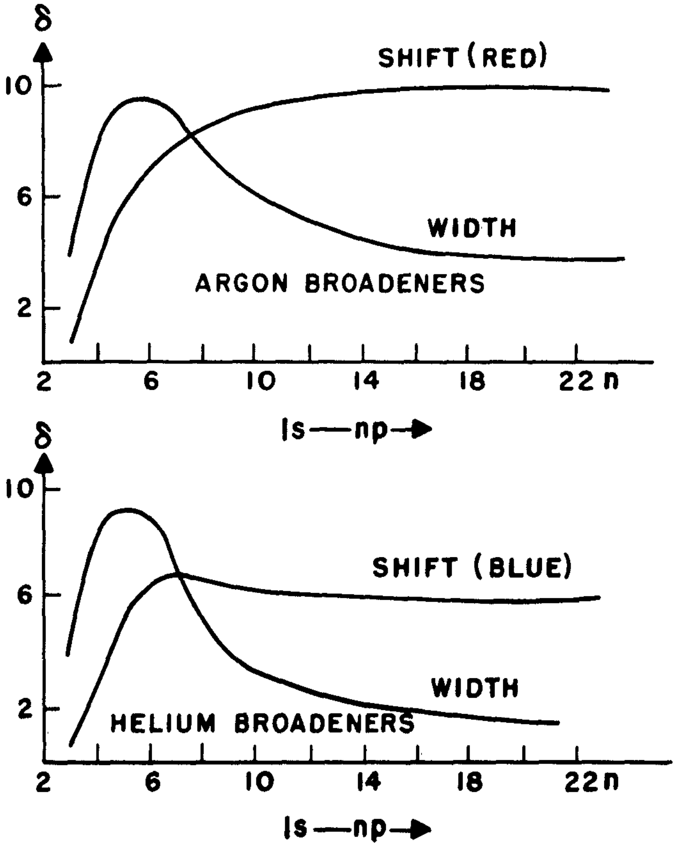

Fig.. (9.3). Line shift and halfwidth as a function of order. (After Fuchtbauer and Schulz.[44])

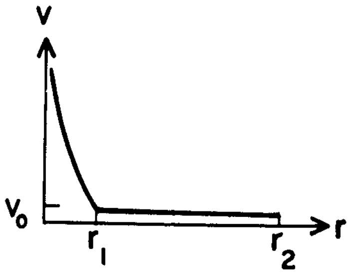

Fig. (9.4). The potential curve due to the high series interactions. (After Reinsberg.[153])

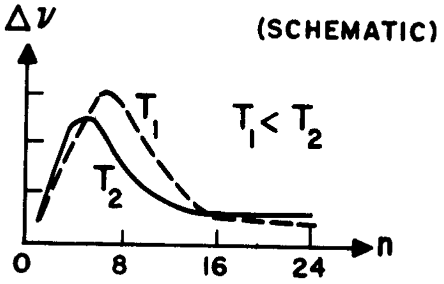

Fig. (9.5). Displacement of level width curve with temperature. (After Reinsberg.[153])

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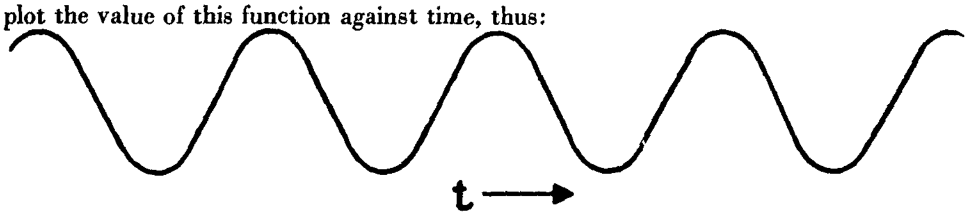
# APPENDIX I

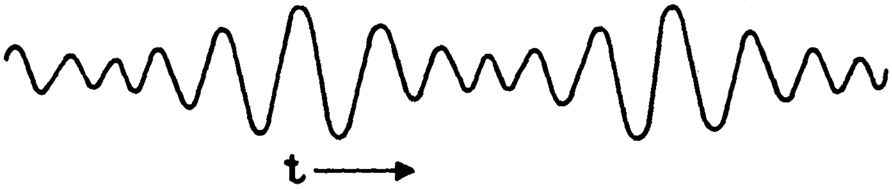
## THE FOURIER ANALYSIS

There often arises the necessity for utilizing a mathematical tool which we see applied by various investigators as the panacea for the line broadening. We refer, of course, to the Fourier analysis. Let us then develop the concept behind the equations which we use, not in a manner to provide rigorous mathematical justification for the result we obtain, — for this we may refer to an almost unlimited number of sources — but after a fashion which will provide us with a physical basis for its use.

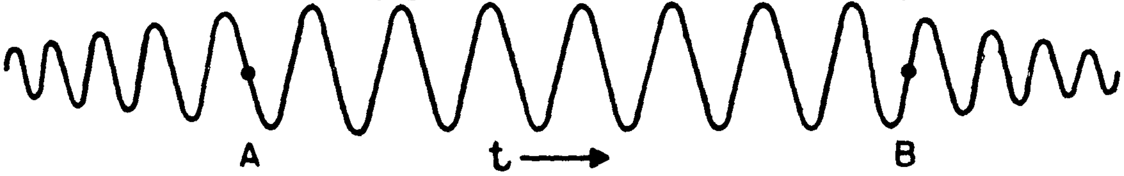
Let us begin with the familiar function $a_1 \sin 2\pi\nu_1 t + b_1 \cos 2\pi\nu_1 t$ where $\nu_1$ is some frequency or other. We may plot the value of this function against time, thus:



Next the function $a_2 \sin 2\pi\nu_2 t + b_2 \cos 2\pi\nu_2 t$ may be added to this, graphically if you wish, to obtain this perhaps, depending on the values we choose for the constants $\nu_1$, $\nu_2$, $a_1$, etc.



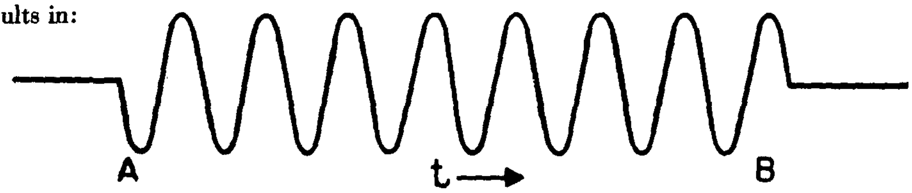
This latter curve indicates the possibility of obtaining, at least approximately, almost any curve by proper choice of the $\nu_i$, $a_i$, $b_i$. If we properly choose, say, ten of the functions, we may obtain:



It would appear intuitively apparent that the extension of the number of cosine and sine functions to infinity results in: of equation:

$$f(t) = \sum_{i=1}^{\infty} a_i \sin \omega_i t + \sum_{i=0}^{\infty} b_i \cos \omega_i t \tag{I.1}$$

where: $\omega_i = \dfrac{2\pi c}{\lambda_i}$



We have thus written an equation (Eq. (I.1)) for a wave beginning at time $A$ and terminating at time $B$. Now the fact that the $\sin \omega_i t$ and the $\cos \omega_i t$ are orthogonal allows us to write:

$$a_i = \text{const} \int f(t) \sin \omega_i t \, dt \qquad b_i = \text{const} \int f(t) \cos \omega_i t \, dt \tag{I.2}$$

The presence of both sine and cosine functions indicates the possibility of transforming to an exponential. This leads to:

$$f(t) = \sum_{i=-\infty}^{+\infty} J(\omega_i) e^{i\omega_i t} \qquad J(\omega_i) = \text{const} \int f(t) e^{-i\omega_i t} dt \tag{I.3}$$

We simply accept the statement that if $\int_{-\infty}^{+\infty} |f(t)| \, dt$ exists, Eq. (I.3) may be rewritten as:

$$f(t) = \int_{-\infty}^{+\infty} J(\omega) e^{i\omega t} d\omega \tag{I.4a}$$

$$J(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} \, dt \tag{I.4b}$$

Eqs. (I.4) are the equations for Fig. (I.1) as given by the Fourier transform.

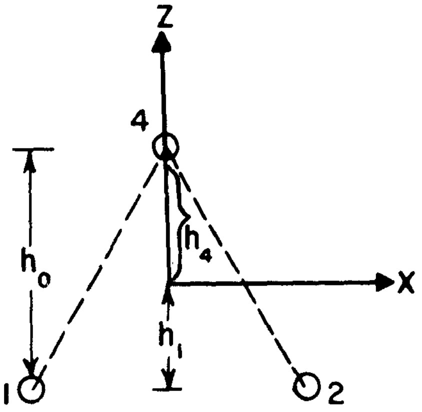
The point which we have attempted to bring out is the manner in which the cut-off wave train of Fig. (I.1) may be built up from an infinite number of infinitely long wave trains of various specific frequencies. Eqs. (I.4) demonstrate the manner in which the various amplitudes weight the various frequencies.

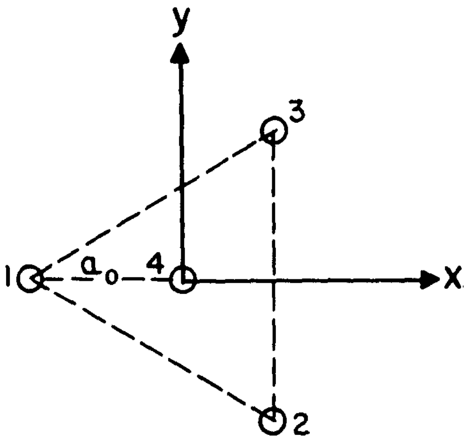
As a final consequence then, in considering the effect of interrupting collisions one might say that their result is for the observer to obtain frequency measurements which indicate to him that an infinite number of wave trains of different frequency and varying strength have replaced the single wave train. This is also the same as saying that an infinite number of state growth coefficients, which give varying probabilities for the various frequencies of photons present in the field after radiation, exist. These state growth coefficients are discussed first in Sec. (4.19). The absolute squares of the coefficients in question yield the probability for the presence of the photons corresponding to the coefficients, and we might consider these individual coefficients as corresponding to individual Fourier components.

# APPENDIX II

## A GROUP THEORY APPLICATION

We propose to discuss here the manner in which group theory may be used to break the vibrational secular determinant into steps. In order to accomplish this let us carry through the procedure for the pyramidal $XY_3$ molecular model of which ammonia is an example. It seems that this should serve as an illustration of the general procedure.





We begin by recalling that our Langrangian may be written as:

$$L = T - V = \widetilde{\|\dot{q}\|}\,\|T\|\,\|\dot{q}\| - \widetilde{\|q\|}\,\|V\|\,\|q\|$$

where $\|\dot{q}\|$ and $\|q\|$ are column vectors, and $\|T\|$ and $\|V\|$ are the matrices of the kinetic and potential energy respectively. Now let us note that, since there are four particles present, twelve Cartesian coordinates will describe the behavior of this assemblage. Let us turn our attention to Fig. (II.1) and determine what covering operations may be performed on the molecules of this figure.

Now a covering operation is defined as an operation (such as a rotation about the $z$-axis of **Fig. (II.1)**) which, when performed on a molecule, leaves the molecule essentially unchanged. We might consider the proper (boreal) rotation of the $XY_3$ molecule through an angle of 120 degrees about the $z$-axis as an example of a covering operation. After this rotation has been carried out, particle 1 is occupying the position previously occupied by particle 2 and so on, $Y$ atoms remain at the corners of the base, and the configuration is considered as indistinguishable from the original one.

A study of Fig. (II.1) tells us that there are six covering operations which may be performed on the molecule in question. These operations are: (1) the identity operation in which all particles are left where they are, (2) a rotation of 120 degrees about the symmetry axis, (3) a rotation of 240 degrees about the symmetry axis, (4) a reflection of all particles through the plane which is perpendicular to the $Y$-plane and which contains particles 1 and 4, (5) reflection through a vertical plane containing 2 and 4, and (6) reflection through a vertical plane containing 3 and 4. Each of these covering operations results in a transformation which may be represented by the matrix equation:

$$\| X \| = \| a \| \, \| X' \|$$

where $\| X' \|$ is a column vector representing the coordinates of a particle prior to one of the covering operations; $\| X \|$ is a column vector representing the coordinates of the particle subsequent to the transformation, and, finally $\| a \|$ is the so-called matrix of the transformation. $\| a \|$ is obviously a mathematical representation of the operation.

The transformation matrices for the six covering operations which we have enumerated may be written out as follows:

$$E = \| E \| = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad A = \| C(120) \| = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$B = \| C(240) \| = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad C = \| \sigma_v(1,4) \| = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$D = \| \sigma_v(2,4) \| = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad F = \| \sigma_v(3,4) \| = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

In the above matrices, $C(\vartheta)$ represents a rotation through an angle $\vartheta$, and $\sigma_v(i,j)$ represents a reflection through a vertical plane containing particles $i$ and $j$.

Let us suppose that we perform the $A$ operation on the molecule and subsequently perform the $B$ operation, and let us represent the performance of these two successive operations as $BA$. When we rotate the molecule through 120 degrees ($A$) and subsequently through 240 degrees ($B$), we arrive at the same final result as if we had left everything where it was ($E$). We then agree that we may write $BA = E$. Let us then form a table as follows: In a top, index row we shall write the right member of a product, in our example $A$. On the left, index column we write the left hand member of the same product, for example, $B$. In the table proper we write the results of these various multiplications, again in our example, $E$. For our six transformation matrices we obtain:

|   | *E* | *A* | *B* | *C* | *D* | *F* |
|---|---|---|---|---|---|---|
| *E* | *E* | *A* | *B* | *C* | *D* | *F* |
| *A* | *A* | *B* | *E* | *F* | *C* | *D* |
| *B* | *B* | *E* | *A* | *D* | *F* | *C* |
| *C* | *C* | *F* | *D* | *E* | *A* | *B* |
| *D* | *D* | *C* | *F* | *A* | *E* | *B* |
| *F* | *F* | *D* | *C* | *B* | *A* | *E* |

Table II.1

as the multiplication table.

Several things may be noted from the multiplication table for our array of transformation matrices. (1) The array contains the so-called identity element, $E$. (2) The result of every possible multiplication of various members of the array appears in the table and is consequently in the array. (3) From the table we see that every member of the array possesses an inverse and that this inverse is in the array. For example: $AA^{-1} = E = AB$ so that $A^{-1} = B$. (4) Multiplication of two operators (as we have defined multiplication) is associative, that is to say: $(AB)C = A(BC)$. As we are, of course, aware, these four attributes of the array mean that, by definition, the array of matrices constitutes a group. This particular group has been generally designated as the symmetry point group $C_{3v}$. The fact that this is a group means that, in addition to a certain aesthetic value which quite impresses the mathematician, it possesses attributes which will be useful to us. In considering these, let us first remark that the element $X$ is the transform of the element $Q$ by the element $P$ if:

$$X = P^{-1}Q\,P$$

Further, two elements, one of which is the transform of the other, are said to be conjugate to each other. Finally, all elements conjugate to each other belong to the same class of the group. As a result of all this, the elements of the $C_{3v}$ group are subdivided into three classes; specifically, $E$ is in a class by itself, the rotations $A$ and $B$ are in the second class, species $A_1$, the reflections $C, D,$ and F fall into a third class, species $A_2$.

Let us approach our next consideration by writing, for example, the element $D$ as:

$$\Gamma(R) = D = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \Gamma^{(3)}(R) & 0 \\ 0 & \Gamma^{(1)}(R) \end{pmatrix} \qquad \text{(II.1)}$$

Now we could suppose that here we have performed a similarity transformation where the unit matrix was our transformation matrix and have reduced the "reducible representation" $\Gamma(R)$ to the two irreducible representations $\Gamma^{(1)}(R)$ and $\Gamma^{(3)}(R)$, these latter now appearing as square, step matrices in $\Gamma(R)$. It so happens that a group will have as many irreducible representations as there are different classes within the group. We thus are in need of one more, namely, $\Gamma^{(2)}(R)$ and the determination of it will furnish a convenient method for the introduction of several rather important facets of group theory.

We let the number of elements in the group be $g$ and the dimension of the matrices in the $i$-th irreducible representation be $d_i$. Now the easily verifiable orthogonality of the various irreducible representations leads to:

$$\sum_R \Gamma_{ab}^{(i)}(R)\, \overline{\Gamma_{cd}^{(j)}(R)} = \frac{g}{(d_i d_j)^{1/2}}\, \delta_{ij}\delta_{ac}\delta_{bd} \tag{II.2}$$

Further, if there are $n$ classes in the group:

$$\sum_{i=1}^{n} d_i^2 = g$$

or, for the specific case of the $C_{3v}$ group:

$$d_1^2 + d_2^2 + d_3^2 = 6$$

and, since $d_1 = 1$ and $d_3 = 2$:

$$d_2 = 1$$

and $\Gamma^{(2)}(R)$ will consist of $1 \times 1$ matrices. One may try the $\Gamma^{(2)}$ in Table II.2 in Table II.1 in order to verify the fact that this representation meets the necessary requirements for an irreducible representation.

| $E$ | $A$ | $B$ | $C$ | $D$ | $F$ | |
|---|---|---|---|---|---|---|
| $(1)$ | $(1)$ | $(1)$ | $(1)$ | $(1)$ | $(1)$ | $\Gamma^{(1)}$ |
| $(1)$ | $(1)$ | $(1)$ | $(-1)$ | $(-1)$ | $(-1)$ | $\Gamma^{(2)}$ |
| $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ | $\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$ | $\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$ | $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ | $\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$ | $\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$ | $\Gamma^{(3)}$ |

Table II.2

Now let us define the characters $\chi$ as the sums of the diagonal elements of the various matrices. A check of the characters of, say, $A$ and $B$ in the various representations shows these two elements of the same class to have the same character for a given irreducible representation. Identical characters for members of the same class proves to be a general situation, and one may construct a character table as follows:

| Species | $1 \cdot C_1(E)$ | $2 \cdot C_2(C_3)$ | $3 \cdot C_3(\sigma_v)$ | |
|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | $\Gamma^{(1)}$ |
| $A_2$ | 1 | 1 | $-1$ | $\Gamma^{(2)}$ |
| $E$ | 2 | $-1$ | 0 | $\Gamma^{(3)}$ |

Table II.3

Next we consider an arbitrary, reducible representative of the $C_{3v}$ group of character $\Xi$. Then this $\Xi$ may be expressed as the sum of the characters of the three irreducible representation as:

$$\Xi = a_1\chi^{(1)} + a_2\chi^{(2)} + a_3\chi^{(3)} \tag{II.3}$$

A consideration of Eq. (II.1) suffices to tell us that, for example:

$$\Xi_D = 1 \cdot \chi^{(1)} + 0 \cdot \chi^{(2)} + 1 \cdot \chi^{(3)}$$

but we need a slightly more general expression for the expansion coefficients, $a_i$, than this.

Writing Eq. (II.3) as:

$$\Xi = \sum_i a_i \chi^{(i)}$$

one may multiply through on the left by $\sum_{m=1}^{n} r_m$ and on the right by $\overline{\chi_m^{(j)}}$ and apply

$$\sum_{m=1}^{n} r_m \chi_m^{(1)} \overline{\chi_m^{(j)}} = g\delta_{ij} \tag{II.3}$$

with the result:

$$a_i = \frac{1}{g} \sum_{m=1}^{n} r_m \Xi_m \overline{\chi_m^{(j)}} \tag{II.4}$$

where $g$ is the number of elements in the group; $r_m$ is the number of elements in the $m$-th class; $\Xi$ is the character of our reducible representation in the $m$-th class, and, finally $\chi_m^{(j)}$ is the character of the $j$-th irreducible representation in the $m$-th class. We have obtained essentially all the group characteristics for which we shall have use, and we now apply these characteristics to our vibrational problem.

To begin with, let us suppose that we have found the normal coordinates of the vibrational problem, and further let us imagine there to be two non-degenerate and two twofold degenerate vibrations. Then:

$$T = \sum_{i=1}^{2} \dot{Q}_i^2 + \sum_{i=3}^{4} (\dot{Q}_{ia}^2 + \dot{Q}_{ib}^2) \tag{II.5a}$$

$$V = \sum_{i=1}^{2} k_i Q_i^2 + \sum_{i=3}^{4} k_i (Q_{ia}^2 + Q_{ib}^2) \tag{II.5b}$$

It is certainly apparent that a covering operation, such as we have detailed, will not affect the kinetic or potential energy. In order that this operation not affect the mathematical expressions for these entities, certain restrictions must be complied with. First, as concerns the non-degenerate coordinates. If $Q_1^2$ is to go into itself as a result of a covering operation then:

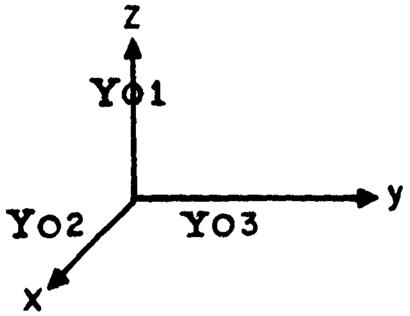
$$RQ_1 = \pm Q_1$$

In other words, only the $\Gamma^{(1)}$ or $\Gamma^{(2)}$ matrices of Table II.2 may operate on a non-degenerate coordinate such as $Q_1$. The value of this observation is more easily perceived by backing up slightly.

Let us suppose that Lagrange's secular determinant is set up in Cartesian coordinates so that, for the $XY_3$ model, the determinant is 12 x 12 and rotational, vibrational, and translational motions have not been separated. A la mode, we would next use the Eckart conditions for this separation, but it is here that group theory may be used to simplify the succeeding vibrational problem. Instead of simply selecting coordinates free of translational and rotational associations, we choose coordinates which react to the covering operations as we know our normal coordinates must. These are, of course, the so-called intermediate symmetry coordinates. For example, we know, after a fashion which we shall detail somewhat later, that two of the $XY_3$ vibrational coordinates must belong to Species $A_1$, that is, they go into themselves under all covering operations. Further, the potential function is not yet diagonalized, so that interactions between certain of the vibrational coordinates are allowed. The potential function must still be invariant with respect to the covering operations so that interactions are only allowed between intermediate symmetry coordinates of the same species. We then see that choosing intermediate symmetry coordinates has the effect of breaking the secular determinant into blocks of easier solution.

Let us conclude with a consideration of how one determines the number of vibrational coordinates belonging to each symmetry species.

Purely for reasons of simplified consideration let us consider a bent $XY_2$ model as illustrated in Fig. (II.2).



In this model a proper (boreal) rotation through an angle of 180° obviously comprises a covering operation. Now if $x_iy_iz_i$ are the coordinates of the $i$-th particle before a proper rotation and $x_i'y_i'z_i'$ those of the same particle after such a rotation, a study of Fig. (II.2) tells us that:

$$\begin{pmatrix} x_1' \\ y_1' \\ z_1' \\ x_2' \\ y_2' \\ z_2' \\ x_3' \\ y_3' \\ z_3' \end{pmatrix} = \left(\begin{array}{c|c} \begin{matrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{matrix} & 0 \\ \hline 0 & \begin{matrix} 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{matrix} \end{array}\right) \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} \qquad \text{(II.6)}$$

In Eq. (II.6) we note that the character of the matrix of this proper rotation — a group element — is given by:

$$\chi(C) = 1 + 2\cos\varphi$$
$$= u_c(1 + 2\cos\varphi) \qquad \text{(II.7)}$$

where $u_c = 1$ is the number of atoms unaffected by the proper rotation, in this case the $X$-atom. Eq. (II.7) then gives the total character — translational + rotational + vibrational — for the proper rotation through an angle $\varphi$.

Next we note that an improper rotation — that is, a proper rotation followed by a reflection through a plane perpendicular to the axis of rotation — may be made to correspond to the reflection $C$, $D$, and $F$ of Table (II.1). For the obtention of the total character under such a performance we may follow a procedure precisely similar to that utilized in obtaining Eq. (II.7) to obtain:

$$\chi(S) = u_s(-1 + 2\cos\varphi) \qquad \text{(II.8)}$$

where now $u_s$ is the number of atoms which are unchanged by the improper rotation.

The unit matrix will replace the matrix of Eq. (II.6) for the identity operation. As a consequence:

$$\chi(E) = 3N \qquad \text{(II.9)}$$

We thus have the total character under the various covering operations. Let us again consider Eq. (II.6). When we transform from the coordinates of this equation to coordinates three of which describe translational motion, three of which describe rotation, and three of which describe internal vibrational motion, this total character should not change. That is to say, the character should be invariant to this coordinate transformation. If we let $XYZ$ be the translational coordinates, $\vartheta$, $\varphi$, $\psi$ the rotational coordinates and $q_1q_2q_3$ the vibrational, the transformation inferred by a covering operation will be:

$$\begin{pmatrix} X' \\ Y' \\ Z' \\ \vartheta' \\ \varphi' \\ \psi' \\ q_1' \\ q_2' \\ q_3' \end{pmatrix} = \left(\begin{array}{c|c|c} \text{Translational} & & 0 \\ \hline 0 & \text{Rotational} & \\ \hline & & \text{Vibrational} \end{array}\right) \begin{pmatrix} X \\ Y \\ Z \\ \vartheta \\ \varphi \\ \psi \\ q_1 \\ q_2 \\ q_3 \end{pmatrix} \tag{II.10}$$

If we call $\chi_{\text{total}}$ the total character, the invariance of $\chi_{\text{total}}$ means that the matrix of the covering operation in Eq. (II.10) will have the same character as the matrix of Eq. (II.6). Let us now designate the translational character, the rotational character, and the vibrational character as $\chi_{\text{trans}}$, $\chi_{\text{rot}}$, and $\Xi_{\text{vib}}$ respectively. Then a consideration of Eq. (II.10) tells us that:

$$\Xi_{\text{vib}} = \chi_{\text{total}} - \chi_{\text{trans}} - \chi_{\text{rot}} \tag{II.11}$$

If we are desirous of obtaining $\Xi_{\text{vib}}$, the next step would appear to be the determination of $\chi_{\text{trans}}$ and $\chi_{\text{rot}}$.

A consideration of Eq. (II.10) is sufficient to tell us that the translational coordinates simply transform as a vector of components $X$, $Y$, and $Z$ -- in a given frame. Thus, our remarks leading to Eqs. (II.7), (II.8), and (II.9) should be equally applicable here. One thus obtains:

$$\chi_{\text{trans}}(C) = 1 + 2\cos\varphi \tag{II.12}$$

$$\chi_{\text{trans}}(S) = -1 + 2\cos\varphi \tag{II.13}$$

Finally then, we must needs find $\chi_{\text{rot}}$. To do this let us first determine the manner in which the angular coordinates $\vartheta$, $\varphi$, and $\psi$ transform.

Let us first recall that the components of the angular momentum **L** are functions of $\dot\vartheta$, $\dot\varphi$, and $\dot\psi$, and, we might note, transform as do $\vartheta$, $\varphi$, and $\psi$. Thus, one may express **L** in Cartesian coordinates and determine the manner in which it transforms from one Cartesian form to another. Now:

$$\mathbf{L} = m_i \sum_i \mathbf{r}_i \times \mathbf{v}_i \doteq m_i \sum \mathbf{r}_i \times \frac{\delta \mathbf{r}_i}{\delta t}$$

or:

$$\delta t\, \mathbf{L} = m_i \sum \mathbf{r}_i \times \delta \mathbf{r}_i$$

so that:

$$\delta t\, L_x = m_i \left[y\delta z - z\delta y\right] \tag{II.14a}$$

$$\delta t\, L_y = m_i \left[z\delta x - x\delta z\right] \tag{II.14b}$$

$$\delta t\, L_z = m_i \left[x\delta y - y\delta x\right] \tag{II.14c}$$

The expression for the transformation of a position vector under a proper rotation may be utilized in Eqs. (II.14) to determine the manner in which the components of $L$ transform. One finds:

$$\begin{pmatrix} L_x' \\ L_y' \\ L_z' \end{pmatrix} = \begin{pmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} \tag{II.15}$$

Under an improper rotation the manner of transformation is given by:

$$\begin{pmatrix} L_x' \\ L_y' \\ L_z' \end{pmatrix} = \begin{pmatrix} -\cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & -\cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} \tag{II.16}$$

Since $\vartheta$, $\varphi$, and $\psi$ will transform in the same fashion:

$$\chi_{\text{rot}}(S) = 1 + 2 \cos \varphi \qquad \text{(II.17)}$$

$$\chi_{\text{rot}}(S) = 1 - 2 \cos \varphi \qquad \text{(II.18)}$$

We may now substitute Eqs. (II.7), II.12), and (II.17) into Eq. (II.11) in order to find the character of the vibrational coordinates under a proper rotation:

$$\begin{aligned} \Xi_{\text{vib}} &= u_c(1 + 2 \cos \varphi) - (1 + 2 \cos \varphi) - (1 + 2 \cos \varphi) \\ &= (u_c - 2)(1 + 2 \cos \varphi) \end{aligned} \qquad \text{(II.19)}$$

The character of the vibrational coordinates under an improper rotation may be found by substituting Eqs. (II.8), (II.13), and (II.18) into Eq. (II.11):

$$\begin{aligned} \Xi_{\text{vib}}(S) &= u_s(-1 + 2 \cos \varphi) - (-1 + 2 \cos \varphi) - (1 - 2 \cos \varphi) \\ &= u_s(-1 + 2 \cos \varphi) \end{aligned} \qquad \text{(II.20)}$$

**Finally:**

$$\Xi_{\text{vib}}(E) = 3N - 6 \qquad \text{(II.21)}$$

Let us now apply our general Eqs. (II.19)–(II.21) to the pyramidal $XY_3$ of Fig. (II.1) to obtain:

| | $\Xi_{\text{vib}}(E)$ | $\Xi_{\text{vib}}(C)$ | $\Xi_{\text{vib}}(\sigma)$ |
|---|---|---|---|
| $\Gamma_{\text{vib}}$ | 6 | 0 | 2 |

Table II.4

Thus, the transformation matrices, which transform the vibrational coordinates according to the covering operations of the $C_{3v}$ group, are possessed of characters which give a group representation as indicated in Table (II.4). Now let us compare this to Table (II.3), the table of the irreducible representations.

We know that the reducible representation of Table II.4 is expressible as a linear combination of the irreducible representations of Table II.3 with the coefficients of this expansion given by Eq. (II.4). If we apply Eq. (II.4) to Tables (II.3) and (II.4) we find:

$$\Gamma_{\text{vib}} = 2 \cdot \Gamma^{(1)} + 0 \cdot \Gamma^{(2)} + 2 \cdot \Gamma^{(3)} \qquad \text{(II.22)}$$

Next, let us consider rather carefully what we have determined.

We consider only the behavior of the vibrational coordinates under a proper rotation. Eq. (II.22) tells us that there will be two of the $\Gamma^{(1)}$ representations and two of the $\Gamma^{(3)}$ which means, according to Table II.2, that:

$$\begin{pmatrix} q_1' \\ q_2' \\ q_{3a}' \\ q_{3b}' \\ q_{4a}' \\ q_{4b}' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & a & 0 & 0 \\ 0 & 0 & -a & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & -a \\ 0 & 0 & 0 & 0 & a & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} q_1 \\ q_2 \\ q_{3a} \\ q_{3b} \\ q_{4a} \\ q_{4b} \end{pmatrix} \qquad \text{(II.23)}$$

where the $q_i$ are the normal coordinates. We note that $a = \dfrac{\pm\sqrt{3}}{2}$ depending on the amount of rotation.

Our conclusions in connection with Eqs. (II.5) now tell us the type of normal coordinates which are to be expected. From Eq. (II.23), two non-degenerate coordinates, $q_1$ and $q_2$, are to be expected. We emphasize the fact that this is the same number as the number of non-degenerate representations $\Gamma^{(1)}$. Further, two twofold degenerate coordinates, the same number as the number of twofold degenerate representations $\Gamma^{(3)}$, are to be anticipated.

Thus, by determining the number of non-degenerate representations in the expansion Eq. (II.22), one finds the number of non-degenerate vibrational modes of which the molecule is possessed and so on for twofold and threefold degenerate vibrations.

# APPENDIX III

## THE MOLECULAR HAMILTONIAN

In obtaining Eq. (2.22), which is what we propose to do, let us begin by writing down Eq. (2.6):

$$2T = M\dot{\rho}^2 + \sum_i m_i v_i^2 + \sum_{\alpha}\sum_{\beta} I_{\alpha\beta}\omega_\alpha\omega_\beta + 2\underline{\omega}\cdot \sum_i m_i \mathbf{r}_i \times \mathbf{v}_i \qquad (2.6)$$

We have observed in Sec. (2.2) — albeit, after a rather cavalier fashion — the manner in which the obtention of normal vibrational coordinates results in the normalization and diagonalization of the vibrational kinetic energy function, namely:

$$\sum m_i v_i^2 = \sum_k \dot{q}_k^2$$

Now let us recall that $\mathbf{r}_i$ may be expressed as the sum of a vibrational equilibrium component $\mathbf{r}_i^0$ and a vibration induced component $\mathbf{r}_i'$. Ergo:

$$\mathbf{r}_i = \mathbf{r}_i^0 + \mathbf{r}_i'$$

In Sec. (2.2) the Eckart conditions — Eqs. (2.16) — were utilized for the purpose of restricting the problem to an internal vibrational one. Here, let us use a modified form of Eq. (2.16a), to wit,

$$\sum m_i \mathbf{r}_i^0 \times \mathbf{v}_i = 0$$

so that Eq. (2.6) becomes:

$$2T = \sum_{\alpha}\sum_{\beta} I_{\alpha\beta}\,\omega_\alpha\omega_\beta + \sum_i m_i v_i^2 + 2\underline{\omega}\cdot\sum_i m_i \mathbf{r}_i' \times \mathbf{v}_i \qquad (\text{III}.1)$$

in which the translational kinetic energy has been neglected.

We will surely agree that $\sum m_i \mathbf{r}_i' \times \mathbf{v}_i$ is — when expanded — an expression in terms of the particle coordinates and time derivatives thereof, and, further, that the $q_k$ are also functions of these coordinates. It then follows that dogged and reasonably intelligent application will yield a transformation like this:

$$\sum_i m_i(\mathbf{r}_i' \times \mathbf{v}_i)_x = \sum_k X_k \dot{q}_k \qquad (\text{III}.2\text{a})$$

$$\sum_i m_i(\mathbf{r}_i' \times \mathbf{v}_i)_y = \sum_k Y_k \dot{q}_k \qquad (\text{III}.2\text{b})$$

$$\sum_i m_i(\mathbf{r}_i' \times \mathbf{v}_i)_z = \sum_k Z_k \dot{q}_k \qquad (\text{III}.2\text{c})$$

where the $X_n$, $Y_n$, $Z_n$ may be expressed as functions of the $q_n$ and certain constant coefficients.

Eq. (III.1) then becomes:

$$2T = \sum_{\alpha}\sum_{\beta} I_{\alpha\beta}\omega_\alpha\omega_\beta + 2\omega_x\sum_k X_k\dot{q}_k + 2\omega_y\sum_k Y_k\dot{q}_k + 2\omega_z\sum_k Z_k\dot{q}_k + \sum_k \dot{q}_k^2 \qquad (\text{III}.3)$$

Now in order to obtain a Hamiltonian from this equation it will first be necessary to re-express it in terms of momentum since it may be recalled that Hamilton's function must needs be expressed in terms of conjugate momenta and coordinates.

There would appear to be no question but that the angular momentum of our system is:

$$\mathbf{P} = \sum_i m_i \mathbf{r}_i \times \dot{\mathbf{r}}_i = \sum_i m_i \mathbf{r}_i \times (\underline{\omega} \times \mathbf{r}_i) + \sum m_i \mathbf{r}_i \times \mathbf{v}_i \qquad (\text{III}.4)$$

since, in a moving frame:

$$\dot{\mathbf{r}} = \mathbf{v} + \underline{\omega} \times \mathbf{r}$$

In any case

$$P_\alpha = \frac{\partial T}{\partial \omega_\alpha}$$

which may be applied to Eq. (III.3) with the result:

$$P_x = \frac{\partial T}{\partial \omega_x} = I_{xx}\omega_x - I_{xy}\omega_y - I_{xz}\omega_z + \sum_k X_k \dot{q}_k \qquad \text{(III.5a)}$$

$$P_y = \frac{\partial T}{\partial \omega_y} = - I_{xy}\omega_x + I_{yy}\omega_y - I_{yz}\omega_z + \sum_k Y_k \dot{q}_k \qquad \text{(III.5b)}$$

$$P_z = \frac{\partial T}{\partial \omega_z} = - I_{xz}\omega_x - I_{yz}\omega_y - I_{zz}\omega_z + \sum_k Z_k \dot{q}_k \qquad \text{(III.5c)}$$

$$P_k = \frac{\partial T}{\partial q_k} = \dot{q}_k + X_k\omega_x + Y_k\omega_y + Z_k\omega_z \qquad \text{(III.5d)}$$

Eqs. (III.5a)-(III.5c) may first be employed in writing Eq. (III.3) as:

$$2T = P_x\omega_x + P_y\omega_y + P_z\omega_z + \Sigma p_k\dot{q}_k \qquad \text{(III.6a)}$$

in which we may substitute for $\dot{q}_k$ from Eq. (III.5d) to obtain:

$$2T = (P_x - p_x)\omega_x + (P_y - p_y)\omega_y + (P_z - p_z)\omega_z + \sum_k p_k^2 \qquad \text{(III.6b)}$$

wherein $p_x = \Sigma X_k p_k$, etc.

Again let us substitute for $\dot{q}_k$ from Eq. (III.5d), this time into Eqs. (III.5a)-(III.5c):

$$\begin{aligned} P_x - p_x &= A\omega_x - D\omega_y - F\omega_z \\ P_y - p_y &= - D\omega_x + B\omega_y - E\omega_z \\ P_z - p_z &= - F\omega_x - E\omega_y + C\omega_z \end{aligned} \qquad \text{(III.6c)}$$

or:

$$\|P_\alpha - p_\alpha\| = \|A\|\,\|\omega_\beta\| \qquad \text{(III.6d)}$$

where:

$$\|A\| = \begin{pmatrix} A & -D & -F \\ -D & B & -E \\ -F & -E & C \end{pmatrix} \qquad \text{(III.6e)}$$

The $\omega_\beta$ coefficients are:

$$\begin{aligned} &A = I_{xx} - \Sigma X_k^2 \ ; \quad B = I_{yy} - \Sigma Y_k^2 \ ; \quad C = I_{zz} - \Sigma Z_k^2 \\ &D = I_{xy} + \Sigma X_k Y_k \ ; \quad E = I_{yz} + \Sigma Y_k Z_k \ ; \quad F = I_{xz} + \Sigma X_k Z_k \end{aligned} \qquad \text{(III.6f)}$$

We multiply Eq. (III.6d) through on the left by $\|A\|^{-1*}$ with the results:

$$\|\omega_\beta\| = \|A\|^{-1}\,\|P_\alpha - p_\alpha\| = \|\chi\|\,\|P_\alpha - p_\alpha\| \qquad \text{(III.7)}$$

and we may substitute into Eq. (III.6b) from Eq. (III.7):

$$\begin{aligned} 2T = {} & \chi_{xx}(P_x - p_x)^2 + \chi_{yy}(P_y - p_y)^2 + \chi_{zz}(P_z - p_z)^2 + 2\chi_{xy}(P_x - p_x)(P_y - p_y) \\ & + 2\chi_{yz}(P_y - p_y)(P_z - p_z) + 2\chi_{xz}(P_z - p_z)(P_x - p_x) + \Sigma p_k^2 \end{aligned} \qquad \text{(III.8a)}$$

We have already noted that:

$$p_x = \Sigma X_k p_k \ ; \quad p_y = \Sigma Y_k p_k \ ; \quad p_z = \Sigma Z_k p_k \qquad \text{(III.8b)}$$

---

*We recall that $a_{ij}^{-1} = \dfrac{A_{ji}}{|a|}$

and a consideration of these relations is sufficient to show that the $p_\alpha$ are the components of the angular momentum which arises from the internal vibration of the molecule. It now remains to transform Eq. (III.8a) to a quantum form.

We agree that the quantum mechanical Hamiltonian operator for a system of $i$ particles is:

$$H = \hbar^2 \Sigma \nabla_i^2 + V \qquad \text{(III.9)}$$

This expression holds in any coordinate system so long as we recall from tensor theory that

$$\nabla^2 = g^{-1/2} \frac{\partial}{\partial q^i} g^{ij} g^{1/2} \frac{\partial}{\partial q^j} \qquad \text{(III.10a)}$$

where:

$$g_{ij} = \sum_l \frac{\partial x^l}{\partial q^i} \frac{\partial x^l}{\partial q^j} \qquad \text{(III.10b)}$$

and some further definitions remain to be accomplished.

In the first place $x^l$ refers to one of the three Cartesian coordinates while $q^i$ and $q^j$ may refer to one of the coordinates in whatever type of frame we transform to. We insist that the transformation is *from* a Cartesian frame, however, and the reason for this is of some importance, if obvious.

Schrodinger originally established that one replaced $p_x$ by $-i\hbar\frac{\partial}{\partial x}$, $p_y$ by $-i\hbar\frac{\partial}{\partial y}$, etc. so that the Cartesian $p^2$ is replaced by the Cartesian $-\hbar^2\nabla^2$. Actually $-\hbar^2\nabla^2$ replaces $p^2$ in any coordinate system, if $\nabla^2$ is as given by Eq. (III.10a) but the partial derivative does not replace the squared momentum component.

As an example of the $g_{ij}$:

$$||g_{ij}|| = \begin{pmatrix} 1 & 0 & 0 \\ 0 & r^2 & 0 \\ 0 & 0 & r^2 \sin^2 \vartheta \end{pmatrix}$$

for the transformation from Cartesian to spherical polar coordinates.

Finally, $g$ is normally defined as:

$$g = \det ||g_{ij}||$$

If $p_i = -\hbar \frac{\partial}{\partial q_i}$ where the $p_i$ and $q_i$ are arbitrary and conjugate, then Eq. (III.9) may thus be rewritten as:

$$H = \tfrac{1}{2} g^{-1/2} \sum_{i,j} p_i g^{ij} g^{1/2} p_j + V \qquad \text{(III.11a)}$$

where

$$||g^{ij}|| = ||g_{ij}||^{-1}$$

In order to conform with the Wilson and Howard notation we redefine $g$ as:

$$g = \det ||g^{ij}||$$

so that Eq. (III.11a) becomes:

$$H = \tfrac{1}{2} g^{\frac{1}{2}} \sum_{i,j} p_i g^{ij} g^{-\frac{1}{2}} p_j + V \qquad \text{(III.11b)}$$

which reduces to:

$$H = \tfrac{1}{2} \Sigma\, g^{ij} p_i p_j + V \qquad \text{(III.12)}$$

for the classical case in which the various factors commute.

Now let us introduce a new set of momenta, $P_m$ such that

$$p_i = \sum_m s_{im} P_m \tag{III.13}$$

where the $P_m$ are not conjugate to any set of coordinates yet established.

We may utilize Eq. (III.12) to obtain an expression for the kinetic energy of our system in terms of the new set of momenta:

$$2T = \sum_{m,n} G^{mn} P_m P_n \tag{III.14a}$$

where

$$G^{mn} = \sum_{i,j} s_{im} g^{ij} s_{jn} \tag{III.14b}$$

Let us next suppose that the Hamiltonian may be expressed as:

$$H = \frac{1}{2} G^{\frac{1}{4}} \sum_{m,n} P_m G^{mn} G^{-\frac{1}{4}} P_n + V \tag{III.15}$$

which we shall see will require that certain conditions be fulfilled (Eqs. (III.3), (III.14b)), and the fact that $G = \det G^{mn} = s^2 g$ may be used in Eq. (III.5) with the result:

$$H = \frac{1}{2} g^{\frac{1}{4}} \sum_{i,j,k,m} s s^{mi} p_i s_{km} s^{-1} g^{kj} g^{-\frac{1}{4}} p_j + V \tag{III.16}$$

It would appear reasonable to require this equation to reduce to Eq. (III.11a), but this reduction means that:

$$\sum_{m,i} s^{mi} p_i s_{km} = \frac{1}{2} p_k s \tag{III.17}$$

The $p_i$ may now be taken as $p_\theta$, $p_\varphi$, $p_\xi$, and $p_k$, that is the momenta conjugate to the three Eulerian angles and to the normal coordinates. The $P_m$ of Eq. (III.13) are, of course, the $P_\alpha$ of Eq. (III.8a).

As an example,

$$P_x = \frac{\partial T}{\partial \omega_x} = \frac{\partial T}{\partial \dot\theta}\frac{\partial \dot\theta}{\partial \omega_x} + \frac{\partial T}{\partial \dot\varphi}\frac{\partial \dot\varphi}{\partial \omega_x} + \frac{\partial T}{\partial \dot\xi}\frac{\partial \dot\xi}{\partial \omega_x} = \frac{\partial \dot\theta}{\partial \omega_x} p_\theta + \frac{\partial \dot\varphi}{\partial \omega_x} p_\varphi + \frac{\partial \dot\xi}{\partial \omega_x} p_\xi$$

and the relations among the Eulerian angles may be used to evaluate the partial derivatives.

Finally:

$$P_i = \sum_m n^{im} p_m \tag{III.18a}$$

where:

$$n^{im} p_m = \begin{pmatrix} \cos\xi \csc\varphi & \sin\xi & \cos\xi \cot\varphi & 0 \\ \sin\xi \csc\varphi & \cos\xi & -\sin\xi \cot\varphi & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_\theta \\ p_\varphi \\ p_\xi \\ p_k \end{pmatrix} \tag{III.18b}$$

The transformation:

$$P_i \to p_\alpha = \sum_m t^{im} P_\alpha$$

where:

$$t^{im} = \begin{pmatrix} 1 & 0 & 0 & -\Sigma X_k \\ 0 & 1 & 0 & -\Sigma Y_k \\ 0 & 0 & 1 & -\Sigma Z_k \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

is next carried out so that, in toto

$$||P_\alpha - p_\alpha|| = ||t^{im}||\,||n^{im}|| - ||p_i|| = ||s_{im}||^{-1}\,||p_i|| = ||s^{im}||\,||p_i|| \qquad \text{(III.19)}$$

and, it is apparent that the $s^{im}$ satisfy the conditions of Eq. (III.17). This means that we may obtain a Hamiltonian from Eq. (III.8a).

A comparison of Eq. (III.12) with Eq. (III.8a) is sufficient to show that the $g^{ij}$ of the former equation correspond to the $\chi_{\alpha\beta}$ of the latter. As a consequence, then, we may write, in analogy with Eq. (III.11b), the Hamiltonian corresponding to Eq. (III.8a):

$$H = \tfrac{1}{2}\,\chi^{\frac{1}{4}} \sum_{\alpha,\beta} (P_\alpha - p_\alpha)\chi_{\alpha\beta}\chi^{-\frac{1}{2}}(P_\beta - p_\beta) + \tfrac{1}{2}\chi^{\frac{1}{4}} \sum_k p_k\,\chi^{-\frac{1}{2}} p_k + V \qquad \text{(III.20)}$$

In order to obtain Eq. (2.22) we must expand this expression remembering that $P_\alpha$ and $p_\alpha$ commute — the rotational and vibrational motions are independent — and, in addition, the $P_\alpha$ and $\chi_{\alpha\beta}$ commute since the latter are functions only of the normal vibrational coordinates. The expansion is then quite straightforward and we obtain:

$$H = \tfrac{1}{2}\sum_{\alpha,\beta}\chi_{\alpha\beta}P_\alpha P_\beta - \sum_\alpha \Upsilon_\alpha P_\alpha + \tfrac{1}{2}\sum_{\alpha,\beta}\chi^{\frac{1}{4}}\,p_\alpha\chi_{\alpha\beta}\chi^{-\frac{1}{2}}\,p_\beta + \tfrac{1}{2}\sum \chi^{\frac{1}{4}}\,p_i\chi^{-\frac{1}{2}}\,p_i + V(q_i) \qquad (2.22)$$

where:

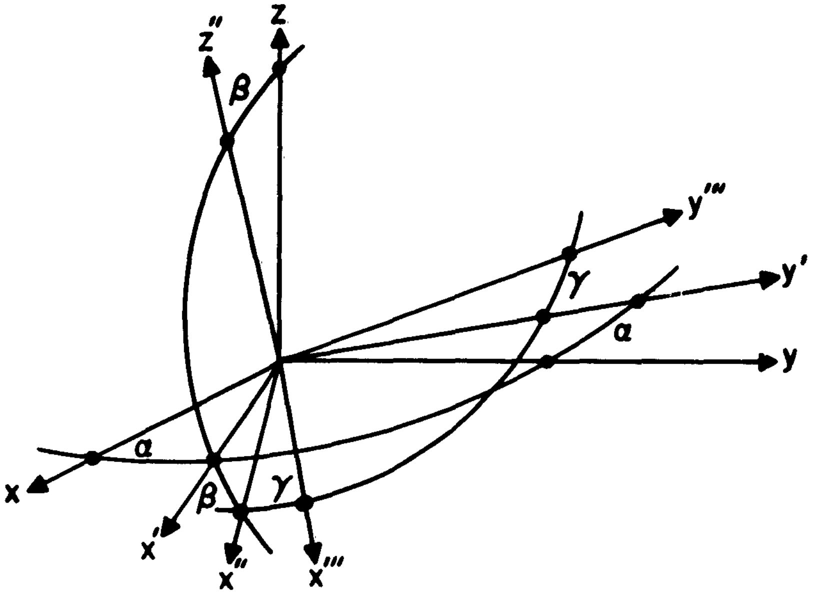
$$\Upsilon_\alpha = \sum_\beta \left\{2\chi_{\alpha\beta}p_\beta + (p_\beta\chi_{\alpha\beta}) + \chi_{\alpha\beta}\chi^{\frac{1}{4}}\,(p_\beta\chi^{-\frac{1}{4}})\right\} \qquad (2.23)$$

In Eq. (2.23) the $p_\beta$ appearing in the parentheses operate only on those terms appearing within the parentheses.

# APPENDIX IV

## THE EULERIAN ANGLES

In considering these rotational coordinates we first turn our attention to the figure:



Now let us begin by remarking the following transformation:

$$\begin{pmatrix} x''' \\ y''' \\ z''' \end{pmatrix} = (a) \begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} = (a')(a) \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = (a'')(a')(a) \begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad \text{(IV.1)}$$

where, from the figure, we may quite readily find:

$$(a'')(a')(a) = \begin{pmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\beta\sin\gamma \\ -\cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix} \qquad \text{(IV.2)}$$

The angular velocities $\dot{\alpha}$, $\dot{\beta}$, and $\dot{\gamma}$ will be measured along $z$, the so-called "line of nodes" $y'$, and $z''$ respectively. In the not unusual circumstance that we are desirous of expressing the angular velocity components in terms of the time derivatives of the Eulerian angles, we could proceed as follows:

Let us determine $\omega_{x'''}$. Firstly $\dot{\alpha}$ is directed along the $z$-axis. Thus from Eq. (IV.2) it has a component $-\sin\beta\cos\gamma$ along the $x'''$-axis. Next $\dot{\beta}$ is directed along the $y'$-axis so that we may see from Figure (IV.1) that it has a component $\sin\gamma$ along the $x'''$-axis. Finally $\dot{\gamma}$ is directed along the $z''$-axis and, since this axis is perpendicular to the $x'''$-axis, will have no component along this $x'''$-axis. Thus:

$$\omega_{x'''} = -\sin\beta\cos\gamma\dot{\alpha} + \sin\gamma\dot{\beta}$$

In like manner are $\omega_{y'''}$ and $\omega_{z'''}$ obtained:

$$\begin{pmatrix} \omega_{x'''} \\ \omega_{y'''} \\ \omega_{z'''} \end{pmatrix} = \begin{pmatrix} -\sin\beta\cos\gamma & \sin\gamma & 0 \\ \sin\beta\sin\gamma & \cos\gamma & 0 \\ \cos\beta & 0 & 1 \end{pmatrix} \begin{pmatrix} \dot{\alpha} \\ \dot{\beta} \\ \dot{\gamma} \end{pmatrix}$$

# APPENDIX V

## SOME POLYNOMIALS AND THEIR EQUATIONS

Gauss' Hypergeometric Equation may be written as:

$$(x^2 - x)y'' + [(1 + \alpha + \beta)x - \gamma]y' + \alpha\beta y = 0 \qquad \text{(V.1a)}$$

where $\alpha$, $\beta$, and $\gamma$ are constants. The Hypergeometric Series (Function),

$$y = F(\alpha,\beta,\gamma;x) = \frac{1}{0!} + \frac{\alpha\beta}{1!\gamma}x + \frac{\alpha(\alpha+1)\beta(\beta+1)}{2!\,\gamma(\gamma+1)}x^2 + \ldots \qquad \text{(V.1b)}$$

furnishes one solution to this equation.

If, in Eq. (V.1a), $x$ is replaced by $\frac{1}{2}(1 - x)$, and $\alpha$, $\beta$ and $\gamma$ are replaced by $l + 1$, $- l$, and 1 respectively, there results Legendre's Equation:

$$(1 - x^2)y'' - 2xy' + l(l + 1)y = 0 \qquad \text{(V.2a)}$$

one solution of which is the Legendre Polynomial:

$$y = P_l(x) = \frac{1\cdot3\cdot5\ldots(2l-1)}{l!}\left\{x^l - \frac{l(l-1)}{2(2l-1)}x^{l-2} + \frac{l(l-1)(l-2)(l-3)}{2\cdot4(2l-1)(2l-3)}x^{l-4}\ldots\right\} \quad l = 0,1,2\ldots \qquad \text{(V.2b)}$$

A slight modification of Eq. (V.2a) results in:

$$(1 - x)y'' - 2xy' + \left[l(l + 1) - \frac{m^2}{1 - x^2}\right]y = 0 \qquad \text{(V.3a)}$$

whose solution is provided by the Associated Legendre Function:

$$y = (1 - x^2)^{m/2}\frac{d^m}{dx^m}P_l(x) \qquad \begin{matrix} l = 0,1,2,\ldots \\ m = 0,1,2\ \ldots \end{matrix} \qquad \text{(V.3b)}$$

The oft-encountered Laguerre Equation may be written as:

$$xy'' + (1 - x)y' + \alpha y = 0 \qquad \text{(V.4a)}$$

a solution of which is the Laguerre Polynomial:

$$y = L_n(x) = (-1)^n\left(\frac{x^n}{0!} - \frac{n^2}{1!}x^{n-1} + \frac{n^2(n-1)^2}{2!}x^{n-2} + \ldots + (-1)^n n!\right); \quad n = 0,1,\ldots \qquad \text{(V.4b)}$$

Further, the Associated Laguerre Polynomial,

$$y = \frac{d^k}{dx^k}L_n(x) = L_n{}^k(x) \qquad \begin{matrix} k = 0,1,2,\ldots, \\ n = 0,1,2,\ldots \end{matrix} \qquad \text{(V.5a)}$$

arises from the equation:

$$xy'' - (k + 1 - x)y' + (\alpha - k)y = 0 \qquad \text{(V.5b)}$$

and the Associated Laguerre Function,

$$y = e^{-k/2}x^{(k-1)/2}L_n{}^k(x) \qquad \begin{matrix} k = 0,1,2,\ldots \\ n = 0,1,2,\ldots \end{matrix} \qquad \text{(V.6a)}$$

is one solution to:

$$xy'' + 2y' + \left[n - \frac{k-1}{2} - \frac{x}{4} - \frac{k^2-1}{4x}\right]y = 0 \qquad \text{(V.6b)}$$

Hermite's Equation,

$$y'' - 2xy' + 2\alpha y = 0 \tag{V.7a}$$

yields the Hermite Polynomial:

$$y = H_n(x) = \frac{(2x)^n}{0!} - \frac{n(n-1)}{1!}(2x)^{n-2} + \frac{n(n-1)(n-2)(n-3)}{2!}(2x)^{n-4} \quad n = 0,1,2,\ldots \tag{V.7b}$$

Finally, Bessel's equation:

$$x^2y'' + xy + (x^2 - n^2)y = 0 \tag{V.8a}$$

has solutions of many forms, but we note only the Bessel function of order $n$

$$y = J_n(x) = \sum_{i=1}^{\infty} \frac{(-1)^i}{\Gamma(i+1)\Gamma(i+n+1)}\left(\frac{x}{2}\right)^{n+2i} \tag{V.8b}$$

as an example of one of these.

# APPENDIX VI

## THE *WKB* APPROXIMATION

It would appear reasonable to suppose that we may write the Schrodinger equation for any one dimensional situation as:

$$\frac{d^2\psi}{dx^2} + k_1^2(x)\psi = 0 \qquad k_1 > 0 \tag{VI.1a}$$

where:

$$k_1(x) = \frac{1}{\hbar}\sqrt{2\mu\,[E - V(x)]} \tag{VI.1b}$$

or:

$$\frac{d^2\psi}{dx^2} - k_2^2(x)\psi = 0 \qquad k_2 > 0 \tag{VI.2a}$$

where:

$$k_2(x) = \frac{1}{\hbar}\sqrt{2\mu\,[V(x) - E]} \tag{VI.2b}$$

The real basis for the *WKB* approximation is quite simple in that it amounts to an assumed eigenfunction of the form:

$$\psi(x) = Ae^{i\frac{u(x)}{\hbar}} \tag{VI.3a}$$

where $u(x)$ is presumed expanded in powers of $\hbar$ as follows:

$$u = u_0 + \hbar u_1 + \hbar^2 u_2 + \ldots \tag{VI.3b}$$

Let us, as an example, substitute Eq. (VI.3a) into Eq. (VI.1a) with the result:

$$i\hbar u'' - u_1^2 + \hbar^2 k_1^2 = 0 \tag{VI.4a}$$

This substitution is followed by yet another; specifically, we substitute Eq. (VI.3b) into Eq. (VI.4a) and separate the result of this operation into a series of equations each of which contains the coefficient of the same order of $\hbar$:

$$- u_0' + 2\mu(E - V) = 0 \tag{VI.4b}$$

$$iu_0'' - 2u_0'u_1' = 0 \tag{VI.4c}$$

The differential equations of Eqs. (VI.4b) and (VI.4c) may be handled by quite ordinary methods in which case they yield solutions:

$$u_0(x) = \pm B_1\hbar \int k_1(x)dx \;\; ; \;\; u_1(x) = \tfrac{1}{2}\, iB_2 ln\, k_1(x) \tag{VI.5a}$$

In most cases it has been supposed that this first order of approximation is sufficient, and when, under this assumption, we substitute Eq. (VI.5a) into Eq. (VI.3b) and then substitute this latter equation into Eq. (VI.3a), we find:

$$\psi(x) = A_1k_1^{-\frac{1}{2}} \exp\left(\pm i \int k_1dx\right) \quad \text{for} \quad V < E \tag{VI.5b}$$

In like manner it may be shown that:

$$\psi(x) = A_2k_2^{-\frac{1}{2}} \exp\left(\pm \int k_2dx\right) \quad \text{for} \quad V > E \tag{VI.5c}$$

The solutions Eq. (VI.5c) are admittedly an approximation, and it seems straightforward to ask under what conditions this approximation may be expected to be valid. In order to determine this let us first look to Eq. (VI.3b), since this series must surely be convergent for the approximation to be a valid one. We ask under what conditions will succeeding terms in this latter equation decrease with reasonable rapidity, that is, under what conditions will $\hbar \frac{u_1}{u_0}$ be small since we are not carrying the approximations any further than to include these terms.

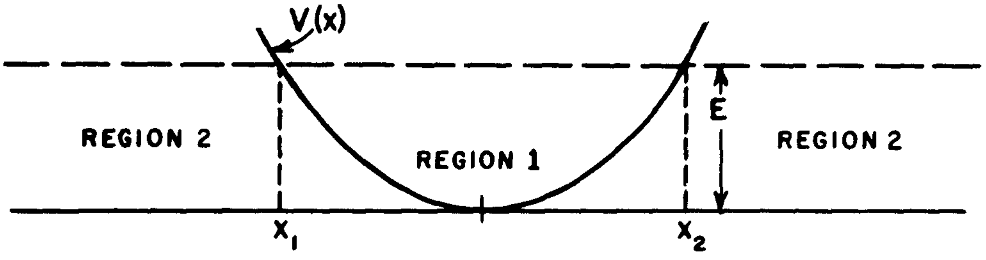
Now $u_0$ increases monotonically so long as $k_1(x)$ is positive since it is simply a measure of the area under the $k_1(x)$ curve. Thus, the rate of change of this function may be expected to be positive and greater than one when our ratio $\hbar \frac{u_1'}{u_0'}$ is small. As a consequence the ratio $\hbar \frac{u_1}{u_0}$ will be small when $\hbar \frac{u_1'}{u_0'}$ is small. From this we may obtain a more meaningful validity equation. Eq. (VI.5a) yields:

$$\left| \hbar \frac{u_1'}{u_0'} \right| = \left| \frac{k_1'}{2k_1^2} \right| \ll 1 \tag{VI.6a}$$

We may recall that the Broglie matter wavelength is $2\pi/k_1$ in the $k_1$ region in our present considerations. This means that Eq. (VI.6) may be expressed as:

$$\frac{\lambda}{4\pi} \left| \frac{dk_1}{dx} \right| \ll k_1 \tag{VI.6b}$$

From this expression it becomes apparent that our validity condition — Eq. (VI.6a) — implies that the momentum (obtainable from $k_1$) is essentially constant over several de Broglie wavelengths. This condition is clearly violated at the so-called turning points of the classical motion which we now discuss.



Let us consider Fig. (VI.1). In this figure an arbitrary potential $V(x)$ and a total energy of a system of mass $\mu$ and momentum $k_1\hbar$ are represented. A classical turning point is, of course, located at $x_1$, since, from a classical point of view, the system, when proceeding from right to left, would be halted at point $x_1$ by equalization of potential and total energy and would be forced to reverse direction. From the quantum viewpoint on the other hand, no such restrictions are imposed, and the system is described by Eq. (VI.5b) in Region 1 and by Eq. (VI.5c) in Regions 2. At the classical turning points, however, the validity condition Eq. (VI.6b) is certainly not fulfilled — we note that $k_1$, for example, goes to zero when approaching from the right — so we may not expect Eqs. (VI.5) to describe our system in this transition region.

It is for this reason that we are required to obtain the so-called connection formulae of Kramers.[88a] Now in order to obtain these formulae one may proceed as follows:

Generally a linear potential function is assumed to be a reasonable approximation right around the turning point. One then may obtain as solutions to Eqs. (VI.1) and (VI.2) functions which contain Bessel functions. Now we desire the asymptotic forms of these equations, initially at least. As an example, we will find the value of the function as $x$ approaches $+\infty$. This will give us — from the figure — the expected value in Region 1 a reasonable distance removed from the turning point at $x_1$. In like manner may the value be found for the functions removed by a little into Regions 2 from the turning point. Finally we determine the manner in which an asymptotic solution in, say, Region 2 will go into one in Region 1, and so on. We find that a decreasing exponential in Region 2 (see Eq. (VI.5b)) will go into an expression of the form

$$k_1^{-\frac{1}{2}}\, 2 \cos\left(\int_{x_1}^{x} k_1 dx + \frac{\pi}{4}\right) \tag{VI.7a}$$

where we may note that a linear combination of the two solutions Eq. (VI.5b) with proper choice of phase will lead to this result. On the other hand an increasing exponential in Region 2 leads to:

$$k_1^{-\frac{1}{2}} \cos\left(\int_{x_1}^{x} k_1 dx - \frac{\pi}{4}\right) \tag{VI.7b}$$

where again the choice of phase in the combination resulting from Eq. (VI.5b) leads to the proper result.

In order to find the restrictions on the considered formulae, we require that the two solutions:

$$k_1^{-\frac{1}{2}} \cos\left(\int_{x_1}^{x} k_1 dx - \frac{\pi}{4}\right)$$

$$k_1^{-\frac{1}{2}} \cos\left(\int_{x}^{x_2} k_1 dx - \frac{\pi}{4}\right)$$

join smoothly at every point $x$ within the interval $x_1$ to $x_2$. This would mean then:

$$\tan\left(\int_{x_1}^{x} k_1 dx - \frac{\pi}{4}\right) = -\tan\left(\int_{x}^{x_2} k_1 dx - \frac{\pi}{4}\right)$$

A solution of this equation yields:

$$\int_{x_1}^{x} k_1 dx = \int_{x}^{x_2} k_1 dx + \left(n + \tfrac{1}{2}\right)\pi$$

or:

$$\int_{x_1}^{x_2} k_1 dx = \left(n + \tfrac{1}{2}\right)\pi \tag{VI.8}$$

which we recognize as the energies of a harmonic oscillator with $n$ a positive integer.

# APPENDIX VII

## OSCILLATOR STRENGTHS

Our interest in oscillator strengths has been principally motivated by a desire to transform classical expressions for spectral intensities into quantum mechanical ones. For this reason it would seem that a good method of investigating oscillator strengths would be to determine classical and quantum intensity or probability expressions and subsequently determine in what manner they are related and, as a consequence, what the oscillator strength which relates them amounts to.

What we propose to do first then is to determine the total energy absorbed per second by a classical oscillator. In order to do so let us first recall that an oscillator of frequency $\nu_0$ has its instantaneous displacement given by:

$$x = A \cos (2\pi\nu_0 t + \varphi) \tag{VII.1}$$

This means that:

$$E = T + V = \tfrac{1}{2} m \dot{x}^2 + \tfrac{1}{2} m\omega x^2 = 2\pi^2 m\nu_0^2 A^2 \tag{VII.2a}$$

From classical electromagnetic theory the mean energy given up by the oscillating dipole over unit time is:

$$<E> = \frac{\omega_0^4}{3\pi c^3} e^2 |x|^2 = \frac{4\omega_0^4}{3\pi c^3} e^2 A^2 = \frac{4\omega_0^4}{3\pi c^3} M^2 \tag{VII.3a}$$

or, over a time $\Delta t$ long compared to the period of oscillation:

$$\Delta E = \frac{4\omega_0^4}{3\pi c^3} M^2 \Delta t \tag{VII.3b}$$

so that Eq. (VII.2a) becomes:

$$E = \frac{8\pi^2 m\nu_0^2}{e^2} M^2 \tag{VII.2b}$$

If we let:

$$\gamma = \frac{8\pi^2}{3} \frac{e^2}{mc^3} \nu_0^2 \tag{VII.4}$$

then Eq. (VII.3b) may be rewritten as:

$$\frac{\Delta \bar{E}}{\Delta t} = 4\pi\gamma E \longleftrightarrow E = E_0 e^{-4\pi\gamma t} \tag{VII.5}$$

We may utilize a derivation similar to that of Sec. (6.13) of the text in order to show that, if a radiation field of density $\Upsilon(\nu)d\nu$ in the frequency interval $\nu$ to $\nu + d\nu$ exists at our oscillator, the energy absorbed by the oscillator from this field per unit of time is:

$$E(\nu) = \Upsilon(\nu) \frac{e^2}{m} \frac{\gamma}{(\nu_0 - \nu)^2 + \gamma^2}$$

From this equation one may immediately obtain:

$$E_{\text{total}} = \int_{-\infty}^{+\nu} E(\nu) d\nu = \Upsilon(\nu_0) \frac{\pi e^2}{m} \tag{VII.6}$$

Now let us suppose that the energy absorbed is present in quanta of energy $h\nu_0$. Then the number of quanta absorbed per second by the oscillator is surely:

$$W_0^a = \Upsilon(\nu_0)\,\frac{\pi e^2}{h\nu_0 m} \tag{VII.7}$$

$W_0^a$ we designate as the classical absorption probability, and it now remains for us to find the quantum probability to which it relates. Firstly we recall the Planck expression for the radiation energy density.

$$\Upsilon(\nu) = \frac{8\pi h\nu^3}{c^3}\,\frac{1}{e^{h\nu/kT} - 1} \tag{VII.8}$$

Following Einstein,[32a] let us suppose that: $A_m^n$ is the probability of a spontaneous emission of radiation by our oscillator $(E_n > E_m)$; $C_m^n\Upsilon(\nu_{nm})$ is the probability of emission induced by the radiation field, and $B_n^m\Upsilon(\nu_{nm})$ is the probability for induced absorption under the aegis of the radiation field of density $\Upsilon(\nu)$. Further let us designate $g_i$ as the degeneracy of the state $i$. Then a Maxwell-Boltzmann distribution would decree that $g_i e^{-h\nu_i/kT}$ oscillators occupy the state $i$. Finally then, the assumption of equilibrium allows us to write the relation among the transitions per second as:

$$g_n e^{-\frac{h\nu_n}{kT}}\left[A_m^n + C_m^n\Upsilon(\nu_{nm})\right] = g_m e^{-\frac{h\nu_m}{kT}} B_n^m\Upsilon(\nu_{nm}) \tag{VII.9}$$

This equation may be solved for $\Upsilon$ with the result:

$$\Upsilon = \frac{g_n A_m^n}{g_m B_n^m e^{h\nu/kT} - g_n C_m^n} \tag{VII.10a}$$

Now if Eq. (VII.8) — the Planck equation — is correct (and we suppose it to be) then $g_m B_n^m = g_n C_m$ so that Eq. (VII.10a) becomes:

$$\Upsilon = \frac{g_n A_m^n}{g_m B_n^m}\left[\frac{1}{e^{h\nu/kT} - 1}\right] \tag{VII.10b}$$

Correctness of the Planck equation requires that the following relation exist between the coefficients of Eq. (VII.10b):

$$\frac{g_n A_m^n}{g_m B_n^m} = \frac{8\pi h\nu^3}{c^3} \tag{VII.11}$$

In our further considerations we shall suppose the coefficient of induced emission $C_m^n$ to be zero since the induced emission is negligible compared to the spontaneous emission for moderate temperatures.

Classically, we may obtain the coefficient of spontaneous emission $A_m^n$ from Eq. (VII.3b) by equating it to the number of photons emitted per second as given by this latter equation:

$$A_m^n = \frac{64\pi^3\nu_{nm}^3}{3hc^3} M_{nm}^2 \tag{VII.12}$$

where now $M_{nm}$ is a moment which we have assigned to the oscillator. Eqs. (VII.11) and (VII.12) then yield:

$$B_n^m = \frac{g_n}{g_m}\frac{8\pi^3}{3h^2} M_{ik}^2 \tag{VII.13a}$$

so that:

$$W_q^a = \Upsilon(\nu_{nm})B_n^m \tag{VII.13b}$$

They are then the probabilities as given by Eqs. (VII.7) and (VII.13b) which are related by the "oscillator strength" of the transition from level $m$ to $n$ as:

$$W_q^a = f_{nm}W_0^a \tag{VII.14}$$

where:

$$f_{nm} = \nu_{nm} M_{nm}{}^2 \frac{g_n}{g_m} \frac{8\pi^2 m}{3h} = \frac{A_m{}^n}{\nu_{nm}{}^2} \frac{g_n}{g_m} \frac{e^3 m}{8\pi^2 e^2} = \nu_{nm} B_n{}^m \frac{hm}{\pi e^2} \tag{VII.15a}$$

$$f_{mn} = -\nu_{mn} M_{mn}{}^2 \frac{8\pi^2 m}{3h} = -\frac{A_m{}^n}{\nu_{mn}{}^2} \frac{c^3 m}{8\pi^2 e^2} = -\nu_{mn} B_{mn} \frac{g_n}{g_m} \frac{hm}{\pi e^2} \tag{VII.15b}$$

for $E_n > E_m$.

The Thomas-Kuhn Summation Theorem, for each level $m$, of an atom,* is:

$$\sum_{\substack{n \\ E_n > E_m}} \nu_{nm} M_{nm}{}^2 \frac{g_n}{g_m} - \sum_{\substack{n \\ E_n < E_m}} \nu_{nm} M_{nm}{}^2 = \frac{3h}{8\pi^2 m} Z \tag{VII.16a}$$

$$\sum_{\substack{n \\ E_n > E_m}} \frac{A_m{}^n}{\nu_{nm}{}^2} \frac{g_n}{g_m} - \sum_{\substack{n \\ E_n < E_m}} \frac{A_n{}^m}{\nu_{nm}{}^2} = \frac{8\pi^2 e^2}{mc^3} Z \tag{VII.16b}$$

$$\sum_{\substack{n \\ E_n > E_m}} \nu_{nm} B_n{}^m - \sum_{\substack{n \\ E_n < E_m}} \nu_{nm} B_m{}^n \frac{g_m}{g_n} = \frac{\pi e^2}{hm} Z \tag{VII.16c}$$

where $Z$ is the number of electrons in the atom, is replaced by the expression:

$$\sum_n f_{nm} = Z \tag{VII.17}$$

Finally, we recall that the time for a classical oscillator amplitude to decay to $1/e$ of its original value is generally taken as the mean life $\tau$. After the fashion in which we obtained the absorption relations Eqs. (VII.14) and (VII.15) we may find:

$$W_q{}^e = f_{mn} \; W_0{}^e \tag{VII.18a}$$

and

$$A_m{}^n = -3 f_{mn} \frac{1}{\tau(\nu_{nm})} \tag{VII.18b}$$

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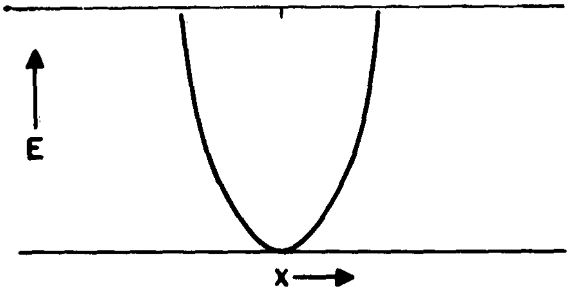
* Up to this point we have spoken only of an oscillator but let us remark that in the quantum derivation of the Einstein coefficients no restriction to oscillators has been imposed. We note further that classically the discretely emitting atom is treated as an oscillator.

# APPENDIX VIII

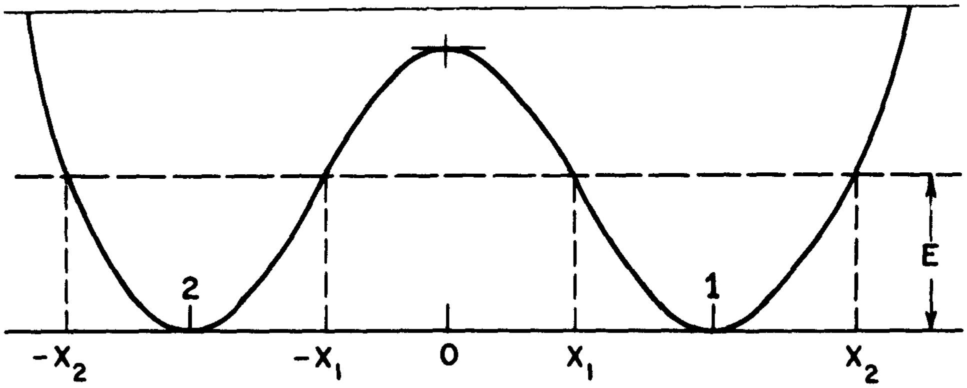
## INVERSION DOUBLING

Let us begin our inversion doubling consideration by referring to the specific example of the $XY_3$ molecule of Appendix II. A study of Fig. (II.1) will be quite helpful.

From the figure in question one may note that a reflection of all particles through the center of mass of the molecule — a sort of turning inside out of the molecule — results in a configuration which we would be hard put to obtain by molecular rotation. For simplicity's sake let us consider the one dimensional approximation of this operation, to wit, let us simply consider the motion of the $X$ atom vertically through the $Y$ plane from its equilibrium position above the plane to what must surely be another equilibrium position below the plane. Before doing this, however, let us remark that, under the assumption of a quadratic potential function for our $X$ atom, we are to suppose a potential curve (in the absence of the mirror potential) like this:



The fact that the $XY_3$ does have a mirror potential, however, changes the look of the potential curve to this:



In Fig. (VIII.2) the two minima are quite obviously located at 1 and 2 while the $Y$ plane is to be found at $x = 0$. The wings of the potential curve correspond to those found in Fig. (VIII.2). Now let us devote our qualitative attention to Fig. (VIII.2) for a moment.

In the figure the system has been assigned the arbitrary energy $E$. Classically, the $X$ atom would be restricted to those regions — namely, the two wells — for which $E > V$. This would be the end of the problem, and we would have a difficult time justifying the effort already expended on it. Quantum mechanists have long been intrigued by barriers though, so that, fortunately, we do have something to consider after all.

If we set up the Schrodinger Equation for the region $x_1 \longleftrightarrow x_2$ or $-x_1 \longleftrightarrow -x_2$ "we may recall that" (and here we probably really will recall that in contradistinction to those recalls limited to the author), the eigenfunction satisfying this equation is oscillatory. Further the Schrodinger Equation for the classically forbidden regions will be satisfied by eigenfunctions consisting of exponential functions. The fact that these latter eigenfunctions do exist within the classically forbidden region $-x_1 \longleftrightarrow x_1$ means, through $\bar{\psi}\psi$, that the $X$ atom may penetrate within and through this barrier region. As a consequence of all this the atom may, in fact, be found in either of the two potential wells. If, say, $\psi_+(x)$ is the function associated with the particle when in the right well and if $\psi_-(x)$ is the function associated with the particle in the left well, then, since the atom may exist in either we are obliged to take two eigenfunctions, namely, the linear combination:

$$\psi_1 = c_1 [\psi_- + \psi_+] \tag{VIII.1a}$$

$$\psi_2 = c_2 [\psi_- - \psi_+] \tag{VIII.1b}$$

for the $X$ atom. Associated with these two eigenfunctions are two eigenvalues of the energy so that our original eigenvalue $E$ (of Fig. VIII.2) has been split into two. We may consider the preceding after a more quantitative fashion.

Let us first consider the even function of $x, \psi_1$, corresponding to the energy $E_+$. To begin with we may take, as solutions to the wave equation in the classically forbidden region $-x_1 < x < x_1$, the solutions displayed as Eq. (VI.5c). A linear combination of them yields:

$$\psi = c(k\hbar)^{-\frac{1}{2}} \cosh \left( \int_0^x k dx \right) \quad -x_1 < x < x_1 \tag{VIII.2a}$$

when $k = \frac{1}{\hbar} \sqrt{2\mu \, |E - V|}$.

If the substitutions:

$$\int_0^x k dx = \int_0^{x_1} k dx - \int_x^{x_1} k dx$$

$$A = \exp \left( \int_0^x k dx \right)$$

are made in Eq. (VIII.2a) the result is:

$$\psi = C(k\hbar)^{-\frac{1}{2}} \left[ A \exp \left( - \int_x^{x_1} k dx \right) + A^{-1} \exp \left( \int_x^{x_1} k dx \right) \right] \; ; \quad -x_1 < x < x_1 \tag{VIII.2b}$$

Now we will agree that some sort of oscillatory solution is required in the region $x_1 < x < x_2$, and a good one would appear to be:

$$\psi_1 = R_+ C(k\hbar)^{\frac{1}{2}} \cos \left[ \int_{x_1}^x k dx - \vartheta_+ \right] \tag{VIII.3a}$$

Substitution will indeed show that Eq. (VIII.3a) will join (VIII.2b) if we suppose:

$$\tan \vartheta_+ = \frac{2A^2 - 1}{2A^2 + 1} \tag{VIII.3b}$$

$$R_+ = \frac{\sqrt{4A^4 + 1}}{2A} \tag{VIII.3c}$$

In the region $x > x_2$ a solution of the form Eq. (VI.5c) is appropriate and it should be quite apparent that the negative exponential must be chosen in order that the eigenfunction may disappear as $x$ approaches infinity. Thus, for this region we choose:

$$\psi_1 = BC(\hbar k)^{-\frac{1}{2}} \exp \left[- \int_{x_2}^{x} kdx\right] \tag{VIII.4}$$

Next, the connection formula Eq. (VI.7a) tells us that Eq. (VIII.4) becomes:

$$\psi_1 = 2BC(\hbar k)^{-\frac{1}{2}} \cos \left[ \int_{x}^{x_2} kdx - \frac{\pi}{4} \right] \tag{VIII.5}$$

We are justified in requiring that the eigenfunctions given by Eqs. (VIII.3a) and (VIII.5) correspond at every point in the region $x_1 < x < x_2$ since they should simply be two ways of writing the same thing. This in turn would allow us to equate $\psi_1'/\psi$ as obtained from the former and the latter equations, namely:

$$\tan \left[ \int_{x_1}^{x} kdx - \vartheta_+ \right] = \tan \left[ \int_{x_2}^{x} kdx + \frac{\pi}{4} \right] \tag{VIII.6}$$

The two angles whose tangents are equated in Eq. (VIII.6) may surely only differ by an integral multiple of $\pi$:

$$\oint kdx = \left(n\pi + \frac{\pi}{4} + \vartheta_+\right)$$

or

$$\oint pdx = \left(n + \frac{1}{4} + \frac{\vartheta_+}{\pi}\right) h \tag{VIII.7}$$

where:

$$p = \sqrt{2\mu \, |E_+ - V|}$$

Beginning with Eq. (VIII.2a) we have devoted our attention to the even eigenfunction. A study of the odd eigenfunction begins with a consideration of the hyperbolic sine in the region $- x_1 < x < x_1$ and finally yields:

$$\oint pdx = \left(n + \frac{1}{4} - \frac{\vartheta_-}{\pi}\right) h \tag{VIII.8a}$$

where now:

$$p = \sqrt{2\mu \, |E_- - V|}$$

also:

$$\tan \vartheta_- = \frac{(2A^2 + 1)}{(2A^2 - 1)} \tag{VIII.8b}$$

After a manner of speaking the work to this point may be considered preliminary to the main step, namely, the obtention of the magnitude of the level splitting due to the mirror potential. In order to obtain the amount of this splitting let us subtract Eq. (VIII.7) from Eq. (VIII.8a):

$$2\sqrt{m}\int_{x_1}^{x_2} \{\sqrt{E_- - V} - \sqrt{E_+ - V}\}\, dx = \frac{(\vartheta_- - \vartheta_+)}{\pi}\, h \tag{VIII.9}$$

and begin by evaluating $(\vartheta_- - \vartheta_+)$.

From Eqs. (VIII.3b) and (VIII.8b):

$$\tan(\vartheta_- - \vartheta_+) = \frac{\tan\vartheta_- - \tan\vartheta_+}{1 + \tan\vartheta_- \tan\vartheta_+} = \frac{8A^2}{8A^4 - 1}$$

Now $A$ is a large quantity so that we may, to a good order of approximation, neglect the one in the denominator. The magnitude of $A$ also indicates, through the defining Eqs. (VIII.3b) and (VIII.8b), that $\vartheta_-$ will be quite near $\vartheta_+$ in value so that the difference, $\vartheta_- - \vartheta_+$, will be small. As a consequence:

$$\vartheta_- - \vartheta_+ \doteq \tan(\vartheta_- - \vartheta_+) \doteq \frac{1}{A^2} \tag{VIII.10}$$

We return to a consideration of Eq. (VIII.9), the left side of which may be rewritten as:

$$2\sqrt{2m}\int_{x_1}^{x_2} \{\sqrt{D + E'} - \sqrt{D + E''}\}\, dx = 2\sqrt{2m}\int \sqrt{D}\left\{\sqrt{1 + \frac{E'}{D}} - \sqrt{1 + \frac{E''}{D}}\right\} dx$$

where:

$$D = E_n - V \;;\quad E' = E_- - E_n \;;\quad E'' = E_+ - E_n$$

The integrand in this latter equation may be expanded with the result:

$$2\sqrt{2m}\int_{x_1}^{x_2} \sqrt{D}\left\{\left[1 + \tfrac{1}{2}\,\frac{E'}{D} + \ldots\right] - \left[1 + \tfrac{1}{2}\,\frac{E''}{D} + \ldots\right]\right\} dx$$

$$= 2\sqrt{2m}\int_{x_1}^{x_2} \tfrac{1}{2}\,\frac{E_- - E_+}{\sqrt{E_n - V}}\, dx = 2m\int_{x_1}^{x_2} \frac{E_- - E_+}{\sqrt{2m(E_n - V)}}\, dx = \frac{h}{\pi A^2}$$

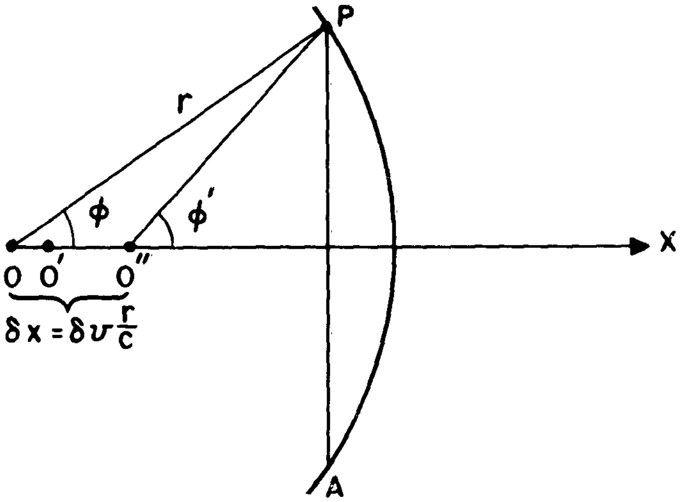
It follows that, if we let $\Delta_n$ denote the splitting of the inversion doubled level:

$$\Delta_n = \frac{h}{2\pi A^2{}_m}\left[\int_{x_1}^{x_2} \frac{dx}{\sqrt{2m(E_n - V)}}\right]^{-1} \tag{VIII.11}$$

# APPENDIX IX

## RADIATION FROM AN ACCELERATED CHARGE

In order to consider this problem let us suppose that the usual physical situation prevails, namely, the situation which is illustrated by Fig. (IX.1) and which may be described as follows:



The electron is taken as being initially at 0 and in uniform motion of velocity $v$ along the $X$-axis. At this point an observer at $P$ is aware of the electron's presence at 0 by virtue of a static electric field which surrounds and accompanies the electron in its uniform motion. At point 0 the electron begins to decelerate and has decelerated to rest by the time it reaches point $0'$ where $00' \ll 00''$ so that we shall later be able to neglect the former distance compared to the latter. This acceleration of the electron causes the propagation of a disturbance in the previously static electronic field toward $P$ with velocity $c$. It will take a time for this disturbance to reach the observer at $P$ who will, of course, be unaware of the existence of such a disturbance until it reaches him. By virtue of this unawareness, he will be under the impression that the electron has proceeded to point $0''$ an impression which will be abetted by the static field of the electron. As a consequence the field will suddenly change, at a time $\frac{r}{c}$ after the deceleration, from the static field corresponding to the electron at point $0''$ to a static field corresponding to the electron at $0'$, or, since $00'$ very small, at 0. This phenomenon forms the basis for the accelerated charge radiation, and let us consider the situation a little more quantitatively.

We begin by recalling Gauss' Law:

$$\oint \mathbf{D} \cdot \mathbf{n} ds = 4\pi e$$

so that over the whole sphere on which, say, $PA$ is an arc of a great circle:

$$D = e$$

It is further apparent that $D$ through a portion of sphere to the right of the plane represented by $PA$ is:

$$D = e\,\frac{\text{sphere area}}{\text{area to right of } PA} = \tfrac{1}{2}\,e\,(1 - \cos\varphi) \qquad \text{(IX.1)}$$

According to our preliminary reasoning then, the sequence of events will be as follows:

First, a field,

$$D = \tfrac{1}{2}\,e\,(1 - \cos\varphi) \qquad \text{(IX.2a)}$$

exists at $P$ which corresponds to the field of the electron before acceleration. During the time $\frac{r}{c}$ — the time required for the acceleration disturbance to reach $P$ — the field at $P$ changes to:

$$D' = \tfrac{1}{2}\,e\,(1 - \cos\varphi') \qquad \text{(IX.2b)}$$

Then, during the time $\delta t$ — the actual duration of the electronic acceleration — the field changes back to that of Eq. (IX.2a). Then from Eqs. (IX.2) one may write:

$$\frac{\delta D}{\delta t} = \frac{D - D'}{\delta t} = \frac{\tfrac{1}{2}\,e\,(\cos\varphi' - \cos\varphi)}{\delta t} = \tfrac{1}{2}\,e\,\frac{\delta\,(\cos\varphi)}{\delta t} = -\tfrac{1}{2}\,e\sin\varphi\,\frac{\delta\varphi}{\delta t} \qquad \text{(IX.3)}$$

On the other hand:

$$\frac{\delta\varphi}{\delta t} = \frac{\delta x}{r}\sin\varphi = \frac{\delta v}{c}\sin\varphi = \frac{1}{c}\sin\varphi\,\frac{\delta v}{\delta t} = -\frac{a}{c}\sin\varphi \qquad \text{(IX.4)}$$

so that Eq. (IX.3) becomes:

$$\frac{\delta D}{\delta t} = -\frac{1}{2}\,\frac{ae}{c}\sin^2\varphi \qquad \text{(IX.5)}$$

From Maxwell's equation relating $\mathbf{H}$ and $\mathbf{D}$ one may obtain:

$$\oint \mathbf{H}\cdot\mathbf{n}\,ds = \frac{1}{c}\int \dot{\mathbf{D}}\cdot\mathbf{n}\,ds = \frac{4\pi}{c}\,\dot{D} \qquad \text{(IX.6a)}$$

or:

$$H(2\pi r\sin\varphi) = \frac{4\pi}{c}\,\frac{1}{2}\,\frac{ae}{c}\sin^2\varphi \qquad \text{(IX.6b)}$$

according to Eq. (IX.5), so that:

$$E = H = \frac{ae}{rc^2}\sin\vartheta \qquad \text{(IX.7)}$$

Now the energy in the field is given by:

$$W = \frac{E^2 + H^2}{8\pi} = \frac{a^2e^2}{4\pi r^2c^4}\sin\varphi \qquad \text{(IX.8)}$$

Since intensity is the energy passing through unit surface in unit time, one next obtains:

$$I = \frac{a^2e^2}{4\pi r^2c^3}\sin^2\varphi \qquad \text{(IX.9)}$$

since the field is propagated with velocity $c$.

In order to find the total power radiated, we must integrate the intensity over a containing sphere:

$$P = \oint I\cdot 2\pi r\sin\varphi\; r\,d\varphi = \frac{2}{3}\,\frac{a^2e^2}{c^3} \qquad \text{(IX.10)}$$

Eq. (IX.10) is the expression which we utilized in Sec. (6.13).

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