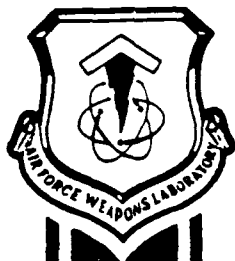


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NEW EFFICIENT METHODS FOR OPTICAL FREQUENCY UP-CONVERSION

A. Elci

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January 1989

Final Report

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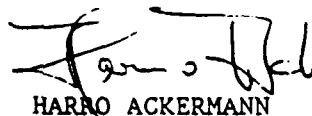


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A theory of the anomalous second harmonic generation in atomic vapors is presented and its possible use to frequency double 1.3 μm radiation at high intensities and large outputs is discussed. A theory of the band structure of superlattices/multiple-quantum-wells is presented, which is a preliminary background to investigations of optical wavemixing in the heterostructure crystals with large nonlinear susceptibilities.					
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1.0 INTRODUCTION

This report contains a theory of the anomalous second harmonic generation (SHG) observed in certain atomic vapors [Refs. 1-9] and a theory of the band structure for superlattices/ multiple -quantum-wells. The first theory suggests that it may be possible to double the 1.3μ radiation at high intensities and large outputs, without consideration of damage inherent to nonlinear crystals. The second is a preliminary background for investigations into radiative interactions within nonlinear heterostructure crystals which have several orders-of-magnitude-larger nonlinear susceptibilities than homogeneous crystals.

The theory of the anomalous SHG is based on global symmetry breakdown in an initially isotropic gas resulting from the off-diagonal order created by the fundamental coherent mode in collision-induced radiative coupling channels. The effect is, therefore, intimately connected with the modification of collision dynamics under applied laser fields. In the new theory, collisional and radiative processes are taken into account simultaneously. It is based upon the Hilbert space of the representation as it is defined by the scattering states of pairs of colliding atoms. It is an alternative to the phenomenological theories used in pressure-induced resonances in four-wave-mixing [Refs. 10 - 11]; to the semiclassical theories used, in collision-induced absorption [Ref. 12] and true and avoided crossings in intense fields [Ref. 13], and to the projection algebra of the density matrices used, for example, in the collisional redistribution of light [Ref. 14].

In Section 2.1 the experimental background of anomalous SHG is described. In Section 2.2 the dynamics of a single collision complex in a coherent radiation field are investigated using the new theoretical approach. This section shows that the Mollow spectrum as well as the spectrum of the Rabi oscillations is modified by collisions. In Section 2.3 the problem of N collision complexes and the quantum description of phase-matching is considered. In Section 2.4 an expression for the macroscopic second harmonic polarization vector is derived. In Section 2.5 a specific gas mixture which might be useful for the doubling of the oxygen-iodine frequency is discussed. In Section 3.0 the band theory of

superlattices/multiple-quantum-wells is discussed. It is formulated in the Bloch representation of one of the constituent materials, and spontaneously exhibits the symmetry breaking along the superlattice axis, which causes the folding of the original Brillouin Zone onto a thin region around the center of the zone. A single homogeneous crystal band splits into many subbands. The series expressions for the energies of these subbands is given and the radiative selection rules are discussed.

2.0 SECOND HARMONIC GENERATION FROM GASES

2.1 EXPERIMENTAL BACKGROUND

The observation of SHG from an isotropic atomic vapor was first reported in 1978 [Ref. 1]. In the experiment atomic Tl vapor was subjected to external dc fields. However, there was SHG from the Tl vapor even when all the external fields were turned off, and when ω was tuned to half the transition frequency between the $6^2P_{1/2}$ and $7^2P_{1/2}$ levels. The experimenters had used an N_2 -pulsed dye laser which produced 7 nsec pulses at a fundamental wavelength $\lambda_\omega = 5860 \text{ \AA}$ (with FWHM 1 to 10 GHz). The Tl vapor was in a heat pipe at a temperature of 860°C . The second harmonic signal was at $\lambda_{2\omega} = 2930 \text{ \AA}$, and its polarization followed the polarization of the fundamental mode. The second harmonic intensity $I_{2\omega}$ scaled as $N^2 I_\omega^2$, where N is the density of the vapor and I_ω is the intensity of the fundamental mode. There was a narrow frequency interval in which SHG occurred. The SHG was destroyed by small detunings of about 2 GHz on either side of the resonance. When an external magnetic field was applied to the vapor, it had no effect on the second harmonic signal $\lambda_{2\omega} = 2930 \text{ \AA}$. This ruled out M1-type transitions. The experimenters advanced the hypothesis that multiphoton ionization of Tl atoms and a subsequent charge separation between faster electrons and slower ions might be responsible for the anomalous SHG. If \vec{E}_0 was a nearly static field arising from multiphoton ionization, then it could cause SHG via four-wave-mixing: $\vec{P}_{2\omega}^{NL} = \chi^{(3)} : \vec{E}_\omega \vec{E}_\omega \vec{E}_0$. However, this hypothesis was not very satisfactory, since it implied that the scaling relationship between $I_{2\omega}$ and I_ω is $I_{2\omega} \propto I_\omega^{2k+2}$, where k is the minimum number of photons required for the ionization of an atom by the fundamental mode. For Tl atoms, $k \geq 3$. Thus, the multiphoton ionization scaling was in contradiction to the observed scaling.

The ionization model was tested in a later experiment [Ref. 3]. The atomic Na vapor in a heat pipe was irradiated with intense $\lambda_\omega = 1.064 \mu\text{m}$ pulses of 28 psec duration and a weak SHG at $\lambda_{2\omega} = 5320 \text{ \AA}$ was observed. The wavelength $\lambda_\omega = 1.064 \mu$ is not resonant with any of the Na transitions. But the experimenters estimated that for intensities

above $5 \times 10^{11} W/cm^2$, the fundamental beam would cause partial ionization of the vapor due to multiphoton transitions. A field-gradient mechanism was suggested to explain the SHG from the original isotropic vapor. In the model, the influence of the multiphoton ionization was secondary; it augmented the SHG caused by the field-gradient mechanism. The latter implied that the dc electric fields in the gas were on the order of 50 V/cm, and that the second harmonic intensity scaled as I_ω^4 .

The two experiments yielded significantly different results. The second harmonic intensities observed under picosecond pulses in Na were several orders of magnitude smaller than those in Tl. The $I_{2\omega}$ had completely different scaling properties with respect to the fundamental beam intensity in the two experiments. Such facts raised strong doubts that the SHG had the same underlying mechanism in the two experiments. These questions were investigated in another set of experiments [Ref. 6]. The experimenters used atomic Na vapor in a cell and a pulsed dye laser whose output could be tuned to some of the Na transitions. The 5P - 3S and 4D - 3S transitions yielded SHG, but the 5S - 3S transition did not yield any SHG. The SHG was tunable about the resonances. The shapes of the tuning curves were sensitive functions of the vapor density. This suggested that the SHG was caused by a bulk interaction. Simultaneously with the SHG, there was a broad-band incoherent fluorescence at 2ω . To test for ionization effects, the experimenters irradiated the cell with intense pulses from a Nd-YAG laser. The pulses had no effect on the SHG. This ruled out multiphoton ionization as the mechanism for the anomalous SHG. The experimenters introduced a higher mode structure into the fundamental beam in order to test for field-gradient effects. This also had no effect on the SHG and ruled out the field-gradient mechanism. Nor could their results be explained by quadrupole transitions, because these yield quantum efficiencies that are six to eight orders of magnitude less than the experimental efficiencies [Refs. 2,6]. The experimenters varied I_ω from $10^5 W/cm^2$ to $10^9 W/cm^2$. For the S - D transitions, they found that $I_{2\omega}$ scaled as I_ω^3 at low intensities. But $I_{2\omega}$ rapidly began to scale as I_ω^2 , and then as I_ω , as I_ω was increased to the values in the upper part of its range.

The anomalous SHG has been observed in other atomic vapors: Li [Ref. 7], Ba [Ref. 4], K [Ref. 9], Hg [Ref. 5], and Zn [Ref. 8]. The experiment with Zn is of special interest in

that an attempt was made to measure the effective electric fields which could generate the observed second harmonic fields obtained from the same atomic levels. The electric fields were 5×10^3 V/cm and 4×10^3 V/cm for the D - S and S - S transitions, respectively. These values are two orders of magnitude larger than the value inferred in Ref. 3.

2.2 A NEW FORMULATION OF THE RADIATIVE COUPLING TO A COLLISION COMPLEX

This section presents the results of the analysis of the coupling of a single collision complex to radiation fields in the Hilbert space of the scattering states. The details of various derivations and further discussions of the implications of the scattering state representation are given in Ref. 15.

The essence of the new method is to pair individual atoms such that one can formally solve for the binary collisions by describing the quantum state of a pair by the scattering state corresponding to a specified asymptotic state of the pair in the limit of vanishing collision potential. If H_A represents the asymptotic Hamiltonian of the two atoms that are paired, and V is the localized collision potential [Ref. 16], then the scattering state corresponding to an asymptotic state $|\psi\rangle$ is given by [Refs. 16-18]

$$|\psi\rangle_+ = \Omega^{(+)}|\psi\rangle \quad (1)$$

$$\Omega^{(\pm)} = 1 + (E - H_A - V \pm i\epsilon)^{-1}V \quad (2)$$

where E is the energy of the asymptotic state $|\psi\rangle$ and is treated as a c -number parameter. The transformation Equation 1 can be viewed as a canonical transformation when there are no bound states of the two atoms induced by V , or even if there are such bound states for an attractive V , provided they can be neglected with little effect on the dynamics of pairs. This follows from a fundamental theorem [Ref. 16] of the Quantum Scattering Theory:

Theorem: To every solution ψ_t of the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi_t = (H_A + V)\psi_t \quad (3)$$

which is orthogonal to all bound states, there corresponds a unique solution ϕ_t of the particle Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \phi_t = H_A \phi_t \quad (4)$$

such that the norm

$$\lim_{t \rightarrow \infty} \|\psi_t - \phi_t\| = 0 \quad (5)$$

Conversely, to every solution of Equation 4 there corresponds exactly one solution of Equation 3 such that Equation 5 holds.

The theorem shows that the asymptotic pair states can be put into one-to-one correspondence with the scattering states in the absence of bound states:

$$|\phi_a(1)\rangle \otimes |\phi_b(2)\rangle \longleftrightarrow |\psi(1,2)\rangle_+ \quad (6)$$

Here the asymptotic states of the pair are written as direct products of atomic states, since the two atoms evolve freely when the collision potential vanishes. In fact, $\Omega^{(+)}$ satisfies [Ref. 17]

$$(\Omega^{(+)})^\dagger \Omega^{(+)} = 1 \quad (7)$$

$$\Omega^{(+)} (\Omega^{(+)})^\dagger = 1 - \sum_{\beta} |\psi_{\beta}\rangle \langle \psi_{\beta}| \quad (8)$$

where $|\psi_{\beta}\rangle$'s are the bound states of $H_A + V$. Thus, $\Omega^{(+)}$ is actually a unitary operator and Equation 1 becomes a unitary transformation, if the bound states are ignored.

If the bound states are to be neglected, then there must be no chemical phase transitions in the gas. In other words, the temperature and the pressure of the gas, as well as the type of atoms (or molecules), must be such that no chemical transformations take place locally or otherwise. The gas may, of course, be a mixture of different chemical species. But each species in the mixture must preserve its chemical identity, and there must be no phase transformations from one species to another.

In the asymptotic limit, the operators describing various properties of a collision complex can be obtained from the atomic operators. To go to the scattering state representation, the asymptotic collision complex operators are transformed by $\Omega^{(+)}$'s and become energy and potential-dependent. For example, let A be an atomic operator such that the corresponding operator of the complex is additive, as given by $A(1) + A(2)$. In the scattering state representation, A is transformed into $A^{(+)}$:

$$A \rightarrow A^{(+)} = [1 + V(E' - H_A - V - i\epsilon)^{-1}]A[1 + (E - H_A - V + i\epsilon)^{-1}V] \quad (9)$$

If A is some moment operator (electric dipole, magnetic dipole, etc.), then $A^{(+)}$ couples to radiation fields in the scattering state representation. In contrast, in the standard theories, it is A that is coupled to radiation fields. The form of Equation 9 shows that the ordinary symmetry arguments and selection rules of the standard theories based on A do not hold in the present approach. The scattering state representation mixes the symmetry properties of the pair of asymptotic atomic states with the collision potential. In general, $A^{(+)}$ has mixed symmetry with respect to rotations, inversions, etc., even if A has a definite symmetry.

In the Kroll-Watson theory of inelastic atom-atom scattering in a laser beam [Ref. 19], the coupling of the collision complex to the radiation field is analyzed by expanding the state of the complex in terms of the actual molecular states, with time-dependent amplitudes. These molecular states are the bound states of the two colliding atoms with potential V . In the present theory these bound states are completely excluded. The quasi-molecular operators are obtained from the free atomic operators by transformations of the type in Equation 9.

Consider the Hamiltonian for two indistinguishable atoms colliding in the presence of radiation fields. The assumption of indistinguishability is not necessary for the formalism; but it simplifies most of the results. This assumption can be readily removed and the results adapted to the case of two nonidentical atoms. When the center of mass (c.o.m.) motions of the atoms are separated from their internal motions, the asymptotic state of the pair can be written as

$$\begin{aligned}\psi_{\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2}(A_1 \vec{X}_1 A_2 \vec{X}_2) &= \langle \vec{X}_1 \vec{X}_2; A_1 A_2 | \alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma \rangle \\ &= \frac{1}{V_{ol} \sqrt{2}} \times \left[\psi_{\alpha_1}(A_1) \psi_{\alpha_2}(A_2) e^{i(\vec{p}_1 \cdot \vec{X}_1 + \vec{p}_2 \cdot \vec{X}_2)} \right. \\ &\quad \left. + \sigma \psi_{\alpha_2}(A_1) \psi_{\alpha_1}(A_2) e^{i(\vec{p}_2 \cdot \vec{X}_1 + \vec{p}_1 \cdot \vec{X}_2)} \right] \quad (10)\end{aligned}$$

where $\vec{X}_{1,2}$ are the atomic c.o.m. positions, $\vec{p}_{1,2}$ are the atomic c.o.m. momenta (divided by \hbar), $A_{1,2}$ are the atomic internal coordinates, and $\alpha_{1,2}$ are the atomic internal quantum numbers. V_{ol} is the volume to which the pair is confined. Since the atoms are indistinguishable, the Hamiltonian is symmetric with respect to the interchange of the two atoms. It follows that the asymptotic eigenstates of the complex can be symmetric or antisymmetric with respect to the interchange of the two atoms. To allow for both possibilities, the variable σ is used. It can assume only two values, +1 and -1. The c.o.m. quantum numbers \vec{p}_1 and \vec{p}_2 are used interchangeably with the total momentum of the pair, $\vec{p} = \vec{p}_1 + \vec{p}_2$, and the relative momentum of the atoms, $\vec{q} = \vec{p}_1 - \vec{p}_2$. The designations for the pair states $|\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma\rangle$ and $|\alpha_1 \alpha_2 \sigma; \vec{p} \vec{q}\rangle$ are used interchangeably. The collision potential V depends on the atomic internal coordinates A_1 and A_2 , and on the interatomic separation $\vec{X}_1 - \vec{X}_2$. V is symmetric with respect to the interchange of the atoms. Its Fourier matrix elements are given by

$$\begin{aligned}V_{\alpha_1 \alpha_2; \alpha'_1 \alpha'_2}(\vec{k}) &= \sum_{A_1 A_2} \frac{1}{V_{ol}} \int d\vec{R} e^{i\vec{k} \cdot \vec{R}} \\ &\quad \times \psi_{\alpha'_1}^*(A_1) \psi_{\alpha'_2}^*(A_2) V(A_1 A_2; \vec{R}) \psi_{\alpha_1}(A_1) \psi_{\alpha_2}(A_2) \quad (11)\end{aligned}$$

The coupling of the complex to radiation fields is described by multipolar couplings. Specifically, the dipole moment density is written as

$$\vec{D}(\vec{r}) = \sum_{j=1}^2 \delta(\vec{r} - \vec{X}_j) \vec{d}_j \quad (12)$$

where \vec{d}_j is the electric dipole moment operator of the j^{th} atom. Although this report focuses on radiative couplings that are given exclusively in terms of the electric dipole moments, the results can readily be generalized to magnetic dipoles, quadrupole moments, etc., by adding further terms to Equation 12 and by treating \vec{D} as a generalized moment density. The Fourier transform of \vec{D} is given by

$$\int d\vec{r} e^{i\vec{k}\cdot\vec{r}} \vec{D}(\vec{r}) = \sum_{j=1}^2 e^{i\vec{k}\cdot\vec{X}_j} \vec{d}_j = \vec{D}(\vec{k}) \quad (13)$$

The asymptotic energy eigenvalues of the complex are designated by $E_{\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2}$:

$$H_A |\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma\rangle = E_{\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2} |\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma\rangle \quad (14)$$

$$E_{\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2} = E_{\alpha_1} + E_{\alpha_2} + \frac{\hbar^2 \vec{p}_1^2}{2m} + \frac{\hbar^2 \vec{p}_2^2}{2m} \quad (15)$$

where E_{α_1} and E_{α_2} are the atomic internal energies. The energy of the complex has the same form (Equation 15) regardless of the sign of σ . The scattering state corresponding to $|\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma\rangle$ is designated with a plus sign:

$$|\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma\rangle_+ = \left[1 + (E_{\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2} - H_A - V + i\epsilon)^{-1} V \right] |\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma\rangle \quad (16)$$

Using the completeness of the scattering states (in the absence of the bound states), the total Hamiltonian is written

$$H = H_A + V + H_T + H_{int} \quad (17)$$

where H_r is the Hamiltonian for the free radiation fields, as

$$\begin{aligned}
H = & \sum_{\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma} E_{\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2} |\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma\rangle_+ + \langle \alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma | \\
& + \sum_{\lambda \vec{k}} \hbar \omega_{\lambda \vec{k}} a_{\lambda \vec{k}}^\dagger a_{\lambda \vec{k}} \\
& + \left\{ i \sum_{\sigma; \alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2; \alpha'_1 \vec{p}'_1 \alpha'_2 \vec{p}'_2; \lambda \vec{k}} g_{\alpha_1 \alpha_2; \alpha'_1 \alpha'_2}^{\sigma \lambda} (\vec{p}_1 \vec{p}_2; \vec{p}'_1 \vec{p}'_2) \right. \\
& \left. \times |\alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma\rangle_+ + \langle \alpha'_1 \vec{p}'_1 \alpha'_2 \vec{p}'_2 \sigma | + \text{herm. conj.} \right\} \quad (18)
\end{aligned}$$

where $a_{\lambda \vec{k}}$ and $a_{\lambda \vec{k}}^\dagger$ are the annihilation and creation operators for the mode propagating with momentum \vec{k} , the polarization index $\lambda \cdot \hat{\epsilon}_{\lambda \vec{k}}$ is the polarization vector, and $\omega_{\lambda \vec{k}}$ is the frequency of the mode. The radiative coupling coefficients are defined by

$$\begin{aligned}
g_{\alpha_1 \alpha_2; \alpha'_1 \alpha'_2}^{\sigma \lambda} (\vec{p}_1 \vec{p}_2; \vec{p}'_1 \vec{p}'_2) = & \left(\frac{2\pi \hbar \omega_{\lambda \vec{k}}}{V_{ol}} \right)^{\frac{1}{2}} \\
& \times \langle \alpha_1 \vec{p}_1 \alpha_2 \vec{p}_2 \sigma | \hat{\epsilon}_{\lambda \vec{k}} \cdot \vec{D}(\vec{k}) | \alpha'_1 \vec{p}'_1 \alpha'_2 \vec{p}'_2 \sigma \rangle_+ \quad (19)
\end{aligned}$$

The matrix elements of \vec{D} between two asymptotic states of the complex are given by

$$\begin{aligned}
\langle \alpha_1 \vec{p}_1 \vec{p}_2 \sigma | \vec{D}(\vec{k}) | \alpha'_1 \vec{p}'_1 \alpha'_2 \vec{p}'_2 \sigma \rangle = & \delta_{\alpha_2 \alpha'_2} \delta(\vec{p}_1, \vec{p}'_1 + \vec{k}) \delta(\vec{p}_2, \vec{p}'_2) \vec{d}_{\alpha_1 \alpha'_1} \\
& + \delta_{\alpha_1 \alpha'_1} \delta(\vec{p}_1, \vec{p}'_1) \delta(\vec{p}_2, \vec{p}'_2 + \vec{k}) \vec{d}_{\alpha_2 \alpha'_2} \\
& + \sigma \left[\delta_{\alpha_2 \alpha'_1} \delta(\vec{p}_1, \vec{p}'_2 + \vec{k}) \delta(\vec{p}_2, \vec{p}'_1) \vec{d}_{\alpha_1 \alpha'_1} \right. \\
& \left. + \delta_{\alpha_1 \alpha'_2} \delta(\vec{p}_1, \vec{p}'_2) \delta(\vec{p}_2, \vec{p}'_1 + \vec{k}) \vec{d}_{\alpha_2 \alpha'_2} \right]
\end{aligned}$$

$$\begin{aligned}
&= \delta(\vec{p}, \vec{p}' + \vec{k}) \left\{ \delta_{\alpha_1, \alpha'_1} \delta(\vec{q}, \vec{q}' + \vec{k}) \vec{d}_{\alpha_1, \alpha'_1} + \delta_{\alpha_1, \alpha'_2} \delta(\vec{q}, \vec{q}' - \vec{k}) \vec{d}_{\alpha_1, \alpha'_2} \right. \\
&\quad \left. + \sigma \left[\delta_{\alpha_2, \alpha'_1} \delta(\vec{q}, -\vec{q}' + \vec{k}) \vec{d}_{\alpha_2, \alpha'_1} + \delta_{\alpha_2, \alpha'_2} \delta(\vec{q}, -\vec{q}' - \vec{k}) \vec{d}_{\alpha_2, \alpha'_2} \right] \right\} \quad (20)
\end{aligned}$$

The subscripts on \vec{d} , are omitted here, because the atoms are indistinguishable, and the atomic matrix elements are designated as $\langle \alpha | \vec{d} | \alpha' \rangle = \vec{d}_{\alpha \alpha'}$. The matrix element in Equation 20 represents a transition in which a photon is absorbed and the total momentum of the complex is increased by \vec{k} . The first two terms are a pair of delta functions located at $\vec{q} = \vec{q}' \pm \vec{k}$. They describe photon absorption by one or the other colliding atom. The other two delta functions at $\vec{q} = -\vec{q}' \pm \vec{k}$ arise from the absorption of the photon accompanied by the exchange of the atoms. These singularities may be called the exchange singularities. If the atoms were not paired and just one atom was being considered, there would be just one delta function singularity, for example at $\vec{p}_1 = \vec{p}_1' + \vec{k}$. Pairing of the atoms doubles the number of singularities. If the paired atoms are identical, the number of singularities is doubled again. If the photon momentum is small compared to the relative momenta of the atoms, $|\vec{k}| \ll |\vec{q}| \simeq |\vec{q}'|$, then the two singularities at $\vec{q} = \vec{q}' \pm \vec{k}$, as well as the exchange singularities, merge together. Note that $|\vec{k}|$ may be completely negligible compared to the total momentum of the complex, yet be significant compared to the relative momentum of the atoms. Merging of the singularities occurs only if $|\vec{k}|$ is also negligible compared to the relative momentum. Finally, for a given set of quantum numbers $\alpha_1 \alpha_2 \alpha'_1 \alpha'_2$, the actual number of singularities appearing in the asymptotic matrix element of \vec{D} depends on how many of the atomic matrix elements $\vec{d}_{\alpha_1, \alpha'_1}$ are nonzero.

Collisions modify the preceding physical picture significantly. The matrix elements of \vec{D} in the scattering state representation are given by

$$\begin{aligned}
& + \langle \alpha_1 \bar{p}_1 \alpha_2 \bar{p}_2 \sigma | \bar{D}(\vec{k}) | \alpha'_1 \bar{p}'_1 \alpha'_2 \bar{p}'_2 \sigma \rangle_+ = \langle \alpha_1 \bar{p}_1 \alpha_2 \bar{p}_2 \sigma | \bar{D} | \alpha'_1 \bar{p}'_1 \alpha'_2 \bar{p}'_2 \sigma \rangle \\
& + \langle \alpha_1 \bar{p}_1 \alpha_2 \bar{p}_2 \sigma | V (E_{\alpha_1, \beta_1, \alpha_2, \beta_2} - H_A - V - i\epsilon)^{-1} \bar{D} | \alpha'_1 \bar{p}'_1 \alpha'_2 \bar{p}'_2 \sigma \rangle \\
& + \langle \alpha_1 \bar{p}_1 \alpha_2 \bar{p}_2 \sigma | \bar{D} (E_{\alpha'_1, \beta'_1, \alpha'_2, \beta'_2} - H_A - V + i\epsilon)^{-1} V | \alpha'_1 \bar{p}'_1 \alpha'_2 \bar{p}'_2 \sigma \rangle \\
& + \langle \alpha_1 \bar{p}_1 \alpha_2 \bar{p}_2 \sigma | V (E_{\alpha_1, \beta_1, \alpha_2, \beta_2} - H_A - V - i\epsilon)^{-1} \bar{D} \\
& \times (E_{\alpha'_1, \beta'_1, \alpha'_2, \beta'_2} - H_A - V + i\epsilon)^{-1} V | \alpha'_1 \bar{p}'_1 \alpha'_2 \bar{p}'_2 \sigma \rangle. \tag{21}
\end{aligned}$$

The collisional parts of Equation 21 can be evaluated by inserting the complete set of the asymptotic states at appropriate places and using Equation 20. To lowest order in V , the collisional part of Equation 36 is given by

$$\begin{aligned}
& \langle \alpha_1 \bar{p}_1 \alpha_2 \bar{p}_2 \sigma | \delta \bar{D}(\vec{k}) | \alpha'_1 \bar{p}'_1 \alpha'_2 \bar{p}'_2 \sigma \rangle \simeq \frac{1}{4} \delta(\vec{p}, \vec{p}' + \vec{k}) \sum_{\alpha''} \\
& \times \left\{ \frac{\mathcal{V}_{\alpha_1 \alpha_2; \alpha'' \alpha'_2} \left(\frac{\vec{q} - \vec{q}' - \vec{k}}{2} \right) + \sigma \mathcal{V}_{\alpha_1 \alpha_2; \alpha'_2 \alpha''} \left(\frac{\vec{q} + \vec{q}' + \vec{k}}{2} \right)}{\left[E_{\alpha_1} + E_{\alpha_2} - E_{\alpha''} - E_{\alpha'_2} + \frac{q^2}{4m} - \frac{(\vec{q}' + \vec{k})^2}{4m} - i\epsilon \right]} \right\} \bar{d}_{\alpha'' \alpha'_1} \\
& + \frac{\left[\mathcal{V}_{\alpha_1 \alpha_2; \alpha'_1 \alpha''} \left(\frac{\vec{q} - \vec{q}' + \vec{k}}{2} \right) + \sigma \mathcal{V}_{\alpha_1 \alpha_2; \alpha'' \alpha'_1} \left(\frac{\vec{q} + \vec{q}' - \vec{k}}{2} \right) \right] \bar{d}_{\alpha'' \alpha'_2}}{\left[E_{\alpha_1} + E_{\alpha_2} - E_{\alpha'_1} - E_{\alpha''} + \frac{q^2}{4m} - \frac{(\vec{q}' - \vec{k})^2}{4m} - i\epsilon \right]} \\
& + \frac{\bar{d}_{\alpha_1 \alpha''} \left[\mathcal{V}_{\alpha'' \alpha_2; \alpha'_1 \alpha'_2} \left(\frac{\vec{q} - \vec{q}' - \vec{k}}{2} \right) + \sigma \mathcal{V}_{\alpha'' \alpha_2; \alpha'_2 \alpha'_1} \left(\frac{\vec{q} + \vec{q}' - \vec{k}}{2} \right) \right]}{\left[E_{\alpha'_1} + E_{\alpha'_2} - E_{\alpha''} - E_{\alpha_2} + \frac{q'^2}{4m} - \frac{(\vec{q} - \vec{k})^2}{4m} - i\epsilon \right]} \\
& + \frac{\bar{d}_{\alpha_2 \alpha''} \left[\mathcal{V}_{\alpha_1 \alpha''; \alpha'_1 \alpha'_2} \left(\frac{\vec{q} - \vec{q}' + \vec{k}}{2} \right) + \sigma \mathcal{V}_{\alpha_1 \alpha''; \alpha'_2 \alpha'_1} \left(\frac{\vec{q} + \vec{q}' + \vec{k}}{2} \right) \right]}{\left[E_{\alpha'_1} + E_{\alpha'_2} - E_{\alpha_1} - E_{\alpha''} + \frac{q'^2}{4m} - \frac{(\vec{q} + \vec{k})^2}{4m} + i\epsilon \right]} \left. \right\} \tag{22}
\end{aligned}$$

A comparison of Equation 22 with Equation 20 shows that: (1) The number of singularities is increased: in other words, new coupling channels are opened up by the scattering process. The new singularities are simple poles, arising from the denominators in Equation 22. They form surfaces in the space of the relative momentum. If the Fourier transform of the collision potential has singularities, then these also contribute to the coupling coefficients. (2) The original as well as the new singularities are broadened. This broadening is due to the appearance of simple pole singularities. The Fourier transform of the collision potential also contributes to this broadening.

Of course, collisionally-opened-up radiative transitions have been observed for a long time [Ref. 20] and are well-known from collision-induced absorption [Ref. 12], field induced avoided crossing [Ref. 13], pressure-induced four wave mixing [Ref. 10], etc. The difference between the present theory and others is that in the other formalisms V enters into the physical picture indirectly, either through linewidths and lineshifts [Ref. 10] or through the calculation of a particular molecular state wave function. In the present formalism, V is directly incorporated into the coupling coefficients of atoms to radiation fields. These coupling coefficients take into account the collisions between the atoms of the complex to all orders in V .

A further discussion of the coupling coefficients between the complex and radiation fields is given in Ref. 15.

In order to obtain an analytically solvable Hamiltonian, some simplifying assumptions are required. Assume that the atoms of the complex are two-level-atoms and that the complex is coupled to just one radiation mode. Furthermore, assume that the momentum exchanged during collisions, as well as the photon momentum, is negligible. The latter assumption means that the atoms of the complex preserve their individual c.o.m. momenta at all times, which is essentially equivalent to the straightline approximation of many of the semiclassical theories of atomic collisions. Finally, assume that $\sigma = +1$ and omit references to σ in the following discussion.

From Equation 10, there are four asymptotic states, which can be written as

$$|0\rangle = \frac{1}{\sqrt{2}} \left[|0; \vec{p}_1\rangle_A \otimes |0; \vec{p}_2\rangle_B + |0; \vec{p}_1\rangle_B \otimes |0; \vec{p}_2\rangle_A \right] \quad (23)$$

$$|1\rangle = \frac{1}{\sqrt{2}} \left[|0; \vec{p}_1\rangle_A \otimes |1; \vec{p}_2\rangle_B + |0; \vec{p}_1\rangle_B \otimes |1; \vec{p}_2\rangle_A \right] \quad (24)$$

$$|2\rangle = \frac{1}{\sqrt{2}} \left[|1; \vec{p}_1\rangle_A \otimes |0; \vec{p}_2\rangle_B + |1; \vec{p}_1\rangle_B \otimes |0; \vec{p}_2\rangle_A \right] \quad (25)$$

$$|3\rangle = \frac{1}{\sqrt{2}} \left[|1; \vec{p}_1\rangle_A \otimes |1; \vec{p}_2\rangle_B + |1; \vec{p}_1\rangle_B \otimes |1; \vec{p}_2\rangle_A \right] \quad (26)$$

Here, the state vectors $|\alpha; \vec{p}_i\rangle_{A,B}$ ($\alpha = 0, 1; i = 1, 2$) refer to the individual atomic states. α designates the internal atomic state, \vec{p}_i the c.o.m. momentum. A, B label the atoms. One should interpret the meaning of, for example, $|0; \vec{p}_1\rangle_A$ as

$$|0; \vec{p}_1\rangle_A \longrightarrow \langle A_a; \vec{X}_A | 0; \vec{p}_1 \rangle = \frac{1}{\sqrt{V_{01}}} e^{i\vec{p}_1 \cdot \vec{X}_A} \psi_0(A_a) \quad (27)$$

where $A_{a,b}$ refers to the sets of the internal variables of the atoms A and B , and $\vec{X}_{A,B}$ to their c.o.m. coordinates. ψ_0 is the wave function for the internal ground state. Under the present approximations, \vec{p}_1 and \vec{p}_2 are constant parameters without dynamical significance. It is therefore entirely sufficient to label these asymptotic states by $|\mu\rangle$ ($\mu = 0, 1, 2, 3$). They are the eigenstates of the asymptotic Hamiltonian H_A :

$$H_A |\mu\rangle = E_\mu^c |\mu\rangle \quad (28)$$

where

$$E_0^c = 2E_0 + \frac{\hbar^2 \vec{p}_1^2}{2m} + \frac{\hbar^2 \vec{p}_2^2}{2m} \quad (29)$$

$$E_1^c = E_2^c = E_0 + E_1 + \frac{\hbar^2 \vec{p}_1^2}{2m} + \frac{\hbar^2 \vec{p}_2^2}{2m} \quad (30)$$

$$E_3^c = 2E_1 + \frac{\hbar^2 \bar{p}_1^2}{2m} + \frac{\hbar^2 \bar{p}_2^2}{2m} \quad (31)$$

The corresponding scattering states are given by

$$|\mu\rangle_+ = \left[1 + (E_\mu^c - H_A - V + i\epsilon)^{-1} V \right] |\mu\rangle \quad (32)$$

which are the eigenstates of $H_A + V$:

$$(H_A + V)|\mu\rangle_+ = E_\mu^c |\mu\rangle_+ \quad (33)$$

The simplified Hamiltonian obtained from Equation 18 can therefore be written as

$$H = \sum_{\mu} E_{\mu}^c |\mu\rangle_+ \langle \mu| + \hbar\omega a^{\dagger} a + \left[i\hbar(g_{10}|1\rangle_+ \langle 0| + g_{20}|2\rangle_+ \langle 0| + g_{31}|3\rangle_+ \langle 1| + g_{32}|3\rangle_+ \langle 2|)d + \text{herm. conj.} \right] \quad (34)$$

where

$$g_{\mu\mu'} = \left(\frac{2\pi\omega}{\hbar V_{ol}} \right)^{\frac{1}{2}} \langle \mu | \hat{\epsilon} \cdot \vec{D} | \mu' \rangle_+ \quad (35)$$

In writing Equation 34, the rotating wave approximation is made and the coupling between $|1\rangle_+$ and $|2\rangle_+$ is omitted, since they have the same energy.

The eigenvalues and eigenstates of the Hamiltonian in Equation 34 can be obtained by writing an arbitrary state $|\psi\rangle$ as a linear superposition of the states of the complex and the radiation field, in the form

$$\begin{aligned} |\psi_n\rangle &= l_0 |0\rangle_+ \otimes |n+2\rangle + l_1 |1\rangle_+ \otimes |n+1\rangle + l_2 |2\rangle_+ \otimes |n+1\rangle + l_3 |3\rangle_+ \otimes |n\rangle \\ &\equiv l_0 |n0\rangle_+ + l_1 |n1\rangle_+ + l_2 |n2\rangle_+ + l_3 |n3\rangle_+ \end{aligned} \quad (36)$$

where $|n\rangle$ designates the radiation state with n quanta ($n \geq 0$). From

$$H|\psi_n\rangle = E|\psi_n\rangle \quad (37)$$

one finds that

$$\begin{bmatrix} E_0^c + (n+2)\hbar\omega & -i\hbar g_{10}^* \sqrt{n+2} & -i\hbar g_{20}^* \sqrt{n+2} & 0 \\ i\hbar g_{10} \sqrt{n+2} & E_1^c + (n+1)\hbar\omega & 0 & -i\hbar g_{31}^* \sqrt{n+1} \\ i\hbar g_{20} \sqrt{n+2} & 0 & E_2^c + (n+1)\hbar\omega & -i\hbar g_{32}^* \sqrt{n+1} \\ 0 & i\hbar g_{31} \sqrt{n+1} & i\hbar g_{32} \sqrt{n+1} & E_3^c + n\hbar\omega \end{bmatrix} \begin{bmatrix} l_0 \\ l_1 \\ l_2 \\ l_3 \end{bmatrix} = E \begin{bmatrix} l_0 \\ l_1 \\ l_2 \\ l_3 \end{bmatrix} \quad (38)$$

Thus, the eigenvalue problem for H is reduced to the diagonalization of a 4×4 hermitian matrix. Denote this matrix by H_n . From

$$\det(H_n - E) = 0 \quad (39)$$

and the definitions

$$E = \hbar\xi + E_1^c + (n+1)\hbar\omega \quad (40)$$

$$\hbar\Delta = E_1^c - E_0^c - \hbar\omega \quad (41)$$

one finds the eigenvalue equation

$$\begin{aligned}
0 = & \xi^4 - \xi^2 \left[\Delta^2 + (n+1)(|g_{31}|^2 + |g_{32}|^2) + (n+2)(|g_{10}|^2 + |g_{20}|^2) \right] \\
& - \xi \Delta \left[(n+1)(|g_{31}|^2 + |g_{32}|^2) - (n+2)(|g_{10}|^2 + |g_{20}|^2) \right] \\
& + (n+1)(n+2) \left[|g_{10}|^2 |g_{32}|^2 + |g_{20}|^2 |g_{31}|^2 \right. \\
& \left. - g_{10}^* g_{20} g_{31}^* g_{32} - g_{10} g_{20}^* g_{31} g_{32}^* \right]
\end{aligned} \tag{42}$$

The indistinguishability of the atoms of the complex and the straightline trajectory assumption introduce certain symmetry relations among $g_{\mu\mu'}$, which simplify Equation 42. These are [see Ref. 15]:

$$g_{01} = g_{02} \tag{43}$$

Similarly,

$$g_{13} = g_{23} \tag{44}$$

It follows from Equation 43 and Equation 44 that the last term of the eigenvalue equation vanishes. One ξ factors out. Designate the roots of Equation 42 by $\xi_{n\lambda}$, where $\lambda = 0, 1, 2, 3$. The ξ - factor gives a root that is zero. Let this root be ξ_{n3} . The remaining three roots are the solutions of the cubic equation

$$\begin{aligned}
0 = & \xi^3 - [2(n+2)|g_{10}|^2 + 2(n+1)|g_{31}|^2 + \Delta^2] \xi \\
& + 2\Delta [(n+2)|g_{10}|^2 - (n+1)|g_{31}|^2]
\end{aligned} \tag{45}$$

Only the real solutions of Equation 45 are acceptable for energy eigenvalues. The number of real solutions of Equation 45 depends on the sign of the quantity

$$w_n = u_n^3 - v_n^2 \quad (46)$$

where

$$u_n = \frac{1}{3}[\Delta^2 + 2(n+2)|g_{10}|^2 + 2(n+1)|g_{31}|^2] \quad (47)$$

and

$$v_n = \Delta[(n+2)|g_{10}|^2 - (n+1)|g_{31}|^2] \quad (48)$$

Since H_n is hermitian, $w_n > 0$, the cubic equation is irreducible and there are three real roots [Ref. 20]:

$$\xi_{n0} = 2\sqrt{u_n} \cos\left(\frac{\phi_n}{3}\right) \quad (49)$$

$$\xi_{n1} = -2\sqrt{u_n} \cos\left(\frac{\pi - \phi_n}{3}\right) \quad (50)$$

$$\xi_{n2} = -2\sqrt{u_n} \cos\left(\frac{\pi + \phi_n}{3}\right) \quad (51)$$

where

$$\phi_n = \tan^{-1}\left(\frac{-\sqrt{w_n}}{v_n}\right) \quad (52)$$

Let $\ell_{n\lambda\mu}$ represent the components of the eigenvector corresponding to the eigenvalue $\xi_{n\lambda}$. If the eigenvalues are not degenerate, then

$$l_{n\lambda 0} = \frac{1}{N_{n\lambda}} [\xi_{n\lambda} (\xi_{n\lambda} - \Delta) - 2(n+1)|g_{31}|^2] \quad (53)$$

$$l_{n\lambda 1} = l_{n\lambda 2} = \frac{i}{N_{n\lambda}} \sqrt{n+2} (\xi_{n\lambda} - \Delta) g_{10} \quad (54)$$

$$l_{n\lambda 3} = -\frac{2}{N_{n\lambda}} \sqrt{(n+1)(n+2)} g_{10} g_{31} \quad (55)$$

where

$$N_{n\lambda} = \left\{ \left[\xi_{n\lambda} (\xi_{n\lambda} - \Delta) - 2(n+1)|g_{31}|^2 \right]^2 + 2(n+2)(\xi_{n\lambda} - \Delta)^2 |g_{10}|^2 + 4(n+1)(n+2)|g_{10}|^2 |g_{31}|^2 \right\}^{1/2} \quad (56)$$

If the eigenvalues are degenerate, an orthonormal set of eigenvectors may be determined directly from the matrix Equation 38. Because H_n is hermitian, the eigenvectors are complete as well as orthonormal:

$$\sum_{\mu} l_{n\lambda\mu}^* l_{n\lambda'\mu} = \delta_{\lambda\lambda'} \quad (57)$$

$$\sum_{\lambda} l_{n\lambda\mu}^* l_{n\lambda\mu'} = \delta_{\mu\mu'} \quad (58)$$

The eigenstates of H are given by

$$|\psi_{n\lambda}\rangle = \sum_{\mu} l_{n\lambda\mu} |n\mu\rangle_+ \quad (59)$$

$$H|\psi_{n\lambda}\rangle = E_{n\lambda} |\psi_{n\lambda}\rangle = [\hbar\xi_{n\lambda} + E_1^c + (n+1)\hbar\omega] |\psi_{n\lambda}\rangle \quad (60)$$

An arbitrary state of the collision complex plus the radiation field can be written as

$$|\psi\rangle = \sum_{n=0}^{\infty} \sum_{\lambda=0}^2 c_{n\lambda}^{(+)} |\psi_{n\lambda}\rangle \quad (61)$$

If the state of the total system at time $t = 0$ is given by a state like Equation 61, then the state at time t is given by

$$|\psi(t)\rangle = e^{-iHt/\hbar} |\psi\rangle = \sum_{n\lambda} c_{n\lambda}^{(+)} e^{-iE_{n\lambda}t/\hbar} |\psi_{n\lambda}\rangle \quad (62)$$

The corresponding density matrix operator is given by

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)| = \sum_{n\lambda n'\lambda'} c_{n\lambda}^{(+)} c_{n'\lambda'}^{(+)*} e^{-i(E_{n\lambda} - E_{n'\lambda'})t/\hbar} |\psi_{n\lambda}\rangle\langle\psi_{n'\lambda'}| \quad (63)$$

If at time $t = 0$ the system can be described only by a mixture of states, for example by the density matrix operator $\rho(0)$, then

$$\rho(0) = \sum_{n\lambda n'\lambda'} |\psi_{n\lambda}\rangle \rho_{n\lambda; n'\lambda'}^{(+)}(0) \langle\psi_{n'\lambda'}| \quad (64)$$

$$\begin{aligned} \rho(t) &= \sum_{n\lambda n'\lambda'} |\psi_{n\lambda}\rangle [e^{-i(E_{n\lambda} - E_{n'\lambda'})t/\hbar} \rho_{n\lambda; n'\lambda'}^{(+)}(0)] \langle\psi_{n'\lambda'}| \\ &= \sum_{n\lambda n'\lambda'} |\psi_{n\lambda}\rangle \rho_{n\lambda; n'\lambda'}^{(+)}(t) \langle\psi_{n'\lambda'}| \end{aligned} \quad (65)$$

Clearly, the specification of either the initial state amplitudes $c_{n\lambda}^{(+)}$ in Equation 62 and Equation 63 or the initial density matrix elements $\rho_{n\lambda; n'\lambda'}^{(+)}(0)$ in Equation 64 is equivalent to a complete solution for the dynamics of the system.

The initial/boundary conditions are specified in the asymptotic limit and for individual atoms. It is assumed that, at $t = 0$, the density matrix of the total system can be factored into an outer product of the density matrix for the complex and the density matrix for the field. These assumptions correspond to a physical picture in which the radiation field and the collision potential are turned on simultaneously at $t = 0$. From Equations 23-26

$$|\mu\rangle = \sum_{\alpha_1 i_1 \alpha_2 i_2} C_{\alpha_1 i_1 \alpha_2 i_2}^{\mu} |\alpha_1; \vec{p}_{i_1}\rangle_A \otimes |\alpha_2; \vec{p}_{i_2}\rangle_B \quad (66)$$

where $\alpha = 0, 1$ designates the internal quantum states of the atoms and $i = 1, 2$ designates the two momenta for the atoms. All of the nonvanishing $C_{\alpha i; \alpha' i'}$'s are equal to $1/\sqrt{2}$:

$$\begin{aligned} C_{01;02}^0 &= C_{02;01}^0 = C_{01;12}^1 = C_{12;01}^1 = C_{11;02}^2 = C_{02;11}^2 \\ &= C_{11;12}^3 = C_{12;11}^3 = \frac{1}{\sqrt{2}} \end{aligned} \quad (67)$$

From Equation 59,

$$\rho_{n\lambda; n'\lambda'}^{(+)}(0) = \langle \psi_{n\lambda} | \rho(0) | \psi_{n'\lambda'} \rangle = \sum_{\mu\mu'} l_{n\lambda\mu}^* l_{n'\lambda'\mu'} \langle n\mu | \rho(0) | n'\mu' \rangle_+ \quad (68)$$

Since both the collision potential and the radiation field are turned on at $t = 0$,

$$\begin{aligned} \rho_{n\lambda; n'\lambda'}^{(+)}(0) &= \sum_{\mu\mu''\mu'''} l_{n\lambda\mu}^* l_{n'\lambda'\mu'''} \rho_{n+m_{\mu}, n'+m_{\mu'}}^{\gamma} (0) \\ &\quad \times \Omega_{\mu\mu''}^{(+)\dagger}(E_{\mu}^c) \rho_{\mu''\mu'''}^c(0) \Omega_{\mu'''\mu'}^{(+)}(E_{\mu'}^c) \end{aligned} \quad (69)$$

$$\rho_{\mu\mu'}^c(0) = \sum_{\substack{\alpha_1, \alpha_2, \alpha_3 \\ \alpha_1', \alpha_2', \alpha_3'}} (C_{\alpha_1, \alpha_2, \alpha_3}^{\mu})^* \rho_{\alpha_1, \alpha_2, \alpha_3}^a(0) \rho_{\alpha_1', \alpha_2', \alpha_3'}^a(0) C_{\alpha_1', \alpha_2', \alpha_3'}^{\mu'} \quad (70)$$

Here $\rho^r(0)$ is the density matrix operator for the field at $t = 0$, $\rho^a(0)$ is the density matrix operator for a single atom, and m_μ is an integer defined by

$$m_\mu = \begin{cases} 2 & \text{for } \mu = 0 \\ 1 & \text{for } \mu = 1, 2 \\ 0 & \text{for } \mu = 3 \end{cases} \quad (71)$$

If the radiation mode is in a coherent state and the average number of quanta is \bar{n} , then

$$\rho_{nn'}^r(0) = \frac{e^{-\bar{n}} (\bar{n})^{\frac{n+n'}{2}}}{\sqrt{n!n'}} \quad (72)$$

Assume that $\rho^a(0)$ is diagonal and the occupation probabilities are given by

$$\rho_{\alpha\alpha; \alpha'\alpha'}^a(0) = \delta_{\alpha\alpha'} \delta_{ii'} f_\alpha(\vec{p}_i) \quad (73)$$

where $f_\alpha(\vec{p}_i)$ is the conditional probability that the internal state of the atom is α , if the atom is in the c.o.m. momentum state \vec{p}_i . For these initial/boundary conditions

$$\begin{aligned} \rho_{n\lambda; n'\lambda'}^{(+)}(t) &= e^{-it[\epsilon_{n\lambda} - \epsilon_{n'\lambda'} + (n-n')\omega]} e^{-\bar{n}} \sum_{\mu\mu'} \\ &\times \frac{(\bar{n})^{\frac{n+m_\mu+n'+m_{\mu'}}{2}}}{\sqrt{(n+m_\mu)!(n'+m_{\mu'})!}} \\ &\times l_{n\lambda\mu}^* l_{n'\lambda'\mu'} F_{\mu\mu'}(\vec{p}_1, \vec{p}_2) \end{aligned} \quad (74)$$

where

$$\begin{aligned}
F_{\mu\mu'}(\vec{p}_1, \vec{p}_2) &= f_0(\vec{p}_1) f_0(\vec{p}_2) \Omega_{\mu_0}^{(+)\dagger}(E_\mu^c) \Omega_{0\mu}^{(+)}(E_{\mu'}^c) \\
&+ f_0(\vec{p}_1) f_1(\vec{p}_2) \Omega_{\mu_1}^{(+)\dagger}(E_\mu^c) \Omega_{1\mu'}^{(+)}(E_{\mu'}^c) \\
&+ f_0(\vec{p}_2) f_1(\vec{p}_1) \Omega_{\mu_2}^{(+)\dagger}(E_\mu^c) \Omega_{2\mu'}^{(+)}(E_{\mu'}^c) \\
&+ f_1(\vec{p}_1) f_1(\vec{p}_2) \Omega_{\mu_3}^{(+)\dagger}(E_\mu^c) \Omega_{3\mu'}^{(+)}(E_{\mu'}^c)
\end{aligned} \tag{75}$$

Taking the trace over the radiation field in Equation 74 and 75 and transforming back to the Hilbert space of the asymptotic states,

$$\rho_{\mu\mu'}^c(t) = \sum_{\mu''\mu'''} \Omega_{\mu\mu''}^{(+)}(E_{\mu''}^c) \rho_{\mu''\mu'''}^{c+}(t) \Omega_{\mu'''\mu'}^{(+)\dagger}(E_{\mu'}^c) \tag{76}$$

where

$$\begin{aligned}
\rho_{\mu\mu'}^{c+}(t) &= e^{-\bar{n}} \sum_{nn'\lambda\lambda'\mu''\mu'''} \delta(n + m_\mu, n' + m_{\mu'}) \\
&\times e^{-it[\xi_{n\lambda} - \xi_{n'\lambda'} - (m_\mu - m_{\mu'})\omega]} \frac{(\bar{n})^{\frac{n+m_{\mu''}+n'+m_{\mu'''}}{2}}}{\sqrt{(n+m_{\mu''})!(n'+m_{\mu'''})!}} \\
&\times l_{n\lambda\mu} l_{n\lambda\mu}^* F_{\mu''\mu'''} l_{n'\lambda'\mu'''} l_{n'\lambda'\mu'}^*
\end{aligned} \tag{77}$$

The elements of the atomic density matrix operator are given by

$$\rho_{\alpha i; \alpha' i'}^a(t) = \sum_{\mu\mu'\alpha''i''} C_{\alpha i; \alpha'' i''}^\mu \rho_{\mu\mu'}^c(t) \left(C_{\alpha' i'; \alpha'' i''}^{\mu'} \right)^* \tag{78}$$

The physically interesting case is the one in which $\bar{n} \gg 1$ and the probability distribution of n 's in Equation 72 is sharply peaked around \bar{n} . If the presence of a moderately intense coherent field is assumed, and also

$$\vec{d}_{10} = \vec{d}_{10}^* \tag{79}$$

$$\mathcal{V}_{11;00} = -\mathcal{V}_{11;00}^* \quad (80)$$

to first order in V and in the limit $\epsilon \rightarrow 0$:

$$g_{10} = \left(\frac{2\pi\omega}{\hbar V_{oi}} \right)^{\frac{1}{2}} \hat{\epsilon} \cdot \vec{d}_{10} \left(1 - \frac{\mathcal{V}_{11;00}}{2E_1 - 2E_0} \right) + O(V^2) \quad (81)$$

$$g_{31} = \left(\frac{2\pi\omega}{\hbar V_{oi}} \right)^{\frac{1}{2}} \hat{\epsilon} \cdot \vec{d}_{10} \left(1 + \frac{\mathcal{V}_{11;00}}{2E_1 - 2E_0} \right) + O(V^2) \quad (82)$$

It follows that, to first order in V :

$$g_{31}^* \simeq g_{10} \equiv g \quad (83)$$

Under these assumptions, the eigenvalue equation becomes

$$\xi^4 - (\Delta^2 + 4\bar{n}|g|^2)\xi^2 = 0 \quad (84)$$

The eigenvalues are

$$\xi_{0,1} = \pm \sqrt{\Delta^2 + 4\bar{n}|g|^2} \equiv \pm \xi' \quad (85)$$

$$\xi_{2,3} = 0 \quad (86)$$

The eigenvectors corresponding to $\pm \xi'$ are, respectively,

$$\underline{l}_0 = \begin{bmatrix} \frac{\xi' - \Delta}{2\xi'} \\ \frac{i}{\xi'} g \sqrt{2\bar{n}} \\ \frac{i}{\xi'} g \sqrt{2\bar{n}} \\ -\frac{\xi' + \Delta}{2\xi'} \end{bmatrix} \quad \underline{l}_1 = \begin{bmatrix} -\frac{\xi' - \Delta}{2\xi'} \\ \frac{i}{\xi'} g \sqrt{2\bar{n}} \\ \frac{i}{\xi'} g \sqrt{2\bar{n}} \\ \frac{\xi' + \Delta}{2\xi'} \end{bmatrix} \quad (87)$$

The eigenvectors corresponding to 0 are

$$\underline{l}_2 = \begin{bmatrix} -\frac{i}{\xi'} g^* \sqrt{2\bar{n}} \\ \frac{\Delta}{\xi' \sqrt{2}} \\ \frac{\Delta}{\xi' \sqrt{2}} \\ -\frac{i}{\xi'} g^* \sqrt{2\bar{n}} \end{bmatrix} \quad \underline{l}_3 = \begin{bmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{bmatrix} \quad (88)$$

Under the present approximations, Equation 76 becomes

$$\rho_{\mu\mu'}^{c+}(t) \simeq \sum_{\lambda\lambda'} e^{-i(\xi_\lambda - \xi_{\lambda'})t} e^{i(m_\mu - m_{\mu'})\omega t} l_{\lambda\mu} \left(\sum_{\mu''} l_{\lambda\mu''}^* F_{\mu''\mu''} l_{\lambda'\mu''} \right) l_{\lambda'\mu'} \quad (89)$$

which can be rewritten as

$$\rho_{\mu\mu'}^{c+}(t) = e^{i(m_\mu - m_{\mu'})\omega t} \left[R_{\mu\mu'}^0 + R_{\mu\mu'}^1 e^{i\xi't} + R_{\mu\mu'}^{-1} e^{-i\xi't} + R_{\mu\mu'}^2 e^{2i\xi't} + R_{\mu\mu'}^{-2} e^{-2i\xi't} \right] \quad (90)$$

The explicit expression for $\rho_{\mu\mu'}^{c+}(t)$ is given in Ref. 15, where Equation (4.48) and Equation (4.49b) show that the quantity ξ' is the generalized Rabi frequency for an atom in the coherent fundamental mode [Ref. 22]. If θ is the angle between the polarization vector and the bare atomic dipole moment

$$\hat{\epsilon} \cdot \vec{d}_{10} = |\vec{d}_{10}| \cos \theta \quad (91)$$

then ξ' can be written as

$$\xi' = |\Delta| \sqrt{1 + \zeta^2 \cos^2 \theta} \quad (92)$$

where

$$\zeta^2 \equiv \frac{4\bar{n}}{\Delta^2} |g(\theta = 0)|^2 \equiv \frac{\Omega_R^2}{\Delta^2} \quad (93)$$

is the square of the ratio of the standard Rabi frequency to detuning, whose magnitude is modified by the collision process. It is seen from Equations 81-83 that the effect of the collision, to first order in V , is to modify the magnitude and the phase of the atomic dipole moment.

The appearance of just one angle variable in Equations 91-93 may be surprising at first glance, since there are two atoms in the complex. However, it was assumed that the two atoms of the complex were indistinguishable. If the internal \vec{d}_{10} were to point in different directions for each atom, then the atoms would be distinguishable. The symmetric and antisymmetric combinations of asymptotic atomic states can still be used for distinguishable atoms. For symmetric combinations, the replacement is

$$\hat{\epsilon} \cdot \vec{d}_{10} \longrightarrow \frac{1}{2} \hat{\epsilon} \cdot \left(\vec{d}_{10}^{(A)} + \vec{d}_{10}^{(B)} \right) \quad (94)$$

in Equations 81-83 for the distinguishable atoms A and B . Formulas for distinguishable atoms are more complicated than those for indistinguishable atoms. The matter is not pursued in this report.

The initial conditions are incorporated into the density matrix solutions through $F_{\mu\mu}$. If the matrix elements of $\Omega^{(+)}$ are expanded in powers of V , then

$$\begin{aligned}
 F_{\mu\mu} = & \delta_{\mu 0} f_0(\vec{p}_1) f_0(\vec{p}_2) + \delta_{\mu 1} f_0(\vec{p}_1) f_1(\vec{p}_2) \\
 & + \delta_{\mu 2} f_0(\vec{p}_2) f_1(\vec{p}_1) + \delta_{\mu 3} f_1(\vec{p}_1) f_1(\vec{p}_2) + O(V^2)
 \end{aligned} \tag{95}$$

In other words, up to and including the first order in V , $F_{\mu\mu}$ is given by the conditional probabilities $f_\alpha(\vec{p}_i)$. The latter is readily obtained when the atoms of the gas obey either the Boltzmann statistics or the Bose-Einstein statistics (since it was assumed that $\sigma = +1$ with respect to the interchange of the atoms of the complex). For the Boltzmann statistics, the probability is that an atom has the c.o.m. momentum \vec{p}_i and that the internal quantum state α is proportional to $\exp\left[-\beta(E_\alpha + \frac{\hbar^2 p_i^2}{2m})\right]$, where $\beta = (k_B T)^{-1}$. Consequently, the conditional probability that the atom with \vec{p}_i is in the state α is given by

$$\begin{aligned}
 f_\alpha(\vec{p}_i) &= \frac{e^{-\beta\left(E_\alpha + \frac{\hbar^2 p_i^2}{2m}\right)}}{\sum_{\alpha'} e^{-\beta\left(E_{\alpha'} + \frac{\hbar^2 p_i^2}{2m}\right)}} \\
 &= \frac{e^{-\beta E_\alpha}}{\sum_{\alpha'} e^{-\beta(E_{\alpha'})}}
 \end{aligned} \tag{96}$$

The f_α 's are thus independent of the c.o.m. momenta. Hence,

$$F_{00} = f_0^2, \quad F_{11} = F_{22} = f_0 f_1, \quad F_{33} = f_1^2 \tag{97}$$

The f_α 's are independent of \vec{p}_i for the Bose-Einstein statistics as well:

$$f_a = \frac{1}{\sum_{a'} \left(\frac{e^{\beta B_a} - 1}{e^{\beta B_{a'}} - 1} \right)} \quad (98)$$

The spectrum of the diagonal matrix elements of $\rho^c(t)$ consists of five peaks at $0, \pm \xi', \pm 2\xi'$. The peaks at $\pm \xi'$ and $\pm 2\xi'$ disappear if $\zeta \ll 1$, that is, if the frequency detuning from the resonance is large compared to the Rabi frequency:

$$\zeta \ll 1 \Rightarrow$$

$$\rho_{00}^{c+}(t) \rightarrow f_0^2,$$

$$\rho_{11}^{c+}(t), \rho_{22}^{c+}(t) \rightarrow f_0(1 - f_0),$$

$$\rho_{33}^{c+}(t) \rightarrow (1 - f_0)^2 \quad (99)$$

In other words, $\rho_{\mu\mu}^{c+}(t)$ is not changed from $\rho_{\mu\mu}^{c+}(0)$, because the coupling to the fundamental mode is negligible. On the other hand, near or at resonance, ρ_{00}^{c+} and ρ_{33}^{c+} have five peaks, but ρ_{11}^{c+} and ρ_{22}^{c+} do not have the components corresponding to $\pm \xi'$:

$$\zeta \gg 1 \Rightarrow$$

$$\begin{aligned} \rho_{00}^{c+}(t) \rightarrow & \frac{1}{4} + \frac{1}{2} \left(f_0 - \frac{1}{2} \right)^2 + \left(f_0 - \frac{1}{2} \right) \cos(\Omega_R | \cos \theta | t) \\ & + \frac{1}{2} \left(f_0 - \frac{1}{2} \right)^2 \cos(2\Omega_R | \cos \theta | t) \end{aligned}$$

$$\begin{aligned} \rho_{11}^{c+}(t), \rho_{22}^{c+}(t) \rightarrow & \frac{1}{4} - \frac{1}{2} \left(f_0 - \frac{1}{2} \right)^2 \\ & - \frac{1}{2} \left(f_0 - \frac{1}{2} \right)^2 \cos(\Omega_R | \cos \theta | t) \end{aligned}$$

$$\begin{aligned} \rho_{33}^{c+}(t) \longrightarrow & \frac{1}{4} + \frac{1}{2} \left(f_0 - \frac{1}{2} \right)^2 - \left(f_0 - \frac{1}{2} \right) \cos(\Omega_R |\cos \theta| t) \\ & + \frac{1}{2} \left(f_0 - \frac{1}{2} \right)^2 \cos(2\Omega_R |\cos \theta| t) \end{aligned} \quad (100)$$

The limits $\zeta \rightarrow \infty$ and $\zeta \rightarrow 0$ will be referred to as the strong and the weak coupling regimes, respectively.

The coherent radiation field creates off-diagonal correlations in the density matrix of the complex. The spectral lines of ρ_{01}^{c+} , ρ_{02}^{c+} , ρ_{03}^{c+} , and ρ_{23}^{c+} are at ω , $\omega \pm \xi'$, and $\omega \pm 2\xi'$. The lines of ρ_{12}^{c+} are at $0, \pm\xi'$, and $\pm 2\xi'$. ρ_{03}^{c+} has spectral lines at 2ω , $2\omega \pm \xi'$, and $2\omega \pm 2\xi'$. These correlations arise from the coupling of the complex to a coherent field. The role of the collision potential is to modify the coupling coefficients to the radiation. In the weak coupling limit, all of these off-diagonal matrix elements vanish: ρ_{03}^{c+} and ρ_{12}^{c+} as ζ^2 ; the others as ζ . In the strong coupling limit:

$$\zeta \rightarrow \infty \implies$$

$$\begin{aligned} \rho_{01}^{c+}, \rho_{02}^{c+} \longrightarrow & \frac{1}{2} e^{i\omega t - i\phi_s} \left(f_0 - \frac{1}{2} \right) \left[\sin(\Omega_R |\cos \theta| t) \right. \\ & \left. + \left(f_0 - \frac{1}{2} \right) \sin(2\Omega_R |\cos \theta| t) \right] \end{aligned}$$

$$\begin{aligned} \rho_{13}^{c+}, \rho_{23}^{c+} \longrightarrow & \frac{1}{2} e^{i\omega t + i\phi_s} \left(f_0 - \frac{1}{2} \right) \left[\sin(\Omega_R |\cos \theta| t) \right. \\ & \left. - \left(f_0 - \frac{1}{2} \right) \sin(2\Omega_R |\cos \theta| t) \right] \end{aligned}$$

$$\rho_{12}^{c+} \longrightarrow \frac{1}{2} \left(f_0 - \frac{1}{2} \right)^2$$

$$\rho_{03}^{\epsilon+} \longrightarrow \frac{1}{2} e^{2i\omega t} \left(f_0 - \frac{1}{2} \right)^2 \left[1 - \cos(2\Omega_R |\cos\theta| t) \right] \quad (101)$$

where $g = |g| \exp(i\phi_g)$. The first four elements in Equation 101 oscillate at $\omega \pm \Omega_R |\cos\theta|$ and $\omega \pm 2\Omega_R |\cos\theta|$, as could be expected from single photon transitions and from the fact that both of the atoms are executing Rabi oscillations with frequency $\Omega_R |\cos\theta|$. It is interesting, however, that for sufficiently large ζ , $\rho_{03}^{\epsilon+}$, which corresponds to polarization at the second harmonic, oscillates at 2ω and $2\omega \pm 2\Omega_R |\cos\theta|$, the components at $2\omega \pm \Omega_R |\cos\theta|$ are suppressed, and that $\rho_{12}^{\epsilon+}$ becomes independent of the radiation field.

Because of the form of $\Omega^{(+)} \Omega^{(+)\dagger}$, $\rho^a(t)$ can be decomposed into three parts. From Equation 2,

$$\begin{aligned} \Omega_{\mu\mu'}^{(+)}(E_{\mu'}) \Omega_{\mu''\mu'''}^{(+)\dagger}(E_{\mu'''}) &= \delta_{\mu\mu'} \delta_{\mu''\mu'''} \\ &+ \left[\delta_{\mu\mu'} \langle \mu'''' | V \frac{1}{E_{\mu''''} - E_{\mu''} - V - i\epsilon} | \mu'' \rangle + \delta_{\mu''\mu'''} \langle \mu | \frac{1}{E_{\mu'} - E_{\mu} - V + i\epsilon} V | \mu' \rangle \right] \\ &+ \langle \mu | \frac{1}{E_{\mu'} - E_{\mu} - V + i\epsilon} V | \mu' \rangle \langle \mu'''' | V \frac{1}{E_{\mu''''} - E_{\mu''} - V - i\epsilon} | \mu'' \rangle \end{aligned} \quad (102)$$

Here the terms are grouped according to the number of kronecker deltas. The term with two kronecker deltas is zeroth order in V . The terms with one kronecker delta are at least of the order of V . The last term is at least of the order of V^2 . One can decompose $\rho^a(t)$ accordingly:

$$\rho^a(t) = \rho^I(t) + \rho^{II}(t) + \rho^{III}(t) \quad (103)$$

$\rho^I(t)$ corresponds to the first term of Equation 102, $\rho^{II}(t)$ corresponds to the terms with one kronecker delta, and $\rho^{III}(t)$ corresponds to the last term of Equation 102. $\rho^I(t)$ can be written as

$$\rho_{\alpha i; \alpha' i'}^I = e^{-i(\alpha - \alpha')\omega t} \sum_{s=0, \pm 1, \pm 2} r_{\alpha i; \alpha' i'}^{Is} e^{is\xi' t} \quad (104)$$

where the elements of r^{Is} are given in Ref. 15. According to Equation 104 the atomic population probability executes the well-known Rabi oscillations. In $\rho^I(t)$, the effect of the scattering on atomic population probabilities is simply to modify the standard Rabi frequency by modifying the coupling coefficient to the radiation field. The off-diagonal elements of $\rho^I(t)$ have spectral components at $\omega, \omega \pm \xi'$, and $\omega \pm 2\xi'$. The components at ω and $\omega \pm \xi'$ correspond to the well-known Mollow triplet in the resonant fluorescence. The components at $\omega \pm 2\xi'$ are generated by the collision process. Their amplitudes are proportional to $\mathcal{V}_{11;00}$ and vanish if the collision potential vanishes. In the limit of strong coupling,

$$\xi \rightarrow \infty \Rightarrow$$

$$\begin{aligned} \rho_{\alpha i; \alpha i}^I(t) &\longrightarrow \frac{1}{4} + (-1)^\alpha \frac{1}{2} \left(f_0 - \frac{1}{2} \right) \cos(\Omega_R |\cos \theta| t) \\ \rho_{0 i; 1 i}^I(t) &\longrightarrow \frac{e^{i\omega t}}{2} \left(f_0 - \frac{1}{2} \right) \left[\cos \phi_\theta \sin(\Omega_R |\cos \theta| t) \right. \\ &\quad \left. - i \left(f_0 - \frac{1}{2} \right) \sin \phi_\theta \sin \left(2\Omega_R |\cos \theta| t \right) \right] \end{aligned} \quad (105)$$

where

$$\sin \phi_\theta = \frac{i\mathcal{V}_{11;00} \cos \theta}{\sqrt{4(E_1 - E_0)^2 + |\mathcal{V}_{11;00}|^2}} \quad (106)$$

These are as one might have expected on the basis of the Rabi oscillations except for the second term in the off-diagonal element. $\rho^{II}(t)$ and $\rho^{III}(t)$ contain the full spectrum

of $\rho^c(t) : 0, \pm\xi', \mp 2\xi', \omega, \omega \pm \xi', \omega \pm 2\xi', 2\omega, 2\omega \pm \xi',$ and $2\omega \pm 2\xi'$. All of the components of $\rho^{II}(t)$ and $\rho^{III}(t)$ vanish as the collision potential vanishes. The appearance of these spectral components as a result of the collision process suggests that, for strong potentials, the Mollow spectrum, as well as the spectrum of the Rabi oscillations, is significantly altered by collisions.

Finally, the density matrix solutions are sensitive to the initial/boundary conditions. At the exact threshold for atomic population inversion, both $\rho^a(t)$ and $\rho^c(t)$ become diagonal and time-independent.

2.3 NONLINEAR LIGHT PROPAGATION

The preceding discussion was confined to a single collision complex in a coherent field. The following discussion concerns the problem of N-collision complexes in a coherent field, where N is a very large number. The complexes are identical but distinguishable. They are initially independent of each other. A quantum theoretical treatment of how a collective mode of the complete system of the coherent fundamental model plus the N-complexes is formed at the second harmonic is presented.

The standard semiclassical theory of two-wave-mixing in gases uses a physical picture in which plane waves proceed from one atomic or molecular system to another. To obtain a measurable wave-mixing, the phases of these waves must match over a macroscopic distance, which requires the analysis of indices of refraction at various frequencies. The following analysis precludes the use of the semiclassical theory for two reasons: (1) The preceding analysis used the quantum theory and a representation which mixes the matter and radiation states for one complex. To be able to use the preceding results in a straightforward way, one must remain within the rigorous picture of the quantum theory. (2) The single complex solutions were obtained for the straightline trajectory approximation in the momentum space representation (hence the photon momentum was suppressed). It is necessary to provide a quantum picture of light propagation and phase matching. This is precisely the quantum theoretical problem of finding a specific collective excitation of a complicated many-body system.

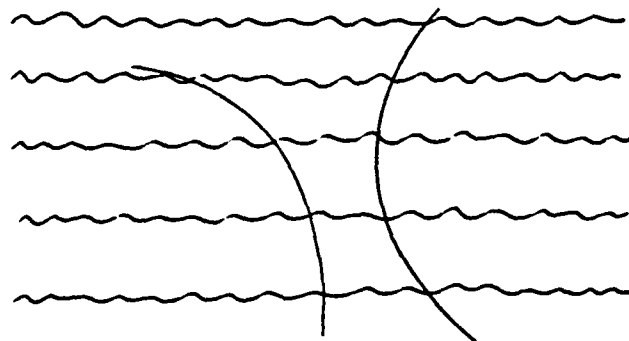
The scattering states forming the basis of the Hilbert space have precisely defined energies. Therefore the scattering time for these states is indefinitely large. These states are also in the momentum space representation. For a scattering state, the spatial extents of the particle trajectories fill the entire volume of the gas. Thus, the phase of a state of the complex plus the radiation field is determined by the contributions of all wavelengths that can be filled in the entire volume and of all points on atomic trajectories. This is illustrated in Fig. (1a). If another pair of atoms is added to the system, the picture shown in Fig. (1b) should be superposed on Fig. (1a). For N pairs, there are N pictures. The collective excitations are given by what survives the N -fold superpositions. Consider the relationship between a macroscopic property of the N -complex system and the corresponding microscopic property of one of the complexes. Of particular interest is the transverse polarization, which is additive.

Without the radiation field, a quantum state of the N independent complexes can be written as

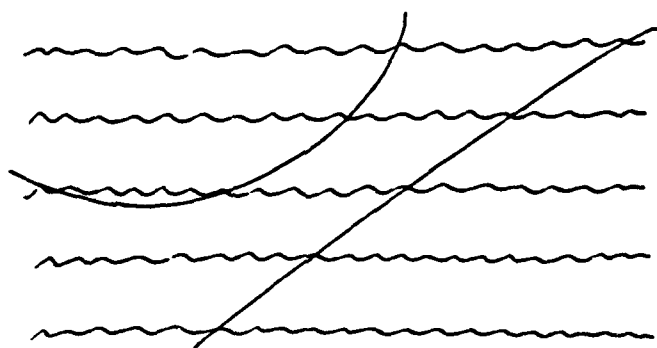
$$|\psi_{\{\mu_1 \dots \mu_n\}}\rangle = \prod_{p=1}^N e^{i\phi_\mu(s_p)} |\mu_p\rangle_+ \quad (107)$$

where $|\mu_p\rangle_+$ designates the scattering state of the p^{th} complex and $\exp[i\phi_\mu(s_p)]$ is an arbitrary phase factor. Since the complexes are independent, relative phases of their states are arbitrary. Here we made the phase ϕ_μ of the p^{th} complex in state $|\mu\rangle_+$ depend on a stochastic variable (or a set of variables) s_p . As one goes from one complex to another, s_p varies randomly. Note that s becomes the angle between \hat{e} and \vec{d}_{10} for a collision complex characterized by Equations 79-83. Equation 107 describes a multiparticle state in which each complex is in a specific state $|\mu\rangle_+$ and the multiparticle state corresponds to a particular configuration $\{\mu_1 \dots \mu_n\}$. An arbitrary state of the N -complex system will be a superposition of such states:

$$|\Psi\rangle = \sum_{\mu_1 \dots \mu_n} C(\mu_1 \dots \mu_n) |\Psi_{\{\mu_1 \dots \mu_n\}}\rangle \quad (108)$$



(a)



(b)

Fig. 1. Schematic illustration of the collision complex + radiation fields system.

The elements of the density matrix for the p^{th} complex (in the scattering state representation) are determined from the amplitudes C and the phases ϕ :

$$\rho_{\mu\mu'}^{C_p+} = e^{-i\phi_\mu(s_p)} \sum_{\mu_1 \dots \mu_{p-1} \mu_{p+1} \dots \mu_n} C^*(\mu_1 \dots \mu_{p-1} \mu \mu_{p+1} \mu_n) \times e^{i\phi_{\mu'}(s_p)} C(\mu_1 \dots \mu_{p-1} \mu' \mu_{p+1} \dots \mu_n) \quad (109)$$

When a coherent radiation field $|\bar{n}\rangle$ is introduced, the state of the total system at $t = 0$ can be written as

$$|\Psi\bar{n}\rangle_{t=0} = \sum_{\mu_1 \dots \mu_n} C(\mu_1 \dots \mu_n) \times \prod_{p=1}^N [e^{i\phi_\mu(s_p)} e^{-\bar{n}/2} \sum_{n=0}^{\infty} \frac{(\bar{n})^{n/2}}{\sqrt{n!}} |n\rangle \otimes |\mu_p\rangle_+] \quad (110)$$

where the state of each complex is associated with the radiation state $|\bar{n}\rangle$.

Consider now the evolution of this system with the total Hamiltonian

$$\mathcal{H} = \sum_p H(s_p) \quad (111)$$

From Equations 36, 60 and 61, one has

$$|(n - m_\mu)\mu\rangle_+ = |n\rangle \otimes |\mu\rangle_+ \quad (112)$$

$$|n\rangle \otimes |\mu\rangle_+ = \sum_\lambda l_{n-m_\mu, \lambda \mu}^* |\psi_{n\lambda}\rangle \quad (113)$$

where m_μ is defined in Equation 71. Therefore,

$$\begin{aligned}
|\Psi\bar{n}\rangle_{t=0} &= \sum_{\mu_1 \dots \mu_n} C(\mu_1 \dots \mu_n) \prod_{p=1}^N \\
&\times [e^{i\phi_{\mu}(s_p)} e^{-n/2} \sum_n \frac{(\bar{n})^{n/2}}{\sqrt{n!}} \sum_{\lambda} l_{n-m_{\mu}, \lambda \mu}^*(s_p) |\psi_{n\lambda}^p\rangle] \quad (114)
\end{aligned}$$

Application of $\exp[-i\mathcal{H} t/\hbar]$ on $|\Psi\bar{n}\rangle_{t=0}$ and the transformation back to the original Hilbert space [using Equation 61] yields

$$\begin{aligned}
|\Psi\bar{n}\rangle_t &= \sum_{\mu_1 \dots \mu_n} C(\mu_1 \dots \mu_n) \prod_{p=1}^N \\
&\times [e^{i\phi_{\mu}(s_p)} e^{-n/2} \sum_n \frac{(\bar{n})^{n/2}}{\sqrt{n!}} \sum_{\lambda \mu'} l_{n-m_{\mu}, \lambda \mu}^*(s_p) \\
&\times l_{n\lambda \mu'}(s_p) e^{-iE_{n\lambda}(s_p)t/\hbar} |n+m_{\mu'}\rangle \otimes |\mu'p\rangle_+] \quad (115)
\end{aligned}$$

Let \mathcal{A} be an operator which describes an additive property of the N complexes:

$$\mathcal{A} = \sum_p A_p \quad (116)$$

where A_p represents the corresponding operator for the p^{th} complex. The expectation value of \mathcal{A} for the state (Equation 115) is given by

$$\begin{aligned}
{}_t\langle\Psi\bar{n}|\mathcal{A}|\Psi\bar{n}\rangle_t &= \sum_{\mu_1 \dots \mu_n \mu'_1 \dots \mu'_n} C^*(\mu_1 \dots \mu_n) C(\mu'_1 \dots \mu'_n) \\
&\times \sum_{p_0=1}^N \left\{ \prod_{p \neq p_0}^N [e^{-i\phi_{\mu}(s_p) + i\phi_{\mu'}(s_p)} e^{-n} \sum_n \frac{(\bar{n})^n}{n!} \sum_{\lambda} \right. \\
&\times l_{n-m_{\mu}, \lambda \mu}(s_p) l_{n-m'_{\mu'}, \lambda \mu'}(s_p)] \left. \right\}
\end{aligned}$$

$$\begin{aligned}
& \times \left\{ e^{-i\phi_\mu(s_{p_0}) + i\phi'_\mu(s_{p_0})} e^{-n} \sum_{nn'} \frac{(\bar{n})^{\frac{n+n'}{2}}}{\sqrt{n!n'}} \sum_{\lambda\lambda'} \right. \\
& \times e^{i[E_{n\lambda}(s_{p_0}) - E_{n'\lambda'}(s_{p_0})]t/\hbar} \sum_{\mu''\mu'''} \delta_{n+m_{\mu''}, n'+m_{\mu'''}} \\
& \times l_{n-m_\mu, \lambda\mu}(s_{p_0}) l_{n\lambda\mu''}^*(s_{p_0}) + \langle \mu'' | A_{p_0} | \mu'''\rangle + \\
& \left. \times l_{n'-m_{\mu'}, \lambda'\mu'}^*(s_{p_0}) l_{n'\lambda'\mu'''}(s_{p_0}) \right\} \quad (117)
\end{aligned}$$

The first curly bracket reduces to a product of Kronecker deltas. This can be seen from the orthogonality of the states $|\psi_{n\lambda}\rangle$. First, from Equations 36, 59 and 61, one has

$$\begin{aligned}
\langle \psi_{n\lambda} | \psi_{n'\lambda'} \rangle &= \sum_{\mu\mu'} l_{n\lambda\mu}^* l_{n'\lambda'\mu'} + \langle \mu | \mu' \rangle + \langle n + m_\mu | n' + m_{\mu'} \rangle \\
&= \delta_{nn'} \sum_{\mu} l_{n\lambda\mu}^* l_{n\lambda'\mu} = \delta_{nn'} \delta_{\lambda\lambda'} \quad (118)
\end{aligned}$$

Second, from the identity.

$$\begin{aligned}
\delta_{nn'} \delta_{\mu\mu'} &= (\langle n' | \otimes \langle \mu' |) \cdot (|n\rangle \otimes |\mu\rangle) \\
&= \sum_{\lambda\lambda'} l_{n'-m_{\mu'}, \lambda'\mu'}^* l_{n-m_\mu, \lambda\mu} \langle \psi_{n'\lambda'} | \psi_{n\lambda} \rangle \\
&= \delta_{nn'} \sum_{\lambda} l_{n-m_{\mu'}, \lambda\mu'}^* l_{n-m_\mu, \lambda\mu} \quad (119)
\end{aligned}$$

one obtains

$$\sum_{\lambda} l_{n-m_{\mu'}, \lambda\mu'}^* l_{n-m_\mu, \lambda\mu} = \delta_{\mu\mu'} \quad (120)$$

Thus,

$$\prod_{p \neq p_0}^N [e^{-i\phi_{\mu}(s_p) + i\phi_{\mu'}(s_p)} e^{-n} \sum_n \frac{(\bar{n})^n}{n!} \sum_{\lambda} \times l_{n-m_{\lambda, \lambda \mu}}(s_p) l_{n-m_{\mu', \lambda \mu'}}^*(s_p)] = \prod_{p \neq p_0}^N \delta_{\mu_p, \mu'_p} \quad (121)$$

The expectation value (Equation 117) becomes

$$\begin{aligned} {}_t \langle \Psi_n | \mathcal{A} | \Psi \bar{n} \rangle_t &= \sum_{p=1}^N \left\{ \sum_{\mu \mu'} \rho_{\mu \mu'}^{c p +} (0) e^{-n} \right. \\ &\times \sum_{n n' \lambda \lambda' \mu'' \mu'''} \delta_{n+m_{\mu'', n'+m_{\mu'''}}} \frac{(\bar{n})^{\frac{n+n'}{2}}}{\sqrt{n!n'!}} \\ &\times e^{i[E_{n\lambda}(s_p) - E_{n'\lambda'}(s_p)]t/\hbar} l_{n-m_{\mu, \lambda \mu}}(s_p) l_{n\lambda \mu'}^*(s_p) \\ &\left. \times l_{n'-m_{\mu', \lambda' \mu'}}^*(s_p) l_{n'\lambda' \mu''} (s_p) + \langle \mu'' | A_p | \mu''' \rangle_+ \right\} \quad (122) \end{aligned}$$

The expression in brackets is the trace of the time-dependent density matrix of the p^{th} complex with the operator A_p :

$$\begin{aligned} {}_t \langle \Psi \bar{n} | \mathcal{A} | \psi \bar{n} \rangle_t &= \sum_{p=1}^N \left[\sum_{\mu \mu'} + \langle \mu | \rho^c(s_p, t) | \mu' \rangle_+ + \langle \mu' | A_p | \mu \rangle_+ \right] \\ &= \sum_p \text{Tr}[\rho^c(s_p, t) A_p] \quad (123) \end{aligned}$$

${}_t \langle \Psi \bar{n} | \mathcal{A} | \Psi \bar{n} \rangle_+$ is a functional of the configuration of the stochastic variables $[s_1 s_2 \dots s_N]$.

Each configuration occurs with a certain probability. To find the macroscopic value of \mathcal{A}

at t , an average over all possible configurations must be taken. For the p^{th} complex, let this stochastic average be designated by

$$\int (ds_p) f(s_p) = \langle f \rangle_s \quad (124)$$

$$\int (ds_p) \cdot 1 = 1. \quad (125)$$

Thus

$$\begin{aligned} \langle {}_t \langle \Psi \bar{n} | \mathcal{A} | \Psi \bar{n} \rangle_t \rangle_s &= \prod_{p=1}^N \int (ds_p)_t \langle \Psi \bar{n} | \mathcal{A} | \Psi \bar{n} \rangle_t \\ &= N \int (ds) \text{Tr}[\rho^c(s, t) \mathcal{A}] \end{aligned} \quad (126)$$

This, now, is the method for obtaining the collective excitations of the entire system directly from the solutions for one complex plus the fundamental mode. The stochastic average of Equation 126 produces the phase matched solutions which can propagate through the N-complex + the radiation fields.

2.4 SECOND HARMONIC GENERATION FROM COLLISION COMPLEXES

Consider the expectation value of the operator \vec{D} :

$$\langle \vec{D}(t) \rangle = \sum_{n\lambda n'\lambda'} \rho_{n\lambda; n'\lambda'}^{(+)}(t) \langle \psi_{n\lambda} | \vec{D} | \psi_{n'\lambda'} \rangle \quad (127)$$

where $\rho_{n\lambda; n'\lambda'}^{(+)}(t)$ is given by Equations 74 and 75. In Equation 127, the angle θ between the atomic dipole moment operator \vec{d}_{10} and the polarization vector $\hat{\epsilon}$ is the stochastic variable. Now use Equation 126 and designate the result by

$$\vec{P}(t) = \frac{N}{\pi} \int_0^\pi d\theta \langle \vec{D}(t) \rangle \quad (128)$$

$\bar{P}(t)$ represents the macroscopic polarization of the N-complex system. The anomalous SHG arises from the spectral components of $P(t)$ which are at $2\omega, 2\omega \pm \xi'$ and $2\omega \pm \xi'$. For an intense coherent field and to lowest order in \mathcal{V} , the amplitude of the component at 2ω is [Ref. 23]:

$$\bar{P}_{SH}(t) \approx -\hat{e} e^{-2i\omega t} \frac{N|\bar{d}_{10}|}{(E_1)^2} (\text{Im} \mathcal{V}_{00;10})(\mathcal{V}_{10;11} - \mathcal{V}_{00;01}) S(\zeta) + c.c. \quad (129)$$

where ζ is given by Equation 93 and

$$S(\zeta) \equiv -\zeta/(1 + \zeta^2) + (3/\zeta) - (3/\zeta^2) \tan^{-1} \zeta. \quad (130)$$

Note that in Ref. 23 a slightly different basis was used, which introduced an extra $\sqrt{2}$ factor in the coupling coefficients. The results are the same otherwise.

Figure 2 shows S versus ζ . For extremely small ζ , S is proportional to ζ . For finite ζ , S increases at first as ζ^2 , then as ζ . To the right of the peak, S is proportional to ζ^{-1} and thus decreases as ζ increases. ζ^2 is proportional to the fundamental intensity I_ω . S^2 is proportional to the second harmonic intensity $I_{2\omega}$. Figure 2 suggests that in terms of intensities,

$$I_{2\omega} \propto \begin{cases} I^3 & \text{for } \Omega_R < 10^{-2} \Delta \\ I_\omega^2 & \Omega_R \sim 10^{-1} \Delta \\ I_\omega & \Omega_R < \Delta \\ I_\omega^{-\frac{1}{2}} & \Omega_R \gg \Delta \end{cases} \quad (131)$$

To be able to compare these results, for example, with the Na-vapor experiments, several complications need to be addressed. In the atomic structure of Na, there are a group of states which have approximately twice the energy of the first excited states. This fact has two influences. One is that in the calculation of $+\langle 0|\bar{D}|3\rangle_+$, they cause a near-resonant-enhancement. The other is that they can directly participate in radiative transitions, coupling both to the second harmonic mode, as well as to the fundamental mode (via two-photon transitions). In other words, the set of basis states in Equations 23-26 must be enlarged to analyze the experiments correctly.

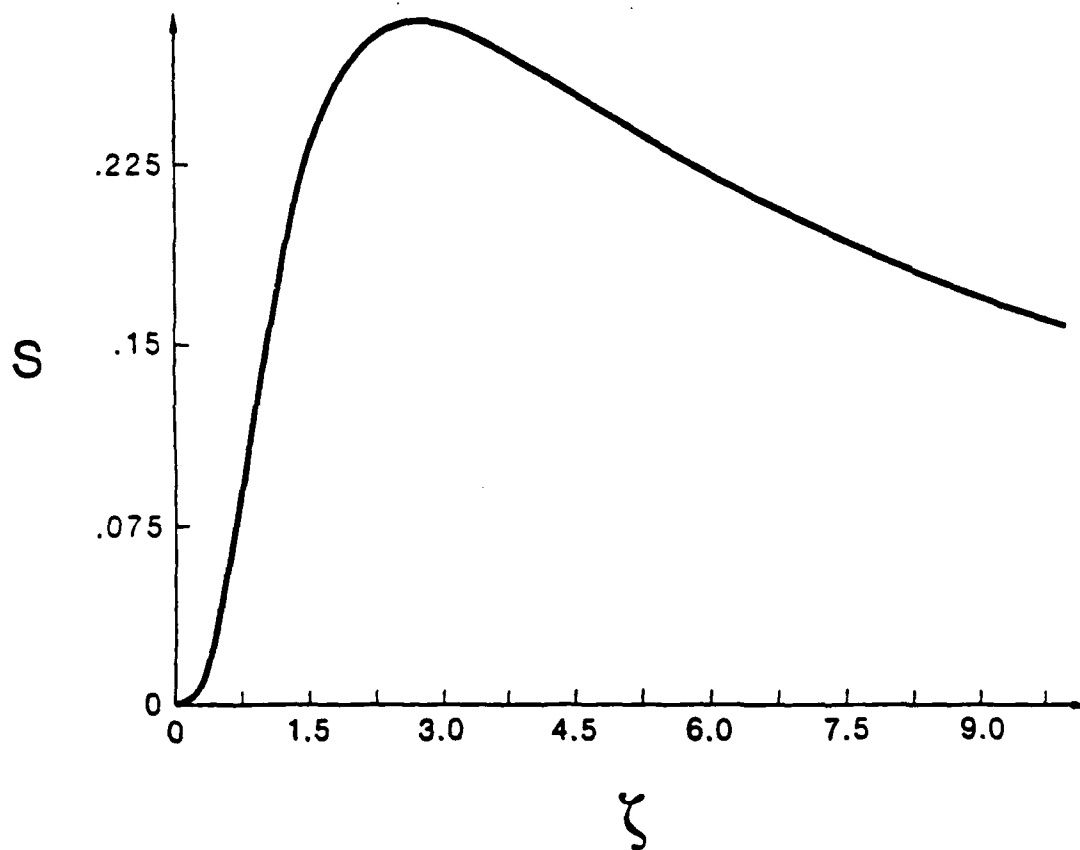


Figure 2. The intensity dependence of the second harmonic polarization.

The near-resonant-enhancement of ${}_+ \langle 0 | \bar{D} | 3 \rangle_+$ may be estimated in the following way. The relevant group of higher excited states may be simulated in the present model by assuming that there is a second excited $\alpha = 2$ state such that $E_2 \approx 2E_1$, but the two energies E_2 and $2E_1$ are sufficiently different so that there is no need to enlarge the set (Equations 23-26) within the rotating-wave-approximation. For the calculation of ${}_+ \langle 0 | \bar{D} | 3 \rangle_+$, the factor

$$\frac{1}{E_1} (\nu_{10;11} - \nu_{00;01})$$

in Equation 129 should be replaced by

$$\frac{\nu_{02;11}}{(2E_1 - E_2)} \left[\frac{\nu_{10;02} + \nu_{10;20}}{E_1} - \frac{\nu_{00;12}}{E_1 + E_2} \right]$$

The comparison of the present theory with the Na-experiment is further complicated by the fact that the experimenters attempted to increase SHG by tuning to a double-photon resonance of the isolated atom. The results of these attempts might have been to induce real population transfers to certain single atom states, creating favorable conditions for stimulated emission from these states, as well as causing the vapor to act as an amplifier to the fundamental mode. As discussed in Section 2.2, nearing a population inversion destroys the coherence of the collision complexes. Without these coherences, there is no collision-induced SHG.

Nevertheless, with the above caveats, it is possible to make preliminary comparisons. The best data for this purpose is provided in Ref. 6. The authors noted that the second harmonic intensity varied as I_ω^3 at first, then I_ω^2 , and at the highest intensities in their experiment, as I_ω . This is precisely the behavior described in Equation 131. Clearly, in their experiments, they were confined to an extremely small region near the origin. In fact, for the data they label as "3s - 4d" tuning, they did not leave the region $\zeta_{ezp} \leq 0.07$, where $I_{2\omega} \sim I_\omega^2$. It follows that their maximum S was about $S_{ez} \approx 0.005$. Figure 2 implies that the maximum possible S is $S_m \approx 0.3$. Their observed quantum efficiencies

(η_{ez}) were on the order of $10^{-4} - 10^{-5}$. Therefore, the present calculations suggest that the maximum possible quantum efficiency in the Na-vapor is on the order of

$$\eta_m = \frac{|S_m|^2}{|S_{ez}|^2} \eta_{ez} \approx -0.04. \quad (132)$$

2.5 A SUITABLE SYSTEM FOR THE DOUBLING OF THE OXYGEN-IODINE FREQUENCY

The preceding discussion on *Na* points out two important features of the collision-induced SHG. The first is that the fundamental frequency should be appropriately detuned from the atomic transition frequency which is to be exploited for SHG. This detuning depends on the intensity of the fundamental mode. The second is that there should be higher excited states at twice the fundamental frequency, which contribute to near-resonant-enhancement of the collisionally-induced coupling coefficient to the second harmonic mode. The latter feature is not a common property of atomic structures. It is, however, much more easily obtained in gas mixtures in which collision complexes of interest are formed by two different types of atoms. In particular, mixtures of *I* atoms with *La* atoms might provide an efficient second harmonic generator at 1.3μ .

Although the preceding discussion was confined to one type of atoms, certain qualitative conclusions may be drawn from it for an optimal system of SHG for the 1.3μ radiation. An analysis of the collision-induced coupling coefficient to the second harmonic mode in Sections 2.1 and 2.4 shows that if the collision complex is composed of an *A* atom and a *B* atom, then there is a term in the coupling coefficient, whose denominator is given by $(E_1^A - E_0^A + E_1^B - E_2^B)$, where $E_0^{A \cdot B}$ is the ground state energy, $E_1^{A \cdot B}$ is the energy of the first excited state, and $E_2^{A \cdot B}$ is the higher excited state. This means that for near resonant enhancement of the coupling coefficient, the sum of the transition energies of the first excited states of the *A* and *B* atoms must be near the transition energy of the second excited state of the *B* atom. It is possible to make this denominator quite small by choosing the *I* atom for *A* and the *La* atom for *B*. The ground state

of the La atom is a ${}^4D_{3/2}$ state. It has a ${}^4F_{5/2}^0$ state which is above the ${}^4D_{3/2}$ state by about $7,000cm^{-1}$. Above the ${}^4F_{5/2}^0$ state, it has a bunch of states: ${}^4F_{5/2}^0[13,600cm^{-1}]$, ${}^4D_{3/2}[14,700cm^{-1}]$, ${}^4D_{1/2}[14,000cm^{-1}]$, ${}^4F_{7/2}^0[15,000cm^{-1}]$, etc. Here the indicated energies are relative to the ground state of the La atom. For the I atom, $E_1^I - E_0^I \simeq 7,600cm^{-1}$. Therefore,

$$(E_1 - E_0) + (E_1^{La} - E_0^{La}) \simeq 14,600cm^{-1}$$

This value is extremely close to the transition energies of the higher excited states of the La atom listed above. One would therefore obtain a strong resonant enhancement of the coupling coefficient.

To be able to provide quantitative estimates, one needs to extend the theory of the previous sections to gaseous mixtures.

3.0 NEW CRYSTALS FOR FREQUENCY UP-CONVERSION

3.1. BAND STRUCTURE OF SUPERLATTICES/MULTIPLE-QUANTUM-WELLS

In heterostructure crystals, such as quantum wells and superlattices, nonlinear susceptibilities are increased several orders of magnitude over those of the composite materials in the homogeneous crystal phase. They are therefore quite attractive for frequency up-conversion, and in particular for harmonic generation. As a preliminary to investigations of their optical interactions, the principal investigator developed a new band theory of superlattices and multiple-quantum-wells (SL/MQWs), whose details of the derivations are given in Refs. 24 and 25.

Since it became possible to grow SL/MQW crystals in the early seventies [Ref. 26], there have been several theoretical approaches to their band structure [Refs. 27-40]. These approaches are generally based on some form of either the envelope function approximation [Refs. 33-36] or the tight binding approximation [Refs. 37-40]. The early empirical results concerning absorption, luminescence, carrier transport, etc. in superlattices could be explained, at least qualitatively, by means of simple quantum wells and Kronig-Penney models [Refs. 27-32]. Later experiments revealed the appearance of certain forbidden transitions [Refs. 41-42]. To explain these, as well as subband energy dispersions, one needs to go to more sophisticated theories in which band mixing occurs [Refs. 35, 36, 43].

In Bastard's envelope function approach [Refs. 33-36], one generalizes Kane's theory [Ref. 44] for the III-V semiconductor compounds to superlattices, and writes a Kane Hamiltonian for each type of material composing the superlattice. The solutions of these effective Hamiltonians are then joined across layer interfaces by means of boundary conditions which require continuity of wave functions and conservation of electron current densities. These calculations ultimately depend on the effective mass concept. The effective mass of the electron is assumed to be position dependent along the superlattice axis (that is to say, along the direction which is vertical to the planes of the superlattice

layers). The space dependence of the effective mass is not calculated, but is postulated to have a certain form; then the results are compared with empirical observations to the extent that this is possible.

Tight binding calculations of superlattices can, in principle, be more accurate than calculations based on the envelope function approximation, but they involve extensive and complex numerical computations. In a tight binding calculation, one uses superpositions of large numbers of electronic orbitals to solve for the eigenvalues and eigenfunctions of a tight binding Hamiltonian [Ref. 45]. Band mixing can be directly incorporated into these computations and optical spectra of superlattices can be reproduced reasonably accurately [Ref. 43].

This report presents a new one-electron theory of superlattices. The homogeneous crystal band structures of the composite materials are assumed to be completely known. A superlattice Hamiltonian in the momentum Bloch representation is obtained, which expresses all of the effects of symmetry breaking in terms of the quantities and parameters related to the homogeneous crystals of the composite materials and the superlattice geometry. Also, series expressions for the superlattice subband energies and wave functions, which can be evaluated systematically with increasing accuracy are presented. The virtue of the new formulation, however, lies in the fact that it provides much greater conceptual clarity and pliability for analytic manipulation than the previous theories.

Consider two types of materials, A and B, whose homogeneous lattice structures match:

$$\vec{R}_A = \vec{R}_B = \vec{R} \quad (\text{lattice translation vectors}) \quad (133)$$

$$\vec{G}_A = \vec{G}_B = \vec{G} \quad (\text{reciprocal lattice vectors}) \quad (134)$$

Assume that the Bloch functions of the homogeneous crystals of these materials are completely known:

$$H_{A,B} = \frac{\vec{p}^2}{2m} + V_{A,B}(\vec{x}) \quad (135)$$

$$H_{A,B} |n\vec{k}\rangle_{A,B} = E_n^{A,B}(\vec{k}) |n\vec{k}\rangle_{A,B}; \langle \vec{x} | n\vec{k} \rangle_{A,B} = \psi_{n\vec{k}}^{A,B}(\vec{x}) \quad (136)$$

Assume that the reciprocal lattice is a simple cubic lattice with one of the principal directions along the \hat{z} -axis. This is a minor simplifying assumption; the results are easily generalized for arbitrary lattice orientations. The reciprocal lattice vectors G_z can be written

$$G_z = \frac{2\pi}{a} M, \quad M = 0, \pm 1, \pm 2, \dots \quad (137)$$

a is the fundamental lattice constant of the homogeneous crystals of A and B . Define

$$l_0 = \frac{L}{a} = \text{a positive integer.} \quad (138)$$

Consider now the geometry shown in Fig. 3. The layers of material A of width L_A are sandwiched in between the layers of material B of width L_B . Assume initially that a finite number, \mathcal{N} , of A layers are embedded in B . In the momentum Bloch representation, let \mathcal{N} become infinite, making the composite structure a superlattice. Keeping \mathcal{N} initially infinite avoids some minor mathematical problems, as discussed in Ref. 24. Let the \hat{z} -axis be vertical to the layers (the superlattice axis). Pick the origin of the coordinate system as symmetrically as possible for the convenience of evaluating certain sums later. If \mathcal{N} is an odd integer, the origin is in the middle of an A layer as shown in Fig. 3a. If \mathcal{N} is even, the origin is in the middle of a B layer as shown in Fig. 3b. In the superlattice limit, whether one starts with odd or even \mathcal{N} does not matter; the results are independent of the initial configuration. For the following choose the initial configuration to be the one shown in Fig. 3a with odd \mathcal{N} . The layers of A and B are assumed to have perfectly sharp plane interfaces.

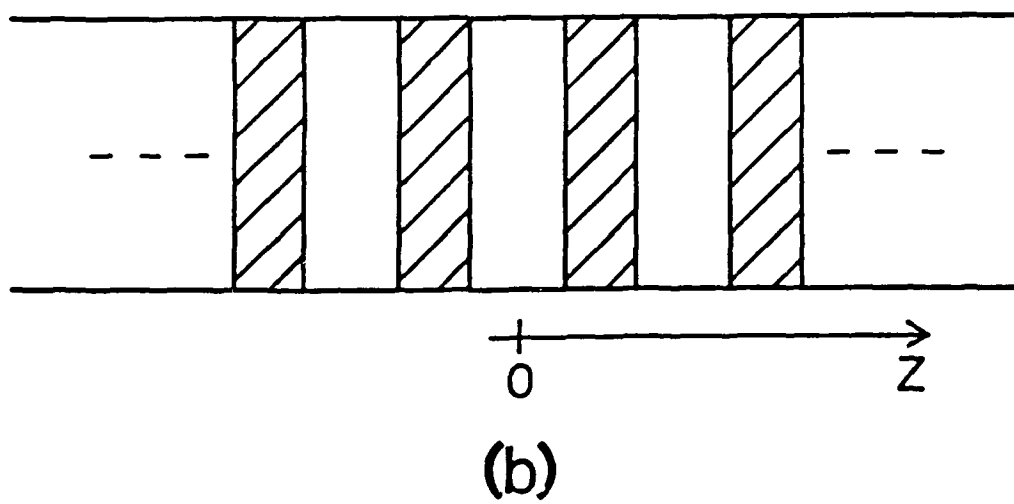
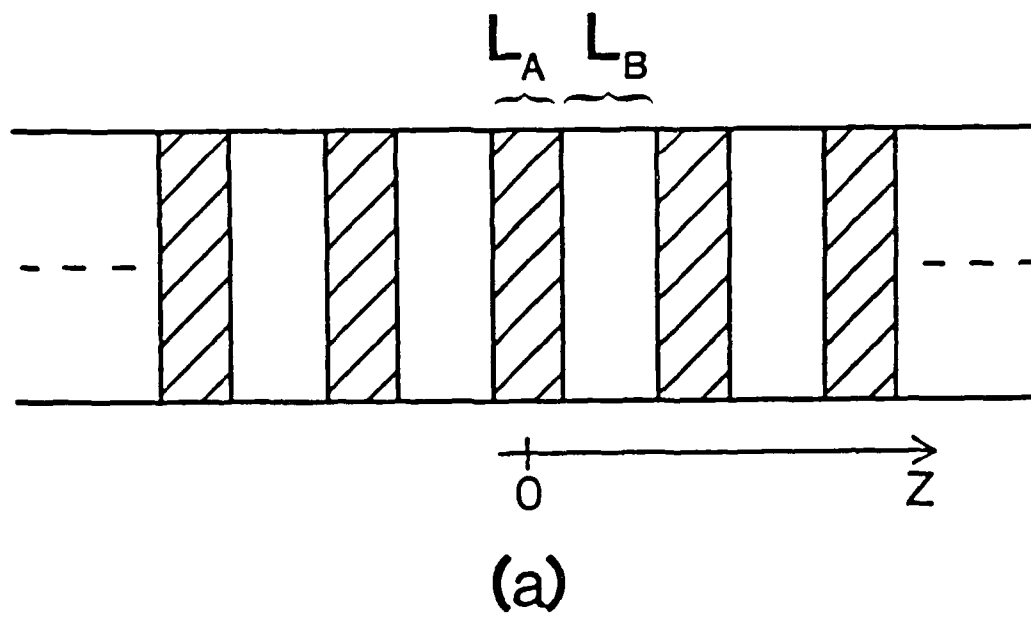


Figure 3. Origin of the coordinates for odd (a) and even (b) \mathcal{N} .

The one-electron Hamiltonian of the composite crystal of Fig. 3a can be written as

$$H = \frac{\bar{p}^2}{2m} + V_B(\bar{x}) + [V_A(\bar{x}) - V_B(\bar{x})] \sum_{s=-\frac{(\mathcal{N}-1)/2}{L}}^{\frac{(\mathcal{N}-1)/2}{L}} \times \left[\theta(z - sL + \frac{1}{2}L_A) - \theta(z - sL - \frac{1}{2}L_A) \right] = \frac{\bar{p}^2}{2m} + V_B(\bar{x}) + H_{AW}(\bar{x}) \quad (139)$$

where θ 's are the step functions, and L is the superlattice period along the superlattice axis:

$$L = L_A + L_B \quad (140)$$

Consider now the matrix elements of this Hamiltonian in the representation defined by the Bloch functions of the B type crystal. In the superlattice limit, namely when

$$\mathcal{N} \rightarrow \infty$$

$$\mathcal{L}_z \rightarrow \infty$$

$$\rho = \frac{\mathcal{N}}{\mathcal{L}_z} = \text{constant} \quad (141)$$

one finds

$${}_B \langle n\bar{k} | H | n'\bar{k}' \rangle_B = \delta_{nn'} \delta(\bar{k}, \bar{k}') E_N^B(\bar{k}) + {}_B \langle n\bar{k} | H_{AW} | n'\bar{k}' \rangle_B \quad (142)$$

$$\begin{aligned} {}_B \langle n\bar{k} | H_{AW} | n'\bar{k}' \rangle_B &= \rho L_A \sum_{lM} \sum_{\vec{G}} \delta(\bar{k}, \bar{k}' + \frac{2\pi l}{L} \hat{z}) \frac{\sin \left[\frac{\pi L_A}{L} (l - l_0 M) \right]}{\left[\frac{\pi L_A}{L} (l - l_0 M) \right]} \\ &\times W(\vec{G}' - \vec{G}) \phi_n^{B*}(\bar{k} - \vec{G}) \phi_n^B(\bar{k} - \vec{G}' - \frac{2\pi l}{L} \hat{z} + \frac{2\pi M}{a} \hat{z}) \end{aligned} \quad (143)$$

where $\phi_n^B(\bar{k})$ is the momentum Bloch function of the crystal type B and $W(\vec{G})$ is related to band offsets:

$$\begin{aligned}
W(\vec{G}) &= \nu_{\vec{G}}^A - \nu_{\vec{G}}^B \\
&= \sum_n \left[E_n^A(0) \phi_n^A(0) \phi_n^{A*}(-\vec{G}) - E_n^B(0) \phi_n^B(0) \phi_n^{B*}(-\vec{G}) \right]
\end{aligned} \tag{144}$$

Next, consider a superlattice eigenstate $|\psi\rangle$. Since the set of B type Bloch states is complete,

$$|\psi\rangle = \sum_{n, \vec{k}} a_n(\vec{k}) |n, \vec{k}\rangle_B \tag{145}$$

Note that the sum over \vec{k} is confined to the Brillouin Zone of the homogeneous crystals.

The time-independent Schrödinger equation for $|\psi\rangle$ is

$$H|\psi\rangle = \sum_{n', \vec{k}'} a_{n'}(\vec{k}') (H_B + H_{AW}) |n', \vec{k}'\rangle_B = \epsilon |\psi\rangle \tag{146}$$

Define

$$\vec{k} = \vec{\kappa} + \frac{2\pi l}{L} \hat{z} \tag{147}$$

such that

$$k_x = \kappa_x$$

$$k_y = \kappa_y$$

$$-\frac{\pi}{L} < \kappa_x < \frac{\pi}{L}$$

$$l = 0, \pm 1, \pm 2, \dots, \pm(l_0 - 1) \tag{148}$$

Let

$$a_{nl}(\vec{\kappa}) = a_n(\vec{\kappa} + \frac{2\pi l}{L}\hat{z}) \quad (149)$$

$$E_{nl}^B(\vec{\kappa}) = E_n^B(\vec{\kappa} + \frac{2\pi l}{L}\hat{z}) \quad (150)$$

$$V_{nl;n'l'}(\vec{\kappa}) = \rho L_A \sum_{M=-\infty}^{+\infty} \frac{\sin[\frac{\pi L_A}{L}(l-l'-l_0 M)]}{[\frac{\pi L_A}{L}(l-l'-l_0 M)]} \Sigma_{\vec{G}\vec{G}'} W(\vec{G}' - \vec{G}) \\ \times \phi_n^B(\vec{\kappa} - \vec{G} + \frac{2\pi l}{L}\hat{z}) \phi_{n'}^B(\vec{\kappa} - \vec{G} + \frac{2\pi M}{a}\hat{z} + \frac{2\pi l'}{L}\hat{z}) \quad (151)$$

Equation 145 becomes

$$[\epsilon - E_{nl}^B(\vec{\kappa})] a_{nl}(\vec{\kappa}) - \sum_{n'l'} V_{nl;n'l'}(\vec{\kappa}) a_{n'l'}(\vec{\kappa}) = 0 \quad (152)$$

Let

$$\alpha_n(\vec{\kappa}) = \begin{pmatrix} a_{nl_0-1}(\vec{\kappa}) \\ a_{nl_0-2}(\vec{\kappa}) \\ \vdots \\ a_{n-l_0+1}(\vec{\kappa}) \end{pmatrix} \quad (153)$$

$$\epsilon_n^B(\vec{\kappa}) = \begin{pmatrix} E_{nl_0-1}^B(\vec{\kappa}) & & & 0 \\ & E_{nl_0-2}^B(\vec{\kappa}) & & \\ & & \ddots & \\ 0 & & & E_{n-l_0+1}^B(\vec{\kappa}) \end{pmatrix} \quad (154)$$

and

$$[\mathcal{V}_{nn'}(\vec{\kappa})]_{ll'} = V_{nl;n'l'}(\vec{\kappa}) \quad (155)$$

Equation 152 can then be written in terms of the $2l_0 - 1$ component spinors α_n and $(2l_0 - 1) \times (2l_0 - 1)$ matrices $\mathcal{V}_{nn'}$ as

$$\sum_{n'} [\mathcal{E}_n^B(\vec{\kappa}) \delta_{nn'} + \mathcal{V}_{nn'}(\vec{\kappa})] \alpha_{n'}(\vec{\kappa}) = \epsilon \alpha_n(\vec{\kappa}) \quad (156)$$

Equations 152 and 156 show that a given band of the homogeneous crystal splits into $2l_0 - 1$ components in the superlattice. The components are the superlattice subbands. There is a correspondence between them and the bound states of quantum wells. The splitting arises entirely from the symmetry breaking along the \hat{z} -axis. The original Brillouin Zone of the homogeneous crystal is partitioned into $2l_0 - 1$ sections. The central piece for $-\frac{\pi}{L} < \kappa_z < \frac{\pi}{L}$ becomes the new Brillouin Zone for the superlattice. The subbands of a band n arise from the folding of the original E_n onto the superlattice Brillouin Zone. Furthermore, the Hamiltonian which determines the subband energies and subband states (in the representation of $\{|n\vec{k}\rangle_B\}$) becomes a supermatrix given by

$$\mathcal{H}_{n_l; n'_{l'}}^{SL}(\vec{\kappa}) = E_{n_l}^B(\vec{\kappa})\delta_{nn'}\delta_{ll'} + V_{n_l; n'_{l'}}(\vec{\kappa}) \quad (157)$$

Note that $\kappa_z = \pm\pi/L$ represent identical points in the superlattice Brillouin Zone, since they are related by the momentum $2\pi\hat{z}/L$. Only one value is needed in the superlattice Brillouin Zone, for example $\kappa_z = +\pi/L$.

Simpler expressions than Equation 151 can be obtained for $V_{n_l; n'_{l'}}$ with the aid of the interband position operator. They are given in Ref. 24.

The energy eigenvalues and eigenstates of Equation 152 may be obtained using Lowdin's theorem [Ref. 46]. Define the matrix function $Z_{n_l; n'_{l'}}(E)$ in terms of the series

$$\begin{aligned} Z_{n_l; n'_{l'}}(E) = & \mathcal{H}_{n_l; n'_{l'}}^{SL} + \sum'_{n_1 l_1} \frac{V'_{n_l; n_1 l_1} V'_{n_1 l_1; n'_{l'}}}{(E - \mathcal{H}_{n_1 l_1}^D)} \\ & + \sum'_{n_1 l_1 n_2 l_2} \frac{V'_{n_l; n_1 l_1} V'_{n_1 l_1; n_2 l_2} V'_{n_2 l_2; n'_{l'}}}{(E - \mathcal{H}_{n_1 l_1}^D)(E - \mathcal{H}_{n_2 l_2}^D)} + \dots \end{aligned} \quad (158)$$

where

$$\mathcal{H}_{n_l}^D = \mathcal{H}_{n_l; n_l}^{SL} \quad (159)$$

$$V'_{n'l;n'l'} = (1 - \delta_{nn'}\delta_{ll'})V_{n'l;n'l'} \quad (160)$$

The primes over the summation signs mean that the sums exclude the nl -terms. An eigenvalue of Equation 152 is given by the solution of the equation

$$\epsilon_{nl}(\vec{\kappa}) = Z_{n'l;n'l}(\epsilon_{nl}(\vec{\kappa})) \quad (161)$$

such that

$$\lim_{W \rightarrow 0} \epsilon_{nl}(\vec{\kappa}) = E_{nl}^B(\vec{\kappa}) \quad (162)$$

The nondegenerate eigenstate corresponding to ϵ_{nl} is given by

$$\psi_{n'l\vec{x}}(\vec{x}) = \eta_{n'l} \left\{ \psi_{n'l\vec{x} + \frac{2\pi l}{L}\vec{x}}^B + \sum'_{n'l'} \frac{Z_{n'l';n'l}(\epsilon_{nl}) \psi_{n'l\vec{x} + \frac{2\pi l'}{L}\vec{x}}^B(\vec{x})}{(\epsilon_{nl} - \chi_{n'l'}^D)} \right\} \quad (163)$$

where

$$\eta_{n'l} = \left[1 + \sum'_{n'l'} \frac{Z_{n'l';n'l}^*(\epsilon_{nl}) Z_{n'l';n'l}(\epsilon_{nl})}{(\epsilon_{nl} - \chi_{n'l'}^D)^2} \right]^{-\frac{1}{2}} \quad (164)$$

Reference 24 describes the procedure in case of degeneracy.

To explore the implications of the preceding results, let us consider a superlattice crystal composed of two-band materials (one conduction and one valence band). Assume that these bands are parabolic in the homogeneous crystal phase and that there is no degeneracy. With further approximations discussed in Ref. 24, the superlattice conduction subbands are given by

$$\begin{aligned} \epsilon_{c0}(\vec{\kappa}) = & E_{c0}^B(\vec{\kappa}) + \rho L_A W(0) + \sum_l \frac{(1 - \delta_{l0}) \rho^2 L_A^2 W^2(0) \cos^2(l\xi) \sin^2\left(\frac{\pi L_A l}{L}\right)}{[E_{c0}^B(\vec{\kappa}) - E_{cl}^B(\vec{\kappa})] \left(\frac{\pi L_A l}{L}\right)^2} \\ & - \sum_l \frac{(1 - \delta_{l0}) \rho^2 L_A^2 W^2(0) \sin^2(l\xi) \sin^2\left(\frac{\pi L_A l}{L}\right)}{[E_{c0}^B(\vec{\kappa}) - E_{v0}^B(\vec{\kappa})] \left(\frac{\pi L_A l}{L}\right)^2} + \dots \end{aligned} \quad (165)$$

for the lowest subband $l = 0$, and

$$\begin{aligned} \epsilon_{c|l}^{\pm}(\vec{\kappa}) = & E_c^B(0) + \rho L_A W(0) + \frac{\hbar^2 \vec{\kappa}^2}{2m_{Bc}} + \frac{2\pi^2 \hbar^2 l^2}{m_{Bc} L^2} \\ & \pm \left[\frac{2\pi^2 \hbar^2 l \kappa_z}{m_{Bc} L} \right]^2 + \rho^2 L_A^2 W^2(0) \cos^2(2l\xi) \frac{\sin^2\left(\frac{2\pi l L_A}{L}\right)}{\left(\frac{2\pi l L_A}{L}\right)^2} \right]^{\frac{1}{2}} \end{aligned} \quad (166)$$

for finite l . Here ξ is a band mixing parameter [see Equation 80 of Ref. 24].

Consider $\epsilon_{c|l}^{\pm}$ given by Equation 166. The first two terms define the position of the energy band, taking into account the band offsets between the two materials. The third term gives mainly the dispersion in the transverse directions. The fourth term comes from the folding of the Brillouin zone and describes the partial localization of the electron. For $L_A = L_B = L/2$, this term becomes

$$\frac{2\pi^2 \hbar^2 l^2}{m_{Bc} L^2} = \frac{\hbar^2}{2m_{Bc}} \left(\frac{\pi l}{L_A} \right)^2 \quad (167)$$

This is identical to the standard expression for a rectangular well of width L_A (for an infinitely deep well).

The above comparison with the quantum well model depends on the fact that the homogeneous crystal bands are parabolic. If they are not parabolic, it is much harder to make a comparison. For some narrow gap semiconductors, conduction and valence bands can be approximated with linear dispersion relations. For example, let

$$E_c^B(\vec{k}) = E_c^B(0) + |\vec{\alpha} \cdot \vec{k}| \quad (168)$$

Conduction subband energies for finite l become

$$\begin{aligned} \epsilon_{c|l}^{\pm}(\vec{\kappa}) = & E_c^B(0) + \frac{1}{2} \left(\left| \vec{\alpha} \cdot \vec{\kappa} + \frac{2\pi l \alpha_z}{L} \right| + \left| \vec{\alpha} \cdot \vec{\kappa} - \frac{2\pi l \alpha_z}{L} \right| \right) \\ & \pm \left[\frac{1}{4} \left(\left| \vec{\alpha} \cdot \vec{\kappa} + \frac{2\pi l \alpha_z}{L} \right| - \left| \vec{\alpha} \cdot \vec{\kappa} - \frac{2\pi l \alpha_z}{L} \right| \right)^2 + \bar{W}^2 C_l^2 S_l^2 \right]^{\frac{1}{2}} \end{aligned} \quad (169)$$

where \tilde{W} , C_l and S_l are defined in Ref. 24. The dependence on $|l|$ here is quite different than in Equation 167.

The last term of Equation 166, which is a square root, makes the subbands nonparabolic in the \hat{z} -direction. In the x, y -directions they are still parabolic. Because of nonparabolicity, one must be careful in assigning an effective mass for a subband. The effective mass can be quite different for $\kappa_x = 0$ and $\kappa_x = \text{finite}$ for nonparabolic bands. For $l \neq 0$, the effective masses as $\kappa_x \rightarrow 0$ are given by

$$\begin{aligned} \frac{1}{m_{c|l}^\pm} &= \frac{1}{\hbar^2} \left(\frac{\partial^2 \epsilon_{c|l}^\pm}{\partial \kappa_x^2} \right)_{\kappa_x = 0} \\ &= \frac{1}{m_{Bc}} \left[1 \pm \frac{4\pi^2 \hbar^2 l^2}{m_{Bc} L^2 \rho L_A |W(0) \cos 2\xi l|} \left| \frac{(2\pi l L_A / L)}{\sin(2\pi l L_A / L)} \right| \right] \end{aligned} \quad (170)$$

For $l = 0$:

$$\frac{1}{m_{c0}} = \frac{1}{m_{Bc}} \left[1 - \frac{2m_{Bc}^2 L^6 \rho^2 W^2(0)}{\pi^6 \hbar^4} \sum_{l=1}^{l_0-1} \frac{1}{l^6} \cos^2(l\xi) \sin^2\left(\frac{\pi l L_A}{L}\right) \pm \dots \right] \quad (171)$$

Note that

$$\frac{m_{c0}}{m_{Bc}} > 1, \quad \frac{m_{c|l}^-}{m_{Bc}} > 1, \quad \frac{m_{c|l}^+}{m_{Bc}} < 1 \quad (172)$$

For large l , the difference of $m_{c|L|}^\mp / m_{Bc}$ from unity becomes more pronounced. These theoretical predictions for the subband effective masses should exhibit themselves in linear and nonlinear susceptibilities through the density of states.

Band mixing occurs throughout the formulas. In the subband energies, band mixing is associated with the parameter ξ . If ξ is zero or some multiple of π , then band mixing does not occur. In the subband wave functions given by Equation 163, the last set of terms under the summation sign represents the band mixing terms. These terms are responsible for the modification of the selection rules for radiative transitions.

When the electronic spin is taken into account, the Hamiltonian (Equation 142) becomes much more complicated. The spin-orbit coupling is discussed in Ref. 25. Here the discussion is restricted to a few comments.

The spin-orbit coupling contributes two terms to the overall Hamiltonian: \mathcal{H}^{S1} [see Equation 19d of Ref. 25] and \mathcal{H}^{S2} [Equation 19e of Ref. 25]. \mathcal{H}^{S1} is related to the presence of the interfaces. When an electron crosses an interface, it experiences a pulse of magnetic field in its rest frame. \mathcal{H}^{S1} describes the coupling of the electron to this field. \mathcal{H}^{S2} arises from the zone-folding of the difference of the spin-orbit interactions of the homogeneous crystals. The present theory suggests that the off-diagonal matrix elements of \mathcal{H}^{S1} is an order of magnitude larger than the matrix elements of \mathcal{H}^{S2} . The main influence of \mathcal{H}^{S1} is on the selection rules for the radiative transitions. These selection rules are modified. The energy shifts of the subbands, however, come mainly from \mathcal{H}^{S2} .

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