Reprinted from THE PHYSICAL REVIEW, Vol. 89, No. 4, 667-671, February 15, 1953
Printed in U. S. A.

The Theory of Electron Diffraction

ROY GLAUBER,* *Norman Bridge Laboratory of Physics, California Institute of Technology, Pasadena, California*
AND
VERNER SCHOMAKER, *Gates and Crellin Laboratories of Chemistry, California Institute of Technology,† Pasadena, California*

(Received October 14, 1952)

It is shown that the omission of an angle-dependent phase factor in the scattering amplitude constitutes a significant error of the Born approximation, as customarily applied to electron diffraction experiments. Some general properties of the scattering amplitude are discussed in relation to the Born approximation and used to derive a simple estimate of the required phase. The theory, thus corrected, is found to remove the need for assuming rather distorted structures in some molecules containing heavy atoms. The effect discussed is present quite generally in the interference of waves scattered by differing potentials and becomes more prominent as the particle energy is lowered. In the Appendix a semiclassical procedure is used to treat the analogous effect in proton diffraction.

THE Born approximation is well known to predict exactly, in the nonrelativistic region, the intensity of electrons scattered by a Coulomb field. Although still a perturbation method, it has seemed in this case nearly immune from the usually attendant inaccuracies and has been widely and successfully used in the analysis of electron diffraction patterns. Confidence in the approximation as ordinarily applied to molecular structure determinations has extended even to a number of cases which have seemed to reveal rather improbable structures. On re-examining several of these (which are briefly noted in Sec. I), we have found that a phase change, heretofore neglected, which takes place on scattering is the probable cause of the anomalies.[1] It may, in extreme cases, lead to strikingly altered conclusions about molecular structure. The error is one characteristic of the Born approximation and appears whenever it is applied to the interference of waves scattered by potentials of different strengths. The phase shift in question, which depends significantly on the effects of screening, is calculated approximately in Sec. II, and the results are then compared with experiment.

I. NATURE OF THE EFFECT

The diffraction patterns of electrons scattered by gases consist of weak concentric rings superposed on the intense forward maximum of Coulomb scattering (modified by screening). Fourier analysis of the ring structure gives the distances between the scattering centers of the molecule. In some molecules containing heavy atoms a curious effect involving these distances has been found. Uranium hexafluoride, in which the effect was first noted, might be expected to show octahedral symmetry about the uranium atom. The molecule has instead appeared rather puzzlingly asymmetric: the calculated curves showing the distribution of interatomic distances[2] have two distinctly separated peaks at 1.87A and 2.17A rather than a single one corresponding to a unique U—F bond length. Information from other sources, however, in no way confirms this picture. The data on infrared spectra, molecular entropy, and the dipole moment are all consistent with the symmetrical structure.[3] Similar apparent asymmetries have also been found to occur in a number of other molecules of the form MX_n, containing single heavy atoms. The distances between the heavy atom and its neighbors are apparently split into two equal groups differing by an amount roughly proportional to $Z_M - Z_X$. For equal atomic numbers as in the heavy molecule I_2, nothing unusual is observed.

We shall not dwell upon the valence-theoretical

* Present address: Lyman Laboratory of Physics, Harvard University, Cambridge 38, Massachusetts.
† Contribution No. 1743.
[1] V. Schomaker and R. Glauber, Nature 170, 290 (1952).
[2] S. H. Bauer, J. Chem. Phys. 18, 27 (1950).
[3] See especially Bigeleisen, Mayer, Stevenson, and Turkevich, J. Chem. Phys. 16, 442 (1948); and Burke, Smith, and Nielsen, J. Chem. Phys. 20, 447 (1952).

attempts which have been made to explain these results. The smoothness of the dependence on nuclear charges indicates an inadequacy of the scattering theory rather than any actual effects of chemical bonding. In demonstrating this we shall show that the molecules in question are in fact as accurately symmetrical as the present diffraction techniques may discern.

Of the various inaccuracies implicit in the conventional calculations, the most obvious, perhaps, is the use of the Born approximation for the atomic scattering amplitudes. Other points more specifically molecular in nature are the neglect of multiple scattering (by the different atoms) and of valence distortion of the charge distribution. A strong dependence on the difference of atomic numbers cannot, however, be produced by either of the latter two effects, whereas interference between corrections to the atomic scattering amplitudes may easily do so. For this reason we assume that the wave scattered by a molecule may still be represented by a superposition of waves $f_j(\mathbf{k}', \mathbf{k})e^{ikr}/r$ scattered by the individual atoms ($j=1, 2, 3, \cdots$) from the direction $\mathbf{k}$ to the direction $\mathbf{k}'$.

The amplitudes $f_j(\mathbf{k}', \mathbf{k})$ may be shown quite generally (see Sec. II) to be complex functions of the scattering angle. It is characteristic of the Born approximation, however, that these amplitudes, given by the familiar matrix element,

$$f_B(\mathbf{k}', \mathbf{k}) = -\frac{m}{2\pi\hbar^2}\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}V(\mathbf{r})d\tau, \qquad (1)$$

are always real for atomic scattering potentials $V(\mathbf{r})$ (or more generally, for any potential unchanged by inversion in the origin). An example close at hand is scattering by a pure Coulomb field, for which the expression (1) predicts exactly the absolute value of the scattered amplitude but omits at the same time a phase factor sensitively dependent on the angle of scattering.[4] Abbreviating the amplitudes for the moment, as $f_j(\theta)$, we take explicit account of their phases by writing them as $|f_j(\theta)|\exp(i\eta_j(\theta))$. The intensity of the scattered electrons averaged over the random orientations of the gas molecules is then proportional to

$$\sum_{i,j} f_i^*(\theta)f_j(\theta)\frac{\sin sr_{ij}}{sr_{ij}} = \sum_{i,j}|f_i(\theta)||f_j(\theta)| \times\cos\{\eta_i(\theta)-\eta_j(\theta)\}\frac{\sin sr_{ij}}{sr_{ij}}, \qquad (2)$$

where $s=|\mathbf{k}-\mathbf{k}'|=(4\pi/\lambda)\sin(\theta/2)$, and r_{ij} is the distance between atoms i and j.

To see the way the phase $\eta(\theta)$ may explain the apparent asymmetry, let us suppose the amplitudes $f_j(\theta)$ are real. Then the sum of the terms contributed by a split pair of distances $r_{ij}=r_0-\delta$ and $r_{ij'}=r_0+\delta$ with similar atoms j and j', would be approximately

$$2|f_j(\theta)||f(\theta)|\cos s\delta\sin sr_0/sr_0. \qquad (3)$$

(The amplitude difference, of order δ/r_0, is neglected.)

This expression is of just the form that would be given by (2) if the phase difference $|\eta_i(\theta)-\eta_j(\theta)|$ were proportional to s, and if no distance splittings at all existed. The scattering angle at which the amplitude of the wave corresponding to (3) first changes sign (and vanishes) is given by $|\eta_i(\theta)-\eta_j(\theta)|=\pi/2$. In practice it is the behavior of the diffraction pattern in the neighborhood of this critical angle that has been principally responsible for the interpretation in terms of bearing fine waves and its implied molecular asymmetry. It is hoped that in future experiments the very faint outer fringes of the diffraction pattern may be observed at scattering angles sufficiently large to include the second critical angle $|\eta_i(\theta)-\eta_j(\theta)|=3\pi/2$. Since these data are lacking, the correct prediction of the scattering angle for which the phase difference is $\pi/2$ is the only quantitative test now available.

Moderate deviations of the phase shift from linearity in s on either side of the single critical angle observed will not very noticeably change the character of the predicted pattern. Indeed the desire that $|\eta_i(\theta)-\eta_j(\theta)|$ be linear in s comes from comparison with the asymmetric model, whose fit to the experimental diffraction pattern, although good, is not beyond improvement. The theoretically predicted phase differences (see Sec. II) which are monotonically increasing functions of s (but not proportional to s) appear in fact to fit the observed patterns more satisfactorily than the asymmetric model.[5]

II. THEORY

Before specializing to the atomic case, it will be useful to discuss several quite general properties of scattering amplitudes. Let us suppose $\psi_{\mathbf{k}}(\mathbf{r})$, $\psi_{\mathbf{k}'}(\mathbf{r})$ and $\psi_{-\mathbf{k}'}(\mathbf{r})$ are solutions of the Schrödinger equation for equal energies arising from initial plane waves in the directions $\mathbf{k}$, $\mathbf{k}'$, and $-\mathbf{k}'$, respectively. They then obey the relations

$$\psi_{-\mathbf{k}'}\nabla^2\psi_{\mathbf{k}}-\psi_{\mathbf{k}}\nabla^2\psi_{-\mathbf{k}'}=0, \qquad (4a)$$

$$\psi_{\mathbf{k}'}^*\nabla^2\psi_{\mathbf{k}}-\psi_{\mathbf{k}}\nabla^2\psi_{\mathbf{k}'}^*=0, \qquad (4b)$$

which, integrated over the volume of a sphere surrounding the scatterer, are immediately expressed as the surface integrals

$$\int_S\left(\psi_{-\mathbf{k}'}\frac{\partial}{\partial r}\psi_{\mathbf{k}}-\psi_{\mathbf{k}}\frac{\partial}{\partial r}\psi_{-\mathbf{k}'}\right)dS=0, \qquad (5a)$$

$$\int_S\left(\psi_{\mathbf{k}'}^*\frac{\partial}{\partial r}\psi_{\mathbf{k}}-\psi_{\mathbf{k}}\frac{\partial}{\partial r}\psi_{\mathbf{k}'}^*\right)dS=0, \qquad (5b)$$

[4] For the exact solution see N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford University Press, London, 1949), second edition, p. 48.

[5] G. Felsenfeld and J. Ibers, private communication.

with dS an element of surface. If the radius of the sphere is made sufficiently large, the wave functions assume their asymptotic values on the surface. We may then substitute

$$\psi_k(r) = \exp(i\mathbf{k}\cdot\mathbf{r}) + f(\mathbf{k}_r, \mathbf{k}) \exp(ikr)/r$$

(where $\mathbf{k}_r$ is a propagation vector in the direction $\mathbf{r}$; $|\mathbf{k}_r| = k$) together with the analogous expressions for the other wave functions. The asymptotic values of the surface integrals for large sphere radii are then easily found and furnish two important relations involving the scattering amplitude. The first of these, coming from (5a), is

$$f(\mathbf{k}', \mathbf{k}) = f(-\mathbf{k}, -\mathbf{k}'), \tag{6}$$

which expresses the reversibility of the scattering between any pair of directions. From (5b) we find the relation

$$\frac{1}{2i}\{f(\mathbf{k}', \mathbf{k}) - f^*(\mathbf{k}, \mathbf{k}')\} = \frac{k}{4\pi}\int f^*(\mathbf{k}'', \mathbf{k}')f(\mathbf{k}'', \mathbf{k})d\Omega_{k''}, \tag{7}$$

in which the vector $\mathbf{k}''$ on the right is integrated over the sphere $|\mathbf{k}''| = k$. For the particular case $\mathbf{k}' = \mathbf{k}$, Eqs. (4b) and (5b) express the conservation of the particle current. Equation (7) then reduces to

$$\mathrm{Im} f(\mathbf{k}, \mathbf{k}) = (k/4\pi)\sigma \tag{8}$$

(where σ is the total scattering cross section), a relation which illustrates how fundamental is the requirement that the amplitude of the scattered wave be complex rather than real.

The more general form of Eq. (7) may be simplified by assuming that the scattering potential has inversion symmetry $V(\mathbf{r}) = V(-\mathbf{r})$. Nothing then is changed by inverting all vectors in the origin, and it follows, in particular, that $f(\mathbf{k}', \mathbf{k}) = f(-\mathbf{k}', -\mathbf{k})$. The latter relation together with the principle of reversibility (6) shows that the scattering amplitude is symmetric:

$$f(\mathbf{k}', \mathbf{k}) = f(\mathbf{k}, \mathbf{k}'). \tag{9}$$

Equation (7), under our assumption, then reduces to

$$\mathrm{Im} f(\mathbf{k}', \mathbf{k}) = \frac{k}{4\pi}\int f^*(\mathbf{k}', \mathbf{k}'')f(\mathbf{k}'', \mathbf{k})d\Omega_{k''}, \tag{10}$$

a relation we shall have frequent occasion to apply.

The reason for the inadequacy of the Born approximation (i.e., the first term of a power series expansion in $\alpha = -Ze^2/\hbar v$) in the present context is easily seen from (10). For $f(\mathbf{k}', \mathbf{k}) = O(\alpha)$ we have $\mathrm{Im} f(\mathbf{k}', \mathbf{k}) = O(\alpha^2)$, from which it follows that the phase increases with α, $\eta(\mathbf{k}', \mathbf{k}) = \arg f(\mathbf{k}', \mathbf{k}) = O(\alpha)$. Clearly then we must either go beyond the first term of the series or employ a fundamentally more accurate formulation of the scattering problem. In the present work we shall use some assumptions based on our experience with Coulomb scattering to simplify the higher terms of the Born series, thereby avoiding a good deal of numerical work but allowing still a reasonable comparison with experiment. We shall leave to a later treatment the refinements introduced by a basically different and more accurate procedure for approximating the scattering amplitude, calculations for which are now in progress.

At the energies at which diffraction experiments are performed (~40 kev), electron wavelengths are substantially smaller than the atomic radius a, ($ka \sim 10$ to 20). For all save small angles ($\theta \sim 1/ka$), therefore, the intensity of scattering is negligibly affected by the screening of atomic fields. For these angles the Rutherford formula and, hence, the Born approximation intensities are nearly exact. At smaller angles the effects of screening are partially accounted for by the structure factor implicit in (1). We shall assume for simplicity that the Born approximation (1) represents the absolute value of the scattering amplitude at all angles. The characteristic features of the simpler diffraction patterns are in any case quite insensitive to the over-all atomic scattering intensities.

The difference between screened and unscreened Coulomb fields becomes particularly important for the phase of the scattering amplitude. For the unscreened field the phase of the exact solution[4] contains principally the coordinate-dependent term $-\alpha \log\{kr(1-\cos\theta)\}$, which increases indefinitely with r, the distance from the scatterer. This is, of course, a property peculiar to the slow decrease of the Coulomb potential and is absent for screened fields. A simple estimate of the phase in the screened case may be obtained by substituting the Born approximation amplitude $f_B(\mathbf{k}', \mathbf{k})$ on the right side of (10) and equating both sides to order α^2. We obtain

$$\eta(\mathbf{k}', \mathbf{k}) = \frac{k}{4\pi f_B(\mathbf{k}', \mathbf{k})}\int f_B(\mathbf{k}', \mathbf{k}'')f_B(\mathbf{k}'', \mathbf{k})d\Omega_{k''}, \tag{11}$$

an expression which is equivalent to the second Born approximation.

To evaluate the phase, we chose as an analytically convenient model of the screened field the exponential form

$$V(r) = -Ze^2e^{-r/a}/r, \tag{12}$$

for which the Born approximation amplitude is

$$f_B(\mathbf{k}', \mathbf{k}) = -2\alpha ka^2/(|\mathbf{k}' - \mathbf{k}|^2a^2 + 1). \tag{13}$$

The angular integration of (11) is not difficult to perform, and the resulting phase, as a function of the scattering angle θ, is

$$\eta(\theta) = -2\alpha\left(1 + \frac{1}{4k^2a^2\sin^2(\theta/2)}\right)A\tanh^{-1}A, \tag{14}$$

with

$$A = \frac{\sin(\theta/2)}{[(1 + (1/2k^2a^2))^2 - \cos^2\theta/2]^{\frac{1}{2}}}. \tag{15}$$

Since $2k^2a^2 \gg 1$ these expressions may be reduced to

$$\eta(\theta) \sim -2\alpha \frac{1+s^2a^2}{sa(4+s^2a^2)^{\frac{1}{2}}} \tanh^{-1}\frac{sa}{(4+s^2a^2)^{\frac{1}{2}}}, \quad (16)$$

in which we have once again used the notation

$$s = |\mathbf{k}' - \mathbf{k}| = 2k \sin(\theta/2).$$

A graph of $|\eta(\theta)/\alpha|$ according to Eq. (16) is given in Fig. 1. For the forward direction, the value $\eta(0) = -\alpha/2$ is quite insensitive to the screening radius. For large angles the phase is asymptotically

$$\eta(\theta) \sim -2\alpha \log(2ka \sin\theta/2), \quad (17)$$

the value of which may in practice be appreciable, even for the lighter elements.

The validity of the expression (16) for the phase, at least for large angles, is somewhat stronger than its derivation by the present perturbation procedure might imply. This may be seen by exploiting the similarity of the large angle scattering by screened and unscreened Coulomb fields.[6] In particular the dependence of the asymptotic phase (17) on θ is the same (apart from an additive constant) as that of the exact Coulomb phase, a fact which implies correctly that for angles $\theta \gg 1/ka$ the scattering amplitudes for the screened and unscreened fields differ only by a phase factor, independent of angle.[7]

In undertaking comparisons with experimental results we shall assume that the estimate of the phase given by (16) is sufficiently accurate to be used directly[8] in

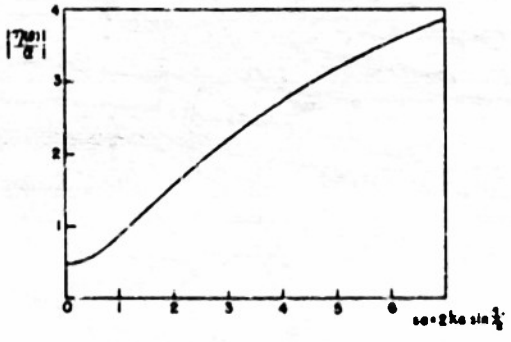

FIG. 1. Graph of the dependence of the phase on scattering angle: $|\eta(\theta)/\alpha|$ *vs* $2ka \sin(\theta/2)$, as given by Eq. (16).

[6] It may also be seen from the work of R. Dalitz [Proc. Roy. Soc. (London) A206, 509 (1951)], who has derived the asymptotic form (17) and shown that its occurrence as a phase is consistent with the third Born approximation as well as the second.

[7] This behavior is implicitly made use of in computing the Coulomb scattering of identical particles when one of them is screened (e.g., p-$\bar{p}$ scattering). The constant phase factor by which the Coulomb and correctly screened solutions differ is not observed. For other potentials the interference effect involved in the scattering of similar particles will also require a knowledge of the angle-dependent part of the phase, omitted in the first Born approximation.

[8] Our procedure here actually goes beyond the second Born approximation, which, strictly speaking, would only consider the terms of (2) to order α^2, and would thereby eliminate the contribution of the phase entirely.

the formalism of Sec. I. The accuracy of this method is difficult to estimate without performing numerically more involved calculations. We may mention, however, that the preliminary results obtained using a more accurate method (based on the smallness of α/ka rather than α) are favorable. They indicate that the accuracy of (16) for $\alpha \sim 1$ is roughly commensurate with that of the screening model (12).

III. COMPARISON WITH EXPERIMENT

While the phase shift we have discussed will modulate the intensities of the diffraction patterns of all heteratomic molecules, its effect is most strongly felt when large differences in the nuclear charges prevail. In such cases the attempt to account in the conventional way for the observed modulation has led, as we have already noted in Sec. I, to the assumption of curiously unsymmetrical molecular structures. For a proper interpretation in the light of the present work, the diffraction data for each of the molecules in question will eventually require detailed re-analysis. A simple way, however, of checking the corrected theory is to show the way in which the treatment based on symmetrical models with phase shifts is able to duplicate the numerical results previously arrived at for the apparent asymmetries. To do this we note by comparing (2) and (3) the approximate relation

$$2\delta = \pi/s_{crit}, \quad (18)$$

in which s_{crit} is the value of $2k \sin(\theta/2)$ for which the phase difference is $\pi/2$. An approximate value of the screening distance, adequate for the calculation is $a = 0.528Z^{-\frac{1}{3}}$A. The predicted apparent "splits" (2δ) that result are listed in Table I along with the corresponding experimental values. Their agreement, it may be seen, is quite close. It follows that for these molecules the diffraction patterns predicted by the present formulation will be in good agreement with those observed. The intensity curve calculated for UF_6 at 40 kev seems to show even better agreement than the previous work for the central and outer parts of the pattern.[4] This is a consequence of the deviation of the phases from proportionality to s.

A large number of electron diffraction studies of molecules containing heavy atoms are on record in which nothing anomalous was observed, a circumstance which no doubt helped delay the recognition of the phase shifts. It is important, therefore, to remark that in all the adequately reported cases, the pattern was observed only at angles at which the phase difference is less than the critical value $\pi/2$.

The phase given by Eq. (16) is increased by lowering the electron energy, and its modulation of the diffraction pattern varies more rapidly with s. The resulting energy dependence of the pattern is a feature absent from any treatment based on the first Born approximation. Some photographs of UF_6, taken at 10 kev do indeed show changes in the direction predicted,[4] and will be analyzed