c. Comparison of Data with Theory

The solid lines on Fig. 9 show the cross sections computed classically for each energy assuming the screened Coulomb potential given in Eq. (6) with the screening radius a computed from Eq. (7). Details of this calculation are given in the paper by Everhart, Stone, and Carbone[7] which tabulates the values of $\sigma(\theta)/b^2$ in center-of-mass coordinates with the quantity b/a as a parameter. The length b is given by

$$b=Z_1Z_2e^2/U', \tag{13}$$

where Z_1e and Z_2e are the nuclear charges of the colliding atoms and U' is the energy of the collision in center-of-mass coordinates. The value of b/a appropriate to the energy in question is determined, and the tabulated cross section is converted to the laboratory coordinate system. The agreement between the measured cross sections and the calculated curves is excellent at 100 kev and fair at 50 and 25 kev. At these latter energies the calculated curves lie below the experimental points by a factor somewhat in excess of the assigned error of measurement.

In order to test whether there was a systematic error in the measurement or apparatus such as an incorrectly determined solid angle, which would affect the absolute values of the experimental cross sections, a second experiment was performed. Helium ions, singly ionized were scattered from argon gas targets and the particle differential cross sections measured as in the argon experiments. These data are plotted in Fig. 10 for 50- and 100-kev incident energy.

The theory is more certain in this case than for argon-argon collisions, since the corresponding value of b/a is small, and the cross sections can be calculated as for Rutherford scattering with almost no correction needed for electron screening. The solid curves on Fig. 10 are the Rutherford curves and the excellent agreement in this case indicates that there is no excessive systematic error.

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Multiple Elastic Scattering in Electron Diffraction by Molecules*

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Electron diffraction patterns from gas molecules containing heavy atoms can be satisfactorily interpreted in terms of a pseudokinematical theory, in which rigorous atomic scattering amplitudes are used, but the Born approximation is retained for expressing the (molecular) interference between the various atomic contributions. It is shown that the correction brought by the second approximation of the pseudokinematical theory, involving multiple scattering on different atoms, is a smooth function of scattering angle and is therefore unimportant in the study of the oscillating interference term.

I. INTRODUCTION

TWO theories are available for the interpretation of electron scattering by gas molecules. In the kinematical theory one assumes that in the scatterer every infinitesimal element of volume scatters under the influence of the incident electron beam only, and that the total amplitude of the wave diffracted in a given direction is obtained by summing the amplitudes scattered by the various elements of volume, including phase factors due to their different locations. These assumptions are valid as long as the scattered intensity is always much weaker than the intensity of the incident beam. Mathematically, the summation over elements of volume is equivalent to taking the Fourier transform of the electrostatic potential distribution within the scatterer. This is also equivalent to applying the Born approximation to the entire problem.

Recently, it has become apparent[1] that the Born approximation is not valid at the voltages currently used in electron diffraction studies (10–80 kev), even in the case of scattering by a single atom. Let us consider the elastic scattering of electrons of velocity v and wavelength λ by a central potential $V(r)$ due to an atom of atomic number Z. If the amplitude of the spherical scattered wave is written as $f(\theta)e^{ikr}/r$ (where θ is the scattering angle and k is $2\pi/\lambda$), it is found that the atomic scattering amplitude $f(\theta)$ is generally complex, unlike the value $f^B(\theta)$ given by the Born approximation, which takes the real value[2]

$$f^B(\theta)=\frac{2k\alpha}{Ze^2}\int_0^\infty V(r)\frac{\sin br}{br}r^2dr=-\frac{2k\alpha}{b^2}\left(1-\frac{F(\theta)}{Z}\right). \tag{1}$$

Here $\alpha=-Ze^2/\hbar v$, $b=2k\sin\frac{1}{2}\theta$, and the x-ray form factor $F(\theta)$ is the Fourier transform of the electronic

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† Contribution No. 2055.

[1] V. Schomaker and R. Glauber, Nature 170, 290 (1952).

[2] Z. G. Pinsker, *Electron Diffraction* (Butterworths Publications, London, 1953), Chap. 7.

density of the atom. On the other hand, the rigorous solutions $f(\theta)$ can be computed by the partial wave method[3] and have been recently tabulated for a number of atoms for the case of 40-kev electrons.[4]

Whereas the kinematical theory assumes that in the scatterer every *infinitesimal element of volume* scatters under the influence of the incident beam only, it is possible to formulate a pseudokinematical theory in which every *atom* scatters under the influence of the incident beam only, the scattering by a single atom being given by the rigorous solution $f(\theta)$. In other words, the Born approximation is only retained for the computation of the total scattering from the atomic contributions. This procedure has been discussed theoretically by Ekstein[5] and has been applied in this laboratory to the scattering of electrons by molecules containing both heavy and light atoms.[1,6] In this way, apparent asymmetries in the structure of these molecules were removed and the variation of the diffraction pattern with different accelerating voltages was satisfactorily accounted for.

In the present work, a physical interpretation of the pseudokinematical theory is given in terms of the successive collisions undergone in the scatterer by an incident electron. The theory will be found to be satisfactory in the case of diffraction by molecules. In a subsequent paper dealing with the diffraction by crystals, a comparison of the pseudokinematical theory with the dynamical theory will be made.

II. THEORY

The fundamental integral equation for the elastic scattering by a potential $V(\mathbf{r})$ is[5]

$$\psi(\mathbf{r})=\psi_0(\mathbf{r})-(m/2\pi\hbar^2)\int G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}')d\tau', \quad (2)$$

where $\psi_0(\mathbf{r})$ is the incident wave $\exp(i\mathbf{k}\cdot\mathbf{r})$ and G is the Green function $|\mathbf{r}-\mathbf{r}'|^{-1}\exp(ik|\mathbf{r}-\mathbf{r}'|)$. If Eq. (2) is solved by iteration, the first step consists in replacing ψ by ψ_0 in the last term and yields the first Born approximation used in the kinematical theory, namely

$$\psi_1(\mathbf{r})=\psi_0(\mathbf{r})-(m/2\pi\hbar^2)\int G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi_0(\mathbf{r}')d\tau'. \quad (3)$$

At large distances from the scatterer the last term of (3) can be rewritten as $f^B(\theta)e^{ikr}/r$, where $f^B(\theta)$ is given by (1). The second Born approximation is obtained by replacing ψ in the last term of (2) by ψ_1:

$$\psi_2(\mathbf{r})=\psi_1(\mathbf{r})+(m/2\pi\hbar^2)^2\int\int G(\mathbf{r},\mathbf{r}'')V(\mathbf{r}'')\times G(\mathbf{r}'',\mathbf{r}')V(\mathbf{r}')\psi_0(\mathbf{r}')d\tau'd\tau''. \quad (4)$$

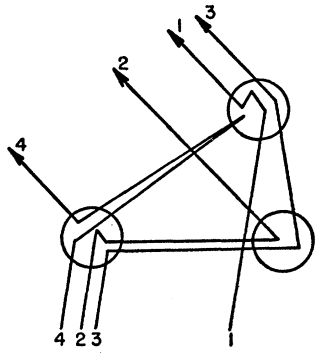

FIG. 1. Electron paths for triple scattering processes in the third Born approximation.

Similarly, the nth Born approximation is obtained by replacing ψ in the last term of (2) by ψ_{n-1}.

A physical interpretation of ψ_1, ψ_2, $\cdots$ in terms of successive collisions undergone by the incident electron in the atom is as follows: In (3), an incident electron is scattered once at point $\mathbf{r}'$ and travels then to the point $\mathbf{r}$ where the scattering is measured, the total amplitude being given by summation over all possible paths. In (4) the contribution of all paths where an electron has been scattered twice (at points $\mathbf{r}'$ and $\mathbf{r}''$) is included, etc.

In the case of a molecule of L atoms of coordinate vectors $\mathbf{a}_i$, the potential can be written as the sum of atomic potentials V_i, namely,

$$V(\mathbf{r})=\sum_{i=1}^{L}V_i(\mathbf{r}-\mathbf{a}_i), \quad (5)$$

provided that valence distortion is neglected. When (5) is substituted in the Born approximation of order n, say, there arise a number of terms referring to the way in which a sequence of n collisions is distributed over the L atoms (or, more strictly, over the L atomic potentials). This number is L^n since every collision in the sequence can occur on any one of the L atoms. Figure 1 shows 4 among the 27 possible paths in the case $n=L=3$. Whereas these four paths are included in the third Born approximation, their relative importance decreases sharply when the number of interatomic jumps along the path increases (zero for path 1, one for path 2, two for paths 3 and 4). Therefore it is appropriate to consider in the same approximation of the theory all the paths with the same number of interatomic jumps (and no longer with the same number of collisions n as in the Born scheme): in the new first approximation, only paths of type 1 (with n ranging from one to infinity) are taken into account, in the

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[3] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), second edition, Chaps. II and VII.

[4] J. A. Ibers and J. A. Hoerni, Acta Cryst. **7**, 405 (1954).

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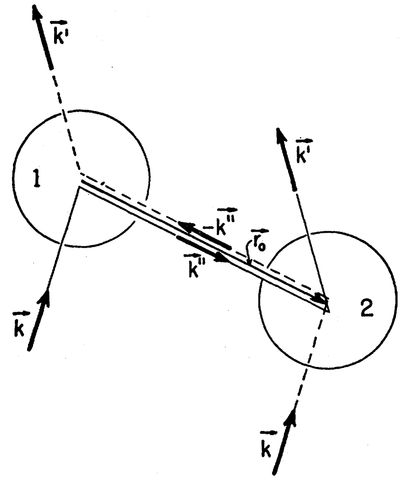

FIG. 2. Double scattering processes for a diatomic molecule.

second approximation paths of type 2 with only one interatomic jump are added, etc. When the molecule reduces to a single atom, the first approximation includes all possible paths and yields the accurate solution $f(\theta)\exp(ikr)/r$.

For a molecule, the first approximation is identical to the pseudokinematical theory defined in the Introduction: since all paths with interatomic jumps are neglected, it is equivalent to adding the various atomic contributions as though every atom scattered under the influence of the incident beam only.

Since the pseudokinematical theory is expressed in terms of the rigorous solutions to single atom problems, the inclusion of possible improvements to these solutions, polarization and electron exchange for instance, is straightforward. On the other hand, the discussion of valence distortion effects (including ionic character of the bonds) would be difficult. In what follows, all these effects will be neglected.

It has already been pointed out that the pseudokinematical theory seems to account satisfactorily for the observed diffraction patterns by gas molecules. We shall now show that such is the case by evaluating approximately the second approximation of the pseudokinematical theory, when electron paths with one interatomic jump are taken into account. Consider a molecule with two atoms 1 and 2 in a fixed orientation defined by the interatomic vector $\mathbf{r}_0$ (Fig. 2). Under the influence of the incident wave of vector $\mathbf{k}$, atom 1 scatters a spherical wave, which in turn is incident on atom 2. If one assumes[7] that r_0 is large enough so that over atom 2 this spherical wave can be approximated by a plane wave of vector $\mathbf{k}''$ parallel to $\mathbf{r}_0$ and of amplitude equal to its actual value at the center of atom 2, namely $f_1(\mathbf{k}'',\mathbf{k})e^{ikr_0}/r_0$, then the amplitude of the twice scattered wave is $f_1(\mathbf{k}'',\mathbf{k})(e^{ikr_0}/r_0)\times f_2(\mathbf{k}',\mathbf{k}'')(e^{ikr}/r)e^{-i\mathbf{k}'\cdot\mathbf{r}_0}$. Here, $\mathbf{k}'$ is parallel to the direction of observation and the phase factor $e^{-i\mathbf{k}'\cdot\mathbf{r}_0}$ arises from the different locations of the two atoms. Similarly, the amplitude of the twice scattered wave when atom 2 scatters first (Fig. 2) is $f_2(-\mathbf{k}'',\mathbf{k})(e^{ikr_0}/r_0)\times f_1(\mathbf{k}',-\mathbf{k}'')(e^{ikr}/r)e^{i\mathbf{k}\cdot\mathbf{r}_0}$. The total scattering is obtained by adding these two terms to the amplitude $F=f_1(\mathbf{k}',\mathbf{k})+f_2(\mathbf{k}',\mathbf{k})e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}_0}$ given by the pseudokinematical theory. The scattered intensity for this particular orientation of the molecule is I/r^2, with

$$I=|F|^2+2\,\mathrm{Re}\{(e^{ikr_0}/r_0)F^*[f_2(\mathbf{k}',\mathbf{k}'')f_1(\mathbf{k}'',\mathbf{k})e^{-i\mathbf{k}'\cdot\mathbf{r}_0}+f_1(\mathbf{k}',-\mathbf{k}'')f_2(-\mathbf{k}'',\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}_0}]\},\quad(6)$$

where terms in $(1/r_0)^2$ are neglected and "Re" means real part. Since the term in $1/r_0$ is a small correction, it is permissible to replace the f values in the last term of (6) by the corresponding f^B values. This is equivalent to retaining in our approximation electron paths with only two collisions and one interatomic jump. Furthermore we compute f^B values for the exponentially screened Coulomb potentials $-Ze^2e^{-r/a}/r$, where $a=0.468Z^{-\frac{1}{3}}$ angstrom. Then (1) yields

$$f^B(\mathbf{k}',\mathbf{k})=A(1-B\cos\langle\mathbf{k}',\mathbf{k}\rangle)^{-1},$$

where $A=-2k\alpha a^2/(2k^2a^2+1)$ and $B=2k^2a^2/(2k^2a^2+1)$.

The observed intensity $\bar{I}/r^2$ is obtained in the usual way by averaging (6) over all orientations of the molecule, namely over all orientations of $\mathbf{r}_0$ (or $\mathbf{k}''$). Averaging $|F|^2$ yields the pseudokinematical expression[1]

$$\bar{I}_{pk}=|f_1|^2+|f_2|^2+2|f_1||f_2|\cos(\eta_1-\eta_2)(\sin br_0)/br_0,\qquad(\eta=\arg f).$$

Consider now one of the four terms which arise from averaging the last term in (6), for instance

$$2(4\pi r_0)^{-1}f_2{}^B(\mathbf{k}',\mathbf{k})\int d\Omega_{\mathbf{k}''}f_2{}^B(\mathbf{k}',\mathbf{k}'')f_1{}^B(\mathbf{k}'',\mathbf{k})\times\cos(kr_0-\mathbf{k}\cdot\mathbf{r}_0),\quad(7)$$

where $\mathbf{k}''$ is integrated over the sphere $|\mathbf{k}''|=k$. We evaluate the integral in spherical coordinates with the polar axis parallel to $\mathbf{k}$. If θ is the angle between $\mathbf{k}$ and $\mathbf{k}'$, α the angle between $\mathbf{k}$ and $\mathbf{k}''$ and φ the angular difference between the azimuthal projections of $\mathbf{k}'$ and $\mathbf{k}''$, the integral in (7) reduces to

$$2\pi S_{12}=\int_0^{2\pi}\int_0^{\pi}\frac{\sin\alpha d\alpha d\varphi A_1A_2\cos kr_0(1-\cos\alpha)}{(1-B_1\cos\alpha)(1-B_2\cos\alpha\cos\theta-B_2\sin\alpha\sin\theta\cos\varphi)}$$

$$=2\pi A_1A_2\int_{-1}^{+1}dx\frac{\cos kr_0(1-x)}{(1-B_1x)(1-B_2{}^2\sin^2\theta-2B_2x\cos\theta+B_2{}^2x^2)^{\frac{1}{2}}}.$$

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[7] This assumption is justified because the regions of effective atomic scattering (shown by circles in Figs. 1 and 2) do not overlap and the interatomic distances, expressed in terms of the wavelength of the incident electrons, are large.

The other terms in (6) can be averaged in a similar way. There results finally

$$\bar{I}=\bar{I}_{pk}+(2/r_0)(S_{12}f_2^B+S_{21}f_1^B)=\bar{I}_{pk}+\bar{I}_1. \qquad (8)$$

III. NUMERICAL EXAMPLE

We shall apply formula (8) to the case of two uranium atoms separated by an arbitrary distance of $r_0=2$ A. Table I shows how the corrective term $\bar{I}_1$ compares with the atomic term, $2|f|^2$, and the molecular term (divided by $\sin br_0$), $2|f|^2/br_0$, in $\bar{I}_{pk}$. The possible importance of $\bar{I}_1$ should be judged relative to the molecular term and not to the total scattering since it is the oscillating molecular term which gives rise to the structure-sensitive part of the diffraction pattern. It is found on plotting the calculated values of $\bar{I}_1$ that they lie on a smooth decreasing curve on which no short range oscillatory feature of frequency comparable with that of the molecular term can be detected. In other words, $\bar{I}_1$ does not affect the positions or the shapes of the diffraction rings and it can merely be considered as an unimportant smooth correction to the smooth background (atomic term and inelastic scattering). The smallness of $\bar{I}_1$ relative to the total scattering is easily understood in terms of formula (6) or Fig. 2: due to the rapid angular decrease of the scattering amplitudes, the only instantaneous orientations of the pair of atoms contributing significantly to $\bar{I}_1$ are those for which $\mathbf{k}''$ or $-\mathbf{k}''$ is about parallel to the average of $\mathbf{k}$ and $\mathbf{k}'$.

The nature, smooth or oscillatory, of the terms in (8) [as well as the neglected terms in (6)], can be discussed on the basis of Figs. 3(a) to 3(f). In each diagram, atoms 1 and 2 have the same instantaneous position and the contribution to the intensity is obtained by multiplying the amplitudes relative to the two paths, together with a phase factor ρ due to the path difference. In cases *a* (an atomic term), *c* [the term (7)], and *e* [a term in $1/r_0^2$ neglected in (6)], ρ is independent of the total scattering angle θ. When these terms are averaged over all orientations of the molecules, they may therefore be expected to be smooth to the same extent as the atomic scattering amplitudes.[8] On the other hand, ρ depends on θ in case *b* (the molecular term), giving rise after averaging to the familiar factor $(\sin br_0)/br_0$. Case *f* (term in $1/r_0^2$) also corresponds to an oscillation, depending here on $\sin[(4k^2-b^2)^{\frac{1}{2}}r_0]$, but for any reasonable form factor its contribution to (6) is negligible, since it always includes scattering angles larger than 90°.

TABLE I. Data on scattering of 39.47-kev electrons ($k=103.75$ A^{-1}) by two uranium atoms 2 A apart.

θ (degrees)	$2\|f\|^2$	$2\|f\|^2/br_0$	$\bar{I}_1$
0	565	···	0.227
2	59.2	8.17	0.178
4	9.25	0.638	0.0953
6	2.79	0.128	0.0471
8	1.13	0.0390	0.0205
10	0.566	0.0157	0.00927
12	0.325	0.00749	0.00498
16	0.128	0.00222	0.00192
20	0.064	0.00089	0.00087

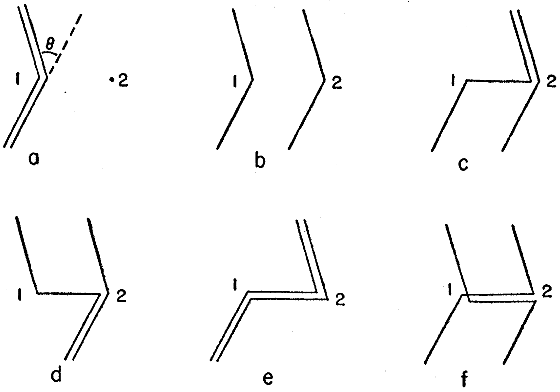

FIG. 3. Scattering diagrams for terms in Eqs. (6) and (8).

The case of two heavy atoms at close distance has been considered, so that Table I sets an upper limit to the importance of the corrective term for a diatomic molecule. For a polyatomic molecule, the correction consists of a sum of terms relative to the various pairs of atoms and becomes more important since the number of pairs grows more rapidly than the number of atoms. It is unlikely, however, to be of any importance in practical work because of the absence of any oscillating feature comparable with the molecular terms. A thorough theoretical treatment should take into account other effects of probably greater importance, namely valence distortion, multiple incoherent intermolecular scattering, and, finally, the possible failure of the Born approximation in the expression for the inelastic atomic scattering.

ACKNOWLEDGMENTS

I wish to thank Professor V. Schomaker for suggesting this problem and for several helpful discussions.

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[8] In case (d) [another term in $1/r_0$ in (6) which contributes to the final expression (8)], ρ depends on θ for a particular orientation of the molecule, but it is easily seen that on averaging over all orientations the same result (8) is obtained as in case (c).