

## Three-atom scattering in gas-phase electron diffraction. II. A general treatment\*<sup>†</sup>

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(Received 24 January 1973)

Intramolecular multiple scattering of electrons by polyatomic gas molecules is investigated with the aid of Glauber's theory of high energy elastic scattering. The key to a simpler and more rapidly convergent expression for dynamic scattering corrections is found in a propitious transformation of variables. An analytical representation of the corrections averaged over molecular rotations and vibrations is presented in a form suitable for routine electron diffraction analyses of molecular structure. Magnitudes and practical considerations in analyses are briefly discussed.

### I. INTRODUCTION

Systematic discrepancies between experiment and theory have been observed in many electron diffraction investigations of the structures of molecules in which heavy atoms are present.<sup>1</sup> Several recent studies<sup>1,2</sup> have established the theoretical basis of the dynamic scattering effect which is chiefly responsible for these discrepancies. The theoretical model conventionally used in diffraction investigations neglects the interference terms generated by electron waves suffering a scattering by more than one atom within the same molecule. It can be shown that this previously neglected interference term is often large enough to give discrepancies much greater than experimental errors.

In a previous paper<sup>1</sup> (hereafter referred to as Paper I), we derived an approximate analytical representation for three-atom scattering using Glauber's approximation<sup>3</sup> for the limiting case in which the distances between atoms are large compared with atomic radii. The result accounts satisfactorily for the discrepancies in  $\text{ReF}_6$  as observed by Jacob and Bartell.<sup>4</sup>

The purpose of the present paper is to outline a new approach based on Glauber's approximation that leads to a convenient analytical expression for a general three-atom scattering case. The advantage of this method lies in its easily recognizable physical basis, in its mathematical simplicity, and in its greater accuracy in comparison with other published analytical approximations. In Sec. II, we introduce the mathematical framework needed for high energy scattering and its application to multiple scattering. A detailed treatment of three-atom scattering and its spherical average is presented in Sec. III. In Sec. IV, considerations of multiple scattering corrections in least squares analyses in electron diffraction are briefly discussed.

### II. GLAUBER'S APPROXIMATION

The effects of double scattering and the interference between single and double scattering in electron diffraction have been studied before<sup>5,2a,b</sup> by numerical methods

and by the Born series approach. It was shown in Paper I that Glauber's approximation<sup>3</sup> leads to a tractable treatment of this multiple scattering effect. Glauber's approximation has been shown to give satisfactory results in the energy range usually used in gas phase electron diffraction.<sup>6</sup>

The Glauber scattering amplitude for a system of scatterers is expressed as<sup>7</sup>

$$f(\mathbf{s}) = (ik/2\pi) \int \exp(i\mathbf{s} \cdot \mathbf{p}) \Gamma(\mathbf{p}) d^2\mathbf{p}, \quad (1)$$

where  $\mathbf{s} = \mathbf{k}_{\text{inc}} - \mathbf{k}_{\text{scatt}}$  with  $\mathbf{k}_{\text{inc}}$  and  $\mathbf{k}_{\text{scatt}}$  representing

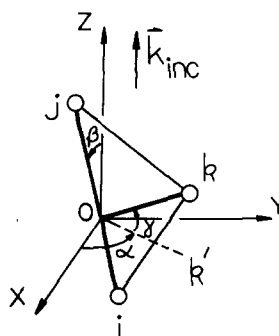


FIG. 1. Three-atom system. Eulerian angles  $\alpha$ ,  $\beta$ , and  $\gamma$  denote the orientation of the system with respect to the space-fixed axes  $XYZ$ . The trajectory of the incident electron is parallel to the  $Z$  axis.

the incident and scattered wave vectors, respectively, and

$$\Gamma(\mathbf{p}) = 1 - \exp[i\chi(\mathbf{p})]. \quad (2)$$

In this expression,  $\chi(\mathbf{p})$  is a phase shift of the scattered particle when it passes through the potential field of the system of scatterers at a particular impact parameter  $\mathbf{p}$ . The relationship between this phase shift and the potential field is given by

$$\chi(\mathbf{p}) = -\frac{m}{\hbar^2 k} \int_{-\infty}^{\infty} V(\mathbf{p}, z) dz, \quad (3)$$

where  $m$  is the mass of the scattered particle. If a static potential is assumed, this approximation is equivalent to the Moliere high energy approximation.<sup>8</sup> If the

interaction between the scatterers and the scattered particle can be approximated by a sum of two-body interactions from individual scatterers in the system, then the phase shift can also be expressed as a sum of phase shifts induced by the individual scatterers, i.e., for an  $N$ -scatterer system,

$$\chi(\mathbf{p}, \mathbf{r}_1, \mathbf{r}_2 \cdots \mathbf{r}_N) = \sum_{i=1}^N \chi_i(\mathbf{p} - \mathbf{p}_i), \quad (4)$$

where  $\mathbf{r}_i$  and  $\mathbf{p}_i$  are, respectively, the position vector of

the  $i$ th scatterer and its projection on the plane perpendicular to the incident wave vector.

Define

$$\Gamma_i(\mathbf{p} - \mathbf{p}_i) = 1 - \exp[i\chi_i(\mathbf{p} - \mathbf{p}_i)]. \quad (5)$$

Then  $\Gamma(\mathbf{p})$  can be conveniently expanded as<sup>9</sup>

$$\Gamma(\mathbf{p}) = \sum_{i=1}^N \Gamma_i - \sum_{i<j} \Gamma_i \Gamma_j + \cdots (-1)^{N-1} \prod_{i=1}^N \Gamma_i, \quad (6)$$

and the scattering amplitude becomes

$$f(\mathbf{s}) = \frac{ik}{2\pi} \left[ \sum_{i=1}^N \exp(i\mathbf{s} \cdot \mathbf{p}_i) \int d^2\mathbf{p} \exp[i\mathbf{s} \cdot (\mathbf{p} - \mathbf{p}_i)] \Gamma_i(\mathbf{p} - \mathbf{p}_i) - \sum_{i<j} \int d^2\mathbf{p} \exp(i\mathbf{s} \cdot \mathbf{p}) \Gamma_i(\mathbf{p} - \mathbf{p}_i) \Gamma_j(\mathbf{p} - \mathbf{p}_j) + \cdots (-1)^{N-1} \int d^2\mathbf{p} \exp(i\mathbf{s} \cdot \mathbf{p}) \prod_{i=1}^N \Gamma_i(\mathbf{p} - \mathbf{p}_i) \right], \quad (7)$$

where the first term denotes the amplitude for single scattering, the second term for double scattering, etc. Hereafter, the individual contributions will be abbreviated as  $f_i(\mathbf{s})$ ,  $f_{ij}(\mathbf{s})$ , etc., respectively.

Now, we consider a general three-atom system as shown in Fig. 1, which is the smallest system that can produce a single-double scattering interference term yielding an oscillatory contribution to the differential cross section, and, hence, is the smallest system capable of causing the discrepancies. For an instantaneous orientation, the scattering amplitude is

$$f(\mathbf{s}) = \sum_i f_i(\mathbf{s}) \exp(i\mathbf{s} \cdot \mathbf{p}_i) + \sum_{i<j} f_{ij}(\mathbf{s}) + \cdots \quad (8)$$

The differential cross section averaged over all orientations is thus given, through lowest-order terms in  $f_{ij}$ , by

$$\begin{aligned} \langle d\sigma/d\Omega \rangle &= \langle |f(\mathbf{s})|^2 \rangle_\Omega \\ &= \sum_i \sum_j f_i^*(\mathbf{s}) f_j(\mathbf{s}) \langle \exp[i\mathbf{s} \cdot (\mathbf{p}_j - \mathbf{p}_i)] \rangle_\Omega \\ &+ 2 \operatorname{Re} \sum_{i<j} \sum_k \langle f_k^*(\mathbf{s}) \exp(-\mathbf{s} \cdot \mathbf{p}_k) f_{ij}(\mathbf{s}) \rangle_\Omega, \quad (9) \\ &= \sum_i \sum_j \langle d\sigma/d\Omega \rangle_{ij} + \sum_{i<j} \sum_k \langle d\sigma/d\Omega \rangle_{ij,k}, \quad (10) \end{aligned}$$

where  $\langle \rangle_\Omega$  denotes the orientational average. The first term, of course, is the conventional atomic ( $i=j$ ) and molecular ( $i \neq j$ ) scattering term. The last term represents the single-double scattering interference term which is the leading term in the multiple scattering effect. Higher-order terms are neglected here because the magnitude is small compared with this term.<sup>1</sup> For the case  $k \neq i \neq j$ , the three-atom term gives oscillatory contributions to the differential cross section and can be evaluated as described in detail in the next section. If  $k$  is equal to either  $i$  or  $j$ , the last term is<sup>2</sup> a monotonic function of  $s$  derivable from the general  $(ij, k)$  term by setting  $r_{ik}$  or  $r_{jk}$  equal to zero.

The factor of two in the last term on the right-hand side of Eqs. (9) and (10) comes from the symmetry of the double scattering amplitude  $f_{ij}(\mathbf{s})$  with respect to the interchange of atoms  $i$  and  $j$ , i.e.,

$$f_{ij}(\mathbf{s}) = f_{ji}(\mathbf{s}). \quad (11)$$

As a consequence of this symmetry, the contribution of each three-atom scattering process to the total differential cross section  $(d\sigma/d\Omega)_{ij,k}$  is also invariant with respect to the interchange of  $i$  and  $j$ . Although this symmetry arises naturally in the Glauber approximation, it is not rigorously adhered to in the exact theory.

### III. ANALYTICAL EXPRESSIONS

An analytical expression for the three-atom scattering is desirable, because it can then be applied conveniently to the routine electron diffraction analysis of molecular structure. Heretofore, the spherical average  $(d\sigma/d\Omega)_{ij,k}$  has been tedious to evaluate either numerically or analytically in a satisfactorily convergent form. Fortunately, the energy of the incident electron used in electron diffraction is sufficiently high that it is permissible to introduce approximations which greatly simplify the orientational averaging process. For high energy scattering, the scattered amplitude is expected to be strongly peaked in the forward direction. Therefore, the magnitude of the double-scattering amplitude  $f_{ij}(\mathbf{s})$  is appreciable only if atom  $i$  and atom  $j$  are nearly eclipsed in the direction of the incident electron. In averaging over all possible orientations of the three-atom system in the space, the contribution of the total three-atom scattering decreases sufficiently rapidly with  $\beta$ , the angle between the vector connecting atoms  $i$  and  $j$  and the  $Z$  axis,<sup>10</sup> that a small angle approximation<sup>11</sup> is applicable.

Consider the three-atom system in the space-fixed coordinate system  $X, Y, Z$ , in which  $\mathbf{k}_{\text{inc}}$  of the incident

electron is chosen to be parallel to the  $Z$  axis. Choose point  $o$  such that  $\mathbf{ok} \perp \mathbf{ij}$ , and take point  $o$  as the origin about which the orientational average is made.

Let  $\mathbf{p}$  be the impact parameter of the incident electron with respect to the origin  $o$ . Define

$$\mathbf{r}_l = \mathbf{o}\mathbf{l}, \quad l = i, j, k,$$

and  $\mathbf{p}_l$  to be the projection of  $\mathbf{r}_l$  on the  $X$ - $Y$  plane. This choice of the origin of the system makes the first order variation of  $\mathbf{p}_k$  with  $\beta$  vanish, i.e.,

$$\lim_{\beta \rightarrow 0} (\partial \mathbf{p}_k / \partial \beta) = 0. \quad (12)$$

To break down the difficult double scattering amplitude  $f_{ij}(\mathbf{s})$ , we propose a new way to separate it into individual scattering amplitudes  $f_i(\mathbf{s})$  and  $f_j(\mathbf{s})$ . Instead of employing an approximate Fourier trans-

form as proposed by Franco and Glauber,<sup>3b</sup> which in this case leads to mathematically tedious, slowly converging terms, we define the following vectors

$$\mathbf{b}_l = \mathbf{p} - \mathbf{p}_l, \quad l = i, j, k, \quad (13)$$

where  $\mathbf{b}_l$  represents the impact parameter of the incident electron with respect to atom  $l$ . From considerations of geometry we find that

$$\mathbf{s} \cdot \mathbf{p} = \mathbf{s}_i \cdot \mathbf{b}_i + \mathbf{s}_j \cdot \mathbf{b}_j, \quad (14)$$

where

$$\mathbf{s}_i = (\mathbf{r}_j / r_{ij}) \mathbf{s},$$

$$\mathbf{s}_j = (\mathbf{r}_i / r_{ij}) \mathbf{s}, \quad (15)$$

and

$$r_{ij} = |\mathbf{r}_j - \mathbf{r}_i| \quad (16)$$

Substitution of (13) and (14) into  $f_{ij}(\mathbf{s})$  gives

$$f_{ij}(\mathbf{s}) = -(ik/2\pi) \int \exp(i\mathbf{s}_i \cdot \mathbf{b}_i) \Gamma_i(\mathbf{b}_i) \exp(i\mathbf{s}_j \cdot \mathbf{b}_j) \Gamma_j(\mathbf{b}_j) d^2\mathbf{p}, \quad (17)$$

and

$$\left( \frac{d\sigma}{d\Omega} \right)_{ij,k} = -2 \operatorname{Re} \left( \frac{ik}{8\pi^3} \right) \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma \int_0^\pi \sin\beta d\beta f_k^*(s) \exp(-i\mathbf{s} \cdot \mathbf{p}_k) \int \exp(i\mathbf{s}_i \cdot \mathbf{b}_i) \Gamma_i(\mathbf{b}_i) \exp(i\mathbf{s}_j \cdot \mathbf{b}_j) \Gamma_j(\mathbf{b}_j) d^2\mathbf{p}, \quad (18)$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  denote the Eulerian angles of the system.<sup>10</sup> The key to simple evaluation of the integrals in (18) is the observation that a proper change of variables allows the integrals of (18) to be separated nicely into a product of integrals closely related to  $f_i(\mathbf{s})$  and  $f_j(\mathbf{s})$ . Therefore, using the geometric relations between  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $b_i$ , and  $b_j$ , we introduce a transformation of the following form:

$$\int d\alpha \int d\gamma \int \sin\beta d\beta \int F(\alpha, \beta, \gamma, \rho, \phi_p) \rho d\rho d\phi_p = \int d\phi \int \int \int F(b_{ix}, b_{iy}, b_{jx}, b_{jy}, \phi) J(\alpha, \beta, \gamma, \rho, \phi_p / b_{ix}, b_{ij}, b_{jx}, b_{jy}, \phi) \times db_{ix} db_{iy} db_{jx} db_{jy}, \quad (19)$$

where  $\phi_p$  is the angle between  $\mathbf{p}$  and the  $X$  axis, and  $J$  is the Jacobian. Details of the transformation are shown in Appendix A. Since a small angle approximation is applicable, all functions containing  $\beta$  are expanded to the  $\beta^2$  term. Also, for sake of calculation, the momentum transfer vector  $\mathbf{s}$  is chosen to lie parallel to the  $X$  axis. This convention has no influence on the spherically averaged intensity, of course. Then the resulting expression for the three-atom scattering is

$$\left( \frac{d\sigma}{d\Omega} \right)_{ij,k} = -2 \operatorname{Re} \left\{ \frac{ik}{8\pi^3 r_{ij}^2} f_k^*(s) \int_0^{2\pi} d\phi \int d^2\mathbf{b}_i \exp(i\mathbf{s}_i \cdot \mathbf{b}_i) \Gamma_i(\mathbf{b}_i) \int d^2\mathbf{b}_j \exp(i\mathbf{s}_j \cdot \mathbf{b}_j) \Gamma_j(\mathbf{b}_j) \times \left[ 1 + \frac{1}{2}\beta^2 (1 + i s r_k \sin^2(\phi - \alpha) \cos\phi + \cos 2(\phi - \alpha)) \right] \right\}. \quad (20)$$

Integrating over  $\phi$  and transforming  $\alpha$ ,  $\beta$  into  $\Delta_x$  and  $\Delta_y$ , where

$$\Delta_x = b_{jx} - b_{ix},$$

$$\Delta_y = b_{jy} - b_{iy}, \quad (21)$$

and noting that

$$J_n(z) = (-1)^n J_n(-z), \quad (22)$$

we obtain

$$\left( \frac{d\sigma}{d\Omega} \right)_{ij,k} = -2 \operatorname{Re} \left\{ \frac{ik}{4\pi^2 r_{ij}^2} f_k^*(s) \int d^2\mathbf{b}_i \exp(i\mathbf{s}_i \cdot \mathbf{b}_i) \Gamma_i(\mathbf{b}_i) \int d^2\mathbf{b}_j \exp(i\mathbf{s}_j \cdot \mathbf{b}_j) \Gamma_j(\mathbf{b}_j) \left[ \left( 1 + \frac{\Delta_x^2 + \Delta_y^2}{2r_{ij}^2} \right) J_0(sr_k) - \frac{\Delta_y^2 - \Delta_x^2}{2r_{ij}^2} J_2(sr_k) + \frac{sr_k}{2r_{ij}^2} (\Delta_y^2 J_1(sr_k) + \frac{1}{4}(\Delta_y^2 - \Delta_x^2) J_3(sr_k) - \frac{3}{4}(\Delta_y^2 - \Delta_x^2) J_1(sr_k)) \right] \right\}. \quad (23)$$

By invoking the recurrence relation of Bessel functions,<sup>12</sup>

$$J_{n+1}(z) = (2n/z)J_n(z) - J_{n-1}(z), \quad (24)$$

we simplify (23) to

$$(d\sigma/d\Omega)_{ij,k} = -2 \operatorname{Re}\{ (ik/4\pi^2 r_{ij}^2) f_k^*(s) \int d^2\mathbf{b}_i \exp(i\mathbf{s}_i \cdot \mathbf{b}_i) \Gamma_i(\mathbf{b}_i) \int d^2\mathbf{b}_j \exp(i\mathbf{s}_j \cdot \mathbf{b}_j) \Gamma_j(\mathbf{b}_j) [(1 + (\Delta_x^2 + \Delta_y^2)/2r_{ij}^2) \times J_0(sr_k) + (\Delta_x^2/2r_{ij}^2) sr_k J_1(sr_k)] \}. \quad (25)$$

It is noted that, from Glauber's approximation,

$$\int d^2\mathbf{b}_l \exp(i\mathbf{s}_l \cdot \mathbf{b}_l) \Gamma_l(\mathbf{b}_l) = (2\pi/ik) f_l(\mathbf{s}_l), \quad l=i, j, k. \quad (26)$$

Let

$$\mathbf{s} = s_x \hat{x} + s_y \hat{y}. \quad (27)$$

Then

$$\int b_{ix} d^2\mathbf{b}_i \exp(i\mathbf{s}_i \cdot \mathbf{b}_i) \Gamma_i(\mathbf{b}_i) = -(2\pi/k) [\partial f_i(\mathbf{s}_i) / \partial s_{ix}], \quad (28)$$

and

$$\int b_{ix}^2 d^2\mathbf{b}_i \exp(i\mathbf{s}_i \cdot \mathbf{b}_i) \Gamma_i(\mathbf{b}_i) = (2\pi i/k) [\partial^2 f_i(\mathbf{s}_i) / \partial s_{ix}^2]. \quad (29)$$

Since  $\mathbf{s}_i \parallel \mathbf{s}_j \parallel \mathbf{s}$ , and they are parallel to the  $X$  axis, the resulting representation has the form,

$$(d\sigma/d\Omega)_{ij,k} = 2 \operatorname{Re}\{ (i/k r_{ij}^2) f_k^*(s) f_i(s_i) f_j(s_j) [(1 + \delta) J_0(sr_k) + \epsilon sr_k J_1(sr_k)] \}, \quad (30)$$

where

$$\delta = (2r_{ij}^2)^{-1} \left\{ -\frac{f_i''(s_i)}{f_i(s_i)} - \frac{f_j''(s_j)}{f_j(s_j)} + 2 \frac{f_i'(s_i) f_j'(s_j)}{f_i(s_i) f_j(s_j)} - \frac{f_i'(s_i)}{s_i f_i(s_i)} - \frac{f_j'(s_j)}{s_j f_j(s_j)} \right\}, \quad (31)$$

and

$$\epsilon = (2r_{ij}^2)^{-1} \left\{ -\frac{f_i''(s_i)}{f_i(s_i)} - \frac{f_j''(s_j)}{f_j(s_j)} + 2 \frac{f_i'(s_i) f_j'(s_j)}{f_i(s_i) f_j(s_j)} \right\}, \quad (32)$$

with

$$f^{(n)}(s) = d^n f(s) / ds^n. \quad (33)$$

It may often be convenient to express the effective diffraction distance  $r_k$  in terms of the valence parameters,

$$r_k = r_{ik} \sin\theta_{jik}, \quad (34)$$

used in Ref. 2. We estimate the magnitudes of  $\epsilon$  and  $\delta$ , for a wide range of combination of atoms  $i$  and  $j$ , to lie in the range  $1 \times 10^{-3}$  to  $3 \times 10^{-2}$  unless  $s$  is small. Therefore  $\delta$  can usually be neglected without significantly affecting the numerical result. However, for an experimentally significant range of angle ( $5 \text{ \AA}^{-1} < s < 25 \text{ \AA}^{-1}$ ) our calculation shows that the magnitude of the coefficient of  $J_1(sr_k)$  term is large enough to modulate both the phase and the magnitude of the oscillatory function  $(d\sigma/d\Omega)_{ij,k}$  appreciably, especially at large values of  $s$ .

If  $\delta$  and higher powers of  $\epsilon$  are discarded and the vibrational average is taken, (30) can be approximately represented by

$$(d\sigma/d\Omega)_{ij,k} = 2 \operatorname{Re}\{ (i/k r_{ij}^2) f_k^*(s) f_i(s_i) f_j(s_j) (1 - \epsilon l_{\perp}^2 s^2) \exp(-l_{\perp}^2 s^2 / 2) J_0[sr_k (1 - \epsilon - \frac{1}{2} \langle \omega^2 \rangle)] \}, \quad (35)$$

where  $l_{\perp}^2$  and  $l_{\parallel}^2$  are the components of the mean square amplitude of vibration of atom  $k$  relative to point  $o$  parallel and perpendicular to  $r_{ij}$ , and where  $\langle \omega^2 \rangle$  is  $l_{\parallel}^2 / r_k^2$ .

For small  $s$ ,  $sr_k$  may be interpreted as the foreshortening of the effective distance between atom  $k$  and atom pair  $i$  and  $j$  due to the average deviation of  $\beta$  from the most favored eclipsing orientation.

#### IV. PRACTICAL CONSIDERATIONS

In Paper I, it was shown that an expression similar to (35), using an approximate value of  $\epsilon$ , gave a correction to the reduced intensity  $M(s)$  for  $\text{ReF}_6$  in good agreement with the experimental  $\Delta M(s) = M(s)_{\text{theoret}} - M(s)_{\text{exptl}}$ . Results by Bonham *et al.* and by Yates<sup>2</sup> also showed similar agreement. It is of some interest to examine the influence of the multiple scattering correction upon the peaks in the radial distribution curve

$f(r)$ . Therefore, the correction to  $f(r)$  was calculated from the Fourier inversion of the correction to the reduced intensity via

$$\Delta f(r)_{\text{calc}} = \int_0^{\epsilon_{\text{max}}} s M(s)_{\text{mult}} \exp(-bs^2) \sin sr ds. \quad (36)$$

A comparison between  $\Delta f(r)_{\text{calc}}$  and  $\Delta f(r)_{\text{exptl}}$  for  $\text{ReF}_6$  obtained from Ref. 4 is shown in Fig. 2. It reveals that the calculated  $\Delta f(r)$  accounts for all the major anomalies

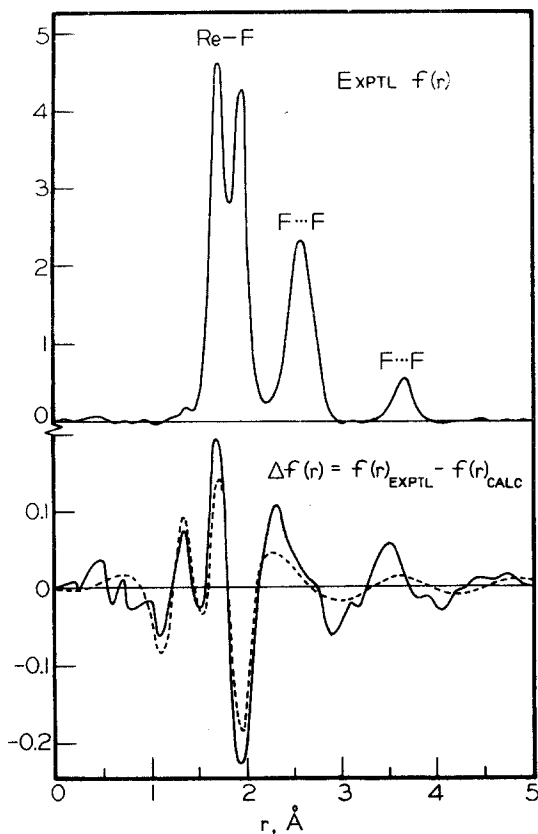


FIG. 2. Upper curve represents the experimental "radial distribution function,"  $f(r)$ , for  $\text{ReF}_6$  (Ref. 4) exhibiting dynamic scattering effects including the splitting of the Re-F peak due to Re intra-atomic multiple scattering. The lower solid curve,  $\Delta f(r)$ , plotted on a tenfold more sensitive scale, is the difference between experiment and theory neglecting interatomic multiple scattering. It includes noise of the order of 1% of the ReF peak height. The dashed curve is the three-atom scattering effect calculated from Eqs. (35) and (36).

originally observed in  $\Delta f(r)_{\text{exp}}$  including the asymmetry of the split ReF peaks and the perturbation of the  $\text{F}\cdots\text{F}$  nonbonded peak. It is worth commenting that, unlike the Shomaker-Glauber failure of the Born approximation,<sup>18</sup> which is caused by a *difference* in atomic number, the three-atom effect may be significant when all atoms involved are heavy, as well as in peaks corresponding to heavy atom-light atom pairs. In Paper I, in Fig. 2 of the present paper, and in the other

calculations by Bonham *et al.* and Yates,<sup>2</sup> it has so far been possible to make only an approximate comparison between  $M(s)_{\text{mult}}$  and  $\Delta M(s)_{\text{exptl}}$  for the chosen case,  $\text{ReF}_6$ . This is because the principal term, (ReF, F) with  $\theta_{ijk} = \pi/2$ , has an effective three-atom diffraction distance,  $r_k(1-\epsilon)$ , virtually the same as the Re-F bond length. Since for large argument,

$$J_0(z) = (\cos z + \sin z) / (\pi z)^{1/2}, \quad (37)$$

the sine component of  $J_0(z)$  for the (ReF, F) term will be in phase with the molecular term of Re-F. The sine component was therefore omitted in the comparison on the ground that it would be largely absorbed by a shift in the vertical scale factor in the least squares fitting. This is not a rigorous comparison, because the sine component of the multiple scattering contribution is modified by an envelope substantially different from that of the molecular interference term. Therefore the sine component corresponding to Eq. (37) cannot be completely absorbed in the least squares fitting. In addition to giving a large discrepancy between theory and experiment, the neglect of the multiple scattering effect in the least squares analysis may alter the apparent index of resolution and distort molecular parameters, especially the amplitude of vibration. A reanalysis with three-atom scattering corrections incorporated properly in the least squares analysis is underway for  $\text{ReF}_6$  and some other compounds with heavy atoms to test the effect upon the derived molecular parameters.

In conclusion, we have shown that a qualitative analytical description of the multiple scattering effect in electron diffraction can be obtained from the Glauber theory. It is simple enough to be applied as a correction in routine analyses for molecular structure. Evidence to date suggests that inclusion of this multiple scattering correction will go far towards eliminating the systematic anomalies previously observed and will put upon a sounder basis the structure analyses of molecules containing heavy atoms.

#### ACKNOWLEDGMENTS

We wish to thank Professor A. C. Yates for helpful discussions leading to an improved mathematical presentation and Mr. Charles Ritz for calculation of the  $\Delta f(r)$  result.

#### APPENDIX A

Transformation (19) can be carried out by establishing the geometric functional relationships between the parameters concerned. Implicit in Fig. 1 are the relations

$$\mathbf{r}_i = r_i(\sin\alpha \sin\beta \hat{i} - \cos\alpha \sin\beta \hat{j} + \cos\beta \hat{k}), \quad (\text{A1})$$

$$\mathbf{r}_j = -r_j(\sin\alpha \sin\beta \hat{i} - \cos\alpha \sin\beta \hat{j} + \cos\beta \hat{k}), \quad (\text{A2})$$

$$\mathbf{r}_k = r_k[(\cos\alpha \cos\gamma - \sin\alpha \cos\beta \sin\gamma) \hat{i} + (\sin\alpha \cos\gamma + \cos\alpha \cos\beta \sin\gamma) \hat{j} + \sin\beta \sin\gamma \hat{k}], \quad (\text{A3})$$

and

$$\mathbf{p}_i = r_i(\sin\alpha\hat{z} - \cos\alpha\hat{y}) \sin\beta, \tag{A4}$$

$$\mathbf{p}_j = -r_j(\sin\alpha\hat{z} - \cos\alpha\hat{y}) \sin\beta, \tag{A5}$$

$$\mathbf{p}_k = r_k[(\cos\alpha \cos\gamma - \sin\alpha \cos\beta \sin\gamma)\hat{z} + (\sin\alpha \cos\gamma + \cos\alpha \cos\beta \sin\gamma)\hat{y}]. \tag{A6}$$

It may be shown from (A1) to (A6) and (13) that

$$\alpha = \tan^{-1}[-(b_{jx} - b_{ix}) / (b_{jy} - b_{iy})], \tag{A7}$$

$$\beta = \sin^{-1}\{(1/r_{ij})[(b_{jx} - b_{ix})^2 + (b_{jy} - b_{iy})^2]^{1/2}\}, \tag{A8}$$

$$\gamma = \tan^{-1}[\sec\beta \tan(\phi - \alpha)], \tag{A9}$$

$$p = (1/r_{ij})[(r_i b_{jx} + r_j b_{ix})^2 + (r_i b_{jy} + r_j b_{iy})^2]^{1/2}, \tag{A10}$$

$$\phi_p = \tan^{-1}[(r_j b_{iy} + r_i b_{jy}) / (r_j b_{ix} + r_i b_{jx})]. \tag{A11}$$

The Jacobian is

$$\begin{aligned} J &= |\partial(\alpha, \beta, \gamma, p, \phi_p) / \partial(b_{ix}, b_{iy}, b_{jx}, b_{jy}, \phi)|, \\ &= (\Delta_x^2 + \Delta_y^2)^{-1/2} \{1 - [(\Delta_x^2 + \Delta_y^2) / r_{ij}^2]\}^{-1/2} [(r_i b_{jx} + r_j b_{ix})^2 + (r_i b_{jy} + r_j b_{iy})^2]^{-1/2} (1 + \frac{1}{2}\beta^2 \cos 2(\phi - \alpha) + O(\beta^4) + \dots). \end{aligned} \tag{A12}$$

The effective diffraction distance between atom  $k$  and atom pair  $i$  and  $j$ , which depends on the orientation of the three-atom system, is expanded as a series in  $\beta$ , where, as in the case of the Jacobian, only terms up to  $\beta^2$  are kept, giving

$$\begin{aligned} p_k &= r_k [1 - \frac{1}{2} \sin^2\gamma \sin^2\beta]^{1/2}, \\ &\simeq r_k [1 - \frac{1}{2} \sin^2(\phi - \alpha)\beta^2 + O(\beta^4) + \dots]. \end{aligned} \tag{A13}$$

Therefore,

$$\exp(i\mathbf{s} \cdot \mathbf{p}_k) = \exp(isr_k \cos\phi) [1 + \frac{1}{2}(i)sr_k \sin^2(\phi - \alpha) \cos\phi\beta^2 + O(\beta^4) + \dots]. \tag{A14}$$

Our choice of the origin simplified this term and, accordingly, the subsequent integrals. Putting (A12) and (14) into (18), keeping only terms up to  $\beta^2$ , we obtain

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega}\right)_{ij,k} &= -2 \operatorname{Re} \left( \frac{ik}{8\pi^3 r_{ij}^2} f_k^*(s) \int_0^{2\pi} d\phi \int d^2\mathbf{b}_i \exp(i\mathbf{s}_i \cdot \mathbf{b}_i) \Gamma_i(\mathbf{b}_i) \int d^2\mathbf{b}_j \exp(i\mathbf{s}_j \cdot \mathbf{b}_j) \Gamma_j(\mathbf{b}_j) \right. \\ &\quad \left. \times \{1 + \frac{1}{2}\beta^2 [1 + isr_k \sin^2(\phi - \alpha) \cos\phi + \cos 2(\phi - \alpha)]\} \right), \end{aligned} \tag{A15}$$

which is identical to (20).

### APPENDIX B

The complex atomic elastic scattering factor for electrons is expressed as

$$f(s) = |f(s)| \exp[i\eta(s)], \tag{B1}$$

where  $|f(s)|$  and  $\eta(s)$  are the absolute value and the phase of the complex quantity, respectively. Then the first and second derivatives of  $f(s)$  with respect to  $s$  can be expressed in terms of the derivatives of  $|f(s)|$  and  $\eta(s)$ :

$$f'(s) = f(s) [|f(s)|' / |f(s)| + i\eta'(s)], \tag{B2}$$

and

$$\begin{aligned} f''(s) &= f(s) [|f(s)|'' / |f(s)| - (\eta'(s))^2] \\ &\quad + i[2(|f(s)|' / |f(s)|)\eta'(s) + \eta''(s)]. \end{aligned} \tag{B3}$$

Tables of  $|f(s)|$  and  $\eta(s)$  exist<sup>14</sup> from which the required derivatives may be obtained by numerical methods. In the present investigation, it proved to be convenient to use the convolution methods for smoothing points and evaluating derivatives of functions as described by Savitzky and Golay.<sup>15</sup>

- \*Research supported by a grant from the National Science Foundation. †Presented in part at the Fourth Austin Symposium on Gas Phase Molecular Structure, Austin, Tx., February 28, 1972. Abstract M16.
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