Three-atom scattering in gas-phase electron diffraction. II. A general
treatment*.†

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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.1 Several recent studies1,2 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 inter­
ference 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 dis­
crepancies much greater than experimental errors.

In a previous paper1 (hereafter referred to as Paper I), we derived an approximate analytical representation for
three-atom scattering using Glauber’s approximation3 for the limiting case in which the distances between
atoms are large compared with atomic radii. The result accounts satisfactorily for the discrepancies in ReFs
as observed by Jacob and Bartell.4

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 diffrac­
tion have been studied before5,6a,b by numerical methods

and by the Born series approach. It was shown in Paper
I that Glauber’s approximation6 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.6

The Glauber scattering amplitude for a system of scatterers is expressed as7

\[ f(s) = (ik/2\pi) \int \exp(is \cdot p) \Gamma(p) d^2p, \]

where \( s = k_{\text{inc}} - k_{\text{scat}} \) with \( k_{\text{inc}} \) and \( k_{\text{scat}} \) representing

the incident and scattered wave vectors, respectively, and

\[ \Gamma(p) = 1 - \exp[i\chi(p)]. \]

In this expression, \( \chi(p) \) 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 \( p \). The relationship between this phase shift and the
potential field is given by

\[ \chi(p) = -\frac{m}{\hbar^2} \int_{-\infty}^{\infty} V(p, z) dz, \]

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.8 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,

$$
\chi(p, r_1, r_2 \cdots r_N) = \sum_{i=1}^{N} \chi_i(p-p_i),
$$

where $r_i$ and $p_i$ are, respectively, the position vector of the $i$th scatterer and its projection on the plane perpendicular to the incident wave vector.

Define

$$
\Gamma_i(p-p_i) = 1 - \exp[i\chi_i(p-p_i)].
$$

Then $\Gamma(p)$ can be conveniently expanded as

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

and the scattering amplitude becomes

$$
f(s) = \frac{i k}{2\pi} \left[ \sum_{i=1}^{N} \exp(is \cdot p_i) \int d^2p \exp[i\chi_i(p-p_i)] \Gamma_i(p-p_i) - \sum_{i<j} \int d^2p \exp(is \cdot p) \Gamma_i(p-p_i) \Gamma_j(p-p_j) + \cdots (-1)^{N-1} \int d^2p \exp(is \cdot p) \prod_{i=1}^{N} \Gamma_i(p-p_i) \right],
$$

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 $f_{ij}(s)$ with respect to the interchange of atoms $i$ and $j$, i.e.,

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

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 $f_{ij}(s)$ 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, that a small angle approximation is applicable.

Consider the three-atom system in the space-fixed coordinate system $X, Y, Z$, in which $k_{inc}$ of the incident
electron is chosen to be parallel to the Z axis. Choose point \( o \) such that \( \mathbf{o} \mathbf{k} \perp \mathbf{ij} \), 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 \( \mathbf{3} \) vanish, i.e.,

\[
\lim_{\mathbf{3} \to \mathbf{0}} \left( \partial \mathbf{p}_k / \partial \mathbf{3} \right) = 0. \quad (12)
\]

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 transform as proposed by Franco and Glauber,\(^{3b}\) 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 \( i \). From considerations of geometry we find that

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

and

\[
\mathbf{r}_{ij} = | \mathbf{r}_i - \mathbf{r}_j |, \quad (16)
\]

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

\[
f_{ij}(\mathbf{s}) = - \left( \frac{ik}{2\pi} \right) \int \exp(i\mathbf{s}_i \cdot \mathbf{b}_i) \Gamma_i(\mathbf{b}_i) \exp(i\mathbf{s}_j \cdot \mathbf{b}_j) \Gamma_j(\mathbf{b}_j) d^2 \mathbf{p}_l, \quad (17)
\]

and

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

where \( \alpha, \beta, \) and \( \gamma \) denote the Eulerian angles of the system.\(^{10}\) The key to simple evaluation of the integrals in (18) is the observation that a proper choice 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 \( \alpha, \beta, \gamma, \mathbf{b}_i, \) and \( \mathbf{b}_j \), we introduce a transformation of the following form:

\[
\int d\alpha d\beta d\gamma \sin\beta d\beta \sin\gamma d\gamma \left[ F(\alpha, \beta, \gamma, \mathbf{p}, \phi_\mathbf{p}) d\mathbf{p} d\phi_\mathbf{p} = \int d\phi_\mathbf{p} \int dF(b_{ix}, b_{iy}, b_{iz}, b_{jx}, b_{jy}, \phi) J(\alpha, \beta, \gamma, \mathbf{p}, \phi_\mathbf{p}/b_{ix}, b_{iy}, b_{iz}, b_{jx}, b_{jy}, \phi) \right] \times d\mathbf{p} \times d\mathbf{p}_l \times d\mathbf{p}_j, \quad (19)
\]

where \( \phi_\mathbf{p} \) 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

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

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

\[
\Delta_x = b_{ix} - b_{is}, \quad (21)
\]

and noting that

\[
J_n(\mathbf{s}) = (-1)^n J_n(-\mathbf{s}), \quad (22)
\]

we obtain

\[
\left( \frac{d\sigma}{d\Omega} \right)_{ij,k} = -2 \text{Re} \left( \frac{ik}{4\pi r_{ij}^2} f_{ij}^*(\mathbf{s}) \int d^2 \mathbf{b}_i \exp(i\mathbf{s}_i \cdot \mathbf{b}_i) \Gamma_i(\mathbf{b}_i) \int d^2 \mathbf{b}_j \exp(i\mathbf{s}_j \cdot \mathbf{b}_j) \Gamma_j(\mathbf{b}_j) \left[ \left( \frac{\Delta_x^2 + \Delta_y^2}{2r_{ij}^2} \right) J_0(\mathbf{s}_k) \right.ight.
\]

\[
- \frac{\Delta_x^2 - \Delta_y^2}{2r_{ij}^2} J_5(\mathbf{s}_k) + \frac{\mathbf{s}_k}{2r_{ij}^2} \left( \Delta_x^2 J_1(\mathbf{s}_k) + \frac{1}{2} (\Delta_y^2 - \Delta_x^2) J_9(\mathbf{s}_k) - \frac{3}{2} (\Delta_y^2 - \Delta_x^2) J_4(\mathbf{s}_k) \right) \right]. \quad (23)
\]
By invoking the recurrence relation of Bessel functions,\textsuperscript{12}
\begin{equation}
J_{n+1}(z) = \frac{2n}{z}J_n(z) - J_{n-1}(z),
\end{equation}
we simplify (23) to
\begin{equation}
\frac{d\sigma}{d\Omega}_{ij,k} = -2 \text{Re}\left\{ \frac{i}{kr_i^2}f_k^*(s)f_i(s)f_j(s) \left[ (1+\delta^2+\epsilon^2) \right] / 2r_i^2 \right\} \times J_0(\delta r_k) + \left( \Delta_2^2/2r_i^2 \right) \delta \epsilon r_k J_1(\delta r_k). \tag{25}
\end{equation}
It is noted that, from Glauber's approximation,
\begin{equation}
\int d^2b_l \exp(i\mathbf{s}_l \cdot \mathbf{b}_l) \Gamma_i(\mathbf{b}_l) = (2\pi/ik)f_i(s_l), \quad l = i, j, k. \tag{26}
\end{equation}
Let
\begin{equation}
s = s_k + s_j \hat{\gamma}. \tag{27}
\end{equation}
Then
\begin{equation}
\int d^2b_l \exp(i\mathbf{s}_l \cdot \mathbf{b}_l) \Gamma_i(\mathbf{b}_l) = -\left( 2\pi/k \right) \left[ \partial f_i(s_l)/\partial s_l \right], \tag{28}
\end{equation}
and
\begin{equation}
\int d^2b_l \exp(i\mathbf{s}_l \cdot \mathbf{b}_l) \Gamma_i(\mathbf{b}_l) = \left( 2\pi/k \right) \left[ \partial^2 f_i(s_l)/\partial s_l^2 \right]. \tag{29}
\end{equation}
Since \( s_i \parallel s_j \parallel s \), and they are parallel to the X axis, the resulting representation has the form,
\begin{equation}
\frac{d\sigma}{d\Omega}_{ij,k} = 2 \text{Re}\left\{ (i/kr_i^2)f_k^*(s)f_i(s)f_j(s) \left[ (1+\delta^2)J_0(\delta r_k) + \epsilon \delta r_k J_1(\delta r_k) \right] \right\}, \tag{30}
\end{equation}
where
\begin{equation}
\delta = (2r_i^2)^{-1} \left\{ \frac{f''(s_i)}{f_i(s_i)} - \frac{f''(s_j)}{f_j(s_j)} + 2\frac{f'(s_i)f'(s_j)}{f_i(s_i)f_j(s_j)} - \frac{f'(s_i)}{s_i f_i(s_i)} - \frac{f'(s_j)}{s_j f_j(s_j)} \right\}, \tag{31}
\end{equation}
and
\begin{equation}
\epsilon = (2r_i^2)^{-1} \left\{ \frac{f''(s_i)}{f_i(s_i)} - \frac{f''(s_j)}{f_j(s_j)} + 2\frac{f'(s_i)f'(s_j)}{f_i(s_i)f_j(s_j)} \right\}, \tag{32}
\end{equation}
with
\begin{equation}
f^{(n)}(s) = d^n f(s)/ds^n. \tag{33}
\end{equation}
It may often be convenient to express the effective diffraction distance \( r_k \) in terms of the valence parameters,
\begin{equation}
r_k = r_{ik} \sin \theta_{ik}, \tag{34}
\end{equation}
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 \( 3 \times 10^{-4} \) unless \( s \) is small. Therefore \( \delta \) can usually be neglected without significantly affecting the numerical result. However, for an experimentally significant range of angle (\( 5 \text{ Å}^{-1} < s < 25 \text{ Å}^{-1} \)) our calculation shows that the magnitude of the coefficient of \( J_1(\delta r_k) \) 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
\begin{equation}
(\Delta \sigma/d\Omega)_{ij,k} = 2 \text{Re}\left\{ (i/kr_i^2)f_k^*(s)f_i(s)f_j(s) \left[ (1+\epsilon^2)J_0(\epsilon r_k) - \epsilon \epsilon r_k J_1(\epsilon r_k) \right] \right\}, \tag{35}
\end{equation}
where \( l_s^2 \) and \( l_{||}^2 \) are the components of the mean square amplitude of vibration of atom \( k \) relative to point 0 parallel and perpendicular to \( r_{ij} \), and \( \delta \) is \( l_s^2/r_k^2 \).

For small \( s \), \( \epsilon r_k \) 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.

\section*{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 ReF\(_6\) in good agreement with the experimental \( \Delta M(s) = M(s)_{\text{theory}} - M(s)_{\text{expt}} \). Results by Bonham \textit{et al.} and by Yates\textsuperscript{6} 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
\begin{equation}
\Delta f(r)_{\text{calc}} = \int_0^{\tau_{\text{max}}} s M(s)_{\text{mult}} \exp(-bs^2) \sin s r ds. \tag{36}
\end{equation}
A comparison between \( \Delta f(r)_{\text{calc}} \) and \( \Delta f(r)_{\text{expt}} \) for 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 \( \text{Re}-\text{F} \) peak due to \( \text{Re} \) 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 \( \text{ReF} \) 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 \( \text{ReF} \) 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,\(^{18}\) 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,\(^2\) it has so far been possible to make only an approximate comparison between \( M(s)_{\text{mult}} \) and \( \Delta M(s)_{\text{exp}} \) for the chosen case, \( \text{ReF}_6 \). This is because the principal term, \( (\text{ReF}, \text{F}) \) with \( \theta_{jk} = \pi/2 \), has an effective three-atom diffraction distance, \( r_b(1 - e) \), virtually the same as the \( \text{Re}–\text{F} \) bond length. Since for large argument,

\[
J_0(z) = \frac{\cos z + \sin z}{(\pi z)^{1/2}},
\]

the sine component of \( J_0(z) \) for the \( (\text{ReF}, \text{F}) \) term will be in phase with the molecular term of \( \text{Re}–\text{F} \). 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.

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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

\[
r_i = r_i(\sin \alpha \sin \beta \theta - \cos \alpha \sin \beta \gamma + \cos \beta k),
\]

\[
r_j = -r_j(\sin \alpha \sin \beta \theta - \cos \alpha \sin \beta \gamma + \cos \beta k),
\]

\[
r_k = r_k[(\cos \alpha \cos \gamma - \sin \alpha \cos \beta \sin \gamma) \hat{\theta} + (\sin \alpha \cos \gamma + \cos \alpha \cos \beta \sin \gamma) \hat{\gamma} + \sin \beta \sin \gamma \hat{k}],
\]

\[
(19)
\]

\[
(A1)
\]

\[
(A2)
\]

\[
(A3)
\]
and
\[ p_i = r_i (\sin \alpha - \cos \phi) \sin \beta, \quad (A4) \]
\[ p_j = - r_j (\sin \alpha - \cos \phi) \sin \beta, \quad (A5) \]
\[ p_k = r_k [(\cos \alpha \cos \gamma - \sin \alpha \cos \beta \sin \gamma) \hat{t} + (\sin \alpha \cos \gamma + \cos \alpha \cos \beta \sin \gamma) \hat{r}]. \quad (A6) \]
It may be shown from (A1) to (A6) and (13) that
\[ \alpha = \tan^{-1} \left[ \frac{- (b_{ja} - b_{ia})}{(b_{ja} - b_{ia})} \right], \quad (A7) \]
\[ \beta = \sin^{-1} \left\{ \left( \frac{1}{r_{ij}} \right) \left[ (b_{ja} - b_{ia})^2 + (b_{ja} - b_{ia})^2 \right]^{1/2} \right\}, \quad (A8) \]
\[ \gamma = \tan^{-1} \left[ \sec \beta \tan (\phi - \alpha) \right], \quad (A9) \]
\[ \rho = \left( \frac{1}{r_{ij}} \right) \left[ (r_i b_{ja} + r_j b_{ia})^2 + (r_i b_{ja} + r_j b_{ia})^2 \right]^{1/2}, \quad (A10) \]
\[ \phi_{\rho} = \tan^{-1} \left[ \frac{r_i b_{ja} + r_j b_{ia}}{(r_i b_{ja} + r_j b_{ia})} \right]. \quad (A11) \]
The Jacobian is
\[ J = \left| \left( \frac{\partial (\alpha, \beta, \gamma, \rho, \phi_{\rho})}{\partial (b_{ia}, b_{ia}, b_{ja}, b_{ia}, \phi)} \right) \right|, \]
\[ = (\Delta_x^2 + \Delta_y^2)^{-1/2} \left[ 1 - \left( \frac{(\Delta_x^2 + \Delta_y^2)}{r_{ij}} \right)^{-1/2} \left[ (r_i b_{ja} + r_j b_{ia})^2 + (r_i b_{ja} + r_j b_{ia})^2 \right]^{-1/2} (1 + \frac{1}{2} \beta^2 \cos 2(\phi - \alpha) + O(\beta^4) + \cdots) \right]. \quad (A12) \]
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
\[ p_k = r_k \left[ 1 - \frac{1}{2} \sin^2 \gamma \sin^2 \beta \right]^{1/2}, \]
\[ \approx r_k \left[ 1 - \frac{1}{2} \sin^2 (\phi - \alpha) \beta^2 + O(\beta^4) + \cdots \right]. \quad (A13) \]
Therefore,
\[ \exp (i \mathbf{r} \cdot \mathbf{p}_k) = \exp \left( i r_k \cos \phi \right) \left[ 1 + \frac{1}{2} (i r_k \sin (\phi - \alpha) \cos \phi \beta^2 + O(\beta^4) + \cdots \right]. \quad (A14) \]
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
\[ \left( \frac{d \alpha}{d \Omega} \right)_{ij,k} = -2 \text{Re} \left( \frac{i k}{8 \pi^2 r_{ij}^2} f_k^*(s) \int_0^{2\pi} d\phi \int d^2 \mathbf{b}_i \exp (i \mathbf{s} \cdot \mathbf{b}_i) \Gamma_i^*(\mathbf{b}_i) \int d^2 \mathbf{b}_j \exp (i \mathbf{s} \cdot \mathbf{b}_j) \Gamma_j(\mathbf{b}_j) \right) \times \left[ 1 + \frac{1}{2} \beta^2 \left[ 1 + i r_k \sin (\phi - \alpha) \cos \phi + \cos 2(\phi - \alpha) \right] \right], \quad (A15) \]
which is identical to (20).

**APPENDIX B**

The complex atomic elastic scattering factor for electrons is expressed as
\[ f(s) = |f(s)| \exp [i \eta(s)], \quad (B1) \]
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 \(\eta(s)\):
\[ f'(s) = f(s) \left[ \frac{f(s)'}{|f(s)|} / |f(s)| + i \eta'(s) \right], \quad (B2) \]
\[ f''(s) = f(s) \left[ f(s)' / |f(s)| - (\eta'(s))^2 \right] + i \left[ 2 \left( |f(s)'| / |f(s)| \right) \eta'(s) + \eta''(s) \right]. \quad (B3) \]
Tables of \(|f(s)|\) and \(\eta(s)\) exist\textsuperscript{14} 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.\textsuperscript{15}
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L. S. Bartell and T. C. Wong, J. Chem. Phys. 56, 2364 (1972), and references therein.


(b) V. Franco and R. J. Glauber, Phys. Rev. 142, 1195 (1966).


The notation in this paper is slightly different from Paper I in order to follow the original notation of Glauber.


A similar expansion appearing in Ref. 2 (c) contained a typographical error. The last term of the expansion should be \((-1)^{N-N_1} \Gamma_{N_1} \) as in (6) instead of \((-1)^{N-N_1-1} \Gamma_{N_1} \).

\( \alpha, \beta, \) and \( \gamma \) are the three Eulerian angles defining the orientation of the molecular system in space. Notation follows H. Margenau and G. M. Murphy. The Mathematics of Physics and Chemistry (Van Nostrand, Princeton, N.J., 1956), 2nd ed., pp. 286-289.


