

TABLE II. The elastic constants of indium antimonide at room temperature obtained from the present measurements (SG) compared with values obtained by Potter^a (P) and McSkimin, Bond, Pearson, Hrostowski^b (M). Results are in units of 10^{12} dynes/cm².

Obs.	Temp.	Freq.	c_{11}	c_{12}	c_{44}
SG	300°K	10 Mc/sec	0.6669	0.3645	0.3020
M	298°K	50 Mc/sec	0.6717	0.3665	0.3018
P	300°K	50 kc/sec	0.6472	0.3265	0.3071

^a See reference 2.

^b See reference 1.

temperature the increased attenuation made the later echoes difficult to range. The uncertainty in ρU^2 for this wave below 77.6°K is estimated at $\pm 1.5\%$. The probable error in c_{11} and c_{12} is about $\pm 1\%$. The various checks on the internal consistency of the data are satisfied to within 0.5% over the entire temperature range.

The results of this work are compared with other determinations of the room temperature elastic constants of indium antimonide in Table II. A Debye characteristic temperature, θ , of $205^\circ \pm 2^\circ\text{K}$ was calculated from the 0°K values of the elastic constants with the aid of the tables given by de Launay.⁵ The calorimetric value is $200^\circ \pm 6^\circ\text{K}$.

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⁵ J. de Launay, J. Chem. Phys. **22**, 1676 (1954).

Compton Scattering of X-Rays from Nonspherical Charge Distributions

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The Waller-Hartree theory for the incoherent Compton scattering of x-rays is extended to include the effects of the inherent nonsphericity of atomic charge distributions. The dependence of the scattering on atomic orientation is treated by a general formalism which depends on the use of the matrix elements of a unitary representation of the group of three-dimensional rotations. Application is made to derive the one-electron scattering matrix elements from atoms with *s*, *p*, and *d* electrons. It is shown that by a proper averaging over all orientations of the scattering vector, "mean" scattering formulas result which may be used directly for predicting the scattering from monatomic gases.

I. INTRODUCTION

A QUANTUM-MECHANICAL theory of the scattering of radiation by a free atom has been given by several authors¹⁻⁴ to account for the observed coherent and incoherent parts of the scattered intensity. Since accurate crystal wave functions are not available, a valuable first approximation to the incoherent Compton scattering function for a crystal may be obtained by considering each atom in the crystal to behave independently of its neighbors, and hence the scattered intensity for the crystal will be given by that determined for the free atoms. This then gives added importance to the available formulas for the free-atom Compton scattering. Of these the one most frequently employed is the Compton-Raman-Wentzel¹⁻³ equation

for the intensity in electron units (e.u.):

$$I_{\text{e.u.}} = Z - \sum_{i=1}^Z |f_{ii}|^2, \quad (1)$$

where *Z* is the number of electrons. To date the most accurate formula, which is based on a nonrelativistic wave equation and on a total atomic wave function expressed as a product of one-electron wave functions which specifically includes the effects of exchange, is that due to Waller and Hartree⁴:

$$I_{\text{e.u.}} = Z - \sum_{j=1}^Z |f_{jj}|^2 - \sum_j \sum_{k \neq j} |f_{jk}|^2, \quad (2)$$

where

$$f_{jk} = \int \psi_j^* \psi_k \exp(i\mathbf{k} \cdot \mathbf{r}) dv, \quad (3)$$

$\kappa = 2\pi/\lambda$; λ is the wavelength of the incident radiation; $\mathbf{S} = \mathbf{s} - \mathbf{s}_0$, where \mathbf{s} , \mathbf{s}_0 are unit vectors along the reflected and incident directions; and the ψ 's are appropriate

¹ A. H. Compton, Phys. Rev. **35**, 925 (1930).

² C. V. Raman, Indian J. Phys. **3**, 357 (1928).

³ G. Wentzel, Z. Physik **43**, 1 (1927).

⁴ I. Waller and D. R. Hartree, Proc. Roy. Soc. (London) **A124**, 119 (1929).

one-electron wave functions. Both Eqs. (1) and (2) have been written (for convenience) without the Breit-Dirac^{5,6} correction factor $(\nu'/\nu)^3$, where ν and ν' are the frequencies of the x-rays before and after scattering.

The extra negative terms in the Waller-Hartree equation arise from application of the Pauli exclusion principle which forbids electronic transitions to an occupied state, and so the summation is over one-electron wave functions of the same spin only.

For spherically symmetrical charge distributions, the incoherent scattering may be calculated directly from Eq. (2) in a rather straightforward way. When the atomic charge distributions are no longer spherically symmetrical, as is the case for many free atoms, the scattering will be dependent on the orientation of the scattering vector, \mathbf{S} . The scattering can no longer be calculated with \mathbf{S} along the polar axis, but must be calculated for an arbitrary orientation of \mathbf{S} . The angular dependence of the scattering intensity must then be treated in a manner suitable for comparison with experiment.

In this paper, a general formalism is presented for calculating the Compton scattering of x-rays which includes the effects of the inherent nonsphericity of the atomic charge distributions in the Waller-Hartree theory. Formulas for all the matrix elements f_{jk} for atoms with s , p , and d electrons are given. Using recently determined Hartree-Fock wave functions,⁷ the predictions of the theory are compared with the experimental results of Walker⁸ for aluminum in the paper which follows.⁹

II. CALCULATION OF f_{jk} FOR SPHERICAL CHARGE DISTRIBUTIONS

If the charge distribution is assumed spherically symmetrical, the scattering is also angle independent and so the matrix elements, f_{jk} , may be calculated by taking the vector \mathbf{S} along the polar axis. Setting $k = \kappa|S| = 4\pi \sin\theta/\lambda$ (2θ is the angle of scattering, not to be confused with the polar angle in what follows), and using the expansion

$$e^{ikr \cos\theta} = \sum_n i^n (2n+1) P_n(\cos\theta) j_n(kr),$$

where the j_n are the spherical Bessel functions, we may write

$$f_{jk} = \sum_n i^n (2n+1) \int \psi_j^*(r) \psi_k(r) P_n(\cos\theta) j_n(kr) dv. \quad (4)$$

Writing ψ_j in the separable form

$$\psi_j = [P_j(r)/r] \Theta(l_j m_j) \Phi(m_j),$$

where $P_j(r)$ is the normalized radial function, $\Theta(l_j m_j)$ the normalized associated Legendre functions (as

defined by Condon and Shortley¹⁰), and $\Phi(m_j)$ the ordinary normalized φ eigenfunctions, and denoting

$$C_n(l_1 m_1; l_2 m_2) = \left(\frac{2}{2n+1} \right)^{\frac{1}{2}} \int_0^\pi \Theta(n m_1 - m_2) \times \Theta(l_1 m_1) \Theta(l_2 m_2) \sin\theta d\theta,$$

we have upon substitution into Eq. (3) and its subsequent integration

$$f_{jk} = \sum_n i^n (2n+1) C_n(l_j m; l_k m) \times \int_0^\infty P_j(r) P_k(r) j_n(kr) dr. \quad (5)$$

Denoting the radial integrals in Eq. (5) by $\langle j_n \rangle$, we see that the f_{jk} terms of Eq. (2) are simply linear combinations of $\langle j_n \rangle$ with coefficients which depend only on the angular dependence of the one-electron wave functions. These coefficients are listed in Table I for the matrix elements, f_{jk} , of s -like, p -like, and d -like one-electron wave functions; the subscripts 0, +, and +2 denote the component of orbital angular momentum along the axis of quantization. When the individual charge density is spherically symmetrical, Eq. (5) reduces to the familiar form

$$\int P_i(r) P_j(r) \frac{\sin kr}{kr} dr = \langle j_0 \rangle.$$

III. SCATTERING MATRIX ELEMENTS FOR NONSPHERICAL CHARGE DISTRIBUTIONS

When the atomic charge distribution is no longer spherically symmetrical, the scattering will be dependent on the orientation of the scattering vector, \mathbf{S} . Hence, the scattering may not be calculated with \mathbf{S} along the polar axis, but must be calculated for an arbitrary orientation of \mathbf{S} .

In Sec. II we saw that there were a number of mathematical simplifications associated with carrying out the integrations of the f_{jk} in a coordinate system in which \mathbf{S} is chosen parallel to the z axis (such as selection rules

TABLE I. Coefficients of $\langle j_n \rangle$ in the expansion of f_{jk} .

f_{jk}	Common coeff.	$\langle j_0 \rangle$	$\langle j_1 \rangle$	$\langle j_2 \rangle$	$\langle j_3 \rangle$	$\langle j_4 \rangle$
$f_{s,s}$	1	1				
f_{s,p_0}	$\sqrt{3}i$		1			
f_{s,d_0}	$\sqrt{5}$			-1		
f_{p_0,p_0}	1	1		-2		
f_{p_+,p_+}	1	1		1		
f_{p_0,d_0}	$3i/\sqrt{15}$		2		-3	
f_{p_+,d_+}	$3i/\sqrt{5}$		1		1	
f_{d_0,d_0}	1	1		-10/7		18/7
f_{d_+,d_+}	1	1		-5/7		-12/7
f_{d_+,d_+2}	1	1		+10/7		3/7

⁵ G. Breit, Phys. Rev. **27**, 362 (1926).

⁶ P. A. M. Dirac, Proc. Roy. Soc. (London) **A111**, 405 (1926).

⁷ D. R. Hartree and A. J. Freeman (unpublished).

⁸ C. B. Walker, Phys. Rev. **103**, 558 (1956).

⁹ A. J. Freeman, Phys. Rev. **113**, 176 (1959), following paper.

¹⁰ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1953), p. 52.

on the magnetic quantum number, m_i). It therefore seems wise, for calculating the scattering when \mathbf{S} is not along z , to transform the one-electron wave functions, ψ_j , from the xyz coordinate system in which they are defined, into a new coordinate frame, $x'y'z'$, in which \mathbf{S} is parallel to z' . In this way, as will be shown later, the matrix elements of Eq. (3) can be calculated as linear combinations of the matrix elements of the spherical Bessel functions, $\langle j_n \rangle$, listed in Table I.

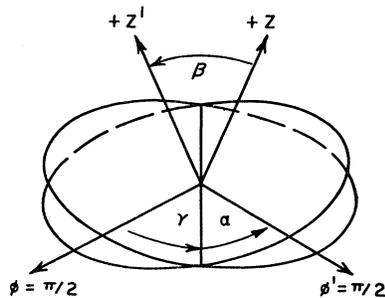
The problem, then, is to transform the one-electron wave functions $\psi_j(r, \theta, \varphi)$ into the rotated coordinate frame, r, θ', φ' . Since the ψ_j have been written in the separable form $[P_j(r)/r] \Theta_{lj}^{m_j}(\cos\theta) \Phi_{m_j}(\varphi)$, we need only find the transformation of the spherical harmonics from the coordinates of one reference frame to another. In general, this is a good deal more complicated than for the usual cases encountered in that the well-known spherical harmonic addition theorem does not suffice. The general problem of the rotation of spherical harmonics has been discussed by Wigner¹¹ and more recently by Corbató,¹² who redefined some of Wigner's factors, such as normalization, choice of Eulerian angles, and use of a left-handed coordinate system. Corbató then defines the rotation of spherical harmonics by

$$P_l^{l'm'}(\cos\theta') \Phi_{m'}(\varphi) = \sum_{l=m}^m \left[\frac{(l-|m|)!}{(l+|m|)!} F_l^{mm'}(\beta) \right. \\ \left. \times e^{-im'\alpha} e^{-im\gamma} \right] P_l^{l|m|}(\cos\theta) \Phi_m(\varphi), \quad (6)$$

where α, β, γ are the Eulerian angles of rotation of the unprimed to the primed coordinate axes. See Fig. 1 for an illustration of these angles. The particular rotation formula given by Eq. (6) was chosen because for $m'=0$, $F_l^{l0}(\beta) = P_l^{l|0|}(\cos\beta)$, and the ordinary addition theorem of spherical harmonics results. The F functions are defined by

$$F_l^{l'm'}(\beta) = (-1)^{\frac{1}{2}(m+|m|+m'+|m'|)} (l+|m|)! (l+|m'|)! \\ \times \sum_t \frac{(-1)^t [\cos(\beta/2)]^{2l+m'-m-2t} [\sin(\beta/2)]^{2l+m-m'}}{(l-m-t)! (l+m'-t)! (l+m-m')! t!}, \quad (7)$$

FIG. 1. Definition of the Euler angles, α, β, γ .



¹¹ E. P. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (F. Vieweg und Sohn, Berlin, 1931).

¹² F. J. Corbató, Ph.D. thesis, Physics Department, Massachusetts Institute of Technology, 1956 (unpublished).

where l has all values giving non-negative factorials. Furthermore, the F function may also be expressed in terms of the hypergeometric function, which in turn is related to the Jacobi polynomial.

The behavior of the spherical harmonics under rotations has also been investigated by group theoretical methods.^{13,14} Representations of the rotation group in three dimensions can be found as linear transformations on the space of analytic functions defined on the surface of a sphere, for which the spherical harmonics form bases for their irreducible subspaces.¹³ Under a rotation R , which transforms a coordinate system r, θ, φ into r, θ', φ' ,

$$\Theta_{l^{m'}}(\cos\theta') \Phi_{m'}(\varphi') = \sum_{m=-l}^l H_l^{mm'}(R) \Theta_l^m(\cos\theta) \Phi_m(\varphi), \quad (8)$$

where the $\Theta_l^m(\cos\theta)$ represent the normalized associated Legendre functions¹⁰ (chosen as normalized because the representations are to be unitary). The $H_l^{mm'}$, called the Herglotz polynomials,¹³ are the matrix elements of a unitary irreducible representation of the group of three dimensional rotations. If the rotation R is described in terms of the Euler angles, then the definitions in Eqs. (6) and (7) are in complete accord with Eq. (8). In either case we see that under a rotation spherical harmonics transform linearly among themselves, which proves our earlier statement that in the rotated system the f_{ij} may be written as linear combinations of the integrals, $\langle j_n \rangle$.

With the rotation R described by the Euler angles, α, β, γ , we may also write

$$H_l^{mm'}(\alpha, \beta, \gamma) = e^{-im'\alpha} H_l^{mm'}(\beta) e^{-im\gamma}. \quad (9)$$

Hence a knowledge of the $H_l^{mm'}(\beta)$ matrix elements completely specifies the total matrix elements $H_l^{mm'}(\alpha, \beta, \gamma)$. The matrix elements $H_l^{mm'}(\beta)$ have symmetry properties which are useful in simplifying the calculations. These symmetries are found by use of the matrix elements of the rotation with $\beta = \pi$ and further successive applications of these rotations, remembering that the $H_l^{mm'}(\beta)$ are real elements of a unitary matrix. Some of the resulting relations are

$$H_l^{mm'}(\pi) = (-1)^{l+m'} \delta_{m, -m'}, \\ H_l^{mm'}(-\pi) = (-1)^{l-m'} \delta_{m, -m'}, \quad (10) \\ H_l^{mm'}(\beta) = H_l^{m'm}(-\beta) = (-1)^{m-m'} H_l^{-m'-m}(\beta) \\ = (-1)^{m-m'} H_l^{m'm}(\beta).$$

These symmetry relations may of course be extended to include the complete matrix elements $H_l^{mm'}(\alpha, \beta, \gamma)$ by use of Eq. (9).

¹³ McIntosh, Kleppner, and Minner, Memorandum Report No. 1097, July, 1957, Ballistic Research Laboratories, Aberdeen Proving Ground, Maryland (unpublished).

¹⁴ W. Magnus, Appendix to R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1953), Vol. I.

A. Scattering from p Electrons

Application of the formulas in Eqs. (6) and (7) to the normalized spherical harmonics for p electrons, $l=1$, results in the matrix $H_l^{mm'}(\beta)$ listed in Table II.

From the $H_l^{mm'}(\beta)$ we readily find the scattering matrix elements of Eq. (3) for p electrons:

$$f_{p_0, p_0} = \int \psi_{p_0}^* \exp(i\mathbf{k}\mathbf{S} \cdot \mathbf{r}) \psi_{p_0} dv = (\cos^2\beta) f_{11} + (\sin^2\beta) f_{11},$$

and

$$f_{p_{\pm}, p_{\pm}} = \int \psi_{p_{\pm}}^* \exp(i\mathbf{k}\mathbf{S} \cdot \mathbf{r}) \psi_{p_{\pm}} dv = \frac{1}{2}(\sin^2\beta) f_{11} + \frac{1}{2}(1 + \cos^2\beta) f_{11},$$

where

$$f_{11} = \int P_p^2(r) [\Theta_1^0(\cos\theta)]^2 e^{ikr \cos\theta} \sin^2\theta d\theta d\varphi dr \quad (12a)$$

is the scattering for a p orbital directed parallel to \mathbf{S} , and

$$f_{11} = \int P_p^2(r) [\Theta_1^1(\cos\theta)]^2 e^{ikr \cos\theta} \sin^2\theta d\theta d\varphi dr \quad (12b)$$

is the scattering for a p orbital directed perpendicular to \mathbf{S} .¹⁵

From Eq. (11) we see that the scattering from a p orbital is completely described by two principal scattering factors and the angle between the scattering vector and the polar axis. Furthermore, for a group of three p electrons forming a half-closed shell in the $4S$ state we find from Eq. (6) that the coherent scattering factor is

$$\sum_{i=1}^3 f_{p_i} = f_{11} + 2f_{11}, \quad (13)$$

and is angle independent. This was to be expected since a half-closed shell has a spherically symmetrical charge distribution and hence the scattering must also be spherically symmetric. This also follows from the unitary nature of the matrix $H_l^{mm'}$, as will be shown later.

We may obtain an "average" scattering factor by averaging over all values of β in either of the equations

TABLE II. The matrix elements $H_l^{mm'}(\beta)$ for p electrons, where for convenience we have listed the matrix elements $H_n^{ik}(\beta)$ instead of the complete matrix elements $H_l^{mm'}(\alpha, \beta, \gamma)$.

$m \setminus m'$	+1	0	-1
+1	$\frac{1}{2}(1 + \cos\beta)$	$\frac{1}{2}\sqrt{2} \sin\beta$	$\frac{1}{2}(1 - \cos\beta)$
0	$-\frac{1}{2}\sqrt{2} \sin\beta$	$\cos\beta$	$\frac{1}{2}\sqrt{2} \sin\beta$
-1	$\frac{1}{2}(1 - \cos\beta)$	$-\frac{1}{2}\sqrt{2} \sin\beta$	$\frac{1}{2}(1 + \cos\beta)$

¹⁵ These results are equivalent to those of R. McWeeny, Acta. Cryst. 4, 513 (1951). McWeeny's method is however not easily generalized for electrons with angular momentum greater than one (p electrons).

in Eq. (6) (since they both give the same result), weighted by the element of solid angle $2\pi \sin\beta d\beta$. Since $\langle \cos^2\beta \rangle_{Av} = \frac{1}{3}$, we find that

$$\langle f_p \rangle_{Av} = \frac{1}{3}(f_{11} + 2f_{11}), \quad (14)$$

which states that the scattering from three p electrons is just three times the average value for one p electron.

These results are all that are needed for calculating the atomic scattering factors which contribute to the coherent scattering. For the incoherent scattering intensities we require the $|f_{ij}|^2$ terms. These are calculated in a similar way to that outlined above, but since the squares of the matrix elements are involved there are certain other complications which enter, especially concerning the angular averages.

Using the expressions in Table II for the rotation of the spherical harmonics, we find that

$$f_{p_0^2} = (\cos^4\beta) f_{11}^2 + (\sin^4\beta) f_{11}^2 + 2(\sin^2\beta \cos^2\beta) f_{11} f_{11}, \quad (15)$$

and

$$f_{p_{\pm}^2} = \frac{1}{4}(\sin^4\beta) f_{11}^2 + \frac{1}{4}(1 + \cos^2\beta)^2 f_{11}^2 + \frac{1}{2} \sin^2\beta (1 + \cos^2\beta) f_{11} f_{11}, \quad (16)$$

which upon averaging in the way already outlined gives

$$\langle f_{p_0^2} \rangle_{Av} = \frac{1}{5} f_{11}^2 + (8/15) f_{11}^2 + (4/15) f_{11} f_{11} = \langle j_0 \rangle^2 + \frac{4}{3} \langle j_2 \rangle^2, \quad (17)$$

$$\langle f_{p_{\pm}^2} \rangle_{Av} = (2/15) f_{11}^2 + (7/15) f_{11}^2 + \frac{2}{3} f_{11} f_{11} = \langle j_0 \rangle^2 + \frac{1}{3} \langle j_2 \rangle^2, \quad (18)$$

where the $\langle j_n \rangle$ are the matrix elements listed in Table I. The results of Eqs. (17) and (18) are in contrast with those of Eq. (14) in that whereas the average scattering factor for different p electrons is the same, the average of the squared scattering factor is not.

From Table I, we have the result that the Compton scattering from a half-closed shell of p electrons, calculated when $\mathbf{S} \parallel \mathbf{z}$, is

$$\sum_{i=1}^3 |f_{ii}|^2 = 3\langle j_0 \rangle^2 + 6\langle j_2 \rangle^2, \quad (19)$$

and is angle independent. But the results of Eqs. (11) and (12) state that when \mathbf{S} has an arbitrary orientation,

$$\sum_{i=1}^3 |f_{ii}|^2 = (\cos^4\beta + \frac{1}{2} \sin^4\beta) f_{11}^2 + [\sin^4\beta + \frac{1}{4}(1 + \cos^2\beta)^2] f_{11}^2 + [2 \sin^2\beta \cos^2\beta + \frac{1}{2} \sin^2\beta (1 + \cos^2\beta)] f_{11} f_{11}, \quad (20)$$

which is certainly not angle independent.

The apparent contradiction is resolved by recognizing that the selection rules prohibiting matrix elements between electrons of different m_l quantum numbers when $\mathbf{S} \parallel \mathbf{z}$ no longer holds for a rotated system. This is so because the orbitals are not eigenfunctions of the

TABLE III. The matrix elements $H_2^{mm'}(\beta)$ for d electrons.

$m \setminus m'$	+2	+1	0	-1	-2
+2	$\cos^4(\beta/2)$	$2 \cos^3(\beta/2) \sin(\beta/2)$	$6^{\frac{1}{2}} \cos^2(\beta/2) \sin^2(\beta/2)$	$2 \cos(\beta/2) \sin^3(\beta/2)$	$\sin^4(\beta/2)$
+1	$-2 \sin(\beta/2) \cos^3(\beta/2)$	$\cos^4(\beta/2) - 3 \cos^2(\beta/2) \times \sin^2(\beta/2)$	$-6^{\frac{1}{2}} [\cos(\beta/2) \sin^3(\beta/2) - \sin(\beta/2) \cos^3(\beta/2)]$	$3 \cos^2(\beta/2) \sin^2(\beta/2) - \sin^4(\beta/2)$	$2 \cos(\beta/2) \sin^3(\beta/2)$
0	$6^{\frac{1}{2}} \cos^2(\beta/2) \sin^2(\beta/2)$	$-6^{\frac{1}{2}} [\cos^3(\beta/2) \sin(\beta/2) - \sin^3(\beta/2) \cos(\beta/2)]$	$\cos^4(\beta/2) + \sin^4(\beta/2) - 4 \cos^2(\beta/2) \sin^2(\beta/2)$	$6^{\frac{1}{2}} [\cos^3(\beta/2) \sin(\beta/2) - \sin^3(\beta/2) \cos(\beta/2)]$	$6^{\frac{1}{2}} \cos^2(\beta/2) \sin^2(\beta/2)$
-1	$-2 \cos(\beta/2) \sin^3(\beta/2)$	$3 \cos^2(\beta/2) \sin^2(\beta/2) - \sin^4(\beta/2)$	$6^{\frac{1}{2}} [\cos(\beta/2) \sin^3(\beta/2) - \sin(\beta/2) \cos^3(\beta/2)]$	$\cos^4(\beta/2) - 3 \cos^2(\beta/2) \times \sin^2(\beta/2)$	$2 \cos^3(\beta/2) \sin(\beta/2)$
-2	$\sin^4(\beta/2)$	$-2 \cos(\beta/2) \sin^3(\beta/2)$	$6^{\frac{1}{2}} \cos^2(\beta/2) \sin^2(\beta/2)$	$-2 \cos^3(\beta/2) \sin(\beta/2)$	$\cos^4(\beta/2)$

orbital angular momentum in the rotated system, as shown in Table II. We must therefore add to Eq. (20) the contributions from all the off-diagonal matrix elements. For p electrons these are

$$|f_{p_0, p_{\pm}}|^2 = \frac{1}{2} \cos^2 \beta \sin^2 \beta (f_{11}^2 + f_{1^2}^2 - 2f_{11}f_{1^2}), \quad (21)$$

$$|f_{p_{\pm}, p_{\mp}}|^2 = \frac{1}{4} \sin^4 \beta f_{11}^2 + (1 + \cos \beta)^2 (\cos \beta - 1)^2 f_{1^2}^2 + 2 \sin^2 \beta (1 + \cos \beta) (\cos \beta - 1) f_{11}f_{1^2}. \quad (22)$$

Therefore, $\bar{\mathfrak{F}} = \sum_i \sum_j |f_{ij}|^2 = 3\langle j_0 \rangle^2 + 6\langle j_2 \rangle^2$, in agreement with the result in Eq. (19), showing that the Compton scattering from a half-closed shell of p electrons is, as expected, spherically symmetric. [As will be shown later, this result follows from the unitary nature of the matrix $H_l^{mm'}(R)$.]

We now also see how to explain the results of Eqs. (17) and (18). The "average" scattering from a single p electron cannot simply be $\frac{1}{3}$ of the scattering from a half-closed shell of p electrons [as is the case for coherent scattering, see Eqs. (13) and (14)], because there are "transition" terms, $|f_{ij}|^2$, which contribute whenever the number of electrons exceeds unity. As these "transition" terms are also dependent on atomic orientation, we may define an average transition scattering contribution in the same way as before. From Eqs. (21) and (22) we find that

$$\langle |f_{p_0, p_{\pm}}|^2 \rangle_{Av} = \frac{3}{5} \langle j_2 \rangle^2, \quad (23)$$

and

$$\langle |f_{p_{\pm}, p_{\mp}}|^2 \rangle_{Av} = (6/5) \langle j_2 \rangle^2.$$

These "mean" formulas, as will be shown later, are useful for making comparisons between theory and experiment.

$p-p$ Transitions

These transition matrix elements occur between p electrons in different shells in the atom. Consider a $3p_0$ orbital outside a closed shell of $2p$ electrons. The required matrix elements are

$$|f_{3p_0, 2p_0}|^2 = (\cos^4 \beta) f_{11}^2 + (\sin^4 \beta) f_{1^2}^2 + 2(\sin^2 \beta \cos^2 \beta) f_{11}f_{1^2}, \quad (24)$$

$$|f_{3p_0, 2p_{\pm}}|^2 = \frac{1}{2} \cos^2 \beta \sin^2 \beta (f_{11}^2 + f_{1^2}^2 - 2f_{11}f_{1^2}),$$

and hence the sum of all possible transition terms is

$$\sum_i \sum_j |f_{ij}|^2 = 2(\cos^2 \beta) f_{11}^2 + 2(\sin^2 \beta) f_{1^2}^2,$$

which upon averaging gives

$$\langle \sum_i \sum_j |f_{ij}|^2 \rangle_{Av} = \frac{2}{3} (f_{11}^2 + 2f_{1^2}^2) = 2\langle j_0 \rangle^2 + 4\langle j_2 \rangle^2. \quad (25)$$

Similarly, for a $3p_{\pm}$ orbital outside a closed shell of $2p$ electrons

$$\sum_i \sum_j |f_{ij}|^2 = (\sin^2 \beta) f_{11}^2 + (1 + \cos^2 \beta) f_{1^2}^2, \quad (26)$$

and

$$\langle \sum_i \sum_j |f_{ij}|^2 \rangle_{Av} = \frac{2}{3} (f_{11}^2 + 2f_{1^2}^2) = 2\langle j_0 \rangle^2 + 4\langle j_2 \rangle^2. \quad (27)$$

$s-p$ Transitions

These are the contributions to Eq. (2) due to "transitions" between electrons in s and p shells. Denoting the scattering contribution in the rotated system by a prime, we have for these matrix elements

$$|f_{s, p_0'}|^2 = \cos^2 \beta |f_{s, p_0}|^2, \quad (28)$$

$$|f_{s, p_{\pm}'}|^2 = |f_{s, p_{\mp}'}|^2 = \frac{1}{2} \sin^2 \beta |f_{s, p_0}|^2.$$

Averaging either of the equations above results in

$$\langle |f_{s, p_0'}|^2 \rangle_{Av} = \langle |f_{s, p_{\pm}'}|^2 \rangle_{Av} = \frac{1}{3} |f_{s, p_0}|^2 = \langle j_1 \rangle^2. \quad (29)$$

These formulas allow us to calculate the scattering for different cases, e.g., atoms with p electrons outside closed s shells or an s electron outside a closed p shell, according to the rules outlined above.

B. Scattering from d Electrons

The transformation properties of d electrons are found by applying the formulas in Eqs. (6) and (7) with $l=2$. The matrix elements $H_2^{mm'}(\beta)$ are listed in Table III.

In terms of these matrix elements and with the following definition,

$$f_m(d) = \int P_d^2(r) [\Theta_2^m(\cos \theta)]^2 e^{ikr \cos \theta} \sin^2 \theta \, d\theta \, d\varphi \, dr, \quad (30)$$

for the scattering factor of a d orbital with $m = |m_l|$, we may write the relation between the scattering factors

in the primed and unprimed coordinate system as

$$\begin{aligned}
f_2'(d) &= \frac{1}{8}(1+6\cos^2\beta+\cos^4\beta)f_2(d) + \frac{1}{2}(1-\cos^4\beta)f_1(d) \\
&\quad + \frac{3}{8}(1-2\cos^2\beta+\cos^4\beta)f_0(d), \\
f_1'(d) &= \frac{1}{2}(1-\cos^4\beta)f_2(d) + (\frac{1}{2}-\frac{3}{2}\cos^2\beta+2\cos^4\beta) \\
&\quad \times f_1(d) + \frac{3}{2}(\cos^2\beta-\cos^4\beta)f_0(d), \quad (31) \\
f_0'(d) &= \frac{3}{4}(1-2\cos^2\beta+\cos^4\beta)f_2(d) \\
&\quad + 3(\cos^2\beta-\cos^4\beta)f_1(d) \\
&\quad + [\frac{1}{4}-\frac{3}{2}\cos^2\beta+(9/4)\cos^4\beta]f_0(d).
\end{aligned}$$

Equations (31) give the variation of the scattering from a particular d orbital as a function of the angle of orientation of the scattering vector. Only for $\beta=0$, in which case $f_m'(d)=f_m(d)$, may we speak of a unique scattering factor, i.e., $f_m(d)$. For $\beta \neq 0$, the symmetry of the orbitals, represented by their momentum quantization, no longer exists and now the scattering factors $f_m'(d)$ are mixtures of the $f_m(d)$. Thus we see that the scattering from d electrons of arbitrary orientation may be completely described by stating the three principal scattering terms and a function of the angle β between the z axis (the polar direction) and the z' axis (the direction of the scattering vector, \mathbf{S}). The geometrical relation which existed for the principal scattering factors for p electrons [see Eq. (11)] is entirely lost since d electrons transform as tensors while p electrons transform as vectors.

Again, for a half-closed shell of d electrons, i.e., all orbitals with different m_l occupied, the coherent scattering factor is

$$\begin{aligned}
\sum_{m_l} f_{m_l}(d) &= 2f_2'(d) + 2f_1'(d) + f_0'(d) \\
&= 2f_2(d) + 2f_1(d) + f_0(d), \quad (32)
\end{aligned}$$

which is of course angle-independent and is the same result obtained if the calculation is made for $\beta=0$. For calculating the Compton scattering intensities, according to the Waller-Hartree expression, Eq. (2), we require the matrix elements $|f_{ij}|^2$. These may be calculated directly from the matrix $H_2^{mm'}$ of Table III in the way already outlined. Since there are 15 independent terms, consisting of linear combinations of products of the $f_m(d)$ with coefficients which are quite complicated trigonometric functions of the angle β , we shall not list them here.

However, as our work strictly applies to the scattering from a monatomic gas only, what we really need, for any actual comparison with experiment, are the "mean" values of these matrix elements. These mean values are defined by averaging over all orientations of the scattering vector, \mathbf{S} , weighted by the element of solid angle $2\pi \sin\beta d\beta$. This follows from the fact that in such a gas the atomic orientation is completely at random, and so the angle β between the polar axis of the atom and the scattering vector, \mathbf{S} , takes on all values. In Table IV we list these matrix elements as linear combinations of

the $\langle j_n \rangle^2$ integrals defined earlier in Table I. It is an interesting consequence of the averaging procedure that the matrix elements do not involve any cross terms involving the $\langle j_n \rangle$ integrals. This feature contributes to simplifying the mathematical calculations in the actual numerical work.

Scattering from a Half-Closed Shell

The unitary properties of the matrix $H_l(R)$ may be used to simplify some of the calculations and to provide some useful general results. As an example, we shall calculate the Compton scattering from any half-closed shell and shall show that it is indeed angle independent. For this we must calculate $\mathfrak{F} = \sum_i \sum_j |f_{ij}|^2$ for an arbitrary orientation of the scattering direction.

In terms of the matrix elements H_{jk} , it follows that

$$f_{ij}' = \sum_k H_{ki} H_{kj}^* f_{kk}, \quad (33)$$

and so

$$\begin{aligned}
\sum_i \sum_j |f_{ij}'|^2 &= \sum_i \sum_j [\sum_k H_{ki} H_{kj}^* f_{kk}] \\
&\quad \times [\sum_l H_{lj} H_{li}^* f_{ll}^*] \quad (34) \\
&= \sum_i \sum_j [\sum_k \sum_l H_{ki} H_{kj}^* H_{lj} H_{li}^* f_{kk} f_{ll}^*].
\end{aligned}$$

For terms in which $l=k$, Eq. (34), reduces to

$$\begin{aligned}
\sum_k [\sum_i \sum_j H_{ki} H_{kj}^* H_{kj} H_{ki}^*] |f_{kk}|^2 \\
= \sum_k [(\sum_i H_{ki} H_{ki}^*)(\sum_j H_{kj} H_{kj}^*)] |f_{kk}|^2. \quad (35)
\end{aligned}$$

Since the matrix $H_l(R)$ is unitary, each of the sums in parentheses in Eq. (35) is equal to one. For the terms $l \neq k$, Eq. (34) becomes

$$\begin{aligned}
\sum_i \sum_j \sum_k \sum_{l \neq k} [H_{ki} H_{kj}^* H_{lj} H_{li}^*] f_{kk} f_{ll}^* \\
= \sum_k \sum_{l \neq k} [(\sum_i H_{ki} H_{li}^*)(\sum_j H_{lj} H_{kj}^*)] f_{kk} f_{ll}^*. \quad (36)
\end{aligned}$$

Again, from the unitary property of $H_l(R)$ each sum in parentheses is zero. Upon combining these results, we see that for any half-closed shell of electrons

$$\mathfrak{F} = \sum_i \sum_j |f_{ij}'|^2 = \sum_k |f_{kk}|^2, \quad (37)$$

a result which is certainly angle independent.

TABLE IV. Mean values of the matrix elements $|f_{ij}|^2$ for d electrons.

$\langle f_{ij}' ^2 \rangle_{Av}$	$\langle j_0 \rangle^2$	$\langle j_2 \rangle^2$	$\langle j_4 \rangle^2$
$\langle f_{2,2'} ^2 \rangle_{Av}$	1	20/49	1/49
$\langle f_{1,1'} ^2 \rangle_{Av}$	1	5/49	16/49
$\langle f_{0,0'} ^2 \rangle_{Av}$	1	20/49	36/49
$\langle f_{2,-2'} ^2 \rangle_{Av}$	0	0	70/49
$\langle f_{2,1'} ^2 \rangle_{Av} = \langle f_{-2,-1'} ^2 \rangle_{Av}$	0	30/49	5/49
$\langle f_{2,-1'} ^2 \rangle_{Av} = \langle f_{-2,1'} ^2 \rangle_{Av}$	0	0	35/49
$\langle f_{2,0'} ^2 \rangle_{Av} = \langle f_{-2,0'} ^2 \rangle_{Av}$	0	20/49	15/49
$\langle f_{1,-1'} ^2 \rangle_{Av}$	0	30/49	40/49
$\langle f_{1,0'} ^2 \rangle_{Av} = \langle f_{-1,0'} ^2 \rangle_{Av}$	0	5/49	30/49

For a half-closed shell of d electrons, we have from Table I and Eq. (37) that the scattering is $5\langle j_0 \rangle^2 + (350/49)\langle j_2 \rangle^2 + (630/49)\langle j_4 \rangle^2$. This is also the result obtained by summing all the contributions of the "mean" scattering contributions in Table IV.

Similarly, for the coherent scattering factor, we have that

$$f = \sum_i f_{ii}' = \sum_i [\sum_j H_{ji} H_{ji}^* f_{jj}] = \sum_j (\sum_i H_{ji} H_{ji}^*) f_{jj}, \quad (38)$$

and therefore

$$f = \sum_i f_{ii}' = \sum_j f_{jj}, \quad (39)$$

which is also invariant.

These results may be shown more simply from the following considerations. For a half-closed shell, the integrals f_{ij} form a matrix \mathbf{F} of which $f = \sum_i f_{ii}$ is its trace. Since the trace of a matrix is invariant under a unitary transformation, the coherent scattering factor, f , is thus seen to be independent of orientation (invariant under rotations in three dimensions).

Now $\mathcal{F} = \sum_i \sum_j |f_{ij}|^2$ is the trace of the square of the matrix \mathbf{F} . By a familiar theorem in matrix theory, we know that if the trace of a matrix is invariant then so is the trace of any power of the matrix.¹⁶ Therefore, it follows that \mathcal{F} as well as f is independent of orientation. These results show us that for any closed or half-closed shells, both the coherent and incoherent scattering functions may be calculated for any orientation of the scattering vector, \mathbf{S} (usually conveniently chosen parallel to the polar axis). In all other cases this invariance is lost and so we must proceed according to the methods already outlined.

s-d Transitions

These are matrix elements of scattering which are due to transitions between s - and d -shell electrons. Again, we shall not write down the complete angular dependence of these terms but shall give only their "mean" values. In each case the averaging procedure gives the same result,

$$\langle |f_{s,d_m'}|^2 \rangle_{Av} = \frac{1}{5} |f_{s,d_0}|^2 = \langle j_2 \rangle^2. \quad (40)$$

¹⁶ I am grateful to Professor G. F. Koster for initially pointing out the possible use of this theorem.

TABLE V. Mean values of the p - d transition matrix elements.

$\langle f_{ij'} ^2 \rangle_{Av}$	$\langle j_1 \rangle^2$	$\langle j_3 \rangle^2$
$\langle f_{p_{\pm}, d_{\pm 2}'} ^2 \rangle_{Av}$	126/105	9/105
$\langle f_{p_{\pm}, d_{\mp 2}'} ^2 \rangle_{Av}$	0	135/105
$\langle f_{p_{\pm}, d_{\pm 1}'} ^2 \rangle_{Av}$	63/105	27/105
$\langle f_{p_{\pm}, d_{\mp 1}'} ^2 \rangle_{Av}$	0	90/105
$\langle f_{p_{\pm}, d_{0'}} ^2 \rangle_{Av}$	21/105	54/105
$\langle f_{p_0, d_{\pm 2}'} ^2 \rangle_{Av}$	0	45/105
$\langle f_{p_0, d_{\pm 1}'} ^2 \rangle_{Av}$	63/105	72/105
$\langle f_{p_0, d_{0'}} ^2 \rangle_{Av}$	84/105	81/105

The total contribution to \mathcal{F} from these s - d terms for half-closed shells of s and d electrons is $10\langle j_2 \rangle^2$.

p-d Transitions

These are contributions to \mathcal{F} due to electronic transitions between p and d shells. The "mean" matrix elements are listed in Table V. From half-closed shells of p and d electrons, the total contribution to the scattering is just $12\langle j_1 \rangle^2 + 18\langle j_3 \rangle^2$.

These are all the matrix elements one needs to calculate the Compton scattering of x-rays from atoms with incomplete d shells. For atoms with f electrons, similar results are obtained by following the methods given earlier in this paper.

IV. CONCLUSION

The effects of the inherent nonsphericity of atomic charge distributions on the Compton scattering may formally be included in a practical way into the Waller-Hartree theory according to the methods outlined in this paper. As illustration, all the matrix elements for the single-electron scattering terms for atoms with s , p , and d electrons have been specifically worked out including their dependence on atomic orientation. By a proper averaging over all orientations of the scattering vector, these matrix elements may be used directly for predicting the scattering from monatomic gases. In the absence of a theory for crystalline scattering, this theory offers the best available means for theoretically determining the Compton scattering from polyatomic systems.

In the paper which follows, a direct comparison between the predictions of theory and experiment is presented for the scattering from aluminum.