

this is equal to

$$\left(\frac{V}{4\pi}\right)^2 (\epsilon - 1)^2 (\mathbf{u} \cdot \mathbf{E})^2 + \frac{1}{\lambda} \mathbf{u} \cdot \nabla_{\mathbf{E}} \left[\frac{V}{4\pi} (\epsilon - 1) \mathbf{u} \cdot \mathbf{E} \right] \quad (34)$$

On expanding ϵ in powers of \mathbf{E} , as in eq. 24, we get

$$\left(\frac{V}{4\pi}\right)^2 (\epsilon^{(0)} - 1)^2 (\mathbf{u} \cdot \mathbf{E})^2 + \frac{V}{4\pi\lambda} (\epsilon^{(0)} - 1) + \frac{V}{4\pi\lambda} \epsilon^{(2)} [\mathbf{E}^2 + 2(\mathbf{u} \cdot \mathbf{E})^2] + 0(\mathbf{E}^4) \quad (35)$$

The first term is exactly what one obtains using the Einstein-Smoluchowski hypothesis. The second term is independent of the field strength. Although it is always present, it is of no interest in light scattering experiments. (One may regard this as the scattered light associated with black body radiation in the system.) The third term on the right-hand side of eq. 35 represents the error in the Einstein-Smoluchowski theory.

After averaging over the ensemble of fluctuations in N and T , and subtracting $(\mathbf{M}_{\text{av}} \cdot \mathbf{u})^2$, we obtain our final result

$$S = S(\text{macro}) + \frac{V}{4\pi\lambda} \epsilon_{\text{av}}^{(2)} [E^2 + 2(\mathbf{u} \cdot \mathbf{E})^2] + 0(E^4) \quad (36)$$

This uses the notation of eq. 14. The term independent of E^2 has been dropped.

The extra term, containing $\epsilon_{\text{av}}^{(2)}$, is responsible for some depolarization. The empirical fact, referred to by Fixman, that small optically isotropic molecules usually show little or no depolarization is clearly related to the well known fact that such molecules show very little dielectric saturation.

Once more we mention that the coefficient $\epsilon_{\text{av}}^{(2)}$ appearing in the correction term in eq. 36 may be slightly in error, as a result of the neglect of saturation in calculating the cavity field. Because this correction is unobservably small in current light scattering experiments, a small error in its estimate is of no concern here.

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Effects of Electron Correlation in X-Ray and Electron Diffraction¹

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The theory of X-ray and electron diffraction by atoms is examined from the standpoint of one-electron and two-electron operators. Elastic scattering depends on one-electron operators and hence, as is well known, may be used to determine the density of *electrons about nuclei*, a one-electron property. On the other hand, it is found that inelastic scattering by atoms possessing more than one electron depends on the distance between planetary electrons. Consequently, the mean density of *electrons about other electrons*, an important two-electron property, can also be determined from diffraction experiments. A procedure for deriving the electron-nuclear and electron-electron radial distribution functions $D(r_i)$ and $P(r_{ij})$ from scattered intensities is presented. It is shown how these functions, in turn, may be used to calculate electronic energies in atoms, including correlation energy. Properties of $D(r_i)$ and $P(r_{ij})$ are illustrated, using helium as an example. An extension of the treatment to molecules and crystals is briefly discussed. Comparisons are made of elastic and inelastic scattering factors calculated from Hartree-Fock wave functions and from wave functions explicitly including electron correlation. Effects of correlation on inelastic factors are found to be appreciable. The influence of correlation on elastic form factors and on Bragg reflection intensities for well-ordered crystals is insignificant, however. The relationship between Debye's 1915 picture of the X-ray scattering process and the very different picture developed in conventional treatments of X-ray crystallography is pointed out. This comparison helps to elucidate the role of electron correlation in X-ray and electron diffraction.

The purpose of this paper is to bring together a few simple ideas, most of which have received attention before, individually. In the aggregate, however, they cast a somewhat different light on X-ray and electron diffraction than the customary approach. Further, they illustrate how diffraction affords an experimental measure of two-electron properties of atoms and molecules in addition to the well-known measure of charge density, a one-electron property.² Indeed, as we shall

(1) Contribution No. 1468. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) n -Electron properties are properties depending on expectation values of n -electron operators. In general, n -electron operators are of the form $Q = \sum q(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$ in which each term in the sum depends on the coordinates of n electrons and in which the terms themselves cannot be written as the sum of m -electron operators with $m < n$. The operator of prime importance in this study is $[\sum \exp(i\mathbf{u} \cdot \mathbf{r}_i)]$, a one-electron operator. The square of its absolute magnitude, which we also encounter, is a two-electron operator.

see, diffraction techniques even offer, in principle, a method for determining total electronic energies of molecules including electron-electron correlation energy. The basic theory for such chemically interesting ideas was developed many years ago but implications have not received the widespread recognition which their simplicity and power warrant. The main reason for this is that the enormous success of conventional X-ray crystallography, which is based on elastic scattering, has quite obscured the significant role of inelastic scattering.

In the following we shall outline those aspects of electron correlation and its effects on the scattering of radiation by atomic systems which seem of general interest to chemists. For sake of brevity and emphasis

of the main ideas, the detailed mathematical treatment of certain points will be deferred until a later paper.

I. X-Ray Diffraction by Gas Atoms

A. Dependence of Intensity on Electronic Wave Functions.—We shall consider the nonrelativistic N electron problem in which the energy of incident photons is large compared with energy differences between bound states of the atom.^{3,4} The theory of the scattering process has been presented in detail by Waller and Hartree.⁵ The resulting expressions for the total intensity, $I_{\text{tot}}(\varphi)$, and the intensity, $I_{\text{elast}}(\varphi)$, elastically scattered by independent atoms initially in state k , are, consistent with the foregoing assumptions

$$I_{\text{tot}}(\varphi) = I_{\text{cl}} \int \psi_k^* \left[\sum_i \exp(i\mathbf{s} \cdot \mathbf{r}_i) \right]^2 \psi_k d\tau \quad (1)$$

and

$$I_{\text{elast}}(\varphi) = I_{\text{cl}} \left| \int \psi_k^* \left[\sum_i \exp(i\mathbf{s} \cdot \mathbf{r}_i) \right] \psi_k d\tau \right|^2 \quad (2)$$

where φ is the total angle of scattering (twice the Bragg angle), I_{cl} is the intensity classically scattered by a point electron as derived by Thomson,⁶ ψ_k is the electronic wave function of the atom, \mathbf{r}_i describes the position of the i th atomic electron, and \mathbf{s} is a vector of magnitude $(4\pi/\lambda) \sin(1/2\varphi)$ and direction $\mathbf{n}_0 - \mathbf{n}$, where \mathbf{n}_0 and \mathbf{n} are unit vectors in the incident and scattered directions, respectively.

It is evident that I_{elast} is a *one-electron* property which, for spherically symmetric atoms or an average over random orientations of aspherical atoms, reduces to the familiar expression

$$I_{\text{elast}}(\varphi) = I_{\text{cl}} \cdot F^2(s) \quad (3)$$

The atomic scattering factor $F(s)$ is given by

$$F(s) = \int_0^\infty D(r) (\sin sr) / sr dr \quad (4)$$

where $D(r)$ is the radial distribution, $4\pi r^2 \rho(r)$, of planetary electrons, $\rho(r)$ is the mean electron density as a function of the distance r from the nucleus, and $s = |\mathbf{s}|$. The function $D(r)$ may be regarded as the sum, $\sum D_i(r)$, of individual electron distributions.

By contrast, I_{tot} is a *two-electron* property⁷ as can be seen by recasting eq. 1 into the form

$$I_{\text{tot}} \varphi = I_{\text{cl}} \sum_i \sum_j \int \psi_k^* [\exp(i\mathbf{s} \cdot \mathbf{r}_{ij})] \psi_k d\tau \quad (5)$$

in which $\mathbf{r}_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i$. The N electron wave function depends on $3N$ spatial coordinates which may be conveniently taken as the components of the vectors $\mathbf{r}_1, \dots, \mathbf{r}_i, \mathbf{r}_{ij}, \mathbf{r}_k, \dots, \mathbf{r}_N$ rather than components of the set $\mathbf{r}_1, \dots, \mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \dots, \mathbf{r}_N$. The wave function implies the electron-electron distribution function $\mathcal{P}_k(\mathbf{r}_{ij})$ for electrons i and j , defined by

$$\mathcal{P}_k(\mathbf{r}_{ij}) = \int \psi_k^* \psi_k d\tau' \quad (6)$$

in which the integration is carried out over all coordinates except those of \mathbf{r}_{ij} . Physically, $\mathcal{P}_k(\mathbf{r}_{ij}) d\tau_{ij}$

(3) In practical analyses relativistic effects are appreciable. We shall regard them as corrections which can be handled in terms of existing theory, as outlined in ref. 4.

(4) A. H. Compton and S. K. Allison, "X-rays In Theory and Experiment," D. Van Nostrand Company, Inc., New York, N. Y., 1935.

(5) I. Waller and D. R. Hartree, *Proc. Roy. Soc. (London)*, **A124**, 119 (1929). Important contributions to the theory were also made by G. Wentzel [*Z. Physik*, **43**, 1, 779 (1927)] and by O. Klein [*ibid.*, **41**, 407 (1927)].

(6) J. J. Thomson, "Conduction of Electricity through Gases," 2nd Ed., Cambridge University Press, England, 1906, p. 325.

(7) Except, of course, for one-electron systems where $\mathbf{r}_i = 0$ and $I_{\text{tot}} = I_{\text{el}}$.

(where $d\tau_{ij} = r_{ij}^2 \sin \theta_{ij} dr_{ij} d\theta_{ij} d\varphi_{ij}$) may be interpreted as the probability that the distance separating electrons i and j lies between r_{ij} and $(r_{ij} + dr_{ij})$ while the polar angles of the vector \mathbf{r}_{ij} , reckoned from any convenient frame of axes, lie between θ_{ij} and $(\theta_{ij} + d\theta_{ij})$ and between φ_{ij} and $(\varphi_{ij} + d\varphi_{ij})$. It is apparent that eq. 5 may be re-expressed, then, as

$$I_{\text{tot}}(\varphi) = I_{\text{cl}} \sum_i \sum_j \int P_k(\mathbf{r}_{ij}) \exp(i\mathbf{s} \cdot \mathbf{r}_{ij}) d\tau_{ij} \quad (7)$$

In the event that the atom is spherically symmetric or that we consider the average over random orientations, eq. 7 simplifies to

$$I_{\text{tot}}(\varphi) = I_{\text{cl}} \sum_i \sum_j \int P_{ij}(r) (\sin sr) / sr dr \quad (8)$$

where $P_{ij}(r)$ is the radial distribution function of electron i with respect to electron j . A mean density, $\rho_{ij}(r)$, of one electron with respect to another may be defined by the relation

$$4\pi r^2 \rho_{ij}(r) = P_{ij}(r) \quad (9)$$

It may be remarked that eq. 8 was first proposed by Debye in 1915,⁸ and is exactly analogous to Debye's 1941 expression⁹ for the scattering of electrons by atomic nuclei in gas molecules. The stimulus prompting the present investigation, in fact, stemmed from the contrast between Debye's equations and the conventional expressions for X-ray scattering.

It is convenient to define a total electron-electron distribution function

$$\begin{aligned} P(r) &= \sum_i \sum_{j \neq i} P_{ij}(r) \\ &= \sum_i \sum_j P_{ij}(r) - N\delta(r) \end{aligned} \quad (10)$$

which is analogous to the total electron-nuclear distribution function $D(r)$. Equation 8 can then be expressed as

$$I_{\text{tot}}(\varphi) = I_{\text{cl}} \left\{ \int_0^\infty P(r) (\sin sr) / sr dr + N \right\} \quad (11)$$

where, as before, N is the number of electrons in the system.

B. Inference of $D(r)$ and $P(r)$ from Scattered Intensities.—The electron-nuclear radial distribution $D(r)$ and the electron-electron radial distribution $P(r)$ are related to elastic and total intensities, respectively, by Fourier sine integrals, as seen in eq. 4 and 11. Experimental radial distribution functions may be deduced from experimental intensity measurements, then, by taking the appropriate sine transforms, or

$$D(r) = (2/\pi) \int_0^\infty sr F(s) \sin sr ds \quad (12)$$

and

$$P(r) = (2/\pi) \int_0^\infty sr [(I_{\text{tot}}/I_{\text{cl}}) - N] \sin sr ds \quad (13)$$

The lack of experimental observations to $s = \infty$ may be handled by a procedure of the sort suggested by Hauptman and Karle.^{10,11} An experimental differen-

(8) P. Debye, *Ann. Physik (Leipzig)*, **46**, 809 (1915); *Physik. Z.*, **24**, 161 (1923); *J. Math. Phys.*, **4**, 133 (1925).

(9) P. Debye, *J. Chem. Phys.*, **9**, 55 (1941).

(10) H. Hauptman and J. Karle, *Phys. Rev.*, **77**, 491 (1950).

(11) L. S. Bartell and L. O. Brockway, *ibid.*, **90**, 833 (1953).

tiation between elastic and total intensity is rarely carried out but it can be done, in principle, and has actually been accomplished in practice by Compton, at least for the larger scattering angles.¹²

Several experimental X-ray determinations of $D(r)$ have been reported in which electron-nuclear distributions were deduced from *total* intensities. In these determinations corrections for inelastic scattering were made using calculations from approximate wave functions. The natural information to be derived from *total* intensities, namely the *electron-electron* distribution function $P(r)$, appears not to have been calculated. Inelastic corrections become smaller relative to total intensities as the atomic number increases. For light atoms, however, the inelastic corrections in the most important angular range are comparable to the elastic intensities. Consequently, the use of approximate wave functions in the deduction of $D(r)$ not only begs the question, logically, but also may lead to serious error. Moreover, in the light of modern developments, since $D(r)$ is a one-electron property which is relatively simple to derive theoretically and since $P(r)$ is a two-electron property which is difficult to calculate, it would seem to be not only more rigorous but also more interesting to seek an experimental measure of $P(r)$ rather than of $D(r)$ from I_{tot} .

C. Inference of Electronic Energies from Scattered Intensities.—The Hamiltonian operator for an atom may be taken, for the present purposes, as

$$H = \sum T_i + \sum V_{ni} + \sum \sum' V_{ij} \quad (14)$$

where the T_i and V_{ni} represent kinetic energy and electron-nuclear potential energy operators and where the V_{ij} operators represent the electron-electron repulsions. The electronic energy for an atom in a given state is the expectation value of H . It is well known that the two-electron operators V_{ij} present the principal obstacle to the deduction of precise solutions of the Schrödinger equation, for their mean magnitude depends on the difficult problem of electron correlation. The distribution functions discussed in a preceding section, however, characterize the electronic behavior sufficiently to establish the electronic energy completely.

The average potential energies are readily seen to be given by

$$\begin{aligned} \sum_n \bar{V}_{ni} &= -e^2 \int_0^\infty \sum_i D_i(r)/r \, dr \\ &= -e^2 \int_0^\infty D(r)/r \, dr \end{aligned} \quad (15)$$

and

$$\begin{aligned} \sum_i \sum_{j \neq i} \bar{V}_{ij} &= e^2 \int_0^\infty \sum_i \sum_{j \neq i} P_{ij}(r)/r \, dr \\ &= e^2 \int_0^\infty P(r)/r \, dr \end{aligned} \quad (16)$$

and it is to be noted especially that the electron correlation energy is fully represented. The total energy can be derived from the mean potential energy by the virial theorem, according to which

$$E = \frac{1}{2} \{ \sum \bar{V}_{ni} + \sum \sum' \bar{V}_{ij} \} \quad (17)$$

for an atom. It is unlikely that determinations of E

(12) A. H. Compton, *Phys. Rev.*, **22**, 409 (1923).

based on experimental diffraction distribution functions will be competitive in accuracy with the best alternative experimental determinations. The diffraction method, however, has the advantage of separating electron-electron and electron-nuclear contributions, and it appears feasible to determine electron-electron repulsion energies with its aid which are better than calculated Hartree-Fock repulsion energies in some cases. Support for this conjecture is given in the following sections.

D. Some Properties of $D(r)$ and $P(r)$.—Although the behavior of $D(r)$ is familiar to all chemists, the distribution function $P(r)$ seems not to have been investigated until recently.¹³ The simplest atom which serves to illustrate the two-electron aspects of $P(r)$ is, of course, helium, an atom for which quite accurate wave functions are available. It is of interest to compare the behavior of $D(r)$ and $P(r)$ calculated according to the correlationless Hartree-Fock wave function¹⁴ and according to the wave function of Roothaan and Weiss¹⁵ which accounts for 92% of the correlation energy. Such a comparison is made in Fig. 1. In Fig. 2 are shown corresponding plots of the electron-nuclear and electron-electron densities $\rho(r)$ and $\rho_{12}(r)$.

As discussed by several authors¹⁶ the Hartree-Fock results are considerably more satisfactory for the one-electron properties $D(r)$ and $\rho(r)$ than for the two-electron properties $P(r)$ and $\rho_{ij}(r)$. The superior electron-electron avoidance allowed by the better wave function is clearly evident in the plots, and the "coulomb hole" near $r = 0$ is graphically portrayed in the best curve for $\rho_{12}(r)$. The difference between the Hartree-Fock and more exact $P(r)$ is substantial and large enough to lend confidence that a precise X-ray study could discriminate between the two.

The functions illustrated in Fig. 1 and 2 were determined from the wave functions by numerical integration and were checked by calculating energies according to eq. 15-17. Published energies were reproduced almost exactly. Further observations on the properties $P(r)$ have been recently reported by Coulson and Neilson,¹³ who outline an analytical method for determining $P(r)$ from certain analytical forms of wave functions.

E. Statistical, Hartree-Fock, and "Exact" Inelastic Scattering Factors.—The inelastic scattering factor $S(s)$ for a spherical atom is defined by the relation

$$I_{\text{tot}}(\varphi) = I_{\text{el}}[F^2(s) + S(s)] \quad (18)$$

A comparison of eq. 18 with eq. 4 and 11 indicates that

$$S(s) = N + \int_0^\infty P(r)(\sin sr)/sr \, dr - \left[\int_0^\infty D(r)(\sin sr)/sr \, dr \right]^2 \quad (19)$$

Plots of $(I_{\text{tot}}/I_{\text{el}})$, $F^2(s)$, and $S(s)$ for helium are shown in Fig. 3, as calculated for the Hartree-Fock and for the more exact wave function of Roothaan and Weiss. It can be seen that correlation effects on the inelastic

(13) C. A. Coulson and A. H. Neilson, *Proc. Phys. Soc. (London)*, **78**, 831 (1961).

(14) C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, *Rev. Mod. Phys.* **32**, 186 (1960).

(15) C. C. J. Roothaan and A. W. Weiss, *ibid.*, **32**, 194 (1960).

(16) L. Brillouin, "Actualités scientifiques et industrielles," No. 159, Hermann et Cie., Paris, 1934; J. Goodisman and W. Klemperer, *J. Chem. Phys.*, **38**, 721 (1963); M. Karplus and H. J. Kolker, *ibid.*, **38**, 1263 (1963).

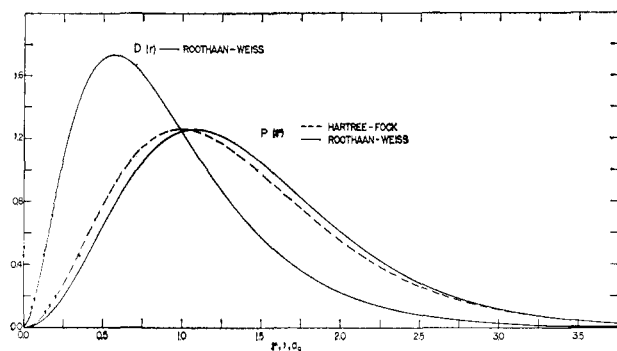


Fig. 1.—Calculated electron-nuclear and electron-electron radial distribution functions $D(r)$ and $P(r)$ for helium. The enhanced electron avoidance implicit in the Rootaan-Weiss wave function in comparison with the Hartree-Fock wave function is clearly evident. The $D(r)$ functions calculated from the two wave functions are indistinguishable from each other in the scale of the above plot.

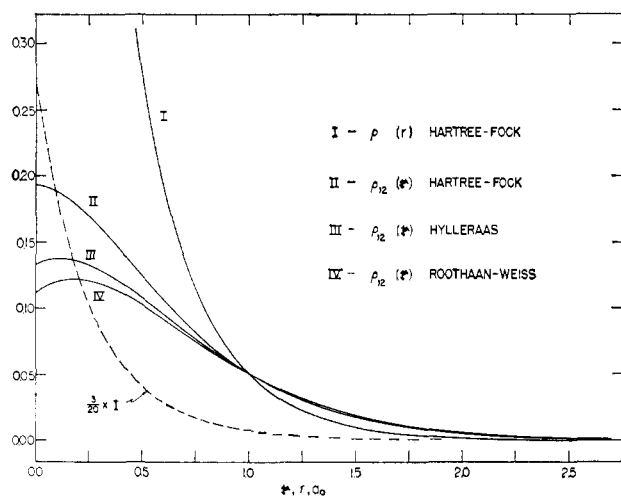


Fig. 2.—Calculated electron-nuclear and mean electron-electron densities $\rho(r)$ and $\rho_{12}(r)$ for helium. The wave functions used were Hartree-Fock [$\varphi(r_1)\varphi(r_2)$], Hylleraas [$(1 + c_{12})\exp(-ar_1 - ar_2)$], and Rootaan-Weiss [$\varphi(r_1)\varphi(r_2)\chi(r,r)$] functions with correlation energy errors of 100%, 30.0%, and 7.9% of the total correlation energy, respectively.

intensity are significant. Also plotted are the 1931 experimental values of Wollan,¹⁷ corrected for relativistic effects. These results are not sufficiently accurate to establish $P(r)$ with any precision but they are not inconsistent with the present calculations.

Inelastic scattering factors as good as Hartree-Fock factors have become generally available only recently.¹⁸ For the most part Heisenberg-Bewilogua scattering factors deduced from the Thomas-Fermi statistical model have been used in the past.¹⁹ The statistical model may be expected to fail more seriously as the number of electrons decreases, and accurate results cannot be expected for helium. For purposes of comparison, numerical values of $S(s)$ calculated for helium are listed in Table I. Computations were based on the statistical model and on Hartree-Fock,¹⁴ Hylleraas,²⁰ and Rootaan-Weiss¹⁵ wave functions.

(17) E. O. Wollan, *Phys. Rev.*, **37**, 862 (1931).

(18) A. J. Freeman, *Acta Cryst.*, **12**, 274 (1959); **13**, 190 (1960); A. J. Freeman and R. E. Watson, U. S. Dept. of Commerce, Office of Technical Services, AD 263,096 (1961).

(19) L. Bewilogua, *Physik Z.*, **32**, 740 (1931).

(20) E. A. Hylleraas, *Z. Physik*, **54**, 347 (1929).

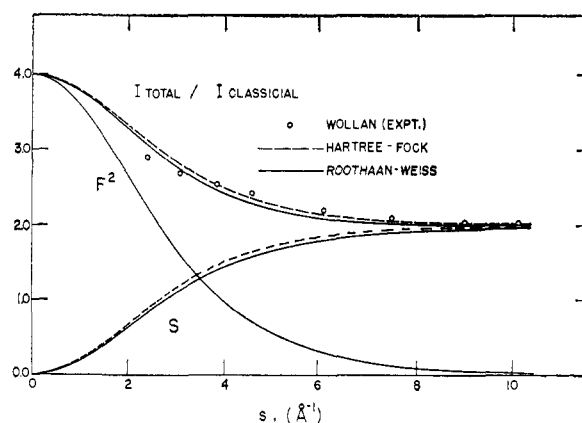


Fig. 3.—Reduced total, elastic [F^2], and inelastic [S] intensities calculated for X-ray scattering by helium. Experimental points due to Wollan are plotted as O's. The elastic intensities calculated from the two wave functions are indistinguishable from each other in the scale of the above plot.

TABLE I
INELASTIC SCATTERING FACTORS, $S(s)$, CALCULATED FOR HELIUM

$\frac{\sin \varphi/2}{\lambda}$	Heisenberg Bewilogua statistical ^a	Hartree-Fock ^b $\varphi(r_1)\varphi(r_2)$	Hylleraas ^c $(1 + c_{12})\cdot$ $\exp(-ar_1 - ar_2)$	Rootaan- Weiss ^d $\varphi(r_1)\varphi(r_2)$ $\chi(r,r)$
0.025	0.49	0.02164	0.01812	0.02052
.050	.79	.08474	.07123	.08032
.075	.99	.1841	.1557	.1744
.100	1.15	.3121	.2659	.2954
.125	1.27	.4596	.3953	.4348
.150	1.38	.6176	.5367	.5840
.175	1.46	.7779	.6835	.7355
.200	1.52	.9336	.8297	.8830
.250	1.63	1.2138	1.1029	1.1485
.300	1.70	1.4382	1.3336	1.3669
.400	1.80	1.7275	1.6526	1.6621
.500	1.86	1.8704	1.8241	1.8219
.600	1.90	1.9376	1.9104	1.9052
.700	1.92	1.9692	1.9533	1.9485
.800		1.9842	1.9748	1.9712

^a Ref. 19. ^b Four term analytical s.c.f. orbital functions, 0% of correlation energy, ref. 14. ^c 70.0% of correlation energy, ref. 20. ^d 92.1% of correlation energy, ref. 15.

F. Physical Description of X-Ray Scattering Process.—A consideration of physical aspects of the scattering process gives some insight into the role of electron correlation in diffraction. Reference books on crystallography customarily describe X-ray diffraction in terms of the following picture:

(1a) An X-ray wave encounters the time-average electron cloud charge of the scatterer and sets it into sympathetic motion.

(2a) Each volume element in the electron cloud radiates a wavelet, the amplitude of which is proportional to the charge density in the volume element.

(3a) At the point of observation the amplitudes arriving from each wavelet are summed, giving the resultant scattered amplitude at that point.

(4a) The intensity is obtained by squaring the absolute magnitude of the scattered amplitude.

In summary, scattered *amplitudes* are averaged over the quantum density of the electrons and the result is squared to get intensities. No manifestation of electron correlation is evident.

By contrast, the original treatment of Debye⁸ and the treatment of Waller and Hartree, according to eq. 1, imply that:

(1b) The X-ray wave encounters an instantaneous distribution of point electrons.

(2b) Scattered amplitudes from the individual point electrons are summed at the point of observation to give an instantaneous total scattered amplitude.

(3b) The instantaneous amplitude is squared to obtain the intensity due to the instantaneous array of point electrons.

(4b) Instantaneous intensities are averaged over the quantum mechanical distribution of geometrical configurations to get the mean total intensity.

In summary, scattered *intensities* are averaged in viewpoint b rather than *amplitudes* as in a. Electron correlation is manifested in the weighting of instantaneous configurations.

Viewpoint b might be interpreted, physically, in terms of the high frequency of X-rays in comparison with natural atomic and molecular frequencies. That is, the time for X-ray scattering is envisioned to be short compared with the time for planetary electrons to move appreciably. This classically expressed interpretation is closely analogous to the popular interpretation of the Franck-Condon principle. It is a useful interpretation but suffers the same deficiency as the Franck-Condon interpretation. If the spectrum of intensity from a system of independent molecules were examined under high resolution, sharp fine structure would be found, as discussed below. In view of the uncertainty relation $\Delta\nu \cdot \Delta t \sim 1$, the existence of fine structure with an energy breadth narrower than spacings between molecular excitation levels would indicate that the duration of the scattering process [or Franck-Condon excitation] is *long* compared with natural molecular periods.

There is really no contradiction between viewpoints a and b, for a corresponds to the elastic intensity and b to the total intensity. This is illustrated in the following. The density $\rho_i(\mathbf{r})$ of electron i is given by the integration of $\psi^* \psi$ over all coordinates except those of electron i . Hence, eq. 2 reduces at once to

$$\begin{aligned} I_{\text{elast}} &= I_{\text{el}} \left| \int \sum_i \rho_i(\mathbf{r}) \exp(i\mathbf{s} \cdot \mathbf{r}) d\tau \right|^2 \\ &= I_{\text{el}} \left| \int \rho(\mathbf{r}) \exp(i\mathbf{s} \cdot \mathbf{r}) d\tau \right|^2 \end{aligned} \quad (20)$$

This equation expresses viewpoint a.

On the other hand, Waller and Hartree have shown that the inelastic intensity scattered in the excitation of atoms from state k to state l is

$$I_{kl} = I_{\text{el}} \left| \int \psi_k^* \left[\sum_i \exp(i\mathbf{s} \cdot \mathbf{r}_i) \right] \psi_l d\tau \right|^2 \quad (21)$$

The total intensity scattered by a system of atoms initially in the k th state is then

$$I_{\text{tot}}(\varphi) = \sum_i I_{kl} \quad (22)$$

Since it is presumed that the set of eigenfunctions $\{\psi_i\}$ is complete, eq. 22 simplifies by application of the closure theorem to eq. 1. This equation expresses viewpoint b.

The momentum exchange between photons and atoms incurred in elastic scattering involves the entire mass of the atoms. The momentum exchange in the inelastic (Compton) scattering involves the planetary electrons, which are thereby excited to higher states. The momentum exchange between photons and electrons, as it were, is associated with positional measure-

ment of the electrons. It is natural, therefore, that correlation shows up in inelastic rather than elastic scattering. Inasmuch as atoms do not have infinite mass, "elastic" scattering is also, of course, to some degree inelastic.

An analogous situation in neutron diffraction has been exploited for some time. Inelastic neutron scattering experiments have been used extensively in the study of correlated motions of nuclei in crystals.²¹ Neutron scattering is particularly effective for this because neutrons have masses comparable to nuclear masses and readily exchange momentum with nuclei. By the same token, it is apparent that inelastic electron scattering would closely parallel inelastic X-ray scattering and serve best as a tool for studying motions of planetary electrons.

II. X-Ray Diffraction by Crystals

For light atoms I_{elast} and I_{tot} are very different and the inelastic contribution is sensitive to electron correlation behavior. It is not immediately obvious, then, that X-ray diffraction by crystals with light atoms is adequately described by the conventional elastic scattering picture alone. It is usually argued that inelastic scattering is incoherent and, hence, unimportant in scattering by crystal lattices. Nevertheless, eq. 21 indicates definite phase relationships for wavelets scattered from volume elements over the entire crystal by each inelastic event. Considerations of this sort originally made it appear worth investigating whether electron correlation might be responsible for anomalous results encountered in crystallography such as the unreasonably short lengths often reported for bonds to hydrogen atoms.²²

The basic relations 1 and 2 of section I-A apply to crystals as well as to individual atoms if the appropriate many-electron wave function for the entire crystal is used. The elastic intensity is sensitive only to electron density, as we have seen. If a simple atomic orbital product wave function is used it may be shown that the only difference between I_{tot} and I_{elast} is a featureless (incoherent) sum of inelastic atomic terms. Any departure between a featureless inelastic intensity and an intensity calculated from a precise wave function must result from the influence of electron correlation on the pair distribution function $\mathcal{P}(\mathbf{r}_{ij})$ of eq. 7.

It is reasonable to assume that correlation effects are significant only for nearest molecular neighbors. Intramolecular dispersion interactions may be high but intermolecular dispersion forces scarcely extend beyond nearest neighbors. It follows that the number of terms in eq. 7 which are influenced by correlation is proportional to the number of molecules in the crystal. The total number of terms, however, is proportional to the square of the number of molecules. Since all terms in the summation of eq. 7 are comparable in magnitude at reflection maxima it would seem that effects of elec-

(21) B. N. Brockhouse and A. T. Stewart, *Rev. Mod. Phys.*, **30**, 236, 250 (1958); "Symposium on Inelastic Scattering of Neutrons by Solids and Liquids," International Atomic Energy Agency, Vienna, 1961.

(22) J. P. Wheatley, *Acta Cryst.*, **6**, 369 (1953); J. A. Ibers, *ibid.*, **14**, 853 (1961); W. C. Hamilton, *Ann. Rev. Phys. Chem.*, **13**, 19 (1962). Ibers' model to explain the fact that C-H distances in electron diffraction studies are longer than in spectroscopic studies is almost certainly wrong, however, because electron diffraction and spectroscopic values agree when spectroscopic values are corrected to mean values. See L. S. Bartell, K. Kuchitsu, and R. J. de Neui, *J. Chem. Phys.*, **35**, 1211 (1961).

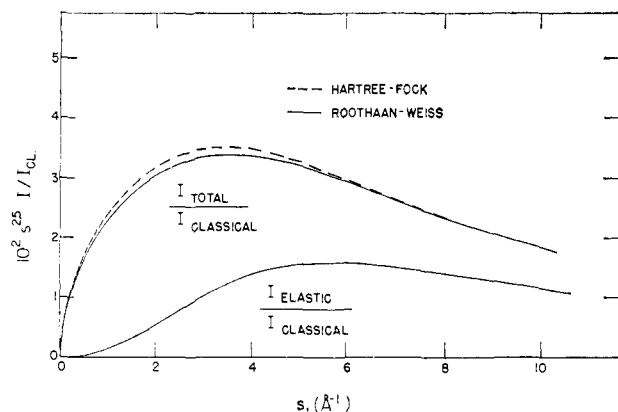


Fig. 4—Total and elastic intensities calculated for electron scattering by helium. Intensities are multiplied by $s^{2.5}$, simulating the action of a rotating sector, to portray most clearly the distinctions between the different curves.

tron correlation are insignificant in crystals with large numbers of well-ordered atoms. Therefore (and to no crystallographer's surprise), the conventional equations of crystallography are accurate and the source of difficulties with hydrogen must lie elsewhere.

III. Electron Diffraction by Gas Atoms and Molecules

The assumptions which must be imposed before electron diffraction is amenable to simple treatment are somewhat more severe than those for X-ray diffraction, as might be expected from the stronger interaction of electrons with matter. As in the case of X-rays, the model considered here is nonrelativistic with the incident energy large compared with atomic excitation energies. If polarization and exchange are ignored and the first Born approximation is applied, expressions for the intensity exactly paralleling eq. 1 and 2 for X-rays result.²³ The wave functions involved, however, include nuclear coordinates as well as electronic coordinates. An interesting consequence is that elastic and total intensities can be reexpressed in terms of viewpoints a and b of section I-F. The only adjustments which must be made are that nuclei as well as planetary electrons scatter wavelets, but with amplitudes $-Z$ times as great, and that I_{cl} for electrons is given by the Rutherford scattering law²⁴ rather than the Thomson equation. This formulation is useful because of its simplicity and power. It is appreciably more precise than the commonly used Debye-Ehrensfer independent atom approximation and has the added virtue of being exceedingly easy to remember.

For a gas molecule the average over random orientations is exactly analogous to eq. 8, or

$$I_{tot}(\varphi) = I_{cl} \sum_{\mu} \sum_{\nu} Z_{\mu} Z_{\nu} \int P_{\mu\nu}(r) (\sin sr) / sr \, dr \quad (23)$$

where the sum is over all particles, nuclei and electrons alike, with Z_{μ} standing for atomic number if μ is a nucleus and standing for -1 if μ is an electron. For a gas atom, eq. 23 reduces to nuclear-nuclear, nuclear-electron, and electron-electron terms, or

$$I_{tot}(\varphi) = I_{cl} \left\{ Z^2 - 2Z \sum_i \int D_i(r) (\sin sr) / sr \, dr + \sum_i \sum_j \int P_{ij}(r) (\sin sr) / sr \, dr \right\} \quad (24)$$

in which i and j denote electrons. The middle term is seen at once from eq. 4 to be $-2ZF(s)$ and the last term is identical with the X-ray double summation in eq. 8 which reduces to $F^2(s) + S(s)$ according to eq. 18, so that

$$I_{tot}(\varphi) = I_{cl} \left\{ Z^2 - 2ZF(s) + [F^2(s) + S(s)] \right\} \\ = I_{cl} \left\{ [Z - F(s)]^2 + S(s) \right\} \quad (25)$$

Equation 25 is the conventional electron diffraction expression for atoms. The corresponding elastic intensity is

$$I_{elst}(\varphi) = I_{cl} [Z - F(s)]^2 \quad (26)$$

Elastic and total intensities for helium calculated using eq. 25 and 26 are shown in Fig. 4 as they would be recorded through an $s^{2.5}$ rotating sector. Electron correlation effects are found to be relatively greater in electron diffraction than in X-ray diffraction since $S/(Z - F)^2$ is greater than S/I^2 in the critical range of scattering angle. Partly offsetting this advantage of electron diffraction over X-ray diffraction as an experimental measure of correlation effects is the greater uncertainty of electron diffraction theory as discussed above.²⁵

It is apparent that I_{tot} for electrons cannot be analyzed to yield either $D(r)$ or $P(r)$ directly. This is in contrast to the X-ray case where $P(r)$ is derivable from I_{tot} alone. If both I_{tot} and I_{elst} are available from electron diffraction, however, both $D(r)$ and $P(r)$ may be derived. An experimental electron diffraction determination of $D(r)$ for argon by Bartell and Brockway,¹¹ which made use of only I_{tot} , is subject to the same criticism as the X-ray determinations discussed in section I-B above.

Further applications of this general approach in electron diffraction, such as the influence of covalent binding effects on scattered intensities, have been discussed recently by Bonham, *et al.*^{23,26} Additional aspects of electron correlation in various states of helium and other light atoms will be published elsewhere along with the details of treatment omitted here.

Acknowledgments.—The authors wish to acknowledge stimulating discussions with Professor P. Debye on diffraction theory. Thanks are due also to Professors R. A. Bonham and H. B. Thompson for helpful suggestions.

(25) It is interesting to note, however, that the expression for the inelastic scattering of electrons is probably not sensitive to errors in the Born approximation. We are indebted to Professor Debye for pointing this out. The Born approximation gives the correct expression for the intensity scattered by an isolated charged particle even though it gives incorrect phases of the scattered waves. It also gives essentially correct interference terms for the scattering by a system of particles of identical charge. It gives incorrect interference terms for a pair of particles of significantly different charge. It would seem, then, that the electron-electron terms of eq. 23, which include the inelastic scattering, are reasonably accurate. The electron-nuclear terms are less reliable but, since they contribute only to the elastic scattering, their uncertainty is less serious in correlation studies. If Born errors are not corrected it is not possible to derive accurate one-electron densities directly from electron scattering data. On the other hand, it may be possible to derive reasonably accurate two-electron distribution functions from uncorrected inelastic scattering data with the aid of theoretical one-electron atom form factors.

(26) R. A. Bonham and T. Iijima, *J. Phys. Chem.*, **67**, 2266 (1963).

(23) For the key steps, see T. Iijima, R. A. Bonham, and T. Ando, *J. Phys. Chem.*, **67**, 1472 (1963).

(24) E. Rutherford, *Phil. Mag.*, **21**, 669 (1911).