The Structure of Atoms from Diffraction Studies

H. HAUPTMAN AND J. KARLE
Naval Research Laboratory, Washington, D. C.
(Received October 31, 1949)

A method is given for obtaining the electron distribution in atoms from diffraction data which makes use of the fact that the distribution function is positive. The property of positiveness affords a basis for extrapolating the scattering data which are determined experimentally over only a finite range. This extrapolation is needed since the formula relating the electron distribution to the scattering function requires that the latter be known over an infinite range. A procedure for the extrapolation is given and the nature of the error is discussed.

THE amplitude of x-rays scattered coherently by free atoms may be expressed according to theory in terms of the electron distribution about the nuclei of these atoms. By means of an inversion procedure the electron distribution may be in turn expressed explicitly in terms of the scattered x-ray amplitude. This suggestive form has lead to several investigations[1–7] with rare gas atoms in which attempts were made to determine the electron distribution. In these experiments scattering data were obtained only over a small range whereas the theory requires that the scattered intensity be known from zero to infinity. A procedure has been developed for extrapolating the data beyond the range covered by experiment which makes use of the fact that the electron distribution about a nucleus is a positive function. Extrapolation procedures used previously had no theoretical basis and caused errors in the final result. It will be shown that exact data known only in a restricted range of angle are sufficient to uniquely determine the positive electron distribution of an atom; the only requirement on the function represented by the data being the existence of all of its derivatives at the origin. If the scattering function is assumed to be analytic, then any finite length determines the remainder of the curve by the principle of analytic continuation, and the concept of positiveness need not be introduced. In practice, of course, experimental data are always obtained with some degree of uncertainty. In this case analyticity offers no useful criterion for extrapolating the data beyond the experimental range. On the other hand, the positiveness of the sine transform of the function does offer a basis for extrapolating the data within a limited range of uncertainty. The uncertainty in the resulting electron distribution will therefore fall within limited bounds which may be evaluated in terms of the uncertainty in the experimental data. In this paper a practical procedure will be developed for extrapolating experimental data which insures that its Fourier sine transform will be positive, and also an evaluation will be made of the error in the final results.

THEORY

The total x-ray intensity scattered by a free atom[8] at an angle θ to the main beam at a distance R is,

$$I_t = I_0 \frac{e^4}{m^2c^4R^2} \cdot \frac{1+\cos^2\theta}{2} [f^2(s)+QZS], \tag{1}$$

where

$$f(s) = \int_0^\infty D(r) \frac{\sin sr}{sr} dr \tag{2}$$

and $Q=1/[1+h(1-\cos\theta)/mc\lambda]^3$. The quantity I_0 is the incident intensity, $(1+\cos^2\theta)/2$ is the polarization factor, S is the incoherent scattering function tabulated by Bewilogua,[9] Q is the relativistic correction, Z is the atomic number, $s=(4\pi \sin\theta/2)/\lambda$, and the quantities e, m, c, h, and λ have their usual definitions. In this paper we are mainly concerned with the quantity $f(s)$ which is called the atomic scattering factor. It is defined in terms of $D(r)=4\pi r^2\rho(r)$ where $\rho(r)$ is the number of electrons per unit volume at a distance r from the atomic nucleus. The square of the scattering factor multiplied by the quantity in front of the bracket in (1) represents the coherent scattered intensity.

A Fourier inversion may be performed on (2) giving,

$$D(r) = \frac{2r}{\pi} \int_0^\infty sf(s) \sin rs ds. \tag{3}$$

The atomic scattering factor, $f(s)$, may be determined experimentally for only a restricted range of s. The practical lower limit of the range is some small value larger than zero and the upper limit is determined by many factors including the wave-length, the sensitivity of the measurements, and the relative magnitudes of the incoherent and coherent scattering. It is evident that $D(r)$ may be reliably obtained from (2) only if $f(s)$ is correctly extrapolated beyond the range in which it has been experimentally determined. The extrapolation

[1] A. H. Compton, Phys. Rev. **35**, 925 (1930).
[2] E. O. Wollan, Phys. Rev. **37**, 862 (1931).
[3] E. O. Wollan, Phys. Rev. **38**, 15 (1931).
[4] G. Herzog, Helv. Phys. Acta **2**, 169, 217 (1929).
[5] G. Herzog, Zeits. f. Physik **69**, 207 (1931).
[6] G. Herzog, Zeits. f. Physik **70**, 583, 590 (1931).
[7] G. Herzog, Helv. Phys. Acta **6**, 508 (1933).
[8] M. H. Pirenne, *The Diffraction of X-Rays and Electrons by Free Molecules* (Cambridge University Press, London, 1946).
[9] L. Bewilogua, Physik. Zeits. **32**, 740 (1931).

TABLE I. Witches of several orders, their cooresponding distribution functions, $D(r)$, and the coordinates of the maxima.

$f(s)$	$D(r)$	r_M	$D(r_M)$
$\frac{1}{(1+bs^2)^2}$	$\frac{r^2}{2b^{3/2}}\exp[-r/(b)^{1/2}]$	$2.0000(b)^{1/2}$	$0.2707/(b)^{1/2}$
$\frac{1}{(1+bs^2)^3}$	$\left(\frac{r^2}{8b^{3/2}}+\frac{r^3}{8b^{4/2}}\right)\exp[-r/(b)^{1/2}]$	$2.7321(b)^{1/2}$	$0.2266/(b)^{1/2}$
$\frac{1}{(1+bs^2)^4}$	$\left(\frac{r^2}{16b^{3/2}}+\frac{r^3}{16b^{4/2}}+\frac{r^4}{48b^{5/2}}\right)\exp[-r/(b)^{1/2}]$	$3.3369(b)^{1/2}$	$0.1991/(b)^{1/2}$
$\frac{1}{(1+bs^2)^5}$	$\left(\frac{5r^2}{128b^{3/2}}+\frac{5r^3}{128b^{4/2}}+\frac{r^4}{64b^{5/2}}+\frac{r^5}{384b^{6/2}}\right)\exp[-r/(b)^{1/2}]$	$3.8622(b)^{1/2}$	$0.1797/(b)^{1/2}$
$\frac{1}{(1+bs^2)^6}$	$\left(\frac{7r^2}{256b^{3/2}}+\frac{7r^3}{256b^{4/2}}+\frac{3r^4}{256b^{5/2}}+\frac{r^5}{384b^{6/2}}+\frac{r^6}{3840b^{7/2}}\right)\exp[-r/(b)^{1/2}]$	$4.3317(b)^{1/2}$	$0.1650/(b)^{1/2}$
$\frac{1}{(1+bs^2)^n}$	$\frac{1}{\Gamma(n)}\left(\frac{\Gamma(2n-3)}{2^{2n-3}\Gamma(n-1)}\cdot\frac{r^2}{b^{3/2}}+\frac{\Gamma(2n-4)}{2^{2n-4}\Gamma(n-2)}\cdot\frac{r^3}{1!b^{4/2}}+\frac{\Gamma(2n-5)}{2^{2n-5}\Gamma(n-3)}\cdot\frac{r^4}{2!b^{5/2}}+\cdots\right)\exp[-r/(b)^{1/2}]$		

procedure given here depends upon the use of a special type of analytic function. It will be indicated, although no formal mathematical proof will be offered, that the uncertainty in the final result for the electron distribution does not depend in the region of interest upon the special type of analytic function used but rather on the restrictiveness of the condition that the Fourier sine transform be positive. The restrictiveness will be shown by developing the formal theory of positive Fourier sine transforms and also by deriving certain of their special properties. The formal theory offers in principle a direct procedure for extrapolating numerical data without resorting to special functions. At its present stage of development, though, this procedure seems to be prohibitively laborious. The evaluation of the error is based on a numerical study involving a large class of examples using two different types of functions. Again the formal theory of positive Fourier sine transforms affords a basis in principle for studying the errors in the resulting electron distribution without resorting to special functions but requires considerable development to make it useful in practice.

NON-NEGATIVE SINE TRANSFORMS

The theory of non-negative Fourier sine transforms may be developed in terms of non-negative Hermitian forms in a manner entirely analogous to that for non-negative Fourier integrals of complex integrand[10] and non-negative Fourier series.[11,12] We define

$$(d/ds)[sf(s)]=\varphi(s)$$

whose value may be obtained from (2) by differentiating with respect to s, giving

$$\varphi(s)=\int_0^\infty D(r)\cos srdr. \tag{4}$$

From (4) we may write

$$\sum_i^m\sum_j \varphi(s_i-s_j)X_i\bar{X}_j = \int_0^\infty D(r)\sum_i^m\sum_j X_i\bar{X}_j\cos(s_i-s_j)rdr, \tag{5}$$

where X_i is an independent variable and $\bar{X}_i$ is its complex conjugate. The right side may be rewritten

$$\int_0^\infty D(r)[\sum_{i=1}^m X_i\cos s_ir\sum_{i=1}^m \bar{X}_i\cos s_ir + \sum_{i=1}^m X_i\sin s_ir\sum_{i=1}^m \bar{X}_i\sin s_ir]dr, \quad m=1,2,\cdots \tag{6}$$

which becomes, since each sum is multiplied by its complex conjugate,

$$\int_0^\infty D(r)[|\sum_{i=1}^m X_i\cos s_ir|^2+|\sum_{i=1}^m X_i\sin s_ir|^2]dr\geq 0. \tag{7}$$

Since $D(r)$ is a non-negative function, the integral is non-negative. We therefore obtain from (5) and (7) the infinite set of non-negative Hermitian forms characterizing the positive Fourier sine transform,

$$\sum_i^m\sum_j \varphi(s_i-s_j)X_i\bar{X}_j\geq 0, \quad m=1,2,\cdots. \tag{8}$$

The necessary and sufficient condition for the Hermitian forms to be non-negative is that the following set of determinants on the coefficients $\varphi(s_i-s_j)$ be non-negative,[13]

$$D_n=\begin{vmatrix}\varphi_0 & \varphi_{-1} & \varphi_{-2} & \cdots & \varphi_{-n}\\ \varphi_1 & \varphi_0 & \varphi_{-1} & \cdots & \varphi_{-(n-1)}\\ \varphi_2 & \varphi_1 & \varphi_0 & \cdots & \varphi_{-(n-2)}\\ \cdots & \cdots & \cdots & \cdots & \cdots\\ \varphi_n & \varphi_{n-1} & \varphi_{n-2} & \cdots & \varphi_0\end{vmatrix}\geq 0, \quad n=0,1,2,\cdots, \tag{9}$$

[10] M. Mathias, Math. Zeits. **16**, 103 (1923).
[11] N. A. Achyeser and M. Krein, Comm. Soc. Math. Kharkoff 4, 9 (1934).
[12] J. Karle and H. Hauptman, Acta Crystallograph. **3**, 181 (1950).
[13] For fixed m, n ranges from zero to $m-1$.

where $\varphi_{ij}=\varphi_{i-j}=\varphi(s_i-s_j)$ is the element in the ith row and jth column and satisfies $\varphi_{ij}=\varphi_{i\alpha}+\varphi_{\alpha j}$. Since φ is an even function, $\varphi_{ij}=\varphi_{ji}$. The determinants (9) may be rewritten to give a bound on φ_n in terms of the other elements. This bound may be written

$$|\varphi_n-\delta_n|\leq r_n, \tag{10}$$

where

$$r_n=D_{n-1}/D_{n-2}, \quad \delta_n=d_n/D_{n-2} \tag{11}$$

and

$$d_n=(-1)^n\begin{vmatrix} \varphi_1 & \varphi_0 & \varphi_{-1} & \cdots & \varphi_{-(n-2)} \\ \varphi_2 & \varphi_1 & \varphi_0 & \cdots & \varphi_{-(n-3)} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \varphi_{n-1} & \varphi_{n-2} & \varphi_{n-3} & \cdots & \varphi_0 \\ 0 & \varphi_{n-1} & \varphi_{n-2} & \cdots & \varphi_1 \end{vmatrix}. \tag{12}$$

The element φ_n is real and is therefore bounded within an interval on the real axis whose center is δ_n and whose length is $2r_n$. It will be shown for a function $f(s)$ whose derivatives exist at the origin that the function known in a finite interval including the origin uniquely determines a positive electron distribution. It is therefore apparent that φ_n, which may be an element beyond the experimental range of s values, is bounded with greater and greater restriction as n and therefore the order of the determinants increases. As n approaches infinity, r_n approaches zero and φ_n becomes a definite point defined as

$$\varphi_\infty=\lim_{n\to\infty}\delta_n. \tag{13}$$

With experimental data there is some uncertainty in the extrapolation owing to the uncertainty in the data. However, the extrapolation of any experimental function consistent with the range of uncertainty of the data must obey the restrictions of (10).

In principle, numerical data can be extrapolated beyond the experimental range by means of (10). The elements $\varphi(s_i-s_j)$ in the experimental range are obtained by finding $(d/ds)[sf(s)]$, $s=s_i-s_j$, from the numerical data. These are used with (10) to extend the function φ. The extension on $f(s)$ may then be found by evaluating

$$sf(s)=\int_0^s \varphi(y)dy. \tag{14}$$

This procedure is quite formidable in its present stage of development. We have therefore devised an extrapolation method which is based upon the application of special functions.

UNIQUENESS PROPERTY

The question of uniqueness may be discussed by means of the Hamburger moment problem[14] which concerns the conclusions that may be drawn about an increasing monotonic function, $\Psi(r)$, given the moments,

$$\mu_n=\int_{-\infty}^{\infty} r^n d\Psi(r), \quad n=0, 1, 2, \cdots. \tag{15}$$

The identification of the moment problem with the problem of non-negative sine transforms may be made by successively differentiating both sides of (2) and then setting s equal to zero. Since $D(r)$ is an even function of r, we obtain

$$\int_{-\infty}^{\infty} r^n D(r)dr=\int_{-\infty}^{\infty} r^n d\Psi(r) = (-1)^{\frac{1}{2}(n^2-n)}\cdot 2(n+1)f^{(n)}(0) \tag{16}$$

where

$$(d/dr)\Psi(r)=D(r). \tag{17}$$

The moments of $D(r)$ are seen to be simply related to the successive derivatives of $f(s)$ at the origin. The function, $\Psi(r)$, according to (17) must be an increasing monotonic function since $D(r)$ is positive for all r. As a corollary to a result of Riesz[15] who studied the Hamburger moment problem, it can be shown that if $D(r)$ drops off at least as fast as $\exp(-kr)$ for some positive k (i.e., $\lim_{r\to\infty}D(r)/\exp(-kr)=0$), $D(r)$ is uniquely determined by its moments. This condition of Riesz may be readily assumed to hold. It may therefore be concluded that the derivatives at the origin of a function, $f(s)$, uniquely determine a positive electron distribution. Since $f(s)$, known in any interval including the origin, determines all its derivatives at the origin, it therefore determines the positive electron distribution. It follows too that any finite portion of the $f(s)$ curve which is connected to a region including the origin by analytic continuation will uniquely determine a positive electron distribution. These conclusions, which relate to functions known exactly, have been drawn without assuming that $f(s)$ is analytic everywhere. They serve to illustrate that positiveness affords extra restrictiveness on exact functions and imply that this restrictiveness may have applications to experimental functions which possess some degree of uncertainty.

EXTRAPOLATION PROCEDURE

The extrapolation method used involves fitting the experimental $f(s)$ data with a function of the type,[16]

$$\sum_{i=1}^{p}\frac{a_i}{(1+b_i s^2)^{n_i}}. \tag{18}$$

This function is used to define $f(s)$ for all s from zero to infinity. The quantities a_i, b_i, and n_i are positive numbers and the value of p depends upon the accuracy de-

[14] J. Shohat and J. Tamarkin, *The Problem of Moments* (American Mathematical Society, New York, 1943).

[15] M. Riesz, Arkiv. f. Mat. Astr. o. Fys. **17**, 1 (1923), (see p. 46).

[16] The function $a/(1+bs^2)$ is known as the witch of Agnesi. We call the function $a/(1+bs^2)^n$ a witch of nth order.

sired and the complexity of the atom being studied. Generally the heavier atoms require more terms in the summation. The values of b_i and n_i must be positive for (18) to remain finite for all values of s. If, in addition, the coefficients a_i are positive, function (18), substituted for $f(s)$ in (3), must give a $D(r)$ which is positive for all values of r. Listed in Table I are examples of some of the simpler functions (18) together with the corresponding functions $D(r)$. In the third and fourth columns the abscissas and ordinates of the maxima of the $D(r)$ are tabulated since these are useful in plotting $D(r)$. If $b_i>0$, each $D(r)$ is seen to be positive for all values of r. Therefore the $D(r)$ which corresponds to any linear combination of the functions $1/(1+b_is^2)^{n_i}$ with positive coefficients will certainly be positive.

The types of functions found to be satisfactory and convenient for lighter atoms have p values up to about five in expression (18) and n_i values equal to integers, none less than two.

The curve fitting procedure which has been developed is divided into two steps. The first step is to approximate the experimental data with a function of the type (18) with all the n_i equal to the same positive integer n. In the second step this approximation is improved by the decomposition of some of the witches into a linear combination of witches of different orders.

The fitting of witches with all the n_i equal to a positive integer n can be reduced to the problem of fitting first-order witches. The experimental $f(s)$ is replaced by the function,

$$\varphi_n(s)=2(n-1)\sum_{i=0}^{n-2}(-1)^i\frac{\binom{n-2}{i}}{(s^2-s_0^2)^{i+1}}\times\int_{s_0}^{s}x(x^2-s_0^2)^i f(x)\,dx, \quad (19)$$

where $\binom{n-2}{i}$ are the binomial coefficients, $\binom{n-1}{0}=1$, and s_0 is the smallest value of s for which $f(s)$ is known. The function $\varphi_n(s)$ is fitted with first-order witches by a procedure which guarantees that the parameters a_i' and b_i' of the first-order witches will be positive. Multiplying a_i' by $(1+b_i's_0^2)^{n-1}$ and leaving b_i' unchanged, we obtain new parameters $a_i=a_i'(1+b_i's_0^2)^{n-1}$ and $b_i=b_i'$ which when substituted into (18) with each n_i equal to n yield a function which is an approximation to $f(s)$. This may be shown by substituting (18) with n_i equal to n for $f(s)$ into (19) and noting that the right-hand side then reduces to a sum of first-order witches with the same b_i but with the a_i replaced by $a_i'=a_i/(1+b_is_0^2)^{n-1}$:

$$\varphi_n(s)=\sum_{i=1}^{p}a_i'/[(1+b_is_0^2)^{n-1}(1+b_is^2)]. \quad (20)$$

We note that

$$\varphi_n(s_0)=\sum_{i=1}^{p}a_i/(1+b_is_0^2)^n=f(s_0)=f_0 \quad (21)$$

so that $f(s)$ and every $\varphi_n(s)$ have the point (s_0, f_0) in common. Finally, if a_i' and b_i' are positive, then so are a_i and b_i.

The procedure for fitting first-order witches to a set of points (s_i, f_i), which guarantees that the a_i and b_i will be positive, has been developed as follows. If the sum of p witches

$$\sum_{i=1}^{p}a_i'/(1+b_is^2)$$

passes through the p points (s_i, f_i), we have a set of p equations

$$\sum_{j=1}^{p}\frac{a_j}{1+b_js_i^2}=f_i, \quad i=1, 2, \cdots, p \quad (22)$$

which are linear in the a_j. These equations may be readily solved for the a_j, giving

$$a_j=\frac{[\prod_{i=1}^{p}(1+b_js_i^2)][(-1)^{\frac{1}{2}(p^2+p)+j}\sum_{i=0}^{p-1}\Lambda_iS_i(b_j)]}{[(-1)^{\frac{1}{2}(p^2-p)}(s_1^2, s_2^2, \cdots, s_p^2)][(-1)^{j-1}\prod_{i\neq j}(b_j-b_i)]}, \quad j=1, 2, \cdots, p \quad (23)$$

where

$$(s_1^2, s_2^2, \cdots, s_p^2)=\prod_{k=i+1}^{p}\prod_{i=1}^{p}(s_i^2-s_k^2)$$
$$=(s_1^2-s_2^2)(s_1^2-s_3^2)\cdots(s_1^2-s_p^2)(s_2^2-s_3^2)\times(s_2^2-s_4^2)\cdots(s_2^2-s_p^2)\cdots(s_{p-1}^2-s_p^2) \quad (24)$$

$$A_i=(s_2^2, s_3^2, \cdots, s_p^2)s_1^{2i}f_1-(s_1^2, s_3^2, s_4^2, \cdots, s_p^2)s_2^{2i}f_2+(s_1^2, s_2^2, s_4^2, \cdots, s_p^2)s_3^{2i}f_3-\cdots, \quad i=0, 1, 2, \cdots, p-1 \quad (25)$$

and $S_i(b_j)$ is the elementary symmetric function of degree i of all the b_k except b_j, e.g.,

$$\begin{aligned}&S_0(b_j)=1,\\ &S_2(b_2)=b_1+b_3+b_4+\cdots+b_p,\\ &S_2(b_1)=b_2b_3+\cdots+b_2b_p+b_3b_4+\cdots+b_3b_p+\cdots+b_{p-1}b_p,\\ &S_{p-1}(b_3)=b_1b_2b_4b_5\cdots b_p.\end{aligned} \quad (26)$$

Since the b_i occur symmetrically in (22), we assume without loss of generality that $b_i>b_j$ if $i<j$. Similarly, we assume that $s_i<s_j$ if $i<j$. Since, if we require the b_i

to be positive each of the expressions

$$\left.\begin{array}{l}\prod_{i=1}^{p}(1+b_j s_i^2)\\ (-1)^{\frac{1}{2}(p^2-p)}(s_1^2, s_2^2, \cdots, s_p^2)\\ (-1)^{j-1}\prod_{i\neq j}(b_j-b_i)\end{array}\right\} \quad (27)$$

appearing in (23) is evidently positive, and since we desire to restrict the b_j so that a_j are positive, we conclude that the only remaining expression appearing in (23) must also be positive:

$$(-1)^{\frac{1}{2}(p^2+p)+j}\sum_{i=0}^{p-1}A_i S_i(b_j)>0, \quad j=1, 2, \cdots, p. \quad (28)$$

We have to determine the b_i, subject to

$$b_1>b_2>\cdots>b_p>0, \quad (29)$$

such that (28) is satisfied. The system of inequalities (28) and (29) has been completely solved for several small values of p. We give solutions sufficient to satisfy (28) and (29) (and therefore $a_i>0$) for $p=3$, 4, 5.

If $p=3$, the necessary and sufficient condition for (28) and (29) to have solutions is that the inequalities

$$\left.\begin{array}{l}(-1)^{i+1}A_i>0, \quad i=0, 1, 2\\ A_1^2-A_0A_2<0\end{array}\right\} \quad (30)$$

be satisfied. If (30) is not fulfilled, then (28) and (29) have no solutions and it is impossible for a sum of three first-order witches with positive parameters to pass through the three points (s_i, f_i). If (30) is fulfilled, then the complete solution of (28) and (29) is given by:

$$\left.\begin{array}{ll}0<b_3<-\dfrac{A_1}{A_2} & \\ b_3<b_2<-\dfrac{A_0+b_3A_1}{A_1+b_3A_2} & \\ -\dfrac{A_0+b_3A_1}{A_1+b_3A_2}<b_1<-\dfrac{A_0+b_2A_1}{A_1+b_2A_2} & \text{if } b_2<-\dfrac{A_1}{A_2}\\ -\dfrac{A_0+b_3A_1}{A_1+b_3A_2}<b_1 & \text{if } b_2\geq-\dfrac{A_1}{A_2}\end{array}\right\} \quad (31)$$

If $p=4$, the necessary and sufficient condition for (28) and (29) to have solutions is that the inequalities

$$\left.\begin{array}{ll}(-1)^{i+1}A_i>0, & i=0, 1, 2, 3\\ A_i^2-A_{i-1}A_{i+1}<0, & i=1, 2\end{array}\right\} \quad (32)$$

be satisfied. If (32) is not fulfilled, then (28) and (29) have no solution and it is impossible for a sum of four first-order witches with positive parameters to pass through the four points (s_i, f_i). If (32) is fulfilled then the complete solution of (28) and (29) is given by:

$$\left.\begin{array}{ll}0<b_4<\alpha & \\ b_4<b_3<-\dfrac{A_1+b_4A_2}{A_2+b_4A_3} & \\ \alpha<b_2<-\dfrac{A_1+b_3A_2}{A_2+b_3A_3} & \text{if } b_3\leq\alpha\\ b_3<b_2<-\dfrac{A_0+(b_3+b_4)A_1+b_3b_4A_2}{A_1+(b_3+b_4)A_2+b_3b_4A_3} & \text{if } b_3\geq\alpha\\ -\dfrac{A_0+(b_2+b_3)A_1+b_2b_3A_2}{A_1+(b_2+b_3)A_2+b_2b_3A_3}<b_1 & \\ <-\dfrac{A_0+(b_2+b_4)A_1+b_2b_4A_2}{A_1+(b_2+b_4)A_2+b_2b_4A_3} & \\ & \text{if } b_3\leq\alpha, \text{ and } b_2<-\dfrac{A_1+b_4A_2}{A_2+b_4A_3}\\ -\dfrac{A_0+(b_2+b_3)A_1+b_2b_3A_2}{A_1+(b_2+b_3)A_2+b_2b_3A_3}<b_1 & \\ & \text{if } b_3\leq\alpha, \text{ and } b_2\geq-\dfrac{A_1+b_4A_2}{A_2+b_4A_3}\\ -\dfrac{A_0+(b_3+b_4)A_1+b_3b_4A_2}{A_1+(b_3+b_4)A_2+b_3b_4A_3}<b_1 & \\ <-\dfrac{A_0+(b_2+b_4)A_1+b_2b_4A_2}{A_1+(b_2+b_4)A_2+b_2b_4A_3} & \\ & \text{if } b_3\geq\alpha, \text{ and } b_2<-\dfrac{A_1+b_4A_2}{A_2+b_4A_3}\\ -\dfrac{A_0+(b_3+b_4)A_1+b_3b_4A_2}{A_1+(b_3+b_4)A_2+b_3b_4A_3}<b_1 & \\ & \text{if } b_3\geq\alpha, \text{ and } b_2\geq-\dfrac{A_1+b_4A_2}{A_2+b_4A_3}\end{array}\right\} \quad (33)$$

where α is the smaller root of the quadratic

$$(A_1^2-A_0A_2)+(A_1A_2-A_0A_3)x+(A_2^2-A_1A_3)x^2=0. \quad (34)$$

If $p=5$, the necessary and sufficient condition for (28) and (29) to have solutions is that the inequalities

$$\left.\begin{array}{ll}(-1)^iA_i>0, & i=0, 1, 2, 3, 4\\ A_i^2-A_{i-1}A_{i+1}<0, & i=1, 2, 3\\ \alpha_2<\alpha_1 & \end{array}\right\} \quad (35)$$

be satisfied where α_i are the smaller roots of the quad-

ratics

$$(A_i^2-A_{i-1}A_{i+1})+(A_iA_{i+1}-A_{i-1}A_{i+2})x+(A_{i+1}^2-A_iA_{i+2})x^2=0, \quad i=1, 2. \quad (36)$$

If (35) is not fulfilled, then (28) and (29) have no solution and it is impossible for a sum of five first-order witches with positive parameters to pass through the five points (s_i, f_i). If (35) is fulfilled, then solutions of (28) and (29) are given by:

$$\left.\begin{aligned} &0<b_5<b_4<b_3<\alpha_2 \\ &\alpha(b_5)<b_2<\alpha(b_4), \quad \alpha(b_5)<b_2<-(A_2+b_5A_3)/(A_3+b_5A_4) \\ &\frac{A_0+(b_2+b_3+b_5)A_1+(b_2b_3+b_2b_5+b_3b_5)A_2+b_2b_3b_5A_3}{A_1+(b_2+b_3+b_5)A_2+(b_2b_3+b_2b_5+b_3b_5)A_3+b_2b_3b_5A_4}<b_1< \\ &\qquad\qquad \frac{A_0+(b_2+b_4+b_5)A_1+(b_2b_4+b_2b_5+b_4b_5)A_2+b_2b_4b_5A_3}{A_1+(b_2+b_4+b_5)A_2+(b_2b_4+b_2b_5+b_4b_5)A_3+b_2b_4b_5A_4} \end{aligned}\right\} \quad (37)$$

where $\alpha(b_5)$ is the smaller root of the quadratic

$$[(A_1^2-A_0A_2)+(A_1A_2-A_0A_3)b_5+(A_2^2-A_1A_3)b_5^2]+[(A_1A_2-A_0A_3)+(A_2^2-A_0A_4)b_5+(A_2A_3-A_1A_4)b_5^2]x+[(A_2^2-A_1A_3)+(A_2A_3-A_1A_4)b_5+(A_3^2-A_2A_4)b_5^2]x^2=0. \quad (38)$$

The method just described for fitting $f(s)$ by a sum of witches of order n will in general not yield solutions for every n since the system of inequalities (28) and (29) may have no solution. This is another indication of the restrictions imposed by positiveness since a solution has been found not to exist in cases where ten arbitrary parameters are available for fitting five points. We have found in practice, however, that if n is chosen sufficiently large then a solution can be found. For convenience n is chosen to be the smallest value for which a solution exists. In this way an approximation to $f(s)$ is obtained which is very good except possibly for the larger values of s and which may be improved as indicated below. If it is desired to improve the approximation use may be made of a set of formulas which permits a witch of any order to be replaced either by a witch of any other order or by a sum of witches of any higher order. These are obtained by writing the Maclaurin expansion for the given witch and also the Maclaurin expansion for the linear combination of higher order witches chosen to approximate the given witch. The first few terms in the expansions are then equated in order to evaluate the coefficients. Typical examples of these formulas are:

$$\left.\begin{aligned} &\frac{1}{1+bs^2}\sim\frac{1}{(1+\frac{1}{2}bs^2)^2}\sim\frac{1}{(1+\frac{1}{3}bs^2)^3}\sim\cdots \\ &\frac{1}{(1+bs^2)^2}\sim\frac{\frac{1}{2}-(1/18)(6)^{\frac{1}{2}}}{[1+(\frac{3}{5}-(1/10)(6)^{\frac{1}{2}})bs^2]^3} \\ &\qquad\qquad +\frac{\frac{1}{2}+(1/18)(6)^{\frac{1}{2}}}{[1+(\frac{3}{5}+(1/10)(6)^{\frac{1}{2}})bs^2]^3} \\ &\frac{1}{1+bs^2}\sim\frac{5/18}{[1+(\frac{1}{2}-(15)^{\frac{1}{2}}/10)bs^2]^2}+\frac{8/18}{[1+\frac{1}{2}bs^2]^2} \\ &\qquad\qquad +\frac{5/18}{[1+(\frac{1}{2}+(15)^{\frac{1}{2}}/10)bs^2]^2} \end{aligned}\right\} \quad (39)$$

It can be readily seen that the leading terms in the Maclaurin expansions of the left and right sides of these expressions are the same. In these formulas and in several others which have been derived the parameters are positive. In order to make efficient use of this adjustment procedure, it is necessary to have a large number of relations such as (39) with an evaluation of the deviation between the left and right sides as a function of s. The particular formula (39) which is chosen is then determined by matching the deviation of the first approximation to $f(s)$ with the deviations of relations (39).

By decomposing a given witch into a sufficiently large number of higher order witches, the given witch may be approximated as accurately as desired over any range. This type of approximation is very accurate for small values of s, but becomes poorer and poorer as s increases, eventually falling off too rapidly or too slowly according as we replace the given witch by higher order ones or by one of lower order. Due to this property, the method is well suited to adjusting the initial approximation which is poor only for large

TABLE II. Wollan's data for neon, $f_N(s)$ (obtained by interpolation from his results), and the fitted functions, $f_1(s)$ and $f_2(s)$.

s	$f_N(s)$	$f_1(s)$	$f_2(s)$
0	10.00	10.00	10.00
1	9.58	9.49	9.54
2	8.41	8.26	8.37
3	6.86	6.81	6.93
4	5.50	5.50	5.57
5	4.51	4.43	4.47
6	3.69	3.62	3.64
7	3.08	3.03	3.04
8	2.59	2.60	2.61
9	2.30	2.28	2.31
10	2.10	2.05	2.09
11	1.90	1.87	1.94
12	1.79	1.74	1.82

values of s if at all. Due to the large number of decompositions of a given witch this method is very flexible and with practice should permit adjustments leading to any desired degree of accuracy.

ERRORS

The examination of 22 different $f(s)$ curves, each with characteristic errors of varying magnitudes as compared to a reference $f(s)$ curve, and their corresponding positive $D(r)$ curves, has permitted an evaluation of the uncertainty in $D(r)$ to be expected from the uncertainties in an experimental $f(s)$. Two different types of functions were used to represent $f(s)$:

$$\sum_i a_i/(1+b_i s^2)^{n_i} \tag{40}$$

and

$$\sum_i a_i \exp(-k_i^2 s^2). \tag{41}$$

In both cases the corresponding $D(r)$ are positive if the parameters in (40) and (41) are positive. It was found that the nature and magnitude of the error in $D(r)$ depended essentially upon the nature and magnitude of the error in $f(s)$ over the interval for which experimental data are obtained, $0<s<s_0$ where s_0 ranges from about 30 to 40. The restriction imposed by the requirement that $D(r)$ be positive is indicated by the fact that the error in $D(r)$ was not sensitive to the form of the functions used. This is further born out by the fact that if an experimental $f(s)$ is extrapolated without the requirement that the associated $D(r)$ be positive, then no general conclusions concerning the character of the error in $D(r)$ may be drawn from an examination of $f(s)$ in the experimental range.

On the basis of our empirical evidence, the following estimates of the error in $D(r)$ as a function of the error in $f(s)$ were obtained:

I. If

$$\left.\begin{array}{lll} |\delta f|<\eta & \text{when} & 0<s<10 \\ \text{and} & & \\ |\delta f|<\epsilon & \text{when} & 10<s<30 \\ \text{then} & & \\ |\delta D|<2\epsilon+2\eta & \text{when} & 0.15<r<1.0 \\ |\delta D|<5\epsilon+2\eta & \text{when} & 0.10<r<1.0 \\ |\delta D|<10\epsilon+2\eta & \text{when} & 0.08<r<1.0 \end{array}\right\}. \tag{42}$$

II. If

$$\left.\begin{array}{lll} |\delta F|<\eta & \text{when} & 0<s<10 \\ \text{and} & & \\ |\delta F|<\epsilon & \text{when} & 10<s<40 \\ \text{then} & & \\ |\delta D|<\epsilon+2\eta & \text{when} & 0.08<r<1.0 \\ |\delta D|<2\epsilon+2\eta & \text{when} & 0.07<r<1.0 \\ |\delta D|<5\epsilon+2\eta & \text{when} & 0.05<r<1.0 \end{array}\right\}. \tag{43}$$

The quantity δF is the relative error in $F(s)$, δD is the relative error in $D(r)$, and $0<\eta<0.03$, $0.01<\epsilon<0.10$. It is assumed that as s approaches zero η approaches zero at least as rapidly as s^2. In this connection it should be noted that the value and first derivative of $f(s)$ are known at $s=0$. In order that the error in $D(r)$ for $r\leq 0.08$ be of the same order of magnitude as the experimental error, it is seen from (42) and (43) that data are required to $s=40$ and beyond.

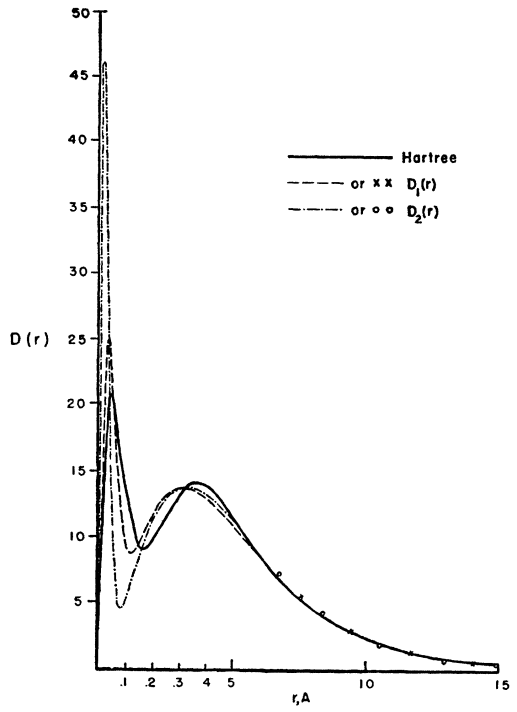

FIG. 1. The two distributions, $D_1(r)$ and $D_2(r)$, corresponding to the functions, $f_1(s)$ and $f_2(s)$, respectively, and the Hartree distribution for neon.

RESULTS

Neon

The application of this method to neon concerns the computation of the electron distribution from the ex-

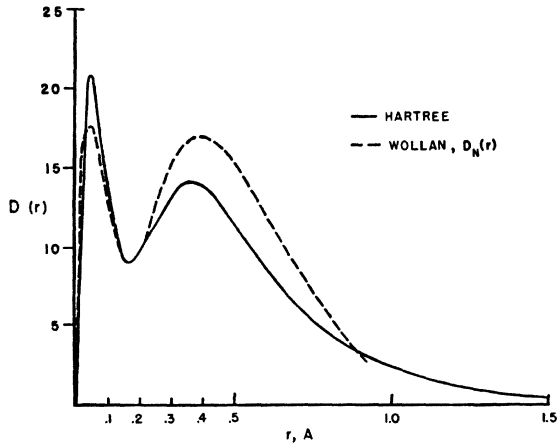

FIG. 2. Wollan's computation of the distribution, $D_N(r)$, corresponding to his data, $f_N(s)$, extrapolated to infinity using the function, $a\exp(-ks)$, and the Hartree distribution for neon.

perimental data of Wollan, although little accuracy can be expected for the inner region from experimental data which extends only to $s=12$. These results were compared with the Hartree distribution for neon.[6,17] The $f(s)$ data obtained by Wollan are given in the second column of Table II. The following functions were fitted to this data:

$$f_1(s)=\sum_{i=1}^{6}\frac{a_i}{(1+k_is^2)^2} \tag{44}$$

$a_1=1.4612$	$k_1=0.000\,28$
$a_2=0.1581$	$k_2=0.011\,00$
$a_3=6.0933$	$k_3=0.022\,60$
$a_4=0.4031$	$k_4=0.039\,899$
$a_5=1.5887$	$k_5=0.058\,40$
$a_6=0.2956$	$k_6=0.065\,00$

$$f_2(s)=\sum_{i=1}^{5}\frac{a_i}{(1+k_is^2)^2} \tag{45}$$

$a_1=1.509\,839$	$k_1=0.000\,077\,778$
$a_2=0.145\,649$	$k_2=0.013\,211$
$a_3=7.886\,528$	$k_3=0.027\,400$
$a_4=0.425\,280$	$k_4=0.042\,178$
$a_5=0.032\,704$	$k_5=0.111\,111.$

The functions $f_1(s)$ and $f_2(s)$ are tabulated in Table II. The two $D(r)$ corresponding to $f_1(s)$ and $f_2(s)$ are plotted in Fig. 1 along with the Hartree distribution. The result obtained from Wollan's data when extrapolated with the function $a\exp(-ks)$, where a and k are determined by the slope and magnitude of the data at the point of joining, is shown in Fig. 2.

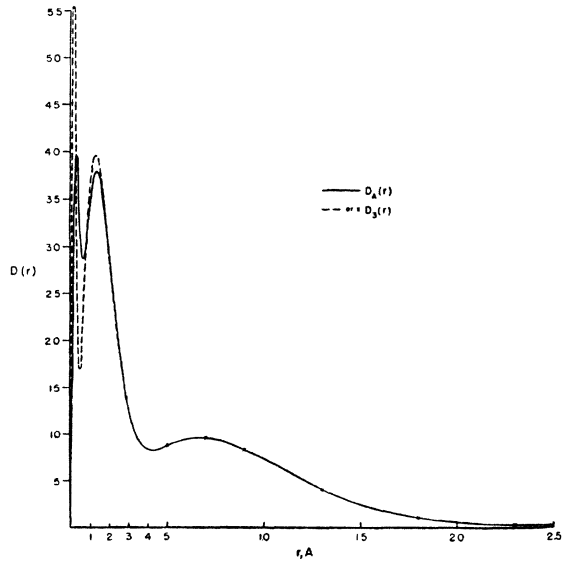

FIG. 3. An analytic distribution, $D_A(r)$, corresponding to the assumed scattering factor for argon, $f_A(s)$, and the distribution, $D_3(r)$, corresponding to the fitted function, $f_3(s)$.

[17] D. R. Hartree, Reports Prog. Phys. **11**, 113 (1946–47).

On the basis of the discussion of errors, it can be expected that very large errors may occur below $r=0.15$, since the experimental data are limited to $s<12$. This is in fact the case as may be seen in Fig. 1. The positive distributions, $D_1(r)$ and $D_2(r)$, however show a uniformly increasing accuracy with increasing r in agreement with the expected behavior of the error. A similar remark concerning $D_N(r)$ in Fig. 2, obtained using the $a\exp(-ks)$ extrapolation, cannot be made. In addition, a computation of the area under $D_N(r)$ shows an excess above the atomic number, 10, and therefore $D_N(r)$ must become negative for larger r in order that the total area be equal to the atomic number.

Argon

In order to study the application of the method to a more complicated atomic structure, a theoretical model for argon closely approximating the Hartree distribution was defined by means of an analytic function,[18]

$$\begin{aligned}D_A(r)=a_1r^2\exp[-r/(k_1)^{1/2}]/2k_1^{3/2}\\+a_2\left[\frac{7r^2}{256k_2^{3/2}}+\frac{7r^3}{256k_2^{4/2}}+\frac{3r^4}{256k_2^{5/2}}\right.\\\left.+\frac{r^5}{384k_2^{6/2}}+\frac{r^6}{3840k_2^{7/2}}\right]\exp[-r/(k_2)^{1/2}]\\+a_3\left[\frac{5r^2}{128k_3^{3/2}}+\frac{5r^3}{128k_3^{4/2}}+\frac{r^4}{64k_3^{5/2}}\right.\\\left.+\frac{r^5}{384k_3^{6/2}}\right]\exp[-r/(k_3)^{1/2}]\end{aligned} \tag{46}$$

$a_1=1.59$	$k_1=0.000\,144$
$a_2=6.95$	$k_2=0.000\,971$
$a_3=9.46$	$k_3=0.030\,999.$

By means of (2) the $f(s)$ corresponding to (46) has been computed. Values of this function $f_A(s)$ are given in the second column of Table III. This function was fitted

TABLE III. A theoretical scattering factor for argon [derived from (46)], and the fitted function $f_3(s)$.

s	$f_A(s)$	$f_3(s)$
0	18.000	18.000
2	13.651	13.652
4	9.181	9.183
8	6.441	6.442
12	4.696	4.698
16	3.313	3.313
20	2.391	2.390
24	1.839	1.842
30	1.406	1.437

[18] Experimental results for the scattering factor for argon have been neither sufficiently accurate nor sufficiently extensive to afford very much instructive information.

with six witches of the fifth order, giving,

$$f_3(s)=\sum_{i=1}^{6}\frac{a_i}{(1+k_i s^2)^5} \tag{47}$$

$a_1=0.006$	$k_1=0.041\,667$
$a_2=9.436$	$k_2=0.031\,033$
$a_3=0.023$	$k_3=0.009\,167$
$a_4=7.217$	$k_4=0.001\,131$
$a_5=0.003$	$k_5=0.000\,833$
$a_6=1.315$	$k_6=0.000\,016\,667.$

The function $f_3(s)$ is tabulated in Table III. The agreement between the two functions is seen to be excellent for the smaller values of s. As s increases, the discrepancy increases to two percent at $s=30$. In Fig. 3 are shown the theoretical $D_A(r)$ and the distribution $D_3(r)$, obtained from the fitted function. It is seen that the two distributions agree very closely except at small values of r in accordance with the expected nature of the error.

In Fig. 4 is shown the result of computing an electron distribution from $f_A(s)$ in the range, $0\leq s\leq 24$, and extrapolating the curve to infinity by means of the function, $a\exp(-ks)$. Again the parameters a and k were chosen so that $a\exp(-ks)$ would agree in magnitude and slope with $f_A(s)$ at $s=24$. It is seen that the two inner maxima are not resolved, the error is relatively large, even for large r and a measurement of the area shows that the curve will eventually become negative.

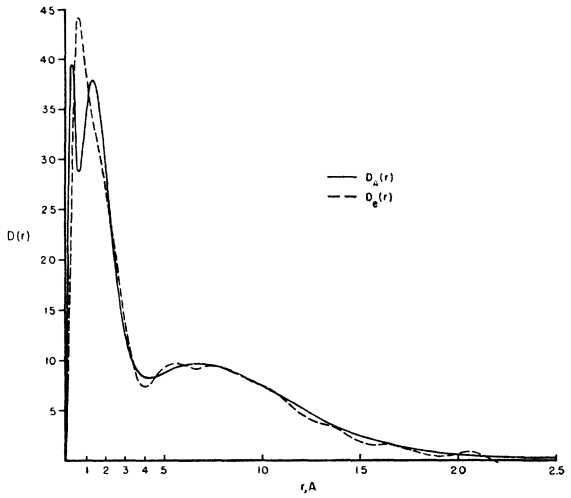

FIG. 4. An analytic distribution, $D_A(r)$, corresponding to the assumed scattering factor for argon, $f_A(s)$, and the distribution, $D_e(n)$, obtained from $f_A(s)$ extrapolated from $s=24$ to infinity by means of the function $a\exp(-ks)$.

CONCLUDING REMARKS

The method presented can be used with x-ray scattering from atoms. It should also prove fruitful with electron scattering but may require further theoretical investigation to improve the atomic scattering formulas. The application of atomic structure studies by the diffraction method to atoms in molecules is also an interesting possibility. It may determine the changes that occur in the electron distributions about atoms when they bind together to form a molecule.

The idea that there are special relationships between the scattering function and the structure of a scatterer which may be represented by a function of one sign is a concept whose usefulness extends beyond the particular application in this paper. Investigations have been in progress applying this idea to scattering experiments involving the determination of particle size and the structure of crystals.[12] In all cases the diffraction experiments yield a limited amount of data. The adjustment and extrapolation of these data consistent with the restrictions imposed by the positiveness of the function describing the structure increases the accuracy and detail of the conclusions that may be drawn.

We wish to thank the Computing Laboratory of the National Bureau of Standards for performing the numerical computations. We also wish to thank Mr. Walter Lynch for drawing the figures.