

## X-Ray Scattering by Aggregates of Bonded Atoms.

### I. Analytical Approximations in Single-Atom Scattering

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An approach is made to the problem of calculating atomic scattering factors for *real* atoms in which both inherent departures from sphericity and the effects of bonding are taken into account. An 'effective' scattering factor for a bonded atom may be defined; the main contribution to this factor is the atomic scattering factor usually employed.

In this paper analytical approximations to atomic wave functions are used in order to obtain closed expressions for the scattering factors of atoms hydrogen to neon. For those atoms which are non-spherical the scattering is dependent on atomic orientation; but it is easily described in terms of two 'principal scattering factors'. There are significant differences between the results of these calculations and those given many years ago by James & Brindley.

#### 1. Introduction

In the customary treatment of the scattering of X-rays by a crystal lattice it is assumed that each atom behaves independently of its neighbours and that the electron distribution in the vicinity of each nucleus is spherically symmetrical. With these assumptions, atomic scattering factors ( $f_0$ )\* have been calculated from Hartree electron distribution curves for a number of atoms by James & Brindley (1931) (henceforth JB). Further assumptions, of an essentially provisional nature, enabled those authors to estimate  $f$  in the case of atoms whose electron distributions were not known with any accuracy. These scattering factors have provided a surprisingly satisfactory basis for the crystal-structure analysis of the past two decades, but recent improvements in technique provide ample evidence of possible inadequacies (see, for example, James & Johnson, 1939; and Franklin, 1950). A more realistic treatment therefore seems desirable and has been made the object of these papers. We shall find it helpful to list at this point the four main assumptions made by JB in their original paper (1931) to which reference may be made for details:

(i) Non-spherical atoms may be dealt with as though spherical, using an electron density which is effectively 'smeared out' by averaging over all orientations in space.

(ii) The contributions to  $f$  arising from electrons in an atom whose electron-density function is not known may be estimated by an interpolation process from the calculated contributions of similar electrons in other atoms.

(iii) The contribution of an electron is not dependent on the state of ionization of the atom. (This assumption plays a vital part in the interpolation process.)

(iv) There is no significant difference between the scattering from an isolated atom and from the same atom engaged in chemical (covalent) or 'metallic' bonding.

A more satisfactory approach, starting from suitable approximate wave functions for the whole electronic system of the molecule or crystal, would not invoke the interpolation assumptions (ii) (iii), and would admit an estimation of the previously ignored effects of inherent non-sphericity (i) and of interatomic interaction (iv).† For three reasons the treatment we shall give falls into two parts, the effects of bonding being dealt with after a preliminary treatment of isolated atoms. In the first place, as will be shown in a subsequent paper, it is possible to define an *effective* atomic scattering factor ( $f^e$ ) for an atom engaged in bond formation, and the main contribution to  $f^e$  is simply  $f$ , the factor for the isolated atom. Secondly, it is desirable to standardize the techniques of dealing with approximate analytical wave functions and to use them in assessing the effect of non-sphericity *within* the atom before considering further refinements. Finally, there are grounds for believing that the effect of bonding is comparatively small.

In this paper, therefore, we consider scattering by single atoms, using analytical wave functions. The calculations are given in detail for atoms up to neon but the methods are generally applicable.

\* The suffix will subsequently be omitted, since we shall deal only with atoms at rest.

† A referee has drawn my attention to a paper by Ewald & Hönl (1936). These authors make elaborate calculations of this kind for the diamond lattice, but their methods are not easily generalized.

## 2. Assumptions and approximations

Our first assumption is that the scattering is completely determined by the integral

$$f = \int \rho(\mathbf{r}) \exp\{i\kappa \mathbf{S} \cdot \mathbf{r}\} d\mathbf{r}, \quad (1)$$

where  $\rho(\mathbf{r}) d\mathbf{r}$  is the probability of finding an electron in the volume element  $d\mathbf{r}$  at  $\mathbf{r}$ ,  $\kappa = 2\pi/\lambda$ , where  $\lambda$  is the wave-length of the incident radiation, and  $\mathbf{S} = \mathbf{s} - \mathbf{s}_0$ , where  $\mathbf{s}$ ,  $\mathbf{s}_0$  are unit vectors along the reflected and incident beams (in crystal analysis  $\mathbf{S}$  is therefore normal to the plane of reflexion).

The electron density  $\rho(\mathbf{r})$  is determined by the wave function of the electrons in the atom. In practice the best many-electron wave function available (for a single electronic configuration) is the determinant

$$\Psi = \begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots \\ \phi_1(2) & \phi_2(2) & \dots \\ \dots & \dots & \dots \end{vmatrix}, \quad (2)$$

where  $\phi_1, \phi_2, \dots$  are one-electron wave functions or orbitals. The density  $\rho(\mathbf{r})$  is expressible, in this approximation, as a sum of the one-electron densities associated with electrons occupying the separate orbitals, provided the latter are orthogonal. Thus

$$\rho(\mathbf{r}) = |\phi_1(\mathbf{r})|^2 + |\phi_2(\mathbf{r})|^2 + \dots$$

In what follows we shall assume a single configuration of this kind because, when an atom is bonded to other atoms, the set of orbitals involved is completely specified.

The most satisfactory one-electron functions would satisfy the Hartree-Fock equations, but, as we wish to deal ultimately with molecules and crystals for which such functions are not available, we must be content with rather cruder functions of similar type. Such functions have been given by Duncanson & Coulson (1944) for the ground states of atoms up to neon. Actually, when atoms are bonded the orbitals associated with the valence shell are somewhat modified but, at this point, consideration of these higher-order effects scarcely seems worth while. In the same way we shall form hybrid valence states by superposition of the unmodified ground-state orbitals.

## 3. Evaluation of the atomic scattering factor

Using the variational wave functions of Duncanson & Coulson, the atomic scattering factor, which is a sum of contributions from the various atomic orbitals, is fairly easily evaluated in any given case. Since, however, the resultant atomic scattering factor is dependent on the orientation of the atom it is necessary to systematize the treatment in some suitable way. First of all the contributions from each type of atomic orbital will be calculated; it will then appear how the synthesis of atomic factors for various electron configurations and orientations may best be brought about.

### Contributions to $f$ from single atomic orbitals

The basic set of atomic orbitals is

$$\left. \begin{aligned} \phi(1s) &= N_{1s} e^{-\mu ar}, & N_{1s} &= (\mu^3 a^3/\pi)^{\frac{1}{2}}, \\ \phi(2s) &= N_{2s} [re^{-\mu r} - Ae^{-\mu br}], & N_{2s} &= (\mu^5/3\pi N)^{\frac{1}{2}}, \\ \phi(2p_x) &= N_{2p} r \cos \theta e^{-\mu cr}, & N_{2p} &= (\mu^5 c^5/\pi)^{\frac{1}{2}}. \end{aligned} \right\} \quad (3)$$

where  $A$  and  $N$  are chosen so as to ensure ortho-normality.\*

### 1s orbitals

The contribution  $f(1s)$  to the scattering factor  $f$  is simply

$$f(1s) = (N_{1s})^2 \int e^{-2\mu ar} \exp\{i\kappa' r \cos \theta\} r^2 \sin \theta d\theta d\phi dr,$$

where, with spherical symmetry, it is convenient to take the reflexion normal  $\mathbf{S}$  as the polar axis and  $\kappa' = \kappa |\mathbf{S}| = 2\kappa \sin \theta$ ,  $\theta$  being the angle of scattering.† Performing the angle integrations,

$$f(1s) = (N_{1s})^2 (4\pi/\kappa') \int_0^\infty r e^{-2\mu cr} \sin \kappa' r dr.$$

All the  $f$ 's can be expressed in terms of the integrals

$$S'_n(c, p) = \int_0^\infty r^n e^{-cr} \sin pr dr,$$

$$C'_n(c, p) = \int_0^\infty r^n e^{-cr} \cos pr dr,$$

which are effectively functions of a single variable since, with  $(p/c) = x$ ,

$$S'_n(c, p) = S_n(x)/c^{n+1}, \quad C'_n(c, p) = C_n(x)/c^{n+1},$$

where

$$S_n(x) = \int_0^\infty t^n e^{-t} \sin xt dt, \quad C_n(x) = \int_0^\infty t^n e^{-t} \cos xt dt. \quad (4)$$

The variable of interest is ultimately  $(\sin \theta/\lambda) = X$  say, and, since  $\kappa' = 4\pi X$ , we write

$$f(1s) = (N_{1s})^2 \left( \frac{\pi}{2\mu^3 a^3} \right) \frac{S_1(x)}{x}, \quad x = \frac{2\pi}{\mu a} X. \quad (5)$$

### 2s orbitals

A similar reduction gives finally

$$f(2s) = 4\pi (N_{2s})^2 \times \left[ \frac{1}{(2\mu)^5} \frac{S_3(x_3)}{x_3} - \frac{2A}{\mu^4(1+b)^4} \frac{S_2(x_2)}{x_2} + \frac{A^2}{(2\mu b)^3} \frac{S_1(x_1)}{x_1} \right], \quad (6)$$

$$\text{where } x_1 = \frac{2\pi}{\mu b} X, \quad x_2 = \frac{4\pi}{\mu(1+b)} X, \quad x_3 = \frac{2\pi}{\mu} X.$$

\* For orthogonality of  $\phi(1s)$  and  $\phi(2s)$ ,

$$A = 3(a+b)^3/\mu(1+a)^4.$$

For normality of  $\phi(2s)$ ,

$$N = [1 - 16A\mu/(1+b)^4 + A^2\mu^2/3b^3].$$

$a, b, c, \mu$  are given by Duncanson & Coulson (1944).

† In what follows there is little opportunity for confusing  $\theta$  with the polar angle.

*2p orbitals*

The  $2p$  and hybrid valence orbitals are no longer spherically symmetrical, and consequently the vector  $\mathbf{S}$  cannot be taken as a convenient polar axis. Consider the scattering from the  $2p_z$  orbital when the vector  $\mathbf{S}$  makes an angle  $\Theta$  with the  $z$  (polar) axis; let the unit vector along this axis be  $\mathbf{k}$  (frame  $\mathbf{i} \mathbf{j} \mathbf{k}$ ) and take a new frame ( $\mathbf{i}' \mathbf{j}' \mathbf{k}'$ ) with  $\mathbf{k}'$  along  $\mathbf{S}$ . Then

$$f(2p) = (N_{2p})^2 \int e^{-2\mu cr} (\mathbf{r} \cdot \mathbf{k})^2 \exp\{i\kappa \mathbf{S} \cdot \mathbf{r}\} d\mathbf{r}.$$

In the new frame

$$\mathbf{k} = \mathbf{k}' \cos \Theta + \mathbf{j}' \sin \Theta, \quad \mathbf{S} = |\mathbf{S}| \mathbf{k}',$$

and therefore

$$f(2p) = (N_{2p})^2 \int e^{-2\mu cr} [z' \cos \Theta + y' \sin \Theta]^2 \exp\{i\kappa' z'\} d\mathbf{r}' \\ = f^{\parallel}(2p) \cos^2 \Theta + f^{\perp}(2p) \sin^2 \Theta,^* \quad (7)$$

$$\text{where } f^{\parallel}(2p) = (N_{2p})^2 \int e^{-2\mu cr} r^2 \cos^2 \theta \\ \times \exp\{i\kappa' r \cos \theta\} r^2 \sin \theta d\theta d\phi dr$$

(the scattering factor for an orbital pointing along  $\mathbf{S}$ ) and

$$f^{\perp}(2p) = (N_{2p})^2 \int e^{-2\mu cr} r^2 \sin^2 \theta \sin^2 \phi \\ \times \exp\{i\kappa' r \cos \theta\} r^2 \sin \theta d\theta d\phi dr$$

(the scattering factor for an orbital perpendicular to  $\mathbf{S}$ ).

The scattering from a  $2p$  orbital pointing in any direction is therefore completely described in terms of  $f^{\parallel}(2p)$ ,  $f^{\perp}(2p)$ , and the inclination of the orbital to the scattering normal  $\mathbf{S}$ .

In terms of the functions  $S_n(x)$ ,  $C_n(x)$  we find

$$f^{\parallel}(2p) = \frac{4\pi(N_{2p})^2}{(2\mu c)^5 x} \left[ S_3(x) + \frac{2C_2(x)}{x} - \frac{2S_1(x)}{x^2} \right], \quad (8)$$

$$f^{\perp}(2p) = \frac{4\pi(N_{2p})^2}{(2\mu c)^5 x^2} \left[ \frac{S_1(x)}{x} - C_2(x) \right], \quad (9)$$

where in each case,  $x = (2\pi/\mu c) X$ .

*(sp) (sp<sup>2</sup>) (sp<sup>3</sup>) valence orbitals*

The only hybrid orbitals we shall consider are those built up from  $2s$  and the various  $2p$  wave functions. As in dealing with the pure  $2p$  orbitals, it is only necessary to consider one member of the set; for simplicity we naturally take the function which points along a co-ordinate axis, say the  $z$  axis. Taking

$$\phi_v = N[\phi(2s) + \lambda\phi(2p)],$$

we have

$$f(\phi_v) = N^2[f(2s) + 2\lambda f(2s2p) + \lambda^2 f(2p)],$$

where the only new term arising is

$$f(2s2p) = \int \phi(2s) \phi(2p) \exp\{i\kappa \mathbf{S} \cdot \mathbf{r}\} d\mathbf{r}.$$

\* The integral arising from the cross-product vanishes.

This term, like  $f(2p)$ , is angle-dependent, and if  $\mathbf{S}$  makes an angle  $\Theta$  with the  $z$  axis a similar reduction shows

$$f(2s2p) = f^{\parallel}(2s2p) \cos \Theta + f^{\perp}(2s2p) \sin \Theta,$$

where  $f^{\perp}(2s2p)$  is identically zero, while

$$f^{\parallel}(2s2p) = \int \phi(2s) \phi(2p_z) \exp\{i\kappa' r \cos \theta\} r^2 \sin \theta d\theta d\phi dr.$$

A straightforward integration gives, with

$$x_1 = \frac{4\pi}{\mu(1+c)} X \quad \text{and} \quad x_2 = \frac{4\pi}{\mu(b+c)} X,$$

$$f^{\parallel}(2s2p) = 4\pi i N_{2s} N_{2p} \left[ \frac{1}{\mu^5(1+c)^5 x_1} \left( \frac{S_2(x_1)}{x_1} - C_3(x_1) \right) \right. \\ \left. - \frac{A}{\mu^4(b+c)^4 x_2} \left( \frac{S_1(x_2)}{x_2} - C_2(x_2) \right) \right] \quad (10)$$

(the factor  $i$  giving a phase shift of  $\frac{1}{2}\pi$  relative to the origin).

A calculation of the scattering from a single hybrid orbital therefore involves only the tabulation of one additional function (10); often, however, as we shall now see, even this can be avoided.

*The atomic scattering factor*

If the functions  $f(1s)$ ,  $f(2s)$ , ... are tabulated for each atom considered, it is immediately possible to add the various contributions and in this way to arrive at an  $f$  depending on the orientation of each occupied  $2p$  orbital with respect to the reflexion normal ( $\mathbf{S}$ ). The calculation is, however, simplified by a suitable decomposition of the electron-density function.

Let us consider first a group of three singly-occupied  $2p$  orbitals, providing a rectangular co-ordinate frame in which the vector  $\mathbf{S}$  has direction cosines ( $l$ ,  $m$ ,  $n$ ). The scattering factor for this system is, by (7),

$$\Sigma f(2p) = (l^2 + m^2 + n^2) f^{\parallel}(2p) + [(1-l^2) + (1-m^2) \\ + (1-n^2)] f^{\perp}(2p),$$

$$\text{i.e.} \quad \Sigma f(2p) = f^{\parallel}(2p) + 2f^{\perp}(2p), \quad (11)$$

which is angle-independent, arising, in fact, from a spherically symmetrical total electron density. Now all the atoms we consider have a unique symmetry axis, namely, that  $2p$  orbital which is distinguished from the rest by the number of electrons it contains; thus in boron only one  $2p$  orbital contains an electron while in oxygen only one  $2p$  orbital contains two electrons. The atomic scattering factor is then expressible in terms of the angle between this axis and  $\mathbf{S}$ , together with two 'principal' factors ( $f^{\parallel}$ ,  $f^{\perp}$ ) referring to scattering in the particular cases  $\Theta = 0$ ,  $\frac{1}{2}\pi$ .

The electron density for fluorine, for example, may be decomposed into two complete shells of three  $2p$  electrons minus one  $2p$  orbital; the total scattering factor is then

$$f = 2f(1s) + 2f(2s) + 2(f^{\parallel}(2p) + 2f^{\perp}(2p)) \\ - 1(f^{\parallel}(2p) \cos^2 \Theta + f^{\perp}(2p) \sin^2 \Theta),$$

and this may be written

$$f = f^{\parallel} \cos^2 \Theta + f^{\perp} \sin^2 \Theta,$$

where  $f^{\parallel} = 2f(1s) + 2f(2s) + f^{\parallel}(2p) + 4f^{\perp}(2p)$

and  $f^{\perp} = 2f(1s) + 2f(2s) + 2f^{\parallel}(2p) + 3f^{\perp}(2p)$

refer to scattering with **S** (respectively) along and perpendicular to the symmetry axis. It is these two principal scattering factors which we shall tabulate.

### Hybrid valence states

In certain valence states involving hybrid orbitals  $f$  is very easily obtained using the result stated in §2; the  $n$ -electron wave function (2) of a configuration based upon  $n$  mutually orthogonal orbitals  $\phi_1, \phi_2, \dots, \phi_n$  gives an electron density which is the sum of the one-electron densities  $|\phi_1|^2, |\phi_2|^2, \dots, |\phi_n|^2$ . Now we may add corresponding elements in any two columns of (2) without altering the value of the determinant. Replacement of  $\phi_1, \phi_2, \dots, \phi_n$  by any linear combination of these orbitals,  $\phi'_1, \phi'_2, \dots, \phi'_n$  therefore gives the same wave function and, if the new functions are also mutually orthogonal,

$$\rho(\mathbf{r}) = \Sigma |\phi(\mathbf{r})|^2 = \Sigma |\phi'(\mathbf{r})|^2.$$

The two sets of one-electron densities,  $|\phi_1|^2, \dots, |\phi_n|^2$  and  $|\phi'_1|^2, \dots, |\phi'_n|^2$  thus yield exactly the same total electron density. This has a general application to certain hybrid states; an example will make this clear. In ( $sp$ ) ( $sp^2$ ) ( $sp^3$ ) hybridization each possible set of valence orbitals is simply a new set of orthogonal combinations of the four available orbitals ( $2s$ ) ( $2p_x$ ) ( $2p_y$ ) ( $2p_z$ ); from above it follows that, provided the whole group of valence orbitals is involved in the electron configuration, the total electron density is independent of the state of hybridization. This is the case in the carbon atom where four electrons are available and in each of the digonal, trigonal and tetrahedral valence states there are four valence orbitals (2, 3 and 4 respectively being hybrids). The total electron density

is thus in each case the sum of the one-electron densities associated with the four basic orbitals involved, i.e.

$$\rho = |\phi(2s)|^2 + |\phi(2p_x)|^2 + |\phi(2p_y)|^2 + |\phi(2p_z)|^2.$$

It follows immediately that the contribution of the valence electron to the atomic scattering factor is

$$f(2s) + f(2p_x) + f(2p_y) + f(2p_z),$$

and that the scattering should be independent of whether the carbon atom is in acetylene, graphite or diamond (the three typical valence states). Moreover, from (11), the electron distribution in the immediate vicinity of such an atom is spherically symmetrical, a result which is not intuitively obvious.

The great importance of states of this kind in carbon chemistry warrants a calculation of the associated scattering factor, but we omit variations, occurring both in carbon and other atoms, in which the valence orbitals are unequally filled. If, for example, one orbital is doubly filled, as with the lone-pair electrons in carbon monoxide (i.e. one orbital occurs twice in the determinantal wave function, combined with different spins) the above result would not apply directly and we should need to add the contribution of an extra hybrid orbital to the complete shell of singly-filled valence orbitals. Cases of this kind must be dealt with individually, using the results already given. It is worth while noting that in such cases there is always a phase shift in the scattered beam relative to that from the centre of the atom.

### 4. General discussion

Table 1 gives the principal atomic scattering factors  $f^{\parallel}$  and  $f^{\perp}$  (or the single factor  $f$  for spherical atoms) for the ground states\* of the neutral atoms hydrogen to neon. For an X-ray reflexion from lattice planes whose normal makes an angle  $\Theta$  with the symmetry axis of an

\* In some cases it would be more correct to speak of the 'prepared state' since, in anticipation of chemical bonding, a single electronic configuration has been specified (cf. § 2).

Table 1. Atomic scattering factors: hydrogen to neon

	X	0	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.25	0.3	0.4	0.5	0.6	0.7	0.8
H	$f$	1.0	0.952	0.829	0.664	0.514	0.383	0.281	0.205	0.150	0.087	0.048	0.019	0.009	0.004	0.002	0.001
He	$f$	2.0	1.964	1.869	1.722	1.544	1.353	1.164	0.987	0.829	0.576	0.397	0.194	0.101	0.056	0.033	0.021
Li	$f$	3.0	2.709	2.263	1.950	1.786	1.675	1.572	1.462	1.348	1.119	0.908	0.576	0.362	0.230	0.150	0.100
Be	$f$	4.0	3.742	3.150	2.553	2.129	1.878	1.736	1.644	1.569	1.424	1.266	0.955	0.695	0.494	0.352	0.253
B	$f^{\parallel}$	5.0	4.710	3.982	3.130	2.423	1.941	1.675	1.539	1.480	1.435	1.383	1.195	0.966	0.759	0.586	0.449
	$f^{\perp}$	5.0	4.802	4.297	3.647	3.042	2.559	2.214	1.981	1.824	1.626	1.486	1.227	0.977	0.764	0.588	0.450
C	$f^{\parallel}$	6.0	5.846	5.417	4.874	4.172	3.565	3.051	2.646	2.340	1.945	1.717	1.435	1.208	0.975	0.814	0.658
	$f^{\perp}$	6.0	5.786	5.213	4.492	3.639	2.941	2.421	2.052	1.813	1.576	1.398	1.342	1.170	0.959	0.807	0.653
C (valence states)	$f$	6.0	5.803	5.271	4.581	3.803	3.137	2.629	2.255	1.999	1.711	1.566	1.368	1.169	0.973	0.795	0.654
N	$f$	7.0	6.822	6.374	5.703	4.890	4.164	3.489	2.892	2.507	2.043	1.697	1.464	1.316	1.156	0.994	0.841
O	$f^{\parallel}$	8.0	7.850	7.396	6.643	5.791	4.915	4.092	3.375	2.790	2.002	1.614	1.365	1.300	1.221	1.110	0.988
	$f^{\perp}$	8.0	7.868	7.526	6.865	6.144	5.383	4.649	3.987	3.422	2.595	2.102	1.647	1.448	1.297	1.150	1.010
F	$f^{\parallel}$	9.0	8.901	8.540	8.024	7.359	6.630	5.885	5.164	4.590	3.454	2.718	1.941	1.615	1.431	1.283	1.146
	$f^{\perp}$	9.0	8.889	8.457	7.834	7.072	6.235	5.396	4.610	3.979	2.826	2.145	1.555	1.388	1.304	1.212	1.105
Ne	$f$	10.0	9.928	9.540	8.991	8.301	7.520	6.699	5.888	5.128	3.839	2.951	1.906	1.549	1.386	1.303	1.207

atom (defined by that  $2p$  orbital which contains a different number of electrons from the other  $2p$  orbitals), it is necessary to use an atomic scattering factor  $f = f^{\parallel} \cos^2 \Theta + f^{\perp} \sin^2 \Theta$ . The actual curves are drawn in Figs. 1–10. For comparison with the JB curves (broken line)  $f^{\parallel}$  and  $f^{\perp}$  are plotted against  $X' = (\sin \theta / \lambda)$  with  $\lambda$  in Ångström units. In Table 1, however,  $f^{\parallel}$  and  $f^{\perp}$  are given in terms of  $X = (\sin \theta / \lambda)$  in atomic units.  $X'$  is readily expressed in terms of  $X$ , using  $X = 0.5282 X'$ .

Perhaps the most striking feature of the curves is the marked effect of non-sphericity on the low- and medium-angle scattering. An accurate estimation of the structure factor for a group of such atoms cannot, therefore, be made unless the orientation of the group in the crystal is at least roughly known; consequently, the effect of non-sphericity cannot be introduced *ab initio* in X-ray analysis but only in the more precise analysis of structures already roughly determined. In the preliminary analysis the most suitable approximate scattering factor for a non-spherical atom is probably

$$\bar{f} = \frac{1}{3}(f^{\parallel} + 2f^{\perp}), \quad (12)$$

in which the  $2p$  electrons are assumed to make a 'mean contribution' defined by (13) of the following paragraph. This factor is not plotted in the figures but lies between the principal factors and in some cases is not very different from the JB curves.

We might now ask how the effect of asphericity of the  $2p$  orbitals ever came to be regarded as small; the answer is provided by an examination of the assumption (iii) (p. 513). If  $f(2p) = f^{\parallel}(2p) \cos^2 \Theta + f^{\perp}(2p) \sin^2 \Theta$  is weighted with an element of solid angle  $d\omega = 2\pi \sin \Theta d\Theta$  and averaged over all orientations  $\Theta$ , the resultant 'mean' scattering factor is

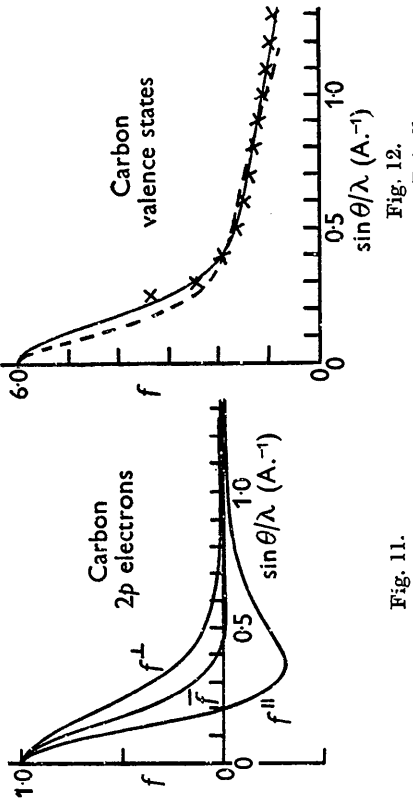
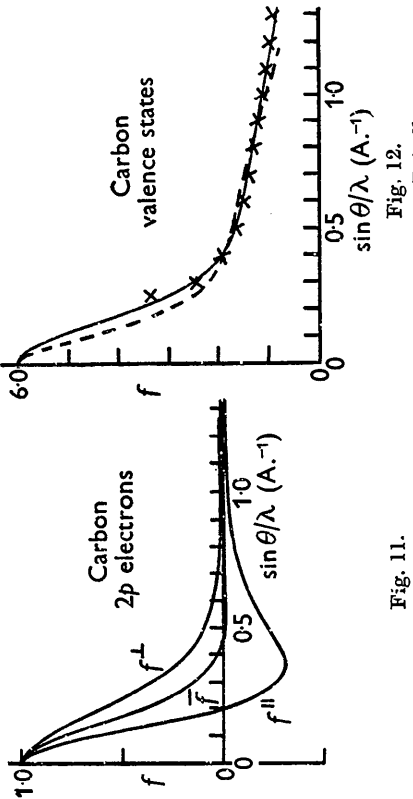
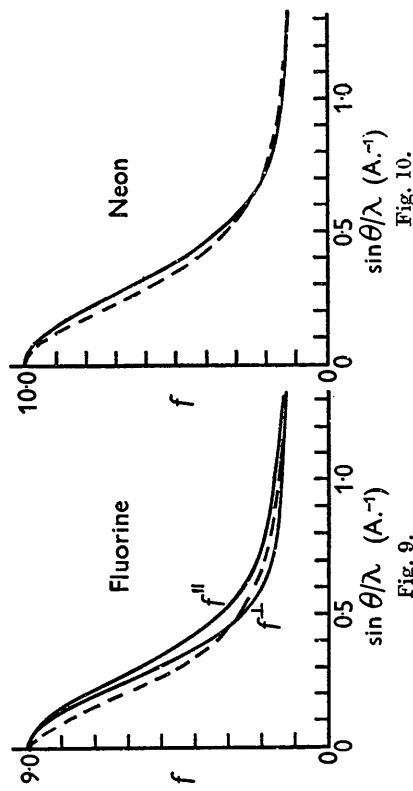
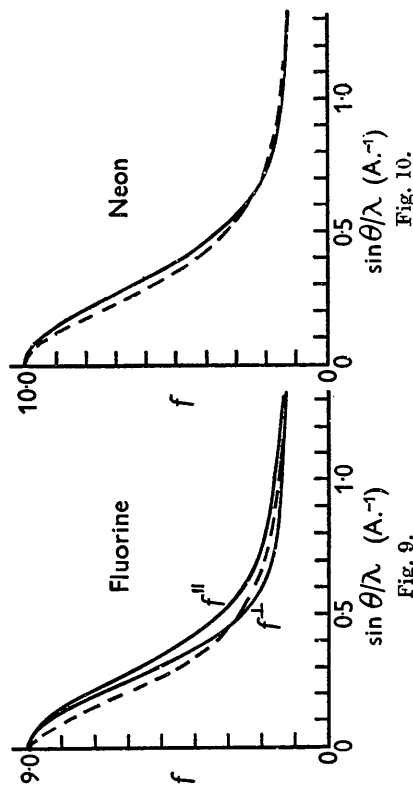
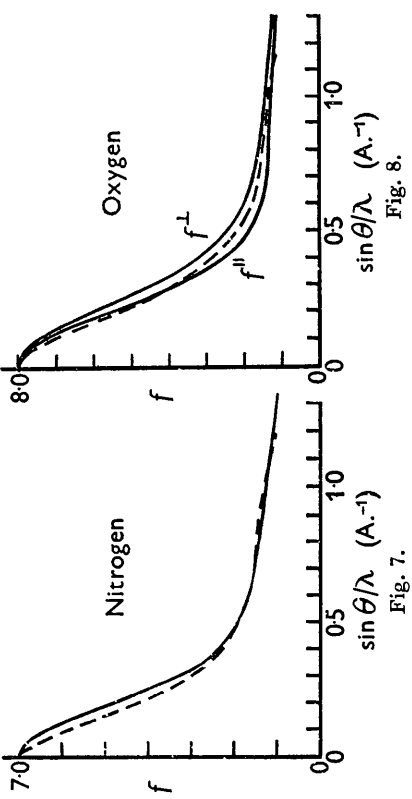
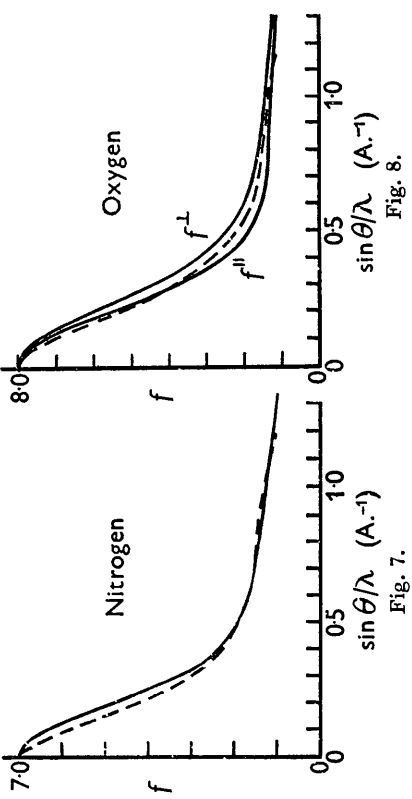
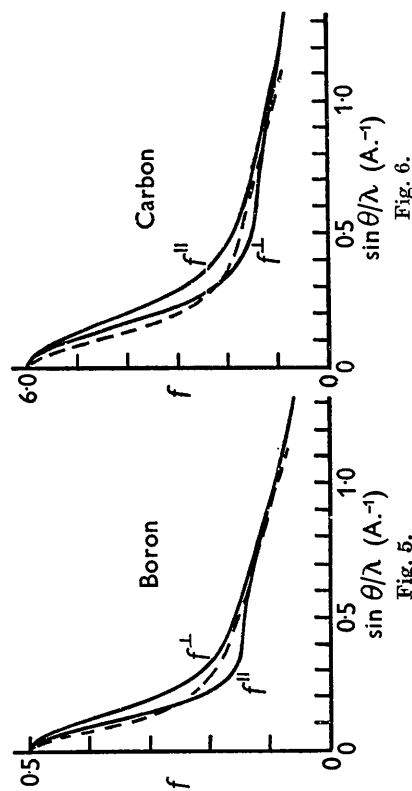
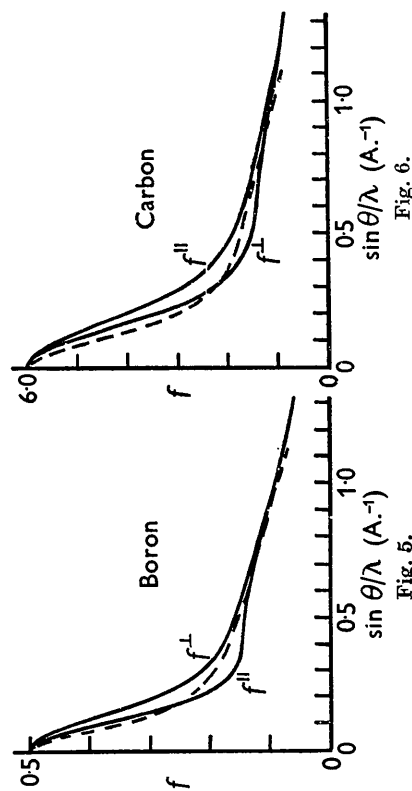
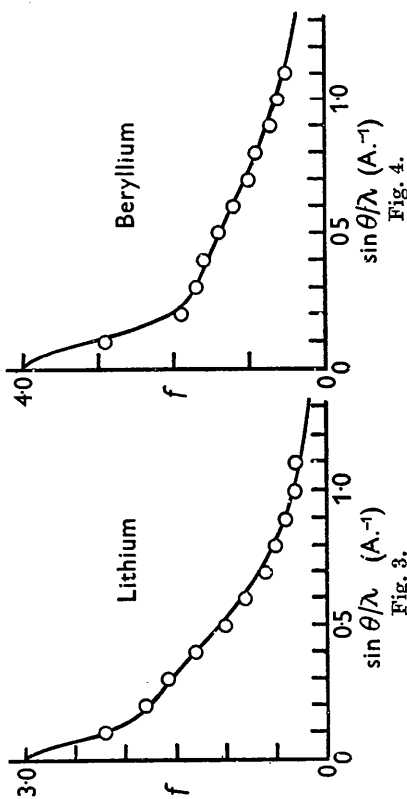
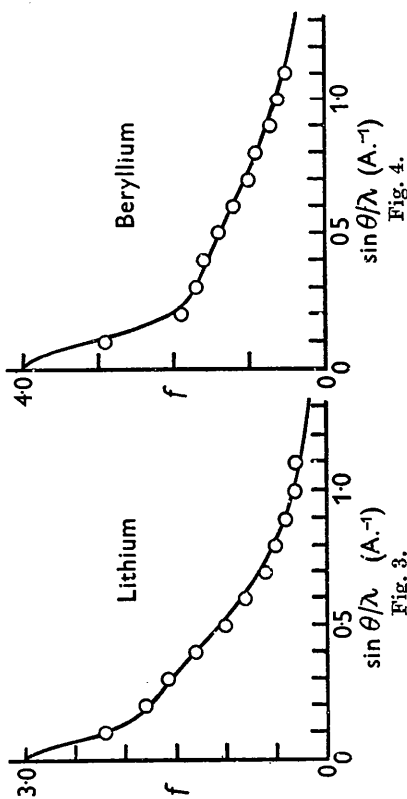
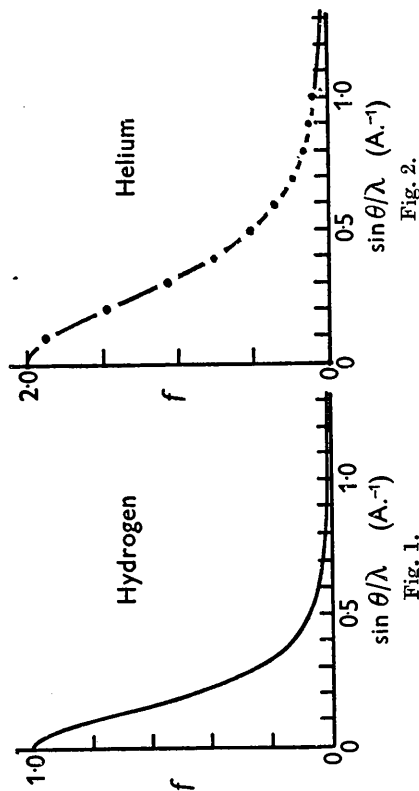
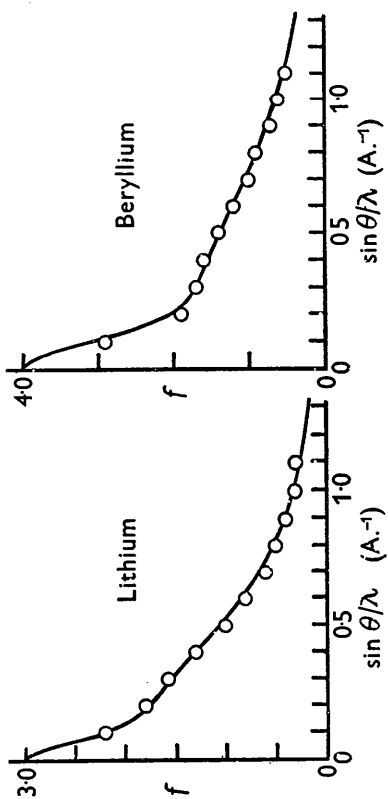
$$\overline{f(2p)} = \frac{1}{3}(f^{\parallel}(2p) + 2f^{\perp}(2p)), \quad (13)$$

and therefore one-sixth of the scattering factor for a closed shell of six  $2p$  electrons. This term corresponds directly, therefore, to the 'contribution per  $2p$  electron' as assessed by James & Brindley. The distinction between the mean contributions,  $\bar{f}(2p)$ , and the extreme contributions  $f^{\parallel}(2p)$  and  $f^{\perp}(2p)$ , is clearly brought out in Fig. 11, where the three curves are plotted for a  $2p$  electron in carbon. While the mean factor  $\bar{f}(2p)$  rapidly becomes insignificant with increasing angle of scattering it is clearly a mistake to conclude that the  $2p$  electrons are ineffective in high-angle scattering; they do, in fact, make a considerable contribution over an important range of angles, the  $f^{\parallel}(2p)$  curve showing very strikingly the effect of interference between the beams scattered from opposite ends of the 'dumb-bell' orbital.

As already stated, the only hybrid valence states considered are the pure digonal, trigonal and tetrahedral states of the carbon atom; there are many instances in which valence states approximating closely to these types exist. The associated scattering

curve is shown in Fig. 12, along with the JB curve. Comparison indicates both a considerable enhancement of the low-angle scattering and a significant divergence in the high-angle region, a result which is of particular interest since experimental evidence has already resulted in the adoption of empirical curves of precisely the form given (Brill, 1950; Franklin, 1950). Indeed, the curve given by Brill (indicated in Fig. 12 by crosses) is almost coincident with our theoretical curve over a wide range. There is, however, still a certain discrepancy in the region of extremely low-angle scattering; if the empirical point is accepted, it is difficult to reconcile with the theory so far developed, for the low-angle peak cannot be so drastically modified by any reasonable modification of the wave function. But it is in precisely this range that we are prepared to find an effective contribution from those regions of the electron density more remote from the nucleus. This, of course, involves the whole question of bonding and lies outside the scope of the present paper.

Finally, some discussion of the accuracy of the curves is desirable. It is difficult to estimate the *absolute* accuracy; but the tables are given to four figures. This would seem necessary for purposes of comparison, since changes of wave function often have a surprisingly small effect on the curves. The only feasible method of making a precise estimate of the accuracy would be to make a comparison with curves computed using wave functions obtained by numerical solution of the Fock equations. This has not yet been attempted, but the basic scheme of calculation need not differ appreciably from that set out in this paper; the Fock functions could be fitted by analytical functions of substantially the same form as those employed here, and the final results would again be expressible in terms of the functions  $S_n(x)$ ,  $C_n(x)$ . However, at least some reassurance can be obtained from the JB curves themselves. Of all the atoms considered in this paper only two, helium and lithium, possess JB curves computed directly from Hartree electron densities (i.e. independently of interpolation techniques and other approximations). Our curves are, perhaps, least reliable for these atoms owing to the predominance of  $1s$  electrons, for which our wave function is of the simple screening-constant type (with one parameter only); any errors due simply to inadequacies of the wave function should then be revealed by comparison with the JB curves which in these two cases could, in principle, be superior. There is scarcely any divergence between the different approximations (Figs. 2 and 3); indeed, it is not easy to detect any real difference, for the points computed by James & Brindley are given only to two- or three-figure accuracy (as indicated in Figs. 2–4). It therefore seems highly improbable that the very marked divergence found in other cases can be attributed to anything but a real failure of the hitherto accepted curves. Although our calculations have been confined to atoms for which rather good analytical wave functions exist, there is no



Figs. 1-10. Principal atomic scattering factors for the 'prepared states' of the neutral atoms hydrogen to neon. Broken lines show the James & Brindley curves. Fig. 11. Mean contribution  $\bar{f}$ , and extreme contributions  $f_{\parallel}$  and  $f_{\perp}$  for a 2p electron in carbon. Fig. 12. Atomic scattering factor for carbon valence state. The broken line is the James & Brindley curve and the crosses are points given by Brill.

reason why similar calculations should not be extended to higher atoms, using Slater-type wave functions. It seems likely that even in these cases the computed functions would be superior to those estimated by interpolation, especially in cases where there is a marked departure from spherical symmetry.

### APPENDIX

The functions

$$S_n(x) = \int_0^\infty t^n e^{-t} \sin xt \, dt, \quad C_n(x) = \int_0^\infty t^n e^{-t} \cos xt \, dt,$$

which appear repeatedly in this and subsequent work, may be tabulated very easily by making use of the following recurrence relations, derived by integration by parts:

$$S_{n+1}(x) = \frac{n+1}{1+x^2} [S_n(x) + xC_n(x)],$$

$$C_{n+1}(x) = \frac{n+1}{1+x^2} [C_n(x) - xS_n(x)].$$

All the functions may be built up from

$$S_0(x) = x/(1+x^2), \quad C_0(x) = 1/(1+x^2),$$

by repeated application of these formulae. This appears to afford the simplest method of systematic tabulation. Moreover, simple and accurate interpolation formulae are easily derived and facilitate the use of such tables.

Individual values of  $S_n(x)$ ,  $C_n(x)$  may be calculated

directly by reduction to a trigonometric form. Thus, with  $x = \tan \alpha$ ,

$$S_n(x) = \Gamma(n+1) \cos^{n+1} \alpha \sin \overline{n+1} \alpha,$$

$$C_n(x) = \Gamma(n+1) \cos^{n+1} \alpha \cos \overline{n+1} \alpha.$$

These formulae are valid when  $n$  is non-integral and would therefore be necessary in using Slater-type wave functions for atoms above neon.

The first few functions of each series (and this is all that is required in the present paper) may, however, be evaluated algebraically by direct recursion from  $S_0(x)$  and  $C_0(x)$ , the expressions reducing to quite simple form.\*

I am greatly indebted to my wife for dealing with the computations involved in this work. My thanks are also due to Prof. C. A. Coulson, F.R.S., for reading the manuscript.

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\* I am indebted to a referee for this remark.