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Aspherical Atomic Scattering Factors for Some Light Atoms in sp^3, sp^2 and sp Hybrid Valence State Approximations

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The atomic scattering powers of N, O, F and P, S, Cl in various sp^3, sp^2 and sp hybrid 'prepared valence state' approximations are examined and compared with the ground-state results for each atom. Numerical values of the 'prepared state' scattering are derived from orbital data given by ground-state calculations of atomic structure. Where possible, Hartree–Fock radial functions are used, but the analytical results of Duncanson & Coulson (1948) and Slater (1930) are also employed.

In hybrid states corresponding to centrosymmetric charge distributions the scattering powers require either two or three 'principal' factors to describe deviations from spherical symmetry and are analogous to aspherical ground-state results. In states where the total distribution is non-centrosymmetric, a further 'principal' factor defines an antisymmetric component of the charge distribution, and the atomic scattering power is then complex.

In many cases, molecular geometry gives sufficient information for straightforward application of 'prepared state' scattering factors in the later stages of detailed structure refinement. The general implications of the results obtained are discussed briefly.

Introduction

The concept of orbital hybridization is long-established, and it provides a useful approach to the directional characteristics which an atom manifests in covalent bond formation. Its value in correlating the geometrical details in a wide variety of molecular stereochemistries has recently been discussed by Coulson (1961), Wells (1962) and Cotton & Wilkinson (1962).

For atoms whose valence shells comprise lone pairs as well as bonding pairs, the general nature of hybrid orbitals implies that the total electron charge distribution about an atomic nucleus may be not only nonspherical but also non-centrosymmetric, and, further, that the 'shape' of the distribution may vary with the state of hybridization assumed. In such cases, allowance for the intrinsic scattering power of these 'shapes' by appropriate atomic scattering factors (f curves) should provide a closer approximation to the bonded-atom scattering effects than that possible when ground state isolated-atom f curves are used in the customary spherically averaged approximation ($\bar{f}$). The desirability of improving on this $\bar{f}$ procedure in refined structure analysis has been urged by McWeeny (1951, 1952, 1953, 1954) as a result of his examinations of X-ray scattering by aggregates of bonded atoms. So far, however, the effect of allowing for valence-state scattering asphericity has not been examined experimentally, so that the influence of the usual $\bar{f}$ treatment on the derivation of atomic position and thermal motion parameters of aspherical atoms is unknown.

A necessary preliminary to such examinations is the derivation of atomic scattering factors which describe approximate 'prepared valence states' that may be invoked, on simple hybrid pictures, to interpret molecular stereochemistry. We report here scattering formulae for the aspherical components associated with various sp^3, sp^2 and sp hybrid states of the atoms in groups V, VI and VII of the second and third rows. Numerical estimates of these components are given, and their relation to ground-state f data is discussed. The present results for P, S and Cl will be subsequently extended to include the formalism associated with possibilities of s–p–d hybridization (Dawson, 1964*b*).

Hybrid valence state scattering approximations

Basic relations

We are concerned with the explicit nature of the general scattering integral

$$f = \int \varrho(\mathbf{r}) \exp\{i\varkappa \mathbf{S}.\mathbf{r}\}\, d\mathbf{r} \tag{1}$$

for an atom whose electrons are described by s- or p-type orbitals, $\varphi(ns)$ and $\varphi(np)$, or by hybrid orbitals, φ_v, based on these two types. McWeeny (1951) (whose notation is used in (1)) has examined this question, and we may summarize his results for our purposes as follows.

For an electron in a hybrid orbital

$$\varphi_v = \sqrt{(1/(1+\lambda^2))}\,[\varphi(ns) + \lambda\varphi(np_z)]\,, \tag{2}$$

where λ is the hybridization or 'mixing' parameter, and

$$\varphi(ns)=\sqrt{(1/4\pi)}\{P_s(r)/r\}\,, \qquad (3)$$

$$\varphi(np_z)=\sqrt{(3/4\pi)}\{P_p(r)/r\}\cos\theta \qquad (4)$$

are the orthonormal s- and p-electron functions (with radial functions $P(r)$, and θ denoting the polar angle), the scattering power has the form

$$f(\varphi_v)=[1/(1+\lambda^2)][f(ns)+\lambda^2 f(np)+2\lambda f(nsnp)]\,. \qquad (5)$$

The latter two components of $f(\varphi_v)$ expand to

$$f(np)=f^{\parallel}(np)\cos^2\Theta+f^{\perp}(np)\sin^2\Theta\,, \qquad (6)$$

$$f(nsnp)=f^{\parallel}(nsnp)\cos\Theta\,, \qquad (7)$$

where Θ defines the angle which the scattering vector $\mathbf{S}$ makes with the positive (see below) axis of φ_v, and the $f^{\parallel}$, $f^{\perp}$ terms denote 'principal' factors when $\mathbf{S}$ is parallel or perpendicular to this axis.

The scattering power for φ_v thus embodies the scattering features associated with pure s- and p-orbitals, *i.e.* $f(ns)$ and $f(np)$, together with a new feature, the cross-term component $f(nsnp)$. Inserting φ_v in (1), where now $\varrho(\mathbf{r})=|\varphi_v|^2$, the different elements in (5), (6) and (7) assume the explicit forms

$$f(ns)=\int_0^\infty P_s^2(r)j_0(kr)\,dr\,,$$

$$f^{\parallel}(np)=\int_0^\infty P_p^2(r)[j_0(kr)-2j_2(kr)]\,dr\,,$$

$$f^{\perp}(np)=\int_0^\infty P_p^2(r)[j_0(kr)+j_2(kr)]\,dr \qquad (8)$$

(so that $\bar{f}(np)=\frac{1}{3}(f^{\parallel}(np)+2f^{\perp}(np))=\int_0^\infty P_p^2(r)j_0(kr)\,dr$),

$$f^{\parallel}(ns\,np)=i\sqrt{3}\int_0^\infty P_s(r)P_p(r)j_1(kr)\,dr\,,$$

where the $j_n(kr)$ are spherical Bessel functions of order n and $k=\varkappa|\mathbf{S}|=4\pi\sin\theta/\lambda$ (θ and λ here being, respectively, half the diffraction angle and the wavelength of the incident radiation).

We see that the new feature which arises in hybrid orbital scattering is $\pi/2$ out of phase with the 'normal' scattering of the component s- and p-orbitals. The total orbital scattering power is thus complex in form, so that

$$f(\varphi_v)=f_c(\varphi_v)+if_a(\varphi_v) \qquad (9)$$

where

$$f_c(\varphi_v)=[1/(1+\lambda^2)]\{f(ns)+\lambda^2[f^{\parallel}(np)\cos^2\Theta+f^{\perp}(np)\sin^2\Theta]\} \qquad (9a)$$

$$f_a(\varphi_v)=-[2\lambda/(1+\lambda^2)][if^{\parallel}(ns\,np)\cos\Theta]\,, \qquad (9b)$$

with $f(ns)$ *etc.* as in (8).

The complex nature of (9) reflects the fact that the overall charge distribution in a hybrid orbital is non-centrosymmetric about the atomic nucleus. The origin of the two components in $f(\varphi_v)$ is shown in Fig. 1, which refers to the sp^3 hybrid orbital of nitrogen given by the Hartree–Fock $P_{2s}(r)$, $P_{2p}(r)$ data of Hartree & Hartree (1948). Fig. 1(*a*) shows contours of φ_v given by (2) on using $\lambda=\sqrt{3}$ and the Hartree–Fock results in (3)* and (4), and Fig. 1(*b*) shows contours of $|\varphi_v|^2$, *i.e.* $\varrho(\mathbf{r})$. The asymmetry of the charge distribution, with its greater extension in the positive direction of the symmetry axis is resolved in Fig. 1(*c*) and (*d*), into the centrosymmetric and non-centrosymmetric (antisymmetric) components which produce the two scattering terms (9*a*) and (9*b*), respectively.

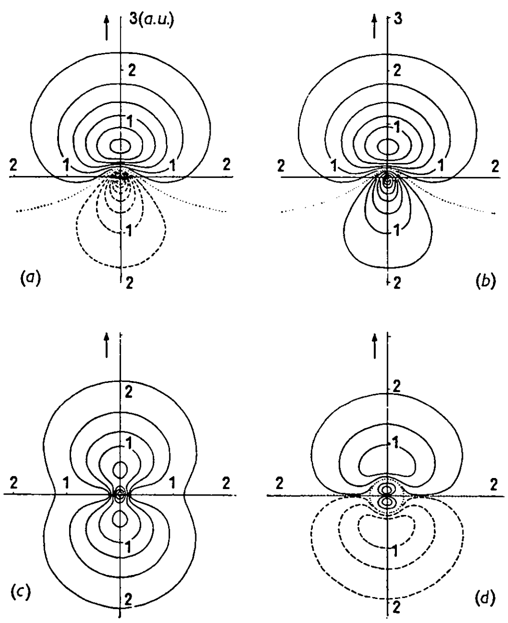

Fig. 1. A tetrahedral hybrid orbital φ_v of nitrogen, in section through the symmetry axis: (*a*) contours of φ_v at intervals of 0·1, with positive values as full lines, the node dotted, and negative values as broken lines; (*b*) contours of $|\varphi_v|^2$ corresponding to those shown for (*a*); (*c*) the centric component of (*b*) given by

$$|\varphi_v|_c^2=|\varphi(2s)|^2/4+3|\varphi(2p)|^2/4\,;$$

(*d*) the antisymmetric component of (*b*) given by

$$|\varphi_v|_a^2=(\sqrt{3}/2)\varphi(2s)\varphi(2p)\,.$$

Total-atom approximations

The total atomic scattering power of a hybrid valence state described in terms of s- and p-electron functions will then be given by appropriate combination of the types of scattering elements given in (8). Following McWeeny (1951), § 2, we assume that the radial functions $P(r)$ applicable to a valence state may be approximated by ground state functions.

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* To accord with convention arising from the use of Slater (1930) radial functions for which the maximum of $P_{2s}(r)$ is positive, the sign of the Hartree–Fock (2*s*) data has been reversed for (2).

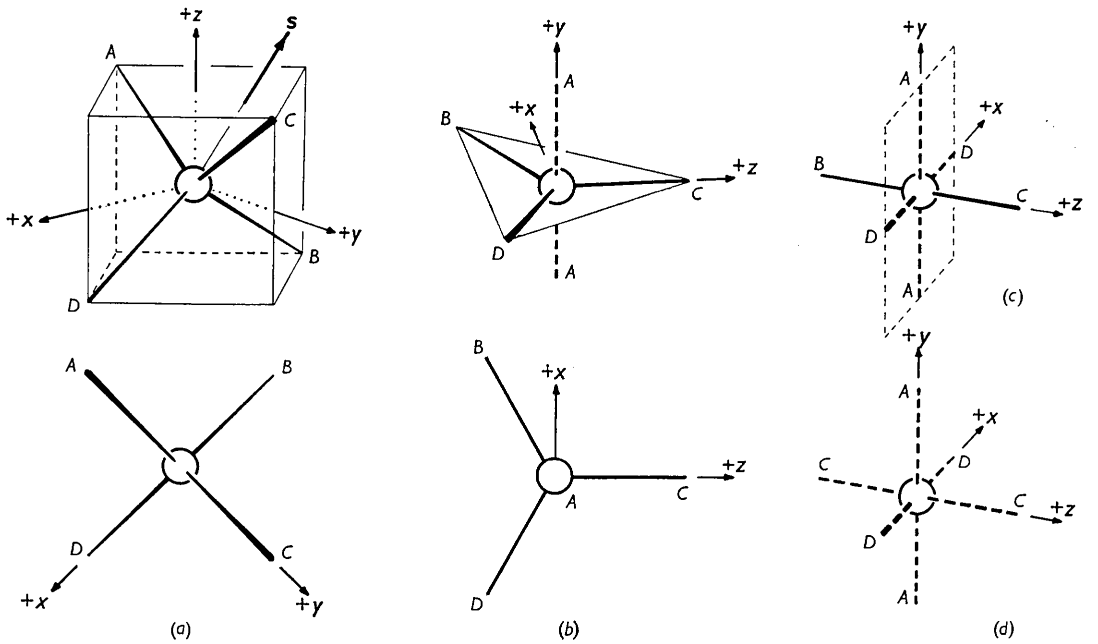

Fig. 2. The geometries of *s–p* hybrid orbitals: (*a*) for sp^3; (*b*) for sp^2; (*c*) for *sp* hybridization; (*d*) ground-state *p*-orbitals.

Scattering formulae for ground and sp^3, sp^2 or sp valence states

The three *s–p* hybrid situations involve the geometries shown in Fig. 2. For sp^3 hybridization, $\lambda=\sqrt{3}$ and there are four hybrid orbitals disposed tetrahedrally about the atom centre: with the atom at the centre of a cube, the positive directions of the orbital axes are along the body diagonals as shown in Fig. 2(*a*). For sp^2 hybridization, $\lambda=\sqrt{2}$ and there are three hybrid orbitals with their symmetry axes disposed at 120° to each other in a plane, with a *p*-orbital perpendicular to this plane (Fig. 2(*b*)). For *sp* hybridization, $\lambda=1$ and there are two hybrid orbitals whose symmetry axes are collinear, while normal to these are two *p*-orbitals whose symmetry axes are normal to each other (Fig. 2(*c*)). The orthogonal geometry of *sp* hybridization is thus similar to that associated with ground state *p*-electron scattering (Fig. 2(*d*)).

Each orbital can accommodate two electrons of opposite spin (constituting a lone pair), and, for the atoms we are to consider here, the number N of electrons per orbital can be one or two. It is convenient to use the A, B, C, D labelling of Fig. 2(*a*)–(*c*), and to denote the various hybrid orbitals as φ_{vj} and the *p*-orbitals as $\varphi(np_k)$ where j or k represent the appropriate A, B *etc.* of the different situations, and also to indicate the respective occupancies of the various orbitals for each atom for each of the hybrid states as, for example, $A^2B^1C^1D^1$.

The combined scattering powers of electrons in these orbitals has the form

$$\sum_j N_j f(\varphi_{vj})+\sum_k N_k f(np_k)\ ,$$

and, for any scattering direction in which **S** makes angles Θ_j with the positive axes of the φ_{vj} and angles Θ_k with the symmetry axes of the $\varphi(np_k)$, we then have, by (6) and (9), that this scattering consists of the centric and acentric components

$$\begin{aligned}\sum_j N_j f_c(\varphi_{vj})+\sum_k N_k f(np_k)=[1/(1+\lambda^2)]\{f(ns)\sum_j N_j\\ +\lambda^2[f^{\parallel}(np)\sum_j N_j\cos^2\Theta_j+f^{\perp}(np)\sum_j N_j\sin^2\Theta_j]\}\\ +f^{\parallel}(np)\sum_k N_k\cos^2\Theta_k+f^{\perp}(np)\sum_k N_k\sin^2\Theta_k \quad (10)\end{aligned}$$

and

$$\begin{aligned}\sum_j N_j f_a(\varphi_{vj})=-[2\lambda/(1+\lambda^2)][if^{\parallel}(ns\ np)\sum_j N_j\cos\Theta_j]\\ =f_a^{\parallel}\sum_j N_j\cos\Theta_j\ . \quad (11)\end{aligned}$$

For the sp^3 case, we have, of course, no summation over k since all orbitals are hybrids. Likewise, for ground state scattering there is no summation over j since only *p*-orbitals are involved (A, C, D, *i.e.* p_y, p_z, p_x, in Fig. 2(*d*)).

The total scattering powers, f, of the atoms in their hybrid valence states include the inner electron scattering, f_{core}, which is spherically symmetric and equal to $2f(1s)$ for the lighter atoms and to $2f(1s)+2f(2s)+6\bar{f}(2p)$ for the heavier ones, so that finally we have, analogous to (9),

$$f=f_c+if_a \quad (12)$$

where f_c results from adding f_{core} to (10) and f_a is (11). For the ground state, the total scattering power is obtained from the appropriate form of (10) on adding not only f_{core} but also the terms $2f(ns)$ where $n=2$ or 3 for the lighter or heavier atoms respectively.

The summations in (10) and (11) relevant to different possible hybrid valence states of the various atoms may be derived systematically by defining direction cosines (p, q, r) for **S** in terms of the orthogonal sets of axes x, y, z shown in Fig. 2. (The different orientations of the axes are chosen to facilitate later comparison of the scattering formulae which apply to different s–p cases). For the sp^3 case, we then have $\cos\Theta_A=(-q\sqrt{2}+r)/\sqrt{3}$, $\cos\Theta_B=-(p\sqrt{2}+r)/\sqrt{3}$, $\cos\Theta_C=(q\sqrt{2}+r)/\sqrt{3}$, $\cos\Theta_D=(p\sqrt{2}-r)/\sqrt{3}$; and for the sp^2 case $\cos\Theta_A=q$, $\cos\Theta_B=(p\sqrt{3}-r)/2$, $\cos\Theta_C=r$, $\cos\Theta_D=(-p\sqrt{3}-r)/2$. The results for the sp case and the ground state are apparent from Fig. 2(*c*) and (*d*), and differ only in the absence of the sp result $\cos\Theta_B(=-r)$ from the ground state where there are only the three p-orbitals. The appropriate summations for different 'prepared' states of the various atoms then follow from assigning single or double occupancy to the orbitals concerned in each instance. For quadrivalent carbon, for example, where one electron is assigned to each of the four orbitals in the three $s-p$ states, we find, as noted earlier by McWeeny (1951), that the total scattering power is independent of the state of hybridization*, is spherically symmetric, and has the form $f_c=2f(1s)+f(2s)+3\bar{f}(2p)$ which is also obtained from Fig. 2(*d*) for the atom regarded as $(1s)^2(2s)^1(2p)^3$. (This does not apply, however, to unusual cases such as carbon monoxide and the isonitriles which involve a lone pair on the carbon atom). A similar, common, spherically symmetric result also applies to the closed shell systems such as neon. With the intermediate atoms, however, the summations in (10) and (11) depend on the state of hybridization and orbital occupancy assumed, and the atomic scattering powers consist, usually, of acentric as well as centric components.

To facilitate comparison of these components in the various 'prepared' states considered, we list explicit formulae appropriate to each case in Table 1. For the group V and VII atoms, the centric components of the total scattering powers can all be described by the common form

$$f_c=f_c^{\parallel}\cos^2\Theta+f_c^{\perp}\sin^2\Theta\,, \qquad (13)$$

while the acentric components have the form

$$f_a=f_a^{\parallel}\cos\Theta\,. \qquad (14)$$

These are analogous to (6) and (7) earlier, and the non-spherical atomic scattering powers therefore involve the three 'principal' factors $f_c^{\parallel}$ *etc.*: it is these factors which are listed in Table 1 for these atoms. For the hybrid possibilities in group VI, however, a more flexible description than (13) and (14) is usually required, and four 'principal' factors are generally necessary. Those listed in Table 1 for these atoms correspond to the description (where necessary) of their scattering powers as

$$f_c=f_1^{\parallel}p^2+f_2^{\parallel}q^2+f_3^{\parallel}r^2,\quad f_a=f_a^{\parallel}r\,, \qquad (15), (16)$$

where (p, q, r) are the direction cosines of **S** for the orthogonal axial systems discussed earlier. The two

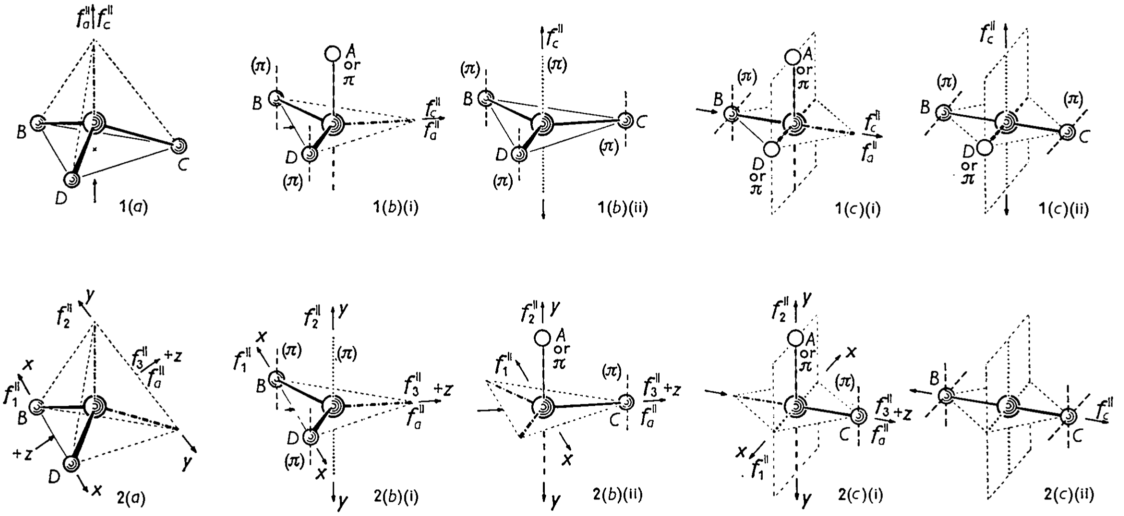

Fig. 3. Diagrammatic representation (see text) of the structural geometries of the axes defining the scattering components of different s–p hybrid possibilities. The f terms are as in Table 1.

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* McWeeny (1954) has shown that it is only when the higher-order effects of interatomic bonding are considered explicitly that small variations in bonded-atom f curves of carbon with state of hybridization are revealed. As Coulson (1962) has noted, discussion of C–C bond lengths in terms of hybridization (see Dewar (1962), and succeeding papers there) must therefore rest on these relatively minor variations in the first-order spherical symmetry of the quadrivalent carbon atom.

Table 1. *Summary of scattering data from hybrid valence state and ground state considerations*

1. Nitrogen and phosphorus

	Atomic state and scattering components*	Remarks on axial definition
1(*a*)	sp^3, as $A^2B^1C^1D^1$ in Fig. 2(*a*) (and Fig. 3). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + (5/4)f(ns) + (15/4)\bar{f}(np)$; $f_c^{\parallel} = \bar{h} - d/2, f_c^{\perp} = \bar{h} + d/4$; $f_a^{\parallel} = (-\sqrt{3}/2)f(sp)$.	Axis for Θ is available from geometry of atoms attached to N (or P). If $A \equiv B \equiv C$, axis is *from* the midpoint of the ABC plane *to* N: if $A \not\equiv B \not\equiv C$, obtain planar starting point by covalent radii considerations (Pauling, 1960).
1(*b*)	sp^2 possibilities (i), as $A^1B^1C^2D^1$ in Fig. 2(*b*) (and Fig. 3). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + (4/3)f(ns) + (11/3)\bar{f}(np)$; $f_c^{\parallel} = \bar{h} - 4d/9, f_c^{\perp} = \bar{h} + 2d/9$; $f_a^{\parallel} = (-2\sqrt{2}/3)f(sp)$.	Regard as a distorted sp^3 form, $\widehat{BND} = 120^\circ$, $\widehat{ANB} = \widehat{AND} = 90^\circ$, and define axis as in 1(*a*). Alternative possibility is a σ–π grouping involving only B and D: axis *to* N *from* a point on the line B–D by approach in 1(*a*).
	(ii), as $A^2B^1C^1D^1$ in Fig. 2(*b*) (and Fig. 3). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + f(ns) + 4\bar{f}(np)$; $f_c^{\parallel} = \bar{h} - 2d/3, f_c^{\perp} = \bar{h} + d/3$; $f_a^{\parallel} = 0$.	Axis for Θ is the normal to the plane of N, B, C, D, and the f curves apply to single (σ-)bond conditions. Evidence of multiple bonding in the planar group requires the consideration of N$^+$ contributions discussed in the text.
1(*c*)	sp possibilities (i), as $A^1B^1C^2D^1$ in Fig. 2(*c*) (and Fig. 3). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + (3/2)f(ns) + (7/2)\bar{f}(np)$; $f_c^{\parallel} = \bar{h} - d/3, f_c^{\perp} = \bar{h} + d/6$; $f_a^{\parallel} = -f(sp)$.	Another distorted sp^3 form, but orthogonal geometry here is ambiguous with ground-state as discussed in text. Axis for Θ is definable only when one atom (B) is triply bonded to N, and the axis is then *from B to* N.
	(ii), as $A^2B^1C^1D^1$ in Fig. 2(*c*) (and Fig. 3). Identical with 1(*b*)(ii) above. (ii)′, variant of (ii) as $A^{3/2}B^1C^1D^{3/2}$. $\bar{h}$ has in 1(*b*)(ii) above; $f_c^{\parallel} = \bar{h} + d/3, f_c^{\perp} = \bar{h} - d/6$; $f_a^{\parallel} = 0$.	The T-shaped geometry for simple σ-bonding of (ii) is improbable, and a linear triatomic, multiply-bonded grouping is more likely. The case of (ii)′ is the form involving radial symmetry of N in the linear group, as discussed in the text, and the axis for Θ is then the direction of the linear group.
1(*d*)	ground state, *i.e.* $A^1C^1D^1$ in Fig. 2(*d*). $g \equiv \bar{f}_c = f_{\text{core}} + 2f(ns) + 3\bar{f}(np)$; $f_a^{\parallel} = 0$.	Spherically symmetric scattering, so no axis required. Ambiguity with 1(*c*)(i) arises as discussed in text.

2. Oxygen and sulphur

1(*a*)	sp^3, as $A^2B^1C^2D^1$ in Fig. 2(*a*) (and Fig. 3). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + (3/2)f(ns) + (9/2)\bar{f}(np)$; $f_1^{\parallel} = \bar{h} + d/2, f_2^{\parallel} = \bar{h} - d/2, f_3^{\parallel} = \bar{h}$; $f_a^{\parallel} = -f(sp)$.	Geometry provides the axes x, y and z. If $B \equiv D$, then x is parallel to the line B–D, y is normal to the plane BOD, z is *from* the midpoint of B–D *to* O. If $B \not\equiv D$, refine x and z by radii considerations of 1(*a*).
2(*b*)	sp^2 possibilities (i), as $A^2B^1C^2D^1$ in Fig. 2(*b*) (and Fig. 3). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + (4/3)f(ns) + (14/3)\bar{f}(np)$; $f_1^{\parallel} = \bar{h} + 5d/9, f_2^{\parallel} = \bar{h} - 4d/9, f_3^{\parallel} = \bar{h} - d/9$; $f_a^{\parallel} = (-2\sqrt{2}/3)f(sp)$.	Regard as a distorted form of sp^3, with $\widehat{BOD} = 120^\circ$, and determine x, y, z as in 2(*a*). Evidence of multiple bonding in the BOD group (Cruickshank, 1962) requires consideration of O$^+$ contributions as discussed in text.
	(ii), as $A^1B^2C^1D^2$ in Fig. 2(*b*) (and Fig. 3). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + (5/3)f(ns) + (13/3)\bar{f}(np)$; $f_1^{\parallel} = \bar{h} - 5d/9, f_2^{\parallel} = \bar{h} + 4d/9, f_3^{\parallel} = \bar{h} + d/9$; $f_a^{\parallel} = (2\sqrt{2}/3)f(sp)$.	Can be regarded as another distorted form of sp^3, with $\widehat{AOC} = 90^\circ$ and axes disposed as in Fig. 3. However, this case is ambiguous as discussed in the text, and information in excess of geometry is required.

* The following abbreviations are employed. The spherically averaged scattering power of any hybrid valence state is denoted as $\bar{h}$, and the analogous scattering power of the ground state as $\bar{g}$; the explicit expressions for $\bar{h}$ and $\bar{g}$ are given, and we have $\bar{h} \equiv \bar{g}$ if $f(ns) = \bar{f}(np)$. We also use $d \equiv (f^{\perp}(np) - f^{\parallel}(np))$, with the two $f(np)$-components as given in (8). Finally, $f(sp) \equiv if^{\parallel}(nsnp)$, where $f^{\parallel}(nsnp)$ is also given in (8).

Table 1. (*cont*).

	Atomic state and scattering components*	Remarks on axial definition
2(*c*)	*sp* possibilities (i), as $A^1B^2C^1D^2$ in Fig. 2(*c*) (and Fig. 3). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + (3/2)f(ns) + (9/2)\bar{f}(np)$; $f_1^{\parallel} = \bar{h} - d/2, f_2^{\parallel} = \bar{h} + d/2, f_3^{\parallel} = \bar{h}$; $f_a^{\parallel} = f(sp)$. (i)′, variant of (i) as $A^{3/2}B^2C^1D^{3/2}$. $\bar{h}$ and $f_a^{\parallel}$ as in (i), but now $f_{1,2,3}^{\parallel} = \bar{h}$.	The orthogonal AOC grouping here has the same ambiguities of axial definition as in 2(*b*)(ii) above, and the same applies to the alternative of a σ–π OC bond. However, the OC group here can be treated in a radially symmetric form as (i)′, when z is *from* O *to* C.
	(ii), as $A^2B^1C^1D^2$ in Fig. 2(*c*) (and Fig. 3). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + f(ns) + 5\bar{f}(np)$; $f_c^{\parallel} = \bar{h} + 2d/3, f_c^{\perp} = \bar{h} - d/3$; $f_a^{\parallel} = 0$.	Only one reference axis is required for the simpler type of scattering here, and Θ is referred to the direction of the linear BOC grouping.
	(iii), as $A^1B^2C^2D^1$ in Fig. 2(*c*). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + 2f(ns) + 4\bar{f}(np)$; $f_c^{\parallel} = \bar{h} - 2d/3, f_c^{\perp} = \bar{h} + d/3$; $f_a^{\parallel} = 0$.	In the orthogonal AOD group, Θ is referred to the axis which is the normal to the group. In the alternative possibilities of multiply bonded OA or OD groups, axial definition is ambiguous (see text) except when O has radial symmetry about its multiple bond: *cf.* 2(*c*)(i), (i)′ above.
2(*d*)	‘ground’ state possibilities (i), as $A^1C^2D^1$ in Fig. 2(*d*). Identical with 2(*c*)(iii) above. (i)′, as $A^{3/2}C^1D^{3/2}$ in Fig. 2(*d*). $\bar{g} \equiv \bar{h}$ of (i); $f_c^{\parallel} = \bar{h} + d/3, f_c^{\perp} = \bar{h} - d/6$; $f_a^{\parallel} = 0$.	Identical situation with that of 2(*c*)(iii). The case of (i)′ is for the radially symmetric situation above, and Θ here refers to the direction of the bond from O. Note that this reference axis for (i)′ is normal to that required for the *f*-components of (i) (and 2(*c*)(iii)).
	3. Fluorine and chlorine	
3(*a*)	*sp*^{3}, *e.g.* $A^1B^2C^2D^2$ in Fig. 2(*a*). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + (7/4)f(ns) + (21/4)\bar{f}(np)$; $f_c^{\parallel} = \bar{h} + d/2, f_c^{\perp} = \bar{h} - d/4$; $f_a^{\parallel} = (\sqrt{3}/2)f(sp)$.	Similar to 1(*a*). Reference axis for Θ is given by the direction of the bond *from* F *to* neighbour (A). We can use this definition for all cases below.
3(*b*)	*sp*^{2} possibilities (i), *e.g.* as $A^2B^2C^1D^2$ in Fig. 2(*b*). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + (5/3)f(ns) + (16/3)\bar{f}(np)$; $f_c^{\parallel} = \bar{h} + 4d/9, f_c^{\perp} = \bar{h} - 2d/9$; $f_a^{\parallel} = (2\sqrt{2/3})f(sp)$.	Evidence of multiple bonding requires that *f* data here be taken as the upper (single bonding) limit to a situation whose lower (double bonding) limit is that of 2(*b*)(ii).
	(ii), as $A^1B^2C^2D^2$ in Fig. 2(*b*). Identical with ground-state 3(*d*) below.	The identity with ground state scattering applies only when the valence state orbitals are built, as here, from ground state data.
3(*c*)	*sp* possibilities (i), *e.g.* as $A^2B^2C^1D^2$ in Fig. 2(*c*). $\bar{h} \equiv \bar{f}_{c,h} = f_{\text{core}} + (3/2)f(ns) + (11/2)\bar{f}(np)$; $f_c^{\parallel} = \bar{h} + d/3, f_c^{\perp} = \bar{h} - d/6$; $f_a^{\parallel} = f(sp)$.	For the possibility of multiple bonding, the lower limit to the case here is given by 2(*c*)(i) or (i)′.
	(ii), *e.g.* as $A^1B^2C^2D^2$ in Fig. 2(*c*). Identical with ground state 3(*d*) below.	For identity conditions, see above. For multiple bonding possibility, the lower limit now is given by 2(*c*)(iii).
3(*d*)	ground state, *e.g.* as $A^2C^1D^2$ in Fig. 2(*d*). $g \equiv \bar{f}_c = f_{\text{core}} + 2f(ns) + 5\bar{f}(np)$; $f_c^{\parallel} = \bar{g} + 2d/3, f_c^{\perp} = \bar{g} - d/3$; $f_a^{\parallel} = 0$.	

descriptions reflect the underlying nature of the centric charge distribution components involved: when these are spheroidal in character, only one reference axis is involved and the form of f_c in (13) suffices; but when they have general ellipsoidal character, three axes must be specified.

The use of molecular geometry in axial assignment and choice of 'prepared valence states'

Apart from enumerating the scattering formulae of the different valence states, Table 1 also comments on the associated problem of defining the reference axes to which the 'principal' factors are related. To amplify the total contents of Table 1 for groups V and VI, we summarize the geometrical disposition of the 'principal' factors in Fig. 3. The orientation of the tetrahedron there differs from that in Fig. 2(*a*) so as to clarify the transition in orbital geometry from the sp^3 to the sp state, but we have retained the A, B *etc.* labelling used in Fig. 2 and the text. The labelling in Fig. 3 is extended, however, to denote not only the orbitals of the central atom (*i.e.* N or O) but also the neighbours bonded to this atom. Singly occupied hybrid orbitals in σ-bonding to neighbours are shown as heavy full lines, and doubly occupied (lone pair) hybrids as chain lines. The corresponding p-orbitals are shown as broken and dotted lines respectively. For the singly occupied p-orbitals, their participation in σ-bonding is indicated by heavier emphasis of one half of their symmetry axes passing through the central atom. The possibilities of π-bonding between central atom and neighbours are also indicated in Fig. 3 by the broken lines, of appropriate orientation, passing through the centres of the neighbours shown as hatched circles. The neighbours shown as open circles are then absent, and these two alternatives are shown in the diagrams as, *e.g.* 'A or π'. The cases of multiple bonding involving contributions from a higher valence state of the central atom (see later) are indicated by the description of a doubly-filled p-orbital of this atom as '(π)'. This same description (π) is used for the neighbour-atom orbitals discussed above.

The geometries involved here are, of course, idealized ones which will rarely be exactly encountered in practice. However, they give useful insight into the value of molecular geometry in both the assignment of reference axes and the choosing of 'prepared state' possibilities. In cases where bond-angle evidence is consistent with approximate sp^3 or sp^2 considerations, then we see from Table 1 and Fig. 3 that a positive choice of reference axes can often be made from the disposition of the atomic groupings observed in the later stages of structure refinement. In other cases, however, where the same geometry applies to more than one 'prepared state' interpretation, the decision as to which scattering components are most appropriate to any system being studied will involve some ambiguity.

The ambiguous cases can be broadly grouped as follows. (1) Situations in which N (or P: hereafter we mention only the lighter member, as in Table 1) is the central atom in orthogonal groupings are consistent with either the sp possibility 1(*c*) (i) or a ground-state interpretation, and this ambiguity persists as the number of adjoining atoms is reduced by double or triple bonding. The two 'prepared state' scattering possibilities for N here have their greatest differences in the presence or absence of an acentric component (Table 1).

(2) A similar problem exists when O occurs in an orthogonal triatomic grouping or is multiply bonded to just one neighbour. Here, geometry cannot resolve the alternatives of an sp^2 state 2(*b*) (ii), sp states 2(*c*) (i) or (i)′, and the states 2(*d*) (i) or (i)′ of Table 1. Again, the most noticeable differences in the alternatives are concerned with the acentric scattering components.

(2A) A further problem related to (2) concerns ambiguity in defining reference axes required for the centric scattering possibilities there. For the sp^2 alternative, the differentiation of y and z axes in the AOC group (2(*b*) (ii) of Fig. 3) requires knowledge of which bond from O involves the p-orbital and which the sp^2 hybrid, since this dictates the axial assignment, as seen in Fig. 3. If only the diatomic group OC is involved, then z is now defined but the resolution of x and y will depend on the availability of additional geometrical information: *e.g.* if C is a member of some associated π-bonded system such as a planar aromatic ring, then the direction of y for O is given by the normal to the planar ring. Exactly similar arguments apply to the sp possibility 2(*c*) (i). Here, however, the dilemma can be circumvented in the OC group by regarding O as having radial symmetry about its bond, in which case the variant 2(*c*) (i)′ in Table 1 can be employed. These arguments can also be extended to the ground state possibility 2(*d*) (i). In this case, the centric scattering involves the simpler form in (13), and the reference axis for $f_c^{\parallel}$ in the orthogonal group AOD (Table 1) is the normal to the group. In the diatomic possibilities, OA or OD, the reference axis can be defined only if the neighbour is a member of an associated π-bonded system. This is analogous to the sp^2 observations above but now, for the example cited there, the reference axis for $f_c^{\parallel}$ will be in the plane of the ring. In other cases, the need for assuming radial symmetry* will involve the scattering description given by the 2(*d*) (i)′ variant in Table 1.

(3) Another possible form of ambiguity concerns certain situations where the observed geometry seemingly permits an explicit choice to be made among the various 'prepared states' examined here. This concerns

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* There may, of course, be real radial symmetry, in which case the variants 2(*c*)(i)′ and 2(*d*)(i)′ are more than just an approximation for overcoming axial indeterminacy. Another case involving radial possibilities is that of N in 1(*c*)(ii) and (ii)′ in Table 1.

cases where significant contributions from valence states higher than those of the neutral atoms may be involved. An example of this possibility is the planar trigonal grouping around N in 1(*b*) (ii) of Table 1 and Fig. 3. As noted there, the scattering components for N in this geometry imply a simple σ-bonded system, whereas structural evidence usually indicates the existence of multiple bonding effects. These require that the N atom be considered as partly in the quadrivalent state, N^+ (this possibility has been extensively discussed by Orville-Thomas (1957) for a variety of geometries), in which case the *p*-orbital normal to the atomic plane is singly rather than doubly occupied. At the level of approximation at which we are working, N^+ thus has spherically symmetric scattering since it is isoelectronic with carbon. Consequently, in a planar grouping showing evidence of extensive multiple bonding, the scattering results for N in 1(*b*) (ii) are probably best regarded only as defining the upper limit to the existing actual situation: they then provide a basis for detailed examination of the way in which the true charge distribution deviates from the aspherical form of the neutral atom. Another instance where N^+ considerations may also apply is the linear triatomic situation in 1(*c*) (ii) or (ii)′ of Table 1. In the case of O, the analogous possibility involving O^+ was noted in 2(*b*) (i) of Table 1, and it may again arise in the linear case of 2(*c*) (ii). For multiple bonding in the *BOD* group of 2(*b*) (i) in Fig. 3, the O^+ considerations set the lower limit of scattering power in this case as the form for N in 1(*b*) (i): we see that the two limits have different details for the centric scattering component but possess the same type of acentric contribution. With the linear *BOC* group of 2(*c*) (ii), the lower limit is probably best described by the radially symmetric form for N in 1(*c*) (ii)′ of Table 1. For group VII, extensive multiple bonding is less likely, but the lower limits for different hybrid possibilities of these atoms are given in Table 1.

It is possible, of course, that these ambiguities may be resolved when evidence other than the observed geometry is available. We consider this briefly in the Discussion below, but otherwise postpone further comments to projected experimental examinations based on the present *f* curves.

Numerical f data for hybrid valence state approximations

The evaluation of the *f* terms in Table 1 is based on ground-state *f* data derived from various approximate treatments available for the different atoms. For the simplified scattering formulae given by the assumption that $f(ns)=f(np)$, we thus require only ground state values of the total $\bar{f}$, $d(np)$ and $f^{\rm II}(ns\,np)$: note that in Table 1 (see footnote there) $\bar{f}$ is written as $\bar{g}$ and $d(np)$ as d. Without this assumption, one-electron *f* components of the total $\bar{f}$ curves are required (to obtain the $\bar{h}$ values of Table 1), and the numerical consequences of this assumption have been examined only for the lighter atoms, N, O and F.

For these atoms, Hartree–Fock values of $\bar{f}$ are available from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and Freeman (1959*a*). The latter has also calculated the aspherical ground state scattering components of O and F, from which the Hartree–Fock values of $d(2p)$ are readily obtained. The terms $f^{\rm II}(2s\,2p)$ arise in the treatment of incoherent Compton scattering (Freeman, 1959*b*, *c*), and the values required here for N, O and F are obtained from his tabulated $f_{2s}f_{2p}$ values by reversing their signs (see first footnote) and applying the factor $\sqrt{3}$ (in (8)). The one-electron components of $\bar{f}$ for these atoms are also given by Freeman (1959*c*), so that only values of $d(2p)$ for N require calculation for evaluating the hybrid scattering curves. Conformity with the other available Hartree–Fock *f* data demands the use of the numerical radial functions of Hartree & Hartree (1948), but we have employed, instead, the more convenient analytical functions of Duncanson & Coulson (1948) used earlier by McWeeny (1951). We have earlier (Dawson, 1961) compared the $d(2p)$ values for O and F from these functions with the Hartree–Fock values, and, as a further simple check for N here, we have used McWeeny's expression for $f^{\rm II}(2s\,2p)$ to calculate values for comparison with the Hartree–Fock values for N noted above.

For the heavier atoms, values of $\bar{f}$ based on the variational poly-detor calculations of Boys & Price (1954) are available for S and Cl (Dawson, 1960), and values of $d(3p)$ for these two systems have been calculated *via* orthogonalized Slater functions for estimating aspherical ground state scattering effects (Dawson, 1961). Extensive Hartree–Fock calculations of all third row atoms performed recently (Watson & Freeman, 1961) have been used to derive values of $\bar{f}$ (Freeman & Watson, 1962). We use here the poly-detor $\bar{f}$ data for S and Cl and the Hartree–Fock data for P, and calculate the $d(3p)$ values required for P from the same basis as in Dawson (1961). The remaining computation of the $f^{\rm II}(3s\,3p)$ terms of the three atoms can also be made conveniently, although at reduced accuracy, in terms of orthogonalized Slater functions in the following way. The orthonormal functions (3) and (4) whose $P(r)$ are required for (8) are then

$$\begin{aligned}\varphi'(3s)=M\{N_{3s}r^2\exp[-c_3r]-Q_1N_{2s}r\exp[-c_2r]\\ -Q_2N_{1s}\exp[-c_1r]\}\end{aligned}$$

and $\varphi'(3p_z)$ as given in Dawson (1961), whose notation we use here. M, Q_1 and Q_2 are constants whose values in terms of the overlap integrals of the simple Slater functions are given by Tomiie & Stam (1958), with their N written as M here to avoid confusion with the normalization constants N_{3s} *etc.* Inserting the functions for $P(r)$ in (8) then yields

Table 2. *Atomic scattering factors for* sp^3 *and* sp^2 *hybrid valence state approximations, at intervals of* $\sin\theta/\lambda$ *in* Å^{-1}

sp^3 N

$\sin\theta/\lambda$	$\bar{f}_c$	$f_c^{\parallel}$	$f_c^{\perp}$	δ	$f_a^{\parallel}$
0·00	7·000	7·000	7·000		0·000
0·05	6·78$_1$	6·75$_9$	6·79$_2$		0·21$_3$
0·10	6·19$_9$	6·11$_8$	6·23$_9$	(−0·01$_6$)	0·38$_6$
0·15	5·42$_0$	5·26$_3$	5·49$_9$		0·48$_7$
0·20	4·59$_2$	4·36$_2$	4·70$_7$	(−0·02$_3$)	0·51$_4$
0·25	3·85$_6$	3·57$_2$	3·99$_8$		0·48$_9$
0·30	3·23$_3$	2·92$_1$	3·38$_9$	(−0·00$_3$)	0·43$_3$
0·35	2·76$_0$	2·44$_5$	2·91$_8$		0·36$_4$
0·40	2·39$_5$	2·09$_6$	2·54$_5$	(0·01$_8$)	0·29$_3$
0·50	1·93$_9$	1·70$_1$	2·05$_8$	(0·02$_5$)	0·17$_3$
0·60	1·69$_4$	1·52$_3$	1·78$_0$	(0·02$_2$)	0·09$_0$
0·70	1·54$_8$	1·43$_1$	1·60$_6$	(0·01$_4$)	0·03$_9$
0·80	1·44$_2$	1·36$_4$	1·48$_1$		0·00$_9$
0·90	1·34$_9$	1·29$_7$	1·37$_5$	(−0·00$_2$)	−0·00$_6$
1·00	1·26$_1$	1·22$_7$	1·27$_8$		−0·01$_4$
1·10	1·17$_1$	1·14$_8$	1·18$_3$	(−0·01$_2$)	−0·01$_7$

sp^2 N

	as $(1s)^2(2p)^1(2s\ 2p)^4$, *i.e.* 1(*b*)(i)					as $(1s)^2(2p)^2(2s\ 2p)^3$, *i.e.* 1(*b*)(ii)		
$\sin\theta/\lambda$	$f_c^{\parallel}$	$f_c^{\perp}$	δ	$f_a^{\parallel}$	$f_a^{\parallel}$	$f_c^{\parallel}$	$f_c^{\perp}$	δ
0·00	7·000	7·000		0·000	(0·000)	7·000	7·000	
0·05	6·76$_1$	6·79$_1$		0·23$_2$	(0·22$_9$)	6·75$_2$	6·79$_6$	
0·10	6·12$_7$	6·23$_5$	(−0·01$_5$)	0·42$_0$	(0·41$_7$)	6·09$_1$	6·25$_3$	(−0·02$_2$)
0·15	5·28$_0$	5·49$_0$		0·53$_0$	(0·53$_8$)	5·21$_1$	5·52$_5$	
0·20	4·38$_7$	4·69$_4$	(−0·02$_1$)	0·55$_9$	(0·58$_5$)	4·28$_5$	4·74$_5$	(−0·03$_2$)
0·25	3·60$_4$	3·98$_2$		0·53$_2$	(0·56$_9$)	3·47$_7$	4·04$_5$	
0·30	2·95$_6$	3·37$_2$	(−0·00$_3$)	0·47$_1$	(0·51$_0$)	2·81$_7$	3·44$_1$	(−0·00$_4$)
0·35	2·48$_0$	2·90$_0$		0·39$_6$	(0·42$_9$)	2·34$_0$	2·97$_0$	
0·40	2·12$_9$	2·52$_8$	(0·01$_5$)	0·31$_9$	(0·34$_3$)	1·99$_6$	2·59$_5$	(0·02$_3$)
0·50	1·72$_7$	2·04$_5$	(0·02$_2$)	0·18$_8$	(0·19$_3$)	1·62$_1$	2·09$_8$	(0·03$_4$)
0·60	1·54$_2$	1·77$_0$	(0·01$_9$)	0·09$_8$	(0·09$_3$)	1·46$_6$	1·80$_8$	(0·02$_9$)
0·70	1·44$_4$	1·60$_0$	(0·01$_2$)	0·04$_2$	(0·03$_5$)	1·39$_2$	1·62$_6$	(0·01$_8$)
0·80	1·37$_3$	1·47$_7$		0·01$_0$	(0·00$_5$)	1·33$_8$	1·49$_4$	
0·90	1·30$_3$	1·37$_2$	(−0·00$_2$)	−0·00$_6$	(−0·00$_9$)	1·28$_0$	1·38$_3$	(−0·00$_3$)
1·00	1·23$_0$	1·27$_6$		−0·01$_5$	(−0·01$_5$)	1·21$_5$	1·28$_4$	
1·10	1·15$_0$	1·18$_1$	(−0·01$_0$)	−0·01$_8$	(−0·01$_6$)	1·14$_0$	1·18$_6$	(−0·01$_6$)

sp^3 O

$\sin\theta/\lambda$	$\bar{f}_c$	$f_1^{\parallel}$	$f_2^{\parallel}$	$f_3^{\parallel}$	δ	$f_a^{\parallel}$
0·00	8·000	8·000	8·000	8·000		0·000
0·05	7·79$_6$	7·81$_7$	7·77$_5$	7·79$_6$		0·23$_3$
0·10	7·24$_8$	7·32$_4$	7·17$_3$	7·24$_8$	(−0·01$_1$)	0·39$_7$
0·15	6·48$_2$	6·62$_5$	6·33$_9$	6·48$_2$		0·51$_9$
0·20	5·63$_0$	5·83$_5$	5·42$_6$	5·63$_0$	(−0·02$_1$)	0·58$_0$
0·25	4·81$_4$	5·06$_3$	4·56$_3$	4·81$_4$		0·58$_6$
0·30	4·09$_3$	4·36$_7$	3·81$_9$	4·09$_3$	(−0·01$_1$)	0·55$_1$
0·35	3·49$_2$	3·77$_3$	3·21$_1$	3·49$_2$		0·49$_5$
0·40	3·00$_8$	3·28$_4$	2·73$_2$	3·00$_8$	(0·00$_5$)	0·42$_7$
0·50	2·33$_7$	2·58$_0$	2·09$_5$	2·33$_7$	(0·01$_5$)	0·29$_2$
0·60	1·94$_5$	2·14$_4$	1·74$_7$	1·94$_5$	(0·01$_8$)	0·18$_2$
0·70	1·71$_4$	1·87$_1$	1·55$_8$	1·71$_4$	(0·01$_5$)	0·10$_4$
0·80	1·56$_7$	1·68$_9$	1·44$_6$	1·56$_7$		0·05$_2$
0·90	1·46$_1$	1·55$_5$	1·36$_8$	1·46$_1$	(0·00$_5$)	0·01$_9$
1·00	1·37$_4$	1·44$_6$	1·30$_2$	1·37$_4$		−0·00$_1$
1·10	1·29$_4$	1·34$_9$	1·23$_9$	1·29$_4$	(−0·00$_4$)	−0·01$_3$

Table 2. (*cont.*)

	*sp*² O									
	as $(1s)^2(2p)^2(2s\ 2p)^4$, *i.e.* 2(*b*)(i)					as $(1s)^2(2p)^1(2s\ 2p)^5$, *i.e.* 2(*b*)(ii)				
$\sin\theta/\lambda$	$f_1^{\parallel}$	$f_2^{\parallel}$	$f_3^{\parallel}$	δ	$f_a^{\parallel}$	$f_1^{\parallel}$	$f_2^{\parallel}$	$f_3^{\parallel}$	δ	$f_a^{\parallel}$
0·00	8·000	8·000	8·000		0·000	8·000	8·000	8·000		0·000
0·05	$7{\cdot}81_9$	$7{\cdot}77_7$	$7{\cdot}79_1$		$0{\cdot}22_0$	$7{\cdot}77_3$	$7{\cdot}81_5$	$7{\cdot}80_1$		$-0{\cdot}22_0$
0·10	$7{\cdot}33_2$	$7{\cdot}18_1$	$7{\cdot}23_1$	$(-0{\cdot}01_5)$	$0{\cdot}37_4$	$7{\cdot}16_4$	$7{\cdot}31_5$	$7{\cdot}26_5$	$(-0{\cdot}00_7)$	$-0{\cdot}37_4$
0·15	$6{\cdot}64_1$	$6{\cdot}35_5$	$6{\cdot}45_0$		$0{\cdot}48_9$	$6{\cdot}32_3$	$6{\cdot}60_9$	$6{\cdot}51_4$		$-0{\cdot}48_9$
0·20	$5{\cdot}85_7$	$5{\cdot}44_8$	$5{\cdot}58_5$	$(-0{\cdot}02_8)$	$0{\cdot}54_6$	$5{\cdot}40_3$	$5{\cdot}81_2$	$5{\cdot}67_5$	$(-0{\cdot}01_4)$	$-0{\cdot}54_6$
0·25	$5{\cdot}09_0$	$4{\cdot}59_3$	$4{\cdot}75_9$		$0{\cdot}55_2$	$4{\cdot}53_8$	$5{\cdot}03_5$	$4{\cdot}86_9$		$-0{\cdot}55_2$
0·30	$4{\cdot}39_7$	$3{\cdot}84_9$	$4{\cdot}03_2$	$(-0{\cdot}01_5)$	$0{\cdot}52_0$	$3{\cdot}78_9$	$4{\cdot}33_7$	$4{\cdot}15_4$	$(-0{\cdot}00_7)$	$-0{\cdot}52_0$
0·35	$3{\cdot}80_4$	$3{\cdot}24_2$	$3{\cdot}43_0$		$0{\cdot}46_7$	$3{\cdot}18_0$	$3{\cdot}74_2$	$3{\cdot}55_4$		$-0{\cdot}46_7$
0·40	$3{\cdot}31_5$	$2{\cdot}76_3$	$2{\cdot}94_7$	$(0{\cdot}00_6)$	$0{\cdot}40_2$	$2{\cdot}70_1$	$3{\cdot}25_3$	$3{\cdot}06_9$	$(0{\cdot}00_3)$	$-0{\cdot}40_2$
0·50	$2{\cdot}60_6$	$2{\cdot}12_1$	$2{\cdot}28_3$	$(0{\cdot}02_0)$	$0{\cdot}27_5$	$2{\cdot}06_8$	$2{\cdot}55_3$	$2{\cdot}39_1$	$(0{\cdot}01_1)$	$-0{\cdot}27_5$
0·60	$2{\cdot}16_6$	$1{\cdot}76_9$	$1{\cdot}90_1$	$(0{\cdot}02_4)$	$0{\cdot}17_2$	$1{\cdot}72_4$	$2{\cdot}12_1$	$1{\cdot}98_9$	$(0{\cdot}01_2)$	$-0{\cdot}17_2$
0·70	$1{\cdot}88_8$	$1{\cdot}57_5$	$1{\cdot}67_9$	$(0{\cdot}02_0)$	$0{\cdot}09_8$	$1{\cdot}54_0$	$1{\cdot}85_3$	$1{\cdot}74_9$	$(0{\cdot}01_0)$	$-0{\cdot}09_8$
0·80	$1{\cdot}70_2$	$1{\cdot}45_9$	$1{\cdot}54_0$		$0{\cdot}04_9$	$1{\cdot}43_2$	$1{\cdot}67_5$	$1{\cdot}59_4$		$-0{\cdot}04_9$
0·90	$1{\cdot}56_5$	$1{\cdot}37_8$	$1{\cdot}44_0$	$(0{\cdot}00_6)$	$0{\cdot}01_8$	$1{\cdot}35_7$	$1{\cdot}54_4$	$1{\cdot}48_2$	$(0{\cdot}00_3)$	$-0{\cdot}01_8$
1·00	$1{\cdot}45_4$	$1{\cdot}31_0$	$1{\cdot}35_8$		$-0{\cdot}00_1$	$1{\cdot}29_4$	$1{\cdot}43_8$	$1{\cdot}39_0$		$0{\cdot}00_1$
1·10	$1{\cdot}35_5$	$1{\cdot}24_5$	$1{\cdot}28_2$	$(-0{\cdot}00_5)$	$-0{\cdot}01_2$	$1{\cdot}23_3$	$1{\cdot}34_3$	$1{\cdot}30_6$	$(-0{\cdot}00_2)$	$0{\cdot}01_2$

	*sp*³ F					*sp*² F					
						as $(1s)^2(2p)^2(2s\ 2p)^5$, *i.e.* 3(*b*)(i)				as $(1s)^2(2p)^1(2s\ 2p)^6$, *i.e.* 3(*b*)(ii)	
$\sin\theta/\lambda$	$\bar{f}_c$	$f_c^{\parallel}$	$f_c^{\perp}$	δ	$f_a^{\parallel}$	$f_c^{\parallel}$	$f_c^{\perp}$	δ	$f_a^{\parallel}$	$f_c^{\parallel}$	$f_c^{\perp}$
0·00	9·000	9·000	9·000		0·000	9·000	9·000		0·000	9·000	9·000
0·05	$8{\cdot}82_0$	$8{\cdot}84_2$	$8{\cdot}80_9$		$-0{\cdot}19_7$	$8{\cdot}84_0$	$8{\cdot}81_0$		$-0{\cdot}21_5$	$8{\cdot}84_9$	$8{\cdot}80_5$
0·10	$8{\cdot}29_3$	$8{\cdot}37_2$	$8{\cdot}25_4$	$(-0{\cdot}00_5)$	$-0{\cdot}32_0$	$8{\cdot}36_3$	$8{\cdot}25_8$	$(-0{\cdot}00_7)$	$-0{\cdot}34_8$	$8{\cdot}39_8$	$8{\cdot}24_0$
0·15	$7{\cdot}53_7$	$7{\cdot}68_3$	$7{\cdot}46_4$		$-0{\cdot}42_4$	$7{\cdot}66_7$	$7{\cdot}47_2$		$-0{\cdot}46_2$	$7{\cdot}73_2$	$7{\cdot}44_0$
0·20	$6{\cdot}69_1$	$6{\cdot}88_8$	$6{\cdot}59_3$	$(-0{\cdot}01_1)$	$-0{\cdot}47_7$	$6{\cdot}86_6$	$6{\cdot}60_4$	$(-0{\cdot}01_5)$	$-0{\cdot}51_9$	$6{\cdot}95_3$	$6{\cdot}56_0$
0·25	$5{\cdot}83_6$	$6{\cdot}06_7$	$5{\cdot}72_1$		$-0{\cdot}48_8$	$6{\cdot}04_1$	$5{\cdot}73_3$		$-0{\cdot}53_1$	$6{\cdot}14_4$	$5{\cdot}68_2$
0·30	$5{\cdot}04_4$	$5{\cdot}29_9$	$4{\cdot}91_7$	$(-0{\cdot}00_9)$	$-0{\cdot}47_5$	$5{\cdot}27_0$	$4{\cdot}93_1$	$(-0{\cdot}01_2)$	$-0{\cdot}51_7$	$5{\cdot}38_3$	$4{\cdot}87_4$
0·35	$4{\cdot}34_8$	$4{\cdot}60_8$	$4{\cdot}21_8$		$-0{\cdot}44_0$	$4{\cdot}57_9$	$4{\cdot}23_2$		$-0{\cdot}47_9$	$4{\cdot}69_5$	$4{\cdot}17_5$
0·40	$3{\cdot}76_0$	$4{\cdot}01_8$	$3{\cdot}63_1$	$(-0{\cdot}00_1)$	$-0{\cdot}39_3$	$3{\cdot}98_9$	$3{\cdot}64_5$	$(-0{\cdot}00_2)$	$-0{\cdot}42_8$	$4{\cdot}10_4$	$3{\cdot}58_8$
0·50	$2{\cdot}87_8$	$3{\cdot}11_2$	$2{\cdot}76_1$	$(0{\cdot}00_6)$	$-0{\cdot}29_2$	$3{\cdot}08_6$	$2{\cdot}77_4$	$(0{\cdot}00_8)$	$-0{\cdot}31_8$	$3{\cdot}19_0$	$2{\cdot}72_2$
0·60	$2{\cdot}31_2$	$2{\cdot}51_3$	$2{\cdot}21_2$	$(0{\cdot}00_9)$	$-0{\cdot}20_2$	$2{\cdot}49_0$	$2{\cdot}22_3$	$(0{\cdot}01_2)$	$-0{\cdot}22_0$	$2{\cdot}57_9$	$2{\cdot}17_8$
0·70	$1{\cdot}95_8$	$2{\cdot}12_3$	$1{\cdot}87_6$	$(0{\cdot}00_9)$	$-0{\cdot}13_1$	$2{\cdot}10_5$	$1{\cdot}88_5$	$(0{\cdot}01_2)$	$-0{\cdot}14_2$	$2{\cdot}17_8$	$1{\cdot}84_8$
0·80	$1{\cdot}73_5$	$1{\cdot}86_8$	$1{\cdot}66_9$		$-0{\cdot}07_6$	$1{\cdot}85_3$	$1{\cdot}67_6$		$-0{\cdot}08_3$	$1{\cdot}91_2$	$1{\cdot}64_6$
0·90	$1{\cdot}58_7$	$1{\cdot}69_4$	$1{\cdot}53_4$	$(0{\cdot}00_6)$	$-0{\cdot}03_6$	$1{\cdot}68_2$	$1{\cdot}53_9$	$(0{\cdot}00_8)$	$-0{\cdot}03_9$	$1{\cdot}73_0$	$1{\cdot}51_6$
1·00	$1{\cdot}48_1$	$1{\cdot}56_7$	$1{\cdot}43_8$		$-0{\cdot}00_1$	$1{\cdot}55_7$	$1{\cdot}44_3$		$-0{\cdot}00_1$	$1{\cdot}59_5$	$1{\cdot}42_4$
1·10	$1{\cdot}39_6$	$1{\cdot}46_3$	$1{\cdot}36_3$	$(0{\cdot}00_1)$	$0{\cdot}03_0$	$1{\cdot}45_6$	$1{\cdot}36_6$	$(0{\cdot}00_1)$	$0{\cdot}03_3$	$1{\cdot}48_5$	$1{\cdot}35_1$

	*sp*³ P				*sp*² P				
					as $(3p)^1(3s\ 3p)^4$			as $(3p)^2(3s\ 3p)^3$	
$\sin\theta/\lambda$	$\bar{f}_c$	$f_c^{\parallel}$	$f_c^{\perp}$	$f_a^{\parallel}$	$f_c^{\parallel}$	$f_c^{\perp}$	$f_a^{\parallel}$	$f_c^{\parallel}$	$f_c^{\perp}$
0·00	15·00	15·00	15·00	0·000	15·00	15·00	0·000	15·00	15·00
0·05	14·47	14·41	14·50	$0{\cdot}34_1$	14·42	14·50	$0{\cdot}37_1$	14·39	14·51
0·10	13·17	12·98	13·26	$0{\cdot}54_0$	13·00	13·25	$0{\cdot}58_8$	12·92	13·30
0·15	11·66	11·36	11·81	$0{\cdot}55_3$	11·39	11·80	$0{\cdot}60_3$	11·25	11·86
0·20	10·34	9·99	10·51	$0{\cdot}43_8$	10·03	10·50	$0{\cdot}47_7$	9·88	10·57
0·25	9·33	9·01	9·49	$0{\cdot}28_3$	9·05	9·47	$0{\cdot}30_8$	8·90	9·54
0·30	8·59	8·34	8·72	$0{\cdot}14_9$	8·37	8·70	$0{\cdot}16_2$	8·26	8·76
0·35	8·02	7·85	8·11	$0{\cdot}05_9$	7·87	8·10	$0{\cdot}06_4$	7·79	8·14
0·40	7·54	7·43	7·59	$0{\cdot}00_8$	7·45	7·59	$0{\cdot}00_9$	7·40	7·61
0·45	7·10	7·04	7·13	$-0{\cdot}01_4$	7·05	7·13	$-0{\cdot}01_6$	7·02	7·14
0·50	6·67	6·64	6·68	$-0{\cdot}02_1$	6·65	6·68	$-0{\cdot}02_3$	6·63	6·69
0·60	5·83	5·83	5·83	$-0{\cdot}01_5$	5·83	5·83	$-0{\cdot}01_7$	5·83	5·83
0·70	5·02	5·03	5·02	$-0{\cdot}00_5$	5·03	5·02	$-0{\cdot}00_6$	5·03	5·02
0·80	4·28	4·29	4·28	$0{\cdot}00_2$	4·29	4·28	$0{\cdot}00_2$	4·29	4·28
0·90	3·64	3·64	3·64	$0{\cdot}00_6$	3·64	3·64	$0{\cdot}00_7$	3·64	3·64
1·00	3·11	3·11	3·11	$0{\cdot}00_8$	3·11	3·11	$0{\cdot}00_8$	3·11	3·11
1·10	2·69	2·69	2·69	$0{\cdot}00_8$	2·69	2·69	$0{\cdot}00_9$	2·69	2·69

Table 2. (*cont.*)

	sp^3 S					sp^2 S							
						as $(3p)^2(3s\,3p)^4$				as $(3p)^1(3s\,3p)^5$			
$\sin\theta/\lambda$	$\bar{f}_c$	$f_1^{\parallel}$	$f_2^{\parallel}$	$f_3^{\parallel}$	$f_a^{\parallel}$	$f_1^{\parallel}$	$f_2^{\parallel}$	$f_3^{\parallel}$	$f_a^{\parallel}$	$f_1^{\parallel}$	$f_2^{\parallel}$	$f_3^{\parallel}$	$f_a^{\parallel}$
0·00	16·00	16·00	16·00	16·00	0·000	16·00	16·00	16·00	0·000	16·00	16·00	16·00	0·000
0·05	15·54	15·59	15·49	15·54	$0{\cdot}35_3$	15·59	15·50	15·53	$0{\cdot}33_3$	15·49	15·58	15·55	$-0{\cdot}33_3$
0·10	14·33	14·49	14·18	14·33	$0{\cdot}58_9$	14·50	14·19	14·30	$0{\cdot}55_6$	14·16	14·47	14·37	$-0{\cdot}55_6$
0·15	12·75	13·02	12·48	12·75	$0{\cdot}65_6$	13·05	12·51	12·69	$0{\cdot}61_8$	12·45	12·99	12·81	$-0{\cdot}61_8$
0·20	11·21	11·55	10·87	11·21	$0{\cdot}58_0$	11·59	10·91	11·14	$0{\cdot}54_7$	10·83	11·51	11·29	$-0{\cdot}54_7$
0·25	9·93	10·27	9·59	9·93	$0{\cdot}43_2$	10·31	9·62	9·85	$0{\cdot}40_7$	9·55	10·24	10·01	$-0{\cdot}40_7$
0·30	8·99	9·29	8·69	8·99	$0{\cdot}27_5$	9·33	8·72	8·92	$0{\cdot}25_9$	8·66	9·26	9·06	$-0{\cdot}25_9$
0·35	8·32	8·56	8·09	8·32	$0{\cdot}14_8$	8·58	8·11	8·27	$0{\cdot}13_9$	8·06	8·53	8·37	$-0{\cdot}13_9$
0·40	7·83	8·00	7·66	7·83	$0{\cdot}06_1$	8·02	7·68	7·79	$0{\cdot}05_7$	7·65	7·98	7·87	$-0{\cdot}05_7$
0·45	7·42	7·53	7·31	7·42	$0{\cdot}01_0$	7·54	7·32	7·40	$0{\cdot}00_9$	7·30	7·52	7·44	$-0{\cdot}00_9$
0·50	7·05	7·11	6·99	7·05	$-0{\cdot}01_6$	7·12	6·99	7·04	$-0{\cdot}01_5$	6·98	7·11	7·06	$0{\cdot}01_5$
0·60	6·31	6·32	6·30	6·31	$-0{\cdot}02_5$	6·33	6·30	6·31	$-0{\cdot}02_3$	6·30	6·32	6·31	$0{\cdot}02_3$
0·70	5·56	5·56	5·57	5·56	$-0{\cdot}01_5$	5·56	5·56	5·56	$-0{\cdot}01_4$	5·57	5·56	5·56	$0{\cdot}01_4$
0·80	4·82	4·81	4·83	4·82	$-0{\cdot}00_4$	4·81	4·83	4·82	$-0{\cdot}00_4$	4·83	4·81	4·82	$0{\cdot}00_4$
0·90	4·15	4·14	4·16	4·15	$0{\cdot}00_4$	4·14	4·16	4·15	$0{\cdot}00_4$	4·16	4·15	4·15	$-0{\cdot}00_4$
1·00	3·56	3·56	3·56	3·56	$0{\cdot}00_8$	3·56	3·56	3·56	$0{\cdot}00_8$	3·56	3·56	3·56	$-0{\cdot}00_8$
1·10	3·07	3·07	3·07	3·07	$0{\cdot}01_0$	3·07	3·07	3·07	$0{\cdot}01_0$	3·07	3·07	3·07	$-0{\cdot}01_0$

	sp^3 Cl				sp^2 Cl				
					as $(3p)^2(3s\,3p)^5$			as $(3p)^1(3s\,3p)^6$	
$\sin\theta/\lambda$	$\bar{f}_c$	$f_c^{\parallel}$	$f_c^{\perp}$	$f_a^{\parallel}$	$f_c^{\parallel}$	$f_c^{\perp}$	$f_a^{\parallel}$	$f_c^{\parallel}$	$f_c^{\perp}$
0·00	17·00	17·00	17·00	0·000	17·00	17·00	0·000	17·00	17·00
0·05	16·55	16·59	16·53	$-0{\cdot}27_7$	16·58	16·53	$-0{\cdot}30_2$	16·60	16·53
0·10	15·33	15·46	15·27	$-0{\cdot}47_9$	15·45	15·27	$-0{\cdot}52_2$	15·50	15·24
0·15	13·68	13·92	13·56	$-0{\cdot}56_5$	13·89	13·58	$-0{\cdot}61_5$	14·00	13·52
0·20	12·00	12·32	11·84	$-0{\cdot}54_1$	12·28	11·86	$-0{\cdot}58_9$	12·42	11·79
0·25	10·55	10·90	10·38	$-0{\cdot}44_5$	10·86	10·40	$-0{\cdot}48_5$	11·02	10·32
0·30	9·44	9·77	9·27	$-0{\cdot}32_2$	9·74	9·29	$-0{\cdot}35_0$	9·88	9·22
0·35	8·64	8·93	8·50	$-0{\cdot}20_5$	8·89	8·51	$-0{\cdot}22_3$	9·02	8·45
0·40	8·07	8·29	7·96	$-0{\cdot}11_2$	8·27	7·97	$-0{\cdot}12_2$	8·37	7·92
0·45	7·65	7·81	7·57	$-0{\cdot}04_8$	7·79	7·58	$-0{\cdot}05_2$	7·87	7·54
0·50	7·29	7·40	7·24	$-0{\cdot}00_9$	7·39	7·24	$-0{\cdot}00_9$	7·44	7·22
0·60	6·64	6·68	6·62	$0{\cdot}02_1$	6·67	6·62	$0{\cdot}02_3$	6·69	6·61
0·70	5·96	5·97	5·96	$0{\cdot}02_0$	5·96	5·96	$0{\cdot}02_2$	5·97	5·96
0·80	5·27	5·26	5·27	$0{\cdot}01_1$	5·26	5·27	$0{\cdot}01_2$	5·26	5·27
0·90	4·60	4·59	4·60	$0{\cdot}00_2$	4·59	4·60	$0{\cdot}00_2$	4·59	4·61
1·00	4·00	3·99	4·00	$-0{\cdot}00_5$	3·99	4·00	$-0{\cdot}00_5$	3·99	4·00
1·10	3·47	3·47	3·47	$-0{\cdot}00_8$	3·47	3·47	$-0{\cdot}00_9$	3·47	3·47

$$
\begin{aligned}
f^{\parallel}(3s\,3p) = i\surd(3M^2/(1-\alpha_{23}^2)) \\
\times \{(A_1/3x_1)[(S_4(x_1)/x_1) - C_5(x_1)] \\
- (Q_1+\alpha_{23})(A_2/3x_2)[(S_3(x_2)/x_2) - C_4(x_2)] \\
+ (Q_1\alpha_{23}A_3/3x_3)[(S_2(x_3)/x_3) - C_3(x_3)] \\
- (Q_2A_4/x_4)[(S_2(x_4)/x_4) - C_3(x_4)] \\
+ (Q_2\alpha_{23}A_5/x_5)[(S_1(x_5)/x_5) - C_2(x_5)]\},
\end{aligned}
$$

where

$$A_4 = 4\pi N_{3s}N_{1s}/(c_3+c_1)^5, \quad A_5 = 4\pi N_{2s}N_{1s}/(c_2+c_1)^4,$$

$$x_4 = 4\pi X/(c_3+c_1), \quad x_5 = 4\pi X/(c_2+c_1) \quad (X = \sin\theta/\lambda),$$

and the other A_n and x_n are defined in Dawson (1961). The integrals $S_n(x)$ and $C_n(x)$ have the simple forms discussed by McWeeny (1951).

The values of the different sp^3 and sp^2 valence state f-components derived from these sources of ground state data are listed in Table 2. Values of the sp states are readily obtained from values of the other states there. The columns for centric scattering in the sp^3 and two sp^2 states are from the simplified expressions using $f(ns) = \bar{f}(np)$. With this simplification, the spherically averaged scattering powers of the different 'prepared' states are the same, and equal to spherically averaged ground state scattering, and these values are denoted $\bar{f}_c$ in the sp^3 group for each atom. The result of not assuming that $f(ns) = \bar{f}(np)$ is shown in the columns headed δ, the values there being those that must be added to the centric values listed for each hybrid state if this simplification is not used: it is clear that only small changes are involved. The values of the acentric components $f_a^{\parallel}$ are for the sense of the axes illustrated in Fig. 3. For the sp^2 state of N as $(1s)^2(2p)^1(2s\,2p)^4$, *i.e.* 1(*b*) (i) earlier, the values of $f_a^{\parallel}$ obtained from Duncanson & Coulson (1948) functions are listed in brackets alongside the Hartree–Fock values: the trend of the small differences between these sets is similar to that noted in values of $d(2p)$ for O and F derived from these two types of radial functions.

Discussion

At this point, it is useful to summarize the general aims of this investigation. We have been concerned with a simple examination of possible charge distributions of atoms containing lone pairs as well as bonding electrons in their valence shells, with a view to assessing the implications of the normal $\bar{f}$-approximation in detailed X-ray structure analysis. The hybrid orbital approach adopted in postulating various 'prepared' valence states, which comply with different idealized geometrical groupings containing these atoms as a central member, is designed to accord with the rather naive concept of a chemical bond based on perfect pairing (Coulson, 1961). The limitations of this concept are apparent in extensive contemporary calculations of molecular structure (see Coulson, 1960; and succeeding papers there), but it nevertheless provides a logical starting point here. The scattering powers of the various 'prepared' states examined represent a natural extension of earlier calculations of aspherical ground state scattering (McWeeny, 1951; Freeman, 1959*a*; Dawson, 1961). Their main function is twofold: firstly, to examine whether valence state considerations modify earlier conclusions regarding suitable strategy to employ in X-ray analysis aiming to define fine details of molecular structure (Dawson, 1961); and secondly, to gain information on the type and magnitude of fine detail we may expect to define in favourable circumstances. We shall only review here briefly some of the general conclusions that emerge from the ground state and prepared state results obtained for the different atoms. Fuller discussion of structure refinement involving acentric atoms is deferred to the accompanying paper (Dawson, 1964*a*) where the sp^3 f-data for N are used to examine position and thermal motion refinement in a hypothetical structure.

For centric scattering, the main differences between the two states occur for group V, where the spherical symmetry of the ground state is replaced in the hybrid states by an aspherical charge distribution component. For group VII, this scattering is aspherical in both states, and the axes required to define it have a common structural definition: the charge distributions are oblately spheroidal, and either identical or else very similar in the two states. For group VI, there is the formal difference that the two axes required for the prolate spheroid of the ground state distribution are replaced (generally) by three axes required for the ellipsoidal distribution associated with the centric valence scattering, but there is again a common relationship in the definition of some axes. Thus, for triatomic groupings, the axis defined as y in 2(*a*) and 2(*b*) (i) and as x in 2(*b*) (ii) and 2(*c*) (i) (Fig. 3) has the same structural description as that employed in ground state scattering, namely, the normal to the plane of the three atoms. In this direction, the ellipsoidal components, $f_2^{\parallel}$ in 2(*a*) and 2(*b*) (i) or $f_1^{\parallel}$ in 2(*b*) (ii) and 2(*c*) (i), are numerically similar to the ground state $f^{\parallel}$ component (see 2(*d*) (i) of Table 1). It is only normal to this direction, in the triatomic plane, that the $f^{\perp}$ component of 2(*d*) (i) is replaced by two valence state components. The allowance for aspherical centric valence scattering for these atoms by a ground state treatment can therefore be regarded as a useful intermediate approximation for cases of geometrical ambiguity discussed in (2) and (2*A*) earlier.

The acentric scattering component of certain hybrid valence states has no counterpart in ground state treatments, and its possible presence has some interesting implications for structure refinement and interpretation. Since it arises from a charge distribution component which is antisymmetric about the atomic centre (Fig. 1(*d*)), the detection of such features in 'difference' maps (Cochran, 1951) of accurately refined (in atomic position and thermal motion) molecular structures should be capable, in principle, of resolving the geometrical ambiguities of axial assignment which were shown earlier to arise in certain prepared states. In the sp^2 state for O in 2(*b*) (ii), for instance, the symmetry axis of these features would be the O–*C* bond direction, thereby eliminating the previous ambiguity of the y- and z-axis directions. Difference maps will, of course, also display any additional features arising from the fact that we are dealing with an assemblage of bonded atoms rather than isolated atoms considered to be in appropriate 'prepared' valence states. The present results can offer no guidance on this question of scattering power differences between 'prepared' and bonded atoms: but the significant examinations of this problem by McWeeny (1952, 1953, 1954), and his final advocacy of 'prepared state' scattering factors, suggest that these differences can be regarded as minor perturbations for even the lighter of the atoms considered here. On this assumption, the antisymmetric charge distribution features discussed above would constitute a source of valuable additional information in applications of difference methods to structure interpretation.

The experimental detection of such features, as well as those associated with aspherical centric scattering if $\bar{f}$ curves are used in a 'difference' procedure, will depend on two broad requirements being satisfied. Firstly, the diffraction data employed must be of high accuracy and reasonably plentiful in the low-angle region, since outer-electron scattering effects are involved and we require measurements over a range of orientations of **S** to the charge distribution axes discussed. This requirement will be governed by the intrinsic nature of the crystallographic system being studied; *i.e.* the size of the unit cell and the systematic absences of the space group. In cases where low-angle

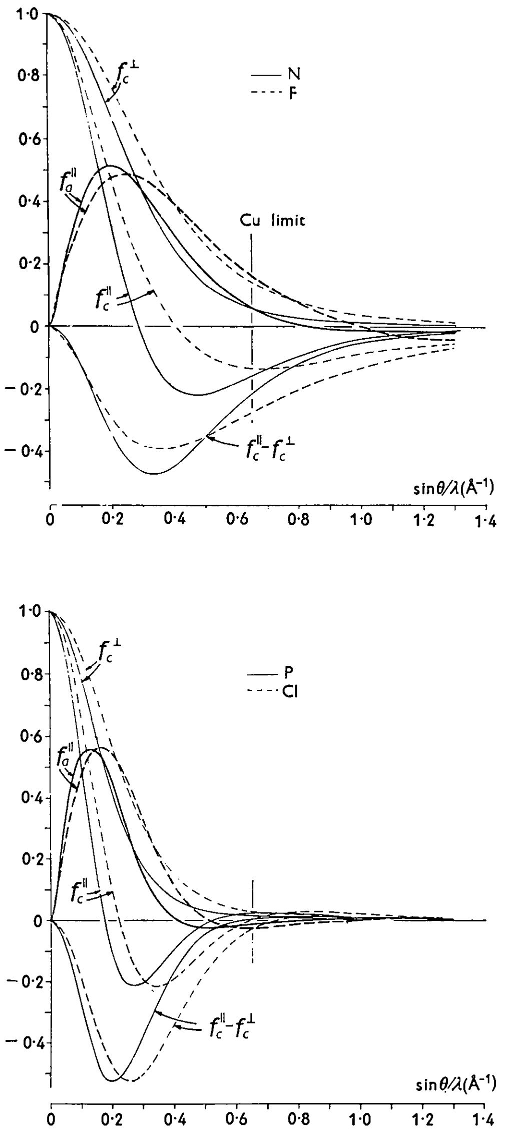

Fig. 4. Comparison of the angular range of the scattering components of an sp^3 hybrid orbital in related second- and third-row atoms.

data are not plentiful, a detailed electron distribution study may still be possible if the molecular system possesses high internal symmetry and a high proportion of aspherical atoms of the same type. Greater chances of success will be offered by second-row rather than third-row atoms since the acentric scattering effects of the former constitute a greater part of the total atomic scattering power and occur over a wider range of $\sin \theta/\lambda$ (Table 2 and Fig. 4). The second requirement is that the nature of the preliminary atomic position and thermal motion refinement must be such as not to obscure the features to be sought for subsequently. This demands the use of high-angle data dominated by inner-electron scattering (McWeeny, 1954; Jeffrey & Cruickshank, 1953). Otherwise, it is likely that the features in Fig 1(*c*) and (*d*) which are of interest may be obliterated by spurious parameter refinement. We examine the possibility of this occurring elsewhere (Dawson, 1964*a*).

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