Aspherical Atomic Scattering Factors for S, S⁻ and Cl

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The spherically-averaged $\bar{f}$-curves for S, S⁻ and Cl recently derived from the ground state poly-detor calculations of Boys & Price (1954) are combined with $f^{\parallel}$ and $f^{\perp}$ values (McWeeny, 1951) calculated for $3p$ electrons described by orthogonalized Slater functions in order to estimate the magnitude and range in $\sin \theta/\lambda$ of aspherical scattering effects in these third-row systems. Comparison of these effects for S and Cl with the results of McWeeny (1951) and Freeman (1959) for $2p$ asymmetry in the lighter analogues O and F shows the reduction in angular range of $3p$ scattering associated with the greater radial extension of $3p$ charge distributions.

The adequacy, for structure analysis, of the Slater-function aspherical modifications to the earlier poly-detor $\bar{f}$-curves is discussed, and the general relevance of these and other calculations of aspherical scattering effects to Cruickshank's (1960) discussion of the use of low temperatures and independent scale determinations in accurate structure investigations is also noted.

Introduction

In deriving new atomic scattering factors recently for the systems S, S⁻ and Cl (Dawson, 1960a) from the poly-detor calculations of Boys & Price (1954), the general coherent scattering integral

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

was used in the simplified form

$$\bar{f} = \int_0^\infty 4\pi r^2 \varrho(r) \sin sr/sr\, dr \tag{2}$$

which describes the spherical approximation to the scattering power of an aspherical charge distribution when averaged over all orientations in space.* Although the use of (2) rather than (1) for aspherical systems has been shown by McWeeny (1951) and Freeman (1959a) to be a rather drastic simplification, its application to Boys & Price's (1954) accurate wave functions is nevertheless valuable for X-ray investigations. The $\bar{f}$-curves derived are not only of general usefulness in structure analyses concerned mainly with atomic-centre location but also, because of their theoretical basis, may be reliably used in more detailed X-ray studies concerned with examining, by 'difference' methods, the aspherical scattering effects which apply to these atoms in any particular chemical structure.

For efficient use of these $\bar{f}$-curves, however, it is clearly desirable to have some guide as to the magnitude and angular (i.e. $\sin \theta/\lambda$) range of scattering asymmetry neglected by using (2). Particularly for refined electron-distribution studies, it is important that the preliminary determinations of atomic position and thermal

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* The notation in (1) and (2) is essentially that of McWeeny (1951) and James (1948).

motion be performed in a manner which does not prejudice the subsequent detection of aspherical scattering effects. While these effects will vary according to changes in the 'prepared' or appropriate valence states (see McWeeny 1951; 1954) of these atoms in different compounds, we may expect that useful information for such studies will result from examining the modifications in the ground-state poly-detor $\bar{f}$-data ($\bar{f}_{PD}$) which are associated with the $3p$-electron asymmetry of these systems.

In this paper, we examine these modifications by using approximate $3p$ wave functions in a McWeeny (1951) treatment. The adequacy of the aspherical results so obtained is discussed, and we also note the general relevance of these results, with those of McWeeny (1951; 1954) and Freeman (1959a), to Cruickshank's (1960) discussion of the use of low temperatures and independent scale determinations in accurate crystal-structure investigations.

Aspherical f-curves for S, S⁻ and Cl

Following McWeeny's treatment of p-electron asymmetry for separable-electron wave-function approximations, we express total aspherical f-curves for these third-row atoms as

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

so that equivalent spherically-averaged f-curves are

$$\bar{f} = \tfrac{1}{3}(f^{\parallel} + 2f^{\perp}) .$$

Here, Θ is the angle which the scattering vector $\mathbf{S}$ makes with the symmetry axis of each system, which is defined as that $3p$ orbital which contains a different number of electrons from the other $3p$ orbitals, and $f^{\parallel}$ and $f^{\perp}$ are the total scattering powers of each

system when $\mathbf{S}$ is parallel and perpendicular, respectively, to this symmetry axis. These 'principal' factors then reduce to

$$f^{\parallel} = \bar{f} - 2a(f^{\perp}(3p) - f^{\parallel}(3p))$$
$$f^{\perp} = \bar{f} + a(f^{\perp}(3p) - f^{\parallel}(3p)) \qquad (3)$$

with $a = \frac{1}{3}$ for S and $a = -\frac{1}{3}$ for S⁻ and Cl, where $f^{\parallel}(3p)$ and $f^{\perp}(3p)$ describe the scattering of a single $3p$-electron for $\mathbf{S}$ parallel and perpendicular to its orbital axis.

In the case of Boys & Price's (1954) poly-detor calculations from which the $\bar{f}_{PD}$ data were derived earlier, this treatment cannot be used directly since the separable-electron approximation does not apply to these calculations and there are no poly-detor '$3p$' functions for calculating $f^{\parallel}(3p)$ and $f^{\perp}(3p)$. However since our main concern here with these two quantities is to obtain an estimate of the extent to which the $\bar{f}_{PD}$ ignore aspherical scattering effects, it is sufficient to calculate them from $3p$ functions which are based on less-exact separable-electron approximations. Two sets of such functions are available for this purpose, either those employed by Boys & Price (1954) in their 'root function' preliminaries to the poly-detor calculations, or those based on Slater (1930) functions. Since the latter are more convenient for computation, and, moreover, it has been shown that their use by Tomiie & Stam (1958) gives $\bar{f}$-results in fair agreement with $\bar{f}_{PD}$ for S and Cl (see Fig. 1 of Dawson, 1960a), we therefore use them here for estimating the effects of $3p$-electron asymmetry.

The orthonormal functions $\varphi'(3p)$ required for (1) are then

$$\varphi'(3p_z) = (1 - \alpha_{23}^2)^{-\frac{1}{2}}[\varphi(3p_z) - \alpha_{32}\varphi(2p_z)]$$
where
$$\varphi(3p_z) = N_{3p}r^2 \cos\theta \exp[-c_3 r],$$
$$\varphi(2p_z) = N_{2p}r \cos\theta \exp[-c_2 r]$$

are unorthogonalized functions with orbital exponents c_3, c_2 given by Slater's (1930) rules, N_{3p} and N_{2p} are normalization constants, and α_{23} is the overlap integral between these functions. Using McWeeny's (1951) treatment and notation, the $3p$ scattering factors then become

$$f^{\parallel}(3p) = (1 - \alpha_{23}^2)^{-1}$$
$$\times \{(A_1/x_1)[S_5(x_1) + (2C_4(x_1)/x_1) - (2S_3(x_1)/x_1^2)]$$
$$- 2\alpha_{23}(A_2/x_2)[S_4(x_2) + (2C_3(x_2)/x_2) - (2S_2(x_2)/x_2^2)]$$
$$+ \alpha_{23}^2(A_3/x_3)[S_3(x_3) + (2C_2(x_3)/x_3) - (2S_1(x_3)/x_3^2)]\},$$
$$f^{\perp}(3p) = (1 - \alpha_{23}^2)^{-1}$$
$$\times \{(A_1/x_1)[-(C_4(x_1)/x_1) + (S_3(x_1)/x_1^2)]$$
$$- 2\alpha_{23}(A_2/x_2)[-(C_3(x_2)/x_2) + (S_2(x_2)/x_2^2)]$$
$$+ \alpha_{23}^2(A_3/x_3)[-(C_2(x_3)/x_3) + (S_1(x_3)/x_3^2)]\}, \qquad (4)$$

where

$$A_1 = 4\pi(N_{3p})^2/(2c_3)^7, \quad A_2 = 4\pi N_{2p}N_{3p}/(c_2 + c_3)^6,$$
$$A_3 = 4\pi(N_{2p})^2/(2c_2)^5$$

$$x_1 = 2\pi X/c_3, \quad x_2 = 4\pi X/(c_2 + c_3), \quad x_3 = 2\pi X/c_2,$$

with $X = \sin\theta/\lambda$, and $\alpha_{23} = (5)^{\frac{1}{2}}A_2/(6A_1A_3)^{\frac{1}{2}}$.

Further reduction gives finally

$$f^{\parallel}(3p) - f^{\perp}(3p) = (1 - \alpha_{23}^2)^{-1}$$
$$\times \{(8/5)(x_1^2(3x_1^2 - 7)/(x_1^2 + 1)^6)$$
$$- 6\alpha_{23}^2[(2/5)(x_2^2(x_2^2 - 7)/(x_2^2 + 1)^5) + x_3^2/(x_3^2 + 1)^4]\}$$

for combination with the $\bar{f}_{PD}$ in (3).

Table 1 lists the poly-detor $\bar{f}$-values, the $f^{\parallel}$ and $f^{\perp}$ modifications to these values given by the above treatment, and also the Slater function values of $\bar{f}(3p)$ obtained from the appropriate combination of equations (4) (which then reduces to the result given by Tomiie & Stam (1958)).

Table 1. *Atomic scattering factors for S, S⁻ and Cl*

sin θ/λ (Å⁻¹)	S				S⁻				Cl			
	$\bar{f}$	$f^{\parallel}$	$f^{\perp}$	$\bar{f}(3p)$	$\bar{f}$	$f^{\parallel}$	$f^{\perp}$	$\bar{f}(3p)$	$\bar{f}$	$f^{\parallel}$	$f^{\perp}$	$\bar{f}(3p)$
0·00	16·00	16·00	16·00	(1·000)	17·00	17·00	17·00	(1·000)	17·00	17·00	17·00	(1·000)
0·05	15·54	15·48	15·57	(0·93₁)	16·45	16·52	16·41	(0·92₉)	16·55	16·60	16·52	(0·94₄)
0·10	14·33	14·13	14·44	(0·75₃)	15·00	15·23	14·89	(0·72₄)	15·33	15·50	15·24	(0·79₆)
0·15	12·75	12·39	12·93	(0·53₀)	13·14	13·52	12·95	(0·48₇)	13·68	14·00	13·53	(0·60₁)
0·20	11·21	10·75	11·43	(0·32₈)	11·36	11·82	11·13	(0·28₃)	12·00	12·43	11·79	(0·40₇)
0·25	9·93	9·47	10·16	(0·17₉)	9·95	10·39	9·72	(0·14₄)	10·55	11·02	10·32	(0·24₉)
0·30	8·99	8·58	9·19	(0·08₈)	8·95	9·32	8·76	(0·06₅)	9·44	9·88	9·22	(0·13₉)
0·35	8·32	8·00	8·47	(0·04₁)	8·27	8·54	8·13	(0·02₉)	8·64	9·02	8·45	(0·07₂)
0·40	7·83	7·61	7·94	(0·02₂)	7·79	7·98	7·70	(0·01₇)	8·07	8·37	7·93	(0·03₇)
0·45	7·42	7·28	7·49	(0·01₇)	7·40	7·51	7·35	(0·01₄)	7·65	7·86	7·54	(0·02₂)
0·50	7·05	6·97	7·09	(0·01₇)	7·05	7·11	7·02	(0·01₅)	7·29	7·44	7·22	(0·01₈)
0·60	6·31	6·29	6·32	(0·02₀)	6·32	6·33	6·32	(0·01₇)	6·64	6·69	6·61	(0·02₀)
0·70	5·56	5·56	5·55	(0·02₀)	5·57	5·56	5·57	(0·01₆)	5·96	5·97	5·96	(0·02₂)
0·80	4·82	4·83	4·81	(0·01₈)	4·83	4·82	4·83	(0·01₄)	5·27	5·26	5·27	(0·02₂)
0·90	4·15	4·16	4·14	(0·01₆)	4·16	4·15	4·16	(0·01₂)	4·60	4·59	4·61	(0·02₀)
1·00	3·56	3·56	3·56	(0·01₂)	3·57	3·57	3·57	(0·00₉)	4·00	3·99	4·00	(0·01₇)
1·10	3·07	3·07	3·07	(0·01₀)	3·08	3·08	3·08	(0·00₇)	3·47	3·47	3·47	(0·01₄)
1·20	2·66	2·66	2·67	(0·00₇)	2·67	2·67	2·67	(0·00₅)	3·02	3·03	3·02	(0·01₁)
1·30	2·34	2·34	2·34	(0·00₅)	2·34	2·35	2·34	(0·00₄)	2·65	2·66	2·65	(0·00₈)

Discussion

The values of $(f^{\perp}(3p)-f^{\parallel}(3p))$ and $\bar{f}(3p)$ obtained here for S and Cl are compared in Figure 1 with similar results for $2p$-electron scattering in the lighter analogues O and F given by the calculations of McWeeny (1951), using Duncanson & Coulson (1944) wave functions, and those of Freeman (1959a,b), using more accurate Hartree-Fock data. The differences between the results for second and third row elements are as expected: the scattering powers of the radially more-extended $3p$ charge distributions are appreciable over a smaller range of $\sin \theta/\lambda$ than is the case with the more compact $2p$ distributions. Apart from such differences however, it is seen that McWeeny's (1951) observations regarding the disparity between rate of fall-off, with $\sin \theta/\lambda$, of the spherically-averaged and aspherical components of $2p$-electron scattering apply equally strongly to $3p$ scattering. (The same also applies to $3d$ scattering (Freeman, 1959a)). Since the number of diffraction data within any limiting value of $\sin \theta/\lambda$ is proportional, in two- and three-dimensions, to $(\sin \theta/\lambda)^2$ and $(\sin \theta/\lambda)^3$ respectively, the consequences of the differences between the $\bar{f}(3p)$ and $(f^{\perp}(3p)-f^{\parallel}(3p))$ are thus considerable: whereas the former decrease so rapidly that only the sparse innermost data are at all affected by this quantity, the latter show that aspherical scattering effects may have, in circumstances where thermal motion is small (see below), an appreciable influence on a large proportion of the data accessible to Cu $K\alpha$-radiation* ($\sin \theta/\lambda \leq 0.65$ Å^{-1}).

Some indication of the approximate nature of the $f^{\parallel}, f^{\perp}$ modifications to $\bar{f}_{PD}$ obtained here via Slater functions is given by the differences between McWeeny's (1951) and Freeman's (1959a,b) results for O and F in Fig. 1. Better estimates of these modifications would be obtained, especially for S and Cl, by combining the $\bar{f}_{PD}$ with $f^{\parallel}(3p)$ and $f^{\perp}(3p)$ values derived from Hartree-Fock radial functions; and such a combination would involve negligible errors associated with the use of the convenient separable-electron treatment discussed earlier, since comparison of poly-detor and Hartree-Fock f-curves and mean radii for Na$^+$ and Ne (Dawson, 1961) shows that only small differences exist between results for positive and neutral systems given by these two methods. However, apart from the fact that Hartree-Fock calculations on these third-row systems have not yet been made, it is doubtful whether the higher numerical accuracy of the 'principal' factors so obtained would be generally useful in X-ray electron-distribution studies involving these atoms, except in those compounds

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* This suggests that, where X-ray study is attempting to determine the state of ionization of an atom, and one of the possibilities is a spherically symmetric state while the other is not, the likelihood of success should be considerably greater than that implied by the small differences, at low angles, between the $\bar{f}$-curves of the two states (Bijvoet &Lonsdale, 1953). Obvious instances here are Cl$^-$ and Cl, or F$^-$ and F.
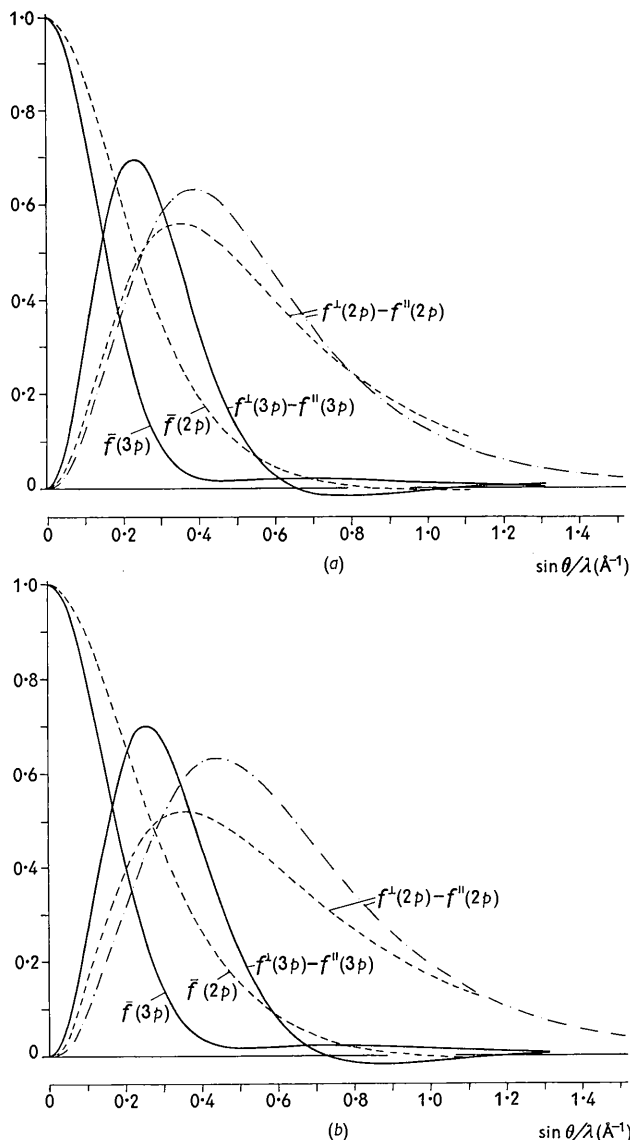

Fig. 1. Comparison of $\bar{f}(3p)$ and $(f^{\perp}(3p)-f^{\parallel}(3p))$ data for S and Cl with analogous results for $2p$ scattering in O and F: (a) is for S and O, and (b) is for Cl and F. The full lines are for S and Cl, the broken lines are for O and F from Freeman (1959a, b), and the chain lines for O and F are from McWeeny (1951).

where it could be demonstrated (by theoretical argument or other physical evidence) that an essentially p-type bonding description is more probable than one involving orbitals based on extensive s–p or s–p–d hybridization. In such compounds, some of which will be considered shortly (Dawson & Hurley, 1962), the higher accuracy of the Hartree-Fock estimates could be valuable in any attempt to define small differences between the aspherical scattering powers of the isolated and bonded atom ($c.f.$ McWeeny, 1954). Usually, however, the aim of an electron-distribution

study will be the demonstration of the presence of bonded-atom scattering asphericity by reference to an accurate free-state $\bar{f}$-curve. It is then more important to estimate the range of $\sin \theta/\lambda$ over which diffraction data may manifest these effects than it is to calculate them accurately for isolated atoms, and the present treatment with Slater functions should satisfy this requirement adequately.

The angular range of aspherical $3p$-scattering influence is in general accord with Freeman's (1959a) results for $3d$-scattering in the first-row transition metals, and adds further weight to earlier observations of McWeeny (1954) and Jeffrey & Cruickshank (1953) stressing the importance of the higher-angle diffraction data accessible to radiation shorter than Cu $K\alpha$ (i.e. Mo $K\alpha$ or Ag $K\alpha$) in the determination of atomic position and thermal motion parameters. Cruickshank (1960) has recently discussed this and other requirements that must be satisfied for accurate single-crystal analysis, and some observations on his comments regarding low-temperature data collection* and the desirability of independent scale determination are relevant here. Using low temperatures, a majority of the data available for structure analysis then depends on the scattering powers of the inner regions of the atomic-charge distributions. This scattering is virtually independent of either bonding or other aspherical effects associated with the outer regions of the charge distributions and may be regarded as essentially spherically symmetric scattering, appropriately modified by thermal and zero-point motion. At first sight, the extensive range of the aspherical scattering effects in second-row atoms (e.g. Figure 1: see also McWeeny (1951) and Freeman (1959a)) suggests that this is not a feasible assumption in these important cases: however the influence of even quite small atomic motion will be so effective in reducing differences between the two extremes, $f^{\parallel}$ and $f^{\perp}$, over the range of $\sin \theta/\lambda$ between Cu- and Mo-limits that it is still realistic for practical purposes to regard this range of scattering as spherically symmetric. This has two important consequences. Firstly it represents a justification for the use of the high-angle regions of isolated-atom $\bar{f}$-curves in the determination of atomic and thermal parameters. Secondly, it suggests that absolute scaling of three-dimensional data may also be achieved satisfactorily by reference to these regions of such $\bar{f}$-curves, provided these have been derived from atomic wavefunction approximations which give reliable scattering descriptions of the inner regions of atomic charge distributions (Black (1955); Dawson (1960a,b; 1961)) relating to differences

* The combination of low temperatures and short radiation favours not only the minimization of anomalous-scattering corrections (e.g. Dauben & Templeton, 1955) but also the accuracy with which the high-angle data are measured, due to reduction in both the influence of thermal motion on the intensities themselves and also the contribution which thermal diffuse scattering makes (together with Compton scattering) to the 'background' against which the intensities are measured).

between $\bar{f}$-curves derived from poly-detor and other approximations). This is the internal scaling process normally employed in structure analysis, and despite some slight indeterminacy arising from the strong correlation between scale and thermal parameters (Cruickshank, 1960), it is likely that such a process will be more reliable* than independent determinations involving reference to external measurements or 'standards'. Accuracy in such determinations involves considerable experimental difficulties, and McDonald (1960), for instance, has noted that the scale of his F's so determined was uncertain to possibly $\pm 5\%$.

The reliability of internal scaling procedures in accurate structure investigations at low temperatures thus bears on the extension here of McWeeny's and Freeman's results on aspherical scattering ranges in isolated atoms at rest and in their ground states. The present work cannot however assess whether, for light (i.e. second-row) atoms, it is important for scaling accuracy that the high-angle regions of $\bar{f}$-curves for valence state rather than ground-state approximations be employed. McWeeny's (1951) and Hoerni & Iber's (1954) results for carbon suggest that further work is desirable, and the examination of the high $\sin \theta/\lambda$ regions of $\bar{f}$-curves of carbon and boron derived from the poly-detor calculations of Boys (1953) for various configurations of these atoms will be reported later.

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* In least-squares calculations, the weights must be chosen correctly, however (see Cruickshank *et al.* (1960)).