Acta Cryst. (1960). **13**, 403

Atomic Scattering Factors from Wave Functions Calculated by the Poly–Detor Method: Cl, Cl$^-$, S and S$^-$

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(*Received* 9 *July* 1959 *and in revised form* 7 *October* 1959)

Earlier atomic scattering factors used for Cl, Cl$^-$ and S in structure analysis are discussed, and new scattering factors for these atoms, and for S$^-$, reported. The new results are based on the ground-state atomic wave functions of Boys & Price (1954) calculated by the variational poly-detor method. A brief description of this method is given with regard to certain features of these wave functions, and it is shown that the atomic scattering factors obtained here represent good, spherically-averaged, approximations to the scattering powers of these atoms in the solid state. The new results are compared with those obtained from self-consistent field and Slater wave functions, and the differences discussed.

Introduction

Improved atomic scattering factors (f-curves) based on self-consistent field (SCF) data in the Hartree–Fock (HF) approximation, which considers the effects of correlation between electrons of like spin i.e. exchange (see Hartree (1957) for discussion of SCF methods), have now been derived for many atoms using the familiar expression

$$f(s) = \int_0^\infty 4\pi r^2 \varrho(r) \sin 4\pi sr/4\pi sr\,dr \qquad (1)$$

appropriate to real or averaged spherical symmetry of the charge distribution in an atom ($s = \sin\theta/\lambda$ and $4\pi r^2\varrho(r)$ is the total radial charge density). Comparison of such HF f-curves with f-curves derived from SCF results in the Hartree (H) approximation, which neglects exchange, shows that the influence of these correlation effects is considerable, particularly on the values of f in the region of small s: the HF values are appreciably higher than the H values due to the radial contraction of the charge distribution, and most notably the 'tail' of the distribution in the region of large r, that occurs when exchange is included in the SCF calculation.

For neutral Cl and S, however, SCF data in either approximation are lacking, so that f-curves for these atoms have been derived by other methods. The James & Brindley (1931) (hereafter JB) results (and those of Viervoll & Øgrim (1949)) are by interpolation, essentially from SCF results for Cl$^-$ in the H approximation (Hartree, 1928, 1933). Interpolation from this base-line has meant, therefore, that, apart from uncertainties in the interpolation process itself, the low-angle regions of the JB curves will be deficient by amounts similar to those in the H f-curve for Cl$^-$. An estimate of these deficiencies can be obtained from comparison of the JB results for Cl$^-$ with the Berghuis *et al.* (1955) results for the HF approximation of Cl$^-$ (Hartree & Hartree, 1936). However, while such an estimate would permit useful correction of base-line errors in the JB values for Cl and S, the resultant f-curves would still be rather unsatisfactory because of interpolation uncertainties that obviously remain. These uncertainties are avoided in the f-curves for Cl and S derived recently by Tomiie & Stam (1958) from Slater functions, but the approximate nature of these functions makes the reliability of these curves again somewhat doubtful.

It is important that f-curves for neutral and ionized states of chlorine and sulphur be known with an adequacy suited to modern methods of structure refinement, since the scattering powers of these atoms are not only large enough to assist in the initial stages of phase determination but also sufficiently small not to impede too seriously the subsequent definition of structural features related to the disposition of associated light atoms. We report here f-curves for Cl, Cl$^-$, S and S$^-$, derived *via* equation (1), which are based on the ground-state wave functions of Boys & Price (1954) calculated by the variational poly-detor (PD) method (Boys, 1950*a*, *b*; 1951*a*, *b*, *c*; 1952; Bernal & Boys, 1952*a*, *b*; Boys, 1953*a*, *b*). In terms of the customary criterion of minimum calculated energy, the PD method represents a considerable improvement over SCF methods as normally employed in complex systems.

In addition to providing adequate spherically-averaged f-curve data for Cl, S and S$^-$, the PD results in the case of Cl$^-$ also permit examination of the suitability of this ion's HF f-curve in detailed structure analysis. Evidence of possible improvement in the HF curve in this regard lies in the discrepancy existing between the observed value of the molar diamagnetic susceptibility and that calculated for the HF charge density. While the HF value is significantly better than the H value (see Table 3) due to the 'tail' contraction produced by exchange, the discrepancy remaining is consistent with a further 'tail' contraction, due either to correlation effects not included in the HF approximation, or to solid-state effects, or both. Tentative indications in accord with this further contraction were obtained in an experimental scattering curve for Cl⁻ derived from the structure analysis of DL-aspartic acid hydrochloride (Dawson, 1960), and are supported by the PD results for Cl⁻ reported here.

Basis of present work

The PD method expresses the total electronic wave function, Ψ, calculated for an atom, in terms of a linear combination of co-detors Φ_r, where the co-detors are themselves linear *co*mbinations of detors (Slater *det*erminants of *or*thonormal single-electron wave functions) with the multiplicity and spatial symmetry of the atomic state considered (Boys, 1950*b*). Thus

$$\Psi = \sum_r Y_r \Phi_r \,,$$

where the coefficients Y_r are determined by the variation method to achieve a minimum value of the total energy. This multi-determinantal form permits efficient allowance to be made in the wave-function calculation for electron correlation effects which cannot be considered in the more-usual single co-detor approximation e.g. the HF approximation. The single-electron wave functions constituting the various detors consist of orthonormal functions whose radial parts φ_i are constructed by linear combination from members of a set of elementary functions of the form $r^n \exp(-\alpha r)$: that is

$$\varphi_i = \sum_{n,\alpha} X_i(n,\alpha) r^n \exp(-\alpha r) \,,$$

where the $X_i(n,\alpha)$ are the coefficients of the members for each of the φ_i constructed. Boys (1950*a*) has shown that the PD calculation will converge to the actual atomic wave function as the set of elementary functions is expanded in number, and all co-detors corresponding to these are included in the variation calculation. In practice, the PD method is generally aimed at obtaining wave functions with energies significantly lower than those given by the HF method, while keeping the amount of numerical work in both cases roughly the same: for this aim, the functions of the elementary set are chosen so that the normal single co-detor approximation (termed the 'root function') is sufficiently good, preferably in terms of the experimental energy if this is known, for the improvements in the calculated energy made by the additional co-detors to be achieved as rapidly as possible. For discussion of the choice of elementary functions, the approximate physical significance of the various co-detors in terms of radial and angular correlation effects and configurational interaction, and for results obtained for various light atoms, see Bernal & Boys (1952*b*) and Boys (1953*a*, *b*).

The PD calculations of Boys & Price (1954) for Cl, Cl⁻, S and S⁻ used elementary functions in the form $r_k^n \exp(-\alpha_k r_k)$, where $r_k = kr$ so that $\alpha_k = \alpha/k$: k, a 'stretching' factor, had the values 17/8 (2·125) for Cl and Cl⁻ and 2 for S and S⁻. These values, whose ratio is that of the atomic numbers, provided compensation for the different nuclear charges, thereby permitting a common set of elementary functions to be used in constructing a common set of φ_i functions for the subsequent PD calculations of each atom. The elementary set, chosen among other things to allow a first-order relativistic correction to be applied to the 1*s* electrons, consisted of the 'stretched' functions

$$\exp(-8r_k),\ \exp(-7r_k),\ r_k\exp(-12r_k),\ r_k\exp(-3r_k),\ r_k^2\exp(-4r_k),\ r_k^2\exp(-3r_k),\ r_k^2\exp(-r_k)\ \text{and}\ r_k^3\exp(-r_k)\,.$$

The ground-state wave functions were expressed in terms of twenty-three co-detors for Cl⁻ and thirty for Cl, S and S⁻, the smaller number for Cl⁻ following from the higher symmetry of this closed-shell ion. Boys & Price (1954) list the co-detor coefficients Y_r obtained for each atom, and the coefficients X_i of the elementary set members used in each of the twelve common φ_i functions employed.

Details of the calculation of the PD radial charge densities from the wave function data of Boys & Price (1954) will be given separately (Dawson & Hurley, 1960), together with the numerical values of $4\pi r^2\varrho(r)$ for each atom. These were obtained by evaluating the 'stretched' elementary functions at intervals $r_k = 2{\cdot}125 r_{\text{HF}}$, where r_{HF} were the intervals used by Hartree & Hartree (1936) for the HF calculation of Cl⁻, so as to permit any differences between the PD and HF *f*-curves for this ion to be examined in terms of differences between the PD and HF total radial charge densities. (These differences are shown in Fig. 2 below). The same intervals apply to Cl since k is also 2·125 here. For S and S⁻, however, where $k=2$, evaluation of the elementary set at the above intervals gave the radial charge densities in these cases at intervals $r = 2{\cdot}125/2\ r_{\text{HF}}$: i.e. $r(\text{S}, \text{S}^-) = 17/16 r(\text{Cl}, \text{Cl}^-)$. This difference in r-intervals has no real consequence, but it is noted here since, as the integrations in equation (1) were done numerically, it has governed the s-intervals at which the PD *f*-curves have been derived.

Results and comparison with earlier values

The isotropic PD *f*-curves for the ground states of Cl, Cl⁻, S and S⁻ are given in the first four columns of Table 1, at intervals in atomic units (a.u.) of $S = 100\,s/Z$, Z being the atomic number. The numerical integrations were performed with tables of $\sin 4\pi sr/4\pi sr$ containing values at r(a.u.)-intervals 0·000 (0·005) 0·300 (0·025) 0·600 (0·050) 4·000 (0·250) 7·000 and s(a.u.)-intervals 0·000 (0·025) 0·200 (0·050) 0·400 (0·100)

Table 1. *Atomic scattering factors from present and earlier work, at intervals S*

S (atomic units) = 100 s/Z

s is $\sin\theta/\lambda$, Z is the atomic number

S	$f(Cl^-)$*	$f(Cl)$*	$f(S^-)$*	$f(S)$*	$f(Cl^-)$†	$f(Cl^-)$‡	$f(Cl)$‡	$\delta f(Cl^-)$§
0·00000	18·000	17·000	17·000	16·000	18·00	18·00	17·00	0·000
0·14706	17·519	16·594	16·560	15·636	17·40	17·48	16·58	
0·29412	16·216	15·488	15·374	14·647	15·88	16·07	15·46	0·420
0·44118	14·445	13·968	13·770	13·292	14·05	14·22	13·92	
0·58824	12·608	12·361	12·116	11·867	12·33	12·35	12·31	0·455
0·73529	11·001	10·921	10·677	10·594	10·91	10·77	10·88	
0·88235	9·755	9·769	9·567	9·576	9·82	9·60	9·76	0·219
1·02941	8·866	8·915	8·770	8·814	9·01	8·80	8·94	
1·17647	8·251	8·301	8·207	8·253	8·39	8·27	8·36	0·081
1·47059	7·466	7·485	7·445	7·461	7·51	7·59	7·60	0·044
1·76471	6·858	6·855	6·810	6·804	6·82	7·01	7·00	0·054
2·05882	6·233	6·223	6·155	6·142	6·17			0·071
2·35294	5·580	5·571	5·482	5·469	5·52	5·73	5·72	0·086
2·94118	4·331	4·324	4·226	4·216	4·32	4·45	4·45	0·108
3·52941	3·316	3·311	3·228	3·219	3·33	3·40	3·41	
4·11765	2·580	2·575	2·515	2·508	2·62	2·63	2·64	
4·70588	2·082	2·077	2·038	2·032	2·12	2·11	2·11	

* Present results from PD total radial charge densities.

† Dawson (1955) from the HF calculation of Cl^-.

‡ Tomiie & Stam (1958) from Slater functions.

§ Brindley & Ridley (1938) from the difference between the HF and 1933 H calculations of Cl^-.

0·800, which were used some years ago (Dawson, 1955) in deriving the HF f-curve also given in Table 1: these HF results are equivalent, to ±0·01 electrons, to those of Berghuis *et al.* (1955), apart from tabulation at different intervals. The choice of r in these tables corresponds, apart from fineness in interval, to r_{HF}, so that the values of s in S for the PD and HF results for Cl and Cl^- in Table 1 (and also for the other results listed there for these atoms) are given by the s-values in the integration tables. For S and S^-, the use of these tables with the PD charge densities calculated at the different r-intervals noted above gives f-values at s-intervals which are 16/17 times those of Cl and Cl^-. The S-intervals thus represent the common basis for recording all PD f-curve derivations together in Table 1. The fineness of r-interval used in the numerical integrations was chosen to satisfy the customary precautions for accuracy, and the extra values of $4\pi r^2\varrho(r)$ necessary were obtained by six-point Lagrangian interpolation (as had been done for the HF curve mentioned above). The adequacy of these intervals and the interpolation procedure was considered satisfactory as the values of the normalizing integral,

$$\int_0^\infty 4\pi r^2 \varrho(r)\,dr$$

determined in this fashion were 18·0003, 17·0003, 17·0002 and 16·0003 electrons for Cl^-, Cl, S^- and S respectively. The values of the PD f-curves given in Table 1 to three decimal places should therefore be accurate to the second place in terms of the wave functions used in their derivation. The results of interpolating these values to the customary s(Å^{-1})-intervals, using $a_{\mathrm{H}} = 0{\cdot}52917$ Å, are given in Table 2.

Earlier f-curve data for Cl, Cl^- and S are also given in the two tables. The values of the HF f-curve for Cl^- in Table 1 have been mentioned above: these values are used here as the interpolation and integration procedures are identical with those of the PD results. The f-curves of Tomiie & Stam (1958) for Cl^- and Cl from Slater functions are also given in Table 1. The last column there lists the δf-values of Brindley & Ridley (1938) obtained from the differences between the radial charge densities for Cl^- in the HF (Hartree & Hartree, 1936) and the later H (Hartree, 1933) calculations, the latter differing from the earlier H (Hartree, 1928) calculation in being of higher numerical accuracy. Details of the integration (r-intervals *etc.*) are not given by Brindley & Ridley (1938), and it is possible that the values of δf at higher angles might change if derived by the procedure used here. Otherwise, the δf- and HF f-values in Table 1 permit estimation of the f-curve for Cl^- in the 1933 H approximation. Table 2 gives the f-curve for Cl^- in the 1928 H approximation obtained by James & Brindley (1928): again, integration details are not available. But apart from the influence of these effects, differences in the two H f-curves for Cl^-, allowing for the different s-intervals in the two tables, will arise mainly from differences in the numerical accuracy of these two SCF calculations. Table 2 also lists the JB curves of Cl and S interpolated from the 1928 H results for Cl^-. The last column of Table 2 gives the f-curve of S for Slater functions, interpolated from the s-intervals used by Tomiie & Stam (1958).

The results for Cl^-, Cl and S in Tables 1 and 2 are shown in Figs. 1(a), (b) and (c) respectively to the s-limit for Mo-radiation. In each case the complete PD f-curve is given for reference, and the remaining curves show the departures, Δf, of the earlier f-curves from these PD results: for example, the Δf-curve of

Table 2. *Atomic scattering factors from present and earlier work, at intervals of* $\sin\theta/\lambda$ (Å^{-1})

$\sin\theta/\lambda$	f(Cl$^-$)*	f(Cl)*	f(S$^-$)*	f(S)*	f(Cl$^-$)†	f(Cl)†	f(S)†	f(S)‡
0·00	18·00	17·00	17·00	16·00	18·00	17·00	16·00	16·00
0·05	17·46	16·55	16·45	15·54	17·11			15·51
0·10	16·03	15·33	15·00	14·33	15·23	14·6	13·6	14·21
0·15	14·12	13·68	13·14	12·75	13·19			12·57
0·20	12·20	12·00	11·36	11·21	11·50	11·3	10·7	11·02
0·25	10·60	10·55	9·95	9·93	10·23			9·80
0·30	9·41	9·44	8·95	8·99	9·30	9·25	8·95	8·94
0·35	8·59	8·64	8·27	8·32	8·60			8·35
0·40	8·03	8·07	7·79	7·83	8·06	8·05	7·85	7·92
0·50	7·28	7·29	7·05	7·05	7·23	7·25	6·85	7·20
0·60	6·64	6·64	6·32	6·31	6·49	6·5	6·0	6·48
0·70	5·97	5·96	5·57	5·56	5·77	5·75	5·25	5·71
0·80	5·28	5·27	4·83	4·82	5·06	5·05	4·5	4·94
0·90	4·61	4·60	4·16	4·15	4·41	4·4	3·9	4·25
1·00	4·01	4·00	3·57	3·56	3·84	3·85	3·35	3·64
1·10	3·48	3·47	3·08	3·07	3·33	3·35	2·9	3·13
1·20	3·03	3·02	2·67	2·66	2·89			2·71
1·30	2·66	2·65	2·34	2·34	2·51			2·37

* Interpolated from the PD results in Table 1.

† f(Cl$^-$) is James & Brindley's (1928) result for the 1928 H calculation of Cl$^-$: f(Cl) and f(S) are James & Brindley's (1931) values interpolated from this result.

‡ Interpolated from Tomiie & Stam (1958) for Slater functions.

the HF results for Cl$^-$ shows the values (f_{HF}–f_{PD}). The vertical scale of the Δf-curves is ten times that of the f-curves. Fig. 1(a) also shows, as closed circles, the departures for the 1933 H f-curve of Cl$^-$, obtained using the δf-values as mentioned above.

Discussion

Both the JB and the Tomiie & Stam (1958) f-curves are seen from Fig. 1 to display departures from the PD results which are essentially the same for Cl$^-$, Cl and S. In the case of the JB f-curves, the greatest errors occur in the low-angle region which is of importance in electron-distribution studies, and the similarity of the deficiencies here shows that their origin lies mainly in the Cl$^-$ base-line used in the JB interpolation procedure, rather than in the interpolation procedure itself. At higher angles, interpolation effects are seen in the JB Δf-curve for S which has values somewhat larger than those for Cl$^-$ and Cl, but, again over this range of s, the main features of each curve reflect the SCF data (1928 H) employed for Cl$^-$. Allowing for the purely numerical effects shown in Fig. 1(a) by the differences associated with the 1933 H data for Cl$^-$, all three JB f-curves thus display the general pattern of errors noted earlier for results based on the radially overextended charge distributions given by the H method: large f-curve deficiencies at small angles, and smaller deficiencies at larger angles. In the case of Tomiie & Stam's (1958) results, which are from Slater functions with the screening parameters given by Slater's (1930) rules, Fig. 1 shows that the contracted nature of the charge distributions for these approximate wave functions produces f-values which, for most of the s-range, are larger than those obtained from the PD calculations. The Slater function f-values are similar to those which must apply to the PD 'root functions', since the results from Slater's rules are practically the same, after 'stretching', as the first, fourth and seventh members of the PD elementary set given earlier: this was the basis on which this set was chosen, the further five members being then included to improve the Slater approximation. The correspondence between Tomiie & Stam's and the 'root function' f-curves will not be exact since all set members are involved in the latter. However, since the dominant members are those relating to Slater's rules, particularly where the 'root function' description of the inner electrons is concerned (see Boys & Price, 1954), the f-curves of the initial PD approximations will be similar, in the region of large s, to those obtained from the Slater functions. The high-angle features of the Tomiie & Stam Δf-curves therefore provide an indication of the improvements which the complete PD calculations make to the initial description of the inner regions of the charge distributions.

Comparison of PD and HF results can be made only for Cl$^-$: for the HF Δf-curve in Fig. 1(a), uncertainties related to integration procedures have been avoided by use of the HF values given in Table 1. Fig. 1(a) shows that the PD and HF results, while agreeing very closely over the s-range between the Cu and Mo limits ($ca.$ $0·7 < s < 1·3$ Å^{-1}), exhibit large differences over most of the s-range appropriate to Cu-radiation ($s < 0·7$ Å^{-1}). These differences cannot be ascribed, however, to the influence of electron correlation effects not accounted for in the HF approximation. Rather, they arise, largely if not entirely, from certain features of the PD approximation to Cl$^-$ which are associated with the common elementary set used in calculating the wave functions of the neutral and ionized atoms. In discussing these wave functions, Boys & Price (1954) observe that the values calculated

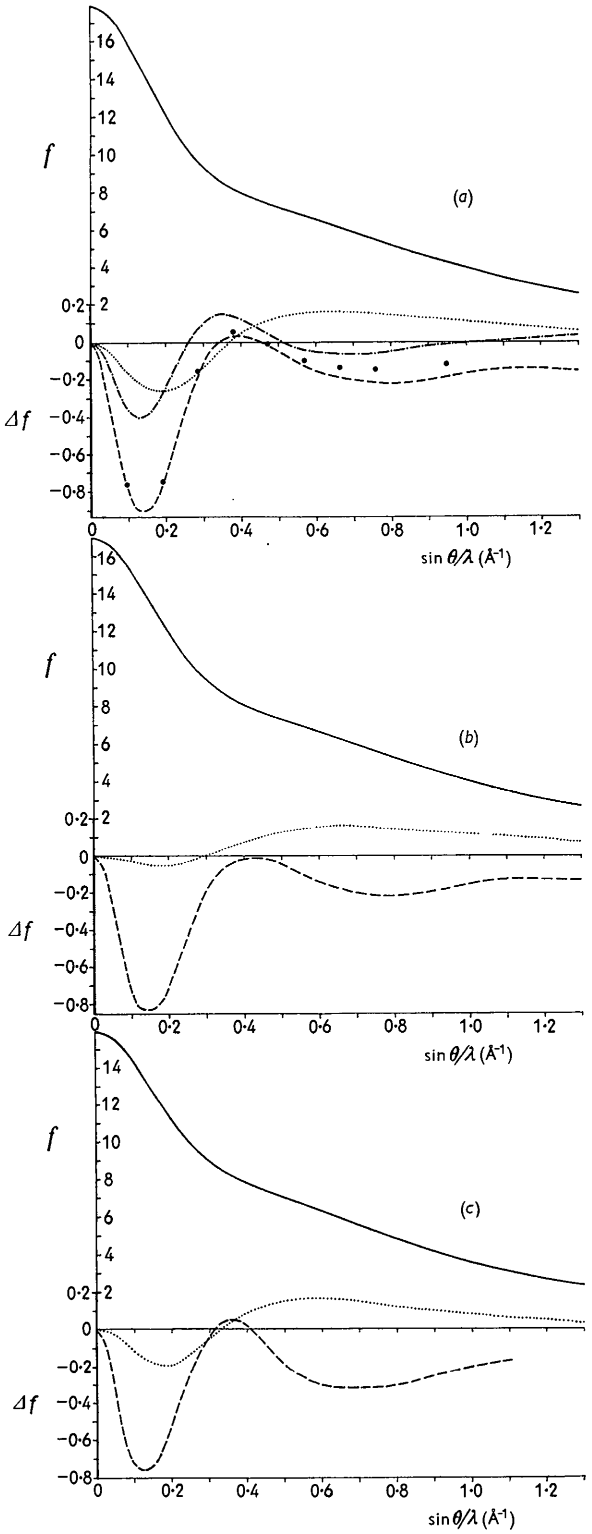

Fig. 1. Comparison of f-curves for (a) Cl^-, (b) Cl and (c) S in terms of the departures Δf shown by earlier f-curves from the PD f-curves represented by the full lines. For Cl^-, the chain line gives the departures shown by the f-curve for the HF total radial charge density, and the closed circles the departures shown by the f-curve for the 1933 H result. The broken lines are for the JB f-curves based on the 1928 H result for Cl^-, and the dotted lines are for Tomiie & Stam's (1958) f-curves for Slater functions.

for the electron affinities of Cl and S indicate that the elementary set is not entirely adequate for describing the negative ions with a precision comparable to that obtained for the neutral atoms. The inadequacy is concerned, primarily, with the set member of greatest radial extension, $r_k^3 \exp(-1r_k)$, which was introduced to improve the Slater (1930) description of the 3s, 3p electrons at large distances from the nuclei. While this term, in association with the other members, is adequate for the 3s distribution, it does not possess sufficient radial extension to allow satisfactory definition, at large r-values, of the 3p distribution in the negative ions: beyond $r \sim 3$ a.u., additional terms such as $r_k^3 \exp(-\frac{1}{2}r_k)$ or $r_k^4 \exp(-\frac{1}{2}r_k)$ become necessary for these electrons in these ions. The absence of such extra terms therefore results in the radial charge densities calculated for these ions having 'tails' more contracted than they would otherwise have been. For Cl^-, Fig. 2 shows (a) the total PD charge density $4\pi r^2 \varrho(r)$ obtained with the basic set listed earlier, and (b) $\Delta(4\pi r^2 \varrho(r))$, the difference (PD − HF) from the HF result. The contraction to smaller r-values of the outer (M) shell distribution in the PD result is seen to be considerable. However, while the bulk of this contraction is to be ascribed to the PD set limitations, such a comparison against HF data must also include the possibility that a PD calculation based on a more extensive set would still produce a 'tail' shorter than the HF result because of better allowance for correlation. Tentative evidence in favour of a correlation contraction* is given by the L-shell features of Fig.

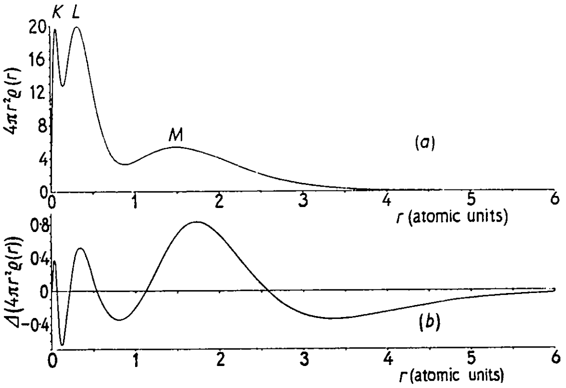

Fig. 2. Comparison of the total radial charge density for Cl^- calculated by the PD and HF methods: (a) is the PD result and (b) the difference (PD–HF).

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* A means of testing this lies in comparing the HF charge densities for Na^+, Ne and F^- with those given by the PD calculations of Bernal & Boys (1952b). The author is indebted to Dr S. F. Boys for making available a form of these PD results which is suitable for such a comparison. The results of this test will be reported later.

2(*b*), since the PD results in this region of *r* should be essentially unaffected by the set limitations which become important only at larger distances. In the case of the *K*-shell features, these arise quite unambiguously from the relativistic correction included in the PD calculation.

Because of the PD set limitations in the negative ions, no detailed assessment of the degree to which the free-state HF *f*-curve of Cl^- may be modified by additional correlation effects can be obtained from the Δf-curve in Fig. 1(*a*). However the nature of the low-angle features of this Δf-curve, which reflect the largely artificial contraction of the outer regions of the PD charge distribution in Fig. 2, do provide an assessment of how the scattering powers of this ion in the free and solid states will differ. In this regard, the molar diamagnetic susceptibility χ of this closed-shell ion, where

$$\chi\ (\text{e.m.u./mol.}) = -0{\cdot}79\,.\,10^{-6}\int_0^\infty r^2[4\pi r^2\varrho(r)]\,dr \qquad (3)$$

(see e.g. Hartree & Hartree, 1936), is a useful guide since χ is sensitive to the outer regions of the charge distribution, which will be most affected by environment. In Table 3, the χ-values calculated for Cl^- from different charge distributions are compared with the experimental value proposed by Brindley & Hoare (1937) from their measurements on powdered alkali halides. The value given by the PD charge distribution is in good agreement with experiment. By itself such a comparison must be accepted with reserve: apart from the experimental difficulties of estimating χ (see Myers, 1952), the Slater function value in Table 3 shows that equation (3) cannot assess the relative merits of different charge distributions over all regions of *r*. When taken in conjunction with Figs. 1(*a*) and 2(*b*), however, the comparison of χ-values indicates that the PD result in Fig. 2(*a*) provides a good spherical approximation to the actual charge distribution, and thus to the actual scattering power, of this ion in the solid state. For S^-, with an unclosed shell, no such comparison is possible but the conclusions regarding the suitability of the spherical approximation represented by the PD *f*-curve of this ion are similar.

Table 3. *Molar diamagnetic susceptibility values for* Cl^- *in units* 10^{-6} cm.^{3}/mol.

Experimental χ	Theoretical χ			
	H	HF	Slater	PD
$-24{\cdot}2$*	$-41{\cdot}3$†	$-30{\cdot}4$†	$-25{\cdot}2$‡	$-23{\cdot}8$§

* Brindley & Hoare's (1937) solid state value: for this ion in solution Selwood (1943) gives $-23{\cdot}4 \pm 1{\cdot}3$.

† Hartree & Hartree (1936) for SCF data with and without exchange.

‡ Myers (1952).

§ For the PD radial charge density in Fig. 2.

In the case of neutral Cl and S whose charge distributions are less extensive than those of Cl^- and S^-, the influence which radial limitations in Boys & Price's elementary set may have on the PD *f*-curves of these atoms will be either totally negligible, or quite minor and confined to the region of small *s*. Certainly, any such features in the spherically-averaged results obtained here with equation (1) will be of quite secondary importance compared with scattering effects related to the intrinsic asymmetry of these open-shell atoms (McWeeny, 1951). The present results for Cl and S can therefore be regarded as a satisfactory basis for demonstration, by electron distribution studies using the difference method (Cochran, 1951), of the open-shell scattering effects which apply to these atoms in any particular structure analysis.

The author is most grateful to Dr A. C. Hurley for advice and stimulating discussion on various aspects of the poly-detor results reported here.

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