

Comparison of Atomic Scattering Factors and Mean Radii for the Charge Distributions in Na⁺, Ne and F⁻ obtained from Hartree-Fock and Polydeter Calculations

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(Received 9 August 1960 and in revised form 29 December 1960)

Bernal & Boys' (1952) poly-determinantal calculations for Na⁺, Ne and F⁻ are used to assess the influence of electron correlation effects beyond exchange on Hartree-Fock results for (a) the atomic scattering factors, (b) the values of the mean radii $\langle r^j \rangle$ of the radial charge densities for $j = -\frac{1}{2}, +\frac{1}{2}, +1, +2$ in

$$\langle r^j \rangle = \int_0^\infty r^j [4\pi r^2 \rho(r)] dr.$$

Comparison of the two sets of $\langle r^j \rangle$ suggests that extended correlation allowance results in charge distributions which are radially more compact than those calculated with allowance for exchange only: for Ne, the poly-deter $\langle r^2 \rangle$ value agrees well with that obtained from measurements of molar diamagnetic susceptibility. However, comparison of the poly-deter and Hartree-Fock f -curves for both Na⁺ and Ne also suggests that the influence of correlation on Hartree-Fock f -curves of complex positive ions and neutral atoms is probably very small. For F⁻, the poly-deter results differ markedly from the Hartree-Fock results for both (a) and (b), and these differences are considered in terms of the elementary set employed by Bernal & Boys.

Introduction

Although improved atomic scattering factors (f -curves) based on Hartree-Fock self-consistent field (SCF) with exchange calculations of atomic charge distributions have now been derived for many atoms and ions, the degree to which the Hartree-Fock scattering description may be modified by the effects of electron correlation not accounted for in such SCF calculations is so far relatively unknown, except for light atoms. There, it has been found that the significant improvements to Hartree-Fock values of total energy which must accompany allowance for correlation (Fröman, 1957) are generally associated with such small changes in the SCF values of charge density (see e.g. Glembotskii *et al.*, 1955 (B); Kibartas *et al.*, 1955 (Be); Green *et al.*, 1959 (He); Löwdin & Rèdei, 1959 (He)) that the errors in Hartree-Fock f -curves of such systems which arise from neglect of correlation will be only very minor ones (Ibers, 1957). Further examination to assess whether a similar correlation insensitivity applies also to SCF charge-density data of heavier atoms is desirable however. Apart from the fact that such data are usually the best presently available over a wide range of atomic number, the adequacy of the Hartree-Fock approximation is relevant to (a), the convenience with which aspherical scattering effects (McWeeny, 1951; Freeman, 1959) may be calculated as a consequence of the total Hartree-Fock scattering power being expressible in terms of individual electron f -contributions, (b) detailed electron-

distribution studies of solid-state scattering such as those of McDonald (1960), and Weiss & deMarco (1958), Batterman (1959*a, b*) and Komura *et al.* (1959).

Table 1. *Hartree-Fock, poly-deter and experimental total energies for Na⁺, Ne and F⁻*
(In Hartree units)

	Na ⁺	Ne	F ⁻
Hartree-Fock	-161.8*	-128.5431†	-99.4591†
Poly-deter	-161.8784*	-128.6920*	-99.5279*
(Poly-deter 'root function')	(-161.2236)*	(-128.1430)*	(-98.9174)*
Experimental	-162.126*	-129.03†	-99.9374†

* Bernal & Boys (1952*b*). The lowness of the Hartree-Fock value for Na⁺ appears to be in doubt.

† Allen (1957).

The variational poly-deter calculations of Bernal & Boys (1952*b*) for the ground states of Na⁺, Ne and F⁻, which yield energy values significantly better than the Hartree-Fock values (Table 1) because of the correlation allowance possible in multi-determinantal approximations, suggest themselves as a means of assessing correlation influence in more complex systems. The poly-deter f -curves, and also various mean radii $\langle r^j \rangle$ (for $j = -\frac{1}{2}, \frac{1}{2}, 1, 2$) of the charge densities, have therefore been evaluated analytically, using

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

$$\langle r^j \rangle = \int_0^\infty r^j [4\pi r^2 \rho(r)] dr, \quad (2)$$

where $s = 4\pi \sin \theta / \lambda$ and $4\pi r^2 \rho(r)$ is the radial charge density, and are compared below with the corresponding results given by the Hartree-Fock approximation. Stepwise comparison of the charge densities over all values of r has not been made, but the $\langle r^j \rangle$ comparison is useful in this regard since $\langle r^2 \rangle$ depends primarily on the outer regions of the distributions whereas $\langle r^{-\frac{1}{2}} \rangle$ is governed more by the inner regions.

Poly-detor and Hartree-Fock results for Na⁺, Ne and F⁻

The poly-detor wave functions for Na⁺, Ne and F⁻, expressed in the (unnormalized) form

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

(§ 7 of Bernal & Boys (1952b): see also Dawson (1960) for a brief description of some aspects of the poly-detor method), are based on sets of ten orthonormal one-electron functions, with radial factors

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

consisting of linear combinations of members of a set of elementary functions $r^n \exp(-\alpha r)$. This set comprises the terms $\exp(-5r)$, $r \exp(-1r)$, $r \exp(-2r)$, $r \exp(-3r)$, $r^2 \exp(-1r)$ and $r^2 \exp(-2r)$, which are related to the elementary set $r^n \exp(-\alpha kr)$ chosen for the three atoms by means of 'stretching' factors k which have the values 11/5, 2 and 9/5 for Na⁺, Ne and F⁻ respectively. The final wave functions consist of the initial 'root function' approximations, composed of 1s-, 2s-, 2p-type functions whose φ_i involve only the first three members of the above elementary set, together with the sixteen co-detors Φ_r which are constructed by single and double replacement of these initial approximations' 1s etc.-functions by other members of the orthonormal sets. For Ne and F⁻, the same sets of φ_i , i.e. the same coefficients $C_i(n, \alpha)$, are used in the poly-detor calculations, while those for Na⁺ are related by a simple transformation.

The electron densities ρ of both the final and initial* approximations can then be expressed in terms of functions of the general form $r^m \exp(-\beta kr)$, each of which is either the square or a cross product of members of the stretched elementary set given above: values of m are thus 0, 1, 2, 3 or 4 and values of β lie in the range 2-10 inclusive. For the complete poly-detor wave functions, the numerical coefficients of the electron-density expansions

* Energywise, these are much poorer than the final approximations (Table 1), and their f -curves and $\langle r^j \rangle$ values cannot be used for assessing correlation influence on SCF results. However the 'root function' results are relevant to the discussion below of the differences between the poly-detor and Hartree-Fock results.

$$\rho(r) = k^3 / 4\pi \sum_{m,\beta} D(m, \beta) (kr)^m \exp(-\beta kr) \quad (3)$$

involve (a), the values of Y_r and $C_i(n, \alpha)$ for each atom, (b), the projective reduction formulae which apply to the vector coupling relationships between the various Φ_r and the 'root functions' (Bernal & Boys, 1952a), and (c), the stretching transformations of § 6 of Bernal & Boys (1952b). The values of $D(m, \beta)$ have been kindly provided by Dr S. F. Boys, and this assistance in the present work is gratefully acknowledged. For the poly-detor 'root functions', coefficients $D'(m, \beta)$ analogous to those of equation (3) are obtained directly from the $C_i(n, \alpha)$ of the φ_i used for these single determinant approximations: in these cases the values of m are restricted to 0, 1 or 2 (see earlier).

The derivation of the poly-detor f -curves then reduces to

$$f(s) = \sum_m k^{m+3} \sum_\beta D(m, \beta) A(m, a; s), \quad (4)$$

where, with $a = \beta k$, the integrals

$$A(m, a; s) = 1/s \int_0^\infty r^{m+1} \exp(-ar) \sin sr dr$$

may be readily evaluated for the various m -values (see e.g. McWeeny (1951)). For the mean radii $\langle r^j \rangle$, substitution of equation (3) in equation (2) gives finally

$$\langle r^j \rangle = k^{-j} \sum_{m,\beta} D(m, \beta) \{(\Gamma(m+3+j)) / \beta^{m+3+j}\}. \quad (5)$$

The values of the f -curves at $\sin \theta / \lambda$ (\AA^{-1}) intervals (using 1 a.u. = 0.52917 \AA) and of $\langle r^j \rangle$ in a.u. for both the final and initial poly-detor approximations are given in Table 2.

The corresponding values of $\langle r^j \rangle$ for the Hartree-Fock results are also given in Table 2. These were obtained by numerical integration of the radial charge densities of Na⁺ (Hartree & Hartree, 1948), Ne (Worsley, 1958a) and F⁻ (Froese, 1957), after using six-point Lagrangian interpolation to obtain additional values at r -intervals sufficiently fine to ensure integration adequacy. The Hartree-Fock f -curves in Table 2 are Freeman's (1959, 1960) for Na⁺ and F⁻ and the average of Freeman's & Worsley's (1959) for Ne. This average is used since the energy of Ne in Table 1 is for Allen's (1957) calculation which is the basis of Freeman's f -curve whereas the $\langle r^j \rangle$ values are for Worsley's results.

Discussion

Two interesting features are shown by the various data listed in Table 2. Firstly, for all three atoms the $\langle r^j \rangle$ values indicate that the charge distributions given by the poly-determinantal approximations are more compact radially than those given by the SCF method with exchange; secondly, whereas the $\langle r^j \rangle$ and f -curve

Table 2. *Poly-detor and Hartree-Fock f-curves and $\langle r^j \rangle$ values for Na⁺, Ne, F⁻*

$\sin \theta/\lambda$ (\AA^{-1})	$f(\text{Na}^+)$			$f(\text{Ne})$			$f(\text{F}^-)$		
	PD	(PDRF) -	HF	PD	(PDRF)	HF	PD	(PDRF)	HF
0.00	10.000	(10.000)	10.000	10.000	(10.000)	10.000	10.000	(10.000)	10.000
0.10	9.552	(9.530)	9.545	9.363	(9.359)	9.351	9.108	(9.219)	8.968
0.20	8.390	(8.332)	8.371	7.824	(7.812)	7.808	7.126	(7.419)	6.924
0.30	6.925	(6.850)	6.891	6.087	(6.070)	6.084	5.188	(5.538)	5.068
0.40	5.509	(5.449)	5.467	4.617	(4.599)	4.617	3.786	(4.072)	3.725
0.50	4.328	(4.294)	4.286	3.536	(3.520)	3.530	2.885	(3.074)	2.843
0.60	3.424	(3.415)	3.391	2.793	(2.782)	2.782	2.323	(2.435)	2.288
0.70	2.771	(2.777)	2.748	2.300	(2.295)	2.288	1.972	(2.035)	1.945
0.80	2.314	(2.326)	2.30	1.976	(1.975)	1.965	1.747	(1.784)	1.729
0.90	2.001	(2.013)	1.992	1.760	(1.765)	1.752	1.596	(1.621)	1.585
1.00	1.785	(1.796)	1.78	1.612	(1.621)	1.608	1.486	(1.507)	1.482
1.10	1.634	(1.645)	1.629	1.504	(1.517)	1.501	1.399	(1.420)	1.398
1.20	1.524	(1.535)	—	1.419	(1.436)	—	1.322	(1.346)	—
1.30	1.438	(1.451)	—	1.346	(1.367)	—	1.251	(1.279)	—
$\langle r^j \rangle$ (a.u.)	Na ⁺			Ne			F ⁻		
$j = -1$	35.256	(35.925)	—	31.178	(31.690)	—	27.376	(28.521)	—
$-\frac{1}{2}$	16.180	(16.234)	16.14 ₀	15.080	(15.143)	15.03 ₂	14.014	(14.366)	13.86 ₅
$+\frac{1}{2}$	7.591	(7.635)	7.61 ₅	8.256	(8.261)	8.28 ₁	8.991	(8.708)	9.21 ₁
$+1$	6.579	(6.690)	6.62 ₁	7.838	(7.859)	7.90 ₀	9.351	(8.732)	9.95 ₈
$+2$	6.344	(6.661)	6.41 ₇	9.150	(9.207)	9.41 ₁	13.120	(11.367)	15.97 ₅

results for Na⁺ and Ne differ only slightly, those for F⁻ differ markedly.

For each atom, the $\langle r^j \rangle$ values show that the main differences between the poly-detor and Hartree-Fock distributions lie in the outer (large r) regions, and the trend of the $\langle r^j \rangle$ differences from Na⁺ to F⁻ is consistent with expectation of the adequacy of the SCF approximation being greater in positive than in negative ions (Hartree & Hartree, 1938). For Ne, the smaller $\langle r^2 \rangle$ value given by the poly-detor result is in good accord with the experimental value $\langle r^2 \rangle_{\text{exp.}} = 9.1$ suggested by measurements of molar diamagnetic susceptibility (Kittel, 1956; Dawson, 1961). Since corresponding $\langle r^2 \rangle_{\text{exp.}}$ values for argon and krypton are also smaller than the $\langle r^2 \rangle$ values given by Hartree-Fock data (see Dawson, 1961), we thus have additional support for inferring from the poly-detor calculations used here that allowance for correlation effects in multi-electron systems will result in charge distributions which are less extensive radially than those given by the SCF method with exchange. It seems clear, however, from the results for Na⁺ and Ne that the influence which correlation allowance will have in modifying the Hartree-Fock f -curves of complex positive ions and neutral atoms is probably sufficiently small to be safely ignored except perhaps in the most detailed X-ray studies. A useful test of these conclusions will be provided when Hartree-Fock radial charge density and f -curve data for neutral chlorine become available for comparison with the results obtained recently (Dawson, 1960) from the poly-detor calculations of Boys & Price (1954).

For F⁻, it is not possible, however, to use the poly-detor results to obtain an assessment of correlation allowance in negative ion Hartree-Fock data which is as unequivocal as that discussed above for

neutral and positive systems. Although the large contractions shown for this ion in Table 2 are similar to results obtained for H⁻ in studies of correlation effects in He-like systems (Hurst, Miller & Matsen, 1958), it would be unwise to interpret the poly-detor results solely in terms of correlation allowance. The situation in Bernal & Boys' (1952*b*) calculation for F⁻ resembles that noted recently (Dawson, 1960) in the calculation of Boys & Price (1954) for Cl⁻: that is, the radial adequacy of the elementary set given earlier does not allow the poly-detor treatment to define completely satisfactorily the outer regions of the F⁻ charge distribution. The radial restrictions here are less severe than those in Cl⁻ in that the poly-detor treatment of F⁻ has expanded the 'root function' distribution considerably (see the $\langle r^j \rangle$ values, and particularly $\langle r^2 \rangle$, in Table 2), whereas for Cl⁻ little expansion was possible, the 'root function' and final distributions there having $\langle r^2 \rangle$ values of 29.33 and 30.07 respectively. The elementary set chosen for Na⁺, Ne and F⁻ has therefore allowed the poly-detor calculations considerable flexibility in improving the 'root function' approximations. Indeed, the large differences between the respective $\langle r^j \rangle$ and f -curves for F⁻ show that the close agreement between initial and final results for Na⁺ and Ne reflects only the excellence of the initial approximations to these systems and not any deficiencies in their final results. For F⁻, however, there must remain uncertainty of the extent to which the final charge distribution would be expanded on using a more extensive elementary set. Consequently no satisfactory estimate of the degree to which correlation allowance will modify Hartree-Fock data of complex negative ions can be made here. Since the SCF approximation is likely to be at least adequate for such systems, as noted earlier,

examination of correlation effects in negative ions of crystallographic interest would be most valuable.

Great thanks are due to Dr S. F. Boys for his kindness in providing the numerical coefficients D of equation (3), and also to Dr A. C. Hurley for advice and many helpful discussions on poly-detor calculations.

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Acta Cryst. (1961). **14**, 1120

Atomic Scattering Amplitudes for Electrons for Some of the Lighter Elements

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(Received 9 August 1960 and in revised form 21 February 1961)

Theoretical mean square radii $\langle r^2 \rangle$ for the atomic charge distributions given by poly-detor, Hartree-Fock and Slater function calculations are used in conjunction with evidence of experimental $\langle r^2 \rangle$ values given by diamagnetic susceptibility measurements to obtain improved estimates of the atomic scattering amplitudes, at zero scattering angle, which apply to the elements F-Ca, and also Kr, in the first Born approximation. Values of the scattering amplitudes at other scattering angles are also obtained, and the new results are compared with results obtained earlier by Ibers (1958) and Vainshtein & Ibers (1958).

In terms of the first Born approximation to the scattering of electrons by neutral spherically symmetric atoms, the atomic scattering amplitudes for electrons $f_{el}(s)$ are real and related to the atomic scattering factors for X-rays $f(s)$ by

$$f_{el}(s) = (8\pi^2 me^2 / h^2) (Z - f(s)) / s^2, \quad (1)$$

where

$$f(s) = \int_0^\infty 4\pi r^2 \rho(r) \sin sr / sr \, dr \quad (2)$$

and $4\pi r^2 \rho(r)$ is the radial charge density, $s = 4\pi \sin \theta / \lambda$ and Z is the atomic number. (For discussion of equation (1) in terms of the true complex scattering amplitude, see e.g. Cowley & Rees (1958)). Ibers (1958)

has recently considered the suitability of the real $f_{el}(s)$ when applied to the interpretation of electron-diffraction data obtained from solids, concluding that the use of the first Born approximation is at present adequate for such purposes, provided that reliable values of $f(s)$ are available for the derivation of $f_{el}(s)$ in the region where s is small. For $f_{el}(0)$, he has shown that the uncertainties which are associated with equation (1) because of the need to extrapolate from $f_{el}(s)$ values for s small can be avoided since

$$f_{el}(0) = (4\pi^2 me^2 / 3h^2) \langle r^2 \rangle, \quad (3)$$

where $\langle r^2 \rangle$, the mean square radius of the atomic charge distribution, is