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Calculations of Coherent Scattering Factors for Helium-Like Ions from a Radially Correlated Wave Function*

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Coherent scattering factors are calculated for helium and helium-like ions from the Hylleraas–Eckart radially correlated wave function. It is suggested that the method may be extended to other atoms with less labor than is required to make Hartree–Fock-type calculations. A sizeable disparity between corresponding correlated and uncorrelated results is noted for H^-; this gradually becomes smaller with increasing atomic number. At the larger values of sin θ/λ, the correlated results for H^- agree quite well with corresponding factors for the hydrogen atom.

Introduction

For a period of nearly two decades the atomic scattering factors given by James & Brindley (1931) were the most widely accepted for use in crystal-structure determinations. Though the agreement with experiment was surprisingly good, the improvement in computational technique and in the X-ray data themselves has stimulated a number of efforts to improve these results. To mention three notable examples, Thomas & Umeda (1957) have recently published a very extensive Thomas–Fermi–Dirac table of factors for Z greater than 24. Berghuis *et al.* (1955) have made extensive Hartree–Fock self-consistent field calculations, and McWeeny (1951) has considered the effects of chemical bonding on the atomic scattering factor.

The present effort is to investigate the effects of including some radial electron correlation by using the Hylleraas (1929)–Eckart (1930) radially correlated wave function for He and He-like ions. Since this wave function is known to give lower calculated energies than can be obtained by the Hartree–Fock approximation, it seems likely that scattering factors calculated from this function may represent an improvement on the self-consistent field results. Further, if this proves to be the case, the method is sufficiently general that it can be applied to other atoms with less labor than is required to make the Hartree–Fock-type calculations.

Theory

In this work the scattering factors are taken to be (see James, 1948)

$$f = \frac{\int \Psi \sum_j \exp\,[ik\mathbf{S}\cdot\mathbf{r}_j]\,\Psi d\tau}{\int \Psi\Psi d\tau}\,, \qquad (1a)$$

where

$$k\mathbf{S}\cdot\mathbf{r}_j = \mu r_j \cos\alpha_j\,, \qquad (1b)$$

$$\mu = 4\pi \sin\theta/\lambda \qquad (1c)$$

and

$$d\tau = d\tau_1 d\tau_2\,, \qquad (1d)$$

$$d\tau_j = r_j^2 \sin\alpha_j d\alpha_j d\varphi_j dr_j\,. \qquad (1e)$$

Since the Hylleraas–Eckart wave function is

$$\Psi = a(1)b(2)+b(1)a(2)\,, \qquad (2)$$

where

$$a(j) = (\mathbf{a}^3/\pi)^{\frac{1}{2}} \exp\,[-\mathbf{a}r_j]\,, \qquad (3a)$$

$$b(j) = (\mathbf{b}^3/\pi)^{\frac{1}{2}} \exp\,[-\mathbf{b}r_j]\,, \qquad (3b)$$

one obtains on substituting equations (2) into (1), after expanding the summation and combining like terms,

$$\begin{aligned} f = (2/N)\Big\{\iint & [a(1)b(2)\exp\,[i\cos\alpha_1\mu r_1][a(1)b(2)]\,d\tau_1 d\tau_2 \\ &+2\iint [a(1)b(2)]\exp\,[i\cos\alpha_1\mu r_1][b(1)b(2)]\,d\tau_1 d\tau_2 \\ &+\iint [b(1)a(2)\exp\,[i\cos\alpha_1\mu r_1][b(1)a(2)]\,d\tau_1 d\tau_2\Big\}, \end{aligned} \qquad (4a)$$

where

$$\begin{aligned} N = 2\int a^2(1)d\tau_1 \int b^2(2)d\tau_2 \\ +2\int a(1)b(1)d\tau_1 \int a(2)b(2)d\tau_2\,. \end{aligned} \qquad (4b)$$

Using the result

$$\int_0^\infty \exp\,[-\alpha r]\,r\sin\mu r dr = \frac{2\mu\alpha}{(\alpha^2+\mu^2)^2}\,, \qquad (5)$$

a straight-forward integration in spherical polar coordinates gives:

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$$f = \left\{ \frac{32\mathbf{a}^4}{(4\mathbf{a}^2+\mu^2)^2} + \frac{256(\mathbf{ab})^4}{\{(\mathbf{a}+\mathbf{b})^2+\mu^2\}^2(\mathbf{a}+\mathbf{b})^2} + \frac{32\mathbf{b}^4}{(4\mathbf{b}^2+\mu^2)^2} \right\} \frac{1}{N}, \quad (6a)$$

where

$$N = 2[1+64(\mathbf{ab})^3/(\mathbf{a}+\mathbf{b})^6]. \quad (6b)$$

All of the new results which are presented in this paper were calculated from equations (6). The parameters **a** and **b** were taken from Shull & Löwdin (1956). The numerical work was performed on an IBM 650 computer.

Results

In Table 1 are given the factors obtained for H$^-$, He, Li$^+$ and Be^{++}.*

Table 1. *Scattering factors computed from radially correlated wave functions*

$\sin\theta/\lambda$ (Å^{-1})	H$^-$	He	Li$^+$	Be^{++}
0·000	2·0000	2·0000	2·0000	2·0000
0·025	1·8591	1·9887	1·9958	1·9978
0·050	1·5659	1·9553	1·9834	1·9914
0·075	1·2865	1·9020	1·9630	1·9807
0·100	1·0638	1·8316	1·9350	1·9660
0·125	0·8867	1·7478	1·9000	1·9472
0·150	0·7417	1·6543	1·8587	1·9247
0·175	0·6207	1·5546	1·8117	1·8987
0·200	0·5193	1 4521	1·7598	1·8693
0·225	0·4344	1·3494	1·7040	1·8369
0·250	0·3635	1·2486	1·6450	1·8017
0·275	0·3044	1·1512	1·5836	1·7641
0·300	0·2554	1·0584	1·5206	1·7243
0·325	0·2148	0·9708	1·4566	1·6827
0·350	0·1811	0·8889	1·3923	1·6395
0·375	0·1531	0·8128	1·3282	1·5951
0·400	0·1299	0·7424	1·2648	1·5497
0·425	0·1106	0·6777	1·2024	1·5036
0·450	0·09455	0·6184	1·1416	1·4570
0·475	0·08110	0·5641	1·0824	1·4102
0·500	0·06982	0·5147	1·0251	1·3634
0·550	0·05233	0·4287	0·9170	1·2706
0·600	0·03979	0·3577	0·8178	1·1799
0·650	0·03067	0·2992	0·7279	1·0923
0·700	0·02394	0·2511	0·6470	1·0086
0·750	0·01892	0·2114	0·5746	0·9294
0·800	0·01512	0·1787	0·5103	0·8549
0·850	0·01221	0·1517	0·4532	0·7853
0·900	0·009949	0·1292	0·4027	0·7206
0·950	0·008183	0·1106	0·3581	0·6607
1·000	0·006785	0·09499	0·3188	0·6055
1·100	0·004772	0·07092	0·2536	0·5082
1·200	0·003446	0·05376	0·2029	0·4266
1·300	0·002547	0·04134	0·1635	0·3586

For the purpose of comparison, and in order to show the trends, these results are compared with those of the simpler approximation where **a** = **b** (as in the usual Slater-type wave functions) and with previously calculated factors for ions of Z up to 6 (see Table 2). In addition, these results are plotted for H$^-$, He, Li$^+$ in Fig. 1.

Discussion

The data given in Table 2 clearly show that the disparity between radially correlated and uncorrelated results is greatest for H$^-$ and gradually becomes smaller with increasing atomic number. Shull & Löwdin's (1956) calculations show a similar trend in

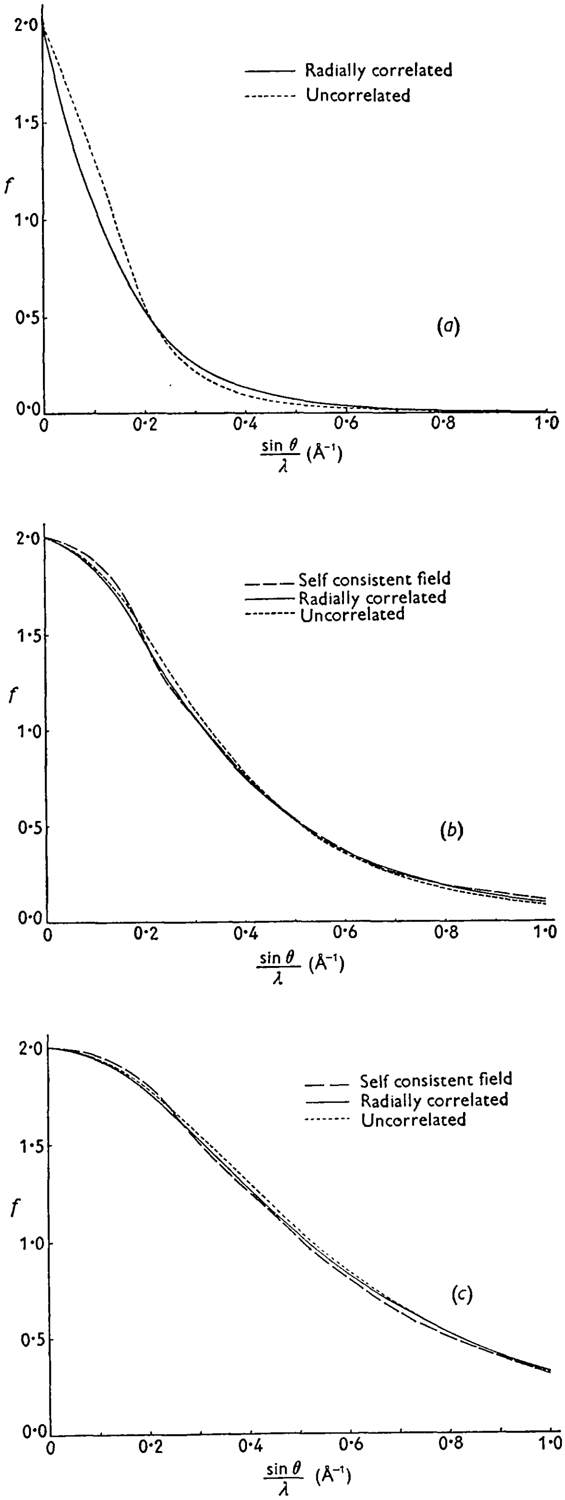

Fig. 1. Atomic scattering factor of (*a*) H$^-$, (*b*) He, (*c*) Li$^+$.

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* A table of these factors with increments of $\sin\theta/\lambda$ of 0·001 will be supplied on request.

Table 2. *Comparison of factors computed from various distributions*

$\sin\theta/\lambda$ (Å^{-1})	0·00	0·10	0·20	0·30	0·40	0·50	0·60	0·70	0·80	1·00	Method
H^-	2·000	1·064	0·519	0·255	0·130	0·0698	0·0398	0·0239	0·0151	0·00679	*R*
	2·000	1·314	0·534	0·207	0·0889	0·0426	0·0225	0·0129	0·00784	0·00336	*N*
He	2·000	1·832	1·452	1·058	0·742	0·515	0·358	0·251	0·179	0·0950	*R*
	2·000	1·853	1·498	1·098	0·761	0·515	0·348	0·237	0·165	0·0839	*N*
	2·000	1·88	1·46	1·05	0·75	0·52	0·35	0·24	0·18	0·11	*H*
Li^+	2·000	1·935	1·760	1·521	1·265	1·025	0·818	0·647	0·510	0·319	*R*
	2·000	1·940	1·776	1·545	1·291	1·046	0·831	0·653	0·510	0·312	*N*
	2·000	1·96	1·8	1·5	1·3	1·0	0·8	0·6	0·5	0·3	*H*
Be^{++}	2·000	1·966	1·869	1·724	1·550	1·363	1·180	1·009	0·855	0·606	*R*
	2·000	1·968	1·876	1·737	1·566	1·381	1·197	1·023	0·865	0·608	*N*
	2·000	2·0	1·9	1·7	1·6	1·4	1·2	1·0	0·9	0·6	*I*
B^{+++}	2·000	1·979	1·919	1·824	1·703	1·566	1·420	1·274	1·132	0·877	*R*
	2·000	1·980	1·922	1·830	1·713	1·578	1·434	1·287	1·144	0·885	*N*
	2·000	1·99	1·9	1·8	1·7	1·6	1·4	1·3	1·2	0·9	*I*
C^{++++}	2·000	1·986	1·945	1·879	1·792	1·689	1·576	1·457	1·335	1·101	*R*
	2·000	1·986	1·946	1·882	1·798	1·698	1·586	1·467	1·347	1·111	*N*

R = Radially correlated.
N = Not radially correlated.
H = Hartree distributions (see James & Brindley, 1931).
I = Interpolated from Hartree distributions (see James & Brindley, 1931).

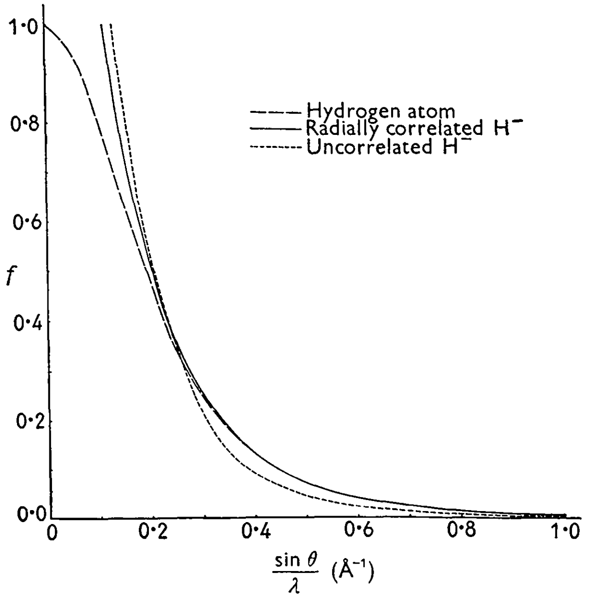

Fig. 2. Comparison of scattering factors for H^- with factors for hydrogen atom.

that electronic energies computed by radially correlated, uncorrelated, and self-consistent field approximations agree better with increasing Z. The James & Brindley (1931) results, interpolated from self-consistent field, do not appear sufficiently accurate to allow this type of comparison.

It is of interest to compare the results for H^- with corresponding scattering factors for the hydrogen atom (see Fig. 2). These results show that the radially correlated H^- factors agree at the higher angles with the hydrogen atom factors, whereas the uncorrelated factors are much smaller. This may be interpreted from the nature of the scattering operator, $\exp[ik\mathbf{S}\cdot\mathbf{r}]$, in the following manner. In any system where Ψ is spherically symmetrical, such as is the case here, equation (1) may be reduced to (see Eucken & Wolf, 1936)

$$f=\int_0^\infty 4\pi r^2\varrho(r)\sin\mu r/\mu r\,dr\ ,$$

where

$$\mu=4\pi\sin\theta/\lambda\ .$$

Then the effect of increasing μ (or $\sin\theta/\lambda$) is to shift the first minimum of $\sin\mu r/\mu r$ toward smaller r values. This reduces the contribution to the integral giving f, of the electron distribution $(4\pi r^2\varrho(r))$ remote from the nucleus (see James, 1948). Alternatively, since f is a Fourier transform of ϱ, variations in the outer region of ϱ affect mainly the inner region of f.

From this well-known fact and the results shown in Fig. 2, we may conclude that the correlated electron density for H^- represents roughly an 'outer' orbital plus a second 'inner' orbital which is very similar to the density for the atom. The 'outer' orbital can be assumed to make a relatively small contribution to f at the large values of $\sin\theta/\lambda$.

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