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X-ray Scattering Factors of Two-Electron Ions from Radially and Angularly Correlated Wave Functions*†

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The X-ray scattering factors for helium and helium-like ions are calculated with radially and angularly correlated wave functions. If the energy criterion for quality of wave functions is used, these new factors are more reliable than those previously derived from radially correlated and restricted Hartree-Fock functions. In parallel trend with the relative magnitude of the electronic correlation energy, the correlation effects on the scattering factors are most pronounced for the lowest member of the isoelectronic series, H^-, and diminish rapidly with increasing nuclear charge. The calculations can be extended to polyelectronic ions without great difficulty.

Introduction

In earlier papers from this laboratory (Hurst, Miller & Matsen, 1958; Hurst & Matsen, 1959), there have been presented X-ray scattering factors, f, for two-, three- and four-electron ions calculated with single configuration functions constructed from antisymmetrized products of Slater orbitals with optimized orbital exponents.‡ These calculations have been made for S ground states and have used s orbitals. The configurations used have fallen in two classes: SODE, i.e. same orbitals for different (paired) electrons and DODE, i.e. different orbitals for different electrons. In this language, the conventional or 'restricted' Hartree-Fock functions (see Pratt, 1956) are SODE calculations which employ self-consistent field (SCF) orbitals. Restricted Hartree-Fock functions have been used to derive most of the Hartree-Fock f values published (Hoerni & Ibers, 1954; Berghuis et al., 1955; Freeman, 1959; Veenendaal et al., 1959). The analytical wave functions constructed from products of hydrogenic or Slater orbitals which were used

for f calculation by Pauling & Sherman (1932) McWeeny (1951) and Tomiie & Stam (1958) are also of the SODE type. SODE wave functions do not permit electronic correlation while DODE wave functions contain some radial correlation (see for example, Löwdin, 1959, for a discussion of correlation in wave functions). The DODE functions yield more accurate energies than the restricted Hartree-Fock functions (Taylor & Parr, 1952; Shull & Löwdin, 1956; Brigman & Matsen, 1957; Hurst, Gray, Brigman & Matsen, 1958; Brigman, Hurst, Gray & Matsen, 1958) while the DODE f values differ from the corresponding Hartree-Fock results particularly for low atomic numbers in a given isoelectronic series.

In the present paper, the effect of correlation on the scattering factors for two-electron ions is further studied by the use of the DODEAC function which adds some angular correlation to the radial correlation of the DODE. The angular correlation is obtained by mixing an additional configuration constructed with angularly dependent orbitals. It has been shown by Silverman, Platas & Matsen (1959) (hereafter abbreviated SP&M) that the DODEAC wave functions yield expectation values for the energy and several other operators which are superior to those calculated from DODE and restricted Hartree-Fock functions and which are quite close to those obtained from more

complex variational wave functions of the Hylleraas type.* An important advantage of both *DODE* and *DODEAC* functions is that correlation is introduced with relatively little loss in simplicity; such functions are sufficiently simple to permit their application to polyelectronic systems without undue difficulty. In contrast, the introduction of correlation in the Hartree–Fock scheme via the superposition of configurations (Glembotskii, Kibartas & Iutsis, 1955; Kibartas, Kavetskis & Iutsis, 1955) or by the use of 'unrestricted,' i.e. *DODE*, Hartree–Fock functions (Pratt, 1956; Wood & Pratt, 1957) is considerably more difficult and in the cases cited has been accomplished with the aid of various simplifying assumptions. Such correlated Hartree–Fock functions have been used for f calculations by Ibers (1957) and by Freeman & Wood (1959).

Calculations

As usual, the coherent atomic scattering factor is computed from (see James, 1948)

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

where

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

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

and

$$d\tau = d\tau_1 d\tau_2 . \quad (1d)$$

Omitting the antisymmetric spin function, the ^1S normalized wave function ψ may be written as

$$\psi = (1+\lambda^2)^{-\frac{1}{2}} \{ N[1s(1)1s'(2) + 1s'(1)1s(2)] \\ + (\lambda/\sqrt{3})[2p_0(1)2p_0(2) + 2p_{+1}(1)2p_{-1}(2) \\ + 2p_{-1}(1)2p_{+1}(2)] \} , \quad (2)$$

where $(1+\lambda^2)^{-\frac{1}{2}}$ is the overall normalization constant, N is the normalization constant for the $(1s1s')$ function and λ is a variational parameter. Wave function (2) was constructed with Slater orbitals. The normalized radial portions of these are

$$R(1s) = 2\mathbf{a}^{3/2} \exp (-\mathbf{a}r) \quad (3a)$$

$$R(1s') = 2\mathbf{b}^{3/2} \exp (-\mathbf{b}r) \quad (3b)$$

$$R(2p) = (2/\sqrt{3})\mathbf{\acute{g}}^{5/2} r \exp (-\mathbf{\acute{g}}r) , \quad (3c)$$

where $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{\acute{g}}$ are the variationally determined orbital exponents. The integration (1a) with wave function (2) is conveniently performed in spherical coordinates. The integration over the $2p$ orbitals was

carried out using the coordinate transformation described by McWeeny (1951). The scattering from a single $2p$ orbital is dependent upon the orientation of the reflexion normal $\mathbf{S}$ in respect to the orbital axis. The $(2p)^2$ wave function, however, has ^1S symmetry so that its contribution

$$f(2p)^2 = \tfrac{2}{3}[f_{\parallel}(2p) + 2f_{\perp}(2p)] \quad (4)$$

to the total scattering factor is angle-independent. Here, $f_{\parallel}(2p)$ is the scattering factor for a $2p$ orbital parallel to $\mathbf{S}$ and $f_{\perp}(2p)$ is the scattering factor for a $2p$ orbital perpendicular to $\mathbf{S}$. The explicit expression for the total scattering factor in modified atomic units* is

$$f = (1+\lambda^2)^{-1} \left\{ 32N^2 \left[\frac{\mathbf{a}^4}{(4\mathbf{a}^2 + \mu^2)^2} + \frac{8(\mathbf{ab})^3}{[(\mathbf{a}+\mathbf{b})^2 + \mu^2]^2(\mathbf{a}+\mathbf{b})^2} \right. \right. \\ \left. \left. + \frac{\mathbf{b}^4}{(4\mathbf{b}^2 + \mu^2)^2} \right] + 128\lambda^2 \mathbf{\acute{g}}^6 \frac{4\mathbf{\acute{g}}^2 - \mu^2}{(4\mathbf{\acute{g}}^2 + \mu^2)^4} \right\} , \quad (5a)$$

where

$$N = [2 + 2S^2(\mathbf{a}, \mathbf{b})]^{-\frac{1}{2}} \quad (5b)$$

and

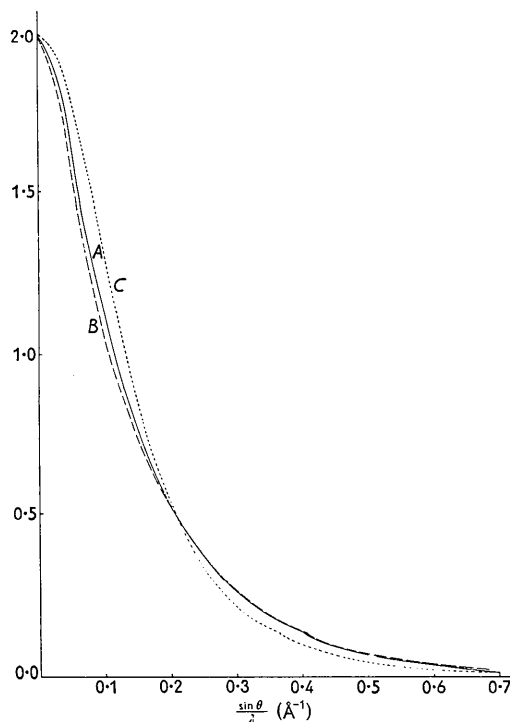$$S(\mathbf{a}, \mathbf{b}) = \int 1s1s' d\tau = \frac{8(\mathbf{ab})^{3/2}}{(\mathbf{a}+\mathbf{b})^3} . \quad (5c)$$

Fig. 1. Comparison of scattering factors for H⁻.
　　$A = DODEAC$, $B = DODE$ and $C = SODE$.

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* Hylleraas type functions (Hylleraas, 1929) introduce correlation by the explicit inclusion of interelectronic terms. Although quite exact wave functions of this type are available for two- and three-electron systems they normally contain many terms and the extension to polyelectronic ions appears impracticable (Pekeris, 1958; James & Coolidge, 1936).

* The modified atomic unit of length, a_M, is given by $a_M = a_0(R_\infty/R_M)$ where $a_0 = 0.529172$ Å is the first Bohr radius for infinite nuclear mass, R_∞ is the Rydberg wave number for infinite nuclear mass and R_M is the Rydberg wave number for the nucleus of mass M. This introduces a first order correction for nuclear motion.

Table 1. *X-ray scattering factors computed from radially and angularly correlated wave functions*

$(\sin\theta/\lambda)$ Å^{-1}	H$^-$	He	Li$^+$	Be^{++}
0·000	2·0000	2·0000	2·0000	2·0000
0·025	1·8882	1·9888	1·9958	1·9978
0·050	1·6338	1·9558	1·9835	1·9914
0·075	1·3616	1·9030	1·9631	1·9808
0·100	1·1258	1·8332	1·9352	1·9660
0·125	0·9314	1·7500	1·9003	1·9473
0·150	0·7713	1·6570	1·8591	1·9248
0·175	0·6391	1·5578	1·8122	1·8988
0·200	0·5296	1·4555	1·7605	1·8695
0·225	0·4393	1·3529	1·7048	1·8371
0·250	0·3648	1·2520	1·6458	1·8020
0·275	0·3036	1·1545	1·5845	1·7644
0·300	0·2533	1·0614	1·5215	1·7246
0·325	0·2120	0·9735	1·4576	1·6830
0·350	0·1780	0·8912	1·3933	1·6399
0·375	0·1500	0·8147	1·3292	1·5955
0·400	0·1269	0·7440	1·2657	1·5501
0·425	0·1078	0·6790	1·2034	1·5040
0·450	0·09193	0·6193	1·1425	1·4575
0·475	0·07871	0·5648	1·0833	1·4107
0·500	0·06766	0·5151	1·0260	1·3639
0·550	0·05058	0·4287	0·9177	1·2711
0·600	0·03838	0·3574	0·8184	1·1803
0·650	0·02954	0·2987	0·7283	1·0927
0·700	0·02303	0·2505	0·6473	1·0090
0·750	0·01818	0·2108	0·5748	0·9298
0·800	0·01452	0·1781	0·5103	0·8552
0·850	0·01171	0·1510	0·4531	0·7856
0·900	0·009543	0·1286	0·4026	0·7208
0·950	0·007845	0·1100	0·3580	0·6609
1·000	0·006503	0·09445	0·3186	0·6057
1·100	0·004571	0·07047	0·2534	0·5083
1·200	0·003299	0·05339	0·2027	0·4266
1·300	0·002438	0·04104	0·1632	0·3586
1·400	0·001838	0·03197	0·1323	0·3021
1·500	0·001410	0·02522	0·1080	0·2552

Equation (5a) reduces to the corresponding *DODE* form for $\lambda = 0$ and further to the *SODE* expression for $\mathbf{a} = (Z - \frac{5}{16}) = \mathbf{b}$ where Z is the nuclear charge. Using equations (5), the scattering factors for H$^-$—Ne^{8+} were calculated. The parameters $\mathbf{a}$, $\mathbf{b}$, $\mathbf{\acute{g}}$ and λ were taken from SP&M. The scattering factors for H$^-$, He, Li$^+$ and Be^{++} as a function of $(\sin\theta/\lambda)$ Å^{-1} are presented in Table 1.* In Table 2, our factors for H$^-$, He, Li$^+$ and C^{4+} are compared with the corresponding analytical *DODE* and *SODE* results as well as with the available SCF calculations. In addition, the various scattering factors for H$^-$ are plotted in Fig. 1.

Discussion and conclusions

From inspection of the data in Table 2, we see that: (*a*) The effect of electronic correlation on f within the isoelectronic series diminishes with increasing nuclear charge. This is in qualitative agreement with the parallel trend in the relative magnitude of the electronic correlation energy. (*b*) The effect of angular correlation diminishes more rapidly than radial correlation with increasing Z. (*c*) The *DODEAC* f values are in general intermediate to the *SODE* and *DODE* values and closer to the latter which is in agreement with the results found for other expectation values, excepting energy (SP&M). This indicates that *DODE* taken alone overemphasizes the radial correlation. (*d*) For larger Z, both *DODE* and *DODEAC* f values are in excellent agreement with SCF results.

The small differences between *DODE* and *DODEAC* values suggest a convergence to greater accuracy in the latter. This point will be considered in a forthcoming publication by Dr R. P. Hurst who has obtained the two-electron scattering factors from a three-term Hylleraas type function. From the above and from the standpoint of the energy criterion, it appears that in general the *DODEAC* scattering factors are superior to the *DODE* and restricted Hartree–Fock results, the correlation effects being most pronounced for the lowest members of an isoelectronic series, i.e. negative ions.

It is our plan to extend these calculations to more complex ions in the near future.

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* Tables of the factors for H$^-$—Ne^{8+} at finer intervals of $(\sin\theta/\lambda)$ Å^{-1} up to a value of $(\sin\theta/\lambda) = 20\cdot0$ will be supplied upon request.

Table 2. *Comparison of scattering factors computed from various wave functions*

$(\sin\theta/\lambda)$ Å^{-1}	0·00	0·10	0·20	0·30	0·40	0·50	0·60	0·70	0·80	0·90	1·00	Method
H$^-$	2·000	1·126	0·530	0·253	0·127	0·0677	0·0384	0·0230	0·0145	0·00954	0·00650	A
	2·000	1·064	0·519	0·255	0·130	0·0698	0·0398	0·0239	0·0151	0·00995	0·00679	B
	2·000	1·314	0·534	0·207	0·0889	0·0427	0·0225	0·0129	0·00784	0·00503	0·00336	C
He	2·000	1·833	1·456	1·061	0·744	0·515	0·357	0·250	0·178	0·129	0·0945	A
	2·000	1·832	1·452	1·058	0·742	0·515	0·358	0·251	0·179	0·129	0·0950	B
	2·000	1·853	1·498	1·098	0·761	0·515	0·348	0·237	0·165	0·116	0·0839	C
	2·000	1·88	1·46	1·05	0·75	0·52	0·35	0·24	0·18	0·14	0·11	H
Li$^+$	2·000	1·935	1·760	1·522	1·266	1·026	0·818	0·647	0·510	0·403	0·319	A
	2·000	1·935	1·760	1·521	1·265	1·025	0·818	0·647	0·510	0·403	0·319	B
	2·000	1·940	1·776	1·545	1·291	1·046	0·831	0·653	0·510	0·399	0·312	C
	2·000	1·936	1·762	1·522	1·264	1·022	0·813	0·642	0·505	0·398	0·316	HF
C^{4+}	2·000	1·986	1·945	1·879	1·792	1·689	1·576	1·457	1·335	1·216	1·101	A
	2·000	1·986	1·945	1·879	1·792	1·689	1·576	1·457	1·335	1·216	1·101	B
	2·000	1·986	1·946	1·882	1·798	1·698	1·586	1·467	1·347	1·227	1·111	C
	2·000	1·986	1·945	1·880	1·794	1·692	1·579	1·459	1·338	1·219	1·104	HF

$A = DODEAC$. $B = DODE$. $C = SODE$. H = Hartree (James & Brindley, 1931a, b). HF = Hartree–Fock (Freeman, 1959).

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A Diffraction Measurement of the Structure of Cu₂O Films Grown on Copper

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A method for the detection of the Bragg maxima of very thin (100–500 Å) oxide films grown on metals is described. The shapes of the maxima are interpreted to give the strain present in the film and its thickness. The method is illustrated by its application to Cu₂O grown on a 110 face of a copper single crystal.

1. Introduction

With the hope of contributing to the understanding of the growth mechanism and structure of oxide films formed on metal surfaces, a series of diffraction experiments were undertaken to determine whether it is possible, during the very early stages of the life of such films (200 Å thick or less), to detect their presence by means of X-rays and, if so, to attempt to interpret the diffraction maxima associated with the oxide film in terms of its thickness and the deviations from crystalline perfection it may experience as it grows. The experiments have been performed with cuprous oxide grown on flat surfaces of copper single

crystals at 250 °C. in one atmosphere of oxygen. Attention has been limited to films grown on (110) faces of the metal crystal. Lawless & Gwathmey (1956) have shown that for this face, there is a simple epitaxial relation between the oxide and the copper substrate: their cube axes are parallel.

Cuprous oxide grown on copper recomends itself because of the uncomplicated well-known cubic crystal structure of the oxide, and the facility with which oxidized metal crystals may be prepared. The conditions for its growth were chosen to avoid contamination with cupric oxide and to obtain a film of uniform thickness. Details of the technique for preparing the films have been described by Young, Cathcart & Gwathmey (1956).

Reported here is a simple X-ray diffraction tech-

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* Operated for the U.S. Atomic Energy Commission by the Union Carbide Corporation.