

Atomic Scattering Factors for Spherical and Aspherical Charge Distributions

BY A. J. FREEMAN

*Materials Research Laboratory, Ordnance Materials Research Office, Watertown, Massachusetts, U.S.A.
and Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts,
U.S.A.*

(Received 4 June 1958)

The atomic scattering factors for forty-five atoms and ions have been calculated from Hartree and Hartree-Fock SCF wave functions and compared with the results of James & Brindley, Berghuis *et al.*, and others.

Principal scattering factors were also calculated along the lines of McWeeny for a number of atoms containing aspherical charge distributions of p electrons.

A general formalism for calculating the coherent scattering of X-rays from non-spherical charge distributions as a function of atomic orientation is presented, based in part on group theoretic methods. For p electrons the results of McWeeny are reproduced. For d electrons, the scattering is completely described in terms of three principal scattering factors and the angle between the scattering vector and the atomic orientation. As illustration, specific numerical calculations are given for several atoms with incomplete d shells. A discussion of the relationship between this treatment and the usual spherical approximation is presented.

1. Introduction

Since the electronic charge distribution determines the atomic scattering factor, there are as many ways of calculating scattering factors as there are electron densities. Thus, form factors have been calculated by (a) Pauling & Sherman (1932) using simple hydrogen-like wave functions with appropriate screening constants, (b) Bragg & West (1928), Debye (1930), and Bewilogua (1931) from Thomas-Fermi electron distribution functions and (c) by James & Brindley (1931a) who used Hartree self-consistent field (SCF) wave functions.

The Thomas-Fermi scheme allows the f values of all the neutral atoms to be easily determined by means of a universal function (independent of z , the atomic number). These f 's are fairly good especially for atoms with high atomic number. Furthermore, it is also at high z that few SCF calculations have been made so that in this region of the periodic table the Thomas-Fermi solution provides the best available atomic scattering factors.

Because only few Hartree solutions were available to them, James & Brindley (J&B in what follows) used an interpolation method to obtain f 's for those atoms not treated by an SCF scheme. The interpolated values are necessarily poor as the number of atoms used in the interpolation procedure was small.

Recently, there has been a determined effort to improve upon the old J&B values in several ways. Viervoll & Øgrim (1949) refined and extended the J&B interpolation scheme by including new SCF results for a number of atoms. McWeeny (1951) used the Slater type atomic orbitals calculated variationally

by Duncanson & Coulson (1944) to calculate f 's for the light atoms hydrogen to neon. Furthermore, McWeeny also calculated the dependence of the scattering on atomic orientation due to the inherent asphericity of the atomic charge distributions.

This effort was further enhanced as experimental evidence appeared (Bacon, 1952) which showed appreciable deviation from the J&B values. Cochran (1953) reported another unsatisfactory feature of the J&B values in giving too diffuse an electronic charge distribution. For these reasons a number of authors decided to use Hartree-Fock functions in order to calculate more exact f values by taking the effects of exchange into account. In this way Hoerni & Ibers (1954, 1957) calculated f 's for the atoms C, N, O, Be and B, and more inclusively Berghuis *et al.* (1955) did the same for some twenty odd atoms.

Since we have been using Hartree-Fock wave functions to calculate Compton scattering functions (Freeman, 1958), we decided to calculate form factors for all atoms and ions for which SCF functions were available in order to augment the previous work and in case of overlap to provide a numerical check on the results.

In the first part of this paper the results of calculations of the atomic scattering factors for some forty-odd atoms and ions using latest SCF atomic wave functions are presented. In the second part a general formula for calculating scattering factors from non-spherical charge distributions as a function of atomic orientation is given along with specific application to several atoms with incomplete p and d shells.

Table 1. Atomic scattering factors

X: SCF charge densities with exchange
 NX: SCF charge densities without exchange

sin θ/λ	Li(X) ¹	Li ⁺ (X) ¹	Be(X) ²	N(X) ³	N ⁻ (X) ³			O ⁺³ (X) ⁴		
	f	f	f	f	f	f _{II}	f _I	f	f _{II}	f _I
0.0	3.000	2.000	4.000	7.000	8.000	8.000	8.000	5.000	5.000	5.000
0.1	2.216	1.936	3.064	6.199	6.688	6.516	6.774	4.760	4.660	4.811
0.2	1.742	1.762	2.060	4.592	4.631	4.300	4.796	4.151	3.878	4.287
0.3	1.513	1.522	1.692	3.233	3.186	2.847	3.355	3.410	3.045	3.592
0.4	1.270	1.264	1.520	2.395	2.364	2.081	2.506	2.745	2.377	2.928
0.5	1.032	1.022	1.362	1.939	1.929	1.711	2.038	2.246	1.923	2.408
0.6	0.823	0.813	1.194	1.694	1.694	1.533	1.774	1.913	1.648	2.046
0.7	0.650	0.642	1.030	1.548	1.551	1.434	1.610	1.701	1.491	1.596
0.8	0.511	0.505	0.876	1.442	1.446	—	—	1.562	—	—
0.9	0.404	0.398	0.739	1.349	1.352	1.290	1.383	1.463	1.338	1.526
1.0	0.319	0.316	0.624	1.261	1.263	—	—	1.382	—	—
1.1	0.257	0.252	0.519	1.171	1.170	1.136	1.187	1.308	1.234	1.344

sin θ/λ	O ⁺² (X) ⁴			O ⁺ (X) ⁴	O(X) ⁴			O ⁻ (X) ⁴			F(X) ⁵		
	f	f _{II}	f _I	f	f	f _{II}	f _I	f	f _{II}	f _I	f	f _{II}	f _I
0.0	6.000	6.000	6.000	7.000	8.000	8.000	8.000	9.000	9.000	9.000	9.000	9.000	9.000
0.1	5.647	5.747	5.597	6.493	7.248	7.148	7.299	7.836	7.970	7.769	8.293	8.398	8.240
0.2	4.776	5.048	4.639	5.298	5.630	5.357	5.766	5.756	6.054	5.607	6.691	6.953	6.650
0.3	3.771	4.136	3.589	4.017	4.093	3.728	4.276	4.068	4.416	3.894	5.044	5.383	4.874
0.4	2.924	3.291	2.740	3.016	3.008	2.640	3.192	2.968	3.292	2.806	3.760	4.104	3.588
0.5	2.327	2.650	2.166	2.356	2.337	2.014	2.499	2.313	2.587	2.176	2.878	3.190	2.722
0.6	1.948	2.213	1.816	1.956	1.945	1.680	2.077	1.934	2.152	1.825	2.312	2.579	2.178
0.7	1.716	1.925	1.611	1.717	1.714	1.505	1.818	1.710	1.880	1.625	1.958	2.178	1.848
0.8	1.568	—	—	1.567	1.567	—	—	1.566	—	—	1.735	—	—
0.9	1.463	1.588	1.401	1.461	1.461	1.336	1.523	1.462	1.562	1.412	1.587	1.730	1.516
1.0	1.378	—	—	1.374	1.374	—	—	1.373	—	—	1.481	—	—
1.1	1.301	1.389	1.279	1.296	1.294	1.221	1.331	1.294	1.352	1.265	1.396	1.485	1.351

sin θ/λ	F ⁻ (X) ⁶	Ne(X) ⁵	Al ⁺³ (X) ⁶	Al ⁺ (X) ⁶	Al(X) ⁷			Si ⁺⁴ (X) ⁸	Si ⁺³ (X) ⁸
	f	f	f	f	f	f _{II}	f _I	f	f
0.0	10.000	10.000	10.00	12.00	13.00	13.00	13.00	10.00	11.00
0.1	8.968	9.350	9.74	10.94	11.21	10.78	11.42	9.79	10.53
0.2	6.924	7.811	9.01	9.22	9.21	8.98	9.32	9.20	9.48
0.3	5.068	6.090	7.97	7.90	7.91	7.87	7.93	8.33	8.34
0.4	3.725	4.620	6.81	6.77	6.80	6.80	6.80	7.31	7.27
0.5	2.843	3.528	5.68	5.70	5.72	5.72	5.72	6.26	6.25
0.6	2.288	2.778	4.68	4.71	4.73	4.72	4.73	5.28	5.30
0.7	1.945	2.283	3.84	3.88	3.89	3.88	3.90	4.42	4.44
0.8	1.729	1.962	3.19	3.22	3.22	—	—	3.70	3.73
0.9	1.585	1.750	2.69	2.70	2.71	2.69	2.72	3.13	3.14
1.0	1.482	1.608	2.31	2.32	2.33	—	—	2.67	2.67
1.1	1.398	1.502	2.04	2.04	2.04	2.04	2.04	2.33	2.34

sin θ/λ	Si(X) ^{7,8}	V ⁺² (X) ⁹	Ti ⁺ (X) ⁹	Mn ⁺² (X) ¹⁰	Mn ⁺ (X) ⁹	Mn(X) ⁹
	f	f	f	f	f	f
0.0	14.00	21.00	21.00	23.00	24.00	25.00
0.1	11.81	20.00	19.76	21.91	22.60	22.57
0.2	9.73	17.59	17.14	19.19	19.41	19.00
0.3	8.37	14.80	14.43	15.96	15.97	15.79
0.4	7.27	12.31	12.09	13.06	13.02	12.97
0.5	6.28	10.37	10.26	10.80	10.77	10.78
0.6	5.34	8.97	8.93	9.19	9.17	9.19
0.7	4.50	7.99	7.98	8.09	8.08	8.08
0.8	3.77	7.30	7.31	7.33	7.32	7.33
0.9	3.18	6.78	6.80	6.77	6.77	6.77
1.0	2.71	6.35	6.37	6.32	6.32	6.33
1.1	2.35	5.96	5.97	5.92	5.92	5.93

Table I (cont.)

$\sin \theta/\lambda$	$C^{+4}(X)^{11}$	$C^{+2}(X)^{11}$	$C^*(X)^{11}$	$Na^+(X)^3$	$Na(X)^3$	$Al^{+2}(X)^{12}$	$K^+(X)^{13}$	$K(X)^{14}$	$Cl^-(X)^{13}$
	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
0.0	2.000	4.000	6.000	10.00	11.00	11.00	18.00	19.00	18.00
0.1	1.986	3.686	5.126	9.54	9.76	10.39	16.68	16.73	15.67
0.2	1.945	2.992	3.581	8.37	8.34	9.17	13.75	13.73	11.97
0.3	1.880	2.338	2.502	6.89	6.89	7.97	10.96	10.97	9.51
0.4	1.794	1.910	1.950	5.47	5.47	6.83	9.04	9.05	8.15
0.5	1.692	1.672	1.685	4.29	4.30	5.73	7.87	7.87	7.29
0.6	1.579	1.533	1.536	3.39	3.40	4.75	7.11	7.11	6.59
0.7	1.459	1.429	1.426	2.74	2.75	3.91	6.51	6.51	5.91
0.8	1.338	1.332	1.322	2.30	2.30	3.25	5.95	5.95	5.23
0.9	1.219	1.233	1.218	1.99	1.99	2.73	5.39	5.39	4.59
1.0	1.104	1.131	1.114	1.78	1.78	2.35	4.84	4.84	4.01
1.1	0.994	1.030	1.012	1.63	1.63	2.07	4.32	4.32	3.49
1.3	0.800	0.838	0.821	1.44	1.44	1.70	3.40	3.40	2.69
1.5	0.638	0.673	0.659	1.31	1.31	1.49	2.71	2.71	2.15
1.7	0.508	0.536	0.524	1.19	1.19	1.35	2.20	2.20	1.81
1.9	0.404	0.427	0.419	1.08	1.08	1.25	1.84	1.84	1.57

$\sin \theta/\lambda$	$Ca^{+2}(X)^{15}$	$Ca^+(X)^{15}$	$Ca(X)^{15}$	$Ga^{+3}(NX)^{16}$	$Ga^+(NX)^{16}$	$Ga(NX)^{16}$
	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
0.0	18.00	19.00	20.00	28.00	30.00	31.00
0.1	16.93	17.21	17.33	27.00	28.15	28.31
0.2	14.40	14.35	14.32	24.42	24.53	24.49
0.3	11.70	11.70	11.71	21.11	20.96	20.96
0.4	9.61	9.63	9.64	17.80	17.72	17.73
0.5	8.25	8.26	8.26	14.91	14.89	14.90
0.6	7.38	7.38	7.38	12.55	12.56	12.57
0.7	6.75	6.75	6.74	10.72	10.74	10.74
0.8	6.22	6.21	6.21	9.35	9.36	9.36
0.9	5.70	5.70	5.70	8.34	8.34	8.35
1.0	5.18	5.19	5.19	7.59	7.59	7.59
1.1	4.68	4.68	4.68	7.03	7.03	7.03
1.3	3.77	3.77	3.77	6.21	6.21	6.22
1.5	3.03	3.03	3.03	5.58	5.58	5.59
1.7	2.44	2.44	2.44	4.98	4.99	4.99
1.9	2.03	2.03	2.03	4.42	4.43	4.43

$\sin \theta/\lambda$	$As^{+3}(NX)^{16}$	$As^{+2}(NX)^{16}$	$As^+(NX)^{16}$	$As(NX)^{16}$	$Tl^{+3}(NX)^{17}$	$Tl^+(NX)^{17}$
	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
0.0	30.00	31.00	32.00	33.00	78.00	80.00
0.1	28.74	29.33	29.79	30.07	75.03	75.87
0.2	25.79	25.86	25.85	25.78	67.94	67.80
0.3	22.47	22.43	22.38	22.32	59.94	59.82
0.4	19.34	19.33	19.33	19.29	52.89	52.91
0.5	16.52	16.54	16.56	16.52	47.15	47.19
0.6	14.07	14.09	14.11	14.08	42.44	42.47
0.7	12.04	12.06	12.07	12.04	38.43	38.44
0.8	10.42	10.43	10.44	10.42	34.88	34.88
0.9	9.17	9.17	9.18	9.17	31.68	31.67
1.0	8.23	8.23	8.23	8.22	28.77	28.76
1.1	7.52	7.52	7.52	7.52	26.16	26.16
1.3	6.55	6.55	6.55	6.55	21.87	21.87
1.5	5.88	5.88	5.88	5.88	18.78	18.78
1.7	5.31	5.31	5.31	5.31	16.62	16.63
1.9	4.78	4.78	4.78	4.77	15.04	15.04

* Ground state configuration.

¹ Fock & Petrashen, 1935.² Hartree & Hartree, 1935.³ Hartree & Hartree, 1948.⁴ Hartree, Hartree & Swirles, 1939.⁵ Allen, 1957.⁶ Froese, 1957.⁷ Hartree & Freeman, 1957.⁸ Hartree, Hartree & Manning, 1941a.⁹ Hartree, 1956.¹⁰ Hartree, 1954.¹¹ Jucys, 1939.¹² Kritschagnia & Petrashen, 1938.¹³ Howland, 1958.¹⁴ Hartree & Hartree, 1938a.¹⁵ Hartree & Hartree, 1938b.¹⁶ Hartree, Hartree & Manning, 1941b.¹⁷ Douglas, Hartree & Runciman, 1955.

2. Table of atomic scattering factors

The results of the computations are given in Table 1 at intervals in $\sin \theta/\lambda$ in \AA^{-1} units, chosen to make our results directly comparable with those of J&B.

The numerical calculations were performed on Whirlwind I, the MIT digital computer using a routine written by Wood (1957). We have calculated the transforms of the individual one-electron wave functions (for all atoms except C, C^{+2} , C^{+4} , Al^{+2} , K, Ga, Ga^{+} , Ga^{+3} , As, As^{+} , As^{+2} , As^{+3} , Tl^{+} and Tl^{+3}) since these are necessary for the Compton scattering calculations and also to allow for possible interpolation for atoms for which SCF wave functions are not available. Space limitations in the computer determined the extent in $\sin \theta/\lambda$ at which the form factors were calculated. The numerical wave functions were used as direct input data after being interpolated to a mesh suitable for machine calculation by a routine written by Corbató (1956). The effect of the interpolation procedure on the numerical accuracy was checked by the normalization condition.

As no SCF wave functions were available for aluminum, a limited Hartree-Fock calculation was carried out by the late D. R. Hartree and the author (1957) using the published results for Al^{+} (Froese, 1957). The $3p$ wave function from this calculation was also used in the calculation of an approximate form factor for silicon quoted in Table 1.

For a number of these atoms, the f values have also been calculated by Hoerni & Ibers (1954) and by Berghuis *et al.* (1955). Nevertheless, the present calculations are useful in that aside from giving some new data over an extended range in $\sin \theta/\lambda$, they also provide a check on the numerical accuracy of both the present and previous works. Comparison with the work of Berghuis *et al.* (1955) shows the numerical agreement to be within several parts in the last figure quoted, or to within the accuracy of the original numerical SCF wave functions. For completeness we have included all our results for these atoms in Table 1.

Berghuis *et al.* (1955) used SCF wave functions for F, F^{-} and Ne which included exchange effects in the $2p$ shell only. In our calculations, more recent Hartree-Fock wave functions were used in which, as is more usual, all exchange effects were included. This difference in charge densities resulted in f values which are about 0.2 units higher for $\sin \theta/\lambda \leq 0.4$. This is typical of the effect of exchange in contracting the radial extension of the charge distribution.

As an illustration of the effects of exchange on the calculated structure factors, we show a comparison of the f values for Mn (Viervoll & Øgrim, 1949) in Fig. 1 and Ti (James & Brindley, 1931*b*) in Fig. 2 obtained by interpolation of the J&B data and our results using Hartree-Fock wave functions. For Mn the agreement is seen to be good only for large $\sin \theta/\lambda$ values, whereas at smaller $\sin \theta/\lambda$ the differences are

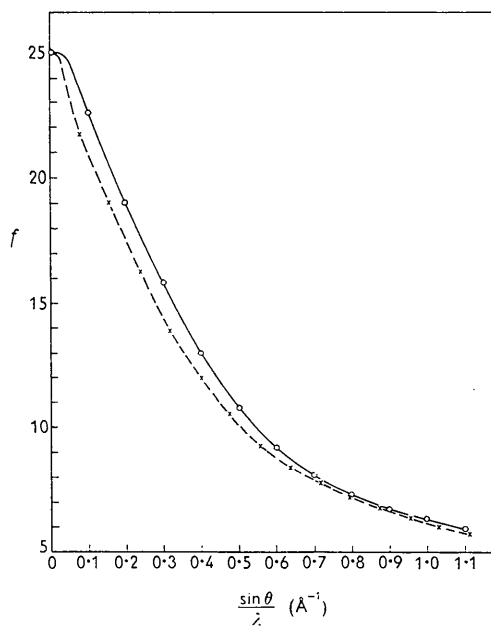


Fig. 1. Atomic scattering factor for Mn. The x's indicate the results of Viervoll & Øgrim; the circles denote our results.

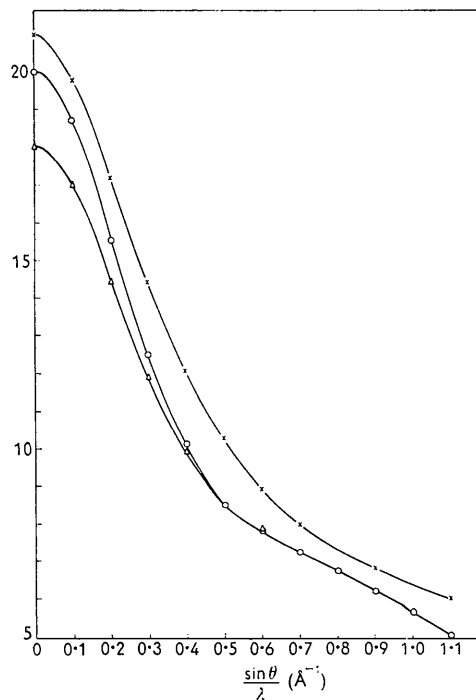


Fig. 2. Atomic scattering factors for titanium. The x's denote our results for Ti^{+} ; the circles are the J&B values for Ti^{+2} ; and the triangles are the J&B values for Ti^{+4} .

as much as 10%. For Ti, we can only compare our Ti^{+} values with those previously obtained for Ti^{+2} and Ti^{+4} . Aside from very small $\sin \theta/\lambda$, where the agreement is necessarily poor due to differences in degree

of ionization, the differences are quite large even for large $\sin \theta/\lambda$, being as much as 20% for intermediate values of $\sin \theta/\lambda$. This comparison rather strongly shows the large deviations which may be expected from the interpolated J&B values. As has been previously noted, and observed in Figs. 1 and 2, the J&B scattering factors generally show a charge distribution which is too diffuse.

As has been previously stated, since few SCF calculations have been carried out for high atomic number the Thomas-Fermi solutions (Landolt & Börnstein, 1950) must be used for calculating atomic scattering factors. Our results for Tl^+ and Tl^{+3} thus offer a good opportunity for comparing the results of the two methods. From Fig. 3 it is seen that the

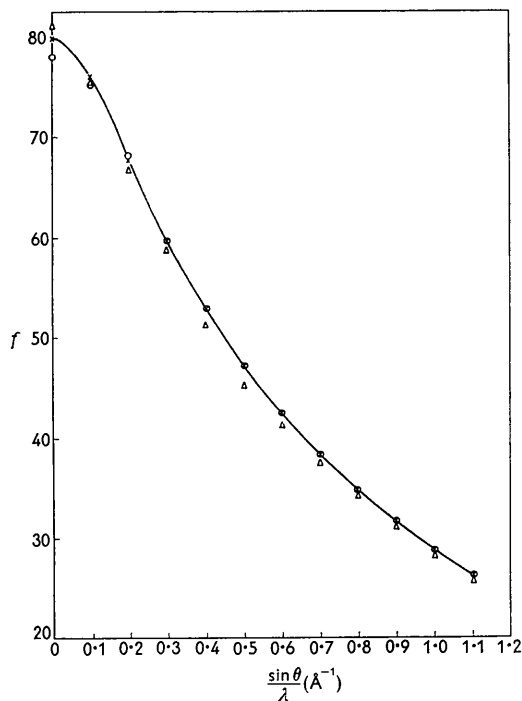


Fig. 3. Atomic scattering factors for thallium. The X's are our results for Tl^+ ; the circles are our results for Tl^{+3} ; and the triangles are the Thomas-Fermi calculations for neutral Tl.

agreement is excellent over the entire range of $\sin \theta/\lambda$; the deviation is nowhere greater than 4%. The inclusion of exchange and relativistic effects into the SCF calculation would of course increase this deviation. In general, however, it appears that the Thomas-Fermi values are indeed quite good for atoms with many electrons.

Atoms in different states of ionization

It has been assumed, in past calculations, that the scattering factors for atoms in different states of ionization were the same, except for very small $\sin \theta/\lambda$. (This assumption is very important to the interpola-

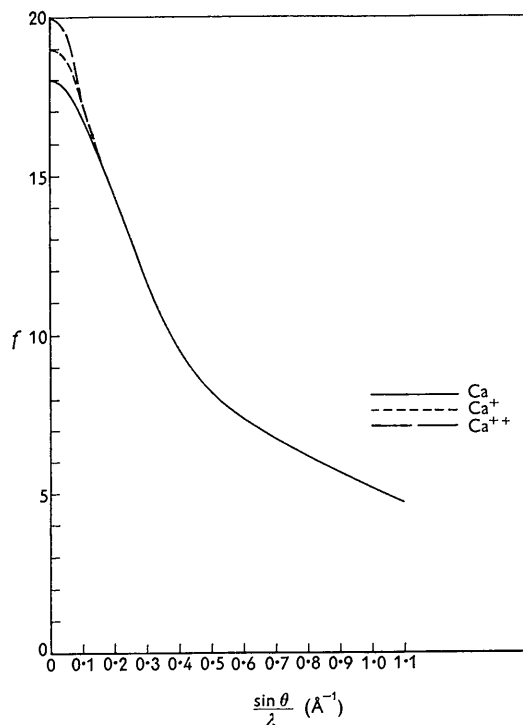


Fig. 4. Atomic scattering factors for Ca, Ca^+ and Ca^{++} .

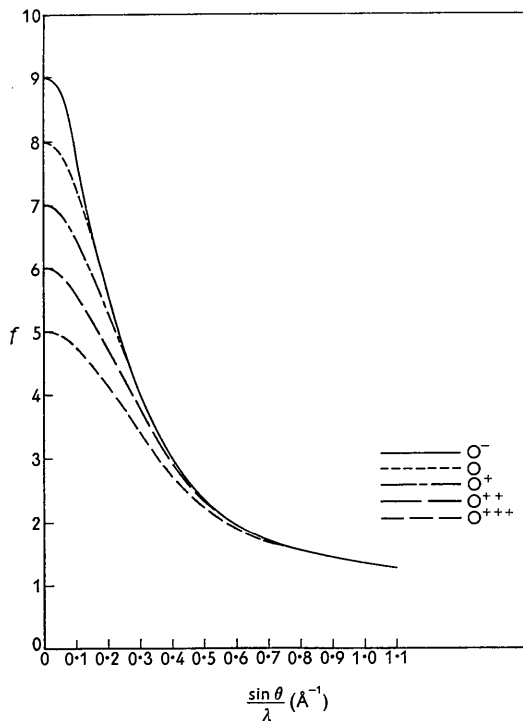


Fig. 5. Atomic scattering factors for some ionized states of oxygen.

tion procedure of J&B.) As there have been few such direct calculations in support of this view, it was decided to investigate the effects of degree of ioniza-

tion on the form factors for those atoms for which SCF wave functions are available. From Table 1 it is seen that in general the form factor varies little with degree of ionization for large $\sin \theta/\lambda$, but that for small $\sin \theta/\lambda$ (often an important experimental region) there are large variations of f with degree of ionization. There are of course individual differences, depending on the particular configuration of the outer electrons. This is seen, for example, by comparing the results obtained for Ca, Ca^+ and Ca^{++} , as shown in Fig. 4, with those for O^- , O , O^+ , O^{++} and O^{+++} , as shown in Fig. 5. For calcium, the outer electrons are $4s$ electrons and so the f curves are different only for the very small $\sin \theta/\lambda$ values at which the $4s$ scattering contribution is important. For oxygen however, the ionized electrons are $2p$ electrons; these contribute to the scattering intensity at larger $\sin \theta/\lambda$ than do the $4s$ electrons and so the differences between f values extend over a larger $\sin \theta/\lambda$ than is the case for calcium. In general though the differences are unimportant for $\sin \theta/\lambda > 0.3$, decreasing in importance with increasing atomic number.

For the atoms and ions listed in Table 1, different electronic wave functions were used for the various states of ionization. The much cruder approximation of subtracting the contribution per electron was not employed.

3. Scattering from aspherical charge distributions (p electrons)

As discussed by McWeeny (1951), the scattering from non-spherical charge distributions is necessarily dependent on the orientation of the scattering vector, \mathbf{S} . He showed that the scattering from a p orbital pointing in any direction is completely described in terms of two scattering factors, f_{\parallel} and f_{\perp} , and the angle β between the orbital axis and the scattering vector \mathbf{S} , f_{\parallel} is the scattering for an orbital pointing along \mathbf{S} while f_{\perp} is the scattering perpendicular to \mathbf{S} . In this language

$$f(p) = f_{\parallel}(p) \cos^2 \beta + f_{\perp}(p) \sin^2 \beta \quad (1)$$

is the scattering from any p orbital and

$$\Sigma f(p) = f_{\parallel}(p) + 2f_{\perp}(p) \quad (2)$$

is the scattering from a half-closed shell of p electrons. $\Sigma f(p)$ in equation (2) is, as expected, spherically symmetric since a half-closed shell has a spherically symmetrical charge distribution.

McWeeny calculated f_{\parallel} and f_{\perp} for the atoms hydrogen through neon, using the Duncanson & Coulson (1944) wave functions described earlier. As Hartree-Fock wave functions are necessarily more exact solutions of the free atom problem, it was decided to calculate these f 's for some of the atoms treated by McWeeny, i.e., oxygen and fluorine, in order to ascertain the effect on the scattering factors due to changes in the wave function. Furthermore, these

potentially useful scattering factors were also calculated for a number of other atoms not previously investigated in this way.

All these atoms have a unique symmetry axis given by that p orbital which contains a number of electrons different from that contained by the other p orbitals; in oxygen, only one orbital is doubly occupied, while in fluorine only one orbital is not doubly occupied. For example, the electron density of oxygen consists of a half-closed shell of $2p$ electrons plus one $2p$ orbital. The total scattering factor may therefore be written as

$$f = 2f(1s) + 2f(2s) + (f_{\parallel}(p) + 2f_{\perp}(p)) + (f_{\parallel}(p) \cos^2 \beta + f_{\perp}(p) \sin^2 \beta) \quad (3)$$

or in turn as

$$f = f_{\parallel} \cos^2 \beta + f_{\perp} \sin^2 \beta, \quad (4)$$

where

$$\begin{aligned} f_{\parallel} &= 2f(1s) + 2f(2s) + 2f_{\parallel}(p) + 2f_{\perp}(p), \\ f_{\perp} &= 2f(1s) + 2f(2s) + f_{\parallel}(p) + 3f_{\perp}(p). \end{aligned} \quad (5)$$

The same procedure can be followed for all the atoms considered. The results are given in Table 1, with f_{\parallel} and f_{\perp} defined by the method shown in equations (4) and (5), and $f = \frac{1}{3}f_{\parallel} + \frac{2}{3}f_{\perp}$ is the average scattering factor (obtained by averaging equation (4) over all values of β) which corresponds to the usual f value for non-spherical atoms.

In Figs. 6 and 7 we plot f , f_{\parallel} and f_{\perp} for atomic oxygen and atomic fluorine obtained from our calculations and those of McWeeny. The agreement is

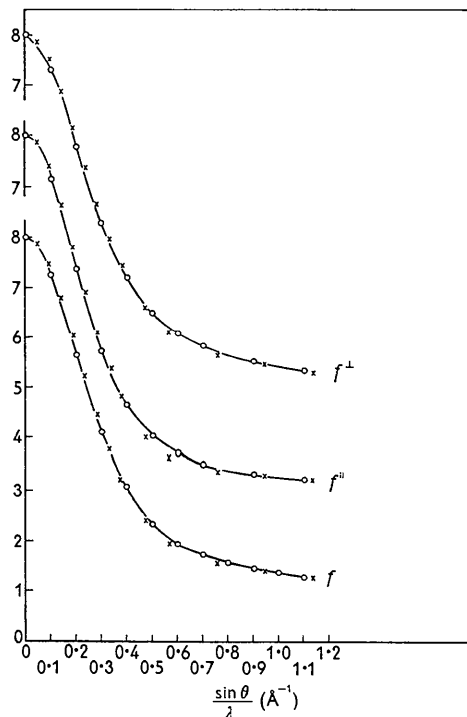


Fig. 6. Principal scattering factors for oxygen. The x 's indicate McWeeny's results and the circles denote our results.

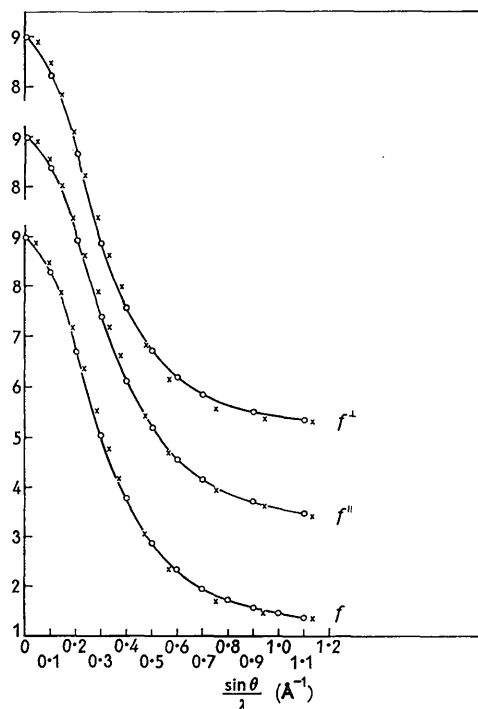


Fig. 7. Principal scattering factors for fluorine. The x 's indicate McWeeny's results and the circles denote our results.

surprisingly good, over most of the range of $\sin \theta / \lambda$, considering the large differences in wave functions. Our values for f for the F & Ne atoms are closer to those of McWeeny than are those of Berghuis *et al.* (1955). This is not surprising since we know that Slater AO's are quite contracted with respect to Hartree-Fock wave functions; the latter in turn are more contracted than are wave functions without exchange (such as those used by Berghuis *et al.*, 1955). This effect shows up in the higher peaking of the scattering factor at low $\sin \theta / \lambda$ for the more contracted wave functions.

4. Scattering from aspherical charge distributions (general formulation)

The scattering function depends upon atomic orientation for all non-spherically symmetrical charge distributions. McWeeny (1951) treated the case of p electrons only, which was particularly simple in that p electrons transform as vectors. For electrons of higher angular momentum, the mathematical complications increase enormously and resort must be made to the methods of group theory.

The basic integrals that appear in a calculation of the scattering factor are the matrix elements

$$f_i = \int \psi_i^* \psi_i \exp [i\kappa \mathbf{S} \cdot \mathbf{r}] dv. \quad (6)$$

$\kappa = 2\pi/\lambda$, λ is the wavelength of the incident radiation, $\mathbf{S} = \mathbf{s} - \mathbf{s}_0$, where \mathbf{s} and \mathbf{s}_0 are unit vectors along

the reflected and incident directions and the ψ_i are the individual one-electron wave functions. If the charge density, $\psi_i^* \psi_i$ is spherically symmetric then the scattering is independent of the orientation of \mathbf{S} and so we may choose \mathbf{S} in a direction most convenient to us. As is generally done in this case, \mathbf{S} is taken parallel to the z axis, along which the orbitals are quantized, as there are then certain selection rules which simplify the mathematics.

In this case, we may use the expansion

$$\exp [ikr \cos \theta] = \sum_n i^n (2n+1) P_n(\cos \theta) j_n(kr)$$

with $k = K|\mathbf{S}|$ and $j_n(kr)$ are the spherical Bessel functions. Writing ψ_i in the separable form $R_i(r)/r \mathcal{O}_l^{m_i}(\cos \theta) \Phi_{m_i}(\varphi)$, with $\mathcal{O}_l^{m_i}(\cos \theta)$ the normalized associated Legendre functions, and substituting into equation (1) we have

$$f_i = \sum_n i^n (2n+1) C_n(l_i m_i; l_i m_i) \int_0^\infty R_i^2(r) j_n(kr) dr. \quad (7)$$

The coefficients $C_n(l_i m_i; l_i m_i)$ are integrals of the product of three Legendre functions and were tabulated by Condon & Shortley (1953). Hence the scattering per electron is just a linear combination of radial integrations of products of radial charge densities and spherical Bessel functions. (In what follows, these radial integrals will be denoted by the symbol $\langle j_n \rangle$.) When the charge density is spherically symmetric equation (7) reduces to the familiar form

$$\int_0^\infty R_i^2(r) \frac{\sin kr}{kr} dr = \langle j_0 \rangle.$$

When the charge density is no longer spherically symmetrical, \mathbf{S} must be taken at an arbitrary direction and the scattering calculated as a function of this orientation, with of course an accompanying loss of the above-mentioned mathematical simplifications. In order to retain these well-known selection rules we adopt a formalism in which the charge densities in equation (6) are transformed from the x, y, z frame in which they are defined into a coordinate system x', y', z' in which \mathbf{S} is parallel to z' . The problem then is to transform the one electron wave functions $\psi_i(r, \theta, \varphi)$ into the rotated coordinate frame, r, θ', φ' defined by \mathbf{S} . But since the ψ_i are written in the separable form $R_i(r)/r \mathcal{O}_l^{m_i}(\cos \theta) \Phi_{m_i}(\varphi)$, we only need find the transformation of the spherical harmonics from the coordinates of one frame into one rotated with respect to it. In general this is a good deal more complicated than for the usual cases encountered in that the well-known spherical harmonic addition theorem does not suffice.

The general problem of the rotation of spherical harmonics has been discussed by Wigner (1931) and Corbató (1956), and by McIntosh *et al.* (1957), who used group theoretic methods. Representations of the rotation group in three dimensions can be found as

linear transformations on the space of analytic functions defined on the surface of a sphere, for which the spherical harmonics form bases for the irreducible subspaces (McIntosh *et al.*, 1957). Under a rotation R , which transforms a coordinate frame r, θ, φ into r', θ', φ'

$$\Theta_n^j(\cos \theta') \Phi_j(\varphi') = \sum_{k=-n}^n H_n^{jk}(R) \Theta_n^k(\cos \theta) \Phi_k(\varphi) \quad (8)$$

with the $\Theta_n^j(\cos \theta)$ representing the *normalized* associated Legendre functions (chosen as normalized because the representations are to be unitary). The H_n^{jk} , called the Herglotz polynomials (McIntosh *et al.*, 1957), are the matrix elements of a unitary irreducible representation of the group of three dimensional rotations. From equation (8) it is seen that under a rotation, the spherical harmonics transform linearly among themselves so that in the rotated system the matrix elements f_i , of equation (6) are linear combinations of the matrix elements in the unrotated system.*

If we define the rotation by the usual choice of Eulerian angles and if β is the angle between the z and z' axes, then for p electrons we reproduce the results of McWeeny† (1951) (see equations (1) and (2)) only with our definitions

* Further details will be given in a forthcoming publication on the Compton scattering from non-spherical charge distributions. (*Phys. Rev.* in press).

† McWeeny's results are derived for a p_z orbital only. As discussed above, this is all that is necessary since for a p shell the atom has a unique symmetry axis specified by that orbital which is either unoccupied or doubly occupied.

$$\begin{aligned} f_{11} &= \int R_p^2(r) [\Theta_1^0(\cos \theta)]^2 \exp [ikr \cos \theta] \sin^2 \theta d\theta d\varphi dr, \\ f_{11} &= \int R_p^2(r) [\Theta_1^1(\cos \theta)]^2 \exp [ikr \cos \theta] \sin^2 \theta d\theta d\varphi dr. \end{aligned} \quad (9)$$

Scattering from incomplete d shells

We have also carried out the analysis for the scattering from electrons of d symmetry. Since d electrons transform as tensors and not simply as vectors, as do p electrons, the simplicity of the geometric relation between f, f_{11} and f_{11} is entirely lost. Still the scattering from d electrons of arbitrary orientation may be completely described by stating three scattering terms and a function of the angle β between the z and z' axes.

Writing

$$f_m(d) = \int R_d^2(r) [\Theta_2^m(\cos \theta)]^2 \times \exp [ikr \cos \theta] \sin^2 \theta d\theta d\varphi dr \quad (10)$$

as the scattering factor of a d orbital with $m = |m_l|$, we find the relation between the scattering factors in the primed to the unprimed system is

$$\begin{aligned} f_2(d) &= \frac{1}{8}(1 + 6 \cos^2 \beta + \cos^4 \beta) f_2'(d) + \frac{1}{2}(1 - \cos^4 \beta) f_1'(d) \\ &\quad + \frac{3}{8}(1 - 2 \cos^2 \beta + \cos^4 \beta) f_0'(d), \\ f_1(d) &= \frac{1}{2}(1 - \cos^4 \beta) f_2'(d) + (\frac{1}{2} - \frac{3}{2} \cos^2 \beta + 2 \cos^4 \beta) f_1'(d) \\ &\quad + \frac{3}{2}(\cos^2 \beta - \cos^4 \beta) f_0'(d), \\ f_0(d) &= \frac{3}{4}(1 - 2 \cos^2 \beta + \cos^4 \beta) f_2'(d) + 3(\cos^2 \beta - \cos^4 \beta) f_1'(d) \\ &\quad + (\frac{1}{4} - \frac{3}{2} \cos^2 \beta + \frac{9}{4} \cos^4 \beta) f_0'(d). \end{aligned} \quad (11)$$

When $\beta = 0$, then $f_m(d) = f_m'(d)$. Equation (11) gives the variation of the scattering from a particular d

Table 2. *Principal scattering factors for d electrons*

$\sin \theta/\lambda$	Ti^{+1}				$V^{+2(1)}$			
	f_2	f_1	f_0	\bar{f}	f_2	f_1	f_0	\bar{f}
0.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.1	0.897	0.724	0.666	0.782	0.935	0.827	0.800	0.865
0.2	0.686	0.242	0.274	0.427	0.791	0.447	0.415	0.578
0.3	0.486	-0.062	0.126	0.195	0.616	0.103	0.163	0.320
0.4	0.331	-0.174	0.077	0.078	0.458	-0.111	0.070	0.153
0.5	0.227	-0.205	0.077	0.024	0.333	-0.210	0.058	0.061
0.6	0.155	-0.190	0.076	0.001	0.239	-0.237	0.073	0.016
0.7	0.108	-0.167	0.084	-0.007	0.172	-0.227	0.087	-0.005
0.9	0.052	-0.111	0.074	-0.009	0.089	-0.170	0.096	-0.013
1.1	0.027	-0.070	0.056	-0.006	0.048	-0.114	0.084	-0.010

$\sin \theta/\lambda$	Mn^{+1}				$Fe^{(2)}$			
	f_2	f_1	f_0	\bar{f}	f_2	f_1	f_0	\bar{f}
0.0	1.00	1.00	1.00	1.00	1.000	1.000	1.000	1.000
0.1	0.94	0.82	0.79	0.86	0.969	0.881	0.852	0.910
0.2	0.79	0.47	0.44	0.59	0.856	0.611	0.580	0.703
0.3	0.62	0.17	0.18	0.35	0.728	0.312	0.324	0.481
0.4	0.48	-0.05	0.11	0.19	0.590	0.092	0.140	0.309
0.5	0.36	-0.15	0.06	0.10	0.473	-0.077	0.079	0.174
0.6	0.27	-0.20	0.06	0.04	0.371	-0.172	0.057	0.091
0.7	0.20	-0.21	0.07	0.01	0.291	-0.219	0.061	0.041
0.9	0.11	-0.18	0.08	-0.01	0.177	-0.230	0.090	-0.003
1.1	0.07	-0.13	0.08	-0.01	0.104	-0.177	0.080	-0.013

(1) Hartree, 1956.

(2) Wood, 1957.

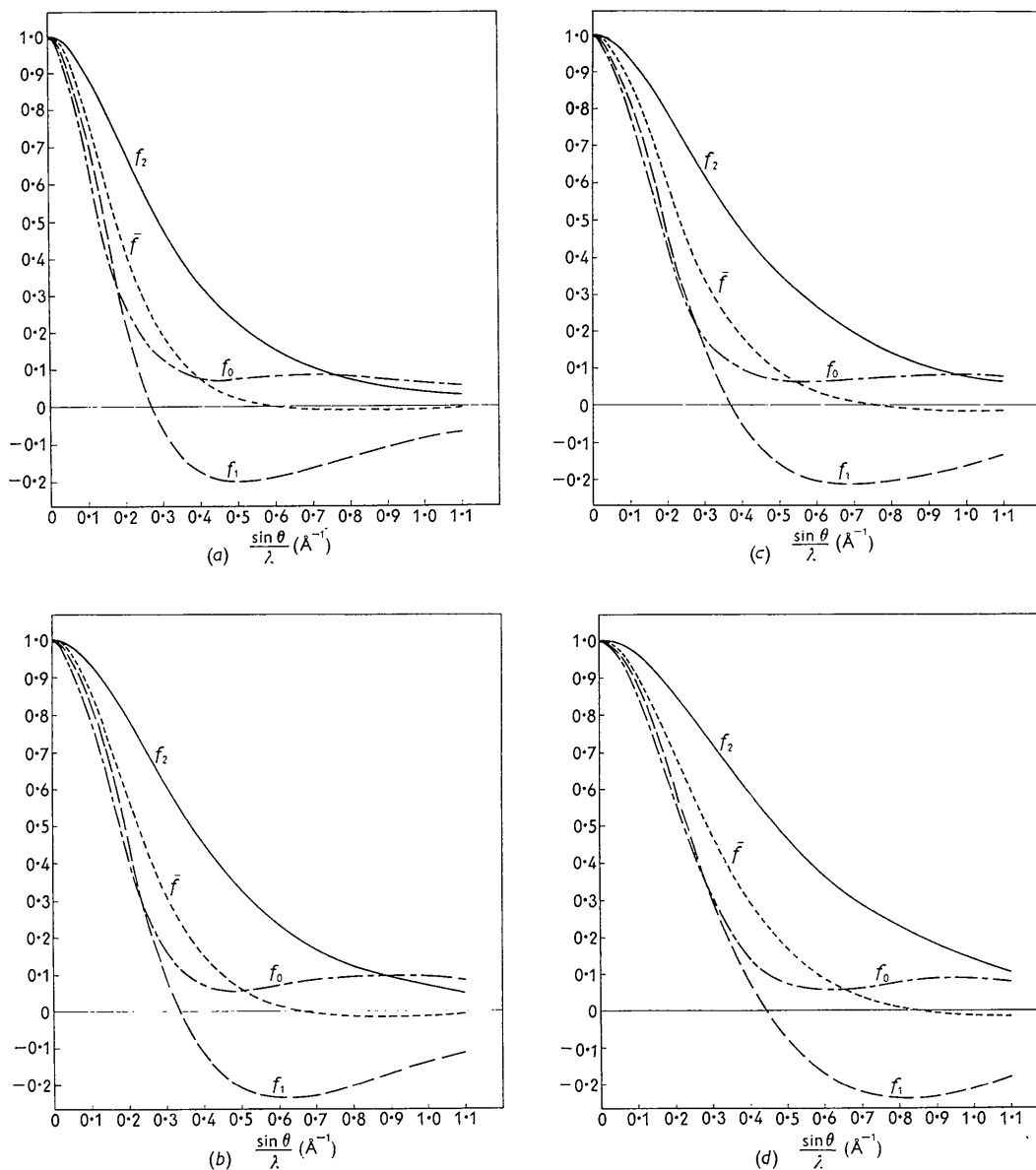


Fig. 8. Principal scattering factors for (a) Ti^+ , (b) V^{+2} , (c) Mn^+ , (d) Fe .

orbital as a function of the angle of orientation of the scattering vector. Only for $\beta = 0$ may we speak of a unique scattering factor, i.e., $f_m(d)$. For $\beta \neq 0$, the symmetry of the orbitals, as represented by their momentum quantization, no longer exists and now the scattering factors $f_m(d)$ are mixtures of the $f'_m(d)$. For the extreme case of $\beta = \pi/2$, for example, equation (11) reduces to

$$\begin{aligned} f_2(d) &= \frac{1}{8}f'_2(d) + \frac{1}{2}f'_1(d) + \frac{3}{8}f'_0(d), \\ f_1(d) &= \frac{1}{2}f'_2(d) + \frac{1}{2}f'_1(d), \\ f_0(d) &= \frac{3}{4}f'_2(d) + \frac{1}{4}f'_0(d). \end{aligned}$$

For a half-closed shell of d electrons, i.e., all orbitals

with different m_l occupied, the total scattering factor is

$$\begin{aligned} \sum_{m_l} f_{m_l}(d) &= 2f'_2(d) + 2f'_1(d) + f'_0(d) \\ &= 2f_2(d) + 2f_1(d) + f_0(d), \end{aligned} \quad (12)$$

which is angle independent and is of course the same result obtained if the calculation is made for $\beta = 0$. (Equation (12) follows also from the unitary nature of the matrix H_n^{jk} of equation (8).)

Following McWeeny (1951), we may define a 'mean' scattering factor per d orbital by averaging equation (11) over all values of β weighted with the element of solid angle $2\pi \sin \beta d\beta$. The result is

$$\overline{f(d)} = \frac{1}{5}(2f_2(d) + 2f_1(d) + f_0(d)) \quad (13)$$

for each m_l value. Comparison of equations (12) and (13) shows that the average scattering from any d orbital is just $\frac{1}{5}$ of the scattering from a half-closed shell of five d electrons.

Unfortunately, for d electrons, we may not carry out the procedure outlined in equations (3), (4) and (5) for the case of p electrons. Here we must tabulate $f_m(d)$ as well as the total scattering factor for the remaining electrons and use the expressions in equation (11) to calculate the total scattering factor as a function of orientation. Table 2 gives the principal scattering factors, $f_m(d)$ along with the mean scattering factor, $\overline{f(d)}$, for the d electrons in Ti^+ , V^{+2} , Mn^+ and Fe as a function of $\sin \theta/\lambda$ in units of \AA^{-1} . These all have a partially filled shell of d electrons and hence an aspherical charge density.

With this result we may understand an apparent paradox. We have seen that even for $\beta = 0$, $f_m(d)$ is a linear combination of the integrals $\langle j_n \rangle$ and not just simply the integral of the standard $j_0 = \sin kr/kr$. In fact

$$\begin{aligned} f_2(d) &= \langle j_0 \rangle + \frac{10}{7} \langle j_2 \rangle + \frac{3}{7} \langle j_4 \rangle, \\ f_1(d) &= \langle j_0 \rangle - \frac{5}{7} \langle j_2 \rangle - \frac{12}{7} \langle j_4 \rangle, \\ f_0(d) &= \langle j_0 \rangle - \frac{10}{7} \langle j_2 \rangle + \frac{18}{7} \langle j_4 \rangle. \end{aligned} \quad (14)$$

How then are we to explain the success of the usual calculations of the scattering factors in which the charge density is assumed spherical and only the $\langle j_0 \rangle$ terms retained? The answer is that the contribution per d electron of J&B corresponds exactly to the 'mean' scattering factor in equation (13). Substituting equation (14) in equation (13) gives

$$\overline{f(d)} = \langle j_0 \rangle = \int R_d^2(r) \cdot \frac{\sin kr}{kr} dr,$$

which is the familiar result obtained by the usual assumption of spherical symmetry. In general, for any orbital symmetry, the mean scattering factor is always just given by $\langle j_0 \rangle$.

As seen from Fig. 8(a), (b), (c) and (d), the $f_m(d)$ contributions differ widely over the range of $\sin \theta/\lambda$ and even become strongly negative. As pointed out by McWeeny (1951) for p electrons, we find that even though the mean factor, $\overline{f(d)}$, becomes small at high $\sin \theta/\lambda$, we may not conclude that the d electrons do not contribute at high $\sin \theta/\lambda$. As seen from Fig. 8(a), (b), (c) and (d) the opposite is true over a large range of angles due to strong interference effects between the radiation scattered from different parts of the charge distribution.

I am indebted to Dr John Wood for his assistance with some of the Whirlwind routines and for his Fe wave functions; to Mrs Joan Stekler of the Joint Computing Group at the Massachusetts Institute of Technology and Mrs Anna Hansen of the Materials Research Laboratory for their help with the hand computations; and to Drs L. C. Allen and L. P. Howland for allowing me the use of their wave functions.

References

- ALLEN, L. C. (1957). Quarterly Progress Report, Solid State and Molecular Theory Group, M.I.T., July 15, p. 52 (unpublished).
- BACON, G. E. (1952). *Acta Cryst.* **5**, 492.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
- BEWILOGUA, L. (1931). *Phys. Z.* **32**, 740.
- BRAGG, W. L. & WEST, J. (1928). *Z. Kristallogr. A*, **69**, 118.
- COCHRAN, W. (1953). *Acta Cryst.* **6**, 812.
- CONDON, E. U. & SHORTLEY, G. H. (1953). *Theory of Atomic Spectra*, p. 178. Cambridge: University Press.
- CORBATÓ, F. J. (1956). Ph.D. Thesis, Physics Dept., M.I.T. (unpublished).
- DEBYE, P. (1930). *Phys. Z.* **31**, 419.
- DOUGLAS, A. S., HARTREE, D. R. & RUNCIMAN, W. A. (1955). *Proc. Camb. Phil. Soc.* **51**, 486.
- DUNCANSON, W. E. & COULSON, C. A. (1944). *Proc. Roy. Soc. Edinb. A*, **62**, 37.
- FREEMAN, A. J. (1958). Quarterly Progress Report, Solid State and Molecular Theory Group, M.I.T., Jan. 15, p. 24 and April 15, p. 7 (unpublished).
- FOCK, V. & PETRASHEN, M. J. (1935). *Phys. Z. Sowjet*, **8**, 547.
- FROESE, C. (1957). *Proc. Camb. Phil. Soc.* **53**, 206.
- HARTREE, D. R. (1954). *Proc. Camb. Phil. Soc.* **51**, 126.
- HARTREE, D. R. (1956). *J. Opt. Soc. Amer.* **46**, 350.
- HARTREE, D. R. & FREEMAN, A. J. (1957) (unpublished results).
- HARTREE, D. R. & HARTREE, W. (1935). *Proc. Roy. Soc. A*, **150**, 9.
- HARTREE, D. R. & HARTREE, W. (1938a). *Proc. Camb. Phil. Soc.* **34**, 550.
- HARTREE, D. R. & HARTREE, W. (1938b). *Proc. Roy. Soc. Lond. A*, **164**, 167.
- HARTREE, D. R. & HARTREE, W. (1948). *Proc. Roy. Soc. A*, **193**, 299.
- HARTREE, D. R., HARTREE, W. & MANNING, M. F. (1941a). *Phys. Rev.* **60**, 857.
- HARTREE, D. R., HARTREE, W. & MANNING, M. F. (1941b). *Phys. Rev.* **59**, 299.
- HARTREE, D. R., HARTREE, W. & SWIRLES, B. (1939). *Philos. Trans. A*, **238**, 229.
- HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
- HOERNI, J. A. & IBERS, J. A. (1957). *Acta Cryst.* **10**, 86.
- HOWLAND, L. P. (1958). *Phys. Rev.* **109**, 1927, exponential fit of the Cl^- & K^+ SCF wave functions with exchange.
- JAMES, R. W. & BRINDLEY, G. W. (1931a). *Phil. Mag.* (7), **12**, 81.
- JAMES, R. W. & BRINDLEY, G. W. (1931b). *Z. Kristallogr. A*, **78**, 470.
- JUCYS, A. (1939). *Proc. Roy. Soc. A*, **173**, 59.
- KRITSCHAGNIA, A. & PETRASHEN, M. (1938). *J. Exp. Theor. Phys.* (U.S.S.R.) **8**, 507.
- LANDOLT, H. H. & BÖRNSTEIN, R. (1950). *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie*, 6th ed., vol. I, p. 301. Berlin: Springer.
- MCINTOSH, H. V., KLEPPNER, A. & MINNER, D. F. (1957). Memorandum Report No. 1097, Ballistic Research Laboratories, Aberdeen Proving Ground, Maryland (unpublished).
- MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.

PAULING, L. & SHERMAN, J. (1932). *Z. Kristallogr. A*, **81**, 1.
 VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.
 WIGNER, E. P. (1931). *Gruppentheorie und ihre Anwend-*

ung auf die Quantenmechanik der Atomspektren. Berlin: Vieweg und Sohn.
 WOOD, J. H. & PRATT, G. W. JR. (1957). *Phys. Rev.* **107**, 995.

Acta Cryst. (1959). **12**, 271

An Atomic Scattering Factor for Iron

BY A. J. FREEMAN

*Materials Research Laboratory, Ordnance Materials Research Office, Watertown, Massachusetts, U.S.A.
 and Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts,
 U.S.A.*

AND J. H. WOOD*

Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

(Received 15 July 1958 and in revised form 29 October 1958)

An atomic scattering factor for iron has been calculated using self consistent field wave functions as calculated by the unrestricted Hartree-Fock method in which Slater's average exchange potential formulation was used to simplify the variational problem. As this results in separate sets of radial wave functions for the two one-electron spin directions, individual one-electron form factors have also been calculated from which neutron scattering functions may be calculated. Comparison is made with the results of Viervoll & Ögrim (1949) and those obtained from the Thomas-Fermi method, with and without exchange.

1

Pratt (1956) has shown that in an atom with net spin there is a different exchange interaction for electrons with m_s of the same sign as the total M_s than for electrons with m_s of opposite sign to that of the total M_s . This effect (called an exchange polarization) results in different variational equations for orbitals of different m_s , if orbitals with the same n , l , and m_l values but different m_s are varied independently. Unlike the usual Hartree-Fock method, which contains the restriction of doubly filled orbitals in closed shells, this method of separate variation with regard to m_s , called the unrestricted Hartree-Fock method (Wood & Pratt, 1957), results in separate sets of radial wave functions for the two one-electron spin directions.

In Slater's (1951) formulation of the self-consistent field treatment of a free atom system, all electrons are considered to move in an average potential field obtained by forming a weighted mean of the exchange charges which appear in the Hartree-Fock procedure. Using this averaged exchange potential, the unrestricted Hartree-Fock equations are further reduced (Wood & Pratt, 1957) to a set of differential equations in which there is one potential acting on all electrons of α spin ($m_s = +\frac{1}{2}$) and another potential for electrons of β spin ($m_s = -\frac{1}{2}$).

* Supported in part by the Army, Navy and Air Force under contract with the Massachusetts Institute of Technology.

Wood & Pratt (1957) have applied this method to calculate SCF wave functions for atomic iron using a single determinant wave function in the $(3d)^6(4s)^2$ configuration to represent the 5D_4 ground state. Five of the six $3d$ -electrons were given α spin, each with the same radial dependence; the sixth $3d$ -electron was given β spin and a radial wave function which is independent of the $3d$ electrons with α spin.

In this paper the results of calculations of the atomic scattering factor for Fe using these SCF wave functions are presented, along with comparisons of scattering factors determined by other methods.

2

The numerical calculations were performed on Whirlwind I, the MIT digital computer using a routine written by Wood (1957). The effect on the numerical accuracy of the integrations was checked by the normalization condition.

3

The results of the computations are listed in Table 1 as a function of $\sin \theta/\lambda$ in Å^{-1} units. Both the individual one-electron form factors, f_i , and the total scattering factor $f = \sum_i f_i$ are listed corresponding to electrons having α or β spin. Since the exchange polarization effects are appreciable only for the wave functions of the $3d$ and $4s$ electrons, appreciable differences in form factors between electrons of opposite spin are