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An Atomic Scattering Factor for Iron

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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 ($m_s = -\frac{1}{2}$).

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 $f = \Sigma_i f_i$ 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

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Table 1. *Scattering factors for* Fe

$\sin\theta/\lambda$	$f_{1s}(\alpha)$	$f_{2s}(\alpha)$	$f_{2p}(\alpha)$	$f_{3s}(\alpha)$	$f_{3p}(\alpha)$	$f_{3d}(\alpha)$	$f_{4s}(\alpha)$
0·0	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
0·1	0·9992	0·9943	0·9949	0·9463	0·9415	0·9104	0·5388
0·2	0·9983	0·9760	0·9803	0·8014	0·7856	0·7027	0·0462
0·3	0·9967	0·9457	0·9563	0·6051	0·5806	0·4805	−0·0371
0·4	0·9950	0·9059	0·9241	0·4030	0·3780	0·3006	−0·0018
0·5	0·9925	0·8566	0·8847	0·2299	0·2124	0·1737	0·0199
0·6	0·9891	0·8004	0·8391	0·1030	0·0963	0·0914	0·0206
0·7	0·9858	0·7385	0·7889	0·0236	0·0265	0·0412	0·0130
0·8	0·9816	0·6734	0·7352	−0·0163	−0·0077	0·0122	0·0053
0·9	0·9766	0·6061	0·6796	−0·0283	−0·0181	−0·0032	0·0003
1·0	0·9716	0·5390	0·6234	−0·0236	−0·0148	−0·0106	−0·0018
1·1	0·9658	0·4733	0·5672	−0·0110	−0·0051	−0·0133	−0·0021

$\sin\theta/\lambda$	$f_{1s}(\beta)$	$f_{2s}(\beta)$	$f_{2p}(\beta)$	$f_{3s}(\beta)$	$f_{3p}(\beta)$	$f_{3d}(\beta)$	$f_{4s}(\beta)$	f
0·0	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	26·00
0·1	0·9999	0·9940	0·9949	0·9458	0·9399	0·8898	0·4886	23·96
0·2	0·9990	0·9756	0·9804	0·7982	0·7799	0·6560	0·0162	20·36
0·3	0·9973	0·9459	0·9566	0·5998	0·5720	0·4310	−0·0322	17·05
0·4	0·9957	0·9055	0·9246	0·3967	0·3685	0·2624	0·0024	14·15
0·5	0·9932	0·8568	0·8851	0·2242	0·2043	0·1488	0·0178	11·77
0·6	0·9898	0·8005	0·8397	0·0987	0·0908	0·0771	0·0167	9·95
0·7	0·9865	0·7385	0·7894	0·0211	0·0235	0·0340	0·0099	8·64
0·8	0·9823	0·6734	0·7359	−0·0173	−0·0089	0·0096	0·0036	7·72
0·9	0·9773	0·6066	0·6804	−0·0284	−0·0182	−0·0033	−0·0002	7·06
1·0	0·9723	0·5396	0·6241	−0·0233	−0·0145	−0·0094	−0·0015	6·57
1·1	0·9664	0·4739	0·5681	−0·0107	−0·0049	−0·0116	−0·0017	6·15

reflected in the table only for these electrons. It is this difference in charge densities which appears in any calculation of the neutron form factor and hence is an important quantity for neutron scattering experiments.

McWeeny (1951) has shown that if the atomic charge density is not spherically symmetrical, the scattering is dependent on the orientation of the scattering vector. For *p* electrons he showed that the scattering from a *p* orbital pointing in any direction is completely described in terms of two principal scattering factors and the angle between the orbital axis and the scattering vector. Freeman (1959a) generalized this work to electrons of arbitrary angular momentum using group theoretic methods and found that for electrons of *d*-like symmetry the scattering from a *d* orbital of arbitrary orientation may be completely described by three principal scattering factors and the angle between the orbital axis and the scattering vector. By averaging over all orientations of the scattering vector, a 'mean' scattering factor is obtained which corresponds exactly to the contribution per electron as determined by James & Brindley (1931). The principal scattering factors for the *d* electrons in iron have been given previously (Freeman, 1959b); only a total 'mean' scattering factor is presented here.

In Fig. 1 we plot for comparison our calculated values of the total 'mean' scattering factor for Fe along with (1) the results of Viervoll & Ögrim (1949), obtained by the interpolation methods of James & Brindley (1931) using SCF wave functions without exchange, and (2) the predictions of the Thomas–Fermi (TF) statistical method without exchange (Landolt & Börnstein, 1950) and with exchange (TFD) as calculated by Thomas & Umeda (1957), as these

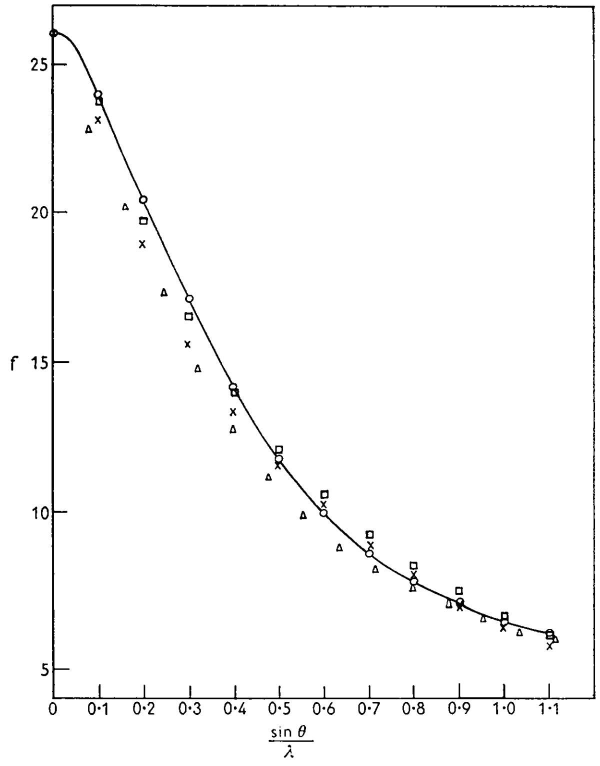

Fig. 1. Atomic scattering factor for Fe. The circles denote our results, the Δ's those of Viervoll & Ögrim (1949), the X's are the TF values and the □'s are the TFD values.

are the only scattering factor data which are available in the literature and are also commonly in use.

Our values are consistently higher than the Viervoll & Ögrim values; the largest deviations are in the range $0{\cdot}1 \leq \sin\theta/\lambda \leq 0{\cdot}5$, and are 10% of our calculated values.* This effect is generally attributed to the inclusion of exchange. But as Wood & Pratt (1957) and Pratt (1952) have pointed out, the Slater method yields total charge densities which are more compact than is the case for the Hartree–Fock scheme and hence their data should result in scattering factors which are higher in the very region observed.

The agreement between our values and those of the TF and TFD calculations is good over most of the range of $\sin\theta/\lambda$.† But whereas the TF values differ at most by 8% only in the region $0{\cdot}2 \leq \sin\theta/\lambda \leq 0{\cdot}4$, with smaller differences elsewhere, the TFD values have their maximum percentage deviations, of about the same amount, in the range $0{\cdot}6 \leq \sin\theta/\lambda \leq 0{\cdot}9$.

4

The magnetic form factor of Fe is sensitive to the shape of the *d* functions in the crystal (Steinberger & Wick, 1949). Weiss (1957) has calculated the magnetic form factor using the $3d$ wave function of α spin and compared his results with experiment. The agreement with experiment is excellent. As Wood & Pratt (1957) have pointed out, this indicates a fault of their calculated charge densities as being more compact than is the actual case for a free atom, a result which is to be expected from the Slater average exchange method.

As already indicated, the exchange polarization effect results in different wave functions for electrons of different spin, the effect being largest for the $3d$ electrons. Beside the obvious neutron magnetic scattering factor due to the unpaired $3d$ electrons, this polarization charge density for the other electrons also gives rise to coherent neutron scattering. Weiss & Freeman (1959) have used the one-electron form factors of Table 1 to calculate this contribution to the neutron scattering factor. While the effect is small, it nevertheless gives rise to a non-negligible coherent neutron scattering, estimated to be equivalent to a scattering amplitude of approximately $0{\cdot}027 \times 10^{-12}$ cm. for 5 unpaired $3d$ electrons.

5

Ideally it would be desirable to have available a scattering factor obtained from an ordinary (restricted) Hartree–Fock calculation in order to be able to determine the importance of exchange polarization effects in the calculation of f values for atoms. Since no such data are available we may only estimate these polarization effects. They appear to be smaller than the effects of exchange in proceeding from a Hartree calculation to a Hartree–Fock calculation. One further complication in any such comparison arises from the fact that the Slater SCF method uses an average potential field for all the electrons. This approximation results in wave functions which are not true solutions of the Hartree–Fock equations, but, as has been indicated, gives charge densities which are more compact than is the actual case for a free atom. Nevertheless, in the absence of solution of the unrestricted Hartree–Fock equations for atomic iron, the f-value given in this paper represents the best scattering factor available to date.

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* This difference is not appreciably affected by the inclusion of the scattering contribution of the $4s$ electrons neglected by Viervoll & Ögrim, since as Qurashi (1954) has shown, these electrons contribute only at $\sin\theta/\lambda \leqq 0{\cdot}15$.

† This is in agreement with similar results obtained earlier for Cu^+ (as pointed out to us by a referee). See Berghuis *et al.* (1955) and Thomas & Umeda (1957).