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Scattering factors for aluminum in the Slater approximation.

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X-ray atomic scattering factors for aluminum are calculated from wave functions resulting from several variants of the Slater exchange approximation and are compared with the experimental and Hartree–Fock values.

It has recently been suggested that Slater's (1951) approximation to the exchange operator appearing in the Hartree–Fock equations for one-electron orbitals of atomic structure could be modified advantageously. Schemes have been put forth by Robinson, Bassani, Knox & Schrieffer (1962), Lenander (1963), Lindgren (1963), and Kohn & Sham (1965). Robinson *et al.* suggested using a Thomas–Fermi screening correction, Kohn & Sham argue for a prefactor of $\frac{2}{3}$, while Lenander and Lindgren suggested a variationally determined parametric form.

It was thought desirable to ascertain the utility of these suggestions by a comparison with experimentally determined data and a series of calculations were undertaken on some simple polyvalent metals. We report herein some results for aluminum. A more extensive report will appear elsewhere.

We employ atomic units with energies expressed in rydbergs and lengths in bohrs. In these units, Slater's operator is

$$V_{ex}(\mathbf{r}) = -6\left[\frac{3}{8\pi}\cdot\varrho(\mathbf{r})\right]^{1/3}. \tag{1}$$

The work of Robinson *et al.* resulted in (1) being multiplied by a screening function

$$F(\alpha)=1-\frac{\alpha^2}{6}-\frac{4}{3}\alpha\tan^{-1}\frac{2}{\alpha}+\frac{\alpha^2}{2}\left(1+\frac{\alpha^2}{12}\right)\ln\left(1+\frac{4}{\alpha^2}\right) \tag{2}$$

with

$$\alpha = k_s/k_f = 0{\cdot}64153158D^{-1/6}(r) \tag{3}$$

where k_s is the screening parameter appearing in the Fermi–Thomas dielectric function for a metal and k_f is the radius of the Fermi sphere in momentum space. $D(r)$ is the radial electron density. Lenander and Lindgren suggested the empirical form for the radial potential

$$V_{ex}(r) = \frac{-C}{r}\left[\frac{81}{4\pi^2}\right]^{1/3} r^{n/3} D^{m/3}(r) \tag{4}$$

with C, n, and m as parameters to be varied until the energy minimum is achieved. In Slater's original suggestion, these three parameters are all equal to one.

Discussion

All the Slater exchange approximation self-consistent field (SCF) calculations were carried out to a self-consistency criterion on $U(r)$ of 10^{-4}, where the radial one-electron potential is defined by

$$V(r) = \frac{-2Z}{r}\,U(r) \tag{5}$$

with Z the atomic number of the nucleus. The scattering factors were calculated in the spherical approximation from the formula

$$f(q) = \int_0^\infty D(r) j_0(qr)\,dr \tag{6}$$

with $D(r)$ the radial electron density and

$$q = 4\pi\frac{\sin\theta}{\lambda} = \frac{2\pi}{a}(h^2+k^2+l^2)^{\frac{1}{2}}. \tag{7}$$

We have used for a, the lattice parameter of aluminum, the value of 4·0496 Å. The numerical integration of (6) was carried out by a nine-point Newton–Cotes procedure and the f values should be as reliable as the wavefunctions from which they were obtained.

In Table 1, we list the atomic scattering factors resulting from the various approximations employed. We have assumed an isolated atom model for the charge distribution and the calculations have been made at the experimental points for comparison (Batterman, Chipman & DeMarco, 1961). The meaning of the symbols in the column headings is as follows:

HF	Hartree–Fock (Clementi, 1965)
HFS	Hartree–Fock–Slater
HFS-WT	Hartree–Fock–Slater with tail correction (Herman & Skillman, 1963)
Scr. HFS	Screened Hartree–Fock–Slater
KS-HFS-WT	Kohn–Sham $\frac{2}{3}$ modification
MHFS-WT	Empirically modified Hartree–Fock–Slater (Lindgren, 1965, Table 3).

Table 1. *Comparison of X-ray scattering factors for aluminum*

hkl	sin θ/λ	f(exp.)	HF	HFS	HFS-WT	Scr. HFS	KS-HFS-WT	MHFS-WT
111	0·21385	8·63 ± 0·14	8·946	9·090	9·084	9·124	8·928	8·984
200	0·24694	8·25 ± 0·14	8·500	8·614	8·621	8·631	8·492	8·529
220	0·34922	7·09 ± 0·13	7·320	7·416	7·423	7·395	7·292	7·320
311	0·40950	6·42 ± 0·12	6·656	6·770	6·773	6·743	6·617	6·655
222	0·42771	6·19 ± 0·13	6·458	6·578	6·579	6·550	6·416	6·457
400	0·49388	5·48 ± 0·15	5·749	5·888	5·888	5·864	5·707	5·753
331	0·53819	4·96 ± 0·14	5·296	5·443	5·442	5·423	5·256	5·304
420	0·55217	4·67 ± 0·13	5·157	5·307	5·306	5·287	5·119	5·166
422	0·60487	4·38 ± 0·15	4·661	4·814	4·812	4·798	4·628	4·674
511	0·64156	4·00 ± 0·16	4·340	4·493	4·491	4·480	4·312	4·355

As can be seen from the Table, there is a notable difference in the results, yet one common attribute persists, *i.e.*, all approximations yield scattering factors larger than experiment. This qualitative result held true in the band model calculations of Arlinghaus (1965). One can see that the MHFS–WT approximation yield values closest to the HF results. Whether this is generally true remains to be ascertained.

All the Slater approximation SCF calculations listed herein were performed with a program written by the author in conjunction with Dr R.A.Moore. Much helpful correspondence with him is gratefully acknowledged.

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Further developments in a likelihood ratio method for the precise and accurate determination of lattice parameters.

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A likelihood ratio method (LRM) was developed by Beu, Musil & Whitney in 1962 which accounted for e_i, the variable component of systematic error in Bragg angle in the process of calculating $\hat{\hat{a}}_0$, the maximum likelihood estimate of the lattice parameter (for cubic materials) under the hypothesis of 'no remaining variable systematic errors' in Bragg angle. In this note, the LRM has been generalized to include the constant component e. $\hat{\hat{a}}_0$, now under two hypotheses of 'no remaining variable systematic errors' and 'no remaining constant systematic error', may be estimated provided the LRM test statistics W_m and U are both less than the corresponding critical values of the χ^2 distribution; in this case, $\hat{\hat{a}}_0$ is the maximum likelihood estimate of the lattice parameter, free of total (variable plus constant) systematic error within the precision of the Bragg angle measurements.

A likelihood ratio method (LRM) has been developed for evaluating in a valid statistical manner the extent of systematic error removal from corrected Bragg angle measurements to aid in the calculation of precise and accurate lattice parameters. (Beu, Musil & Whitney, 1962; hereafter called reference 1; Beu, Musil & Whitney, 1963). The original LRM was based on a hypothesis H of 'no remaining (variable) systematic errors' ('variable' was not explicitly stated in H of reference 1) in the corrected Bragg angle data and on an assumption that the algebraic sum of the variable error components (e_i) is zero, namely $\sum_i e_i = 0$. Such an assumption is required to keep the maximum likelihood estimates $\hat{\hat{a}}_0$, $\hat{a}_0$, $\hat{e}_i$, *etc.* (reference 1) from becoming indeterminate and to provide unique values for these estimates. In so doing, however, the e_i automatically become only one component of the total systematic error, namely, the variable component. The purpose of this note is to introduce the constant component e into LRM theory so as to complete the generality of the LRM. With e, the LRM becomes completely general since e'_i, the total remaining systematic error, can be determined from e_i and e alone according to: $e'_i = e_i + e$.

A brief review of the original LRM theory is given to introduce the modification based on e. Complete details including additional definitions, derivations, calculation procedure and an example are given in a comprehensive report available from the authors (Beu & Whitney, 1965). The pertinent assumptions of the original LRM are:

$$E(\psi_{i\alpha}) = \theta_i + e_i \tag{1}$$

$$\sum_i e_i = 0 \tag{2}$$

where

$E(\psi_{i\alpha})$ is the expected or mean value of $\psi_{i\alpha}$ (αth measurement of the ith Bragg angle) corrected for all known systematic errors.

ψ_i is the average of n_i measurements of $\psi_{i\alpha}$.

θ_i is the true but unknown value of the ith Bragg angle.

e_i is the unknown variable systematic error remaining in the measured ith Bragg angle after correcting for all known systematic errors.

$E(\psi_{i\alpha})$, ψ_i, θ_i, and e_i are all measured in degrees θ.

The maximum likelihood estimate of the lattice parameter $\hat{\hat{a}}_0$ (for cubic materials) under the hypothesis (H_1)* of 'no remaining variable systematic errors' in the ψ_i is calculated using a test statistic (W_m) which is distributed like χ^2 (Mood, 1950). W_m is based on H_1, on assumptions (1) and (2), and on the maximum likelihood estimates $\hat{a}_0$, $\hat{\theta}_i$, $\hat{e}_i$, and $\hat{\sigma}_i$ (standard deviation estimate of the ith Bragg angle). By comparing the numerical value of W_m with w_ε (a critical value of the χ^2 distribution), H_1 is or is not re-

* H_1 in this note is identical with H in reference 1.