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Errors Arising from Numerical Use of the Mott Formula in Electron Image Simulation

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Abstract

The Mott formula relating the electron scattering factor to that for X-rays is inaccurate in its numerical form in the small-angle region. Effects of the inaccuracy on both kinematic and dynamical diffraction have been investigated. Some artifacts arising from the inaccuracy have been found in simulated electron microscopy images. A modified form for the Mott formula, which minimizes the error, is proposed. However, for any accurate and reliable calculation only those electron scattering factors derived directly from the atomic potential can be used.

Introduction

For all the theories and calculations concerned with the dynamical interaction between electrons and crystalline materials, a knowledge of the crystal potential is essential. Among all the other ways of setting up the crystal potential, the most commonly used method is the one using atomic scattering factors $f(s)$ which have been computed and tabulated for elements under various approximations (Doyle & Cowley, 1973). It is the purpose of this paper to make a survey of the procedures for setting up the crystal potential, the approximations used and their effects on the calculated potential field as well as on the final simulated lattice images. We do not address the fact that tabulated scattering factors are approximate in that they refer to isolated atoms or ions and do not take into account the redistributions of electrons in crystals. It will become evident that the current practices involve errors, even within the limitations of the assumption of isolated-atom scattering factors. The dynamical and surface calculations require that much more attention be paid to the accuracy of the atomic scattering factors than in the case of kinematic scattering.

Computation

The atomic scattering factor for electrons is defined as the Fourier transform of the atomic potential,

$$f_e(s) = (2\pi me/h^2)F[\varphi(r)]$$
$$= (8\pi^2 me/h^2)\int_0^\infty \varphi(r)[\sin(sr)/sr]r^2\,dr. \qquad (1)$$

Here F denotes Fourier transform, $s = 4\pi\lambda^{-1}\sin\theta$ and $\varphi(r)$ is the atomic potential for isolated spherically symmetrical atoms or ions.

A further formulation for obtaining the atomic scattering factor for electrons is that due to Mott & Massey (1965) by the use of Poisson's equation relating the potential and charge-density distribution,

$$f_e(s) = (8\pi^2 me^2/h^2)[Z - f_X(s)]/s^2, \qquad (2)$$

where $f_X(s)$ is the atomic scattering factor for X-rays.

A detailed calculation of the atomic scattering factors requires the total wave function of an atom. However, the wave function is known exactly only for the hydrogen atom. Scattering factors published for all other atoms are approximate, and are reliable only insofar as the electron wave function employed in the calculation is a reliable representation of the true wave function. Various methods of approximating the total wave function of an atom have been developed. The relativistic Hartree-Fock equation (RHF) provides the most accurate generally calculable atomic wave functions. The RHF equation given by Grant (1961) has been solved numerically and programmed by Coulthard (1967) with the magnetic-interaction terms and off-diagonal Lagrange parameters omitted. Calculations performed by Doyle & Turner (1968) yield the total charge densities $\rho(r)$ and atomic potential $\varphi(r)$, and therefore the atomic scattering factors for X-rays and electrons.

The applications of these numerical discrete scattering factors to the calculation of electron diffraction and electron microscopy image simulation are inconvenient. It was considered desirable to express $f_e(s)$ for each element by a single analytical expression from which values could be calculated for any values of s and any electron energy. Analytical approximations to $f_e(s)$, of the form

$$f_e(s) = \sum_{i=1}^{n} a_i \exp(-b_i s^2) + c \qquad (3)$$

where a_i, b_i and c are parameters determined by curve fitting procedures, were originally introduced by Vand, Eiland & Pepinsky (1957) for X-ray scattering factors, and by Smith & Burge (1962) for electron scattering factors.

Since values of $f_X(s)$ are generally available in the literature, and also because our very limited knowledge of the potential field in crystals is an even greater

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obstacle to the derivation of useful values of $f_e(s)$ than it is to the derivation of useful values of $f_X(s)$ (Ibers, 1958), the Mott formula (2) has been used as a basis for most of the dynamical calculations to obtain the electron scattering factors.

The Mott formula, in its approximate numerical form, can be written as

$$f_e(s) = (8\pi^2 me^2/h^2)\left[Z - \sum_{i=1}^{n} a_i \exp(-b_i s^2) - c\right]\Big/ s^2. \tag{4}$$

The limiting expression of the formula, as s approaches zero, takes the form

$$f_e(0) = \lim_{s\to 0}(8\pi^2 me^2/h^2) \times\left[\sum_{i=1}^{n} a_i b_i - \left(\sum_{i=1}^{n} a_i + c - Z\right)\Big/ s^2\right]. \tag{5}$$

Finite errors are unavoidable in the numerical calculations of the X-ray atomic scattering factors and in the Gaussian curve-fitting procedures. The limiting expression (5) turns out to be divergent as $s=0$ because, in its analytical approximate form,

$$f_X(0) = \sum_{i=1}^{n} a_i + c \neq Z. \tag{6}$$

An improved form of the Mott formula which takes account of the fact that $f_X(0) = Z$ can be introduced:

$$\begin{aligned} f_e(s) &= (8\pi^2 me^2/h^2) \times\left[f_X(0) - \sum_{i=1}^{n} a_i \exp(-b_i s^2) - c\right]\Big/ s^2 \\ &= (8\pi^2 me^2/h^2)\left\{\sum_{i=1}^{n} a_i[1 - \exp(-b_i s^2)]\right\}\Big/ s^2, \end{aligned} \tag{7}$$

with the corresponding limiting form as $s \to 0$,

$$f_e(0) = (8\pi^2 me^2/h^2)\left(\sum_{i=1}^{n} a_i b_i\right). \tag{8}$$

The divergence problem is hence avoided and the atomic scattering amplitude takes only finite values for small-angle scattering.

The electron scattering factors as functions of the parameter s are shown in Fig. 1. Fig. 1(a) is obtained from (4). As s goes to the small-angle region of the same order as that of the discrepancy between $f_X(0)$ and Z, the electron scattering factor begins to increase enormously and is divergent as $s=0$. Curve (b) is obtained from (3) by using the Gaussian fitting parameters from Doyle & Turner (1968). The parameters are based on the numerical calculations from the relativistic Hartree–Fock equation and are considered as the most reliable representation of the true electron scattering factors. Hereafter these are called the HFP (HF, parameterized) electron scattering factors. Curve (c) is from (7), the improved numerical form of the Mott formula. As can be seen from Fig. 1, this formula, like the original approximate numerical Mott formula, works very well for s greater than 0·15 but becomes less accurate and begins to deviate from the HFP electron scattering factor when s become smaller than 0·13. The reason for these deviations lies in the nature of the Mott formula. From (7) it is obvious that if the error for the X-ray scattering factor calculation is of the order of 10^{-2}, then for large s the error for the electron scattering factor will be of the same order as for the X-ray case but it will become more and more severe as s goes to zero. For $s \sim 10^{-2}$, the error in the electron scattering factor will then be of the order of 1. Compared with its value at $s=0$, this is a 10% error and is expected to be important under certain circumstances.

The potential fields resulting from the three types of electron scattering factors are shown at Fig. 2 for a single Au atom. The most remarkable differences between the fields are in the averaged potential. The averaged potential from the Mott formula and X-ray

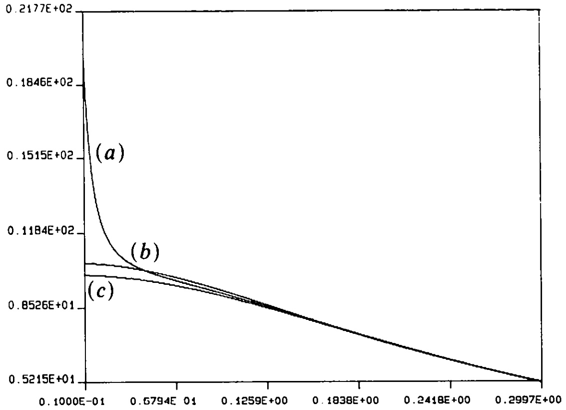


Fig. 1. The electron scattering factors of an Au atom vs s. Curve (a) is from the Mott formula, (b) from the fitting parameters for electron scattering and (c) from the improved Mott formula.

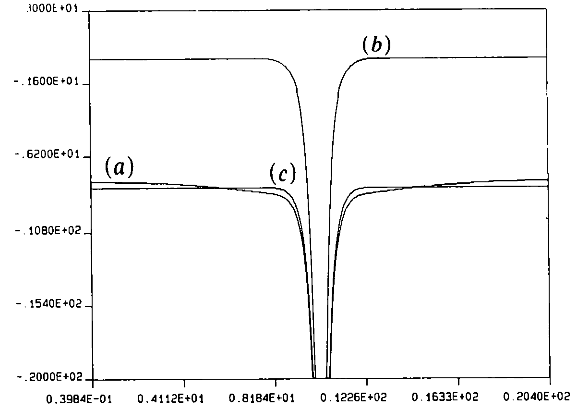


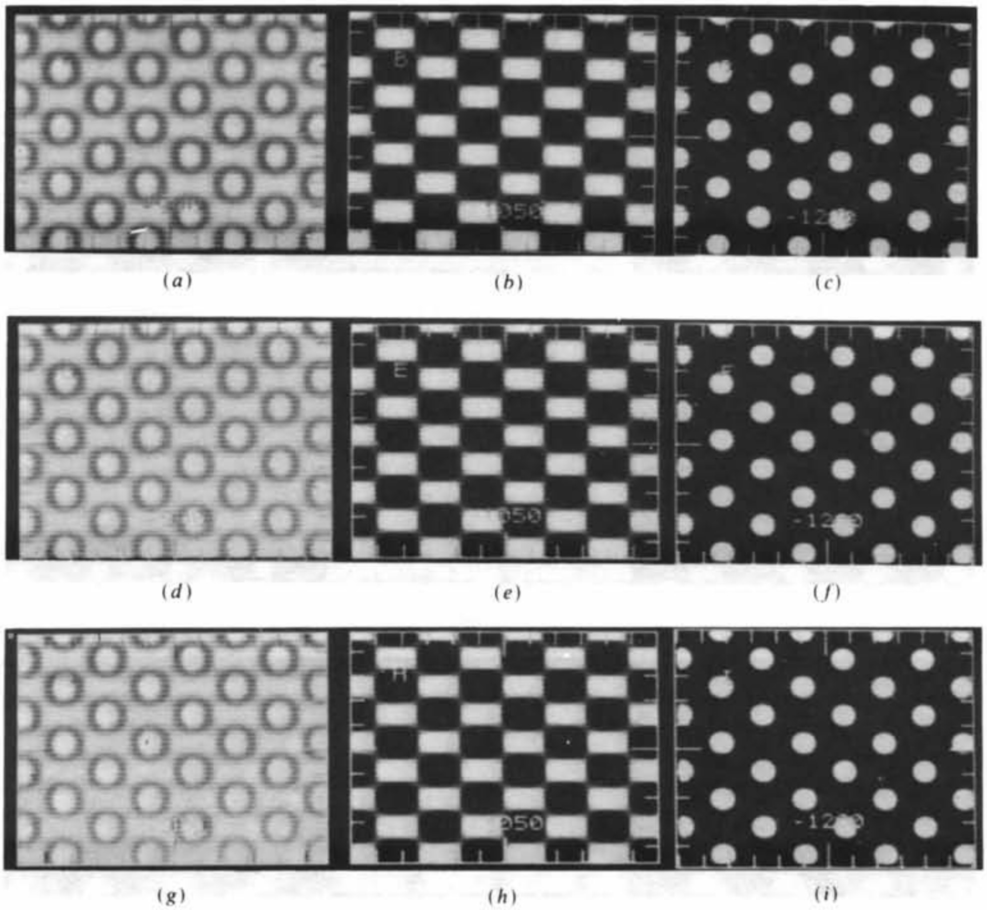
Fig. 2. Potential distributions of a single Au atom. (a), (b) and (c) correspond to curves (a), (b) and (c) in Fig. 1 respectively.

scattering factor is of the order of −8 (Figs. 2*a*,*c*), while the value from the HFP electron scattering factor is about 0 (Fig. 2*b*). This difference in the average potential values is a direct consequence of the discrepancies in the atomic scattering factors at the small-*s* region, because the zeroth Fourier component of the potential field corresponds to the averaged potential.

Figs. 3 and 4 are high-resolution electron microscopy (HREM) images simulated by the multislice method (Cowley & Moodie, 1957). The electron scattering factors from (7) are used in Figs. 3(*a*)-(*c*) and 4(*a*)-(*c*), the scattering factors from (5) are used in Figs. 3(*d*)-(*f*) and 4(*d*)-(*f*), while Figs. 3(*g*)-(*i*) and 4(*g*)-(*i*) are obtained from the HFP electron scattering factors. The simulations have been done for 100 keV electrons and a gold crystal with the electron beam along the ⟨110⟩ direction. Fig. 3 shows simulated images for a crystal of 28·9 Å thickness. The differences between the images from different types of scattering factors are minor; the images are not sensitive to the scattering factor in the small-angle region at this thickness. For the larger crystal thickness (Fig. 4) of 289 Å, the differences are very pronounced. Artifacts are produced by using improper scattering factors (Figs. 4*b* and *e*).

Results and discussion

It was shown in the previous section that if the specimen is so thin and the real-space periodicity so small that the single scattering events are dominant in the diffraction processes, the final simulated images are not sensitive to the values of the electron scattering factor in the small-angle region. For scattering from a crystal only discrete values of the atomic scattering factor which correspond to the diffracted beams are important to the diffracted-beam intensities calculation and the image simulation. For a crystal of periodicity *A* in real space, the smallest value of *s* which is significant to the kinematic diffraction calculation is of the order of $1/A$. If, further, this value of *s* is larger than the critical value s_0, a point above which the Mott formula is accurate in its numerical form, the



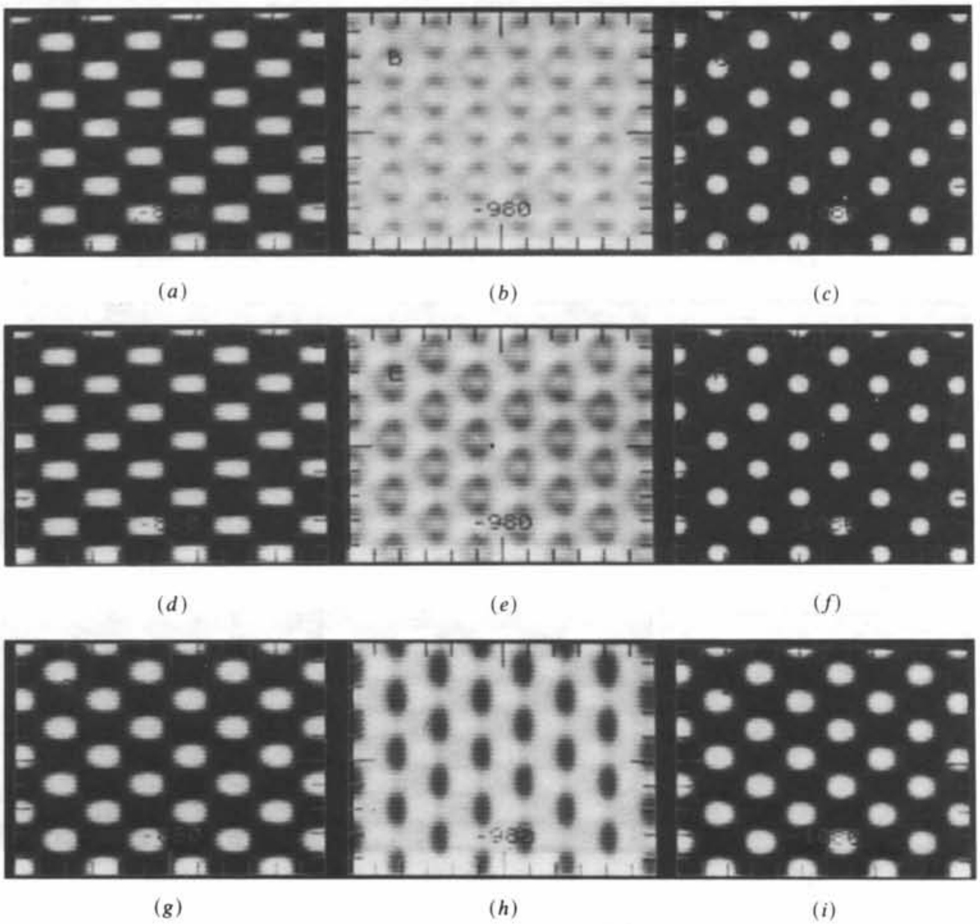
(*a*) (*b*) (*c*)
(*d*) (*e*) (*f*)
(*g*) (*h*) (*i*)

Fig. 3. Simulated electron microscopy images for Au in [110] orientation. The crystal thickness $t = 29{\cdot}8$ Å and the defocus $\Delta f = -900$ (*a*, *d* and *g*), −1050 (*b*, *e* and *h*) and −1200 Å (*c*, *f* and *i*). The images are calculated using equation (7) (*a*, *b* and *c*), equation (5) (*d*, *e* and *f*) and the HFP scattering factors (*g*, *h* and *i*).

inaccuracy in the scattering factors in the small-angle region below s_0 will not affect the diffraction calculation. On the other hand, if the periodicity A is large enough so that $1/A$ is less than s_0, the scattering factor at some points s below s_0 will contribute to the final diffracted-beam intensities, and introduce some errors into the diffraction calculation. Some artifacts may then appear in the simulated images even in the kinematic diffraction case.

Roughly speaking, the scattering factor in the small-angle region corresponds to the long-range atomic potential distribution. If the atoms are far apart then it will be those asymptotic values of the atomic potential that dominate the crystal potential in the region between the atoms. Further, in the Fourier space it is the small-angle components that are responsible for the asymptotic form of the atomic potential and therefore the crystal potential in the region between the atoms. It is expected that the computed crystal potential will be more sensitive to the accuracy in the atomic scattering factors in the small-angle region when a large atomic spacing is involved.

Surface-image simulation (Marks, 1984; Peng & Cowley, 1986) is one of the situations in which both a large unit-cell dimension and large atomic spacings are involved. The periodic-continuation assumptions (Cowley, 1981) needs to be used in order to deal with the essentially non-periodic object, and a large unit-cell dimension normal to the surface must be used to avoid interference between the extended unit cells. The calculated crystal potential within one unit cell is shown in Fig. 5. Fig. 5(*b*) is obtained from the X-ray scattering factor and the original Mott formula. The divergence of the scattering factor at small values of s results in an artificial long tail in the atomic potential and, in the surface case, a long tail around the crystal surface. For some surface-potential-sensitive technique, like reflection electron microscopy (REM), this representation of the surface potential will not give the correct results. Fig. 5(*c*) is from the improved Mott formula. The resulting surface potential is much better than in Fig. 5(*b*) but still gives a wrong potential value outside the surface in the vacuum and an incorrect averaged potential inside the crystal in comparison with that of Fig. 5(*a*), which



(*a*) (*b*) (*c*)

(*d*) (*e*) (*f*)

(*g*) (*h*) (*i*)

Fig. 4. Simulated electron microscopy images as for Fig. 3 but with $t = 289$ Å. Defocus values used in the simulation are $\Delta f = -880$ (*a*, *d* and *g*), -980 (*b*, *e* and *h*) and -1080 Å (*c*, *f* and *i*).

is obtained from the HFP electron scattering factor and is considered to be the most reliable representation of the real case.

For thick crystals the interaction between the incident electron beam and the crystal potential is characterized by multiscattering events. In consequence, the discrepancies in the small-s region between the electron scattering factors in the various approximations begin to affect the diffracted-beam intensities. The artifacts observed in Fig. 4 stem from the dynamical processes to which the small-angle scattering factor is important.

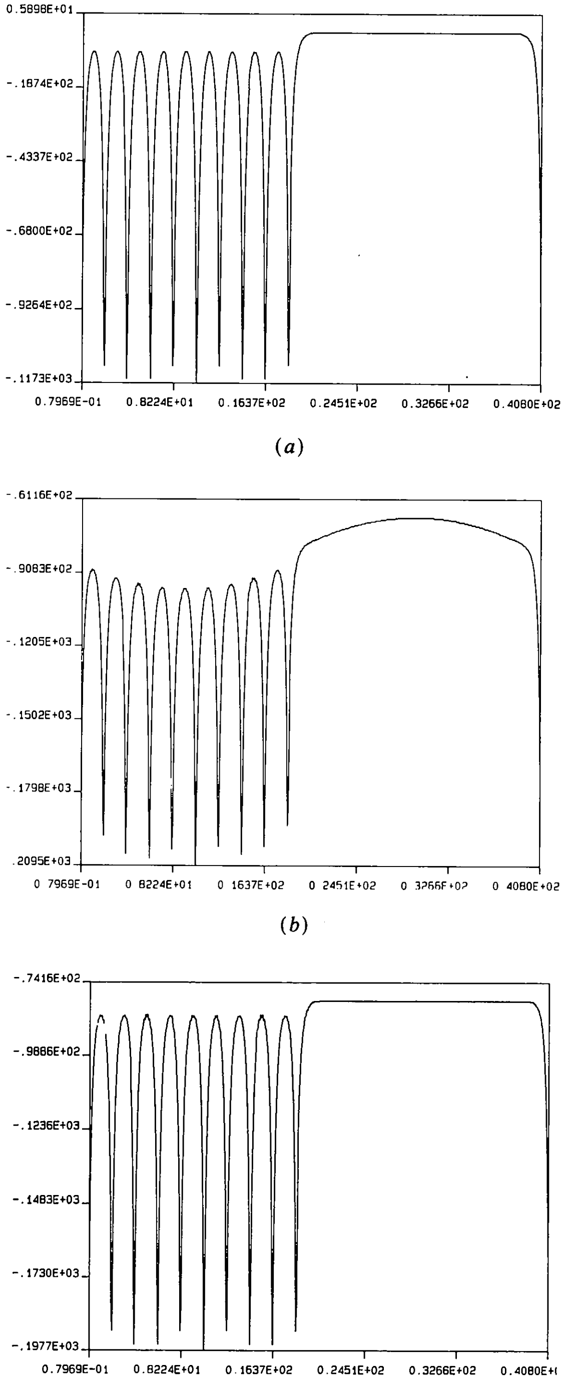


Fig. 5. Surface potential distribution obtained from (a) the HFP electron scattering factor; (b) the X-ray scattering factor and Mott formula; (c) the improved Mott formula.

Summary

For larger unit-cell dimensions or for a thick crystal when the diffraction processes are dominated by multiscattering events, the inaccuracy in the atomic scattering factors in the small-angle region will affect the diffracted-beam intensities and result in some artifacts in the simulated electron microscopy images. The inaccuracy of the atomic scattering factors in the small-angle region can come from the improper use of the Mott formula in its numerical form and is emphasized by the nature of the formula. The resulting effects in the electron-microscopy-images simulation are severe and misleading in certain circumstances. For any accurate reliable dynamical calculation and image simulation the use of parameterized X-ray scattering factors and the Mott formula must be avoided. Only the electron scattering factor derived directly from the atomic potential can be used (Doyle & Turner, 1968; Jiang & Li, 1984).

Note added in proof. It should be noted that some, but not all, of the current multi-slice computer programs include the improper use of the Mott formula. Michael O'Keefe incorporated the improved form of the Mott formula, equations (7) and (8), in the *SHRLI* program he wrote in 1980.

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Normalization Factors for Spherical Harmonic Density Functions

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Abstract

Normalization factors N_{lm} for spherical harmonic density functions c_{lmp} defined by $\int N_{lm}|c_{lmp}|\,d\tau = 2-\delta_{l0}$ have been derived for $l \le 7$, from both analytical and numerical integration methods.

Introduction

The increasing accuracy of X-ray diffraction data has led to more widespread use of spherical atom scattering formalisms. In the multipole formalism the atomic density is described by a series of real spherical harmonic functions y_{lmp} with $p = +$ or $-$, multiplied by a normalized radial function $R(r)$ (Dawson, 1967; Stewart, 1976; Hansen & Coppens, 1978; Kurki-Suonio, 1968; Price & Maslen, 1978). The functions y_{lmp} are defined as

$$y_{lmp} = N_{lmp} P_l^m(\cos\theta) \begin{matrix} \cos m\varphi & \text{for } p=+ \\ \sin m\varphi & \text{for } p=- \end{matrix} \qquad (1)$$

where $P_l^m(\cos\theta)$ are the associated Legendre polynomials (Arfken, 1970). A number of authors (Price & Maslen, 1978; Hansen & Coppens, 1978) have normalized the angular functions y_{lmp} such that

$$\begin{aligned} \int |y_{lmp}(\theta,\varphi)|\,d\tau &= 1 \quad \text{if } l=0 \\ &= 2 \quad \text{if } l>0. \end{aligned} \qquad (2)$$

We shall adopt the convention that density functions normalized according to (2) are labelled d_{lmp} (Coppens, 1988).

For a monopole function ($l=0$) the normalization implies that a population parameter $P_{00}=1$ corresponds to a population of one electron, while for the higher-order poles $P_{lm}=1$ implies that one electron has been shifted from the negative to the positive lobes of the function. Normalization factors N_{lm} for $l \le 4$ have been published (Hansen & Coppens, 1978). Though truncation of the expansion at $l=4$ is often warranted, this is not always the case. In particular, in highly symmetric environments the lowest symmetry-allowed multipole with $m \ne 0$ may be of higher order than four in l. An example is an atom at a site with sixfold symmetry, for which the first allowed multipole with non-zero m is y_{66+}. We report here on the values of N_{lm} as defined by (1) and (2) for $l \le 7$.

Method of calculation

From (1) and (2) N_{lm} is given by

$$N_{lm} = 1/I_{lm}J_m \quad \text{or} \quad N_{lm} = 2/I_{lm}J_m \qquad (3)$$

with

$$I_{lm} = \int_{-1}^{+1} |P_l^m(z)|\,dz$$

and

$$J_m = \int_0^{2\pi} |\cos m\varphi|\,d\varphi$$

or

$$J_m = \int_0^{2\pi} |\sin m\varphi|\,d\varphi,$$

which gives

$$J_m = 4 \text{ for } m>0; \quad J_m = 2\pi \text{ for } m=0.$$

Evaluation of I_{lm} requires calculation of the roots of the equation $P_l^m(z)=0$ and integration between boundaries equal to the root values. This is most easily done when the associated Legendre functions are expressed as a series in powers of z:

$$P_l^m(z) = (1/l!2^l)(1-z^2)^{m/2} p_{lm}(z), \qquad (4)$$

where

$$p_{lm}(z) = \sum_{k=k_i}^{l} A_k z^{2k-l-m}$$

with

$$A_k = \frac{(-1)^{k-l} l!}{k!(l-k)!} \frac{(2k)!}{(2k-l-m)!}$$

$$k_i = \begin{matrix} (l+m)/2 & \text{if } l+m \text{ odd} \\ (l+m+1)/2 & \text{if } l+m \text{ even.} \end{matrix}$$

Thus $p_{lm}(z)$ is a polynomial of degree $l-m$. Since the exponent increases by two between successive terms either even or odd powers occur.

The integration (2) requires evaluation of the roots of p_{lm}. As it is not possible to find analytically the roots of a polynomial of degree larger than 4, the

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