Aspherical electron scattering factors and their parameterizations for elements from H to Xe

Jin-Cheng Zheng, Lijun Wu and Yimei Zhu


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Aspherical electron scattering factors and their parameterizations for elements from H to Xe

Jin-Cheng Zheng,a,b* Lijun Wub and Yimei Zhub

*Department of Physics, and the Institute of Theoretical Physics and Astrophysics, Xiamen University, Xiamen 361005, People’s Republic of China, and bBrookhaven National Laboratory, Upton, New York 11973, USA. Correspondence e-mail: jczheng@xmu.edu.cn

The formalism for, and the values of, aspherical electron scattering factors using relativistic wavefunctions are presented. The parameterizations of electron form factors valid for a full range of scattering vectors from 0.0 to 6.0 Å⁻¹ were obtained for atoms with atomic number 1 (H) to 54 (Xe) by fitting a linear combination of Gaussian functions. Eight Gaussians were needed to achieve high-quality fittings. The tabulated aspherical p- and d-orbital parameters are invaluable for probing orbital electrons and calculating high-resolution electron microscopy images and diffractions, especially those involving interfaces and defects.

1. Introduction

Incident electrons are very sensitive to the redistribution of valence charge at small scattering angles compared with X-rays because electrons ‘see’ the electrostatic Coulomb potential (the positively charged nucleus screened by electrons), while X-rays ‘see’ the total ground-state density of electrons in the crystal (Zheng et al., 2005). However, regardless of their high sensitivity, the spherical form factors of neutral atoms are traditionally used in electron crystallography and electron microscopy to simulate electron diffraction patterns and atomic images to compare with experimental findings. Thus, there is an urgent need to tabulate aspherical form factors that can describe orbital electrons for a wide range of elements, including transition metal elements, so that we gain an understanding of charge redistribution in materials and, subsequently, of their functionality (Zhu et al., 2007). Recently, detectable changes of more than 10% of the contrast were demonstrated in high-resolution image calculations with and without taking orbital electrons into account (Deng & Marks, 2006), suggesting the exciting possibility of visualizing the local symmetry of a given electronic state in real space. In this article, we first examine the sensitivity of electron scattering factors to orbital asphericity, and then we provide the parameterizations of electron form factors for atoms with atomic number ranging from 1 (H) to 54 (Xe). Our aspherical electron form factors might well afford a better description of the experimentally observed exit-waves in electron diffraction and imaging after they pass through the sample, thereby allowing more accurate comparisons between the experiments and the density functional theory of functional materials.

2. General expression of electron scattering factor

The electron scattering amplitude, or electron form factor for the atomic or ionic cases, can be expressed as the Fourier transform of the crystal potential \( \phi(r) \),

\[
f^{(e)}(s) = K \int \phi(r) \exp(i2\pi q \cdot r) \, dr,
\]

where \( K \) is a coefficient. The electron scattering amplitude can also be obtained from the X-ray scattering amplitude \( f^{(x)}(s) \) through Mott’s formula (Mott & Massey, 1965)

\[
f^{(e)}(s) = A[Z - f^{(x)}(s)]/s^2,
\]

where

\[
f^{(x)}(s) = \int \rho(r) \exp(i2\pi q \cdot r) \, dr,
\]

\( \rho(r) \) is charge density, \( s = |s| = \sin \theta/\lambda \) and \( q = 2\pi \). The coefficient \( A = |e|/16\pi^2 \varepsilon_0 = 0.023934 \) when \( s \) is measured in the unit of Å⁻¹, the unit of \( f^{(x)}(s) \) is given as the charge of the electron, and the unit of \( f^{(e)}(s) \) is in \( A \); \( Z \) is the positive nuclear charge.

3. Angular-dependent expression of electron scattering factor for aspherical orbitals

The formulae given above are generalized for both spherical and aspherical charge distributions. For the former, the spherical charge density, only the radial component of the scattering vector should be considered. However, for the aspherical case, the charge distribution is anisotropic and thus the scattering amplitudes depend strongly upon the direction of the scattering vector. The X-ray atomic scattering factors for aspherical charge distributions were established many decades ago (McWeeny, 1951; Dawson, 1964; Freeman, 1959; Weiss & Freeman, 1959). However, the effect of orbital asphericity on electron scattering factors has not received much attention compared with their X-ray counterpart. In the following, we establish the theoretical grounds of the underlying factors in electron scattering for aspherical charge distributions. We also examine the sensitivity of electron scattering to orbital asphericity.
To describe the angular-dependent electron scattering factor for aspherical orbitals, we replace \( \rho(r) \) in equation (3) with the product of the \( i \)th and \( j \)th orbital wavefunctions, that is, \( \psi_i(r)\psi_j(r) \), and then expand both orbital wavefunctions and the term \( \exp(i\mathbf{q} \cdot \mathbf{r}) \) into expressions of spherical harmonics \( Y_{lm}(\theta, \phi) \), namely

\[
\psi_i(r) = R_i(r)Y_{lm}(\theta, \phi) \tag{4}
\]

and

\[
\exp(i\mathbf{q} \cdot \mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(Sr) Y_{lm}(\beta, \gamma) Y_{lm}(\theta, \phi), \tag{5}
\]

respectively. One can write down the expression of the angular-dependent electron scattering factor as

\[
f^{(e)}_{ij}(s, \beta, \gamma) = A \left[ Z - \sum_n D_{n0}(\beta, \gamma) \langle \hbar n \rangle_l \right] / s^2, \tag{6}
\]

where

\[
D_{n0}(\beta, \gamma) = [(4\pi)(2n+1)]^{1/2} r_n C_n(l_m,i,l_m) \times \Theta_n^{m-m_0}(\beta) \Phi_m^{m_0}(\gamma) \tag{7}
\]

and

\[
\langle \hbar n \rangle_l = \int_0^s R_i R_j \langle \alpha \rangle_{n0}(Sr) d r. \tag{8}
\]

Here, \( R_i(r) \) is the radial function, \( j_i(Sr) \) or \( j_j(Sr) \) are the spherical Bessel functions of the order \( l \) or \( n \), and \( |\mathbf{S}| = 4\pi s \). \( \beta \) and \( \gamma \) are angular coordinates of \( \mathbf{q} \) or \( \mathbf{S} \), and \( \theta \) and \( \phi \) are angular coordinates of \( \mathbf{r} \). \( C_n(l_m,i,l_m) \) is the integral of the product of three associated Legendre functions. \( \Theta_n^{m-m_0}(\beta) \) and \( \Phi_m^{m_0}(\gamma) \) are \( \beta \)- and \( \gamma \)-dependent portions of spherical harmonics, respectively.

From the above expression, it is clearly seen that the electron scattering factor depends not only on \( s \), but also upon the angles \( \beta \) and \( \gamma \). Here, \( \beta \) is the angle between the scattering vector \( \mathbf{q} \) and the \( z \) axis of the orbital, and \( \gamma \) is the azimuthal angle of \( \mathbf{q} \). The sensitivity of the electron scattering factor to orbital asphericity (hereafter denoted as asphericity) can be defined as

\[
\zeta^{(e)}_{\text{asph}}(s, \beta, \gamma) = \frac{f^{(e)}_{\text{asph}}(s, \beta, \gamma) - f^{(e)}_{\text{sp}}(s)}{f^{(e)}_{\text{sp}}(s)}, \tag{9}
\]

where \( f^{(e)}_{\text{asph}}(s, \beta, \gamma) \) and \( f^{(e)}_{\text{sp}}(s) \) are the aspherical and spherical electron scattering factors, respectively.

The \( s \) orbital (not to be confused with the italic \( s \), which refers to the scattering vector) has spherical symmetry, its electron scattering factor (normalized to one electron) is independent of the angles,

\[
f^{(e)}_{s}(s) = A(1 - \langle \hbar n \rangle_s) / s^2 = f^{(e)}_{\text{sp}}(s), \tag{10}
\]

and therefore its asphericity is zero, i.e., \( \zeta^{(e)}_{\text{asph}}(s) = 0 \). For the \( p \) orbital, the electron scattering factor has a two-dimensional shape and can be expressed as

\[
f^{(e)}_{p}(s) = \left( \frac{3}{2} \sin^2 \beta \right) f^{(e)}_{\text{p,sp}}(s) + \left( \cos^2 \beta - \frac{1}{2} \sin^2 \beta \right) f^{(e)}_{p_1}(s), \tag{11}
\]

where

\[
f^{(e)}_{\text{p,sp}}(s) = \frac{A}{s^3} (1 - \langle j_0 \rangle_p), \tag{12}
\]

\[
f^{(e)}_{p_1}(s) = \frac{A}{s^3} (1 - \langle j_0 \rangle_p + 2\langle j_2 \rangle_p), \tag{13}
\]

One can immediately obtain the asphericity of the \( p \) orbital as

\[
\zeta^{(e)}_{\text{p,asph}}(s, \beta) = \left( \frac{3}{2} \sin^2 \beta - 1 \right) + \left( \cos^2 \beta - \frac{1}{2} \sin^2 \beta \right) \frac{f^{(e)}_{p}(s)}{f^{(e)}_{\text{p,sp}}(s)}. \tag{14}
\]

For the \( d \) orbital, the expression of electron scattering factors is much more complicated than that of the \( p \) and \( s \) orbitals. The three principal electron scattering factors based on the expression of the X-ray scattering factor (Freeman, 1959; Weiss & Freeman, 1959) can be written as

\[
f^{(e)}_{d_4}(s) = \frac{A}{s^3} \left( 1 - \langle j_0 \rangle_d + \frac{10}{7} \langle j_2 \rangle_d - \frac{18}{7} \langle j_4 \rangle_d \right), \tag{15}
\]

\[
f^{(e)}_{d_2}(s) = \frac{A}{s^3} \left( 1 - \langle j_0 \rangle_d + \frac{5}{7} \langle j_2 \rangle_d + \frac{12}{7} \langle j_4 \rangle_d \right), \tag{16}
\]

\[
f^{(e)}_{d_4}(s) = \frac{A}{s^3} \left( 1 - \langle j_0 \rangle_d - \frac{10}{7} \langle j_2 \rangle_d - \frac{3}{7} \langle j_4 \rangle_d \right). \tag{17}
\]

Here, scattering vectors are along the \( z \) axis of the \( d \) orbitals. The electron scattering factor for five individual \( d \) orbitals can be put into three groups: \( d(zx) \) and \( d(zy) \); \( d(xy) \) and \( d(x^2 - y^2) \); and \( d(3z^2 - r^2) \). For any scattering vector \( \mathbf{q}(x', y', z') \) with an angle \( \beta \) between the \( z' \) and \( z \) axes of the \( d \) orbital, the scattering factors can be written as

\[
f^{(e)}_{d_4}(s) = a_1(\beta)f^{(e)}_{d_4}(s) + a_2(\beta)f^{(e)}_{d_4}(s) + a_3(\beta)f^{(e)}_{d_4}(s), \tag{18}
\]

\[
f^{(e)}_{d_2}(s) = b_1(\beta)f^{(e)}_{d_2}(s) + b_2(\beta)f^{(e)}_{d_2}(s) + b_3(\beta)f^{(e)}_{d_4}(s), \tag{19}
\]

\[
f^{(e)}_{d_2}(s) = c_1(\beta)f^{(e)}_{d_2}(s) + c_2(\beta)f^{(e)}_{d_2}(s) + c_3(\beta)f^{(e)}_{d_4}(s), \tag{20}
\]

where

\[
a_1(\beta) = \frac{1}{4} - \frac{3}{2} \cos^2(\beta) + \frac{9}{4} \cos^4(\beta), \tag{21}
\]

\[
a_2(\beta) = 3 \cos^2(\beta) - 3 \cos^4(\beta), \tag{22}
\]

\[
a_3(\beta) = \frac{3}{4} - \frac{3}{2} \cos^2(\beta) + \frac{3}{4} \cos^4(\beta), \tag{23}
\]

\[
b_1(\beta) = \frac{3}{2} \cos^2(\beta) - \frac{3}{2} \cos^4(\beta), \tag{24}
\]

\[
b_2(\beta) = \frac{1}{2} - \frac{3}{2} \cos^2(\beta) + 2 \cos^4(\beta), \tag{25}
\]

\[
b_3(\beta) = \frac{1}{2} - \frac{1}{2} \cos^2(\beta), \tag{26}
\]
Then, the total charge density can be written as
\[ n_{ij}^{s}(\beta) = \frac{3}{8} - \frac{3}{4} \cos^2(\beta) + \frac{3}{8} \cos^2(\beta), \]  
(27)
\[ c_{ij}(\beta) = \frac{1}{2} - \frac{1}{2} \cos^2(\beta), \]  
(28)
\[ c_{ij}(\beta) = \frac{1}{8} + \frac{3}{4} \cos^2(\beta) + \frac{1}{8} \cos^2(\beta). \]  
(29)

3.1. Explicit expressions based on analytical Slater-type relativistic atomic wavefunctions

The sensitivity to asphericity of the orbitals can be explicitly expressed in analytical form provided that the orbital wavefunctions are known. To illustrate this point, we use Slater-type relativistic (Dirac–Fock) atomic wavefunctions (Su & Coppens, 1998; Macchi & Coppens, 2001; Kim et al., 2008) to derive the analytical expressions for several quantities of interest. The analytical expressions of the radial function for each \( i \)th orbital are given by
\[ R_{\text{orb}}^{i}(n_{ij}, \xi_{ij}, c_{ij}) = \sum_{j=1}^{m} A_{ij} r^{n_{ij}-1} \exp(-\xi_{ij} r), \]  
(30)
where \( n_{ij} \) is the principal quantum number of the \( i \)th orbital with the basis function \( j \), and \( c_{ij} \) and \( \xi_{ij} \) are the parameters of the basis function. The coefficient of the Slater-type function is written as
\[ A_{ij} = \sum [(2n_{ij})!]^{1/2} (2\xi_{ij})^{n_{ij}+1/2} c_{ij}. \]  
(31)
The values of \( n_{ij} \), \( c_{ij} \) and \( \xi_{ij} \) were obtained by Su & Coppens (1998) through fitting the relativistic atomic ground-state wavefunctions obtained by the Dirac–Fock method. The charge density from any \( i \)th orbital can be obtained as
\[ \rho_{\text{orb}}^{i}(r) = P_{i} R_{\text{orb}}^{i}(n_{ij}, \xi_{ij}, c_{ij})^{2}. \]  
(32)
Then, the total charge density can be written as
\[ \rho(r) = \sum_{i} \rho_{\text{orb}}^{i}(r) = \sum_{i} P_{i} R_{\text{orb}}^{i}(n_{ij}, \xi_{ij}, c_{ij})^{2}, \]  
(33)
where \( P_{i} \) is the electron population in the \( i \)th orbital. Therefore, the orbital-dependent density and the total radial density are written, respectively, as
\[ R_{\text{den}}^{i}(r) = r^{2} \rho_{\text{orb}}^{i}(r) = P_{i} r^{2} R_{\text{orb}}^{i}(n_{ij}, \xi_{ij}, c_{ij})^{2}, \]  
(34)
and
\[ R_{\text{den}}^{\text{tot}}(r) = \sum_{i} P_{i} r^{2} R_{\text{orb}}^{i}(n_{ij}, \xi_{ij}, c_{ij})^{2}. \]  
(35)
The radial integrals are obtained as follows
\[ \langle j_{k} \rangle_{i} = \sum_{m} \sum_{b} A_{m,b} G_{N,k}(S, \Lambda), \]  
(36)
where \( G_{N,k}(S, \Lambda) \) is the closed-form expression for the Fourier transform of the Slater-type functions,
\[ G_{N,k}(S, \Lambda) = \int_{0}^{\infty} r^{N} \exp(-\Lambda r) j_{k}(Sr) \, dr, \]  
(37)
given by Su & Coppens (1990). Here, the variables are defined as
\[ N = n_{ij} + n_{ij}, \quad S = 4\pi s \quad \text{and} \quad \Lambda = \xi_{ij} + \xi_{ij}. \]  
(38)

3.2. Parameterization of the aspherical electron scattering factor

Using an existing database of relativistic atomic wavefunctions provided by Coppens and co-workers (Su & Coppens, 1998; Macchi & Coppens, 2001; Kim et al., 2008) as input, we calculate the spherical and aspherical electron scattering factors according to equations (10), (12), (13), (15), (16), (17) and (36). We also obtain electron scattering factors for core electrons. We then fit the spherical and aspherical electron scattering factors to the data using a least-squares fitting approach.

Figure 1
Comparison of fitting residuals with a different number of Gaussian functions (Fe atom as an example). (a) \( \Delta F \), the absolute difference between the original and fitting electron scattering factor. (b) \( \Delta F/F \), the relative difference (in %). The symbol \( gn \) (\( n = 4, 5, 6, 7, 8 \)) refers to the number \( n \) of Gaussian functions. \( s \) is the scattering vector in Å.
The root of the mean square (RMS) of the deviation between the numerical and fitted electron scattering factors is defined as (Peng et al., 1996).

\[
\sigma = \left( \frac{1}{m} \sum_{j=1}^{m} \left[ f(s_j) - \sum_{i=1}^{N} a_i \exp(-b_i s_j^2) \right]^2 \right)^{1/2}.
\]

One can choose a suitable \( N \) number, i.e. the number of Gaussian functions used to fit the RMS data. It is clear that the more Gaussian functions that are included, the more accurate the fit is. After several numerical tests, we found that it is necessary to use eight Gaussian functions in order to achieve a high-quality fitting. Taking an Fe atom as an example, Fig. 1 compares the fitting of the two sets ofdata and shows that the larger scattering vector \( s \) approaching zero, while the 

\[ f(s) = \sum_{i=1}^{N} a_i \exp(-b_i s^2). \]

(39)

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(39)

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\]
The RMSs for the case of $Z = 1$ to $Z = 54$ are shown in Fig. 3 and Table 2. From Figs. 1–3, it is obvious that the quality of fitting with eight Gaussians is significantly improved.

### 4. Applications and discussion

Here we give some examples to illustrate the application of the parameterization and to the orientation of the outermost p orbital. For a single p orbital in O, one can use the parameters for $f(p0)$ to calculate the atomic total electron scattering factor of equation (4) and the spherical electron scattering factor from equation (11) (the orientation of the p orbital is determined by the angle of $\beta$). In Fig. 4(a), we compare the electron scattering factors of a single p orbital in H to Xe (neutral atoms) using five Gaussians. In Fig. 4(b), we compare the electron scattering factors of $\beta = 0$ to 180 degrees parallel to the p orbital.

### 5. Conclusions

Comparison of the root mean square deviation of the fitting residual for a neutral Fe atom as a function of $\beta$. Figure 3 and Table 2. From Figs. 1–3, it is obvious that the quality of fitting with eight Gaussians is significantly improved.
Table 1 (continued)

<table>
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<th>Label</th>
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<th>$b_3$</th>
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**ii)** aspherical $\beta = \pi/2$, scattering direction is perpendicular to the $p$ orbital, namely, $f_p$ ($\theta_{p}$) = $-1/f_{p}^\perp$ cases. It is clear that the effect of the orientation of the $p$ orbital on the electron scattering factor is significant: the aspherical scattering factor can be almost twice as large as (or as small as about 3/2 of the size) for the outermost pair for (or parallel) different cases at low angle range angles. One might wonder how the orientation of the outermost pair, using the electron scattering factor, considering that, in realistic electron diffraction, one normally measures the total electron scattering factor. Therefore, we also plot the total electron scattering factor of the atom with consideration of the orbits (see Figs. 4b).

For the electronic configuration, one can calculate directly from the electron scattering factor, considering that, in realistic electron diffraction, one normally measures the total electron scattering factor. Therefore, we also plot the total electron scattering factor of the atom with consideration of the orbits (see Figs. 4b).

For the spherical case, one can calculate directly from the electron scattering factor, considering that, in realistic electron diffraction, one normally measures the total electron scattering factor. Therefore, we also plot the total electron scattering factor of the atom with consideration of the orbits (see Figs. 4b).
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The principal electron scattering factors for the Fe d orbitals are shown in Fig. 5(b). The labels ‘parallel’ and ‘perpendicular’ refer to the orbital of the excess p electron, as shown in Fig. 4(b) with the labels ‘parallel’ and ‘perpendicular’, respectively. Obviously, the modification of the total electron scattering factor due to the orientation of even one single p orbital cannot be ignored, as, for example, the changes can be as large as 10 or 5% when the oxygen p orbitals are parallel or perpendicular to the scattering vector, respectively, compared with the spherical one.

The aspherical effects of d orbitals are significant enough to change much attention because in many functional materials, the orbital ordering, which is mainly due to the orientation of d orbitals, plays an important role in determining their functionality. Therefore, the significance of the electron scattering factor due to the anisotropic d orbitals, and whether such asphericity can be detected accurately becomes interesting and important for fundamental research. Here, we will first show the dispersion of the three principal electron scattering factors for the Fe d orbitals [calculated from equations (15)–(17)], taking Fe as an example, are shown in Fig. 5. The curve of $R_f^{(i)}$ ($i$ = 1, 2, 3) and those of $R_f^{(i)}$ and $R_f^{(2)}$ exhibit the most significant dispersion, while the difference between $R_f^{(1)}$ and $R_f^{(2)}$ is much smaller. This is mainly due to the different sign for the $\langle j_3 \rangle$ and $\langle j_2 \rangle$ terms. The common feature for those three curves is that the largest dispersion is located at small scattering angles. The values of $R_f^{(1)}$ and $R_f^{(2)}$ could be used to two times from the third scattering for the orbitals of Fe electron scattering factors, as shown in Fig. 5(b) with the labels ‘parallel’ and ‘perpendicular’, respectively.
Here, $\eta$ is the azimuthal angle of the scattering vector. One can calculate $B(\beta, \gamma)$ in terms of the Miller indices, $hkl$, for a cubic crystal (Weiss & Freeman, 1959):

$$B(\beta, \gamma) = h^2 + k^2 + l^2 - 3(h^2k^2 + h^2l^2 + k^2l^2),$$

and $\eta = 0.25 \cos \theta$. The electron scattering factor of the $T_{2g}$ orbital is much larger than that of the $E_g$ orbital. This clearly shows the significant signature of orbital degeneracy.

Figs. 4 and 5 clearly show that the smaller the angular scattering factor, the larger the anisotropic effects.

Based on equations (41) and (42), one can plot the electron scattering factors of $T_{2g}$ and $E_g$ orbitals as a function of $\beta$ and $\gamma$. To illustrate this, we plot the scattering factors for $T_{2g}$ and $E_g$ orbitals, as shown in Fig. 6. The electron scattering factor of the $T_{2g}$ orbital is much larger than that of the $E_g$ orbital. This clearly shows the significant signature of orbital degeneracy.

Figs. 4 and 5 also clearly show that the smaller the angular scattering factor, the larger the anisotropic effects.
Here we compare the electron scattering factors of an Fe crystal calculated from our parameters using formulae described above with those calculated from density functional theory (DFT). For DFT calculations, we use the full potential plane wave method, as implemented in the WIEN2k package (Blaha et al., 2001). The experimental lattice constant (2.87 Å) of a body centered cubic (b.c.c.) Fe crystal, ferromagnetic configuration, and the method of local density approximation (LDA) are used. The magnetic moment calculated is 2.20 μB, which is in good agreement with the experimental value.

The low-order structure factor, f(200), obtained by DFT calculation is 2.13 Å. The value of f(200) calculated using Table 3 is 2.16 Å when all the d electrons occupy Fe T2g orbitals, respectively. It is clear that the electron population of T2g and Eg electrons. It has been shown that in Fe, d orbitals show an aspherical effect when the occupation of the T2g state is about 64.8% (Ohba et al., 1982), which is in fairly good agreement with the results of the present work. With this tested T2g population, we thus obtain f(200) = 2.12 Å, in fairly good agreement with DFT calculations.

The asphericity can be more clearly seen by comparing the experimental results of special photoemission reflections with the same s = 3.891 Å. For those paired reflections, the sphericity of the electron scattering factors are the same. In other words, for the orthogonal case, for the sphericity, the case of the paired electron scattering factors is equal to the aspherical case, if for the case of the spherical factor can be larger or smaller than 1.0 for example. Fe crystal, electron scattering factors f(330) and f(411) have the same s = 0.7391 Å⁻¹, but the ratio of Fe crystal, electron scattering factors f(330) and f(411) is 0.7391 Å⁻¹. This difference is surprising.

Table 1 (continued)

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**Figure 6**

The electron scattering factors for T2g and Eg orbitals of Fe in a cubic field. The angles are chosen to be β = 0 and γ = 0.
0.7820 Å; their ratio is $f(330)/f(411) = 1.0027$, or $(330)^2/f(411)^2 = 1.0054$, with a 64.8% $T_{2g}$ population. Because there is no measured electron structure factor ratio for Fe available, we transfer the electron structure factor into X-ray structure factor through the Mott formula, $f_e(x) = f_x(x) = 1.012$, which is very close to experimental data (1.020; Diana & Mazzone, 1974; Ohba et al., 1982) and previous theoretical results [1.015 (Duff & Das, 1971), 1.028 (Philips & Weiss, 1972) or 1.004 (Callaway & Wang, 1977)]. The structure factor ratio is strongly dependent on the populations of $T_{2g}$ or $E_g$ orbitals. There is a long history of determining the asphericity of charge distribution in transition metals, and the main focus is on how accurately the population of $T_{2g}$ or $E_g$ can be measured. Apart from the previously measured 64.8% $T_{2g}$ population (e.g. Ohba et al., 1982) in Fe, a more recent γ-ray diffraction study suggested a much smaller value, 62.5% (Jauh & Reehuis, 2007). With this new value of $T_{2g}$ population, we obtain $f_{e}(330)/f_{x}(411) = 1.0031$, in perfect agreement with γ-ray data (1.0033; Jauh & Reehuis, 2007). It has also been argued that the LDA calculations may be inadequate to describe the asphericity of d orbitals in transition metals (e.g. Di Fabrizio et al., 1989). This will provide a new application for the quantitative electron diffraction technique since it has very high sensitivity to the tiny dispersion in low-order structure factors (Zheng et al., 2005). The formulae and parameterizations shown in this paper can certainly provide a convenient and efficient tool for such analysis, especially for systems where the anisotropic arrangement of orbitals is more important than charge redistribution isotropically, such as orbital occupancy and ordering in transition metal oxides (Jiang et al., 2002).

Regarding the parameterization of the electron scattering factor, one might wonder why the existing parameterization of the X-ray scattering factor is not directly converted using the Mott formula. In principle, one can calculate the electron scattering factor by using available X-ray scattering factors in the literature through the Mott formula. In practice, this can be done only for a large scattering angle. However, for a small scattering angle, such direct conversion from fitted X-ray scattering factors becomes less accurate, because the fitting errors in X-ray scattering factors become significant when $s$ approaches zero. Such problems have been discussed in the literature (see, for example, Peng & Cowley, 1988; Peng et al., 1996). To illustrate this point further, we compare the electron scattering factors of Ni obtained from our method (i.e. from Table 1) with those directly converted from the X-ray scattering factors of Rez et al. (1994) and Su & Coppens (1997), as shown in Fig. 7. It is clear that, if the electron scattering factors are obtained by directly converting the X-ray scattering factor parameterization, they diverge at small scattering angles and thus are incorrect. Therefore, it is necessary to fit the electron scattering factor using a wavefunction or potential in order to obtain accurate parameterization, especially for $s$ approaching zero.

One more advantage of the parameterization of the electron scattering factor compared with that of the X-ray counterpart is the convenient and accurate calculation of the mean inner potential (MIP). MIP or average Coulomb potential (O’Keeffe & Spence, 1994), the electron scattering factor when $s = 0$, attracts a lot of attention owing to advances in holography and the use of Fresnel imaging to characterize interfaces (Rez et al., 1994; Wu et al., 2004). Using the X-ray scattering factor, one needs to calculate the coefficient of $s^4$ that fits the charge density near $s = 0$ to obtain MIP (Rez et al., 1994). However, with the parameterization of the total electron scattering factor as listed in Table 1, one can easily calculate the MIP simply using $\sum_i$, without any further fitting. For example, for Fe and Ni, we obtain MIP = 7.168869 and 6.573553 Å, respectively, in good agreement with previous results, 7.168993 and 6.570390 Å, calculated from the atomic second moments $\langle r^2 \rangle$ (Su & Coppens, 1997).

5. Conclusions

We have derived the angular-dependent expression of the electron scattering factor for aspherical orbitals. To explore the sensitivity of the scattering factor to the anisotropy of orbital electrons, we used Slater-type relativistic atomic wavefunctions to derive analytical expressions for several quantities of interest. Using an existing database of relativistic atomic wavefunctions, we have calculated the values of the aspher-
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Error analysis for fitting of the total electron scattering factor as listed in Table 1.

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References