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Orientation-Dependent Scattering Factors for Overlap Electron Density

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The scattering from the overlap electron density $\psi^*_{i\alpha}(\mathbf{r}-\mathbf{r}_\alpha)\,\psi_{j\beta}(\mathbf{r}-\mathbf{r}_\beta)$ between two orbitals on stationary atoms at $\mathbf{r}_\alpha = 0$ and $\mathbf{r}_\beta$ may be expressed as

$$\chi_{i\alpha j\beta}(\mathbf{k}) = \int \psi^*_{i\alpha}(\mathbf{r}-\mathbf{r}_\alpha)\,\psi_{j\beta}(\mathbf{r}-\mathbf{r}_\beta)\exp i\mathbf{k}.(\mathbf{r}-\mathbf{r}_\alpha)\,\mathrm{d}V = \sum_{l=|m|}^{\infty} i^l \mu_{lm}(k)\,Y^R_{lm}(\mathbf{k}),$$

where $\mu_{lm}(k)$ is an orientation-independent term. $Y^R_{lm}(\mathbf{k})$ are spherical harmonics, where the scattering vector $\mathbf{k}$ is defined in spherical coordinates (k,θ_k,φ_k) and $\theta_k = 0$ corresponds to the direction $\mathbf{R} = \mathbf{r}_\beta - \mathbf{r}_\alpha$. $m = M_\beta - M_\alpha$, where M_α and M_β are the magnetic quantum numbers of the two orbitals defined about the direction $\mathbf{R}$. The general case is described and more detailed expressions are given for overlaps involving s, p_x, p_y, p_z orbitals.

Introduction

The X-ray structure factor for the reciprocal-lattice vector $\mathbf{k}$ may be expressed as $F(\mathbf{k}) = \int \rho(\mathbf{r}) \times \exp(i\mathbf{k}.\mathbf{r})\,\mathrm{d}V_r$, where $k = 4\pi\sin\theta/\lambda$ and $\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \rho'(\mathbf{r}) + i\rho''(\mathbf{r})$. $\rho(\mathbf{r})$ is the dynamically averaged scattering density at $\mathbf{r}$, $\rho_0(\mathbf{r})$ is the dynamically averaged electron density at $\mathbf{r}$, and $\rho'(\mathbf{r})$ and $\rho''(\mathbf{r})$ are wavelength-dependent contributions.

It is also useful to describe the structure factor as

$$F(\mathbf{k}) = \sum_\alpha f_\alpha(\mathbf{k})\,T_\alpha(\mathbf{k})\exp(i\mathbf{k}.\mathbf{r}_\alpha),$$

where $f_\alpha(\mathbf{k})\,T_\alpha \exp(i\mathbf{k}.\mathbf{r}_\alpha)$ is the contribution to $F(\mathbf{k})$ from the αth atom whose most probable nucleus position is $\mathbf{r}_\alpha$. $f_\alpha(\mathbf{k})$ can be evaluated from a static model where all nuclei are at their most probable positions. $T_\alpha(\mathbf{k})$ may then be regarded as a thermal smearing function which accounts for atomic vibrations. From a theoretical viewpoint $T_\alpha(\mathbf{k})$ is not easy to calculate and recent efforts by Ruysink & Vos (1974), Stevens, Rys & Coppens (1977) and Scheringer (1977) show the complexity of the problem and the approximations that must be made.

However, if $T_\alpha(\mathbf{k})$ is regarded as being experimentally determined, a better model than that of an isolated spherical atom or ion is advantageous. The lack of easy to use, orientation-dependent scattering factors for overlap electron density between atoms has restricted the advancement of such procedures. Original efforts to evaluate scattering from overlap electron density used Slater-type functions (McWeeny, 1952) but Gaussian-type functions (McWeeny, 1953) have been used for all practical purposes since then. However, a simple formulation using Slater-type orbitals is possible and this is the subject of this and the following paper (Rae & Wood, 1978).

The wavelength-independent term of $f_\alpha(\mathbf{k})$ may be described as

$$f_{0\alpha}(\mathbf{k}) = \int \rho_{0\alpha}(\mathbf{r}-\mathbf{r}_\alpha) \exp i\mathbf{k}.(\mathbf{r}-\mathbf{r}_\alpha)\,\mathrm{d}V_r,$$

where $\rho_{0\alpha}(\mathbf{r}-\mathbf{r}_\alpha)$ is the electron density associated with the αth atom in the static model. We can describe the pth electron as being in a molecular orbital

$$\psi^p(\mathbf{r}) = \sum_{i,\alpha} a^p_{i\alpha}\,\psi_{i\alpha}(\mathbf{r}-\mathbf{r}_\alpha),$$

where $a^p_{i\alpha}$ is a coefficient and $\psi_{i\alpha}$ is the ith member of an orthonormalized set of single-atom wave functions at $\mathbf{r}_\alpha$. We can thus say

$$\rho_{0\alpha}(\mathbf{r}-\mathbf{r}_\alpha) = \tfrac{1}{2}\sum_{i\beta j}[b_{i\alpha j\beta}\,\psi^*_{i\alpha}(\mathbf{r}-\mathbf{r}_\alpha)\,\psi_{j\beta}(\mathbf{r}-\mathbf{r}_\beta) + b^*_{i\alpha j\beta}\,\psi_{i\alpha}(\mathbf{r}-\mathbf{r}_\alpha)\,\psi^*_{j\beta}(\mathbf{r}-\mathbf{r}_\beta)],$$

where $b_{i\alpha j\beta} = \sum_p (a^p_{i\alpha})^*\,a^p_{j\beta}$ and $\sum_\alpha \rho_{0\alpha}(\mathbf{r}-\mathbf{r}_\alpha) = \rho_0(\mathbf{r})$. It is useful to assume $b_{i\alpha j\beta} = \delta_{ij}\delta_{\alpha\beta}$ if i refers to an *inner shell* electron orbital. δ_{ij} has its usual meaning ($\delta_{ij} = 1$ if $i=j$, 0 otherwise). The $b_{i\alpha j\beta}$ may be theoretically determined from quantum-mechanical calculations but they are intrinsically refineable parameters of the X-ray diffraction experiment. Obviously, constrained refinement is an essential feature of an experimental approach.

We must also include the wavelength-dependent terms of $f_\alpha(\mathbf{k}) = f_{0\alpha}(\mathbf{k}) + f'_\alpha(\mathbf{k}) + if''_\alpha(\mathbf{k})$, where $f'_\alpha(\mathbf{k})$ and $f''_\alpha(\mathbf{k})$ correspond to the contribution of the αth atom to $\rho'(\mathbf{r})$ and $\rho''(\mathbf{r})$ respectively. It is usual to assume that these terms are the same as for an isolated spherical atom.

Notations used in this paper are explained in the Appendix. Throughout this paper we assume only integral quantum numbers.

Theory

We wish to evaluate integrals of the type

$$\chi_{i\alpha j\beta}(\mathbf{k}) = \int \psi^*_{i\alpha}(\mathbf{r}-\mathbf{r}_\alpha)\,\psi_{j\beta}(\mathbf{r}-\mathbf{r}_\beta) \exp i\mathbf{k}.(\mathbf{r}-\mathbf{r}_\alpha)\,\mathrm{d}V,$$

and hence

$$f_{0\alpha}(\mathbf{k}) = \sum_{i\beta j} \tfrac{1}{2}[b_{i\alpha j\beta}\,\chi_{i\alpha j\beta}(\mathbf{k}) + b^*_{i\alpha j\beta}\,\chi^*_{i\alpha j\beta}(-\mathbf{k})]. \quad (1)$$

We can describe $\psi_{i_\alpha}(\mathbf{r}-\mathbf{r}_\alpha)$ as $R_\alpha(r_1)\Theta_{L_\alpha M_\alpha}(\theta_1)\Phi_{M_\alpha}(\varphi_1)$, and $\psi_{j\beta}(\mathbf{r}-\mathbf{r}_\beta)$ as $R_\beta(r_2)\Theta_{L_\beta M_\beta}(\theta_2)\Phi_{M_\beta}(\varphi_2)$, where $\mathbf{r}_1 = \mathbf{r}-\mathbf{r}_\alpha$ has polar coordinates (r_1,θ_1,φ_1), and $\mathbf{r}_2 = \mathbf{r}-\mathbf{r}_\beta$ has polar coordinates (r_2,θ_2,φ_2). A simpler notation is $\psi_{i\alpha}(\mathbf{r}_1) = R_\alpha(r_1)\,Y_{L_\alpha M_\alpha}(\mathbf{r}_1)$, and $\psi_{j\beta}(\mathbf{r}_2) = R_\beta(r_2)\,Y_{L_\beta M_\beta}(\mathbf{r}_2)$. We must expand $\psi_{j\beta}(\mathbf{r}_2)$ about $\mathbf{r}_\alpha$ and to do this we use the expansion

$$r_2^{L_\beta}\,Y_{L_\beta M_\beta}(\mathbf{r}_2) = \sum_{\substack{L_1\\ L_1+L_2=L_\beta}} \left\{\frac{4\pi(2L_\beta+1)!}{(2L_1+1)!(2L_2+1)!}\right\}^{1/2} \times \sum_{\substack{M_1\\ M_1+M_2=M_\beta}} \langle L_1L_2M_1M_2|L_\beta M_\beta\rangle \times r_1^{L_2}\,Y_{L_2M_2}(\mathbf{r}_1)(-R)^{L_1}\,Y_{L_1M_1}(\mathbf{R}) \quad (2)$$

propounded by Moshinsky (1959); $\mathbf{R} = \mathbf{r}_\beta - \mathbf{r}_\alpha = \mathbf{r}_1 - \mathbf{r}_2$. We also use the well-known expression

$$\exp i\mathbf{k}.\mathbf{r}_1 = 4\pi\sum_l \sum_{m=-l}^{l} (-1)^m i^l j_l(kr_1)\,Y_{lm}(\mathbf{k})\,Y_{l-m}(\mathbf{r}_1) \quad (3)$$

(Stewart, 1969; Antosiewicz, 1968). Using (2) and (3) we can then say

$$\chi_{i\alpha j\beta}(\mathbf{k}) = \sum_{l,m} i^l(-1)^m\,Y_{lm}(\mathbf{k})[4\pi(2L_\beta+1)!]^{1/2} \times \sum_{\substack{L_1,M_1\\ L_1+L_2=L_\beta}} (-R)^{L_1}\,Y_{L_1M_1}(\mathbf{R})\frac{\langle L_1L_2M_1M_2|L_\beta M_\beta\rangle}{[(2L_1+1)!(2L_2+1)!]^{\frac{1}{2}}} \times 4\pi\int R_\alpha(r_1)R_\beta(r_2)\frac{r_1^{L_2}}{r_2^{L_\beta}} \times j_l(kr_1)\,Y^*_{L_\alpha M_\alpha}(\mathbf{r}_1)\,Y_{l-m}(\mathbf{r}_1)\,Y_{L_2M_2}(\mathbf{r}_1)\,\mathrm{d}V.$$

We have yet to choose the axial directions that define our polar coordinates and if we now choose $\theta_1 = 0$ to correspond to the direction $\mathbf{R}$ then $M_1 = 0$, $M_2 = M_\beta$ and $m = M_\beta - M_\alpha$ for a non-zero contribution to $x_{i\alpha j\beta}(\mathbf{k})$. We will use the notation $Y^R_{LM}(\mathbf{r})$ to denote that $\mathbf{r}$ is defined relative to $\mathbf{R}$. Now,

$$4\pi Y^*_{L_\alpha M_\alpha}(\mathbf{r}_1)\,Y_{lM_\alpha-M_\beta}(\mathbf{r}_1)\,Y_{L_2M_\beta}(\mathbf{r}_1) = (-1)^{M_\alpha}\sum_{L,L_3}(2l+1)(2L_\alpha+1)\,C^l(L_3M_\alpha,L_2M_\beta) \times C^{L_\alpha}(L0,L_3M_\alpha)\,Y_{L0}(\mathbf{r}_1) \quad (4)$$

with coefficients C^l given by Condon & Shortley (1935). If we now change notation to use exclusively $3j$ coefficients (Rotenberg, Bivins, Metropolis & Wooten, 1959) we obtain

$$\chi_{i\alpha j\beta}(\mathbf{k}) = \sum_{l=|m|}^{\infty} i^l \mu_{lm}(\mathbf{k})\, Y^R_{lm}(\mathbf{k}), \quad m = M_\beta - M_\alpha, \quad (5)$$

where

$$\begin{aligned}\mu_{lm}(\mathbf{k}) &= [4\pi(2l+1)(2L_\alpha+1)(2L_\beta+1)]^{1/2}(-1)^{L_\beta} \\ &\times [(2L_\beta+1)!]^{1/2}(-1)^{M_\alpha} \sum_{\substack{L_1 \\ L_1+L_2=L_\beta}} (-R)^{L_1} \\ &\times \left[\frac{(2L_1+1)(2L_2+1)}{(2L_1+1)!(2L_2+1)!}\right]^{1/2} \begin{pmatrix} L_1 & L_2 & L_\beta \\ 0 & M_\beta & -M_\beta \end{pmatrix} \\ &\times \sum_{L,L_3} (2L+1)(2L_3+1) \\ &\times \begin{pmatrix} L_3 & L_2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_3 & L_2 & l \\ M_\alpha & -M_\beta & m \end{pmatrix} \begin{pmatrix} L & L_3 & L_\alpha \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & L_3 & L_\alpha \\ 0 & -M_\alpha & M_\alpha \end{pmatrix} \\ &\times I_{lLL_2}(k), \end{aligned} \quad (6)$$

$$I_{lLL_2}(k) = \frac{1}{4\pi}\int R_\alpha(r_1)\, R_\beta(r_2) \frac{r_1^{L_2}}{r_2^{L_\beta}} j_l(kr_1) P_L(\cos\theta)\, \mathrm{d}V, \quad (7)$$

is an axially symmetric integral, the evaluation of which is discussed in Rae & Wood (1978). It should be noted that for the special case where $\mathbf{R} = 0$ the only non-zero contribution to $\mu_{lm}(k)$ is when $L = L_1 = 0$, $L_2 = L_\beta$ and $L_3 = L_\alpha$. Then

$$\mu_{lm}(k) = (-1)^m [4\pi(2l+1)]^{1/2} C^l(L_\alpha M_\alpha, L_\beta M_\beta) \times \langle j_l(k)\rangle_{\alpha\beta}, \quad (8)$$

where

$$\langle j_l(k)\rangle_{\alpha\beta} = \int_0^{\infty} R_\alpha(r_1) R_\beta(r_1) j_l(kr_1)\, r_1^2\, \mathrm{d}r_1, \quad (9)$$

is a special case of the more general integral $I_{lLL_2}(k)$. The result agrees with that of Stewart (1969) obtained with only single-centre overlaps. The maximum value of L is $l + L_\alpha + L_2$.

We see that the scattering factors are evaluated by redefining $\mathbf{k}$ relative to various bonds $\mathbf{R} = \mathbf{r}_\beta - \mathbf{r}_\alpha$. We thus wish to describe functions $Y_{LM}(\mathbf{r})$ defined relative to standard reference axes $\mathbf{X}$, $\mathbf{Y}$, $\mathbf{Z}$ as combinations of functions $Y^R_{LN}(\mathbf{r})$ defined relative to axes $\mathbf{X}^R$, $\mathbf{Y}^R$, $\mathbf{Z}^R$, where $\mathbf{Z}^R$ is in the direction $\mathbf{R}$:

$$Y^R_{LN}(\mathbf{r}) = \sum_M A_{MN}\, Y_{LM}(\mathbf{r}), \quad Y_{LM}(\mathbf{r}) = \sum_N A^*_{MN}\, Y^R_{LN}(\mathbf{r}). \quad (10)$$

We shall transform the axial system in two stages. Let $\mathbf{R}$ have polar coordinates (R, θ_R, φ_R) relative to the standard reference axes. We first rotate by φ_R about $\mathbf{Z}$. This creates $\mathbf{Y}^R$ normal to $\mathbf{R}$. We then rotate by θ_R about $\mathbf{Y}^R$ to create $\mathbf{Z}^R$ in the $\mathbf{R}$ direction. This is equivalent to first rotating by θ_R about $\mathbf{Y}$ followed by a rotation of φ_k about $\mathbf{Z}$ enabling the evaluation of A_{MN} (Brink & Satchler, 1968) as

$$A_{MN} = \exp(-iM\varphi_R)\, d^L_{MN}(\theta_R), \quad (11)$$

where

$$\begin{aligned} d^L_{MN}(\theta) &= \sum_t (-1)^t \\ &\times \frac{[(L+N)!(L-N)!(L+M)!(L-M)!]^{1/2}}{(L+N-t)!(L-M-t)!t!(t+M-N)!} \\ &\times \cos^p\frac{\theta}{2}\sin^q\frac{\theta}{2}, \end{aligned} \quad (12)$$

$p = 2L + N - M - 2t$, $q = 2t + M - N$ and t has any integer value that gives only non-negative numbers for the evaluation of factorials;

$$d^L_{MN}(\theta) = d^L_{-N-M}(\theta) = d^L_{NM}(-\theta) = (-1)^{M-N} d^L_{NM}(\theta). \quad (13)$$

Table 1. *Functional forms $\chi_{i\alpha j\beta}(k)$ for overlaps between real functions*

Note $m_1 = M_\beta - M_\alpha$, $m_2 = M_\beta + M_\alpha$, $M_\alpha > 0$, $M_\beta > 0$, $\mu_{lm}(k) = \mu_{l-m}(k)$.

$\psi_{i\alpha}(\mathbf{r}_1)/R_\alpha(r_1)$	$\psi_{j\beta}(\mathbf{r}_2)/R_\beta(r_2)$	$\chi_{i\alpha j\beta}(\mathbf{k})$
$Y^R_{L_\alpha 0}(\mathbf{r}_1)$	$Y^R_{L_\beta 0}(\mathbf{r}_2)$	$\sum_{l=0}^{\infty} i^l \mu_{l0}(k)\, Y^R_{l0}(\mathbf{k})$
$Y^R_{L_\alpha 0}(\mathbf{r}_1)$	$Y^R_{L_\beta M_\beta,c}(\mathbf{r}_2)$	$\sum_{l=M_\beta}^{\infty} i^l \mu_{lM_\beta}(k)\, Y^R_{lM_\beta,c}(\mathbf{k})$
$Y^R_{L_\alpha 0}(\mathbf{r}_1)$	$Y^R_{L_\beta M_\beta,s}(\mathbf{r}_2)$	$\sum_{l=M_\beta}^{\infty} i^l \mu_{lM_\beta}(k)\, Y^R_{lM_\beta,s}(\mathbf{k})$
$Y^R_{L_\alpha M_\alpha,c}(\mathbf{r}_1)$	$Y^R_{L_\beta 0}(\mathbf{r}_2)$	$(-1)^{M_\alpha} \sum_{l=M_\alpha}^{\infty} i^l \mu_{lM_\alpha}(k)\, Y^R_{lM_\alpha,c}(\mathbf{k})$
$Y^R_{L_\alpha M_\alpha,s}(\mathbf{r}_1)$	$Y^R_{L_\beta 0}(\mathbf{r}_2)$	$(-1)^{M_\alpha} \sum_{l=M_\alpha}^{\infty} i^l \mu_{lM_\alpha}(k)\, Y^R_{lM_\alpha,s}(\mathbf{k})$
$Y^R_{L_\alpha M_\alpha,c}(\mathbf{r}_1)$	$Y^R_{L_\beta M_\beta,c}(\mathbf{r}_2)$	$\frac{1}{\sqrt{2}} \sum_{l=\lvert m_1\rvert}^{\infty} i^l \mu_{lm_1}(k)\, Y^R_{lm_1,c}(\mathbf{k}) + \frac{(-1)^{M_\alpha}}{\sqrt{2}} \sum_{l=m_2}^{\infty} i^l \mu_{lm_2}(k)\, Y^R_{lm_2,c}(\mathbf{k})$
$Y^R_{L_\alpha M_\alpha,s}(\mathbf{r}_1)$	$Y^R_{L_\beta M_\beta,s}(\mathbf{r}_2)$	$\frac{1}{\sqrt{2}} \sum_{l=\lvert m_1\rvert}^{\infty} i^l \mu_{lm_1}(k)\, Y^R_{lm_1,c}(\mathbf{k}) - \frac{(-1)^{M_\alpha}}{\sqrt{2}} \sum_{l=m_2}^{\infty} i^l \mu_{lm_2}(k)\, Y^R_{lm_2,c}(\mathbf{k})$
$Y^R_{L_\alpha M_\alpha,c}(\mathbf{r}_1)$	$Y^R_{L_\beta M_\beta,s}(\mathbf{r}_2)$	$\frac{1}{\sqrt{2}} \sum_{l=\lvert m_1\rvert}^{\infty} i^l \mu_{lm_1}(k)\, Y^R_{lm_1,s}(\mathbf{k}) + \frac{(-1)^{M_\alpha}}{\sqrt{2}} \sum_{l=m_2} i^l \mu_{lm_2}(k)\, Y^R_{lm_2,s}(\mathbf{k})$
$Y^R_{L_\alpha M_\alpha,s}(\mathbf{r}_1)$	$Y^R_{L_\beta M_\beta,c}(\mathbf{r}_2)$	$\frac{-1}{\sqrt{2}} \sum_{l=\lvert m_1\rvert}^{\infty} i^l \mu_{lm_1}(k)\, Y^R_{lm_1,s}(\mathbf{k}) + \frac{(-1)^{M_\alpha}}{\sqrt{2}} \sum_{l=m_2}^{\infty} i^l \mu_{lm_2}(k)\, Y^R_{lm_2,s}(\mathbf{k})$

We can define real functions

$$Y_{LM,c}(\mathbf{r}) = \frac{1}{\sqrt{2}}\,[Y_{L-M}(\mathbf{r}) + (-1)^M\, Y_{LM}(\mathbf{r})]$$

and

$$Y_{LM,s}(\mathbf{r}) = \frac{i}{\sqrt{2}}\,[Y_{L-M}(\mathbf{r}) - (-1)^M\, Y_{LM}(\mathbf{r})].$$

If we do so then the axial transformation above gives

$$\begin{aligned}
Y_{L0}(\mathbf{r}) &= d^L_{00}(\theta_R)\, Y^R_{L0}(\mathbf{r}) + \sum_{N>0} \sqrt{2}\, d^L_{N0}(\theta_R)\, Y^R_{LN,c}(\mathbf{r}),\\
Y_{Lm,c}(\mathbf{r}) &= \sqrt{2}\, d^L_{0M}(\theta_R) \cos M\varphi_r\, Y^R_{L0}(\mathbf{r})\\
&\quad + \sum_{N>0} [d^L_{NM}(\theta_R) + (-1)^M d^L_{N-M}(\theta_R)]\\
&\quad \times \cos M\varphi_R\, Y^R_{LN,c}(\mathbf{r})\\
&\quad + \sum_{N>0} [-d^L_{NM}(\theta_R) + (-1)^M d^L_{N-M}(\theta_R)]\\
&\quad \times \sin M\varphi_R\, Y^R_{LN,s}(\mathbf{r}),\\
Y_{LM,s}(\mathbf{r}) &= \sqrt{2}\, d^L_{0M}(\theta_R) \sin M\varphi_R\, Y^R_{L0}(\mathbf{r})\\
&\quad + \sum_{N>0} [d^L_{NM}(\theta_R) + (-1)^M d^L_{N-M}(\theta_R)]\\
&\quad \times \sin M\varphi_R\, Y^R_{LN,c}(\mathbf{r})\\
&\quad - \sum_{N>0} [-d^L_{NM}(\theta_R) + (-1)^M d_{N-M}(\theta_R)]\\
&\quad \times \cos M\varphi_R\, Y^R_{LN,s}(\mathbf{r}).
\end{aligned} \tag{14}$$

In particular, when $L = 1$

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} \cos\theta_R \cos\varphi_R & -\sin\varphi_R & \sin\theta_R\cos\varphi_R \\ \cos\theta_r \sin\varphi_R & \cos\varphi_R & \sin\theta_R \sin\varphi_R \\ -\sin\theta_R & 0 & \cos\theta_R \end{pmatrix} \begin{pmatrix} p^R_x \\ p^R_y \\ p^R_z \end{pmatrix}. \tag{15}$$

The overlap between real functions can be evaluated as combinations of terms of the form contained in (5). Table 1 contains expressions for $\chi_{i\alpha j\beta}(\mathbf{k})$ for the overlap of real orbitals.

If we define γ_{lm} as

$$\gamma_{lm} = \left[\frac{(2l+1)}{4\pi}\,\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2}, \tag{16}$$

then $Y^R_{l0}(\mathbf{k}) = \gamma_{l0} P^0_l(\cos\theta_k)$, and for $m > 0$

$$Y^R_{lm,c}(\mathbf{k}) = \sqrt{2}\gamma_{lm} P^m_l(\cos\theta_k)\cos m\varphi_k,$$

$$Y^R_{lm,s}(\mathbf{k}) = \sqrt{2}\gamma_{lm} P^m_l(\cos\theta_k)\sin m\varphi_k$$

$$Y^R_{l-m,c}(\mathbf{k}) = (-1)^m \sqrt{2}\gamma_{lm} P^m_l(\cos\theta_k)\cos m\varphi_k$$

and

$$Y^R_{l-m,s}(\mathbf{k}) = -(-1)^m \sqrt{2}\gamma_{lm} P^m_l(\cos\theta_k)\sin m\varphi_k.$$

We should note that $m_1 = M_\beta - M_\alpha$ in Table 1 can have any integer value. Functional forms of $\gamma_{lm}\mu_{lm}(k)$ for overlaps between s and p orbitals are given in Table

Table 2. *Functional forms of $\gamma_{lm_1}\mu_{lm_1}(k)$ and $\gamma_{lm_2}\mu_{lm_2}(k)$, where $m_1 = M_\beta - M_\alpha$, $m_2 = M_\beta + M_\alpha$*

The functions are identical if either M_α or $M_\beta = 0$.

L_α	M_α	L_β	M_β	Value
0	0	0	0	$(2l+1)\,I_{ll0}(k)$
0	0	1	0	$3^{1/2}[(l+1)I_{ll+11}(k) + lI_{ll-11}(k) - R(2l+1)\,I_{ll0}(k)]$
1	0	0	0	$3^{1/2}[(l+1)I_{ll+10}(k) + lI_{ll-10}(k)]$
0	0	1	1	$\left(\frac{3}{2}\right)^{1/2}[-I_{ll+11}(k) + I_{ll-11}(k)]$
1	1	0	0	$\left(\frac{3}{2}\right)^{1/2}[I_{ll+10}(k) - I_{ll-10}(k)]$
1	0	1	0	$3\left\{\frac{(l+1)(l+2)}{(2l+3)} I_{ll+21}(k) + \frac{l(l-1)}{(2l-1)} I_{ll-21}(k) + \left[\frac{(l+1)^2}{(2l+3)} + \frac{l^2}{(2l-1)}\right] I_{ll1}(k) - R[(l+1)\,I_{ll+10}(k) + lI_{ll-10}(k)]\right\}$
1	0	1	1	$\frac{3}{\sqrt{2}}\left\{-\frac{(l+2)}{(2l+3)} I_{ll+21}(k) + \frac{(l-1)}{(2l-1)} I_{ll-21}(k) - \left[\frac{(l+1)}{(2l+3)} - \frac{l}{(2l-1)}\right] I_{ll1}(k)\right\}$
1	1	1	0	$\frac{3}{\sqrt{2}}\left\{\frac{(l+2)}{(2l+3)} I_{ll+21}(k) - \frac{(l-1)}{(2l-1)} I_{ll-21}(k) + \left[\frac{(l+1)}{(2l+3)} - \frac{l}{(2l-1)}\right] I_{ll1}(k) - R[I_{ll+10}(k) - I_{ll-10}(k)]\right\}$
1	1	1	1	$\gamma_{l0}\mu_{l0}(k) = \frac{3}{2}\left\{\frac{(l+1)(l+2)}{(2l+3)}[I_{ll1}(k) - I_{ll+21}(k)] + \frac{l(l-1)}{(2l-1)}[I_{ll1}(k) - I_{ll-21}(k)]\right\}$ $\gamma_{l2}\mu_{l2}(k) = \frac{3}{2}\left\{\frac{1}{(2l+3)}[I_{ll1}(k) - I_{ll+21}(k)] + \frac{1}{(2l-1)}[I_{ll1}(k) - I_{ll-21}(k)]\right\}$

Table 3. *Functional forms of $\chi_{i\alpha j\beta}(k)$ for overlaps between real s and p orbitals*

$\gamma_{lm}\mu_{lm}(k)$ values are given in Table 2 for the appropriate $L_\alpha M_\alpha$, $L_\beta M_\beta$ combination.

	$\varphi_{i\alpha}(\mathbf{r}_1)$	$\varphi_{j\beta}(\mathbf{r}_2)$	$\chi_{i\alpha j\beta}(k)$
(1)	s	s	$\sum_{l=0}^{\infty} i^l \gamma_{l0}\mu_{l0}(k) P_l^0(\cos\theta_k)$
	s	p_z	
	p_z	s	
	p_z	p_z	
(2)	s	p_x	$\sqrt{2}\sum_{l=1}^{\infty} i^l \gamma_{l1}\mu_{l1}(k) P_l^1(\cos\theta_k)\cos\varphi_k$
	p_z	p_x	
(3)	s	p_y	$\sqrt{2}\sum_{l=1}^{\infty} i^l \gamma_{l1}\mu_{l1}(k) P_l^1(\cos\theta_k)\sin\varphi_k$
	p_z	p_y	
(4)	p_x	s	$-\sqrt{2}\sum_{l=1}^{\infty} i^l \gamma_{l1}\mu_{l1}(k) P_l^1(\cos\theta_k)\cos\varphi_k$
	p_x	p_z	
(5)	p_y	s	$-\sqrt{2}\sum_{l=1}^{\infty} i^l \gamma_{l1}\mu_{l1}(k) P_l^1(\cos\theta_k)\sin\varphi_k$
	p_y	p_z	
(6)	p_x	p_y	$-\sum_{l=2}^{\infty} i^l \gamma_{l2}\mu_{l2}(k) P_l^2(\cos\theta_k)\sin 2\varphi_k$
	p_y	p_x	
(7)	p_x	p_x	$\sum_{l=0}^{\infty} i^l \gamma_{l0}\mu_{l0}(k) P_l^0(\cos\theta_k) - \sum_{l=2}^{\infty} i^l \gamma_{l2}\mu_{l2}(k) P_l^2(\cos\theta_k)\cos 2\varphi_k$
(8)	p_y	p_y	$\sum_{l=0}^{\infty} i^l \gamma_{l0}\mu_{l0}(k) P_l^0(\cos\theta_k) + \sum_{l=2}^{\infty} i^l \gamma_{l2}\mu_{l2}(k) P_l^2(\cos\theta_k)\cos 2\varphi_k$

2. Functional forms of $\chi_{i\alpha j\beta}(\mathbf{k})$ for these orbitals are given in Table 3. Functional forms of $\chi_{i\alpha j\beta}(\mathbf{k})$ are given in Table 4 for the special case when both orbitals are on the same atom.

APPENDIX

Associated Legendre polynomial:

$$P_l^m(\cos\theta) = \sin^m\theta \frac{d^m}{d\cos\theta^m} P_l(\cos\theta).$$

Legendre polynomial:

$$P_l(\cos\theta) = \frac{1}{2^l l!}\frac{d^l}{d\cos\theta^l}(\cos^2\theta - 1)^l, \quad p_l(1) = 1.$$

Table 4. *Functional forms of $\chi_{i\alpha j\alpha}(k)$ for overlaps between real orbitals on the same atom*

$\mathbf{k}$ has direction cosines (t_1, t_2, t_3) relative to the axial system used for orbitals. $\langle j_l(k)\rangle$ is defined in (9). The omitted expressions are obtained by permutation of the $t_1 t_2 t_3$ indices.

$\psi_{i\alpha}(\mathbf{r})$	$\psi_{j\alpha}(\mathbf{r})$	$\chi_{i\alpha j\alpha}(\mathbf{k})$
s	s	$\langle j_0(k)\rangle$
s	p_z	$i\sqrt{3}t_3\langle j_1(k)\rangle$
p_z	p_z	$\langle j_0(k)\rangle + (1-3t_3^2)\langle j_2(k)\rangle$
p_x	p_y	$-3t_1t_2\langle j_2(k)\rangle$

Spherical harmonics:

$$\text{For } m \ge 0,\ Y_{lm}(\theta,\varphi) = (-1)^m \left[\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2} \times P_l^m(\cos\theta)\exp im\varphi$$

$$Y_{l-m}(\theta,\varphi) = \left[\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\cos\theta)\exp - im\varphi.$$

Product of spherical harmonics:

$$Y_{l_1m_1}(\theta,\varphi)\,Y_{l_2m_2}(\theta,\varphi) = \sum_l \alpha_l\, Y_{lm_1+m_2}(\theta,\varphi),$$

where

$$\alpha_l = \left(\frac{2l_1+1}{4\pi}\right)^{1/2} C^{l_1}(lm_1+m_2, l_2m_2)$$

$$= (-1)^{-m_1-m_2}\left[\frac{(2l+1)(2l_1+1)(2l_2+1)}{4\pi}\right]^{1/2} \times \begin{pmatrix} l & l_1 & l_2 \\ -m_1-m_2 & m_1 & m_2\end{pmatrix}\begin{pmatrix} l & l_1 & l_2 \\ 0 & 0 & 0\end{pmatrix}.$$

3-j symbols and Wigner coefficients:

$$\begin{pmatrix} l & l_1 & l_2 \\ m & m_1 & m_2\end{pmatrix} = \frac{(-1)^{l-l_1-m_2}}{(2l_2+1)^{1/2}}\langle ll_1mm_1|l_2-m_2\rangle.$$

Spherical Bessel function:

$$j_{-1}(z) = \frac{\cos z}{z}, \quad j_0(z) = \frac{\sin z}{z}$$

$$j_{n+1}(z) = \frac{(2n+1)}{z} j_n(z) - j_{n-1}(z).$$

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Calculation of Integrals for Overlap Electron Density Scattering Factors

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A new method is given for the calculation of integrals

$$I_{lLL_2}(k)=\frac{1}{4\pi}\int R_\alpha(r_1)R_\beta(r_2)\frac{r_1^{L_2}}{r_2^{L_\beta}}j_l(kr_1)P_L(\cos\theta_1)\,\mathrm{d}V$$

which are needed to evaluate orientation-dependent scattering factors for the overlap electron density between orbitals on stationary atoms at $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$, where $\mathbf{r}_1=\mathbf{r}-\mathbf{r}_\alpha$, $\mathbf{r}_2=\mathbf{r}-\mathbf{r}_\beta$ and $\mathbf{R}_\alpha(r_1)$ and $R_\beta(r_2)$ are Slater-type radial functions. The integration may be reduced to the sum of an algebraic term and a one-dimensional numeric integration between 0 and R, where $\mathbf{R}=\mathbf{r}_\beta-\mathbf{r}_\alpha$.

Introduction

Let $\psi_{i\alpha}(\mathbf{r}_1)=R_\alpha(r_1)Y^R_{L_\alpha M_\alpha}(\mathbf{r}_1)$ and $\psi_{j\beta}(\mathbf{r}_2)=R_\beta(r_2)\times Y^R_{L_\beta M_\beta}(\mathbf{r}_2)$ be orbitals on stationary atoms at $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$ respectively, where $\mathbf{r}_1=\mathbf{r}-\mathbf{r}_\alpha$ and $\mathbf{r}_2=\mathbf{r}-\mathbf{r}_\beta$. The X-ray scattering from the overlap electron density $\psi^*_{i\alpha}(\mathbf{r}_1)\,\psi_{j\beta}(\mathbf{r}_2)$ may then be expressed (Rae, 1978) as

$$\chi_{i\alpha j\beta}(\mathbf{k})=\sum_{l=|m|}^{\infty} i^l\mu_{lm}(k)\,Y^R_{lm}(\mathbf{k}),\quad m=M_\beta-M_\alpha. \tag{1}$$

The scattering vector $\mathbf{k}$ has polar coordinates (k,θ_k,φ_k) defined relative to a local axial system, where $\theta_k=0$ corresponds to the direction $\mathbf{R}=\mathbf{r}_\beta-\mathbf{r}_\alpha$. Likewise, $\mathbf{r}_1$ has polar coordinates (r_1,θ_1,φ_1) and $\mathbf{r}_2$ has polar coordinates $(r_2\theta_2,\varphi_2)$ relative to the same axes. $Y^R_{L_\alpha M_\alpha}(\mathbf{r}_1)$, $Y^R_{L_\beta M_\beta}(\mathbf{r}_2)$, $Y^R_{lm}(\mathbf{k})$ are spherical harmonics with the appropriate polar coordinates defined above. The evaluation of $\mu_{lm}(k)$ requires the calculation of axially symmetric integrals

$$I_{lLL_2}(k)=\frac{1}{4\pi}\int R_\alpha(r_1)R_\beta(r_2)\frac{r_1^{L_2}}{r_2^{L_\beta}}j_l(kr_1)P_L(\cos\theta_1)\,\mathrm{d}V, \tag{2}$$

where $k=4\pi\sin\theta/\lambda$, θ being the Bragg angle. The evaluation of these integrals for Slater-type orbitals is the subject of this paper.

Theory

We expand $R_\beta(r_2)/r_2^{L_\beta}$ about r_α as

$$R_\beta(r_2)/r_2^{L_\beta}=\sum_{L'=0}^{\infty}(2L'+1)P_{L'}(\cos\theta_1)U_{L'}(r_<,r_>), \tag{3}$$

where $U_{L'}(r_<,r_>)$ is a function of $r_<$ and $r_>$ and $P_{L'}(\cos\theta_1)$ is a Legendre polynomial of order L'. $r_<$ is the smaller and $r_>$ the greater of r_1 and R. (3) enables us to say

$$I_{lLL_2}(k)=\int_0^\infty R_\alpha(r_1)r_1^{L_2}j_l(kr_1)\,U_L(r_<,r_>)\,r_1^2\,\mathrm{d}r, \tag{4}$$

from the orthogonality of Legendre polynomials, *i.e.*

$$\frac{2L+1}{4\pi}\int_{-1}^{1}\int_0^{2\pi}P_L(\cos\theta_1)P_{L'}(\cos\theta_1)\,\mathrm{d}\cos\theta_1\,\mathrm{d}\varphi_1=\delta_{LL'},$$

where $\delta_{LL'}=1$ if $L=L'$, 0 if $L\neq L'$.