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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

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

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

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

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

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

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

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

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

Coulson (1937) has shown how to evaluate the functions $U_L(r_<,r_>)$ where $R_\beta(r_2)$ is a combination of Slater-type functions $r_2^{N_\beta-1}\exp(-\zeta_2 r_2)$, where $N_\beta > L_\beta$. We start with the expansion

$$\exp(-\zeta_2 r_2)/r_2 = \sum_{L=0}^{\infty}(2L+1)P_L(\cos\theta_1)\,a_{L,0}(r_<,r_>), \quad (5)$$

where

$$a_{L,0}(r_<,r_>) = \zeta^2 f_L(y) g_L(z), \quad (6)$$

$y = \zeta_2 r_<$ and $z = \zeta_2 r_>$, $f_L(y) = (\pi/2y)^{\frac{1}{2}} I_{L+\frac{1}{2}}(y)$ and $g_L(z) = (2/\pi z)^{\frac{1}{2}} K_{L+\frac{1}{2}}(z)$, where $I_{L+\frac{1}{2}}(y)$ and $K_{L+\frac{1}{2}}(z)$ are modified spherical Bessel functions (Antosiewicz, 1968). Definitions of $f_L(y)$ and $g_L(z)$ and various recursion relations are given in the Appendix.

Now

$$\exp(-\zeta_2 r_2) = \frac{\mathrm{d}}{\mathrm{d}\zeta_2}\frac{\exp(-\zeta_2 r_2)}{r_2}$$

and so

$$\exp(-\zeta_2 r_2) = \sum_{L=0}^{\infty}(2L+1)P_L(\cos\theta_1)\,a_{L,1}(r_<,r_>), \quad (7)$$

where

$$\begin{aligned} a_{L,1}(r_<,r_>) &= \frac{\mathrm{d}}{\mathrm{d}\zeta_2}[\zeta_2 f_L(\zeta_2 r_<) g_L(\zeta_2 r_>)] \\ &= -y f_{L-1}(y) g_L(z) + z f_L(y) g_{L+1}(z) \\ &= z g_{L-1}(z) f_L(y) - y g_L(z) f_{L+1}(y) \end{aligned} \quad (8)$$

from relations detailed in the Appendix.

We can now use the cosine rule, $r_2^2 = r_1^2 + R^2 - 2r_1 R\cos\theta_1$, and say

$$\begin{aligned} r_2^{N_\beta-1}\exp(-\zeta_2 r_2) = {} & [r_<^2 + r_>^2 - 2r_< r_> P_1(\cos\theta_1)] \\ & \times [r_2^{N_\beta-3}\exp(-\beta r_2)], N_\beta > 1, \end{aligned}$$

so that

$$r_2^{N_\beta-1}\exp(-\zeta_2 r_2) = \sum_{L=0}^{\infty}(2L+1)P_L(\cos\theta_1)\,a_{L,N_\beta}(r_<,r_>), \quad (9)$$

where

$$\begin{aligned} a_{L,N_\beta}(r_<,r_>) = {} & (r_<^2 + r_>^2)\,a_{L,N_\beta-2}(r_<,r_>) \\ & - \frac{2r_< r_>}{(2L+1)}[L a_{L-1,N_\beta-2}(r_<,r_>) \\ & + (L+1)\,a_{L+1,N_\beta-2}(r_<,r_>)], \end{aligned} \quad (10)$$

since

$$\begin{aligned} P_1(\cos\theta_1)P_L(\cos\theta_1) = {} & [LP_{L-1}(\cos\theta_1) + (L+1) \\ & \times P_{L+1}(\cos\theta_1)]/(2L+1). \end{aligned}$$

Thus for $r_1 < R$ we have the functional form $a_{L,N_\beta}(r_1,R)$ but for $r_1 > R$ we have a different functional form $a_{L,N_\beta}(R,r_1)$. Likewise we can say $U_L(r_<,r_>)$ has the functional form $U_L(r_1,R)$ for $r_1 < R$ and the functional form $U_L(R,r_1)$ for $r_1 > R$. For computational purposes the integral $I_{lLL_2}(k)$ can be rearranged so that $I_{lLL_2}(k) = V_{lLL_2}(k) + W_{lLL_2}(k)$, where

$$V_{lLL_2}(k) = \int_0^{\infty} R_\alpha(r_1)\,r_1^{L_2} j_l(kr_1)\,U_L(R,r_1)\,r_1^2\,\mathrm{d}r_1 \quad (11)$$

and

$$\begin{aligned} W_{lLL_2}(k) = {} & \int_0^{R} R_\alpha(r_1)\,r_1^{L_2} j_l(kr_1)[U_L(r_1,R) \\ & - U_L(R,r_1)]\,r_1^2\,\mathrm{d}r_1. \end{aligned} \quad (12)$$

$W_{lLL_2}(k)$ has to be calculated numerically but the evaluation of $V_{lLL_2}(k)$ has an exact algebraic form. We note that when $R = 0$, (*i.e.* both orbitals on the same atom) we need only consider (11) with $L = 0$.

The evaluation of $V_{lLL_2}(k)$

Let us first consider the finiteness of the integral component

$$\begin{aligned} & \frac{1}{4\pi}\int r_1^{N_\alpha-1}\exp(-\zeta_1 r_1)\,r_2^{N_\beta-1}\exp(-\zeta_2 r_2)\,\frac{r_1^{L_2}}{r_\gamma^{L_\beta}} \\ & \quad \times j_l(kr_1)P_L(\cos\theta_1)\,\mathrm{d}V \\ & = \int_0^{\infty} r_1^M \exp(-\zeta_1 r_1)\,j_l(kr_1)\,a_{L,N}(R,r_1)\,\mathrm{d}r_1, \end{aligned}$$

where $M = N_\alpha + L_2 + 1$ and $N = N_\beta - L_\beta$. As r_1 tends to zero, $a_{L,N}(R,r_1)$ varies as $1/r_1^{L+1}$ and $j_l(kr_1)$ varies as r_1^l so that $r_1^M j_l(kr_1)\,a_{L,N}(R,r_1)$ varies as $r_1^{N_\alpha+l+L_2-L}$.

Now, the maximum value of L for a given l and L_2 is $l + L_\alpha + L_2$ (Rae, 1978), so that $r_1^M j_l(kr_1)\,a_{L,N}(R,r_1)$ varies as $r_1^{N_\alpha-L_\alpha}$ as r_1 tends to zero. Thus the function being integrated to evaluate $V_{lLL_2}(k)$ is zero at the origin, since $N_\alpha > L_\alpha$ for Slater-type functions. The function being integrated to evaluate $W_{lLL_2}(k)$ goes to zero at both $r_1 = 0$ and $r_1 = R$.

The evaluation of $V_{lLL_2}(k)$ requires the evaluation of integral components of the type

$$A_{lmn} = \int_0^{\infty} r_1^m j_l(kr_1)\exp(-\zeta_1 r_1)\,g_n(\zeta_2 r_1)\,r_1^2\,\mathrm{d}r_1,$$

where $l \geq 0$, $n \geq 0$ and $m > n - l - 1$. All these integrals are finite, as are integrals with $m = n - l - 1$. For integrals with $m = n - l - 1$, the function being integrated has a finite non-zero value at $r_1 = 0$. These latter integrals are also needed for successful use of the recursion formulae which relate the A_{lmn} integrals.

Now $\zeta_1 A_{lmn} = -\int_0^\infty r_1^{m+2} j_l(kr_1)\, g_n(\zeta_2 r_1)\, \mathrm{d}\exp(-\zeta_1 r_1)$

$$= (m+2) A_{lm-1n} + \int_0^\infty r_1^{m+1} \exp(-\zeta_1 r_1)\left[r_1 g_n(\zeta_2 r_1) \frac{\mathrm{d}j_l}{\mathrm{d}r_1}(kr_1) + r_1 j_l(kr_1) \frac{\mathrm{d}g_n}{\mathrm{d}r_1}(\zeta_2 r_1)\right] \mathrm{d}r_1 + \lim_{r_1 \to 0} [r_1^{m+2} j_l(kr_1)\, g_n(\zeta_2 r_1)].$$

From information given in the Appendix we can say

$$\zeta_1 A_{lmn} = (m - l - n) A_{lm-1n} + kA_{l-1mn} - \zeta_2 A_{lmn-1} + \lim_{r_1 - 0} [r_1^{m+2} j_l(kr_1) g_n(\zeta_2 r_1)] \quad (13)$$

and

$$\zeta_1 A_{lmn} = (m + l + 1 - n) A_{lm-1n} - kA_{l+1mn} - \zeta_2 A_{lmn-1} + \lim_{r_1 \to 0} [r_1^{m+2} j_l(kr_1) g_n(\zeta_2 r_1)]. \quad (14)$$

When $n = l = 0$ (13) becomes

$$(\zeta_1 + \zeta_2) A_{0m0} = mA_{0m-10} + kA_{-1m0} \text{ for } m \geq 0. \quad (15)$$

When $n = 0, l = -1$ (14) becomes

$$(\zeta_1 + \zeta_2) A_{-1m0} = mA_{-1m-10} - kA_{0m0} + \delta_{m0}/k\zeta_2 \text{ for } m \geq 0, \quad (16)$$

where $\delta_{m0} = 1$ if $m = 0$, 0 if $m > 0$.

Now, for $m = -1$ we have (*CRC Handbook of Chemistry and Physics*, 1971)

$$\zeta_2 kA_{0-10} = \int_0^\infty \frac{\sin kr_1}{r_1} \exp -(\zeta_1 + \zeta_2) r_1 \, \mathrm{d}r_1 = \omega = \arctan [k/(\zeta_1 + \zeta_2)], \quad (17)$$

where $0 \leq \omega \leq \pi/2$ so that $\cos\omega = (\zeta_1 + \zeta_2)/D$ and $\sin\omega = k/D$ where $D = [k^2 + (\zeta_1 + \zeta_2)^2]^{1/2}$.

For the case when $m = 0$ (15) and (16) give

$$k\zeta_2 A_{000} = \sin\omega/D \quad (18)$$

and

$$k\zeta_2 A_{-100} = \cos\omega/D. \quad (19)$$

For $m > 0$ (15) and (16) give

$$A_{-1m0} = m[\cos\omega A_{-1m-10} - \sin\omega A_{0m-10}]/D$$

and

$$A_{0m0} = m[\sin\omega A_{-1m-10} + \cos\omega A_{0m-10}]/D.$$

We can thus say

$$\zeta_2 A_{0-10} = \omega/k \quad (20)$$

$$k\zeta_2 A_{-1m0} = m! \cos(m+1)\omega/D^{m+1} \quad m \geq 0 \quad (21)$$

$$\zeta_2 A_{0m0} = m! \sin(m+1)\omega/kD^{m+1} \quad m \geq 0. \quad (22)$$

When $k = 0$ we obtain

$$\lim_{k \to 0} k\zeta_2 A_{-1m0} = m!/(\zeta_1 + \zeta_2)^{m+1}, \quad m \geq 0 \quad (23)$$

and

$$\lim_{k \to 0} \zeta_2 A_{0m0} = (m+1)!/(\zeta_1 + \zeta_2)^{m+2}, \quad m \geq -1. \quad (24)$$

We note that $A_{lmn} = 0$ when $k = 0$ for the finite A_{lmn} integrals with $l > 0$. We now use the recursion formula

$$j_{l+1}(kr_1) = \frac{(2l+1)}{kr_1} j_l(kr_1) - j_{l-1}(kr_1)$$

so that

$$kA_{l+1mn} = (2l+1) A_{lm-1n} - kA_{l-1mn}. \quad (25)$$

If all the finite A_{lm-10} and A_{l-1m0} are known, (25) produces all A_{l+1m0} with $m \geq -l$. The remaining finite A_{l+1m0}, $m = -(l+1)$ and $-(l+2)$, are obtained from (13) for the $n = 0$ case, *i.e.*

$$(l - m) A_{l+1m0} = kA_{lm+10} - (\zeta_1 + \zeta_2) A_{l+1m+10}. \quad (26)$$

The recursion formula

$$g_{n+1}(\zeta_2 r_1) = \frac{(2n+1)}{\zeta_2 r_1} g_n(\zeta_2 r_1) + g_{n-1}(\zeta_2 r_1)$$

may now be used to create all finite A_{lmn} from

$$\zeta_2 A_{lmn+1} = (2n+1) A_{lm-1n} + \zeta_2 A_{lmn-1} \quad (27)$$

with $A_{lm0} = A_{lm-1}$ known.

The evaluation of $W_{lLL_2}(k)$

The integral for $W_{lLL_2}(k)$ has to be evaluated numerically. $I_{lLL_2}(k)$ will have a magnitude less than 1·0 but $V_{lLL_2}(k)$ and $W_{lLL_2}(k)$ will have magnitudes which depend on the magnitudes of the ζ_2 values used to describe $R_\beta(r_2)$. The greater the value of ζ_2 the greater the value of $W_{lLL_2}(k)$ and the greater the number of significant figures and data points required to obtain $I_{lLL_2}(k)$ to the required accuracy. Functions of $R_\beta(r_2)$ for bonding electrons have reasonably small values of ζ_2 if a single ζ function is used. However multi-ζ functions (Clementi & Roetti, 1974) include larger values of ζ_2, and the use of multi-ζ functions can increase $W_{lLL_2}(k)$ by a factor as large as 10^3 slowing convergence to the required accuracy. The advantage of reducing the numeric integral to a range 0 to R is then

largely lost. A compromise is the most efficient solution to the problem. $U_L(r_<,r_>)$ is described as $U'_L(r_<,r_>)$ + $U''_L(r_<,r_>)$ where $U'_L(r_<,r_>)$ is the low-ζ component and $U''_L(r_<,r_>)$ is the high-ζ component. Thus $I_{lLL_2}(k)$ = $I'_{lLL_2}(k)$ + $I''_{lLL_2}(k)$, where the low-ζ component $I'_{lLL_2}(k)$ is evaluated from (11), (12) but the high-ζ component is evaluated numerically as

$$I''_{lLL_2}(k) = \int_0^{R+R'} R_\alpha(r_1) r_1^{L_2} j_l(kr_1) U''_L(r_<,r_>) r_1^2 \, dr_1, \quad (28)$$

where R' may be quite small, since $U''_L(r_<,r_>)$ has a rapid exponential decay when $r_1 > R$.

A program has been written to evaluate the above integrals. It was found advantageous to cut the range of the numeric integrals into sixteenths to allow for different rates of convergence in different sections of the range. Convergence of the integration is worst near $r_1 = 0$ and initial trial calculations are found necessary to optimize the calculation. It should also be noted that, as the scattering vector **k** changes, only $j_l(kr)$ changes so that storage of $R_\alpha(r_1) r_1^{L_2} U_L(r_<,r_>) r_1^2$ values is advantageous. It should also be pointed out that the use of the recursion formulae in the Appendix for the evaluation of $j_l(x)$ and $f_L(y)$ has serious round-off errors as x or y approaches zero so that the series expansions given in the Appendix should be used for small x, y. Likewise, if we define $G_n(z) = z^{n+1} g_n(z)$, the recursion formula $G_{n+1}(z) = (2n + 1)G_n(z) + z^2 G_{n-1}(z)$, $G_0(z) = \exp(-z)$, $z^2 G_{-1}(z) = z \exp(-z)$ is less prone to round-off error for small z.

APPENDIX

Spherical Bessel function $j_l(x)$:

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

$$j_{l+1}(x) = \frac{(2l+1)}{x} j_l(x) - j_{l-1}(x)$$

$$x \frac{d}{dx} j_l(x) = -(l+1) j_l(x) + x j_{l-1}(x)$$

$$= l j_l(x) - x j_{l+1}(x),$$

$$j_l(x) = x^l \sum_{m=0}^{\infty} \frac{2^{l+m}(l+m)!(-\frac{1}{2}x^2)^m}{m!(2l+2m+1)!}, \quad l \geq 0.$$

Modified spherical Bessel function

$$f_L(y) = (\pi/2y)^{\frac{1}{2}} I_{L+\frac{1}{2}}(y):$$

$$f_0(y) = \frac{\sinh y}{y}, f_{-1}(y) = \frac{\cosh y}{y}$$

$$f_{L+1}(y) = -\frac{(2L+1)}{y} f_L(y) + f_{L-1}(y)$$

$$y \frac{d}{dy} f_L(y) = -(L+1) f_L(y) + y f_{L-1}(y)$$

$$= L f_L(y) + y f_{L+1}(y)$$

$$f_L(y) = y^L \sum_{m=0}^{\infty} \frac{2^{L+m}(L+m)!(\frac{1}{2}y^2)^m}{m!(2L+2m+1)!}, \quad L \geq 0.$$

Modified spherical Bessel function

$$g_L(z) = (2/\pi z)^{\frac{1}{2}} K_{L+\frac{1}{2}}(z):$$

$$g_0(z) = g_{-1}(z) = \frac{\exp(-z)}{z}$$

$$g_{L+1}(z) = \frac{(2L+1)}{z} g_L(z) + g_{L-1}(z)$$

$$z \frac{d}{dz} g_L(z) = -(L+1) g_L(z) - z g_{L-1}(z)$$

$$= L g_L(z) - 2 g_{L+1}(z)$$

$$g_L(z) = g_{-L-1}(z) = (-1)^{L+1}[f_L(z) - f_{-L-1}(z)].$$

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