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Generalized Scattering Factors and Generalized Fourier Transforms

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Abstract

A method is proposed for evaluating generalized X-ray scattering factors (Fourier transforms of products of atomic orbitals) in the two-center case with Slater-type orbitals. This method is especially appropriate if one of the Slater exponents is considerably larger than the other.

Introduction

In a previous paper (Avery, 1978), an approximate method was proposed for calculating the generalized scattering factor

$$X_{\mu\nu}(\mathbf{S}) \equiv \int d^3x \exp(i\mathbf{S}.\mathbf{x})\chi_\mu(\mathbf{x}-\mathbf{a})\chi_\nu(\mathbf{x}-\mathbf{b}) \quad (1)$$

in the two-center case where χ_μ and χ_ν are Slater-type atomic orbitals (see also Harris & Michels, 1967; Avery, 1975; Stewart, 1969; Monkhorst & Harris, 1972; Graovac, Monkhorst & Zivkovic, 1973; Avery & Watson, 1977). In the present paper, an alternative method will be discussed. This method is especially appropriate in the special case where one of the Slater exponents is much larger than the other.

Suppose, for example, that χ_μ and χ_ν are 1*s* Slater-type atomic orbitals located on different centers, so that

$$\begin{aligned} \chi_\mu &= N_1 \exp(-\zeta'|\mathbf{x}-\mathbf{a}|), \\ \chi_\nu &= N_2 \exp(-\zeta|\mathbf{x}-\mathbf{b}|), \end{aligned} \quad (2)$$

where $\zeta' \gg \zeta$ and where N_1 and N_2 are normalizing constants. Since χ_μ is much more sharply localized in space than χ_ν, it follows that the main contribution to the generalized scattering factor $X_{\mu\nu}$ will come from the region in which χ_μ is localized, *i.e.* the region near $\mathbf{x} = \mathbf{a}$. Therefore, we can approximate $X_{\mu\nu}$ by expanding χ_ν about the point $\mathbf{x} = \mathbf{a}$.

Expansion of χ_ν about $\mathbf{x} = \mathbf{a}$

Let

$$\mathbf{R} = \mathbf{b} - \mathbf{a}, \quad (3)$$

then

$$|\mathbf{x}-\mathbf{b}| = |\mathbf{x}-\mathbf{a}-\mathbf{R}| \quad (4)$$

and, in our illustrative example,

$$\begin{aligned} X_{\mu\nu}(\mathbf{S}) &= N_1 N_2 \exp(i\mathbf{S}.\mathbf{a}) \int d^3x \exp\{i\mathbf{S}.(\mathbf{x}-\mathbf{a}) \\ &\quad - \zeta'|\mathbf{x}-\mathbf{a}| - \zeta|\mathbf{x}-\mathbf{a}-\mathbf{R}|\} \\ &= N_1 N_2 \exp(i\mathbf{S}.\mathbf{a}) \int d^3x \exp(i\mathbf{S}.\mathbf{x} \\ &\quad - \zeta'|\mathbf{x}| - \zeta|\mathbf{x}-\mathbf{R}|). \end{aligned} \quad (5)$$

We now expand $|\mathbf{x}-\mathbf{R}|$ in the series

$$|\mathbf{x}-\mathbf{R}| = R \sum_{l=0}^{\infty} Q_l(\gamma) \left(\frac{r}{R}\right)^l, \quad (6)$$

where

$$\begin{aligned} \gamma &\equiv \frac{\mathbf{x}.\mathbf{R}}{rR} = \cos\theta, \\ r &\equiv |\mathbf{x}|, \end{aligned} \quad (7)$$

and

$$\begin{aligned} Q_0 &= 1 \\ Q_1 &= -\gamma \\ Q_2 &= \tfrac{1}{2}(1-\gamma^2) \\ Q_3 &= \tfrac{1}{2}(\gamma-\gamma^3) \\ Q_4 &= \tfrac{1}{8}(-1+6\gamma^2-5\gamma^4) \\ Q_5 &= \tfrac{1}{8}(-3\gamma+10\gamma^3-7\gamma^5), \textit{ etc.} \end{aligned} \quad (8)$$

and, in general,

$$Q_l(\gamma) = \frac{1}{2l-1}\{P_{l-2}(\gamma) - P_l(\gamma)\} \ (l \geq 2). \quad (9)$$

In (9), the P_l's are Legendre polynomials. From (6) and (8) we have

$$\begin{aligned} &\exp(-\zeta|\mathbf{x}-\mathbf{R}|) \\ &= \exp(-\zeta R + \zeta r\gamma) \exp\left\{-\zeta R \sum_{l=2}^{\infty} Q_l(\gamma)\left(\frac{r}{R}\right)^l\right\} \\ &= \exp(-\zeta R + \boldsymbol{\kappa}.\mathbf{x}) \exp\{a_2 r^2 + a_3 r^3 + a_4 r^4 + \ldots\} \end{aligned}$$

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$$= \exp(-\zeta R + \boldsymbol{\kappa}.\mathbf{x}) \Big\{ 1 + (a_2 r^2 + a_3 r^3 + \ldots) + \frac{1}{2!}(a_2 r^2 + a_3 r^3 + \ldots)^2 + \frac{1}{3!}(a_2 r^2 + a_3 r^3 + \ldots)^3 + \ldots \Big\}$$

$$= \exp(-\zeta R + \boldsymbol{\kappa}.\mathbf{x}) \Big\{ 1 + a_2 r^2 + a_3 r^3 + \left(a_4 + \frac{1}{2} a_2 a_2\right) r^4 + (a_5 + a_2 a_3) r^5 + \ldots \Big\}, \quad (10)$$

where

$$\boldsymbol{\kappa} = \frac{\zeta}{R}\mathbf{R} \quad (11)$$

and

$$a_l = \zeta \frac{Q_l(\gamma)}{R^{l-1}}. \quad (12)$$

Collecting terms in the various Legendre polynomials, we obtain

$$\exp(-\zeta|\mathbf{x}-\mathbf{R}|) = \exp(-\zeta R + \boldsymbol{\kappa}.\mathbf{x}) \sum_{l=0}^{\infty} P_l(\gamma) g_l(r), \quad (13)$$

where

$$g_0 = 1 - \frac{\zeta R}{3}\left(\frac{r}{R}\right)^2 + \frac{(\zeta R)^2}{15}\left(\frac{r}{R}\right)^4 + \ldots$$

$$g_1 = -\frac{\zeta R}{5}\left(\frac{r}{R}\right)^3 + \frac{2}{35}(\zeta R)^2\left(\frac{r}{R}\right)^5 + \ldots$$

$$g_2 = \frac{\zeta R}{3}\left(\frac{r}{R}\right)^2 - \frac{\zeta R}{7}\left(1 + \frac{2}{3}\zeta R\right)\left(\frac{r}{R}\right)^4 + \ldots$$

$$g_3 = \frac{\zeta R}{5}\left(\frac{r}{R}\right)^3 - \frac{\zeta R}{9}\left(1 + \frac{4}{5}\zeta R\right)\left(\frac{r}{R}\right)^5 + \ldots$$

$$g_4 = \frac{\zeta R}{7}\left(1 + \frac{\zeta R}{5}\right)\left(\frac{r}{R}\right)^4 + \ldots$$

$$g_5 = \frac{\zeta R}{9}\left(1 + \frac{2}{7}\zeta R\right)\left(\frac{r}{R}\right)^5 + \ldots, \textit{etc.} \quad (14)$$

We have tested this expansion numerically, and find that for $\zeta R \leq 10$, the terms shown in (14) are sufficient to give five-figure accuracy for $r/R \leq 0{\cdot}1$.

In the range $0{\cdot}1 \leq (r/R) \leq 0{\cdot}2$, the terms shown in (14) give three- or four-figure accuracy. Greater precision could of course be obtained by extending the expansion of higher powers of $(r/R)^l$. Notice that when $\gamma = \pm 1$, $Q_l(\gamma) = 0$ for $l \geq 2$; and therefore when $\gamma = \pm 1$, we have the exact relationship:

$$\exp(-\zeta|\mathbf{x}-\mathbf{R}|) = \exp(-\zeta R + \boldsymbol{\kappa}.\mathbf{x}). \quad (15)$$

From this it follows that

$$\sum_{l=0}^{\infty} P_l(1) g_l(r) = \sum_{l=0}^{\infty} g_l(r) = 1$$

and

$$\sum_{l=0}^{\infty} P_l(-1) g_l(r) = \sum_{l=0}^{\infty} (-1)^l g_l(r) = 1, \quad (16)$$

so that

$$\sum_{l=0,2,4,\ldots}^{\infty} g_l(r) = 1 \quad \text{and} \quad \sum_{l=1,3,5,\ldots}^{\infty} g_l(r) = 0. \quad (17)$$

Substituting (13) into (5), we have

$$X_{\mu\nu}(\mathbf{S}) = N_1 N_2 \exp(i\mathbf{S}.\mathbf{a} - \zeta R) \times \int d^3 x \exp\{i(\mathbf{S} - i\boldsymbol{\kappa}).\mathbf{x} - \zeta' r\} \times \sum_{l=0}^{\infty} P_l\left(\frac{\mathbf{x}.\mathbf{R}}{rR}\right) g_l(r). \quad (18)$$

Generalized Fourier transforms

From (18), we see that if we let

$$\boldsymbol{\xi} = \mathbf{S} - i\boldsymbol{\kappa}, \quad (19)$$

the integral will resemble a Fourier transform, except that the scattering vector $\boldsymbol{\xi}$ will be complex. Therefore it will be helpful in evaluating integrals of this type if we can generalize Fourier transform techniques to include cases where the scattering vector is complex. One can show by analytic continuation that the identity

$$\exp(i\boldsymbol{\xi}.\mathbf{x}) = \sum_{l=0}^{\infty} i^l (2l+1) P_l\left(\frac{\boldsymbol{\xi}.\mathbf{x}}{\xi r}\right) j_l(\xi r) \quad (20)$$

is valid when $\boldsymbol{\xi}$ is complex. In (20),

$$\xi = (\boldsymbol{\xi}.\boldsymbol{\xi})^{1/2} = \{(\mathbf{S} - i\boldsymbol{\kappa}).(\mathbf{S} - i\boldsymbol{\kappa})\}^{1/2}, \quad (21)$$

where the j_l's are spherical Bessel functions of order l, and the P_l's are Legendre polynomials. It does not matter which of the two values of the square root is chosen for ξ, since the phase factor cancels out of the expansion in (20). Substituting (20) into (18), and making use of the identity

$$\int d\Omega P_l\left(\frac{\boldsymbol{\xi}.\mathbf{x}}{\xi r}\right) P_{l'}\left(\frac{\mathbf{x}.\mathbf{R}}{rR}\right) = \frac{4\pi}{2l+1} \delta_{ll'} P_l\left(\frac{\boldsymbol{\xi}.\mathbf{R}}{\xi R}\right), \quad (22)$$

we obtain for the generalized scattering factor of (18):

$$X_{n\nu}(\mathbf{S}) = 4\pi N_1 N_2 \exp(i\mathbf{S}.\mathbf{a} - \zeta R) \times \sum_{l=0}^{\infty} i^l P_l\left(\frac{\boldsymbol{\xi}.\mathbf{R}}{\xi R}\right) \int_0^{\infty} dr\, r^2 g_l(r) j_l(\xi r) e^{-\zeta' r}. \quad (23)$$

The functions $g_l(r)$ which appear in (23) are expressed in terms of powers of r/R by (14). Therefore, $X_{\mu\nu}(\mathbf{S})$ can be expressed in terms of radial integrals of the form:

$$J_{n,l} \equiv \int_0^\infty \mathrm{d}r\, r^n j_l(\xi r) e^{-\zeta' r}. \tag{24}$$

These integrals are easy to evaluate (see Stewart, 1969; Harris, 1973; Avery & Cook, 1974; Avery & Watson, 1977). By integration one obtains:

$$J_{1,0} = \frac{1}{\xi^2 + \zeta'^2}$$

$$J_{2,0} = \frac{2\zeta'}{(\xi^2 + \zeta'^2)^2} \tag{25}$$

and the integrals $J_{n,l}$ with higher values of n and l are obtained from the recursion relations:

$$J_{\nu+1,\nu} = \left(\frac{2\nu\xi}{\xi^2 + \zeta'^2}\right) J_{\nu,\nu-1}$$

$$J_{\nu+2,\nu} = \zeta' \left(\frac{2\nu + 2}{\xi^2 + \zeta'^2}\right) J_{\nu+1,\nu}$$

$$J_{\mu+1,\nu} = \frac{1}{\xi^2 + \zeta'^2} \{2\mu\zeta' J_{\mu\nu} - (\mu + \nu)(\mu - \nu - 1) J_{\mu-1,\nu}\}. \tag{26}$$

In terms of these integrals, the generalized scattering factor of our example becomes:

$$X_{\mu\nu}(\mathbf{S}) = 4\pi N_1 N_2 \exp(i\mathbf{S}.\mathbf{a} - \zeta R) \times \left\{\left(J_{2,0} - \frac{\zeta}{3R} J_{4,0} + \frac{\zeta^2}{15R^2} J_{6,0} + \ldots\right) + \frac{i\boldsymbol{\xi}.\mathbf{R}}{\xi R}\left(\frac{-\zeta}{5R^2} J_{5,1} + \frac{2}{35}\frac{\zeta^2}{R^3} J_{7,1} + \ldots\right) + \ldots\ etc.\right\}. \tag{27}$$

In applying this method, it should be remembered that

$$\xi^2 = S^2 - \zeta^2 - 2i\frac{\zeta}{R}(\mathbf{S}.\mathbf{R}) \tag{28}$$

is a complex number and that ξ is also complex.

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