common scale and a value of 10·0 for bond lengths and 2·0 for angles produces a well-behaved refinement with acceptable residual values for the constrained bond lengths and angles. Since the slack constraints should not be expected to hold exactly, smaller weights are used once the refinement produces constrained values that are within reasonable limits of expected values.

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Generalized X-ray Scattering Factors. An Approximate Method for the Two-Centre Case with Slater-Type Orbitals

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A general method is described for calculating the Fourier transform of a product of two Slater-type atomic orbitals located on different atomic centres. The method is approximate, but can be carried to any desired degree of accuracy.

Introduction

Let $\chi_\mu(\mathbf{x}-\mathbf{a})$ be an atomic orbital of type μ centred on an atom at the point **a**, while $\chi_\nu(\mathbf{x}-\mathbf{b})$ is an atomic orbital of type ν centred on an atom at the point **b**. The Fourier transform of the product of two such functions:

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

is called a generalized scattering factor. Here **S** is the scattering vector, and $\mathbf{R} \equiv \mathbf{a}-\mathbf{b}$ is the interatomic distance. Scattering factors of this type are important in comparing the results of X-ray charge-density measurements with calculated charge densities, and also have applications in the evaluation of molecular Coulomb and exchange integrals (Harris & Michels, 1967; Avery, 1975). They have been studied extensively by Stewart (1969*b*), Monkhorst & Harris (1972), Graovac, Monkhorst & Zivkovic (1973), Avery & Watson (1977) and others. The one-centre case is easy to evaluate in simple closed form, both with Slater-type basis functions and with Cartesian Gaussian basis functions. The two-centre case is also easy to evaluate with Cartesian Gaussian basis functions. However, the two-centre case with Slater-type basis functions is extremely difficult, and, in this case, it has not yet been possible to evaluate the generalized scattering factors in simple closed form. Therefore it is desirable to obtain approximate expressions which will cover this case.

Approximate expressions

Let us define the Fourier transform of a function $f(\mathbf{x})$ as:

$$f^t(\mathbf{S}) \equiv \frac{1}{\sqrt{(2\pi)^3}} \int d^3x \exp(i\mathbf{S}.\mathbf{X}) f(\mathbf{x}). \tag{2}$$

Then

$$[f(\mathbf{x}-\mathbf{a})]^t = \frac{\exp(i\mathbf{S}.\mathbf{a})}{\sqrt{(2\pi)^3}} \int d^3x \exp[i\mathbf{S}.(\mathbf{x}-\mathbf{a})] f(\mathbf{x}-\mathbf{a})$$
$$= \exp(i\mathbf{S}.\mathbf{a}) f^t(\mathbf{S}). \tag{3}$$

From (1) we have:

$$X_{\mu\nu} = \sqrt{(2\pi)^3}\,[f(\mathbf{x}-\mathbf{a})g(\mathbf{x}-\mathbf{b})]^t \tag{4}$$

where

$$f(\mathbf{x}) = \chi_\mu(\mathbf{x})$$
$$g(\mathbf{x}) = \chi_\nu(\mathbf{x}). \tag{5}$$

Let us split the function f into 'hard' and 'soft' parts:

$$f = f_h + f_s, \tag{6}$$

where

$$f_h(\mathbf{x}) \equiv \exp\left[-\left(\frac{r}{r_0}\right)^2\right] f(\mathbf{x}) \qquad (7)$$

and

$$f_s(\mathbf{x}) \equiv \left\{1 - \exp\left[-\left(\frac{r}{r_0}\right)^2\right]\right\} f(\mathbf{x}). \qquad (8)$$

If we choose a small value for r_0, for example, $r_0 = 0{\cdot}25$ atomic units, then $f_h(\mathbf{x} - \mathbf{a})$ will be localized in the near neighbourhood of the point $\mathbf{x} = \mathbf{a}$. Similarly, if we split g in the same way, so that

$$g = g_h + g_s \qquad (9)$$

$$g_h(\mathbf{x}) = \exp\left[-\left(\frac{r}{r_0}\right)^2\right] g(\mathbf{x}) \qquad (10)$$

$$g_s(\mathbf{x}) = \left\{1 - \exp\left[-\left(\frac{r}{r_0}\right)^2\right]\right\} g(\mathbf{x}), \qquad (11)$$

then $g_h(\mathbf{x} - \mathbf{b})$ will be localized in the near neighbourhood of the point $\mathbf{x} = \mathbf{b}$. If we neglect the overlap between $f_h(\mathbf{x} - \mathbf{a})$ and $g_h(\mathbf{x} - \mathbf{b})$, then the Fourier transform in (4) becomes:

$$[f(\mathbf{x}-\mathbf{a})g(\mathbf{x}-\mathbf{b})]^t \simeq [f_s(\mathbf{x}-\mathbf{a})g_s(\mathbf{x}-\mathbf{b})]^t + [f_s(\mathbf{x}-\mathbf{a})g_h(\mathbf{x}-\mathbf{b})]^t + [f_h(\mathbf{x}-\mathbf{a})g_s(\mathbf{x}-\mathbf{b})]^t, \qquad (12)$$

where we have introduced the approximation:

$$f_h(\mathbf{x}-\mathbf{a})g_h(\mathbf{x}-\mathbf{b}) \simeq 0. \qquad (13)$$

Let us now introduce a further approximation. We let

$$f_s(\mathbf{x}) \simeq \left\{1 - \exp\left[-\left(\frac{r}{r_0}\right)^2\right]\right\} f'(\mathbf{x}) \qquad (14)$$

where $f'(\mathbf{x})$ is a Gaussian approximation to the Slater-type orbital $f(\mathbf{x})$. In other words, we replace the exponential factor $\exp(-\zeta r)$ in $f(\mathbf{x})$ by its Gaussian approximation:

$$\exp(-\zeta r) \simeq \sum_j C_j \exp(-\alpha_j r^2). \qquad (15)$$

The constants C_j and α_j are chosen so that the fit is good for $r > r_0$. [For methods of fitting, see Stewart (1969*a*)]. However, there can be a small region around the nucleus where the fit is poor. Having made the approximation (14), we can then evaluate the transform

$$\left\{\left[1 - \exp\left(-\frac{|\mathbf{x}-\mathbf{a}|^2}{r_0^2}\right)\right] f'(\mathbf{x}-\mathbf{a}) \times \left[1 - \exp\left(-\frac{|\mathbf{x}-\mathbf{b}|^2}{r_0^2}\right)\right] g'(\mathbf{x}-\mathbf{b})\right\}^t \qquad (16)$$

exactly (Chandler & Spackman, 1978).

Let us now turn our attention to the term $[f_s(\mathbf{x} - \mathbf{a})g_h(\mathbf{x} - \mathbf{b})]^t$ in (12). In the neighbourhood of $\mathbf{x} = \mathbf{b}$, we can make the approximation:

$$f_s(\mathbf{x}-\mathbf{a}) \simeq f(\mathbf{x}-\mathbf{a}). \qquad (17)$$

We now expand $f(\mathbf{x} - \mathbf{a})$ in a Taylor series about $\mathbf{x} = \mathbf{b}$, and retain only the zeroth-order term. Then, using (17), (10), (2) and (3), we obtain:

$$[f_s(\mathbf{x}-\mathbf{a})g_h(\mathbf{x}-\mathbf{b})]^t \simeq \exp(i\mathbf{S}.\mathbf{b})f(\mathbf{b}-\mathbf{a}) \times \left\{\exp\left[-\left(\frac{r}{r_0}\right)^2\right] g(\mathbf{x})\right\}^t. \qquad (18)$$

The term $[f_h(\mathbf{x} - \mathbf{a})g_s(\mathbf{x} - \mathbf{b})]^t$ can be evaluated in a similar way, so that finally we obtain:

$$\begin{aligned}
&[f(\mathbf{x}-\mathbf{a})g(\mathbf{x}-\mathbf{b})]^t \\
&\quad \simeq \left\{\left[1 - \exp\left(-\frac{|\mathbf{x}-\mathbf{a}|^2}{r_0^2}\right)\right] f'(\mathbf{x}-\mathbf{a}) \times \left[1 - \exp\left(\frac{|\mathbf{x}-\mathbf{b}|^2}{r_0^2}\right)\right] g'(\mathbf{x}-\mathbf{b})\right\}^t \\
&\quad + \exp(i\mathbf{S}.\mathbf{b})f(\mathbf{b}-\mathbf{a})\left\{\exp\left[-\left(\frac{r}{r_0}\right)^2\right] g(\mathbf{x})\right\}^t \\
&\quad + \exp(i\mathbf{S}.\mathbf{a})g(\mathbf{a}-\mathbf{b})\left\{\exp\left[-\left(\frac{r}{r_0}\right)^2\right] f(\mathbf{x})\right\}^t,
\end{aligned} \qquad (19)$$

where f' and g' are Gaussian approximations to the Slater-type orbitals f and g. All the terms in (19) are easy to evaluate in closed form. Notice that in the high-frequency limit we obtain:

$$[f(\mathbf{x}-\mathbf{a})g(\mathbf{x}-\mathbf{b})]^t \underset{S\to\infty}{\Rightarrow} \exp(i\mathbf{S}.\mathbf{b})f(\mathbf{b}-\mathbf{a})g^t(\mathbf{S}) + \exp(i\mathbf{S}.\mathbf{a})g(\mathbf{a}-\mathbf{b})f^t(\mathbf{S}) \qquad (20)$$

since, for Slater-type orbitals,

$$\left\{\exp\left[-\left(\frac{r}{r_0}\right)^2\right] f(\mathbf{x})\right\}^t \underset{S\to\infty}{\Rightarrow} f^t(\mathbf{S}) \qquad (21)$$

and since the first term on the right-hand side of (19) falls off more rapidly than (21) for large values of S. The method described here is approximate, but it can be carried to any desired degree of accuracy by using more terms in the expansion (15) and by correspondingly reducing the value of r_0. Also, more terms can be retained in the expansion of $f(\mathbf{x} - \mathbf{a})$ about $\mathbf{x} = \mathbf{b}$.

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The Vicissitudes of the Low-Quartz Crystal Setting or the Pitfalls of Enantiomorphism

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To I. Koda, who in 1929 *first proposed to use coordinate systems of both hands*

Based on a literature study, the following proposals endeavour to combine the advantages of previous conventions for setting low-quartz crystals: (1) Knowing that symmetry axes are parallel to the edges of the smallest hexagonal cell, place *Oz* along the 3-axis and *Ox*, *Oy*, *Ou* along the *macroscopic* 2-axes. (2) Direct the polar axes positively toward the *s* and *x* faces, if present, or toward the positive charge developed on extension by piezoelectric test. (3) Match the hand of the coordinate system to that of the structural screw; thus, the right-handed coordinate system (RHCS) for the known right screw (RS) of laevorotatory quartz. (4) Let the coordinate axis that *coincides* with a 2-axis *in the structure* be *Ox*[100]. These rules result in both enantiomorphs obeying Lang's mnemonic rule and being in the *r*(+) setting, in which $\{10\bar{1}1\}$ symbolizes the major rhombohedron *r*, defined by $I_{\rm obs}(10\bar{1}1) > I_{\rm obs}(01\bar{1}1)$. Low quartz has only one structure. It should be published only for the RS ($P3_121$) and in the RHCS: anyone can visualize the LS enantiomorph by plotting the atomic coordinates in the LHCS. This policy should apply to any enantiomorphous substance with known absolute configuration. If a crystal structure, determined in the RHCS, turns out to have a LS, transform to LHCS and publish the new coordinates, which also fit the *standard RS in RHCS*, but add, 'Known only as LS' or 'Observed as LS'.

Introduction

Various settings have been used in the literature for the description of low quartz, and several attempts at uniformization have been made. Colliding interests of the parties involved have hampered progress. Proposed conventions have conflicted on many points: (1) What criterion will identify a crystal as 'right' or 'left' and, concomitantly, how to express the optical rotatory power [Biot (1817) *vs* Herschel (1822) conventions], and whether it is possible to correlate the hand of the screw axis ('geometrical or structural helix') with that of the 'optical helix'; (2) the hand of the coordinate system; (3) the sense of the rotation that will define a screw rotation; (4) whether to adopt the *r* or the *z* setting, that is, giving the symbol $\{10\bar{1}1\}$ to the 'major rhombohedron' *r* or to the 'minor rhombohedron' *z*; (5) how to orient the polar twofold axes; (6) what to call the coordinate axis that is chosen to coincide with a twofold axis in the crystal structure (*x*, *y* or *u*). Committees have disagreed on whether to use a single (right-handed) coordinate system for both right and left quartz, or one system for right quartz and the other for left quartz; in the latter choice, an additional question comes up at the present time, now that it is possible to determine the absolute configuration of an enantiomorph – should the hand of the coordinate system match that of the geometrical helix or that of the optical helix? Finally a number of misprints in key publications increased the confusion. None of the above difficulties, which deal mostly with matters of convention, would by itself create any problem. Taken together, however, they lead to so many possibilities that they constitute a real obstacle to the mastering of the literature.

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