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Structure-Factor Calculations with Anisotropic Thermal Parameters

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An atom having anisotropic thermal motion may be represented in the structure-factor calculation by two or four isotropic fractional atoms, placed symmetrically about the atom centre and at small distances from it. By this procedure it is possible to calculate the contributions of anisotropically vibrating atoms to the structure factors in the same way as for isotropic atoms without the necessity of introducing new constants for a fictitious distorted lattice. The justification and accuracy of this approximation in the range of observed intensities are discussed, and an estimate is given for the separation between these isotropic fractional atoms. The agreement between this method and the correct representation of the anisotropic thermal motion for practical cases is shown to be extremely high.

Introduction

Early in the course of refinement of structures, different anisotropic thermal parameters for some of the atoms often are clearly indicated in the Fourier maps and one is confronted with the problem of whether and how to allow for these effects in further refinement. In structures containing a few heavy atoms among a larger number of lighter atoms, the intensity distribution of the small-angle reflections is dominated by the scattering from the heavier atoms. The accuracy with which the positions of the light atoms can be determined depends to a great extent on the correct estimation of the phases and amplitudes of the contributions from the heavy atoms to the large-angle reflections. If these heavy atoms have marked anisotropic thermal motions, then good representation of these anisotropies in the assumed structure model becomes an important factor in the accurate determination of the positions of the light atoms. For example, during the refinement of codeine hydrobromide dihydrate which contains one bromine atom and 24 light atoms (excluding hydrogens) in the asymmetric unit cell, the assignment of anisotropic thermal parameters to the bromine atom alone improved the discrepancy factor from 19% to 14% for the whole structure in one cycle of refinement; this corresponds to a reduction from 40% to 26% considering the contributions of the light atoms only. Although this refinement was for a centrosymmetric projection it is to be expected that the effect would be even more pronounced for data of non-centrosymmetric structures where phases also would be appreciably affected.

The methods which have been described for estimating the effect of anisotropy of an atom on its scattering contribution to any reflection require a different distorted lattice for the temperature-factor calculation of each anisotropically vibrating atom as well as the undistorted lattice for scattering factors, and this is of a definite disadvantage in mechanized calculations on medium-size computers. The method described in this paper has the advantage of allowing for the anisotropic thermal vibration of some of the atoms, to a good degree of approximation within the practical range of observation, without the necessity of changing the logic of machine programs designed for isotropic atoms only. This is achieved by replacing an anisotropic atom by two or four isotropic fractional atoms. When only a few atoms in the structure are to be assigned anisotropic thermal parameters this procedure usually results in increasing the total number of atoms included in the structure-factor calculation by only a small fraction of the original number. However, for those structures in which a large percentage of the atoms have to be assigned anisotropic thermal parameters it may be better to employ a structure-factor program that allows for the anisotropic thermal motion in the usual way.

Principle of method

Cochran (1954) has shown that the surfaces of constant scattering factor round an atom which has anisotropic thermal vibration are ellipsoids specified by the distribution

$$f(\xi, \eta, \zeta) = f_0(S) \exp\left[-2\pi^2\{\xi^2 u_x^2 + \eta^2 u_y^2 + \zeta^2 u_z^2\}\right], \quad (1)$$

where $f_0(S)$ is the scattering of the atom at rest, u_x^2, u_y^2, u_z^2 are its mean-square displacements along the principal directions of vibration (which may not coincide with the crystallographic axes), (x, y, z) and (ξ, η, ζ) are the rectangular components of the vectors r in real space, and S in reciprocal space, respectively. The magnitude of S is $2 \sin \theta/\lambda$, and the components (B_x, B_y, B_z) of the temperature factors along those principal directions are given by the relations $B_x = 8\pi^2 u_x^2$, ... etc.

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In equation (1), by writing for the isotropic part not the scattering from an atom at rest but from an atom having a suitable isotropic temperature factor B, we get

$$f(\xi, \eta, \zeta) = f_B(S) \exp\left[-(\Delta B_x \xi^2 + \Delta B_y \eta^2 + \Delta B_z \zeta^2)/4\right], \quad (2)$$

where B is chosen to be less than or equal to the smallest of B_x, B_y, B_z so that ΔB_x, ΔB_y, ΔB_z are all positive. The electron-density distribution which gives the scattering corresponding to equation (2) is the convolution of the Fourier transforms of the two terms on the right hand side of equation (2). Thus,

$$\varrho_{aniso}(r_1) = \iiint_r \varrho^B_{iso}(r+r_1) \, . \, 8(\pi^3/\Delta B_x \Delta B_y \Delta B_z)^{\frac{1}{2}} \times \exp\left[-4\pi^2\left(\frac{x^2}{\Delta B_x} + \frac{y^2}{\Delta B_y} + \frac{z^2}{\Delta B_z}\right)\right] dx\,dy\,dz, \quad (3)$$

where ϱ^B_{iso} is the electron density corresponding to an atom which has isotropic temperature factor B, and the integration extends over the whole of real space. In this case the Gaussian distribution function represents only the difference between the anisotropic thermal motion and the assumed isotropic part; hence the distribution is concentrated near the centre of the atom, and a further simplification in the range of practical importance becomes justifiable. This is done by replacing the sharp Gaussian distribution

$$2(\pi/\Delta B_x)^{\frac{1}{2}} \exp\left[-4\pi^2 x^2/\Delta B_x\right]$$

by the two Dirac functions $\{\frac{1}{2}\delta(x+\sigma_x) + \frac{1}{2}\delta(x-\sigma_x)\}$, of half weight each, with their peaks symmetrically placed about the atom centre and at distances $\pm\sigma_x$ from it, where σ_x is the standard deviation of the distribution. Applying similar approximations along y and z we get

$$\varrho_{aniso}(r_1) = \iiint_r \left[\tfrac{1}{8}\varrho^B_{iso}(r+r_1)\right] \times \delta(x \pm \sigma_x)\delta(y \pm \sigma_y)\delta(z \pm \sigma_z)\,dx\,dy\,dz, \quad (4)$$

where $\sigma_x = [\Delta B_x/(8\pi^2)]^{\frac{1}{2}}$, ... etc. With the usual definition of δ, the convolution in equation (4) reduces to repetition of the isotropic distribution $\frac{1}{8}\varrho^B_{iso}(r)$ at the eight points $(\pm\sigma_x, \pm\sigma_y, \pm\sigma_z)$.

Taking the separation (Δx) equal to σ_x is good enough to a first degree of approximation, but in actual fact the value of Δx which should be chosen depends on the anisotropy parameter ΔB_x and the range of ξ where good fit between the two representations is most important. Also, since a scattering-factor curve having isotropic temperature factor B falls off fairly rapidly for increasing values of ξ, therefore good fit is most important in the range of small values of $\xi(\Delta B_x)^{\frac{1}{2}}$. By trial, we have found that within the practical range of observation and for average B values, the best fit between the correct and approximate representations of the anisotropy corresponds to a separation

$$\Delta x \simeq 0{\cdot}96\sigma_x \quad \text{or} \quad 0{\cdot}108(\Delta B_x)^{\frac{1}{2}}\ \text{Å}, \quad (5)$$

where ΔB_x is in Å^2, and similarly for the separations Δy and Δz.

Application of method to practical cases

In order to illustrate the accuracy of such a representation consider the two-dimensional case of an anisotropically vibrating atom with $B_y = B$, $B_x = B + \Delta B_x$. This atom is represented by two atoms of half weight each and isotropic thermal parameter B, placed symmetrically about the atom centre and distant $(\pm\Delta x, 0)$ from it, where Δx corresponds to ΔB_x as given by equation (5). The scattering from such a representation in the ξ direction in reciprocal space is given by

$$f_1(\xi) = f_0(\xi) \exp\left[-B\xi^2/4\right] \cos 2\pi\xi\Delta x, \quad (6)$$

whereas the correct factor is given by

$$f_2(\xi) = f_0(\xi) \exp\left[-B\xi^2/4\right] \exp\left[-\Delta B_x \xi^2/4\right]. \quad (7)$$

Thus the present method is equivalent to representing an exponential function by a cosine function for small values of the argument. The validity of this representation for all practical ranges is seen from Fig. 1 which gives the graphs of the two functions $\exp -\Delta B\xi^2/4$ and $\cos 2\pi\xi\Delta x$ against $(\xi(\Delta B_x)^{\frac{1}{2}})$. For the practical case with $\Delta B = 1$ Å^2 the discrepancy between the two representations within the Cu $K\alpha$ sphere of reflection (which corresponds to an outside

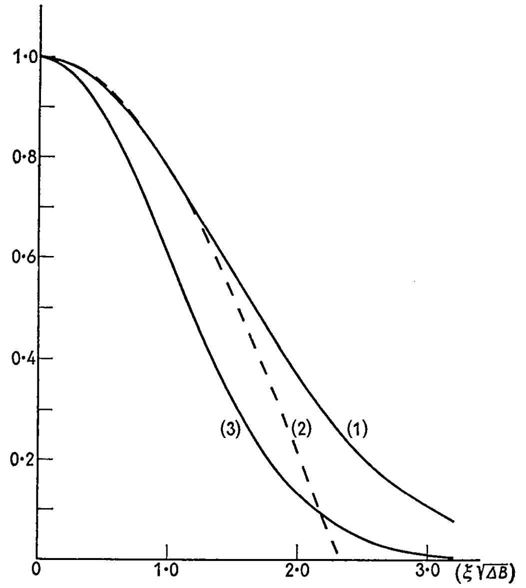

Fig. 1. Graphs of (1) the exact expression $\exp(-\Delta B_x \xi^2/4)$, (2) the δ-function approximation $\cos 2\pi\xi\Delta x$, (3) the expression $\exp(-2\Delta B_x \xi^2/4)$ for an assumed isotropic part of the temperature factor equal to twice the anisotropic component. All graphs are drawn against $\xi(\Delta B_x)^{\frac{1}{2}}$, where $\xi = 2 \sin \theta/\lambda$.

range of $\xi(\Delta B_x)^{\frac{1}{2}}=1\cdot3$) is better than 2%. Furthermore, the scattering of the atom is reduced primarily by the isotropic part of the thermal vibration. The fall due to an isotropic temperature factor which is double the anisotropic part ΔB_x is shown in curve (3) of Fig. 1. The combined factor to be applied to each $f_0(\xi)$ value for different ξ (or $2 \sin \theta/\lambda$) in the highly anisotropic case of $B=2$ Å^2 and $\Delta B=1$ Å^2 as calculated using expressions (6) and (7) are given in Fig. 2 as graphs (1) and (2) respectively. It is seen that the agreement between the two curves is very good throughout the region where the scattering is appreciable. Similarly good agreement can be obtained in other cases, say with $B=4$ Å^2 and $\Delta B=2$ Å^2 merely by changing the scale of Fig. 2. Further, it may be pointed out that anisotropies so high as to have $\Delta B=\frac{1}{2}B$ are rare and represent the largest value of the anisotropies usually encountered. In this case, the reason why a value of $\Delta x < \sigma_x$ gives a better overall fit between the functions $\cos 2\pi\xi\Delta x$ and $\exp(-\Delta B_x\xi^2/4)$ of equations (6) and (7) respectively, can be seen by considering their series expansions.

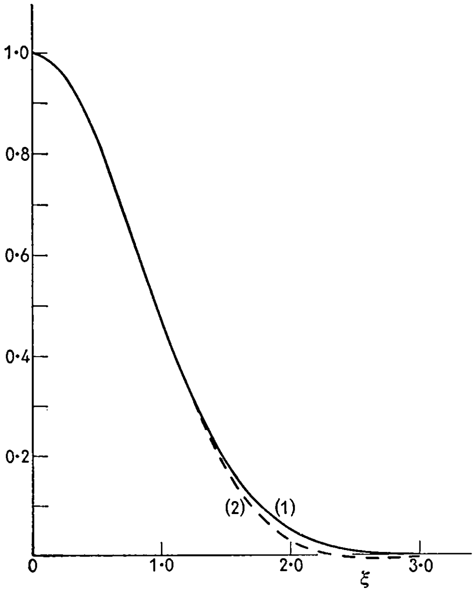

Fig. 2. Graphs of the combined functions corresponding to $B=2\cdot0$ Å^2 and $\Delta B=1\cdot0$ Å^2 as calculated (1) by the correct expression, (2) by the δ-function approximation for the anisotropic part, drawn against ξ.

Special cases

It is seen from equation (4) that in the general case, an atom having an anisotropic thermal vibration can be represented by a constellation of eight atoms of $\frac{1}{8}$ weight each at the eight points ($\pm\Delta x$, $\pm\Delta y$, $\pm\Delta z$), symmetrically placed about the centre of the atom. However, further simplification can always be obtained by choosing the isotropic temperature factor equal to the smallest of B_x, B_y, B_z, say $B=B_x$. In this case, only four atoms of $\frac{1}{4}$ weight each at (0, $\pm\Delta y$, $\pm\Delta z$) are required for representation of the anisotropic atom. Further simplification is possible in the case when the vibration tensor is an ellipsoid of revolution about the major axis, say z, so that $B_x=B_y<B_z$; and only two atoms of half weight each at (0, 0, $\pm\Delta z$) are enough for the representation. However, this last simplification cannot be applied in the case when the ellipsoid is obtained by revolution along the minor axis so that $B_x=B_y>B_z$, say, then since ΔB has to be positive the four-fold repetition is necessary to give a correct representation.

Thus, in the general case the anisotropically vibrating atom can be represented by four repetitions of isotropic atoms of $\frac{1}{4}$ weight each and this number is further reduced to two of $\frac{1}{2}$ weight each in the favourable case where the vibration ellipsoid is an ellipsoid of revolution obtained by rotation around the major axis.

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