maxima. This result is not surprising because low $l$ terms contribute a substantial portion of the whole Patterson function (after omitting the $l=0$ term) under the conditions of the test. However, as discussed in the article, these very low-$l$ terms can hinder the true solution from showing up. This is clearly shown in Fig. 8, where the terms $l=2,4$ were omitted from the calculations. It is worth noticing that the two omitted terms contributed 86% of the Patterson squared norm.

References


Measurability of Bijvoet Differences in Triclinic, Monoclinic and Orthorhombic Crystals. II

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Abstract

The probability that the Bijvoet ratio $X$ for the observed reflections of a given crystal is greater than any particular value $X_0$ depends on space-group symmetry, the number of anomalous scatterers per asymmetric unit and the parameters $k$ and $\sigma^2$. Numerical values for this probability are obtained as a function of $X_0$ for different values of $k$ and $\sigma^2$ for the triclinic, monoclinic and orthorhombic crystals containing $p$ ($=1,2,3$ or 4) anomalous scatterers per asymmetric unit. These results are provided in the form of compact tables; Fortran programs that are useful in computing this probability for any given situation are also provided.

1. Introduction

The success of the anomalous-scattering method of structure determination strongly depends on the measurability of Bijvoet differences. The measurability is defined as the probability of the event $\{(X \geq 0.1) \cap (y_{\text{min}} \geq 0.3)\}$ (Velurugan & Parthasarathy, 1984; VP, hereafter) where $X$ is the Bijvoet ratio and $y_{\text{min}}$ is the minimum value of the normalized structure-factor magnitudes for the reflection $H$ and the inverse reflection $\bar{H}$. Owing to the importance of the anomalous-scattering method, particularly due to the advent of synchrotron radiation as a source for diffraction studies, it would be useful to know a priori, in the case of a given crystal, the percentage of observed reflections for which the Bijvoet ratio $X$ would be greater than any specific value $X_0$, say. This information can be obtained from the probability value for the event $\{(X \geq X_0) \cap (y_{\text{min}} \geq 0.3)\}$ ($= D$, say) and we shall denote this probability by $M(X_0,0.3)$. The values of $M(X_0,0.3)$ for the particular case of $X_0=0.1$ were obtained in VP for the triclinic, monoclinic and orthorhombic crystals containing one or two heavy atoms per asymmetric unit for values of $k$ (i.e. the ratio of the imaginary to the total real part of the atomic scattering factor of the anomalous scatterer) up to 0.6. Under a pronounced anomalous-scattering effect, $k$ can have larger values for some of the heavy atoms. For example, the values

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2. Theoretical considerations

In this paper we shall follow the notation of VP. In particular, we shall use \( \sigma^2 \) to denote the fractional contribution to local mean intensity from the group of anomalous scatterers relative to the whole structure. We shall present the results corresponding to the non-centrosymmetric space-group categories 1, 3, 5 and 6 belonging to the triclinic, monoclinic and orthorhombic systems [see p. 59 of Lipson & Cohran (1966) for details of the space-group categories]. Since the theoretical expressions needed for the evaluation of \( M(X_0, 0.3) \) are available in VP, we shall give only the final expression needed for computing the numerical tables in this paper.

The theoretical expression for \( M(X_0, 0.3) \) in the case of a non-centrosymmetric crystal containing \( n \) atoms in the asymmetric unit of which \( p \) atoms are anomalous scatterers (of the same type) and the remaining \( q (= n - p) \) are normal scatterers of similar scattering power is known to be [see equation (42) of VP]

\[
M(X_0, 0.3) = Pr(D) = \int \cdots \int 2y_0 \exp (-y_0^2) \, d\tau \quad (1)
\]

where \( d\tau \) is a volume element in the \((3p+2)\)-dimensional Cartesian \((y_0, \psi_0, \theta_1', \phi_1', \psi_1', \ldots, \theta_p', \phi_p', \psi_p')\) space. Equation (1) is valid for the space-group categories 5 and 6. For crystals of space-group category 3, \( d\tau \) is the volume element in the \((2p+2)\)-dimensional \((y_0, \psi_0, \theta_1, \phi_1, \ldots, \theta_p, \phi_p)\) space. For crystals of space-group category 1, \( d\tau \) is the volume element in the \((p+2)\)-dimensional \((y_0, \psi_0, \theta_1, \ldots, \theta_p)\) space. Thus (1) involves \((p+2)\)-fold, \((2p+2)\)-fold, \((3p+2)\)-fold and \((3p+2)\)-fold integrals for the space-group categories 1, 3, 5 and 6 respectively. The theoretical expressions for \( X \) and \( y_{min} \) in terms of the random variables involved in (1) are given by [see equation (27) of VP]

\[
X = C_1E_py_0|\sin(2\pi\psi_0)|/[C_2E_p^2 + \sigma^2y_0^2]
+ C_3E_p\cos(2\pi\psi_0) \quad (2)
\]

\[
y_{min} = \{\min [a + b(\cos 2\pi\psi_0 + k \sin 2\pi\psi_0),
\quad a + b(\cos 2\pi\psi_0 - k \sin 2\pi\psi_0)]\}^{1/2} \quad (3)
\]

where \( a \) and \( b \) are defined to be

\[
a = C_4E_p^2/(\sigma p) + C_5y_0^2, \quad b = C_6E_py_0/(\sigma p)^{1/2}.
\]

The quantities \( C_n \), \( n = 1 \) to 6, depend on \( k, \sigma^2 \) and \( p \) and these are defined in equations (29) and (35) of VP. \( E_p \) is defined to be [see equation (22) of VP]

\[
E = \left\{ \sum_{j=1}^{p} \xi_{np}(\theta_j', \phi_j', \psi_j') \right\}^2 + \left[ \sum_{j=1}^{p} \eta_{np}(\theta_j', \phi_j', \psi_j') \right]^{1/2}. \quad (4)
\]

3. Discussion

The multiple integrals in (1) for the various space-group categories are to be computed by the Monte Carlo method for different values of \( X_0, p, k \) and \( \sigma^2 \). The results obtained for the space-group categories 1, 3, 5 and 6 corresponding to \( p = 1, 2, 3, 4 \) are given in Tables 1 to 16.* These tables contain the values of \( M(X_0, 0.3) \) corresponding to \( \sigma^2 = 0.02, 0.05, 0.10, 0.15, 0.20, 0.30, 0.40 \) and 0.50 and \( k = 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.40, 0.60, 0.80 \) and 0.90. Tables 1–4 are for space-group category 1 and pertain to the cases \( p = 1, 2, 3, 4 \) respectively. Tables 5–8 are for space-group category 3 and pertain to the cases \( p = 1, 2, 3, 4 \) respectively. Tables 9–12 are for space-group category 5 and pertain to the cases \( p = 1, 2, 3, 4 \) respectively. Tables 13–16 are for space-group category 6 and pertain to the cases \( p = 1, 2, 3, 4 \) respectively.

The variation of \( M(X_0, 0.3) \) as a function of \( X_0 \) is shown in Fig. 1 for the space-group category 5 corresponding to the following typical situation: \( p = 1, \sigma^2 = 0.10 \) and \( k = 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.40, 0.60, 0.80 \) and 0.90. The ordinate corresponding to \( X_0 = 0 \) for any curve represents the probability of the event \( \{X \geq 0\} \cap \{y_{min} \geq 0.3\} \) and this event is equivalent to the event \( \{y_{min} \geq 0.3\} \) (= \( D_0 \), say) since all the reflections satisfy the trivial condition that \( X \geq 0 \). Though the probability for the event \( D_0 \) is a

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* Tables 1 to 16 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43890 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
function of \( k \) and \( \sigma^2_0 \), it is found to be insensitive to changes in \( k \) and \( \sigma^2_0 \). For example, the values of \( P_r(D_0) \) (corresponding to \( k = 0.05 \)) are found to be 0.907 and 0.902 when \( \sigma^2_0 = 0.05 \) and 0.30 respectively and the values of \( P_r(D_0) \) (corresponding to \( \sigma^2_0 = 0.05 \)) are found to be 0.907 and 0.852 for \( k = 0.05 \) and 0.90 respectively. It is seen from Fig. 1 that the curves for \( M \) fall steeply to zero when \( k \) is small. For larger values of \( k \), the curves fall relatively slowly. Thus, while it is hardly possible to find any reflection having a Bijvoet ratio greater than 0.25 when \( k = 0.05 \), more than 61\% of reflections would have a Bijvoet ratio greater than 0.25 when \( k = 0.9 \). Curves for other values of \( k \), \( \sigma^2_0 \) and \( \rho \) and for other space-group categories exhibit similar trends and hence are not shown. Since \( M \) varies differently in the different regions of \( \sigma^2_0 \) and \( k \), values of \( M \) are given in Tables 1-16 at convenient unequal intervals of \( X_0 \).

In connection with the theoretical evaluation of \( M(X_0, 0.3) \) for any given \( X_0 \) for a particular crystal, the following points may be noted. Since \( M \) is a function of \( k \) and \( \sigma^2_0 \) and since these are, in turn, functions of \((\sin \theta)/\lambda\), it follows that \( M \) will also be a function of \((\sin \theta)/\lambda\). Hence it is necessary to obtain an average value of \( M \) (\( \langle M \rangle \), say) for the crystal. \( \langle M \rangle \) for a particular crystal can be obtained from the local values of \( M \) by giving weights proportional to the relative number of reflections in the various ranges of \((\sin \theta)/\lambda\). It can easily be shown that

\[
\langle M \rangle = \frac{3}{S_{\text{max}}^3} \int_0^{S_{\text{max}}} Ms^2 \, ds,
\]

where \( s \) stands for \((\sin \theta)/\lambda\) and \( S_{\text{max}} \) is the maximum value of \((\sin \theta)/\lambda\) for the data. The value of \( \langle M \rangle \) for any situation (i.e. for given crystal, radiation and data) is to be obtained by carrying out the integration in (5) numerically. The values of \( M \) needed for the numerical integration can be obtained from the appropriate table of values of \( M \) by interpolation. Reasonably good values of \( \langle M \rangle \) can be obtained by employing the following simpler procedure: (i) Obtain the mean values of \( k \) and \( \sigma^2_0 \) for the data. (ii) Use these mean values to compute the value of \( \langle M \rangle \) from the appropriate deposited table by a two-dimensional interpolation method (Abramowitz & Stegun, 1965). Fortran programs for calculating the value of \( \langle M(X_0, 0.3) \rangle \) corresponding to any fixed \( X_0 \) for a given crystal by this method are also available as deposited material.*

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* See deposition footnote.

References


