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The Estimation of Two-Phase and Three-Phase Invariants in *P*1 when Anomalous Scatterers are Present

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Abstract

The method of joint probability distributions is applied for the estimation of two-phase and three-phase invariants when anomalous scatterers are present. The conclusive formulae are von Mises functions and give expected values of the phases lying anywhere between 0 and 2π without ambiguity.

Symbols and notation

$\mathbf{h} = (h,k,l)$ vectorial index of a reflection

$f = f' + if''$ atomic scattering factor; f' is its real part and may include an anomalous real effect, f'' is its imaginary part, thermal factor is also included

N number of atoms in the unit cell

$F_{\mathbf{h}} = F'_{\mathbf{h}} + F''_{\mathbf{h}}$ structure factor with vectorial index **h**, where

$$F'_{\mathbf{h}} = \sum_{j=1}^{N} f'_j \exp 2\pi i\mathbf{h}\mathbf{r}_j$$

$$F''_{\mathbf{h}} = i\sum_{j=1}^{N} f''_j \exp 2\pi i\mathbf{h}\mathbf{r}_j$$

$E_{\mathbf{h}}$ normalized structure factor

$R_{\mathbf{h}}, \varphi_{\mathbf{h}}$ modulus and phase of $E_{\mathbf{h}}$

$G_{\mathbf{h}}, \psi_{\mathbf{h}}$ modulus and phase of $E_{-\mathbf{h}}$.

Other locally used symbols are defined in the text.

1. Introduction

Anomalous scattering effects occur because the atomic scattering factor is in general a complex number so that at a given wavelength a scattering component $F''_{\mathbf{h}}$ for $F_{\mathbf{h}}$ arises which has a phase advance over the $F'_{\mathbf{h}}$ component. Because of this phase difference the structure amplitudes $F_{\mathbf{h}}$ and $F_{-\mathbf{h}}$ of Friedel pairs of reflections are unequal for non-centrosymmetric crystals.

Anomalous dispersion methods are traditionally used: (i) to determine the absolute configuration of molecules and to resolve the well known twofold ambiguity in the phases determined by the single isomorphous replacement method (Bijvoet, 1949, 1951, 1954); (ii) to determine the position of the anomalous scatterers by a Patterson synthesis with $\{|F_{\mathbf{h}}| - |F_{-\mathbf{h}}|\}^2$ coefficients (Rossmann, 1961).

The advent of synchrotron radiation as a tunable source for X-ray diffraction experiments has opened new prospects for the methods of crystal structure determination, particularly for the X-ray analysis of proteins. Indeed, the tunability of synchrotron radiation allows the use of a wavelength for which the anomalous component of the scattering factor even for not-so-heavy atoms becomes rather large. In this way it is no longer necessary to introduce heavy atoms in the protein structure in order to secure non-negligible anomalous dispersion effects.

The joint probability distribution methods have already been applied by several authors to structure factors with complex scattering factors. Parthasarathy & Srinivasan (1964) derived the statistical distribution of the difference in intensity between Bijvoet pairs of reflections.

Kroon, Spek & Krabbendam (1977) successfully incorporated anomalous dispersion techniques into direct methods by means of a procedure which generalizes the classical method of phase determination from Bijvoet inequalities and involves the estimation of sine invariants. As in the classical case a twofold ambiguity (α, $\pi - \alpha$) persists in the estimates of the invariants and no probabilistic criterion was suggested for ranking the estimates in order of accuracy. In a subsequent paper Heinerman, Krabbendam, Kroon & Spek (1978) presented a statistical approach which leads to a joint probability of the phase $\varphi_{\rm I} = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\overline{\mathbf{h}+\mathbf{k}}}$ of a triple product and $\varphi_{\rm II} = \varphi_{-\mathbf{h}} + \varphi_{-\mathbf{k}} + \varphi_{\mathbf{h}+\mathbf{k}}$, the Friedel-related triple product. The new approach gives more accurate estimates of the sine invariants but is unable to overcome the twofold ambiguity (α, $\pi - \alpha$). Since their theory uses triple-product magnitudes and not the magnitudes of the individual structure factors, the authors suggested the

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use of the joint probability distribution function $P(E_{\mathbf{h}}, E_{-\mathbf{h}}, E_{\mathbf{k}}, E_{-\mathbf{k}}, E_{\mathbf{h+k}}, E_{\overline{\mathbf{h+k}}})$ in order to calculate more accurate values of the invariants. At the XIIth IUCr Congress in Ottawa, Hauptman (1981) presented some results arising from the study of the joint probability distribution $P(R_{\mathbf{h}}, G_{\mathbf{h}}, \varphi_{\mathbf{h}}, \psi_{\mathbf{h}})$. On the same occasion results were also presented concerning the study of the six-variate aforementioned joint probability distribution $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h+k}}, E_{-\mathbf{h}}, E_{-\mathbf{k}}, E_{-\mathbf{h-k}})$. Let us denote

$$R_1 = |E_{\mathbf{h}}|, \quad R_2 = |E_{\mathbf{k}}|, \quad R_3 = |E_{\mathbf{h+k}}|,$$
$$G_1 = |E_{-\mathbf{h}}|, \quad G_2 = |E_{-\mathbf{k}}|, \quad G_3 = |E_{-\mathbf{h-k}}|,$$
$$\varphi_1 = \varphi_{\mathbf{h}}, \quad \varphi_2 = \varphi_{\mathbf{k}}, \quad \varphi_3 = \varphi_{\mathbf{h+k}},$$
$$\psi_1 = \varphi_{-\mathbf{h}}, \quad \psi_2 = \varphi_{-\mathbf{k}}, \quad \psi_3 = \varphi_{-\mathbf{h-k}}.$$

The three-phase invariants

$$\Phi_1 = \psi_1 + \psi_2 + \varphi_3 \qquad \Phi_2 = \varphi_1 - \psi_2 - \varphi_3$$
$$\Phi_3 = \psi_1 - \varphi_2 + \varphi_3 \qquad \Phi_4 = \varphi_1 + \varphi_2 - \varphi_3$$
$$\Phi_5 = \psi_1 + \psi_2 - \psi_3 \qquad \Phi_6 = \varphi_1 - \psi_2 + \psi_3$$
$$\Phi_7 = \psi_1 - \varphi_2 - \psi_3 \qquad \Phi_8 = \varphi_1 + \varphi_2 + \psi_3$$

were estimates, given the six magnitudes R_1, R_2, R_3, G_1, G_2, G_3, *via* unimodal von Mises functions. According to Hauptman, the expected values of the invariants lie between 0 and 2π without ambiguity. This result was unexpected in view of the fact that with the classical method it is impossible to obtain an unambiguous result for the individual structure-factor phases.

Hauptman's preliminary account did not give rise to the supposition that his primitive random variables were in direct space. For, in a paper on the four-phase structure invariant in $P\bar{1}$ (Hauptman & Green, 1976), Hauptman still suggests (in polemic with the author of this paper) that using atomic coordinates as primitive random variables would lead to a distribution of structure factors less appropriate than that obtained when reciprocal vectors are considered as primitive random variables.

Owing to the controversial results obtained by Hauptman we started with statistical calculations on this problem. For the sake of brevity the mathematical techniques are not described in this paper: a detailed account of them may be found in a recent book (Giacovazzo, 1980).

In § 2 the joint probability distribution $P(R_{\mathbf{h}}, G_{\mathbf{h}}, \varphi_{\mathbf{h}}, \psi_{\mathbf{h}})$ and related distributions are calculated: a comparison with a result of Parthasarathy & Srinivasan (1964) is also given. We explicitly note that these authors were mostly interested in the distributions of the diffraction magnitudes and related quantities so they did not involve phases in their calculations. On the other hand, their theory is worked out for structures containing one, two and many anomalous scatterers (all assumed to be alike) in addition to a large number of non-anomalous scatterers. For the sake of simplicity, in our approach the number of anomalous scatterers is assumed to be large, even if of different type. Such a limitation should not be critical, and we expect that the application of our theoretical result may prove useful even in the cases in which one or few anomalous scatterers are present in the unit cell. Furthermore, our theory does not consider the case of structures with a large number of anomalous scatterers with a centric configuration, even if our results hold to a first approximation. Our conclusive formulas do not depend on the values of the overall isotropic thermal factor, which may be supposed unknown. Even if the formulas were explicitly derived in $P1$ they may be applied in any non-centrosymmetric space group provided none of the three reflections giving rise to the triplet is centrosymmetric.

In § 3, the six-variate joint probability distribution function has been derived. In § 4 the conclusive formulae estimating three-phase invariants are given. In § 5 estimations are made about the information provided by the *a priori* knowledge of the six magnitudes for the estimation of the triple invariants.

Two new efforts are encouraged by the present theory: (i) the study of suitable joint probability distributions for the estimation of three-phase invariants when two wavelengths are used for diffraction data collection. Such work is suggested by the advent of synchrotron radiation and the relative ease of performing two-wavelength experiments. The results could be useful for the structure determination of proteins on their own or as supports for geometrical two-wavelength techniques (Cascarano, Giacovazzo, Peerdeman & Kroon, 1982); (ii) a new formulation of the theory of representation of structure seminvariants and invariants (Giacovazzo, 1977) when different sets of diffraction data arising from the same or isomorphous crystals are available.

2. The joint probability distribution $P(R_{\mathbf{h}}, G_{\mathbf{h}}, \varphi_{\mathbf{h}}, \psi_{\mathbf{h}})$ and related distributions in $P1$

In order to give statistical meanings to some basic parameters frequently used in this and the following sections we first calculate the characteristic function $C(u_1, u_2, v_1, v_2)$ of the distribution $P(A_{\mathbf{h}}, A_{-\mathbf{h}}, B_{\mathbf{h}}, B_{-\mathbf{h}})$, where u_1, u_2, v_1, v_2 are carrying variables associated with $A_{\mathbf{h}}, A_{-\mathbf{h}}, B_{\mathbf{h}}, B_{-\mathbf{h}}$. $A_{\mathbf{h}}$ and $A_{-\mathbf{h}}$ are the real parts of $E_{\mathbf{h}}$ and $E_{-\mathbf{h}}$, respectively, $B_{\mathbf{h}}$ and $B_{-\mathbf{h}}$ are the imaginary parts.

We introduce the following notation:

$$\sum = \sum_{j=1}^{N} (f_j'^2 + f_j''^2),$$

the average value of $|F_{\mathbf{h}}|^2$ at a given $|\mathbf{h}|$,

$$c_1 = \sum_{j=1}^{N} (f_j'^2 - f_j''^2)/\Sigma,$$

$$c_2 = 2 \sum_{j=1}^{N} f_j' f_j''/\Sigma,$$

$$c = [1 - (c_1^2 + c_2^2)]^2.$$

After some calculations we obtain:

$$C(u_1, u_2, v_1, v_2) \simeq \exp\{-\tfrac{1}{4}(u_1^2 + u_2^2 + v_1^2 + v_2^2) - \tfrac{1}{2}c_1(u_1 u_2 - v_1 v_2) - \tfrac{1}{2}c_2(u_1 v_2 + u_2 v_1)\}. \quad (1)$$

The joint probability distribution $P(A_{\mathbf{h}}, A_{-\mathbf{h}}, B_{\mathbf{h}}, B_{-\mathbf{h}})$ is the Fourier transform of (1). If we make the variable changes

$$u_1' = u_1/\sqrt{2}, \quad u_2' = u_2/\sqrt{2},$$
$$v_1' = v_1/\sqrt{2}, \quad v_2' = v_2/\sqrt{2},$$
$$A_1' = \sqrt{2}A_1, \quad A_2' = \sqrt{2}A_2,$$
$$B_1' = \sqrt{2}B_1, \quad B_2' = \sqrt{2}B_2,$$

we obtain

$$P(A_{\mathbf{h}}', A'_{-\mathbf{h}}, B_{\mathbf{h}}', B'_{-\mathbf{h}}) \simeq \frac{1}{(2\pi)^2} \frac{1}{\sqrt{c}} \times \exp\left\{-\frac{1}{2\sqrt{c}}(A_1'^2 + A_2'^2 + B_1'^2 + B_2'^2 - 2c_1 A_1' A_2' + 2c_1 B_1' B_2' - 2c_2 A_1' B_2' - 2c_2 A_2' B_1')\right\}, \quad (2)$$

which is a four-dimensional normal distribution. c is the determinant of the matrix of second-order moments $\mathbf{c}$ given by

$$\mathbf{c} = \begin{vmatrix} 1 & c_1 & 0 & c_2 \\ c_1 & 1 & c_2 & 0 \\ 0 & c_2 & 1 & -c_1 \\ c_2 & 0 & -c_1 & 1 \end{vmatrix}.$$

We have thus defined the statistical meanings of c_1, c_2 and c which play a central role in the theory.

By suitable variable changes the more useful distribution

$$P(R_{\mathbf{h}}, G_{\mathbf{h}}, \varphi_{\mathbf{h}}, \psi_{\mathbf{h}}) \simeq \frac{1}{\pi^2} \frac{R_{\mathbf{h}} G_{\mathbf{h}}}{\sqrt{c}} \exp\left\{-\frac{R_{\mathbf{h}}^2 + G_{\mathbf{h}}^2}{\sqrt{c}} + 2\frac{R_{\mathbf{h}} G_{\mathbf{h}}}{\sqrt{c}}[c_1 \cos(\varphi_{\mathbf{h}} + \psi_{\mathbf{h}}) + c_2 \sin(\varphi_{\mathbf{h}} + \psi_{\mathbf{h}})]\right\} \quad (3)$$

is obtained. From (3) other relevant distributions may be obtained. For example:

(*a*) The conditional probability distribution function

$$P(\varphi_{\mathbf{h}}, \psi_{\mathbf{h}}|R_{\mathbf{h}}, G_{\mathbf{h}}) \simeq \frac{1}{4\pi^2 I_0(Q)} \exp\left\{\frac{2R_{\mathbf{h}} G_{\mathbf{h}}}{\sqrt{c}} \times [c_1 \cos(\varphi_{\mathbf{h}} + \psi_{\mathbf{h}}) + c_2 \sin(\varphi_{\mathbf{h}} + \psi_{\mathbf{h}})]\right\}, \quad (4)$$

where

$$Q = \frac{2R_{\mathbf{h}} G_{\mathbf{h}}}{\sqrt{c}} [c_1^2 + c_2^2]^{1/2}.$$

Denoting $\Phi = \varphi_{\mathbf{h}} + \psi_{\mathbf{h}}$, the more useful conditional probability distribution

$$P(\Phi|R_{\mathbf{h}}, G_{\mathbf{h}}) \simeq \frac{1}{2\pi I_0(Q)} \exp\{Q \cos(\Phi - q)\} \quad (5)$$

is readily derived, where

$$\cos q = \frac{c_1}{[c_1^2 + c_2^2]^{1/2}}, \quad \sin q = \frac{c_2}{[c_1^2 + c_2^2]^{1/2}}.$$

Equation (5) is a von Mises function. q is the most probable value of Φ: a large value of the parameter Q suggests that the phase relation $\Phi = q$ is reliable. If c_2 goes to zero (no anomalous scatterers) then c_1 goes to 1 and c to zero so that (5) correctly becomes a Dirac delta function with $q = 0$.

(*b*) The marginal probability density

$$P(R_{\mathbf{h}}, G_{\mathbf{h}}) \simeq \frac{4R_{\mathbf{h}} G_{\mathbf{h}}}{\sqrt{c}} \exp\left\{-\frac{R_{\mathbf{h}}^2 + G_{\mathbf{h}}^2}{\sqrt{c}}\right\} I_0(Q). \quad (6)$$

In terms of diffraction intensities the distribution (6) becomes

$$P(I_{\mathbf{h}}, J_{\mathbf{h}}) \simeq \frac{1}{\sqrt{c}} \exp\left\{-\frac{I_{\mathbf{h}} + J_{\mathbf{h}}}{\sqrt{c}}\right\} I_0(Q),$$

where $I_{\mathbf{h}} = R_{\mathbf{h}}^2$ and $J_{\mathbf{h}} = G_{\mathbf{h}}^2$. Then the probability density for $\Delta = |I_{\mathbf{h}} - J_{\mathbf{h}}|$ is readily obtained:

$$P(\Delta) = \frac{1}{c^{1/4}} \exp\left(-\frac{\Delta}{c^{1/4}}\right). \quad (7)$$

If we denote $\Delta_n = \Delta/c^{1/4}$, from (7) (8) follows:

$$P(\Delta_n) = \exp(-\Delta_n). \quad (8)$$

In the Appendix we show that (8) is identical to a previous result [Parthasarathy & Srinivasan, 1964, equation (23)].

3. The joint probability distribution function $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h}+\mathbf{k}}, E_{-\mathbf{h}}, E_{-\mathbf{k}}, E_{-\mathbf{h}-\mathbf{k}})$ in $P1$

We introduce the carrying variables $P_i, Q_i, p_i, q_i, i = 1, 2, 3$, associated with $R_i, G_i, \varphi_i, \psi_i, i = 1, 2, 3$, respectively. We calculate the characteristic function $C(R_i, G_i, \varphi_i, \psi_i, i = 1, 2, 3)$ retaining terms up to $1/\sqrt{N}$ order. Its Fourier transform gives the required joint probability distribution function

$$P(R_1, R_2, R_3, G_1, G_2, G_3, \varphi_1, \varphi_2, \varphi_3, \psi_1, \psi_2, \psi_3)$$

$$\simeq \frac{R_1 R_2 R_3 G_1 G_2 G_3}{(2\pi)^{12}} \int_0^\infty \cdots \int_0^\infty \int_0^{2\pi} \cdots \int_0^{2\pi} P_1 P_2 P_3$$

$$\times Q_1 Q_2 Q_3 \exp \Big\{ -i \sum_{i=1}^{3} [R_i P_i \cos(\varphi_i - p_i)$$

$$+ G_i Q_i \cos(\psi_i - q_i)] - \sum_{i=1}^{3} [\tfrac{1}{4}(P_i^2 + Q_i^2)$$

$$+ \tfrac{1}{2} c_{1i} P_i Q_i \cos(p_i + q_i)$$

$$+ \tfrac{1}{2} c_{2i} P_i Q_i \sin(p_i + q_i)]$$

$$- i[t_1 Q_1 Q_2 P_3 \cos(q_1 + q_2 + p_3)$$

$$+ b_1 Q_1 Q_2 P_3 \sin(q_1 + q_2 + p_3)$$

$$+ t_2 P_1 Q_2 P_3 \cos(p_1 - q_2 - p_3)$$

$$- b_2 P_1 Q_2 P_3 \sin(p_1 - q_2 - p_3)$$

$$+ t_3 Q_1 P_2 P_3 \cos(q_1 - p_2 + p_3)$$

$$+ b_3 Q_1 P_2 P_3 \sin(q_1 - p_2 + p_3)$$

$$+ t_4 P_1 P_2 P_3 \cos(p_1 + p_2 - p_3)$$

$$+ b_4 P_1 P_2 P_3 \sin(p_1 + p_2 - p_3)$$

$$+ t_4 Q_1 Q_2 Q_3 \cos(q_1 + q_2 - q_3)$$

$$+ b_4 Q_1 Q_2 Q_3 \sin(q_1 + q_2 - q_3)$$

$$+ t_3 P_1 Q_2 Q_3 \cos(p_1 - q_2 + q_3)$$

$$+ b_3 P_1 Q_2 Q_3 \sin(p_1 - q_2 + q_3)$$

$$+ t_2 Q_1 P_2 Q_3 \cos(q_1 - p_2 - q_3)$$

$$- b_2 Q_1 P_2 Q_3 \sin(q_1 - p_2 - q_3)$$

$$+ t_1 P_1 P_2 Q_3 \cos(p_1 + p_2 + q_3)$$

$$+ b_1 P_1 P_2 Q_3 \sin(p_1 + p_2 + q_3)] \Big\} \, dp_1 \, dp_2 \, dp_3$$

$$\times dq_1 \, dq_2 \, dq_3 \, dP_1 \, dP_2 \, dP_3 \, dQ_1 \, dQ_2 \, dQ_3,$$

where

$$c_{11} = \left[\sum_{j=1}^{N} f_j'^2(\mathbf{h}) - f_j''^2 \right] / \Sigma_1,$$

$$c_{12} = \left[\sum_{j=1}^{N} f_j'^2(\mathbf{k}) - f_j''^2 \right] / \Sigma_2,$$

$$c_{13} = \left[\sum_{j=1}^{N} f_j'^2(\mathbf{h}+\mathbf{k}) - f_j''^2 \right] / \Sigma_3,$$

$$c_{21} = 2 \left[\sum_{j=1}^{N} f_j'(\mathbf{h}) f_j'' \right] / \Sigma_1,$$

$$c_{22} = 2 \left[\sum_{j=1}^{N} f_j'(\mathbf{k}) f_j'' \right] / \Sigma_2,$$

$$c_{23} = 2 \left[\sum_{j=1}^{N} f_j'(\mathbf{h}+\mathbf{k}) f_j'' \right] / \Sigma_3,$$

$$\Sigma_1 = \sum_{j=1}^{N} [f_j'^2(\mathbf{h}) + f_j''^2],$$

$$\Sigma_2 = \sum_{j=1}^{N} [f_j'^2(\mathbf{k}) + f_j''^2],$$

$$\Sigma_3 = \sum_{j=1}^{N} [f_j'^2(\mathbf{h}+\mathbf{k}) + f_j''^2],$$

$$t_1 = \frac{1}{(\Sigma_1 \Sigma_2 \Sigma_3)^{1/2}} \sum_{j=1}^{N} \{ f_j'(\mathbf{h}) f_j'(\mathbf{k}) f_j'(\mathbf{h}+\mathbf{k}) - f_j''^2 [f_j'(\mathbf{h}) + f_j'(\mathbf{k}) + f_j'(\mathbf{h}+\mathbf{k})] \},$$

$$b_1 = \frac{1}{(\Sigma_1 \Sigma_2 \Sigma_3)^{1/2}} \sum_{j=1}^{N} \{ f_j'' [f_j'(\mathbf{h}) f_j'(\mathbf{k}) + f_j'(\mathbf{h}) f_j'(\mathbf{h}+\mathbf{k}) + f_j'(\mathbf{k}) f_j'(\mathbf{h}+\mathbf{k})] - f_j''^3 \},$$

$$t_2 = \frac{1}{(\Sigma_1 \Sigma_2 \Sigma_3)^{1/2}} \sum_{j=1}^{N} \{ f_j'(\mathbf{h}) f_j'(\mathbf{k}) f_j'(\mathbf{h}+\mathbf{k}) + f_j''^2 [-f_j'(\mathbf{h}) + f_j'(\mathbf{k}) + f_j'(\mathbf{h}+\mathbf{k})] \},$$

$$b_2 = \frac{1}{(\Sigma_1 \Sigma_2 \Sigma_3)^{1/2}} \sum_{j=1}^{N} \{ f_j'' [f_j'(\mathbf{h}) f_j'(\mathbf{k}) + f_j'(\mathbf{h}) f_j'(\mathbf{h}+\mathbf{k}) - f_j'(\mathbf{k}) f_j'(\mathbf{h}+\mathbf{k})] + f_j''^3 \},$$

$$t_3 = \frac{1}{(\Sigma_1 \Sigma_2 \Sigma_3)^{1/2}} \sum_{j=1}^{N} \{ f_j'(\mathbf{h}) f_j'(\mathbf{k}) f_j'(\mathbf{h}+\mathbf{k}) + f_j''^2 [f_j'(\mathbf{h}) - f_j'(\mathbf{k}) + f_j'(\mathbf{h}+\mathbf{k})] \},$$

$$b_3 = \frac{1}{(\Sigma_1 \Sigma_2 \Sigma_3)^{1/2}} \sum_{j=1}^{N} \{ f_j'' [f_j'(\mathbf{h}) f_j'(\mathbf{k}) - f_j'(\mathbf{h}) f_j'(\mathbf{h}+\mathbf{k}) + f_j'(\mathbf{k}) f_j'(\mathbf{h}+\mathbf{k})] + f_j''^3 \},$$

$$t_4 = \frac{1}{(\Sigma_1 \Sigma_2 \Sigma_3)^{1/2}} \sum_{j=1}^{N} \{ f_j'(\mathbf{h}) f_j'(\mathbf{k}) f_j'(\mathbf{h}+\mathbf{k}) + f_j''^2 [f_j'(\mathbf{h}) + f_j'(\mathbf{k}) - f_j'(\mathbf{h}+\mathbf{k})] \},$$

$$b_4 = \frac{1}{(\Sigma_1 \Sigma_2 \Sigma_3)^{1/2}} \sum_{j=1}^{N} \{ f_j'' [-f_j'(\mathbf{h}) f_j'(\mathbf{k}) + f_j'(\mathbf{h}) f_j'(\mathbf{h}+\mathbf{k}) + f_j'(\mathbf{k}) f_j'(\mathbf{h}+\mathbf{k})] + f_j''^3 \}.$$

The complicated definitions arise from the fact that we cannot assume an identical unitary scattering curve for the various atoms. After lengthy calculations we obtain the following joint probability density:

$$\begin{aligned}
P(R_1, R_2, R_3, G_1, G_2, G_3, \varphi_1, \varphi_2, \varphi_3, \psi_1, \psi_2, \psi_3) \\
\simeq \frac{1}{\pi^6} R_1 R_2 R_3 G_1 G_2 G_3 \frac{1}{(c_1 c_2 c_3)^{1/2}} \\
\times \exp\Bigg\{ \sum_{i=1}^{3} \frac{1}{\sqrt{c_i}} [-R_i^2 - G_i^2 \\
+ 2c_{1i} R_i G_i \cos(\varphi_i + \psi_i) \\
+ 2c_{2i} R_i G_i \sin(\varphi_i + \psi_i)] \\
+ T_1 G_1 G_2 R_3 \cos(\psi_1 + \psi_2 + \varphi_3) \\
+ B_1 G_1 G_2 R_3 \sin(\psi_1 + \psi_2 + \varphi_3) \\
+ T_2 R_1 G_2 R_3 \cos(\varphi_1 - \psi_2 - \varphi_3) \\
+ B_2 R_1 G_2 R_3 \sin(\varphi_1 - \psi_2 - \varphi_3) \\
+ T_3 G_1 R_2 R_3 \cos(\psi_1 - \varphi_2 + \varphi_3) \\
+ B_3 G_1 R_2 R_3 \sin(\psi_1 - \varphi_2 + \varphi_3) \\
+ T_4 R_1 R_2 R_3 \cos(\varphi_1 + \varphi_2 - \varphi_3) \\
+ B_4 R_1 R_2 R_3 \sin(\varphi_1 + \varphi_2 - \varphi_3) \\
+ T_4 G_1 G_2 G_3 \cos(\psi_1 + \psi_2 - \psi_3) \\
+ B_4 G_1 G_2 G_3 \sin(\psi_1 + \psi_2 - \psi_3) \\
+ T_3 R_1 G_2 G_3 \cos(\varphi_1 - \psi_2 + \psi_3) \\
+ B_3 R_1 G_2 G_3 \sin(\varphi_1 - \psi_2 + \psi_3) \\
+ T_2 G_1 R_2 G_3 \cos(\psi_1 - \varphi_2 - \psi_3) \\
+ B_2 G_1 R_2 G_3 \sin(\psi_1 - \varphi_2 - \psi_3) \\
+ T_1 R_1 R_2 G_3 \cos(\varphi_1 + \varphi_2 + \psi_3) \\
+ B_1 R_1 R_2 G_3 \sin(\varphi_1 + \varphi_2 + \psi_3) \Bigg\}, \qquad (9)
\end{aligned}$$

where

$$\begin{aligned}
c_i &= [1 - (c_{1i}^2 + c_{2i}^2)]^2, \quad i = 1, 2, 3, \\
T_1 &= 2(c_{13} S_2 - c_{23} S_4 - S_1)/\sqrt{c_3}, \\
T_2 &= 2(c_{13} S_6 + c_{23} S_8 - S_5)/\sqrt{c_3}, \\
T_3 &= 2(c_{13} S_5 - c_{23} S_7 - S_6)/\sqrt{c_3}, \\
T_4 &= 2(c_{13} S_1 + c_{23} S_3 - S_2)/\sqrt{c_3}, \\
B_1 &= 2(c_{13} S_4 + c_{23} S_2 - S_3)/\sqrt{c_3}, \\
B_2 &= 2(c_{13} S_8 - c_{23} S_6 - S_7)/\sqrt{c_3}, \\
B_3 &= 2(c_{13} S_7 + c_{23} S_5 - S_8)/\sqrt{c_3}, \\
B_4 &= 2(c_{13} S_3 - c_{23} S_1 - S_4)/\sqrt{c_3}. \\
S_1 &= (-Z_2 + c_{12} Z_3 - c_{22} Z_7)/\sqrt{c_2}, \\
S_2 &= (-Z_1 + c_{12} Z_4 - c_{22} Z_8)/\sqrt{c_2}, \\
S_3 &= (-Z_6 + c_{12} Z_7 + c_{22} Z_3)/\sqrt{c_2}, \\
S_4 &= (-Z_5 + c_{12} Z_8 + c_{22} Z_4)/\sqrt{c_2}, \\
S_5 &= (-Z_4 + c_{12} Z_1 + c_{22} Z_5)/\sqrt{c_2}, \\
S_6 &= (-Z_3 + c_{12} Z_2 + c_{22} Z_6)/\sqrt{c_2}, \\
S_7 &= (-Z_8 + c_{12} Z_5 - c_{22} Z_1)/\sqrt{c_2}, \\
S_8 &= (-Z_7 + c_{12} Z_6 - c_{22} Z_2)/\sqrt{c_2},
\end{aligned}$$

and

$$\begin{aligned}
Z_1 &= (t_4 - c_{11} t_3 - c_{21} b_3)/\sqrt{c_1}, \\
Z_2 &= (t_1 - c_{11} t_2 + c_{21} b_2)/\sqrt{c_1}, \\
Z_3 &= (t_3 - c_{11} t_4 - c_{21} b_4)/\sqrt{c_1}, \\
Z_4 &= (t_2 - c_{11} t_1 - c_{21} b_1)/\sqrt{c_1}, \\
Z_5 &= (b_4 + c_{11} b_3 - c_{21} t_3)/\sqrt{c_1}, \\
Z_6 &= (b_1 - c_{11} b_2 - c_{21} t_2)/\sqrt{c_1}, \\
Z_7 &= (b_3 + c_{11} b_4 - c_{21} t_4)/\sqrt{c_1}, \\
Z_8 &= (-b_2 + c_{11} b_1 - c_{21} t_1)/\sqrt{c_1}.
\end{aligned}$$

From (9) the conditional probability distribution (10) is obtained by application of standard techniques:

$$\begin{aligned}
P(\varphi_1, \varphi_2, \varphi_3, \psi_1, \psi_2, \psi_3 | R_i, G_i, i = 1, 2, 3) \\
\simeq \frac{1}{L} \exp\Bigg\{ \sum_{i=1}^{3} [R_i G_i A_{0i} \cos(\varphi_i + \psi_i - \xi_{0i})] \\
+ G_1 G_2 R_3 A_1 \cos(\psi_1 + \psi_2 + \varphi_3 - \xi_1) \\
+ R_1 G_2 R_3 A_2 \cos(\varphi_1 - \psi_2 - \varphi_3 - \xi_2) \\
+ G_1 R_2 R_3 A_3 \cos(\psi_1 - \varphi_2 + \varphi_3 - \xi_3) \\
+ R_1 R_2 R_3 A_4 \cos(\varphi_1 + \varphi_2 - \varphi_3 - \xi_4) \\
+ G_1 G_2 G_3 A_4 \cos(\psi_1 + \psi_2 - \psi_3 - \xi_4) \\
+ R_1 G_2 G_3 A_3 \cos(\varphi_1 - \psi_2 + \psi_3 - \xi_3) \\
+ G_1 R_2 G_3 A_2 \cos(\psi_1 - \varphi_2 - \psi_3 - \xi_2) \\
+ R_1 R_2 G_3 A_1 \cos(\varphi_1 + \varphi_2 + \psi_3 - \xi_1) \Bigg\}, \qquad (10)
\end{aligned}$$

where L is a constant whose value is not critical for our purposes,

$$A_{0i} = 2\left(\frac{c_{1i}^2 + c_{2i}^2}{c_i}\right)^{1/2}, \quad \cos \xi_{0i} = \frac{c_{1i}}{(c_{1i}^2 + c_{2i}^2)^{1/2}},$$

$$\sin \xi_{0i} = \frac{c_{2i}}{(c_{1i}^2 + c_{2i}^2)^{1/2}}, \quad i = 1, 2, 3;$$

$$A_i = (T_i^2 + B_i^2)^{1/2}, \quad \cos \xi_i = T_i/(T_i^2 + B_i^2)^{1/2},$$

$$\sin \xi_i = B_i/(T_i^2 + B_i^2)^{1/2}, \quad i = 1, 2, 3, 4.$$

It may be noted that A_{0i} are terms of order $1/(N)^0$, while the other terms, A_i, are of order $1/\sqrt{N}$ (however, the A_i's may have large moduli).

4. Some useful conditional probability distributions

For practical applications it is useful to know the conditional probability distributions of the various Φ_i given the six magnitudes $R_1, R_2, R_3, G_1, G_2, G_3$. Some probabilistic considerations will be made for the conditional probability $P(\Phi_1|R_i, G_i,\ i=1,2,3)$ which are also valid for the other distributions $P(\Phi_j|R_i, G_i,\ i=1,2,3)$.

We will use in this section the function $D(x) = I_1(x)/I_0(x)$, where I_0 and I_1 are the modified Bessel functions of order zero and one, respectively, according to the following notation:

$$D_1 = D(A_{01}R_1G_1),\quad D_2 = D(A_{02}R_2G_2),$$
$$D_3 = D(A_{03}R_3G_3).$$

(*a*) *The conditional probability* $P(\Phi_1|R_i, G_i, i=1,2,3)$

We obtain

$$P(\Phi_1|\ldots) \simeq \frac{1}{2\pi I_0(\Omega_1)}\exp[\Omega_1\cos(\Phi_1-\omega_1)],$$

where $\Omega_1 = [\theta_1^2 + \gamma_1^2]^{1/2}$,

$$\begin{aligned}\theta_1 = [&G_1G_2R_3A_1\cos\xi_1 + R_1G_2R_3A_2D_1\cos(\xi_2-\xi_{01})\\ &+ G_1R_2R_3A_3D_2\cos(\xi_3+\xi_{02})\\ &+ G_1G_2G_3A_4D_3\cos(\xi_4+\xi_{03})\\ &+ R_1R_2R_3A_4D_1D_2\cos(\xi_4-\xi_{01}-\xi_{02})\\ &+ R_1G_2G_3A_3D_1D_3\cos(\xi_3-\xi_{01}-\xi_{03})\\ &+ G_1R_2G_3A_2D_2D_3\cos(\xi_2+\xi_{02}+\xi_{03})\\ &+ R_1R_2G_3A_1D_1D_2D_3\\ &\times\cos(\xi_1-\xi_{01}-\xi_{02}-\xi_{03})],\end{aligned}$$

$$\begin{aligned}\gamma_1 = [&G_1G_2R_3A_1\sin\xi_1 - R_1G_2R_3A_2D_1\sin(\xi_2-\xi_{01})\\ &+ G_1R_2R_3A_3D_2\sin(\xi_3+\xi_{02})\\ &+ G_1G_2G_3A_4D_3\sin(\xi_4+\xi_{03})\\ &- R_1R_2R_3A_4D_1D_2\sin(\xi_4-\xi_{01}-\xi_{02})\\ &- R_1G_2G_3A_3D_1D_3\sin(\xi_3-\xi_{01}-\xi_{03})\\ &+ G_1R_2G_3A_2D_2D_3\sin(\xi_2+\xi_{02}+\xi_{03})\\ &- R_1R_2G_3A_1D_1D_2D_3\\ &\times\sin(\xi_1-\xi_{01}-\xi_{02}-\xi_{03})],\end{aligned}$$

$$\cos\omega_1 = \theta_1/\Omega_1,\quad \sin\omega_1 = \gamma_1/\Omega_1.$$

ω_1, the expected value of Φ_1, may lie anywhere between 0 and 2π. The reliability of the phase indication $\Phi_1 = \omega_1$ may be very high even for large structures because it depends on eight contributions all of order $1/\sqrt{N}$.

(*b*) *The conditional probability* $P(\Phi_4|R_i, G_i, i=1,2,3)$*

We obtain

$$P(\Phi_4|\ldots) \simeq \frac{1}{2\pi I_0(\Omega_4)}\exp[\Omega_4\cos(\Phi_4-\omega_4)],$$

where $\Omega_4 = [\theta_4^2 + \gamma_4^2]^{1/2}$,

$$\begin{aligned}\theta_4 = [&R_1R_2R_3A_4\cos\xi_4 + G_1R_2R_3A_3D_1\cos(\xi_3-\xi_{01})\\ &+ R_1G_2R_3A_2D_2\cos(\xi_2+\xi_{02})\\ &+ R_1R_2G_3A_1D_3\cos(\xi_1-\xi_{03})\\ &+ R_1G_2G_3A_3D_2D_3\cos(\xi_3+\xi_{02}-\xi_{03})\\ &+ G_1R_2G_3A_2D_1D_3\cos(\xi_2-\xi_{01}+\xi_{03})\\ &+ G_1G_2R_3A_1D_1D_2\cos(\xi_1-\xi_{01}-\xi_{02})\\ &+ G_1G_2G_3A_4D_1D_2D_3\\ &\times\cos(\xi_4-\xi_{01}-\xi_{02}+\xi_{03})],\end{aligned}$$

$$\begin{aligned}\gamma_4 = [&R_1R_2R_3A_4\sin\xi_4 - G_1R_2R_3A_3D_1\sin(\xi_3-\xi_{01})\\ &+ R_1G_2R_3A_2D_2\sin(\xi_2+\xi_{02})\\ &+ R_1R_2G_3A_1D_3\sin(\xi_1-\xi_{03})\\ &+ R_1G_2G_3A_3D_2D_3\sin(\xi_3+\xi_{02}-\xi_{03})\\ &- G_1R_2G_3A_2D_1D_3\sin(\xi_2-\xi_{01}+\xi_{03})\\ &- G_1G_2R_3A_1D_1D_2\sin(\xi_1-\xi_{01}-\xi_{02})\\ &- G_1G_2G_3A_4D_1D_2D_3\\ &\times\sin(\xi_4-\xi_{01}-\xi_{02}+\xi_{03})],\end{aligned}$$

$$\cos\omega_4 = \theta_4/\Omega_4,\quad \sin\omega_4 = \gamma_4/\Omega_4.$$

(*c*) *The conditional probability* $P(\varphi_i|\ldots)$ *or* $P(\psi_i|\ldots)$

In the usual applications of direct methods a phase $\varphi_{\mathbf{h}}$ is assigned when at least one pair of phases $\varphi_{\mathbf{k}}$ and $\varphi_{\mathbf{h}+\mathbf{k}}$ and three moduli are *a priori* known. The theory developed in this paper suggests that a larger variety of *a priori* information may be conceived. Some examples are described below in order to show how different may be the conclusive formulae in different situations. For the sake of simplicity, in the examples we constantly assume that the six magnitudes are *a priori* known.

Let us suppose that φ_2 and φ_3 are known but ψ_1, ψ_2, ψ_3 are unknown. Then φ_1 may be assigned by means of the von Mises distribution

* The other conditional probability distribution equations $P(\Phi_j|R_i, G_i, i=1,2,3)$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38435 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$$P(\varphi_1|\ldots) \simeq \frac{1}{2\pi I_0(\Omega_4)} \exp\{\Omega_4 \cos(\varphi_1 - \tau_1 - \omega_4)\} \quad (11)$$

where $\tau_1 = -\varphi_2 + \varphi_3$. Ω_4 and ω_4 are defined below. A different formula must be applied for the estimation of φ_1, when φ_2, φ_3, ψ_1, ψ_2, ψ_3 are all *a priori* known. We obtain

$$P(\varphi_1|\ldots) \simeq \frac{1}{2\pi I_0(\Omega_4')} \exp\{\Omega_4' \cos(\varphi_1 - \omega_4')\} \quad (12)$$

where $\Omega_4' = [\theta_4'^2 + \gamma_4'^2]^{1/2}$,

$$\begin{aligned}\theta_4' = [&R_1 G_1 A_{01} \cos(\psi_1 - \xi_{01}) \\ &+ R_1 G_2 R_3 A_2 \cos(\psi_2 + \varphi_3 + \xi_2) \\ &+ R_1 R_2 R_3 A_4 \cos(\varphi_2 - \varphi_3 - \xi_4) \\ &+ R_1 G_2 G_3 A_3 \cos(\psi_2 - \psi_3 + \xi_3) \\ &+ R_1 R_2 G_3 A_1 \cos(\varphi_2 + \psi_3 - \xi_1)],\end{aligned}$$

$$\begin{aligned}\gamma_4' = [&-R_1 G_1 A_{01} \sin(\psi_1 - \xi_{01}) \\ &+ R_1 G_2 R_3 A_2 \sin(\psi_2 + \varphi_3 + \xi_2) \\ &- R_1 R_2 R_3 A_4 \sin(\varphi_2 - \varphi_3 - \xi_4) \\ &+ R_1 G_2 G_3 A_3 \sin(\psi_2 - \psi_3 + \xi_3) \\ &- R_1 R_2 G_3 A_1 \sin(\varphi_2 + \psi_3 - \xi_1)],\end{aligned}$$

$$\cos \omega_4' = \theta_4'/\Omega_4', \quad \sin \omega_4' = \gamma_4'/\Omega_4'.$$

As a final example we suppose that φ_2, φ_3, ψ_2, ψ_3 are known *a priori* and ψ_1 is unknown. Then φ_1 may be estimated *via* the von Mises distribution

$$P(\varphi_1|\ldots) \simeq \frac{1}{2\pi I_0(\Omega_4'')} \exp\{\Omega_4'' \cos(\varphi_1 - \omega_4'')\}, \quad (13)$$

where $\Omega_4'' = [\theta_4''^2 + \gamma_4''^2]^{1/2}$,

$$\begin{aligned}\theta_4'' = [&G_1 G_2 R_3 A_1 D_1 \cos(\psi_2 + \varphi_3 - \xi_1 + \xi_{01}) \\ &+ R_1 G_2 R_3 A_2 \cos(\psi_2 + \varphi_3 + \xi_2) \\ &+ G_1 R_2 R_3 A_3 D_1 \cos(\varphi_2 - \varphi_3 + \xi_3 - \xi_{01}) \\ &+ R_1 R_2 R_3 A_4 \cos(\varphi_2 - \varphi_3 - \xi_4) \\ &+ G_1 G_2 G_3 A_4 D_1 \cos(\psi_2 - \psi_3 - \xi_4 + \xi_{01}) \\ &+ R_1 G_2 G_3 A_3 \cos(\psi_2 - \psi_3 + \xi_3) \\ &+ G_1 R_2 G_3 A_2 D_1 \cos(\varphi_2 + \psi_3 + \xi_2 - \xi_{01}) \\ &+ R_1 R_2 G_3 A_1 \cos(\varphi_2 + \psi_3 - \xi_1)],\end{aligned}$$

$$\begin{aligned}\gamma_4'' = [&G_1 G_2 R_3 A_1 D_1 \sin(\psi_2 + \varphi_3 - \xi_1 + \xi_{01}) \\ &+ R_1 G_2 R_3 A_2 \sin(\psi_2 + \varphi_3 + \xi_2) \\ &- G_1 R_2 R_3 A_3 D_1 \sin(\varphi_2 - \varphi_3 + \xi_3 - \xi_{01}) \\ &- R_1 R_2 R_3 A_4 \sin(\varphi_2 - \varphi_3 - \xi_4) \\ &+ G_1 G_2 G_3 A_4 D_1 \sin(\psi_2 - \psi_3 - \xi_4 - \xi_{01}) \\ &+ R_1 G_2 G_3 A_3 \sin(\psi_2 - \psi_3 + \xi_3) \\ &- G_1 R_2 G_3 A_2 D_1 \sin(\varphi_2 + \psi_3 + \xi_2 - \xi_{01}) \\ &- R_1 R_2 G_3 A_1 \sin(\varphi_2 + \psi_3 - \xi_1)],\end{aligned}$$

$$\cos \omega_4'' = \theta_4''/\Omega_4'', \quad \sin \omega_4'' = \gamma_4''/\Omega_4''.$$

Equations (11), (12) and (13) are very different from one another. Indeed, Φ_4' contains a term of order $1/(N)^0$ and four terms of order $1/\sqrt{N}$, while Ω_4 and Ω_4'' ($\Omega_4 \neq \Omega_4''$) contain only terms of order $1/\sqrt{N}$. Other examples may be easily conceived. It is clear now that different amounts of *a priori* information produce different probabilistic formulae which, in their turn, may be readily obtained by standard techniques *via* the distribution (10).

5. Conclusive remarks

While this paper was under examination by the referees the paper by Hauptman (1982) on the same subject appeared in *Acta Cryst.* A comparison between the two papers is mandatory.

The following may be observed:

(*a*) In spite of the quite different notation, the conclusive formulae coincide. That is not surprising: indeed this time Hauptman preferred to use, according to our habit, the atomic positions as the primitive random variables. Two incongruities (probably clerical errors) were found in Hauptman's paper: (1) on p. 636, where γ_3 is defined, the line

$$C_{HK\bar{L}}[1 - (C_H C_K C_L - C_H S_K S_L$$

should be replaced by

$$C_{HK\bar{L}}[1 - (C_H C_K C_L + C_H S_K S_L;$$

(2) on p. 637, where $C_{\bar{2}}$ is defined, the line

$$+ \xi_3 + \zeta_2) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \cos \zeta_2]$$

should be replaced by

$$+ \xi_3 + \zeta_2) + R_{\bar{1}} R_2 R_{\bar{3}} \cos \zeta_2].$$

(*b*) The conclusive formulae estimating triplet invariants are unimodal and are not in complete agreement with some probabilistic results by Heinerman *et al.* (1978). We cannot conclude that those results are wrong because in our approach, as in Heinerman *et al.*'s approach, a number of approximations were introduced which may be responsible for the disagreement. For example, a critical point in our mathematical approach (as well as in Hauptman's procedure) is the passage from (10) to the various conditional probability distributions $P(\Phi_j|R_i, G_i, i = 1, 2, 3)$. We had to integrate exponential expressions containing a term of order N^0 and several terms of order $N^{-1/2}$. In order to obtain simple final distributions we approximated the terms of order $N^{-1/2}$ by the formula $e^x \simeq 1 + x$ without considering the fact that, when anomalous dispersion is present, terms of order $N^{-1/2}$ may be numerically equivalent to the N^0-order terms. The final formulae estimating Φ_j were von Mises distributions but it is very likely that the true distributions are not of von Mises type.

(*c*) Hauptman's and our procedure estimate triplet invariants *via* the joint probability distribution of six structure factors. In principle the approach is more general than Heinerman *et al.*'s (1978) procedure, which only involves triple-product magnitudes. On the other hand, with respect to the classical algebraic methods, it is able to exploit the positivity of the electron density. This property probably helps to overcome the (α, $\pi - \alpha$) ambiguity, at least from a formal point of view. New efforts in the field will probably lead to more efficient formulae.

(*d*) Using the presumed known coordinates of the ferrodoxin from *Peptococcus aerogenes* (Adman, Sieker & Jensen, 1973), which crystallizes in $P2_12_12_1$ with $M_r \simeq 6000$, we calculated 3328 structure factors up to 2 Å resolution. The eight iron atoms in the molecule were assumed to be anomalous scatterers with $f' = -1{\cdot}18$ and $f'' = 3{\cdot}20$. Our results suggest the following considerations: (1) for a given triplet the Ω_i's, $i = 1, \ldots, 8$, are slightly different from one another. For example, for the case $R_{\mathbf{h}}, G_{\mathbf{h}} = 2{\cdot}44, 2{\cdot}81$, $R_{\mathbf{k}}, G_{\mathbf{k}} = 2{\cdot}33, 2{\cdot}42$, $R_{\mathbf{h+k}}, G_{\mathbf{h+k}} = 1{\cdot}65, 2{\cdot}00$, $\Omega_i = 2{\cdot}22$ always for $i = 1, 2, \ldots, 8$. This is mainly because $D_i \simeq 1$ always, $i = 1, 2, 3$. Thus all the Φ_i's corresponding to a given triplet are estimated with about the same reliability. Such behaviour may mainly be due to the reason discussed in (*b*); (2) the Φ's can in principle be estimated everywhere between 0 and 2π, but the majority are actually estimated around 2π. That may be because $\langle |I_{\mathbf{h}} - \mathscr{I}_{\mathbf{h}}|/(I_h + \mathscr{I}_h)\rangle$ is small (Parthasarathy, 1967) when many identical anomalous scatterers are present. This situation favours estimates of the Φ_i's around 2π;* (3) the accuracy with which triplet phases are appraised is overestimated (see also Table 2 in Hauptman's paper). This may depend on the numerical approximations discussed in (*b*). Hauptman's results seem more accurate than ours, but all his calculations are carried out with double precision (approximately 15 significant digits) and error-free diffraction data. Our calculations were made by rescaling error-free diffraction data by a standard k curve. Our opinion is that the efficiency of the formulae is remarkably influenced by the scaling and normalization procedures of the diffraction data.

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* Even when the triple phases are far from 2π.

APPENDIX

Parthasarathy & Srinivasan (1964) denote by $P \gg 1$ the number of anomalous scatterers of the same type in the unit cell, and by Q the number of non-anomalous scatterers. Following their notation we write

$$\sigma_P^2 = \sum_{j=1}^{P} f'^2_{Pj}, \quad \sigma_Q^2 = \sum_{j=1}^{Q} f^2_{Qj}, \quad k'' = f_P''/f_P',$$

where k'' depends on $|\mathbf{h}|$.

Our c_1, c_2 and c are defined as

$$c_1 = \frac{\sigma_P^2 + \sigma_Q^2 - k''^2\sigma_P^2}{\sigma_P^2 + \sigma_Q^2 + k''^2\sigma_P^2},$$

$$c_2 = \frac{2k''\sigma_P^2}{\sigma_P^2 + \sigma_Q^2 + k''^2\sigma_P^2},$$

$$\sqrt{c} = \frac{4k''^2\sigma_P^2\sigma_Q^2}{(\sigma_P^2 + \sigma_Q^2 + k''^2\sigma_P^2)^2}.$$

Parthasarathy & Srinivasan obtain, for

$$x = \frac{||F_{\mathbf{h}}|^2 - |F_{-\mathbf{h}}|^2|}{4k''\sigma_P\sigma_Q},$$

the following distribution:

$$P(x) = 2\exp(-2x). \qquad (A1)$$

Since $\Delta_n = 2x$ our distribution (8) coincides with ($A1$).

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