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The Probabilistic Estimation of Triplet Invariants: the Formula P_{13}

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Abstract

The second representation of a triplet invariant [Giacovazzo (1977). *Acta Cryst.* A33, 933–944] is a collection of special quintets. In the present paper, the triplet is embedded in many more additional quintets obtained in a special way by symmetry operations on the indices of the structure factors. The method of joint probability distribution functions has been used to derive a formula for estimating triplets *via* the information contained in the basis and in the cross terms of the quintet invariants. The P_{10} formula [Cascarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori (1984). *Acta Cryst.* A40, 278–283] is a special case of the new formula, here called P_{13}. The new expression has been applied to practical cases.

Symbols and abbreviations

$C \equiv (\mathbf{R},\mathbf{T})$ — Symmetry operator. $\mathbf{R}$ is the rotation component, $\mathbf{T}$ is the translation component.

$E_{\mathbf{h}} = |R_{\mathbf{h}}| \exp(i\varphi_{\mathbf{h}})$ — Normalized structure factor.

$\varepsilon_{\mathbf{h}} = R_{\mathbf{h}}^2 - 1$

$\Phi_3 = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3}$ — With $\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = 0$.

m — Number of symmetry operators.

N — Number of atoms in the primitive unit cell.

$D_1(x) = I_1(x)/I_0(x)$ — Ratio of the two modified Bessel functions of order 1 and 0, respectively.

Introduction

In accordance with Giacovazzo (1977), the second representation $\{\psi\}_2$ of the triplet phase invariant Φ_3 is the collection of special quintets

$$\psi_2 = \Phi_3 + \varphi_{\mathbf{kR}_i} - \varphi_{\mathbf{kR}_j}, \quad i = 1,....,m, \qquad (1)$$

where $\mathbf{k}$ is a free vector in reciprocal space. The collection of the basis and cross magnitudes of the various quintets ψ_2 is called the second phasing shell of Φ_3:

$$\{B\}_2 = \{R_{\mathbf{h}_1}, R_{\mathbf{h}_2}, R_{\mathbf{h}_3}, R_{\mathbf{k}}, R_{\mathbf{h}_1 \pm \mathbf{kR}_i}, R_{\mathbf{h}_2 \pm \mathbf{kR}_i}, R_{\mathbf{h}_3 \pm \mathbf{kR}_i}\},$$

$$i = 1,...,m.$$

A formula was derived (Cascarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori, 1984) that can be used to estimate Φ_3 given the moduli in $\{B\}_2$:

$$P(\Phi_3|\{B\}_2) \simeq [2\pi I_0(G)]^{-1} \exp(G \cos \Phi_3),$$

where

$$G = C(1 + Q)$$

$$C = 2R_{h_1}R_{h_2}R_{h_3}/N^{1/2}$$

$$Q = \sum_k \left[\frac{\sum_{i=1}^{m}{}' A_{k,i}/N}{1 + (\varepsilon_{h_1}\varepsilon_{h_2}\varepsilon_{h_3} + \sum_{i=1}^{m}{}' B_{k,i})/2N} \right]$$

$$A_{k,i} = \varepsilon_k[\varepsilon_{h_1 + kR_i}(\varepsilon_{h_2 - kR_i} + \varepsilon_{h_3 - kR_i})$$
$$+ \varepsilon_{h_2 + kR_i}(\varepsilon_{h_1 - kR_i} + \varepsilon_{h_3 - kR_i})$$
$$+ \varepsilon_{h_3 + kR_i}(\varepsilon_{h_1 - kR_i} + \varepsilon_{h_2 - kR_i})]$$

$$B_{k,i} = \varepsilon_{h_1}[\varepsilon_k(\varepsilon_{h_1 + kR_i} + \varepsilon_{h_1 - kR_i})$$
$$+ \varepsilon_{h_2 + kR_i}\varepsilon_{h_3 - kR_i} + \varepsilon_{h_2 - kR_i}\varepsilon_{h_3 + kR_i}]$$
$$+ \varepsilon_{h_2}[\varepsilon_k(\varepsilon_{h_2 + kR_i} + \varepsilon_{h_2 - kR_i})$$
$$+ \varepsilon_{h_1 + kR_i}\varepsilon_{h_3 - kR_i} + \varepsilon_{h_1 - kR_i}\varepsilon_{h_3 + kR_i}]$$
$$+ \varepsilon_{h_3}[\varepsilon_k(\varepsilon_{h_3 + kR_i} + \varepsilon_{h_3 - kR_i})$$
$$+ \varepsilon_{h_1 + kR_i}\varepsilon_{h_2 - kR_i} + \varepsilon_{h_1 - kR_i}\varepsilon_{h_2 + kR_i}].$$

The prime to the summation warns the reader that precautions have to be taken to avoid duplication of contributions. The denominator of Q is never allowed to be less than unity. Furthermore, ε is assumed to be zero for nonmeasured reflections (this corresponds to the less-biased assumption of $R = 1$). As a consequence of the space-group algebra, systematically absent reflections do not provide any contribution to the formula (the practice in the applications is to assume $\varepsilon = 0$ for these reflections also).

The distribution $P(\Phi_3|\{B\}_2)$ was denoted P_{10} in order to emphasize the fact that the formula explores reciprocal space by means of a ten-node figure. G may be positive or negative: if $G < 0$, the triplet phase is estimated close to π. Long experience with SIR88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) and SIR92 (Altomare, Cascarano, Giacovazzo, Guagliardi, Burla, Polidori & Camalli, 1994), two packages for direct phasing of crystal structures, proved that:

(a) a limited number of k vectors, chosen among the largest R values, are sufficient for accurate estimates of Φ_3;

(b) P_{10} is much more efficient than the Cochran (1955) formula, its use often making the difference between success and failure.

The basic reason for the success of P_{10} may be described in the following way. For any k vector, the

$6m$ cross magnitudes of Φ are

$$R_{h_1 + kR_1}, R_{h_1 - kR_1}, R_{h_2 + kR_1}, R_{h_2 - kR_1}, R_{h_3 + kR_1}, R_{h_3 - kR_1}$$
$$R_{h_1 + kR_2}, R_{h_1 - kR_2}, R_{h_2 + kR_2}, R_{h_2 - kR_2}, R_{h_3 + kR_2}, R_{h_3 - kR_2}$$
$$\vdots \qquad\qquad (2)$$
$$R_{h_1 + kR_m}, R_{h_1 - kR_m}, R_{h_2 + kR_m}, R_{h_2 - kR_m}, R_{h_3 + kR_m}, R_{h_3 - kR_m}.$$

From the magnitudes in the ith line of (2), six quadrupoles arise:

$$\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1} - \varphi_{kR_i} + \varphi_{h_1 + kR_i}$$
$$- \varphi_{h_2} + \varphi_{kR_i} + \varphi_{h_2 - kR_i} - \varphi_{h_3} - \varphi_{h_1 + kR_i} - \varphi_{h_2 - kR_i}$$

$$\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1} - \varphi_{kR_i} + \varphi_{h_1 + kR_i}$$
$$- \varphi_{h_2} - \varphi_{h_1 + kR_i} - \varphi_{h_3 - kR_i} - \varphi_{h_3} + \varphi_{kR_i} + \varphi_{h_3 - kR_i}$$

$$\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1} + \varphi_{kR_i} + \varphi_{h_1 - kR_i}$$
$$- \varphi_{h_2} - \varphi_{kR_i} + \varphi_{h_2 + kR_i} - \varphi_{h_3} - \varphi_{h_1 - kR_i} - \varphi_{h_2 + kR_i} \qquad (3)$$

$$\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1} - \varphi_{h_2 + kR_i} - \varphi_{h_3 - kR_i}$$
$$- \varphi_{h_2} - \varphi_{kR_i} + \varphi_{h_2 + kR_i} - \varphi_{h_3} + \varphi_{kR_i} + \varphi_{h_3 - kR_i}$$

$$\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1} + \varphi_{kR_i} + \varphi_{h_1 - kR_i}$$
$$- \varphi_{h_2} - \varphi_{h_1 - kR_i} - \varphi_{h_3 + kR_i} - \varphi_{h_3} - \varphi_{kR_i} + \varphi_{h_3 + kR_i}$$

$$\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1} - \varphi_{h_2 - kR_i} - \varphi_{h_3 + kR_i}$$
$$- \varphi_{h_2} + \varphi_{kR_i} + \varphi_{h_2 - kR_i} - \varphi_{h_3} - \varphi_{kR_i} + \varphi_{h_3 + kR_i},$$

each of which gives a recognizable contribution to P_{10}. The P_{10} formula is an efficient way of simultaneously exploiting the information contained in a quite large number of quadrupoles. The question is now whether (3) are the only quadrupoles exploitable via the second representation of Φ_3. Other types of quadrupoles do exist; for example,

$$\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_2} - \varphi_{kR_i} + \varphi_{h_2 + kR_i}$$
$$- \varphi_{h_3} + \varphi_{kR_j} + \varphi_{h_3 - kR_j}$$
$$- \varphi_{h_1} - \varphi_{(h_2 + kR_i)R_p} - \varphi_{(h_3 - kR_j)R_s} \qquad (4)$$

is also a quadrupole, provided

$$h_1 + h_2 R_p + h_3 R_s + kR_i R_p - kR_j R_s = 0.$$

Quadrupole (4) is structurally different from quadrupoles (3) because it involves magnitudes contained in two lines of (2) and also because the sum of the four triplets in (4) is no longer strictly equal to zero. In the paper by Cascarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori (1984), quadrupoles like (3) were called type I, quadrupoles like (4) type II. If the sum D of the four triplet phases in (4) is calculated, one obtains

$$D = 2\pi[h_2 T_p + h_3 T_s + k(T_i - T_j + R_i T_p - R_j T_s)].$$

When $D = 0$, the quadrupole is called consistent (Viterbo & Woolfson, 1973); it is inconsistent in the other cases. Since quadrupoles (3) are all consistent, P_{10} cannot exploit any inconsistent quadrupole. It is therefore of some interest to understand if some quintets exist that are referred to quadrupoles (4)

and then to introduce a formalism able to involve such quintets. Then, quadrupoles of types I and II could be simultaneously exploited. This is the first aim of this paper.

Algebraic considerations

Let

$$\psi_2 = \varphi_{\mathbf{h}_1\mathbf{R}_p} + \varphi_{\mathbf{h}_2\mathbf{R}_q} + \varphi_{\mathbf{h}_3} + \varphi_{\mathbf{kR}_i} - \varphi_{\mathbf{kR}_j}, \qquad (5)$$

where $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$ and $\mathbf{k}$ are chosen so as to satisfy the condition

$$\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q + \mathbf{h}_3 + \mathbf{k}(\mathbf{R}_i - \mathbf{R}_j) = 0. \qquad (6)$$

The quintet (5) differs from Φ_3 by a known phase shift:

$$\psi_2 = \Phi_3 - 2\pi[\mathbf{h}_1\mathbf{T}_p + \mathbf{h}_2\mathbf{T}_q + \mathbf{k}(\mathbf{T}_i - \mathbf{T}_j)].$$

Therefore, any method estimating ψ_2 also provides an estimate of Φ_3. Finding for each set of four vectors $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$ and $\mathbf{k}$ all the combinations of four matrices $\mathbf{R}_p$, $\mathbf{R}_q$, $\mathbf{R}_i$ and $\mathbf{R}_j$ for which (6) is satisfied is too long a job, even for fast computers. Thus, we prefer to limit our study to three subsets of quintets (5); more precisely, to the following cases:

Case I

$$\{\varphi_{\mathbf{h}_1\mathbf{R}_p} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3} + \varphi_{\mathbf{kR}_i} - \varphi_{\mathbf{kR}_i\mathbf{R}_p}\} \qquad (7)$$

under the condition

$$(\mathbf{h}_1 - \mathbf{kR}_i)(\mathbf{R}_p - \mathbf{I}) = 0. \qquad (8)$$

Case II

$$\{\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2\mathbf{R}_p} + \varphi_{\mathbf{h}_3} + \varphi_{\mathbf{kR}_i} - \varphi_{\mathbf{kR}_i\mathbf{R}_p}\} \qquad (9)$$

under the condition

$$(\mathbf{h}_2 - \mathbf{kR}_i)(\mathbf{R}_p - \mathbf{I}) = 0. \qquad (10)$$

Case III

$$\{\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3\mathbf{R}_p} + \varphi_{\mathbf{kR}_i} - \varphi_{\mathbf{kR}_i\mathbf{R}_p}\} \qquad (11)$$

under the condition

$$(\mathbf{h}_3 - \mathbf{kR}_i)(\mathbf{R}_p - \mathbf{I}) = 0. \qquad (12)$$

For each set of four vectors $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$ and $\mathbf{k}$, we need now to identify only the two matrices $\mathbf{R}_p$ and $\mathbf{R}_i$ that satisfy (8), (10) or (12). Since the three cases have similar properties, we focus our attention on case I: results are then easily extended to cases II and III.

Let us consider for case I the generic quintet (7). Its phasing shell consists of the following 13 magnitudes:

$$\{R_{\mathbf{h}_1}, R_{\mathbf{h}_2}, R_{\mathbf{h}_3}, R_{\mathbf{k}}, R_{\mathbf{h}_1\mathbf{R}_p+\mathbf{kR}_i}, R_{\mathbf{h}_1-\mathbf{kR}_i}, R_{\mathbf{h}_2+\mathbf{kR}_i},$$

$$R_{\mathbf{h}_2-\mathbf{kR}_i\mathbf{R}_p}, R_{\mathbf{h}_3+\mathbf{kR}_i}, R_{\mathbf{h}_3-\mathbf{kR}_i\mathbf{R}_p}, R_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2}, R_{\mathbf{h}_1(\mathbf{R}_p-\mathbf{I})-\mathbf{h}_2},$$

$$R_{\mathbf{kR}_i(\mathbf{R}_p-\mathbf{I})}\}. \qquad (13)$$

In accordance with (8), the vector $\mathbf{kR}_i(\mathbf{R}_p - \mathbf{I})$ can be rewritten as $\mathbf{h}_1(\mathbf{R}_p - \mathbf{I})$. This notation emphasizes the fact that, when $\mathbf{k}$ varies over reciprocal space and p is kept constant, $\mathbf{kR}_i(\mathbf{R}_p - \mathbf{I})$ remains constant. Therefore, the last three terms in (13) depend only on $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$ and $\mathbf{R}_p$.

When $\mathbf{R}_p = \mathbf{I}$, the 13 magnitudes reduce to ten, which constitute the second phasing shell of Φ_3 (*i.e.* the set $\{B\}_2$). Accordingly, the formulation used for deriving the P_{10} expression is a particular case of the theory described here.

It should be noted that, because of (8), $\mathbf{h}_1 - \mathbf{kR}_i$ is a special reflection marked by a Wilson coefficient $\eta \neq 1$ [*i.e.* η rotation matrices exist for which $(\mathbf{h}_1 - \mathbf{kR}_i)\mathbf{R}_p = \mathbf{h}_1 - \mathbf{kR}_i]$.* According to (7), the phase shift between ψ_2 and Φ_3 reduces to $\Delta = 2\pi(\mathbf{h}_1 - \mathbf{kR}_i)\mathbf{T}_p$; therefore, $\Delta \neq 0$ only if $(\mathbf{h}_1 - \mathbf{kR}_i)$ is a systematic absence, otherwise $\Delta = 0$.

We also note that equation (8) may be written as

$$\mathbf{h}_1\mathbf{R}_p + \mathbf{kR}_i = \mathbf{h}_1 + \mathbf{kR}_i\mathbf{R}_p. \qquad (14)$$

If $\mathbf{C}_p$ represents a symmetry operator of order 2, then $(\mathbf{h}_1\mathbf{R}_p + \mathbf{kR}_i)$ is also a special reflection with $\eta \neq 1$. Indeed,

$$\mathbf{h}_1\mathbf{R}_p + \mathbf{kR}_i = (\mathbf{h}_1 + \mathbf{kR}_i\mathbf{R}_p^{-1})\mathbf{R}_p = (\mathbf{h}_1 + \mathbf{kR}_i\mathbf{R}_p)\mathbf{R}_p$$

and, according to (14),

$$(\mathbf{h}_1 + \mathbf{kR}_i\mathbf{R}_p)\mathbf{R}_p = \mathbf{h}_1 + \mathbf{kR}_i\mathbf{R}_p \quad \text{for } \mathbf{R}_p \neq \mathbf{I}.$$

We conclude that at least one cross reflection of the quintets (7) is always special; when it coincides with a systematic absence, the phase shift between ψ_2 and Φ_3 is different from zero.

Quintet (7) exploits the following 14 quadrupoles [for simplicity we often denote $\mathbf{h}_1(\mathbf{R}_p - \mathbf{I}) - \mathbf{h}_2 = \mathbf{h}_1\mathbf{R}_p + \mathbf{h}_3$]:

(a) $\quad \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{kR}_i} + \varphi_{\mathbf{h}_1-\mathbf{kR}_i}$
$\quad\quad - \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{kR}_i} + \varphi_{\mathbf{h}_2+\mathbf{kR}_i}$
$\quad\quad - \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{h}_1-\mathbf{kR}_i} - \varphi_{\mathbf{h}_2+\mathbf{kR}_i}$

(b) $\quad \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{kR}_i} + \varphi_{\mathbf{h}_1-\mathbf{kR}_i}$
$\quad\quad - \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1-\mathbf{kR}_i} - \varphi_{\mathbf{h}_3+\mathbf{kR}_i}$
$\quad\quad - \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{kR}_i} + \varphi_{\mathbf{h}_3+\mathbf{kR}_i}$

(c) $\quad \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_p} - \varphi_{\mathbf{h}_1(\mathbf{R}_p-\mathbf{I})}$
$\quad\quad - \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1\mathbf{R}_p} + \varphi_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2}$
$\quad\quad - \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2} + \varphi_{\mathbf{h}_1(\mathbf{R}_p-\mathbf{I})}$

(d) $\quad \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_p} - \varphi_{\mathbf{h}_1(\mathbf{R}_p-\mathbf{I})}$
$\quad\quad - \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_3} + \varphi_{\mathbf{h}_1(\mathbf{R}_p-\mathbf{I})}$
$\quad\quad - \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{h}_1\mathbf{R}_p} + \varphi_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_3}$

(e) $\quad \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{h}_1\mathbf{R}_p} - \varphi_{\mathbf{h}_3} + \varphi_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_3}$
$\quad\quad - \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{kR}_i\mathbf{R}_p} + \varphi_{\mathbf{h}_2-\mathbf{kR}_i\mathbf{R}_p}$
$\quad\quad - \varphi_{\mathbf{kR}_i} - \varphi_{\mathbf{h}_2-\mathbf{kR}_i\mathbf{R}_p} - \varphi_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_3}$

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* In the literature, the Wilson coefficient is usually called ε or p. Here, it is called η to avoid a conflict with other symbols.

(f) $\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1 R_p} - \varphi_{h_3} + \varphi_{h_1 R_p + h_3}$
$\quad - \varphi_{h_2} - \varphi_{kR_i} + \varphi_{h_2 + kR_i}$
$\quad + \varphi_{kR_i R_p} - \varphi_{h_2 + kR_i} - \varphi_{h_1 R_p + h_3}$

(g) $\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1 R_p} - \varphi_{kR_i} + \varphi_{h_1 R_p + kR_i}$
$\quad - \varphi_{h_2} + \varphi_{kR_i R_p} + \varphi_{h_2 - kR_i R_p}$
$\quad - \varphi_{h_3} - \varphi_{h_1 R_p + kR_i} - \varphi_{h_2 - kR_i R_p}$

(h) $\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1 R_p} - \varphi_{kR_i} + \varphi_{h_1 R_p + kR_i}$
$\quad - \varphi_{h_2} - \varphi_{h_1 R_p + kR_i} - \varphi_{h_3 - kR_i R_p}$
$\quad - \varphi_{h_3} + \varphi_{kR_i R_p} + \varphi_{h_3 - kR_i R_p}$ (15)

(i) $\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1 R_p} - \varphi_{h_2} + \varphi_{h_1 R_p + h_2}$
$\quad + \varphi_{kR_i R_p} - \varphi_{h_3} + kR_i - \varphi_{h_1 R_p} + h_2$
$\quad - \varphi_{h_3} - \varphi_{kR_i} + \varphi_{h_3 + kR_i}$

(j) $\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1 R_p} - \varphi_{h_2} + \varphi_{h_1 R_p + h_2}$
$\quad - \varphi_{kR_i} - \varphi_{h_3 - kR_i R_p} - \varphi_{h_1 R_p + h_2}$
$\quad - \varphi_{h_3} + \varphi_{kR_i R_p} + \varphi_{h_3 - kR_i R_p}$

(k) $\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1 R_p} - \varphi_{h_2 + kR_i} - \varphi_{h_3 - kR_i R_p}$
$\quad - \varphi_{h_2} - \varphi_{kR_i} + \varphi_{h_2 + kR_i}$
$\quad - \varphi_{h_3} + \varphi_{kR_i R_p} + \varphi_{h_3 - kR_i R_p}$

(l) $\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{h_1 R_p} - \varphi_{h_2 - kR_i R_p} - \varphi_{h_3 + kR_i}$
$\quad - \varphi_{h_2} + \varphi_{kR_i R_p} + \varphi_{h_2 - kR_i R_p}$
$\quad - \varphi_{h_3} - \varphi_{kR_i} + \varphi_{h_3 + kR_i}$

(m) $\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{kR_i} + \varphi_{kR_i R_p} - \varphi_{kR_i(R_p - I)}$
$\quad - \varphi_{h_1 R_p} - \varphi_{h_2} + \varphi_{h_1 R_p + h_2}$
$\quad - \varphi_{h_3} - \varphi_{h_1 R_p + h_2} + \varphi_{h_1(R_p - I)}$

(n) $\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} - \varphi_{kR_i} + \varphi_{kR_i R_p} - \varphi_{kR_i(R_p - I)}$
$\quad - \varphi_{h_1 R_p} - \varphi_{h_3} + \varphi_{h_1 R_p + h_3}$
$\quad - \varphi_{h_2} - \varphi_{h_1 R_p + h_3} + \varphi_{h_1(R_p - I)}.$

The reader will easily verify that (15) has some quadrupoles in common with (3). Such an overlap will be reflected in the probabilistic formula estimating triplets via 13 moduli, which will therefore have terms in common with P_{10}.

The conditional probabilistic formula
$$P(\Phi_3 | R_{h_1}, ..., R_{h_1(R_p - I)})$$

Let us consider the quintet (case I of the preceding section)

$$\varphi_{h_1 R_p} + \varphi_{h_2} + \varphi_{h_3} + \varphi_{kR_i} - \varphi_{kR_i R_p}. \quad (16)$$

The method of joint probability distribution functions of structure factors (Hauptman & Karle, 1953; Klug, 1958; Giacovazzo, 1980) is used to derive the conditional probability

$$P(\Phi_3 | R_{h_1}, R_{h_2}, R_{h_3}, R_k, R_{h_1 R_p + kR_i}, R_{h_1 - kR_i}, R_{h_2 + kR_i},$$

$$R_{h_2 - kR_i R_p}, R_{h_3 + kR_i}, R_{h_3 - kR_i R_p}, R_{h_1 R_p + h_2}, R_{h_1 R_p + h_3},$$

$$R_{h_1(R_p - I)}).$$

under the condition (8).

For the sake of simplicity, we do not give any detail about the mathematical derivation. We only underline that k is a free vector that can vary over reciprocal space and that R_i is a rotation matrix that can vary freely over the set of rotation matrices included in the space group. Once the vector kR_i and the matrix R_p satisfy (8), then the conditional probability of Φ_3 given 13 magnitudes is calculated. Contributions arising from different k and different R_i can be combined with each other to give the general formula

$$P(\Phi_3 | ...) \simeq [2\pi I_0(G')]^{-1} \exp(G' \cos\Phi_3), \quad (17)$$

where

$$G' = C(1 + Q')$$

$$Q' = \sum_k \left[\frac{\sum_{i=1}^{m} {}' A'_{k,i}/N}{1 + \left(\varepsilon_{h_1}\varepsilon_{h_2}\varepsilon_{h_3} + \sum_{i=1}^{m} {}' B'_{k,i}\right)/2N} \right]$$

$$A'_{k,i} = \sum_{p=1}^{m} {}' \{\varepsilon_k[\varepsilon_{h_1 - kR_i}(\varepsilon_{h_2 + kR_i} + \varepsilon_{h_3 + kR_i})$$

$$+ \varepsilon_{h_1 R_p + kR_i}(\varepsilon_{h_2 - kR_i R_p} + \varepsilon_{h_3 - kR_i R_p})$$

$$+ \varepsilon_{h_1 R_p + h_2}(\varepsilon_{h_3 + kR_i} + \varepsilon_{h_3 - kR_i R_p})$$

$$+ \varepsilon_{h_1 R_p + h_3}(\varepsilon_{h_2 + kR_i} + \varepsilon_{h_2 - kR_i R_p})$$

$$+ \varepsilon_{h_2 + kR_i}\varepsilon_{h_3 - kR_i R_p} + \varepsilon_{h_3 + kR_i}\varepsilon_{h_2 - kR_i R_p}]$$

$$+ \tfrac{1}{4}(\varepsilon_k - 2)\varepsilon_{h_1(R_p - I)}(\varepsilon_{h_1 R_p + h_2} + \varepsilon_{h_1 R_p + h_3})\} \cos\Delta$$

$$+ \tfrac{1}{4}(\varepsilon_{h_1} - 2)\varepsilon_{h_1(R_p - I)}(\varepsilon_{h_1 R_p + h_2} + \varepsilon_{h_1 R_p + h_3})$$

$$\Delta = 2\pi(h_1 - kR_i)T_p$$

$$B'_{k,i} = \sum_{p=1}^{m} {}' \{\varepsilon_{h_1}[\varepsilon_k(\varepsilon_{h_1 R_p + kR_i} + \varepsilon_{h_1 - kR_i})$$

$$+ \varepsilon_{h_2 + kR_i}\varepsilon_{h_3 - kR_i R_p} + \varepsilon_{h_2 - kR_i R_p}\varepsilon_{h_3 + kR_i}$$

$$+ \varepsilon_{h_2}\varepsilon_{h_1 R_p + h_2} + \varepsilon_{h_3}\varepsilon_{h_1 R_p + h_3}]$$

$$+ \varepsilon_{h_2}[\varepsilon_k(\varepsilon_{h_2 + kR_i} + \varepsilon_{h_2 - kR_i R_p}) + \varepsilon_{h_1 R_p + kR_i}\varepsilon_{h_3 - kR_i R_p}$$

$$+ \varepsilon_{h_1 - kR_i}\varepsilon_{h_3 + kR_i} + \varepsilon_{h_1 R_p + h_3}\varepsilon_{h_1(R_p - I)}]$$

$$+ \varepsilon_{h_3}[\varepsilon_k(\varepsilon_{h_3 + kR_i} + \varepsilon_{h_3 - kR_i R_p}) + \varepsilon_{h_1 R_p + kR_i}\varepsilon_{h_2 - kR_i R_p}$$

$$+ \varepsilon_{h_1 - kR_i}\varepsilon_{h_2 + kR_i} + \varepsilon_{h_1 R_p + h_2}\varepsilon_{h_1(R_p - I)}]$$

$$+ \varepsilon_k[\varepsilon_{h_1 R_p + h_3}(\varepsilon_{h_2 + kR_i} + \varepsilon_{h_2 - kR_i R_p})$$

$$+ \varepsilon_{h_1 R_p + h_2}(\varepsilon_{h_3 + kR_i} + \varepsilon_{h_3 - kR_i R_p})]\}.$$

The formula P_{13}

Let us now consider case II. The quintet (9) may be written as

$$\psi_2 = \varphi_{h_2 R_p} + \varphi_{h_1} + \varphi_{h_3} + \varphi_{kR_i} - \varphi_{kR_i R_p}$$

and depends on the ordered set of magnitudes

$$\{R_{h_2}, R_{h_1}, R_{h_3}, R_k, R_{h_2 R_p + kR_i}, R_{h_2 - kR_i}, R_{h_1 + kR_i},$$

$$R_{h_1-kR_iR_p}, R_{h_3+kR_i}, R_{h_3-kR_iR_p}, R_{h_2R_p+h_1}, R_{h_2R_p+h_3},$$

$$R_{h_2(R_p-1)}\}. \tag{18}$$

The quintet (11) may be written as

$$\psi_2 = \varphi_{h_3R_p} + \varphi_{h_2} + \varphi_{h_1} + \varphi_{kR_i} - \varphi_{kR_iR_p}$$

and depends on the ordered set of magnitudes

$$\{R_{h_3}, R_{h_2}, R_{h_1}, R_k, R_{h_3R_p+kR_i}, R_{h_3-kR_i}, R_{h_2+kR_i},$$

$$R_{h_2-kR_iR_p}, R_{h_1+kR_i}, R_{h_1-kR_iR_p}, R_{h_3R_p+h_2}, R_{h_3R_p+h_1},$$

$$R_{h_3(R_p-1)}\}. \tag{19}$$

The ordered set (13) has its image in the ordered set (18) if h_1 is replaced by h_2 and *vice versa*. Accordingly, the ordered set (19) is the image of the ordered set (13) if h_1 and h_3 change their roles. In conclusion, the same formula holds for all the cases if the positions of the magnitudes in (13), (18) and (19) are considered rather than their indices. Then, the final formula P_{13}, collecting contributions from different cases and from different k's, may be written

$$P_{13} = P(\Phi_3|\ldots) \simeq [2\pi I_0(G'')]^{-1}\exp(G''\cos\Phi_3),$$

$$\tag{20}$$

where

$$G'' = C(1+Q'')$$

$$Q'' = \sum_{cases}{}' \sum_k{}' \left[\frac{\sum_{i=1}^{m}{}' A'_{k,i}/N}{1 + \left(\varepsilon_{h_1}\varepsilon_{h_2}\varepsilon_{h_3} + \sum_{i=1}^{m}{}' B'_{k,i}\right)/2N} \right]$$

$$A'_{k,i} = \sum_{p=1}^{m}{}' [\varepsilon_4(\varepsilon_6\varepsilon_7 + \varepsilon_6\varepsilon_9 + \varepsilon_5\varepsilon_8 + \varepsilon_5\varepsilon_{10} + \varepsilon_9\varepsilon_{11}$$

$$+ \varepsilon_{10}\varepsilon_{11} + \varepsilon_7\varepsilon_{12} + \varepsilon_8\varepsilon_{12} + \varepsilon_7\varepsilon_{10} + \varepsilon_8\varepsilon_9)$$

$$+ \tfrac{1}{4}(\varepsilon_4 - 2)\varepsilon_{11}\varepsilon_{13} + \tfrac{1}{4}(\varepsilon_4 - 2)\varepsilon_{12}\varepsilon_{13}]\cos\Delta$$

$$+ \tfrac{1}{4}(\varepsilon_1 - 2)\varepsilon_{11}\varepsilon_{13} + \tfrac{1}{4}(\varepsilon_1 - 2)\varepsilon_{12}\varepsilon_{13}$$

$$B'_{k,i} = \sum_{p=1}^{m}{}' [\varepsilon_1(\varepsilon_4\varepsilon_5 + \varepsilon_4\varepsilon_6 + \varepsilon_7\varepsilon_{10} + \varepsilon_8\varepsilon_9$$

$$+ \varepsilon_2\varepsilon_{11} + \varepsilon_3\varepsilon_{12})$$

$$+ \varepsilon_2(\varepsilon_4\varepsilon_7 + \varepsilon_4\varepsilon_8 + \varepsilon_5\varepsilon_{10} + \varepsilon_6\varepsilon_9 + \varepsilon_{12}\varepsilon_{13})$$

$$+ \varepsilon_3(\varepsilon_4\varepsilon_9 + \varepsilon_4\varepsilon_{10} + \varepsilon_5\varepsilon_8 + \varepsilon_6\varepsilon_7 + \varepsilon_{11}\varepsilon_{13})$$

$$+ \varepsilon_4(\varepsilon_7\varepsilon_{12} + \varepsilon_8\varepsilon_{12} + \varepsilon_9\varepsilon_{11} + \varepsilon_{10}\varepsilon_{11})].$$

The subscripts to ε indicate the position of the related magnitude in (13), (18) and (19).

First application of the formula P_{13}

In order to check the practical effectiveness of P_{13} for $R_p \neq I$, we have suitably modified the *SIR*92

Table 1. *Code name, space group and crystallographic and chemical data for the test structures*

Structure code*	Space group	Molecular formula	Z
AX118[a]	Pccn	$C_{19}H_{21}N_2O_3Cl$	8
AZET	Pca2₁	$C_{21}H_{16}ClNO$	8
BED	I4	$C_{26}H_{26}N_4O_4$	8
BOBBY	P2₁3	$Na^+Ca^{2+}[N(CH_2CO_2)_3]^{3-}$	4
CUIMID	P3₂21	$C_6H_8N_4ClCu$	6
DIAM	P4₂/n	$C_{14}H_{20}O$	8
DIOLE	I$\bar{4}$2d	$C_{10}H_{18}O_2$	16
FEGAS[b]	P6₃/mmc	$Fe_2Ga_2S_5$	2
INOS	P2₁/n	$C_6H_{12}O_6 \cdot H_2O$	8

References: (a) distributed by the crystallographic group in York (unpublished). (b) Cascarano, Douggy-Smiri & Nguyen-Huy Dung (1987).

* Complete references for most of the structures are not given, for the sake of brevity. The reader is referred to magnetic tapes distributed by the crystallographic group in Göttingen.

program. Triplets are sought among the NLAR reflections with largest R values (NLAR is fixed by the program) and estimated according to the Cochran (1955) formula, P_{13} and P_{10}. The Cochran formula

$$P(\Phi_3) \simeq [2\pi I_0(C)]^{-1}\exp(C\cos\Phi_3)$$

is here denoted P_3 for brevity.

Nine test structures were used for which Table 1 gives references, space groups and main crystal data. The P_{10} and P_{13} formulas require that the vector k be allowed to vary over a number of reflections. *SIR*92 fixed for P_{13} the same number of k vectors used for P_{10}; N_k is this value (see Table 2) and $\langle N_{kR_i}\rangle$ is the average number of the kR_i vectors involved in the quintets (1) exploited for each triplet by P_{10}. For algebraic reasons, only a subset of the vectors kR_i will satisfy (8), (10) or (12); we denote by $\langle N'_{kR_i}\rangle$ the average number of quintets of type (7), (9) or (11) exploited for each triplet by P_{13}. The relative efficiencies of P_3 and P_{13} can be deduced from Tables 3 and 4, where triplet estimates are ranked as a function of ARG (ARG = C or G'' according to circumstances). In Table 3, n is the number of triplets with $|C|$ or $|G''|$ larger than ARG; nw is the number of wrong estimates. In Table 4, $\langle|\Phi|\rangle$ is the average absolute deviation of the triplet phase from 2π (in °).

Tables 3 and 4 show that P_{13} is an efficient tool both for ranking positive triplets and for picking up negative ones. It proves to be a formula more accurate than P_3 and therefore may constitute a useful alternative to it. In the same tables, we show the corresponding statistics obtained for P_{10}. It is immediately seen that P_{13}, calculated for $R_p \neq I$ (*i.e.* P_{10} contribution excluded), is not better than P_{10} and is highly correlated with it. In order to have a simple figure for measuring the relative efficiency of the three formulas, we calculated for each structure the

Table 2. *Parameters for each test structure*

NTRIP is the number of triplets calculated by *SIR*92. For the other symbols see the main text.

Structure code	NLAR	NTRIP	N_k	$\langle N_{kR_i} \rangle$	$\langle N'_{kR_i} \rangle$	ρ_3	ρ_{10}	ρ_{13}	ρ_{10+13}
AX118	300	7025	46	156	60	0.200	0.635	0.503	0.644
AZET	342	8000	60	186	50	0.156	0.406	0.284	0.413
BED	286	4585	64	186	1	0.176	0.282	0.183	0.281
BOBBY	68	2217	32	196	21	0.329	0.732	0.427	0.736
CUIMID	198	4204	33	120	5	0.224	0.657	0.284	0.657
DIAM	260	6455	46	162	41	0.193	0.553	0.430	0.571
DIOLE	182	6508	42	230	34	0.179	0.275	0.212	0.280
FEGAS	71	1334	30	180	320	0.311	0.773	0.543	0.785
INOS	304	3572	56	99	17	0.188	0.660	0.412	0.656

Table 3. *Triplet statistics for AX118*

The P_{13} formula has been calculated for $R_p \neq I$.

			P_{13}				P_{10}			
			Positive estimated triplets		Negative estimated triplets		Positive estimated triplets		Negative estimated triplets	
	P_3									
ARG	n	nw	n	nw	n	nw	n	nw	n	nw
0.4	6823	843	3435	53	93	14	3794	17	131	19
0.8	2672	143	2672	24	14	1	2919	8	11	0
1.2	740	13	1514	11	3	0	1547	1	1	0
1.6	197	0	831	1	1	0	675	0		
2.0	56	0	425	0	1	0	276	0		

Table 4. *Triplet statistics for AZET*

The P_{13} formula has been calculated for $R_p \neq I$.

			P_{13}				P_{10}			
			Positive estimated triplets		Negative estimated triplets		Positive estimated triplets		Negative estimated triplets	
	P_3									
ARG	n	$\langle |\Phi| \rangle$ (°)	n	$\langle |\Phi| \rangle$ (°)	n	$\langle |\Phi| \rangle$ (°)	n	$\langle |\Phi| \rangle$ (°)	n	$\langle |\Phi| \rangle$ (°)
0.4	8000	50.5	5708	44.4	87	87.6	5373	40.3	55	109.9
1.2	1409	38.8	1972	35.5	9	121.2	2341	32.0	1	122.0
2.0	95	27.2	521	29.4	2	89.5	597	25.8		
3.2			111	25.4			67	22.3		
4.4			25	26.9			4	23.0		

correlation coefficient

$$\rho = \frac{\langle (\cos \varphi_T - \langle \cos \varphi_T \rangle)[D_1(ARG) - \langle D_1(ARG) \rangle] \rangle}{\langle (\cos \varphi_T - \langle \cos \varphi_T \rangle)^2 \rangle^{1/2} \langle (D_1(ARG) - \langle D_1(ARG) \rangle)^2 \rangle^{1/2}},$$

where $\cos \varphi_T$ is the true cosine of the triplet and $D_1(ARG)$ is the expected value of the triplet cosine according to P_3, P_{10} and P_{13} (ARG $= C$, G and G'' in the three cases). Accordingly, for each test structure three correlation factors ρ_3, ρ_{10} and ρ_{13} are calculated, which correspond to the Cochran, P_{10} and P_{13} formulas, respectively (see Table 2). It is easily seen that:

(1) ρ_{13} is always larger than ρ_3. The indications of Tables 3 and 4 are therefore confirmed.

(2) ρ_{10} is always much higher than ρ_3. This corroborates the well documented higher efficiency of P_{10} with respect to the Cochran formula.

(3) For low-symmetry space groups, $\langle N'_{kR} \rangle$ is very small; consequently, P_{13} does not provide a relevant

improvement on P_3 performance. We then decided to recalculate P_{13} after having increased the value of N_k and, as a consequence, the value of $\langle N'_{kR} \rangle$. The results are given in Table 5 and show that ρ_{13} generally increases even if for low-symmetry space groups (*i.e.* for BED) conditions (8), (10) or (12) are hardly satisfied.

(4) In most cases, ρ_{13} is significantly close to ρ_{10}. This correlation seems not to be random and suggests a supplementary algebraic and statistical analysis of the P_{13} formula.

Algebraic and statistical analysis of the P_{13} formula
$$P(\Phi_3 | R_{h_1}, ..., R_{h_1(R_p - 1)})$$

If the $R_p = I$ condition (8) is verified for any kR_i, then the $A'_{k,i}$ and $B'_{k,i}$ terms coincide with terms $A_{k,i}$ and $B_{k,i}$ in P_{10}. Thus, the present formulation encompasses the P_{10} formalism. However, some theoretical and practical drawbacks limit the usefulness of the present theory. For example, as for P_{10},

Table 5. *Parameters* N_k, $\langle N'_{kR} \rangle$ *and* ρ_{13} *for the test structures*

The correlation coefficient has been calculated using the P_{13} formula with $\mathbf{R}_p \neq \mathbf{I}$.

Structure code	N_k	$\langle N'_{kR} \rangle$	ρ_{13}
AX118	150	185	0.556
AZET	150	126	0.314
BED	150	3	0.175
BOBBY	68	45	0.447
CUIMID	150	24	0.344
DIAM	150	116	0.464
DIOLE	150	129	0.233
FEGAS	71	770	0.635
INOS	150	44	0.440

the prime to the summation warns the reader that precautions have to be taken in order to avoid duplications of contributions [*i.e.* if $\mathbf{R}_p$ is a symmetry operator of order two ($\mathbf{R}_p = \mathbf{R}_p^{-1}$), then $A'_{k,i}$ and $B'_{k,i}$ do not change when $\mathbf{R}_i$ is replaced by $-\mathbf{R}_i\mathbf{R}_p$]. While duplications of contributions can be easily avoided for P_{10}, a computer program able to eliminate all of them in (20) is too time consuming even for a fast computer. Thus, (20) would be less efficient in practice than theoretically expected.

Let us now compare (17) with P_{10}, with special attention to the comparison between $A_{k,i}$ and $A'_{k,i}$ ($A_{k,i}$ and $A'_{k,i}$ influence the sign of $\cos \Phi_3$, while $B_{k,i}$ and $B'_{k,i}$ are only scaling factors). We note:

(a) The term $\varepsilon_k \varepsilon_{h_1-kR_i}(\varepsilon_{h_2+kR_i} + \varepsilon_{h_3+kR_i})$ is both in $A_{k,i}$ and in $A'_{k,i}$ [the quadrupoles (15a) and (15b) are also in (3)] but is multiplied in $A'_{k,i}$ by $\cos \Delta$. This is not a contradiction. Indeed, $\Delta \neq 2\pi n$ only if the reflection with vectorial index $\mathbf{h}_1 - \mathbf{kR}_i$ is systematically absent – but in this case the term itself vanishes.

(b) If $\mathbf{R}_i$ is replaced by $\mathbf{R}_i\mathbf{R}_p^{-1}$ and $\mathbf{R}_p$ is a symmetry operator of order two, then the term $\varepsilon_k \varepsilon_{h_1R_p+kR_i}(\varepsilon_{h_2-kR_iR_p} + \varepsilon_{h_3-kR_iR_p})$ [from quadrupoles (15g) and (15h)] is replaced by $\varepsilon_k \varepsilon_{h_1+kR_i}(\varepsilon_{h_2-kR_i} + \varepsilon_{h_3-kR_i})$, which is also included in $A_{k,i}$ (this is not true if $\mathbf{R}_p$ is not a symmetry operator of order two). The fact that in $A'_{k,i}$ the term is multiplied by $\cos \Delta$ is not a contradiction. In the section dedicated to algebraic considerations, we showed that, if $\mathbf{R}_p^{-1} = \mathbf{R}_p$, then $\mathbf{h}_1\mathbf{R}_p + \mathbf{kR}_i$ is a special reflection with $\eta \neq 1$. Therefore, $\Delta \neq 2\pi n$ only if the reflection with vectorial index $\mathbf{h}_1\mathbf{R}_p + \mathbf{kR}_i$ is a systematically absent reflection – but in this case the term itself vanishes.

(c) For a fixed $\mathbf{R}_p$, the term $\frac{1}{4}(\varepsilon_{h_1} - 2)\varepsilon_{h_1(R_p-1)} \times (\varepsilon_{h_1R_p+h_2} + \varepsilon_{h_1R_p+h_3})$ [from quadrupoles (15c) and (15d)] does not change with $\mathbf{k}$. Consequently, its role in (17) is statistically irrelevant. In addition, it is based on special quadrupoles [see relationships (15)] involving Σ_1 relations that are unreliable for complex structures. An analogous conclusion holds for the term $\frac{1}{4}(\varepsilon_k - 2)\varepsilon_{h_1(R_p-1)}(\varepsilon_{h_1R_p+h_2} + \varepsilon_{h_1R_p+h_3})$ arising from quadrupoles (15m) and (15n).

Table 6. P_{13} *triplet statistics calculated using only the contributions of quadrupoles* (15k) *and* (15l)

AX118

ARG	Positive estimated triplets		Negative estimated triplets	
	n	nw	n	nw
0.4	3512	144	62	21
0.8	2527	70	13	11
1.2	1338	23	2	0
1.6	738	12		
2.0	400	6		

AZET

ARG	Positive estimated triplets		Negative estimated triplets	
	n	$\langle |\Phi| \rangle$ (°)	n	$\langle |\Phi| \rangle$ (°)
0.4	6435	47.7	17	96.0
1.2	1805	39.2	4	139.2
2.0	343	34.3		
3.2	56	29.5		
4.4	5	25.2		

(d) The term $\varepsilon_k[\varepsilon_{h_1R_p+h_2}(\varepsilon_{h_3+kR_i} + \varepsilon_{h_3-kR_iR_p}) + \varepsilon_{h_1R_p+h_3}(\varepsilon_{h_2+kR_i} + \varepsilon_{h_2-kR_iR_p})]$ arising from quadrupoles (15i), (15j), (15f) and (15e) is present in both A' and B'. When it is large, it contributes to make A'/N meaningful, but at the same time it makes $B'/2N$ large so automatically reducing its own influence on (17). Generally, large values of this term are associated with large variance values. This strange behaviour may be explained thus: while typical quadrupoles strengthening Φ_3 involve triplets each of which contains $\mathbf{h}_1$, $\mathbf{h}_2$ or $\mathbf{h}_3$, quadrupoles (15e), (15f), (15i) and (15j) do not satisfy this condition. They are based on two-phase seminvariants [for example, the sum of the last two triplets in the quadrupole (15e) is the two-phase seminvariant $\varphi_{h_1(R_p-1)-h_2} - \varphi_{h_2} - 2\pi\mathbf{kR}_i\mathbf{T}_p]$, which are unreliable for complex structures.

(e) The term $\varepsilon_k[\varepsilon_{h_2+kR_i}\varepsilon_{h_3-kR_iR_p} + \varepsilon_{h_3+kR_i}\varepsilon_{h_2-kR_iR_p}]$ arising from quadrupoles (15k) and (15l) is not present in $A_{k,i}$: it contains useful information supplementary to that provided by P_{10}. In particular, it is able to exploit quadrupoles of type (4) (not accessible to P_{10}) because it involves magnitudes contained in two different lines of (2).

It should be worthwhile to calculate the role of the quadrupoles (15k) and (15l) in the P_{13} formula. We neglect in $A'_{k,i}$ all the terms but $\varepsilon_4(\varepsilon_7\varepsilon_{10} + \varepsilon_8\varepsilon_9)$ and in $B'_{k,i}$ all the terms but $[\varepsilon_1(\varepsilon_7\varepsilon_{10} + \varepsilon_8\varepsilon_9) + \varepsilon_2(\varepsilon_4\varepsilon_7 + \varepsilon_4\varepsilon_8) + \varepsilon_3(\varepsilon_4\varepsilon_9 + \varepsilon_4\varepsilon_{10})]$. The results for AX118 and AZET are shown in Table 6. We see that the simple use of the information contained in the quadrupole (4) is able to identify negative triplets and to efficiently rank the positive ones. The phase indications provided by quadrupoles (15k) and (15l) agree well with those obtained through the complete P_{13} formula (see Tables 3 and 4). We have combined the contributions from quadrupoles (15k) and (15l) with contributions from P_{10} just by adding the corresponding

numerators and respective denominators (terms can be considered as statistically independent). The correlation coefficient ρ has then been calculated for the test structures; it is shown in the last column of Table 2. It is seen that ρ_{10+13} is slightly better than ρ_{10} but the improvement is not really significant.

Concluding remarks

A probabilistic theory has been presented that is based on the representation of a given triplet phase by a family of special quintet phases. The information contained in the basis and in the cross terms of such quintets is used for estimating the triplet phase. The formulation is quite general and includes the well known P_{10} formula as a particular case. The final formula, called P_{13}, proved more efficient than the Cochran (1955) formula; in particular, it is able, as well as P_{10}, to recognize negative triplets. A strong correlation has been found between P_{10} and P_{13}, both from the theoretical point of view and in practical applications. The additional information exploited by P_{13} does not seem to be of sufficient quality for substantially improving the efficiency of P_{10} and, in addition, P_{13} is much more time consuming. Does this theory demonstrate the limits to which one can go with the embedding scheme? It is too early to conclude thus.

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Derivation of Wyckoff Positions of N-Dimensional Space Groups. Theoretical Considerations

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Abstract

An algorithm to calculate Wyckoff positions of n-dimensional space groups is developed and a detailed theoretical background is supplied. The algorithm is based on concepts of symmetry support and of translational normalizer

1. Introduction

It has become attractive to view quasicrystals as objects whose structure can be derived from a higher-dimensional crystal. This approach is based on the fact that the bright spots occurring in a diffraction pattern of a quasicrystal can be indexed by a finite number n, $n > 3$, of integers and that the positions and intensities of Bragg peaks display a point symmetry forbidden in three-dimensional crystals. The corresponding Z-module of rank n, sometimes called Fourier module (Janssen, 1991) of the related density function, can be interpreted as the reciprocal lattice of a certain n-dimensional lattice T, invariant under the symmetry group L of the diffraction pattern, where L is a representative of some Laue class. Usually, from L and from the statistical