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The joint probability distribution function of structure factors with rational indices. VI. Cases with reduced dimensionality

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Abstract

The probabilistic formulas relating standard and mixed type reflections (these last show integral and half-integral indices) are derived. It is shown that probabilistic estimates can be obtained by using particular sections of the three-dimensional reciprocal space. The concept of structure invariant is extended to define the wider class of structure quasi-invariant. Their statistical behaviour is briefly discussed with the help of some practical tests.

1. Symbols and notation

Papers by Giacovazzo & Siliqi (1998), Giacovazzo, Siliqi, Carrozzini *et al.* (1999), Giacovazzo, Siliqi, Altomare *et al.* (1999), Giacovazzo, Siliqi & Fernández-Castaño (1999) and Giacovazzo, Siliqi, Fernández-Castaño & Comunale (1999) will be referred to as papers I, II, III, IV and V, respectively. The notation here adopted is essentially that used in papers IV and V, to which the reader is referred.

2. Introduction

In paper IV, the joint probability distribution

$$P(A_{\mathbf{p}}, B_{\mathbf{p}}, A_{\mathbf{q}_1}, B_{\mathbf{q}_1}, \ldots, A_{\mathbf{q}_n}, B_{\mathbf{q}_n}) \qquad (1)$$

was derived, where A and B are the real and imaginary parts of the structure factor F, and $\mathbf{p}_j$ and $\mathbf{q}_j$, $j = 1, \ldots, n$, are rational indices. The distribution (1) may be written in the form

$$P(\mathbf{X}) = P(X_1, X_2, \ldots, X_{2n+1}, X_{2n+2}),$$

where the variable X_j represents $A_{\mathbf{p}}$, $B_{\mathbf{p}}$, $A_{\mathbf{q}}$, $B_{\mathbf{q}}$ according to the value of j (*i.e.* $X_1 = A_{\mathbf{p}}$, $X_2 = B_{\mathbf{p}}$, $X_3 = A_{\mathbf{q}_1}$, $X_4 = B_{\mathbf{q}_1}$, $X_5 = A_{\mathbf{q}_2}, \ldots$). The final distribution may be written in the form

$$P(\mathbf{X}) = (2\pi)^{-(n+1)}(\det \lambda)^{1/2} \exp\Bigg(-\tfrac{1}{2}\sum_{j=1}^{2n+2} \lambda_{jj} d_j^2 - \sum_{j=2}^{2n+2} \lambda_{1j} d_1 d_j - \sum_{j=3}^{2n+2} \lambda_{2j} d_2 d_j - \sum_{j_1 > j_2 = 3}^{2n+2} \lambda_{j_1 j_2} d_{j_1} d_{j_2} \Bigg), \qquad (2)$$

where

$$\lambda = \mathbf{K}^{-1}, \quad \mathbf{K} = \begin{vmatrix} K_{11} & K_{12} & \ldots & K_{1,2n+2} \\ K_{21} & K_{22} & \ldots & K_{2,2n+2} \\ \vdots & \vdots & \ddots & \vdots \\ K_{2n+2,1} & K_{2n+2,2} & \ldots & K_{2n+2,2n+2} \end{vmatrix}.$$

$\mathbf{K}$ is the variance–covariance matrix [by definition, $(\det \mathbf{K}) > 0$].

From (2), formulas estimating $A_{\mathbf{p}}$ or $B_{\mathbf{p}}$ given the prior knowledge of $A_{\mathbf{q}}$ and $B_{\mathbf{q}}$, for $\mathbf{q} = 1, \ldots, n$, were derived [see relationships (GPR1)–(GPR8) of paper IV]. Such formulas require the inversion of the matrix $\mathbf{K}$, which is a difficult and rather lengthy job if n is large.

The calculations become very simple in the canonical case: *e.g.* when $\mathbf{p}$ is a half-integral index and the $\mathbf{q}$'s are standard indices (*option 1*) or, *vice versa*, when $\mathbf{p}$ is a Miller index and the $\mathbf{q}$ are half-integral indices (*option 2*). In this case, the matrix $\mathbf{K}$ assumes the form

$$\mathbf{K} = \begin{vmatrix} K_{11} & 0 & 0 & K_{14} & 0 & K_{16} & 0 & K_{18} & \ldots & K_{1,2n+2} \\ 0 & K_{22} & K_{23} & 0 & K_{25} & 0 & K_{27} & 0 & \ldots & 0 \\ 0 & K_{23} & K_{33} & 0 & 0 & 0 & 0 & 0 & \ldots & 0 \\ K_{14} & 0 & 0 & K_{44} & 0 & 0 & 0 & 0 & \ldots & 0 \\ 0 & K_{25} & 0 & 0 & K_{55} & 0 & 0 & 0 & \ldots & 0 \\ K_{16} & 0 & 0 & 0 & 0 & K_{66} & 0 & 0 & \ldots & 0 \\ 0 & K_{27} & 0 & 0 & 0 & 0 & K_{77} & 0 & \ldots & 0 \\ K_{18} & 0 & 0 & 0 & 0 & 0 & 0 & K_{88} & \ldots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ K_{1,2n+2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & K_{2n+2,2n+2} \end{vmatrix} \qquad (3)$$

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and the inversion of **K** is no longer necessary. Then the following formulas were derived:

$$\begin{aligned}\langle A_{\mathbf{p}}|\{A_{\mathbf{q}}, B_{\mathbf{q}}\}\rangle &= \sum_{\mathbf{q}}\{[K_{14}(\mathbf{p},\mathbf{q})/K_{02}(\mathbf{q})][B_{\mathbf{q}} - K_{01}(\mathbf{q})]\}\\ &= \sum_{\mathbf{q}}\{\Sigma_{11}(\mathbf{p},\mathbf{q})/[\Sigma_2(\mathbf{q})(1-2s_{\mathbf{q}}^2)]\\ &\quad \times (s_{\mathbf{p}+\mathbf{q}} + s_{\mathbf{q}-\mathbf{p}})\}[B_{\mathbf{q}} - \Sigma_1(\mathbf{q})s_{\mathbf{q}}] \quad \text{(CPR1)}\end{aligned}$$

$$\begin{aligned}V_{A_{\mathbf{p}}} &= K_{20}(\mathbf{p}) - \sum_{\mathbf{q}}[K_{14}^2(\mathbf{p},\mathbf{q})/K_{02}(\mathbf{q})]\\ &= \tfrac{1}{2}\Big[\Sigma_2(\mathbf{p}) - \sum_{\mathbf{q}}\big(\{\Sigma_{11}^2(\mathbf{p},\mathbf{q})/[\Sigma_2(\mathbf{q})](1-2s_{\mathbf{q}}^2)\}\\ &\quad \times (s_{\mathbf{p}+\mathbf{q}} + s_{\mathbf{q}-\mathbf{p}})^2\big)\Big] \quad \text{(CPR2)}\end{aligned}$$

$$\begin{aligned}\langle B_{\mathbf{p}}|\{A_{\mathbf{q}}, B_{\mathbf{q}}\}\rangle &= K_{01}(\mathbf{p}) + \sum_{\mathbf{q}}[K_{23}(\mathbf{p},\mathbf{q})/K_{20}(\mathbf{q})]A_{\mathbf{q}}\\ &= \Sigma_1(\mathbf{p})s_{\mathbf{p}} + \sum_{\mathbf{q}}\{[\Sigma_{11}(\mathbf{p},\mathbf{q})/\Sigma_2(\mathbf{q})]\\ &\quad \times (s_{\mathbf{p}+\mathbf{q}} + s_{\mathbf{p}-\mathbf{q}})\}A_{\mathbf{q}} \quad \text{(CPR3)}\end{aligned}$$

$$\begin{aligned}V_{B_{\mathbf{p}}} &= K_{02}(\mathbf{p}) - \sum_{\mathbf{q}}[K_{23}^2(\mathbf{p},\mathbf{q})/K_{20}(\mathbf{q})]\\ &= \tfrac{1}{2}\Big(\Sigma_2(\mathbf{p})(1-2s_{\mathbf{p}}^2) - \sum_{\mathbf{q}}\{[\Sigma_{11}^2(\mathbf{p},\mathbf{q})/\Sigma_2(\mathbf{q})]\\ &\quad \times (s_{\mathbf{p}+\mathbf{q}} + s_{\mathbf{p}-\mathbf{q}})^2\}\Big). \quad \text{(CPR4)}\end{aligned}$$

In terms of pseudonormalized structure factors, equations (CPR1)–(CPR4) may be rewritten as follows (see paper V):

$$\begin{aligned}\langle A_{\mathbf{p}}^N|\{A_{\mathbf{q}}^N, B_{\mathbf{q}}^N\}\rangle &\approx \sum_{\mathbf{q}}[(s_{\mathbf{p}+\mathbf{q}} + s_{\mathbf{q}-\mathbf{p}})/(1-2s_{\mathbf{q}}^2)]\\ &\quad \times [B_{\mathbf{q}}^N - (N_{\text{eff}})^{1/2}s_{\mathbf{q}}] \quad \text{(CPRN1)}\end{aligned}$$

$$V_{A_{\mathbf{p}}^N} \approx \tfrac{1}{2}\Big\{1 - \sum_{\mathbf{q}}[(s_{\mathbf{p}+\mathbf{q}} + s_{\mathbf{q}-\mathbf{p}})^2/(1-2s_{\mathbf{q}}^2)]\Big\} \quad \text{(CPRN2)}$$

$$\langle B_{\mathbf{p}}^N|\{A_{\mathbf{q}}^N, B_{\mathbf{q}}^N\}\rangle \approx (N_{\text{eff}})^{1/2}s_{\mathbf{p}} + \sum_{\mathbf{q}}(s_{\mathbf{p}+\mathbf{q}} + s_{\mathbf{p}-\mathbf{q}})A_{\mathbf{q}}^N \quad \text{(CPRN3)}$$

$$V_{B_{\mathbf{p}}^N} \approx \tfrac{1}{2}\big[(1-2s_{\mathbf{p}}^2) - \sum_{\mathbf{q}}(s_{\mathbf{p}+\mathbf{q}} + s_{\mathbf{p}-\mathbf{q}})^2\big]. \quad \text{(CPRN4)}$$

In the first part of this paper, we will show that structure factors can also be estimated by exploiting special sections (planes or rows) of the reciprocal lattice. To do that, we introduce the following definition: a vectorial index is said to be of mixed type if some of its components are integers and some are half-integers, *e.g.* (p_1, p_2, l), (p_1, k, p_3), (h, p_2, p_3), (h, k, p_3), (h, p_2, l), (p_1, k, l) are all indices of mixed type. We will consider the case in which **p** is of mixed type while the **q**'s are standard Miller indices or, *vice versa*, **p** is a standard index and the **q**'s are of mixed type. We will show that the simplifications of the canonical case also hold for these instances. Accordingly, from now on they will be classified as *options three–six* of the canonical case, in the following order:

(*a*) *option three*: **p** is of type (p_1, p_2, l) or (p_1, k, p_3) or (h, p_2, p_3), and the **q**'s are Miller indices;

(*b*) *option four*: the reverse situation of *option three*;

(*c*) *option five*: **p** is of type (h, k, p_3) or (h, p_2, l) or (p_1, k, l) and the **q**'s are Miller indices;

(*d*) *option six*: the reverse situation of *option five*.

Our probabilistic formulas, estimating real and imaginary parts of $F_{\mathbf{p}}$, can be compared with the geometrical formulas obtained by Mishnev (1996) *via* the method of the Hilbert transform. The reader can easily verify that our approach encompasses Mishnev relations owing to the fact that we are able to provide probabilistic estimates for any subset of data.

The second part of this paper is devoted to triplet-invariant estimates when the triplets are constituted by reflections with rational indices. The concept of 'quasi-invariant' will be introduced to describe triplets of reflections for which the sum of the indices is close but not equal to zero. Their statistical behaviour will be briefly described.

3. The canonical case: probabilistic formulas for *options three* and *four*

In paper IV, the joint probability distribution $P(A_{\mathbf{p}}, B_{\mathbf{p}}, A_{\mathbf{q}}, B_{\mathbf{q}})$ was derived, where **p** and **q** are any rational indices. The final expression for such a distribution [see equation (I.4)] holds for the canonical case too, and may be specialized for *options three* and *four* by properly defining the values of the cumulants. Let us consider the case in which (*option three* of the canonical case):

$$\mathbf{p} = (p_1, p_2, l_1) \quad \text{and} \quad \mathbf{q} = (h, k, l_2)$$

under the conditions

$$l_1 \neq l_2, \quad l_1 \neq 0. \tag{4}$$

According to §3 of paper IV, the cumulants depend on the parameters $\Sigma_1(\mathbf{p})$, $\Sigma_2(\mathbf{p})$, $\Sigma_1(\mathbf{q})$, $\Sigma_2(\mathbf{q})$, $\Sigma_{11}(\mathbf{p},\mathbf{q})$, $c_{\mathbf{p}}$, $s_{\mathbf{p}}$, $c_{2\mathbf{p}}$, $s_{2\mathbf{p}}$, $c_{\mathbf{q}}$, $s_{\mathbf{q}}$, $c_{2\mathbf{q}}$, $s_{2\mathbf{q}}$, $c_{\mathbf{p}+\mathbf{q}}$, $c_{\mathbf{p}-\mathbf{q}}$, $s_{\mathbf{p}+\mathbf{q}}$, $s_{\mathbf{p}-\mathbf{q}}$. While the Σ parameters depend only on the crystal structure (and, therefore, they do not need to be redefined for each special case), the c and s parameters require specific calculations. Since

$$\begin{aligned}c_{\mathbf{p}} &= \cos(\pi p_s)c_{p_1/2}c_{p_2/2}c_{p_3/2}\\ s_{\mathbf{p}} &= \sin(\pi p_s)c_{p_1/2}c_{p_2/2}c_{p_3/2}\\ c_{p_i} &= \sin(2\pi p_i)/(2\pi p_i)\\ s_{p_i} &= [1-\cos(2\pi p_i)]/(2\pi p_i),\end{aligned}$$

the following results easily follow:

(*a*) owing to the fact that at least one component of the vectorial indices $\mathbf{p}$ and $\mathbf{q}$ are integers,

$$c_{\mathbf{p}} \equiv s_{\mathbf{p}} \equiv c_{\mathbf{q}} \equiv s_{\mathbf{q}} \equiv c_{2\mathbf{p}} \equiv s_{2\mathbf{p}} \equiv c_{2\mathbf{q}} \equiv s_{2\mathbf{q}} \equiv c_{\mathbf{p}+\mathbf{q}} \equiv s_{\mathbf{p}+\mathbf{q}} \equiv c_{\mathbf{p}-\mathbf{q}} \equiv s_{\mathbf{p}-\mathbf{q}} \equiv 0;$$

(*b*)

$$\begin{aligned} &K_{10}(\mathbf{p}) \equiv K_{01}(\mathbf{p}) \equiv K_{10}(\mathbf{q}) \equiv K_{01}(\mathbf{q}) \equiv 0 \\ &K_{20}(\mathbf{p}) = K_{02}(\mathbf{p}) = \Sigma_2(\mathbf{p})/2 \\ &K_{20}(\mathbf{q}) = K_{02}(\mathbf{q}) = \Sigma_2(\mathbf{q})/2 \\ &K_{12}(\mathbf{p}) \equiv K_{34}(\mathbf{p}) \equiv 0; \end{aligned}$$

(*c*)

$$K_{13}(\mathbf{p},\mathbf{q}) \equiv K_{14}(\mathbf{p},\mathbf{q}) \equiv K_{23}(\mathbf{p},\mathbf{q}) \equiv K_{24}(\mathbf{p},\mathbf{q}) \equiv 0.$$

The same results also occur for the *fourth option* of the canonical case; *i.e.*

$$\mathbf{p} = (h, k, l_2) \quad \text{and} \quad \mathbf{q} = (q_1, q_2, l_1),$$

with

$$l_2 \neq l_1, \quad l_2 \neq 0. \tag{5}$$

It may be concluded that, for *options three* and *four* of the canonical case, under the conditions (4) and (5), the joint probability distribution $P(A_{\mathbf{p}}, B_{\mathbf{p}}, A_{\mathbf{q}}, B_{\mathbf{q}})$ is nothing but the product of the two Wilson distributions:

$$P(A_{\mathbf{p}}, B_{\mathbf{p}}, A_{\mathbf{q}}, B_{\mathbf{q}}) \approx P_W(A_{\mathbf{p}}, B_{\mathbf{p}}) P_W(A_{\mathbf{q}}, B_{\mathbf{q}}).$$

Let us consider the case in which $\mathbf{p}$ and $\mathbf{q}$ belong to the reciprocal-lattice plane defined by l = constant:

$$\mathbf{p} = (p_1, p_2, l), \quad \mathbf{q} = (hkl), \quad \text{with} \quad l \neq 0. \tag{6}$$

In this case,

$$c_{\mathbf{p}} \equiv s_{\mathbf{p}} \equiv c_{\mathbf{q}} \equiv s_{\mathbf{q}} \equiv c_{2\mathbf{p}} \equiv s_{2\mathbf{p}} \equiv c_{2\mathbf{q}} \equiv s_{2\mathbf{q}} \equiv c_{\mathbf{p}+\mathbf{q}} \equiv s_{\mathbf{p}+\mathbf{q}} \equiv s_{\mathbf{p}-\mathbf{q}} \equiv 0$$

but

$$\begin{aligned} c_{\mathbf{p}-\mathbf{q}} &= \cos \pi (p_s - q_s) c_{(p_1-q_1)/2} c_{(p_2-q_2)/2} \\ &= -\pi^{-2}[(p_1-q_1)(p_2-q_2)]^{-1}. \end{aligned}$$

Furthermore,

$$\begin{aligned} &K_{10}(\mathbf{p}) \equiv K_{01}(\mathbf{p}) \equiv K_{10}(\mathbf{q}) \equiv K_{01}(\mathbf{q}) \equiv 0 \\ &K_{20}(\mathbf{p}) = K_{02}(\mathbf{p}) = \Sigma_2(\mathbf{p})/2 \\ &K_{20}(\mathbf{q}) = K_{02}(\mathbf{q}) = \Sigma_2(\mathbf{q})/2 \\ &K_{12}(\mathbf{p}) \equiv K_{34}(\mathbf{p}) \equiv K_{14}(\mathbf{p},\mathbf{q}) = K_{23}(\mathbf{p},\mathbf{q}) = 0 \end{aligned}$$

but

$$K_{13}(\mathbf{p},\mathbf{q}) \equiv K_{24}(\mathbf{p},\mathbf{q}) \equiv 0.5\Sigma_{11}(\mathbf{p},\mathbf{q}) c_{\mathbf{p}-\mathbf{q}}.$$

We can now consider the distribution

$$P(A_{\mathbf{p}}, B_{\mathbf{p}}, A_{\mathbf{q}_1}, B_{\mathbf{q}_1}, A_{\mathbf{q}_2}, B_{\mathbf{q}_2}, \ldots, A_{\mathbf{q}_n}, B_{\mathbf{q}_n})$$

under the condition that $\mathbf{q}_i \equiv (h_i, k_i, l)$ (in this case, we try to estimate $F_{\mathbf{p}}$ from reflections belonging to the same section of the reciprocal lattice). The above cumulant expressions suggest that the matrix $\mathbf{K}$ has the form

$$\mathbf{K} = \begin{vmatrix} K_{11} & 0 & K_{13} & 0 & K_{15} & 0 & K_{17} & 0 & \ldots & 0 \\ 0 & K_{22} & 0 & K_{24} & 0 & K_{26} & 0 & K_{28} & \ldots & K_{2,2n+2} \\ K_{13} & 0 & K_{33} & 0 & 0 & 0 & 0 & 0 & \ldots & 0 \\ 0 & K_{24} & 0 & K_{44} & 0 & 0 & 0 & 0 & \ldots & 0 \\ K_{15} & 0 & 0 & 0 & K_{55} & 0 & 0 & 0 & \ldots & 0 \\ 0 & K_{26} & 0 & 0 & 0 & K_{66} & 0 & 0 & \ldots & 0 \\ K_{17} & 0 & 0 & 0 & 0 & 0 & K_{77} & 0 & \ldots & 0 \\ 0 & K_{28} & 0 & 0 & 0 & 0 & 0 & K_{88} & \ldots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & K_{2,2n+2} & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & K_{2n+2,2n+2} \end{vmatrix},$$

which is not coincident with equation (IV.3), but may be algebraically treated in a similar way to that described in paper IV. After the necessary calculations, not shown for brevity, we obtain, for *option three*, the following relationships:

$$\langle A_{\mathbf{p}} | \{A_{\mathbf{q}}, B_{\mathbf{q}}\} \rangle = \sum_{\mathbf{q}} \{[\Sigma_{11}(\mathbf{p},\mathbf{q})/\Sigma_2(\mathbf{q})] c_{\mathbf{p}-\mathbf{q}}\} A_{\mathbf{q}} \tag{7}$$

$$\begin{aligned} V_{A_{\mathbf{p}}} &= \Sigma_2(\mathbf{p})/2 - \sum_{\mathbf{q}} \{K_{13}^2(\mathbf{p},\mathbf{q})/[\Sigma_2(\mathbf{q})/2]\} \\ &= \Sigma_2(\mathbf{p})/2 - \tfrac{1}{2} \sum_{\mathbf{q}} \{[\Sigma_{11}^2(\mathbf{p},\mathbf{q})/\Sigma_2(\mathbf{q})] c_{\mathbf{p}-\mathbf{q}}^2\} \end{aligned} \tag{8}$$

$$\langle B_{\mathbf{p}} | \{A_{\mathbf{q}}, B_{\mathbf{q}}\} \rangle = \sum_{\mathbf{q}} \{[\Sigma_{11}(\mathbf{p},\mathbf{q})/\Sigma_2(\mathbf{q})] c_{\mathbf{p}-\mathbf{q}}\} B_{\mathbf{q}} \tag{9}$$

$$V_{B_{\mathbf{p}}} = \Sigma_2(\mathbf{p})/2 - \tfrac{1}{2} \sum_{\mathbf{q}} \{[\Sigma_{11}^2(\mathbf{p},\mathbf{q})/\Sigma_2(\mathbf{q})] c_{\mathbf{p}-\mathbf{q}}^2\}. \tag{10}$$

In a pseudonormalized form, we can rewrite (7)–(10) as

$$\langle A_{\mathbf{p}}^N | \{A_{\mathbf{q}}^N, B_{\mathbf{q}}^N\} \rangle = \sum_{\mathbf{q}} c_{\mathbf{p}-\mathbf{q}} A_{\mathbf{q}}^N \tag{MCPR1}$$

$$V_{A_{\mathbf{p}}^N} = 0.5\left(1 - \sum_{\mathbf{q}} c_{\mathbf{p}-\mathbf{q}}^2\right) \tag{MCPR2}$$

$$\langle B_{\mathbf{p}}^N | \{A_{\mathbf{q}}^N, B_{\mathbf{q}}^N\} \rangle = \sum_{\mathbf{q}} c_{\mathbf{p}-\mathbf{q}} B_{\mathbf{q}}^N \tag{MCPR3}$$

$$V_{B_{\mathbf{p}}^N} = 0.5\left(1 - \sum_{\mathbf{q}} c_{\mathbf{p}-\mathbf{q}}^2\right). \tag{MCPR4}$$

In accordance with §1.4 of paper V, we estimate structure-factor moduli and phases as follows:

$$|E_{\mathbf{p}}|_{\text{est}}^2 = \langle |E_{\mathbf{p}}|^2 \big| \{|E_{\mathbf{q}}|, \phi_{\mathbf{q}}\} \rangle = \langle |A_{\mathbf{p}}^N|^2 \big| \ldots \rangle + \langle |B_{\mathbf{p}}^N|^2 \big| \ldots \rangle, \tag{MCPR5}$$

$$\langle \phi_{\mathbf{p}} | \ldots \rangle = \tan^{-1}[\langle B_{\mathbf{p}}^N | \ldots \rangle / \langle A_{\mathbf{p}}^N | \ldots \rangle], \tag{MCPR6}$$

with variance

$$V_{|E_{\mathbf{p}}|} = \sigma_{|E_{\mathbf{p}}|}^2 = V_{A_{\mathbf{p}}^N} + V_{B_{\mathbf{p}}^N}. \tag{MCPR7}$$

It may be shown that the formulas (MCPR1)–(MCPR7) hold also for *option four*. We observe:

(i) $A_{\mathbf{p}}$ depends on the prior knowledge of the $A_{\mathbf{q}}$'s and not, as in (CPRN1)–(CPRN4) (full three-dimensional case), on the $B_{\mathbf{q}}$'s. Equivalently, the estimate of $B_{\mathbf{p}}$ depends on the prior information of the $B_{\mathbf{q}}$'s.

(ii) Only one reciprocal-lattice plane contributes to the estimation of $F_{\mathbf{p}}$. *E.g*:

(*a*) If $\mathbf{p} = (p_1, p_2, l_3)$, then only the plane (h, k, l_3) contributes. Then

$$c_{\mathbf{p}-\mathbf{q}} = -\pi^{-2}[(p_1 - h)(p_2 - k)]^{-1}.$$

(*b*) If $\mathbf{p} = (p_1, k_2, p_3)$, then only the plane (h, k_2, l) contributes to estimate $F_{\mathbf{p}}$. Then,

$$c_{\mathbf{p}-\mathbf{q}} = -\pi^{-2}[(p_1 - h)(p_3 - l)]^{-1}.$$

(*c*) If $\mathbf{p} = (h_1, p_2, p_3)$, then only the plane (h_1, k, l) contributes to $\langle F_{\mathbf{p}} | \ldots \rangle$. Then,

$$c_{\mathbf{p}-\mathbf{q}} = -\pi^{-2}[(p_2 - k)(p_3 - l)]^{-1}.$$

4. A special case of *options three* and *four*

Let us consider the case in which (*option three*)

$$\mathbf{p} = (p_1, p_2, 0) \quad \text{and} \quad \mathbf{q} = (h, k, 0).$$

We can look at this situation as a special section of the three-dimensional lattice or a full bi-dimensional situation.

Then,

$$\begin{aligned} c_{\mathbf{p}} &= -\pi^{-2}(p_1 p_2)^{-1} \\ c_{\mathbf{p}-\mathbf{q}} &= -\pi^{-2}[(p_1 - h)(p_2 - k)]^{-1} \\ c_{\mathbf{p}+\mathbf{q}} &= -\pi^{-2}[(p_1 + h)(p_2 + k)]^{-1} \end{aligned}$$

$$s_{\mathbf{p}} \equiv c_{\mathbf{q}} \equiv s_{\mathbf{q}} \equiv c_{2\mathbf{p}} \equiv s_{2\mathbf{p}} \equiv c_{2\mathbf{q}} \equiv s_{2\mathbf{q}} \equiv s_{\mathbf{p}+\mathbf{q}} \equiv s_{\mathbf{p}-\mathbf{q}} \equiv 0.$$

Accordingly, the cumulants of the distribution $P(A_{\mathbf{p}}, B_{\mathbf{p}}, A_{\mathbf{q}}, B_{\mathbf{q}})$ are:

$$\begin{aligned} K_{10}(\mathbf{p}) &= \Sigma_1(\mathbf{p}) c_{\mathbf{p}} \\ K_{01}(\mathbf{p}) &= K_{10}(\mathbf{q}) = K_{01}(\mathbf{q}) = 0 \\ K_{20}(\mathbf{p}) &= \Sigma_2(\mathbf{p})(1 - 2c_{\mathbf{p}}^2)/2 \\ K_{02}(\mathbf{p}) &= \Sigma_2(\mathbf{p})/2 \\ K_{20}(\mathbf{q}) &= K_{02}(\mathbf{q}) = \Sigma_2(\mathbf{q})/2 \\ K_{12}(\mathbf{p}) &= K_{34}(\mathbf{q}) = K_{14}(\mathbf{p}, \mathbf{q}) = K_{23}(\mathbf{p}, \mathbf{q}) = 0 \\ K_{13}(\mathbf{p}, \mathbf{q}) &= \Sigma_{11}(\mathbf{p}, \mathbf{q})(c_{\mathbf{p}+\mathbf{q}} + c_{\mathbf{p}-\mathbf{q}})/2 \\ K_{24}(\mathbf{p}, \mathbf{q}) &= \Sigma_{11}(\mathbf{p}, \mathbf{q})(c_{\mathbf{p}-\mathbf{q}} - c_{\mathbf{p}+\mathbf{q}})/2. \end{aligned}$$

Let us consider, for *option four*, the case in which

$$\mathbf{p} = (h, k, 0) \quad \text{and} \quad \mathbf{q} = (q_1, q_2, 0).$$

Then, $c_{\mathbf{p}} \equiv 0$, $c_{\mathbf{q}} = -\pi^{-2}(q_1 q_2)^{-1}$ and

$$\begin{aligned} c_{\mathbf{p}-\mathbf{q}} &= -\pi^{-2}[(p_1 - h)(p_2 - k)]^{-1} \\ c_{\mathbf{p}+\mathbf{q}} &= -\pi^{-2}[(p_1 + h)(p_2 + k)]^{-1}. \end{aligned}$$

The same procedure described in §3 leads to the following formulas, valid for both options:

$$\langle A_{\mathbf{p}} | \{A_{\mathbf{q}}, B_{\mathbf{q}}\} \rangle = K_{10}(\mathbf{p}) + \sum_{\mathbf{q}} [K_{13}(\mathbf{p}, \mathbf{q})/K_{20}(\mathbf{q})] \times [A_{\mathbf{q}} - K_{10}(\mathbf{q})] \qquad (11)$$

$$V_{A_{\mathbf{p}}} = K_{20}(\mathbf{p}) - \sum_{\mathbf{q}} [K_{13}^2(\mathbf{p}, \mathbf{q})/K_{20}(\mathbf{q})] \qquad (12)$$

$$\langle B_{\mathbf{p}} | \{A_{\mathbf{q}}, B_{\mathbf{q}}\} \rangle = \sum_{\mathbf{q}} [K_{24}(\mathbf{p}, \mathbf{q})/K_{02}(\mathbf{q})] B_{\mathbf{q}} \qquad (13)$$

$$V_{B_{\mathbf{p}}} = K_{02}(\mathbf{p}) - \sum_{\mathbf{q}} [K_{24}^2(\mathbf{p}, \mathbf{q})/K_{02}(\mathbf{q})]. \qquad (14)$$

For *option three*, equations (11)–(14), in terms of pseudonormalized structure factors, reduce to

$$\langle A_{\mathbf{p}}^N | \{A_{\mathbf{q}}^N, B_{\mathbf{q}}^N\} \rangle \approx (N_{\text{eff}})^{1/2} c_{\mathbf{p}} + \sum_{\mathbf{q}} (c_{\mathbf{p}+\mathbf{q}} + c_{\mathbf{p}-\mathbf{q}}) A_{\mathbf{q}}^N \qquad (15)$$

$$V_{A_{\mathbf{p}}^N} = \tfrac{1}{2} - [1/2(1 - 2c_{\mathbf{p}}^2)] \sum_{\mathbf{q}} (c_{\mathbf{p}+\mathbf{q}} + c_{\mathbf{p}-\mathbf{q}})^2 \qquad (16)$$

$$\langle B_{\mathbf{p}}^N | \{A_{\mathbf{q}}^N, B_{\mathbf{q}}^N\} \rangle = \sum_{\mathbf{q}} (c_{\mathbf{p}-\mathbf{q}} + c_{\mathbf{p}+\mathbf{q}}) B_{\mathbf{q}}^N \qquad (17)$$

$$V_{B_{\mathbf{p}}^N} = \tfrac{1}{2} - \tfrac{1}{2} \sum_{\mathbf{q}} (c_{\mathbf{p}-\mathbf{q}} - c_{\mathbf{p}+\mathbf{q}})^2, \qquad (18)$$

where

$$c_{\mathbf{p}} = -\pi^{-2}(p_1 p_2)^{-1}, \quad c_{\mathbf{p}\pm\mathbf{q}} = -\pi^{-2}[(p_1 \pm h)(p_2 \pm k)]^{-1}.$$

For *option four*, equations (11)–(14) reduce to

$$\langle A_{\mathbf{p}}^N | \{A_{\mathbf{q}}^N, B_{\mathbf{q}}^N\} \rangle = \sum_{\mathbf{q}} [(c_{\mathbf{p}+\mathbf{q}} + c_{\mathbf{p}-\mathbf{q}})/(1 - 2c_{\mathbf{q}}^2)] \times [A_{\mathbf{q}}^N - (N_{\text{eff}})^{1/2} c_{\mathbf{q}}] \qquad (19)$$

$$V_{A_{\mathbf{p}}^N} = \tfrac{1}{2} - \tfrac{1}{2} \sum_{\mathbf{q}} [(c_{\mathbf{p}+\mathbf{q}} + c_{\mathbf{p}-\mathbf{q}})^2/(1 - 2c_{\mathbf{q}}^2)] \qquad (20)$$

$$\langle B_{\mathbf{p}}^N | \{A_{\mathbf{q}}^N, B_{\mathbf{q}}^N\} \rangle = \sum_{\mathbf{q}} (c_{\mathbf{p}-\mathbf{q}} - c_{\mathbf{p}+\mathbf{q}}) B_{\mathbf{q}}^N \qquad (21)$$

$$V_{B_{\mathbf{p}}^N} = \tfrac{1}{2} - \tfrac{1}{2} \sum_{\mathbf{q}} (c_{\mathbf{p}-\mathbf{q}} - c_{\mathbf{p}+\mathbf{q}})^2. \qquad (22)$$

5. The canonical case: probabilistic formulas for *options five* and *six*

Let us consider the case in which

$$\mathbf{p} = (p_1, k_1, l_1) \quad \text{and} \quad \mathbf{q} = (h, k_2, l_2)$$
$$\text{with } k_1 \neq k_2 \text{ and/or } l_1 \neq l_2.$$

In accordance with §3, the distribution

Table 1. *Statistical outcome for the estimates of the reflections of type (h, p_2, p_3) estimated from the standard structure factors via equations (MCPR5)–(MCPR7)*

NM is the number of reflections of type (h, p_2, p_3) with $|E|_{\rm est}/\sigma_{|E|}$ larger than RATIO.

RATIO	NM	ERR (°)	R
0.0	4638	24.86	0.22
1.2	3930	18.30	0.20
3.0	2424	11.89	0.17
4.8	1220	8.91	0.14
6.6	520	7.22	0.12
8.4	174	6.19	0.11
10.2	55	4.80	0.08
12.0	17	3.88	0.10

Table 2. *Statistical outcome for the estimates of the standard reflections from mixed reflections of type (h, p_2, p_3)*

NI is the number of standard reflections with $|E|_{\rm est}/\sigma_{|E|}$ larger than RATIO.

RATIO	NM	ERR (°)	R
0.0	4100	24.38	0.23
1.2	3539	18.07	0.21
3.0	2221	11.26	0.18
4.8	1153	8.59	0.15
6.6	515	6.95	0.13
8.4	193	6.09	0.11
10.2	71	5.85	0.08
12.0	26	5.19	0.06

$$P(A_{\mathbf{p}}, B_{\mathbf{p}}, A_{\mathbf{q}}, B_{\mathbf{q}}) \equiv P(A_{\mathbf{p}}, B_{\mathbf{p}})P(A_{\mathbf{q}}, B_{\mathbf{q}})$$

does not provide any information on $A_{\mathbf{p}}$ or $B_{\mathbf{p}}$ given $(A_{\mathbf{q}}, B_{\mathbf{q}})$. Suppose now that $k_1 \equiv k_2$ and $l_1 \equiv l_2$. In this case,

$$c_{\mathbf{p}} \equiv s_{\mathbf{p}} \equiv c_{\mathbf{q}} \equiv s_{\mathbf{q}} \equiv c_{2\mathbf{p}} \equiv s_{2\mathbf{p}} \equiv c_{2\mathbf{q}} \equiv s_{2\mathbf{q}} \equiv c_{\mathbf{p}+\mathbf{q}} \equiv c_{\mathbf{p}-\mathbf{q}} \equiv s_{\mathbf{p}+\mathbf{q}} \equiv 0$$

but

$$s_{\mathbf{p}-\mathbf{q}} = \pi^{-1}(p_1 - q_1)^{-1}.$$

Furthermore,

$$\begin{aligned} K_{10}(\mathbf{p}) &\equiv K_{01}(\mathbf{p}) \equiv K_{10}(\mathbf{q}) \equiv K_{01}(\mathbf{q}) \equiv 0 \\ K_{20}(\mathbf{p}) &= K_{02}(\mathbf{p}) = \Sigma_2(\mathbf{p})/2 \\ K_{20}(\mathbf{q}) &= K_{02}(\mathbf{q}) = \Sigma_2(\mathbf{q})/2 \\ K_{12}(\mathbf{p}) &\equiv K_{34}(\mathbf{q}) \equiv K_{13}(\mathbf{p}, \mathbf{q}) = K_{24}(\mathbf{p}, \mathbf{q}) = 0 \\ K_{14}(\mathbf{p}, \mathbf{q}) &= -K_{23}(\mathbf{p}, \mathbf{q}) \equiv \Sigma_{11}(\mathbf{p}, \mathbf{q}) s_{\mathbf{q}-\mathbf{p}}/2. \end{aligned}$$

Therefore, $A_{\mathbf{p}}$ and $B_{\mathbf{p}}$ may be estimated *via* the reflections belonging to a lattice row according to:

$$\langle A_{\mathbf{p}} | \{A_{\mathbf{q}}, B_{\mathbf{q}}\}\rangle = \sum_{\mathbf{q}} \{[\Sigma_{11}(\mathbf{p}, \mathbf{q})/\Sigma_2(\mathbf{q})] s_{\mathbf{q}-\mathbf{p}}\} B_{\mathbf{q}} \quad (23)$$

$$V_{A_{\mathbf{p}}} = 0.5\left(\Sigma_2(\mathbf{p}) - \sum_{\mathbf{q}} \{[\Sigma_{11}^2(\mathbf{p}, \mathbf{q})/\Sigma_2(\mathbf{q})] s_{\mathbf{q}-\mathbf{p}}^2\}\right) \quad (24)$$

$$\langle B_{\mathbf{p}} | \{A_{\mathbf{q}}, B_{\mathbf{q}}\}\rangle = -\sum_{\mathbf{q}} \{[\Sigma_{11}(\mathbf{p}, \mathbf{q})/\Sigma_2(\mathbf{q})] s_{\mathbf{q}-\mathbf{p}}\} A_{\mathbf{q}} \quad (25)$$

$$V_{B_{\mathbf{p}}} = 0.5\left(\Sigma_2(\mathbf{p}) - \sum_{\mathbf{q}} \{[\Sigma_{11}^2(\mathbf{p}, \mathbf{q})/\Sigma_2(\mathbf{q})] s_{\mathbf{q}-\mathbf{p}}^2\}\right). \quad (26)$$

In terms of normalized structure factors,

$$\langle A_{\mathbf{p}}^N | \{A_{\mathbf{q}}^N, B_{\mathbf{q}}^N\}\rangle = \sum_{\mathbf{q}} s_{\mathbf{q}-\mathbf{p}} B_{\mathbf{q}}^N \quad (27)$$

$$V_{A_{\mathbf{p}}^N} = 0.5\left(1 - \sum_{\mathbf{q}} s_{\mathbf{q}-\mathbf{p}}^2\right) \quad (28)$$

$$\langle B_{\mathbf{p}}^N | \{A_{\mathbf{q}}^N, B_{\mathbf{q}}^N\}\rangle = -\sum_{\mathbf{q}} s_{\mathbf{q}-\mathbf{p}} A_{\mathbf{q}}^N \quad (29)$$

$$V_{B_{\mathbf{p}}^N} = 0.5\left(1 - \sum_{\mathbf{q}} s_{\mathbf{q}-\mathbf{p}}^2\right). \quad (30)$$

In conclusion, the reflections $F_{p_1 k_2 l_3}$ may be evaluated by exploiting the prior knowledge of the reflections $F_{h k_2 l_3}$, where h is a free index. Analogously, the formulas (23)–(30) can be applied to the equivalent cases in which:

(*a*) $\mathbf{p} = (h_1 p_2 l_3)$ and $\mathbf{q} = (h_1 k l_3)$ with free k index. In this case,

$$s_{\mathbf{q}-\mathbf{p}} = \pi^{-1}(p_2 - k)^{-1};$$

(*b*) $\mathbf{p} = (h_1 h_2 p_3)$ and $\mathbf{q} = (h_1 h_2 l)$ with free l index. In this case,

$$s_{\mathbf{q}-\mathbf{p}} = \pi^{-1}(p_3 - l)^{-1}.$$

6. Experimental tests for cases with reduced dimensionality

In the following calculations, we have used SCHWARZ [Schweizer (undated); a = 9.049, b = 13.609, c = 13.650 Å, α = 72.79, β = 86.37, γ = 85.21°; $C_{46}H_{70}O_{27}$; space group $P1$] as the test structure. To compare the estimates with the true values, we have computed, from the published atomic parameters, the normalized structure factors $E_{\rm true}$ of the standard and the mixed-type reflections. In Table 1, we show the number (NM) of reflections of type $(h, p_2 p_3)$ with $|E|_{\rm est}/\sigma_{|E|}$ larger than RATIO [as estimated from the standard structure factors *via* equations (MCPR5)–(MCPR7)], the relative average phase error (ERR) and the discrepancy index R given by

$$R = \sum \big| |E|_{\rm est} - |E|_{\rm true} \big| \Big/ \sum |E|_{\rm true}.$$

All the standard reflections were used to estimate each mixed-type reflection. We observe that:

(i) $|E|_{\rm est}/\sigma_{|E|}$ is a good ranking parameter that is able to pick up the reflections accurately determined.

Table 3. *Statistics for the other options considered in* §3

Reflection type	NR	ERR (°)	R
(h, p_2, p_3) from (h, k, l)	4638	24.9	0.22
(p_1, k, p_3) from (h, k, l)	4752	27.0	0.25
(p_1, p_2, l) from (h, k, l)	4674	27.5	0.26
(h, k, l) from (h, p_2, p_3)	4100	24.4	0.23
(h, k, l) from (p_1, k, p_3)	4100	24.0	0.22
(h, k, l) from (p_1, p_2, l)	4100	26.1	0.24

Table 4. *JAMILAS: triplets found among reflections with* $|E| > 1.8$

The entries refer to (*a*) triplets with integral indices, (*b*) triplets constituted by two rational index reflections and one integral index reflection. NTRIPL = number of triplets with $G > \text{ARG}$, $\langle|\Phi|\rangle$ is the average value of $|\Phi|$.

(*a*) ARG	NTRIPL	$\langle\|\Phi\|\rangle$	(*b*) ARG	NTRIPL	$\langle\|\Phi\|\rangle$
0.0	11794	24.4	0.0	3079	18.5
2.0	11201	23.6	2.0	2716	18.1
3.8	3150	17.7	3.8	343	18.7
5.5	633	13.6	5.5	39	21.8
9.0	34	8.7	9.0	2	16.5

(ii) Both ERR and R decrease with $|E|_{\text{est}}/\sigma_{|E|}$. When this last parameter falls to values smaller than unity, the estimates are unreliable (the value of ERR for the 708 reflections with $|E|_{\text{est}}/\sigma_{|E|} < 1.2$ is 61°).

In Table 2, the reverse case is considered [standard reflections are estimated from mixed-type reflections of type (hp_2p_3)]. The results are of equivalent quality. In Table 3, we show some statistics over the other options considered in §3. The tests prove the efficiency of our probabilistic formulas.

7. About triplet invariants and triplet quasi-invariant estimates

Triplet invariants involving integral index reflections play a fundamental role for the solution of the phase problem: their value does not depend on the origin and can be evaluated from the diffraction magnitudes. Do triplets involving rational indices preserve the same properties? The answer is certainly yes because:

(i) If $F_{\mathbf{p}_1}, F_{\mathbf{p}_2}, F_{\mathbf{p}_3}$ are a triple of reflections with rational indices, with $\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3$ satisfying $\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 = 0$, then

$$F'_{\mathbf{p}_1}F'_{\mathbf{p}_2}F'_{\mathbf{p}_3} = F_{\mathbf{p}_1}F_{\mathbf{p}_2}F_{\mathbf{p}_3}\exp[-2\pi i(\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3)\mathbf{X}_0] = F_{\mathbf{p}_1}F_{\mathbf{p}_2}F_{\mathbf{p}_3} \qquad (31)$$

as for integral index triplets. In (31), $\mathbf{X}_0$ is a general origin shift and F' is the structure factor calculated with respect to the new origin. Equation (31) suggests the following definition: $F_{\mathbf{p}_1}F_{\mathbf{p}_2}F_{\mathbf{p}_3}$ is a triplet invariant if $\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 = 0$ for $\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3$ rational indices.

Table 5. *BOBBY: triplets found among reflections with* $|E| > 1.8$

The entries refer to (*a*) triplets with integral indices, (*b*) triplets constituted by two rational index reflections and one integral index reflection. NTRIPL = number of triplets with $G > \text{ARG}$, $\langle|\Phi|\rangle$ is the average value of $|\Phi|$.

(*a*) ARG	NTRIPL	$\langle\|\Phi\|\rangle$	(*b*) ARG	NTRIPL	$\langle\|\Phi\|\rangle$
0.0	2569	42.9	0.0	10758	49.3
0.8	2458	41.9	0.8	9630	47.5
2.0	678	26.3	2.0	1220	45.5
3.8	67	19.1	3.8	75	57.0
5.5	5	18.8	5.5	9	29.7

Table 6. *SCHWARZ: triplets found among reflections with* $|E| > 1.6$

The entries refer to (*a*) triplets with integral indices, (*b*) triplets constituted by two rational index reflections and one integral index reflection. NTRIPL = number of triplets with $G > \text{ARG}$, $\langle|\Phi|\rangle$ is the average value of $|\Phi|$.

(*a*) ARG	NTRIPL	$\langle\|\Phi\|\rangle$	(*b*) ARG	NTRIPL	$\langle\|\Phi\|\rangle$
0.0	3852	35.7	0.0	5532	35.5
1.2	3696	35.3	1.2	5050	34.2
2.0	1465	28.0	2.0	1356	28.0
3.8	106	18.8	3.8	49	18.7
5.5	15	12.7	5.5	4	12.2

(ii) The triplet phase probability will be based on the positivity and on the atomicity of the electron density, as for traditional triplet invariants. We argue then that the Cochran (1955) relationship

$$P(\Phi) \approx [2\pi I_0(G)]^{-1}\exp(G\cos\Phi), \qquad (32)$$

where $\Phi = \phi_{\mathbf{p}_1} + \phi_{\mathbf{p}_2} + \phi_{\mathbf{p}_3}$ and $G = 2|E_{\mathbf{p}_1}E_{\mathbf{p}_2}E_{\mathbf{p}_3}|/N^{1/2}$, will hold for rational index triplets too.

The general efficiency of (32) is checked in Tables 4, 5 and 6 for two types of triplets (triplets involving three half-integral reflections cannot exist): (*a*) triplets constituted by integral index reflections; (*b*) triplets involving two half-integral and one integral index reflection [*e.g.* $\mathbf{p}_1 \equiv (2.5, 3.5, \overline{1.5})$, $\mathbf{p}_2 \equiv (4.5, \overline{8.5}, 6.5)$, $\mathbf{p}_3 \equiv (\bar{7}, 5, \bar{5})$].

We have used JAMILAS [Dobson *et al.* (1990), $K_4C_{64}H_{28}N_8O_{20}S_4$; $a = 9.377$, $b = 12.495$, $c = 15.321$ Å, $\alpha = 93.536$, $\beta = 99.335$, $\gamma = 90.173$°; space group $P1$]; BOBBY [Barnett (undated); Na^+Ca^{2+}. $N(CH_2CO_2)_3^{3-}$; $a = 9.626$ Å; space group $P2_13$] and SCHWARZ as test structures. In this second case, we expanded cubic to triclinic symmetry to simulate a $P1$ group. In both cases, structure factors were calculated from the published coordinates. The tests clearly show that the Cochran formula can be applied to both types of triplet invariants without any relevant modification. Indeed, the triplet

Table 7. *JAMILAS: quasi-triplets found among reflections with $|E| > 1.8$*

The entries in (*a*) refer to triplet quasi-invariants for which $\Delta_i = 0$ or ±0.2 for $i = 1, 2, 3$; the entries in (*b*) refer to triplet quasi-invariants for which $\Delta_i = 0$ or ±0.4 for $i = 1, 2, 3$. NQTRIPL = number of triplet quasi-invariants with $G >$ ARG, $\langle|\Phi|\rangle$ is the average value of $|\Phi|$.

(*a*)

ARG	NTRIPL	$\langle\|\Phi\|\rangle$
0.0	3161	29.2
2.0	2828	28.9
3.8	458	23.8
5.5	153	18.1
9.0	18	12.6

(*b*)

ARG	NTRIPL	$\langle\|\Phi\|\rangle$
0.0	3657	51.9
2.0	3403	51.4
3.8	633	50.0
5.5	292	46.6
9.0	77	46.8

Table 8. *BOBBY: quasi-triplets found among reflections with $|E| > 1.8$*

The entries in (*a*) refer to triplet quasi-invariants for which $\Delta_i = 0$ or ±0.2 for $i = 1, 2, 3$; the entries in (*b*) refer to triplet quasi-invariants for which $\Delta_i = 0$ or ±0.4 for $i = 1, 2, 3$. NQTRIPL = number of triplet quasi-invariants with $G >$ ARG, $\langle|\Phi|\rangle$ is the average value of $|\Phi|$.

(*a*)

ARG	NTRIPL	$\langle\|\Phi\|\rangle$
0.0	3062	47.9
1.2	2743	47.4
2.0	767	46.8
3.8	60	65.5
4.4	24	76.1

(*b*)

ARG	NTRIPL	$\langle\|\Phi\|\rangle$
0.0	1914	78.9
1.2	1706	79.5
2.0	363	81.3
3.8	90	78.0
4.4	60	81.2

phase deviations from zero are of the same order for the two types of invariants and for any value of *G*.

When rational indices are used, it may be much easier to find indices $\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3$ whose vectorial sum is close to zero rather than exactly equal to zero. Therefore, an important question may be: how is the phase Φ distributed when $\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3$ is close but not equal to zero? For example, is Φ expected to be close to zero if

$$\mathbf{p}_1 = (3, 6, \bar{4}), \quad \mathbf{p}_2 = (2.48, 3.18, 2.37),$$
$$\mathbf{p}_3 = (\overline{5.40}, \overline{9.02}, 1.48)$$

and $|E_{\mathbf{p}_1}|, |E_{\mathbf{p}_2}|, |E_{\mathbf{p}_3}|$ are all large? Of course, (31) will no longer hold, but the triplet quasi-invariants could 'on average' retain phase values close to zero, and therefore they could be used for crystal structure solution. More precisely, it may be expected that the Cochran formula will approximately hold when the $|\Delta_i|$'s are small and will fail when they are sufficiently large. This expectation is confirmed by Tables 7, 8 and 9. Sections (*a*) of the tables refer to triplet quasi-invariants for which $\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 = (\Delta_1, \Delta_3, \Delta_3)$, where Δ_i may be 0 or ±0.2 for $i = 1, 2, 3$; sections (*b*) refer to quasitriplets for which $\Delta_i = 0$ or ±0.4 for $i = 1, 2, 3$. For example, in sections (*a*), the statistics include cases for which $(\Delta_1, \Delta_3, \Delta_3) = (0.2, 0, 0), (0.2, -0.2, 0), (0.2, 0.2, -0.2)$ *etc*.

Table 9. *SCHWARZ: quasi-triplets found among reflections with $|E| > 1.6$*

The entries in (*a*) refer to triplet quasi-invariants for which $\Delta_i = 0$ or ±0.2 for $i = 1, 2, 3$; the entries in (*b*) refer to triplet quasi-invariants for which $\Delta_i = 0$ or ±0.4 for $i = 1, 2, 3$. NQTRIPL = number of triplet quasi-invariants with G > ARG, $\langle|\Phi|\rangle$ average value of $|\Phi|$.

(*a*)

ARG	NTRIPL	$\langle\|\Phi\|\rangle$
0.0	3346	50.5
1.2	3145	50.0
2.0	937	46.8
3.8	86	44.0
5.5	14	35.3

(*b*)

ARG	NTRIPL	$\langle\|\Phi\|\rangle$
0.0	2665	73.2
1.2	2465	73.2
2.0	842	71.0
3.8	232	74.5
5.5	66	73.8

It is seen that the reliability of the triplet quasi-invariants which moderately deviate from the invariance condition [sections (*a*) of Tables 7, 8 and 9] is still comparable with the invariant reliability in Tables 4, 5 and 6, while it is remarkably worse for sections (*b*) of Tables 7, 8 and 9 for which higher values of $|\Delta_i|$ have been used. Quite interesting is the case of BOBBY, for which the average phase value $\langle\Phi\rangle$, relatively large also for invariants, increases in Table 8, section (*b*), enough to make the parameter *G* an unuseful descriptor of the triplet quasi-invariant reliability.

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