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The Role of Symmetry in the Estimation of Triplet Invariants: Theoretical Considerations and Applications

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Abstract

A simplified probabilistic theory of triplet invariants making full use of the space-group symmetry is described. Practical aspects concerning the application of the theory to the solution of real crystal structures are discussed: in particular, the number and the possible role of so-called symmetry-consistent and -inconsistent triplets in the structure-determination process are discussed together with a practical algorithm for their identification.

Symbols and abbreviations

$E_{\mathbf{h}} = |E_{\mathbf{h}}| \exp i\varphi_{\mathbf{h}}$: normalized structure factor.
N: number of atoms in the unit cell.
τ: centring order of the unit cell.
$N_{\rm pr} = N/\tau$: number of atoms in the primitive unit cell.
t: number of atoms in the asymmetric unit.
Z_j: atomic number of the jth atom.

$$\sigma_n = \sum_{j=1}^{N} Z_j^n.$$

$$\sum(\mathbf{h}) = \sum_{j=1}^{N} f_j^2(\mathbf{h}).$$

$N_{\rm eq} = (\sigma_3\sigma_2^{-3/2})^{-2}$: equals N when all the atoms in the unit cell are of the same atomic species.
m: order of the space group.
$\mathbf{C}_s \equiv (\mathbf{R}_s, \mathbf{T}_s)$: sth symmetry operator.
$\mathbf{C}_s r_j = \mathbf{R}_s r_j + \mathbf{T}_s$.
$\Delta_{s,r} = 2\pi(\mathbf{kT}_s + \mathbf{lT}_r)$.
$p_{\mathbf{h}}$: Wilson's power (or statistical weight) of a structure factor. It equals the number of times for which $\mathbf{h}(\mathbf{I} - \mathbf{R}_n) = 0$ for $n = 1, 2, \ldots, m$. If the cell is centred, $p_{\mathbf{h}} = \tau\varepsilon_{\mathbf{h}}$, where $\varepsilon_{\mathbf{h}}$ is calculated by involving in the equations $\mathbf{h}(\mathbf{I} - \mathbf{R}_n) = 0$ only the symmetry operators not related by a centring vector.
I_i: modified Bessel function of order i.
$D_i(x) = I_i(x)/I_0(x)$.

1. Introduction

Triplets

$$\Phi_1 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} \quad (\mathbf{h} + \mathbf{k} + \mathbf{l} = 0) \qquad (1a)$$

and

$$\Phi_2 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{kR}_s} + \varphi_{\mathbf{lR}_r} \quad (\mathbf{h} + \mathbf{kR}_s + \mathbf{lR}_r = 0) \qquad (1b)$$

are symmetry equivalent. Since

$$\Phi_2 = \Phi_1 - \Delta_{s,r}, \qquad (1c)$$

it may be said that Φ_1 and Φ_2 are symmetry consistent if $(\mathbf{kT}_s + \mathbf{lT}_r)$ is an integer value, otherwise they are said to be symmetry inconsistent.

The existence of inconsistent triplets in $P2_12_12_1$ was pointed out by Hauptman & Karle (1956). A probabilistic approach for the estimation of triplet invariants which takes into account the space-group symmetry was described by Giacovazzo (1974*a*, *b*): accordingly, the triplet reliability parameter $G = 2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}|/N_{\rm eq}^{1/2}$ derived by Cochran (1955) for $P1$ structures should be replaced by

$$G' = \frac{2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}|}{N_{\rm eq}^{1/2}} \left\langle \frac{\xi(\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{l})}{m(p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{l}})^{1/2}} \right\rangle \qquad (2)$$

where ξ is the trigonometric part of the structure factor. The above results were confirmed and extended by Pontenagel & Krabbendam (1983); they found that in the eleven pairs of enantiomorphously related space groups there are triple products for which (2) may be a complex value.

A general algebraic point of view for the study of the coexistence of symmetry-related invariants (and seminvariants) was provided by the method of representations (Giacovazzo, 1976). According to this method, the first representation of a triplet is the set of triplets

$$\{\varphi_h + \varphi_{\mathbf{kR}_s} + \varphi_{\mathbf{lR}_r}\}$$

which are obtained from (1*a*) when $\mathbf{R}_s$ and $\mathbf{R}_r$ vary over the set of rotation matrices of the space group. In a recent paper by Han & Langs (1988) the 230 space groups were examined in order to identify conditions which permit symmetry-inconsistent triplets. A useful table describing such conditions for the various space groups was presented. The matter was reexamined (Giacovazzo, 1989) in order to:

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(*a*) complete the results by Han & Langs, who missed conditions for cubic space groups and neglected triplets with symmetry-restricted phase values;

(*b*) provide an algorithm for the discovery of symmetry-inconsistent triplets in any space group, in order to avoid the use of the large Han & Langs table.

All the above-mentioned papers paid attention to the theoretical aspects of the problem. So far no paper has been devoted to the practical aspects: *i.e.* how large the number of symmetry-consistent and -inconsistent triplets may be for crystal structures of mineralogical or of chemical interest; what advantages, for the success of a direct procedure for phase solution, really arise from triplet estimates making full use of space-group symmetry. In particular, it could be interesting to learn about the possible disturbance that symmetry-inconsistent triplets, when not recognized, may introduce against the success of a direct procedure. To give a reasonable answer to these problems is one of the purposes of this paper. Also we want to describe an algorithm for the identification of symmetry-equivalent triplets and a practical formula for their estimation.

2. A procedure for the estimation of triplet invariants

Triplet invariants may be estimated according to recent methods (Castleden, 1987; Peschar & Schenk, 1987) which utilize the space-group symmetry in deriving the joint probability distributions of structure factors. Such methods lead to reliability parameters which coincide with those derived by Giacovazzo (1974*a*, *b*) and Pontenagel & Krabbendam (1983). Thus the first problem to be faced in a practical procedure for triplet estimation is that of identifying how many triplets (1*b*) can be calculated for each triplet (1*a*). Triplets of type

$$\varphi_{\mathbf{h}\mathbf{R}_n}+\varphi_{\mathbf{k}\mathbf{R}_n}+\varphi_{\mathbf{l}\mathbf{R}_n} \qquad n=1,\ldots,m$$

are trivial: they never present phase shift with respect to the triplet Φ_1 defined by (1*a*) and can always be neglected. A simple way for obtaining equivalent triplets is to modify the usual $\sum_2$ procedures (see Main, 1985, for a related process) in order to identify, when they exist, all the triplets constituted by the same three reflections. According to the signs, four types of triplets, all with the same reliability parameter G, can coexist in a $\sum_2$ list:

$$n_1 \quad n_2 \quad n_3 \quad \Delta_1 \qquad (3a)$$

$$n_1 \quad -n_2 \quad n_3 \quad \Delta_2 \qquad (3b)$$

$$n_1 \quad n_2 \quad -n_3 \quad \Delta_3 \qquad (3c)$$

$$n_1 \quad -n_2 \quad -n_3 \quad \Delta_4 \qquad (3d)$$

where n_i is the code number of the standard reflection (in decreasing order of $|E|$), Δ_i is the generic triplet phase shift. If n_1, n_2, n_3 are all reflections of general type, each type of triplet in (3) is not symmetry equivalent to the others. In this case they can be simultaneously used, without any supplementary probabilistic consideration, in direct procedures for phase determination as independent phase relationships. A brief supplementary analysis of pairs of such triplets is presented in § 3.

Two triplets of the same type [*i.e.* with identical signs in (3)] are symmetry equivalent by definition; but also triplets of different type may be symmetry equivalent. For example, if the reflection n_2 in (3*b*) or n_3 in (3*c*) or n_2 and n_3 in (3*d*) have symmetry-restricted phase values then (3*b*), (3*c*), (3*d*) are all symmetry equivalent to (3*a*). For example, for (3*b*) we can write

$$\varphi_{\mathbf{k}_a\mathbf{R}_i}=-\varphi_{\mathbf{k}_a}=\varphi_{\mathbf{k}_a}-2\pi\mathbf{k}_a\mathbf{T}_i \qquad (4)$$

where the subscript a to $\mathbf{k}$ denotes the standard reflection and $\mathbf{R}_i$ is the matrix for which $\mathbf{k}\mathbf{R}_i=-\mathbf{k}$. Then (3*b*) may be transformed into

$$n_1 \quad n_2 \quad n_3 \quad \Delta_2'$$

where $\Delta_2'=\Delta_2-2\pi\mathbf{k}_a\mathbf{T}_i=\Delta_2-2\varphi_{p\mathbf{k}_a}$, and $\varphi_{p\mathbf{k}_a}$ is one of the two symmetry-permitted phases of the reflection $\mathbf{k}_a$.

It may be noted that (3*a*) and (3*d*) are also symmetry equivalent [as well as (3*b*) and (3*c*)] if n_1 has restricted phase values. Indeed, (3*d*) may be the first transformed into

$$-n_1 \quad n_2 \quad n_3 \quad -\Delta_4$$

and then, by applying (4) to reflection $\mathbf{h}$, it is again transformed into

$$n_1 \quad n_2 \quad n_3 \quad (-\Delta_4-2\varphi_{p\mathbf{h}_a}).$$

If all of n_1, n_2, n_3 have symmetry-restricted phases then all the triplets (3) are symmetry equivalent. The above considerations suggest that all symmetry-equivalent triplets can be easily referred to a unique representative triplet, say $\Phi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}$. If full use of space-group symmetry is made then (*A*.5) and (*A*.6) may be applied to such a triplet so that it may be stored in a $\sum_2$ list as

$$n_1 \quad n_2 \quad n_3 \quad \Delta_f+\Delta \quad G'$$

where (see Appendix)

$$\tan\Delta_f=(\textstyle\sum''\sin\Delta_{s,r})/(\sum''\cos\Delta_{s,r})=T/B \qquad (5)$$

is the expected value of Φ and

$$G'=\frac{2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}|}{(N_{eq})_{pr}^{1/2}}\frac{1}{(\varepsilon_{\mathbf{h}}\varepsilon_{\mathbf{k}}\varepsilon_{\mathbf{l}})^{1/2}}(T^2+B^2)^{1/2}. \qquad (6)$$

Three cases can occur.

(I) All symmetry-equivalent triplets have the same $\Delta_{s,r}$ value. Then $\Delta_f = \Delta_{s,r}$ and

$$G' = \frac{2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}|}{(N_{eq})^{1/2}_{pr}} \frac{q}{(\varepsilon_{\mathbf{h}}\varepsilon_{\mathbf{k}}\varepsilon_{\mathbf{l}})^{1/2}} = Gw,$$

which is a non-vanishing real value. The phase of the representative triplet is then expected to be zero: the reliability parameter G' differs from Cochran's G parameter by a factor w arising from space-group symmetry (see Table 1 in Giacovazzo, 1974*b*).

(II) Symmetry-equivalent triplets have different values of $\Delta_{s,r}$ but they lead to $T = 0$ and $B = 0$. Then G' is equal to zero and the triplet is symmetry inconsistent. Triplets symmetry restricted to $\pm\pi/2$ in $P2_12_12_1$ are a typical example. Let us examine

$$\Phi_1 = \varphi_{h_1,k_1,0} + \varphi_{-h_1,0,l_1} + \varphi_{0,-k_1,-l_1}$$

with odd values of $(h_1 + k_1 + l_1)$. The symmetry-equivalent triplet

$$\begin{aligned}\Phi_2 &= \varphi_{h_1,k_1,0} + \varphi_{-h_1,0,-l_1} + \varphi_{0,-k_1,+l_1} \\ &= \Phi_1 + \pi(h_1 + k_1 + l_1)\end{aligned}$$

can be found, giving opposite phase indication. Such a triplet, once identified, can be excluded from any active use in the phasing process.

(III) Symmetry-equivalent triplets have different $\Delta_{s,r}$ values, but $T \neq 0$ and/or $B \neq 0$. Then the phase of the representative triplet is expected to differ from 2π according to the non-vanishing reliability parameter given by (6). This is the case explicitly identified by Pontenagel & Krabbendam: such triplets can help to fix the enantiomorph in the phasing process.

In order to illustrate this case, let us consider, in space group $P3_1$,

$$[(x, y, z); (\bar{y}, x-y, z+\tfrac{1}{3}); (\bar{x}+y, \bar{x}, z+\tfrac{2}{3})],$$

the triplet invariant

$$\Phi_1 = \varphi_{30\bar{3}} + \varphi_{\bar{3}31} + \varphi_{0\bar{3}2}.$$

A symmetry-equivalent triplet

$$\begin{aligned}\Phi_2 &= \varphi_{30\bar{3}} + \varphi_{0\bar{3}1} + \varphi_{\bar{3}32} = \varphi_{30\bar{3}} + \varphi_{(\bar{3}31)\mathbf{R}_3} + \varphi_{(0\bar{3}2)\mathbf{R}_2} \\ &= \Phi_1 - \Delta_{3,2} = \Phi_1 - 2\pi/3\end{aligned}$$

may be calculated. Then according to (5) and (6) we obtain $\Delta_f = \pi/3$ and $G' = G$. The example given by Pontenagel & Krabbendam in their Appendix V for space group $P4_1$,

$$[(x, y, z), (\bar{x}, \bar{y}, z+\tfrac{1}{2}), (\bar{y}, x, z+\tfrac{1}{4}), (y, \bar{x}, z-\tfrac{1}{4})],$$

may be treated in the same way. Indeed, the pair of triplets

$$\Phi_1 = \varphi_{221} + \varphi_{\bar{4}01} + \varphi_{2\bar{2}\bar{2}}$$

and

$$\begin{aligned}\Phi_2 &= \varphi_{221} + \varphi_{0\bar{4}1} + \varphi_{\bar{2}2\bar{2}} = \varphi_{221} + \varphi_{(\bar{4}01)\mathbf{R}_4} + \varphi_{(2\bar{2}\bar{2})\mathbf{R}_2} \\ &= \Phi_1 - \Delta_{4,2} = \Phi_1 + \pi/2\end{aligned}$$

may be represented by Φ_1, for which the expected value $\Delta_f = -\pi/4$ and the reliability parameter $G' = G \times 2^{1/2}$ may be calculated. The application of (5) and (6) to triplets constituted by restricted phase reflections is trivial in the cases I and II. In order to illustrate case III, we consider, in space group $P4_12_12_1$ [equivalent positions

$$\begin{aligned}&(x, y, z); (\bar{x}, \bar{y}, z+\tfrac{1}{2}); (x+\tfrac{1}{2}, \bar{y}+\tfrac{1}{2}, \bar{z}+\tfrac{3}{4}); \\ &(\bar{x}+\tfrac{1}{2}, y+\tfrac{1}{2}, \bar{z}+\tfrac{1}{4}); (\bar{y}, \bar{x}, \bar{z}+\tfrac{1}{2}); (y, x, \bar{z}); \\ &(y+\tfrac{1}{2}, \bar{x}+\tfrac{1}{2}, z+\tfrac{3}{4}); (\bar{y}+\tfrac{1}{2}, x+\tfrac{1}{2}, z+\tfrac{1}{4})],\end{aligned}$$

the triplet

$$\Phi_1 = \varphi_{1,\bar{1},\bar{19}} + \varphi_{1,1,12} + \varphi_{\bar{2}07}.$$

If space-group symmetry is not taken into account, Φ_1 is expected to be close to 2π. However, the values of $\varphi_{1,\bar{1},\bar{19}}$, $\varphi_{1,1,12}$ and $\varphi_{\bar{2}07}$ are symmetry restricted to $(0, \pi)$, $(0, \pi)$, $(-\pi/4, 3\pi/4)$ respectively, so that the triplet Φ_1 is itself restricted to $(-\pi/4, 3\pi/4)$. If full use of symmetry is made, a triplet symmetry equivalent to Φ_1 may be calculated:

$$\begin{aligned}\Phi_2 &= \varphi_{1,\bar{1},\bar{19}} + \varphi_{\bar{1},\bar{1},12} + \varphi_{027} \\ &= \varphi_{1,\bar{1},\bar{19}} + \varphi_{(1,1,12)\mathbf{R}_2} + \varphi_{(\bar{2}07)\mathbf{R}_8} \\ &= \Phi_1 - \Delta_{2,8} = \Phi_1 + \pi/2.\end{aligned}$$

According to (5) and (6), a phase shift $\Delta_f = -\pi/4$ and a reliability parameter $G' = G \times 2^{1/2}$ ($\varepsilon_i = 1$ for $i = 1, 2, 3$) are associated with the representative triplet. Now the expected value of the triplet is consistent with phase restrictions imposed by symmetry.

Some supplementary considerations on the practical consequences of the above result are useful. Suppose that in a phasing process $\varphi_{1,1,12}$ and $\varphi_{\bar{2}07}$ have already been fixed to 0 and $-\pi/4$ respectively. If no use is made of the present theory, $\varphi_{1,\bar{1},\bar{19}}$ will be assigned the value $+\pi/4$. Since this is inconsistent with the permitted value of $\varphi_{1,\bar{1},\bar{19}}$ the tangent routine will associate with $\varphi_{1,\bar{1},\bar{19}}$, its permitted value closest to $\pi/4$, *i.e.* 2π, with reliability parameter equal to $G/2^{1/2}$. If the present theory is used, $\varphi_{1,\bar{1},\bar{19}}$ will assume the value

$$\varphi_{1,\bar{1},\bar{19}} = -\varphi_{1,1,12} - \varphi_{\bar{2}07} - \pi/4 = 0$$

with reliability parameter equal to $G/2^{1/2}$.

3. Special pairs of triplets

In a paper by Giacovazzo & Vicković (1980) (but see also Hauptman & Green, 1978) special quartets of type

$$\Psi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{hR}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{kR}} = 2(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}}) - 2\pi(\mathbf{h}+\mathbf{k})\mathbf{T}$$

were studied in order to estimate in non-centrosymmetric groups the so-called two-phase variants, fixed by the relationship $2(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}}) = \Psi + 2\pi(\mathbf{h}+\mathbf{k})\mathbf{T}$.

Table 1. *BOBBY; special pairs of triplets*

For simplicity Miller indices are not given and reflections are identified by the code number.

			G	Δ				G	Δ				G	Δ
7	20	51	1·90	π	7	−21	−64	1·73	0	7	51	64	1·35	0
70	−20	−51	1·90	0	7	21	64	1·73	π	7	−51	−64	1·35	π
	$(\varphi_7)_{true}=252°$					$(\varphi_7)_{est}=90, 270°$					$\alpha=\sum G_iD_1(G_i)=3·179$			
14	−35	−38	1·51	π										
14	35	38	1·51	π										
	$(\varphi_{14})_{true}=173°$					$(\varphi_{14})_{est}=0, 180°$					$\alpha=\sum G_iD_1(G_i)=0·912$			
19	38	40	1·32	0	19	−38	−50	1·23	0					
19	−38	−40	1·32	π	19	38	50	1·23	π					
	$(\varphi_{19})_{true}=244°$					$(\varphi_{19})_{est}=90, 270°$					$\alpha=\sum G_iD_1(G_i)=1·386$			
32	48	−55	0·99	π										
32	48	55	0·99	π										
	$(\varphi_{55})_{true}=35°$					$(\varphi_{55})_{est}=0, 180°$					$\alpha=\sum G_iD_1(G_i)=0·446$			
50	−62	64	0·73	0										
50	62	−64	0·73	0										
	$(\varphi_{50})_{true}=18°$					$(\varphi_{50})_{est}=0, 180°$					$\alpha=\sum G_iD_1(G_i)=0·252$			

If Ψ is estimated close to π and $(\mathbf{h}+\mathbf{k})\mathbf{T}$ is an integer value, then $(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}})$ is close to $\pm\pi/2$. So phase estimates are obtained which are enantiomorph sensitive.

While three-phase and upper-order variants can be defined *via* special sextets, octets and so on, there is no way of defining one-phase variants by the same technique. However, in favourable space groups special triplets exist which provide estimates for one-phase variants. Let us suppose, for example, that a pair of triplets, constituted by non-centrosymmetrical phases, can be found such as

$$\Phi_1=\varphi_{\mathbf{h}_a}+\varphi_{\mathbf{k}_a\mathbf{R}_\mu}+\varphi_{\mathbf{l}_a\mathbf{R}_\nu}=\varphi_{\mathbf{h}_a}+\varphi_{\mathbf{k}_a}+\varphi_{\mathbf{l}_a}+\Delta_1 \qquad (7)$$

$$\Phi_2=\varphi_{\mathbf{h}_a}-\varphi_{\mathbf{k}_a\mathbf{R}_p}+\varphi_{\mathbf{l}_a\mathbf{R}_q}=\varphi_{\mathbf{h}_a}-\varphi_{\mathbf{k}_a}+\varphi_{\mathbf{l}_a}+\Delta_2 \qquad (8)$$

where

$$\Delta_1=-2\pi(\mathbf{k}_a\mathbf{T}_\mu+\mathbf{l}_a\mathbf{T}_\nu)$$

and

$$\Delta_2=-2\pi(-\mathbf{k}_a\mathbf{T}_p+\mathbf{l}_a\mathbf{T}_q)$$

respectively. Since Φ_1 and Φ_2 are not symmetry equivalent and both are expected to be close to 2π,

$$2\varphi_{\mathbf{k}_a}=\Phi_1-\Phi_2-\Delta_1+\Delta_2\simeq\Delta_2-\Delta_1$$

from which

$$\varphi_{\mathbf{k}_a}\simeq\tfrac{1}{2}(\Delta_2-\Delta_1)+n\pi. \qquad (9)$$

The reliability parameter for the phase relationship (9) is the β value which satisfies

$$D_1(\beta)=D_1(G_1)D_1(G_2)$$

where G_1 and G_2 are the reliability parameters for the triplets Φ_1 and Φ_2 respectively.

The same reflection $E_{\mathbf{k}}$ may be involved in more pairs of triplets of type (7), (8). The phase indications (9) may then be combined by a tangent-like formula in order to obtain more reliable estimates for $\varphi_{\mathbf{k}_a}$.

The application of such considerations to the crystal structure BOBBY (see Tables 2 and 3 for relevant data and references) yields the results collected in Table 1. The agreement of results with the theory is satisfactory.

Table 2. *Crystallographic data for the eleven structures selected for study*

Structure*	Chemical formula	Space group	Z
TPALA	$C_{28}H_{42}N_4O_7$	$P2_1$	2
ERGO	$C_{28}H_{44}O$	$P2_12_12_1$	8
AZET	$C_{21}H_{16}ClNO$	$Pca2_1$	8
APAPA	$C_{30}H_{37}N_{15}O_{16}P_2.6H_2O$	$P4_12_12$	8
MGHEX	$C_{48}H_{68}N_{12}MgO_{12}.2ClO_4.4CH_3CN$	$P3_1$	3
NO55	$C_{20}H_{24}N_4$	$Fdd2$	16
GOLDMAN2	$C_{28}H_{16}$	Cc	8
TUR10	$C_{15}H_{24}O_2$	$P6_122$	12
DIOLE	$C_{10}H_{18}O_2$	$I\bar{4}2d$	16
DIAM	$C_{14}H_{20}O$	$P4_2/n$	8
BOBBY	$Na^+.Ca^{2+}.N(CH_2CO)_3^-$	$P2_13$	4

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

4. Experimental

Eleven crystal structures having different structural complexity and covering a large variety of space groups have been used as experimental tests. For each structure the code name, the space group and the chemical formula are quoted in Table 2. Tests were performed by means of a modified version of *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) in order to provide data concerning occurrences of special and of general triplets respectively and to check advantages and/or drawbacks arising from the use of probabilistic formula which estimate triplet phase by making full use of the space-group symmetry.

In Table 3 NRIF is the number of the largest $|E|$'s chosen by *SIR*88 for active use in the phasing procedure; in Table 4 NRIF is the number of the smallest $|E|$'s chosen by *SIR*88 for psi-zero triplets and negative quartets. The number of triplets found in each of two $\sum_2$ lists is divided into general triplets (each

Table 3. *Data for active triplets*

Structure	NRIF	Active triplets: General	Special I	Special II	Special III	Pairs
TPALA	306	3564	45	-	-	-
ERGO	382	3889	149	2	-	-
			(46)	(2)		
AZET	342	3244	815	-	-	-
			(16)			
APAPA	426	4319	135	9	14	-
			(25)	(8)	(13)	
MGHEX	489	4104	2	-	10	2
			(-)		(-)	
NO55	246	3820	194	-	-	-
			(29)			
GOLDMAN	374	3200	801	-	-	-
			(-)			
TUR10	219	3715	361	27	-	-
			(125)	(20)		
DIOLE	182	3603	408	4	-	2
			(19)	(4)		
DIAM	260	5083	3	10	-	-
			(3)	(10)		
BOBBY	68	2171	62	-	-	8
			(1)			

Table 4. *Data for psi-zero triplets*

Structure	NRIF	Psi-zero triplets: General	Special I	Special II	Special III	Pairs
TPALA	100	2566	8	-	-	-
ERGO	100	3866	134	2	-	-
			(47)	(2)		
AZET	100	3465	535	-	-	-
			(29)			
APAPA	100	3786	193	11	21	-
			(48)	(9)	(13)	
MGHEX	100	3985	5	10	-	-
			(-)	(-)		
NO55	100	3865	135	-	-	-
			(25)			
GOLDMAN	100	2870	633	-	-	-
			(-)			
TUR10	100	3724	276	59	-	-
			(138)	(52)		
DIOLE	35	3618	369	4	-	5
			(29)	(4)		
DIAM	100	3974	26	6	-	-
			(26)	(6)		
BOBBY	38	1110	104	10	-	-
			(1)	(5)		

of them has no symmetry equivalents) and special triplets (for each of them two or more symmetry equivalents exist). Special triplets are then classified according to the types I, II or III described in § 2: for each structure the numbers of special triplets having symmetry-restricted phase values are quoted in parentheses on a second line. The number of special pairs of triplets described in § 3 are also given.

Tables 3 and 4 show that:

(*a*) the number of special triplets increases with space-group symmetry. Mirror and glide planes are more effective than proper symmetry axes in generating special triplets, as expected;

Table 5. *Combined figures of merit (CFOM) and R values*

Structure	Protocol 1 CFOM	Protocol 1 *R*	Protocol 2 CFOM	Protocol 2 *R*
TPALA	0·221	0/24	0·186	0/24
ERGO	0·530	0/72	0·469	0/72
AZET	0·372	0/30	0·335	0/30
APAPA	0·957	6/60	0·967	4/72
MGHEX	0·866	0/96	0·868	0/96
NO55	0·260	0/32	0·784	1/36
GOLDMAN	0·239	0/24	0·221	0/24
TUR10	0·882	6/36	0·819	6/36
DIOLE	0·813	4/30	0·776	4/36
DIAM	0·987	7/32	0·981	7/32
BOBBY	0·168	35/160	0·161	38/192

(*b*) special triplets of type I are more frequent than those of types II or III. The full use of symmetry can change only their reliability parameter ($G \Rightarrow G'$) but not the expected phase values. Thus they should often have little effect in the phasing process;

(*c*) special pairs of triplets (as defined in § 3) are infrequent and are expected to be of very limited use.

In order to check the effectiveness of the formulas (5) and (6) with respect to Cochran estimates, *SIR*88 was run according to two different protocols: in the first one five symbolic phases (magic-integer procedure) and Cochran estimates were used; in the second one five symbolic phases and formulas (5) and (6) were applied. The results are shown in Table 5: in columns 2 and 3 the highest values of the combined figure of merit (CFOM) and the number of correct solutions over the number of trials (R) are shown according to protocol 1; in columns 4 and 5 the same results are given for protocol 2.

The following conclusions arise:

(i) the effectiveness of the two protocols in solving crystal structures is rather similar: the main advantage for protocol 2 is that it solves NO55.

(ii) CFOM's are not very different. In particular PSI0 and NQUEST proved rather insensitive to the use of symmetry.

5. Concluding remarks

A simplified probabilistic theory for triplet phase estimation making full use of the space-group symmetry has been described. The connections of such a theory with the representations method of structure invariants and seminvariants have also been revealed. Practical applications show that in most cases the standard Cochran formula for triplet invariants and the use of the tangent formula are sufficient tools for the solution of the phase problem. For high-symmetry space groups the application of the theory here described can sometimes provide supplementary information sufficient for the solution of a crystal structure which could not be solved by standard techniques. In order to reduce computing time the appli-

cation of the theory to PSI0 triplets and to negative quartets for calculating FOM's may be skipped without compromising the success of the phasing process.

APPENDIX

Let

$$E_{\mathbf{h}} = \sum_{j=1}^{t} \nu_j(\mathbf{h}) \sum_{s=1}^{m} \exp 2\pi i \mathbf{h}\mathbf{C}_s\mathbf{r}_j$$

be the normalized structure factor with vectorial index $\mathbf{h}$, where

$$\nu_j(\mathbf{h}) = f_j(\mathbf{h}) \Big/ \left[\tau \varepsilon_{\mathbf{h}} \sum_{N} (\mathbf{h})\right]^{1/2}.$$

Instead of calculating the complete trivariate distribution $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}})$ with $\mathbf{h}+\mathbf{k}+\mathbf{l}=0$, as done by Giacovazzo (1974*a*), we limit ourselves to calculating the expression for the reliability parameter for a triplet phase in any space group. This will make reading easier for crystallographers not familiar with distributions theory and will elucidate the role played by symmetry in the estimation of triplets.

It is easily seen that the parameter G obtained by Cochran in $P1$ coincides with $2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}|\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}\rangle$. Indeed, in $P1$

$$E_{\mathbf{h}} = \sum_{j=1}^{N} \nu_j(\mathbf{h}) \exp 2\pi i \mathbf{h}\mathbf{r}_j$$

and

$$\begin{aligned}\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}\rangle &= \sum_{j=1}^{N} \nu_j(\mathbf{h})\nu_j(\mathbf{k})\nu_j(\mathbf{l}) \\ &\quad \times \langle \exp 2\pi i[\mathbf{k}(\mathbf{r}_{j_1} - \mathbf{r}_{j_3}) + \mathbf{l}(\mathbf{r}_{j_2} - \mathbf{r}_{j_3})]\rangle \\ &= \sum_{j=1}^{N} \nu_j(\mathbf{h})\nu_j(\mathbf{k})\nu_j(\mathbf{l}) \\ &= \sum_{j=1}^{N} \frac{f_j(\mathbf{h})f_j(\mathbf{k})f_j(\mathbf{l})}{[\sum_N (\mathbf{h}) \sum_N (\mathbf{k}) \sum_N (\mathbf{l})]^{1/2}} \\ &= \frac{1}{N_{\mathrm{eq}}^{1/2}}. \end{aligned} \qquad (A.1)$$

Calculate now $\langle E_{\mathbf{h}}E_{\mathbf{h}}E_{\mathbf{h}}\rangle$ for any space group:

$$\begin{aligned}\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}\rangle &= \sum_{j=1}^{t} \nu_j(\mathbf{h})\nu_j(\mathbf{k})\nu_j(\mathbf{l}) \\ &\quad \times \left\langle \sum_{s_1,s_2,s_3=1}^{m} \exp 2\pi i[\mathbf{k}(\mathbf{C}_{s_1} - \mathbf{C}_{s_3}) \right. \\ &\quad \left. + \mathbf{l}(\mathbf{C}_{s_2} - \mathbf{C}_{s_3})]\mathbf{r}_j \right\rangle. \end{aligned} \qquad (A.2)$$

With the choice $\mathbf{C}_{s_1} = \mathbf{C}_s\mathbf{C}_{s_3}$, $\mathbf{C}_{s_2} = \mathbf{C}_r\mathbf{C}_{s_3}$ (and therefore $\mathbf{R}_{s_1} = \mathbf{R}_s\mathbf{R}_{s_3}$, $\mathbf{T}_{s_1} = \mathbf{R}_s\mathbf{T}_{s_3} + \mathbf{T}_s$) (*A*.2) is equivalent to

$$\begin{aligned}\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}\rangle &= \sum_{j=1}^{t} \nu_j(\mathbf{h})\nu_j(\mathbf{k})\nu_j(\mathbf{l}) \\ &\quad \times \sum_{s,r,s_3=1}^{m} \langle \exp 2\pi i\{[\mathbf{k}(\mathbf{R}_s - \mathbf{I}) \\ &\quad + \mathbf{l}(\mathbf{R}_r - \mathbf{I})]\mathbf{R}_{s_3}\mathbf{r}_j + \mathbf{k}(\mathbf{R}_s\mathbf{T}_{s_3} + \mathbf{T}_s - \mathbf{T}_{s_3}) \\ &\quad + \mathbf{l}(\mathbf{R}_r\mathbf{T}_{s_3} + \mathbf{T}_r - \mathbf{T}_{s_3})\}\rangle \end{aligned} \qquad (A.3)$$

For general $\mathbf{h}$, $\mathbf{k}$, $\mathbf{l}$ reflections and for primitive cells non-vanishing contributions to the average on the right-hand side of (*A*.3) (mostly but not always) arise when $\mathbf{R}_s = \mathbf{I}$ or $\mathbf{R}_r = \mathbf{I}$ and $\mathbf{R}_{s_3}$ is whichever (m cases). Since $tm = N$, (*A*.3) transforms into (*A*.1) and Cochran's reliability parameter G is obtained.

If $\mathbf{h}$, $\mathbf{k}$, $\mathbf{l}$ are general reflections but the cell is centred then additional non-vanishing contributions arise when $\mathbf{R}_s$ and $\mathbf{R}_r$ are related to $\mathbf{I}$ by a centring vector: in all there will be $\tau^2 m$ contributions to the average and (*A*.3) transforms into

$$\begin{aligned}\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}\rangle &= \left[\sum_{j=1}^{t} \nu_j(\mathbf{h})\nu_j(\mathbf{k})\nu_j(\mathbf{l})\right] m\tau^2 \\ &= \tau^2 \sum_{j=1}^{N} \nu_j(\mathbf{h})\nu_j(\mathbf{k})\nu_j(\mathbf{l}) \\ &= \tau^2 \frac{\sum_{j=1}^{N} f_j(\mathbf{h})f_j(\mathbf{k})f_j(\mathbf{l})}{\tau^{3/2}[\sum_N (\mathbf{h}) \sum_N (\mathbf{k}) \sum_N (\mathbf{l})]^{1/2}} \\ &= \left(\frac{\tau}{N_{\mathrm{eq}}}\right)^{1/2} = \frac{1}{(N_{\mathrm{eq}})_{\mathrm{pr}}^{1/2}} \end{aligned}$$

where $(N_{\mathrm{eq}})_{\mathrm{pr}}$ refers to the primitive unit cell. This result, in accordance with Giacovazzo (1974*b*), suggests that the value of N_{eq} to be used in any $\sum_2$ list has to be calculated on the basis of the primitive cell.

If $\mathbf{h}$, $\mathbf{k}$, $\mathbf{l}$ are special reflections with $\varepsilon_{\mathbf{h}}$ or $\varepsilon_{\mathbf{k}}$ or $\varepsilon_{\mathbf{l}}$ different from unity (but not only in this case as shown in the text), more non-vanishing contributions to the average arise in the right-hand term of (*A*.3). In this more general case

$$\begin{aligned}\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}\rangle &= \frac{1}{(N_{\mathrm{eq}})_{\mathrm{pr}}^{1/2}} \frac{1}{(\varepsilon_{\mathbf{h}}\varepsilon_{\mathbf{k}}\varepsilon_{\mathbf{l}})^{1/2}} \\ &\quad \times \sum'' \exp 2\pi i\{\mathbf{k}(\mathbf{R}_s\mathbf{T}_{s_3} + \mathbf{T}_s - \mathbf{T}_{s_3}) \\ &\quad + \mathbf{l}(\mathbf{R}_r\mathbf{T}_{s_3} + \mathbf{T}_r - \mathbf{T}_{s_3})\} \end{aligned} \qquad (A.4)$$

where the double prime to the summation means that symmetry operators vary among the m/τ symmetry operators not related by a centring vector, with the supplementary condition that

$$\mathbf{k}(\mathbf{R}_s - \mathbf{T}) + \mathbf{l}(\mathbf{R}_r - \mathbf{I}) = 0.$$

In this case $\mathbf{kR}_s + \mathbf{lR}_r = \mathbf{k} + \mathbf{l}$ so that (*A*.4) may be simplified to

$$\langle E_\mathbf{h} E_\mathbf{k} E_\mathbf{l} \rangle = \frac{1}{(N_{eq})_{pr}^{1/2}} \frac{1}{(\varepsilon_\mathbf{h}\varepsilon_\mathbf{k}\varepsilon_\mathbf{l})^{1/2}} \sum'' \exp[i\Delta_{s,r}]. \quad (A.5)$$

According to (5) the expected value of $\Phi = \varphi_\mathbf{h} + \varphi_\mathbf{k} + \varphi_\mathbf{l}$ is then defined by

$$\tan \Delta_f = (\sum'' \sin \Delta_{s,r})/(\sum'' \cos \Delta_{s,r}) = T/B$$

where $\Delta_{s,r} = +2\pi(\mathbf{kT}_s + \mathbf{lT}_r)$. Accordingly, the reliability parameter of the phase estimate is given by

$$G' = \frac{2|E_\mathbf{h} E_\mathbf{k} E_\mathbf{l}|}{(N_{eq})_{pr}^{1/2}} \frac{1}{(\varepsilon_\mathbf{h}\varepsilon_\mathbf{k}\varepsilon_\mathbf{l})^{1/2}} (T^2 + B^2)^{1/2} \quad (A.6)$$

Finally, the conditional probability distribution of Φ given $|E_\mathbf{h}|, |E_\mathbf{k}|, |E_\mathbf{l}|$ in any space group and for any triple (**h**, **k**, **l**) is given by

$$P(\Phi \,||E_\mathbf{h} E_\mathbf{k} E_\mathbf{l}|) = [2\pi I_0(G')] \exp[G' \cos(\Phi - \Delta_f)]. \quad (A.7)$$

Even if explicitly obtained for non-centric phase triplets, these results are easily extended to any kind of triplet with three-phase restricted structure factors. Indeed, the expected value of Φ will always be defined by $\tan \Delta f$: a hyperbolic tangent expression can then define which of the two allowed phase values is more probable (see § 2).

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Angular Distribution of Reflections in Laue Diffraction

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Abstract

An analysis is presented of the angular distribution of reflections in Laue diffraction, with particular application to the spatial overlap problem in synchrotron macromolecular crystallography. Spatial overlaps of spots on the detector occur when the angular separations of adjacent diffracted beams are very small. The maximum density of spots occurs at $\theta_c = \sin^{-1}(\lambda_{min} D^*/2)$ and the majority of spots in this region of θ have short wavelengths. At higher θ the mean wavelength increases steadily. On a flat detector the spots of a Laue pattern lie on intersecting conics. Each conic corresponds to a zone plane of reciprocal-

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