Direct Methods and Structures Showing Superstructure Effects.

II. A Probabilistic Theory of Triplet Invariants

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(Received 21 November 1985; accepted 8 May 1986)

Abstract

A probabilistic theory of triplet invariants is provided which may be used when pseudotranslations occur in the crystal structure. The final formula for estimating a triplet phase invariant in centrosymmetric space groups is of Cochran-Woolfson type, in non-centrosymmetric space groups of von Mises type with maximum at 2π; single phases are determined via a special tangent formula. Thus the usual algorithms for phase expansion and refinement can be employed with few modifications. Parameters occur in the von Mises and tangent formulae which are markedly different from the usual ones. In particular, the reliability of each triplet depends not only on |Eh|, |Ek|, but also on the actual h, k, h-k indices and on the nature of the pseudotranslations. An automatic phasing procedure and some applications are also described for the solution of superstructures and other structures showing pseudotranslations.

Symbols and abbreviations

φh, φk,...: phase of Eh, Ek,...
Rh, Rk,...: moduli of Eh,Ek,... respectively.
\([σ_1], [σ_2], [σ_N]...= \sum Z_j\), where Z_j is the atomic number of the jth atom and the summation is made over the p, q, N,... atoms.
Ch = { \([σ_2]^2 + [σ_3]^2\}^{1/2}.
I_0: modified Bessel function of order zero.
N: number of atoms in the cell.
m: order of the space group.
p: number of atoms (symmetry-equivalent included) whose positions are related by the pseudotranslations u.
q: number of atoms (symmetry-equivalent included) whose positions are not related by the pseudotranslations u.
t_p: number of independent atoms which generate the p atoms when the pseudotranslations u and the symmetry operators C_s, s = 1, 2,..., m, are applied.
t_q: number of independent atoms which generate the q atoms by application of the symmetry operators C_s, s = 1, 2,..., m.
n_i: order of the pseudotranslation u_i.

For other symbols see paper I (Cascarano, Giacovazzo & Liuč, 1985b).

1. Introduction

Since the pioneering works by Lipson & Woolfson (1952), Rogers & Wilson (1953) and Hauptman & Karle (1953) it was clear that rational dependence of atom coordinates should affect both the statistics of normalized structure factors and the reliability of triplet phase relationships. The mere renormalization procedure proposed by Hauptman & Karle (1959) to overcome problems imposed by systematically weak and strong reflections was unsuccessful in several cases. Indeed, it implies that triplets involving reflexions from weak reflexion sets are as reliable as triplets from strong sets, which is in contradiction with Sayre's equation (Gramlich, 1975).

In some cases, it is relatively easy to determine the substructural unit: then the superstructure may be found by techniques particularly devoted to recovering the complete from the partial structure (Prick, Beurskens & Gould, 1983; Camalli, Giacovazzo & Spagna, 1985). However, the main aim of this paper is that of determining at the same time both the positions of the substructural and those of the superstructural atoms by taking into account the information (often available) on pseudotranslational symmetry. Such information may be derived by different methods: we quote, among others, that described by Cascarano, Giacovazzo & Liuč (1985a, b), which suggests, via a statistical analysis of the diffraction intensities, the possible presence of a pseudotranslational symmetry. The method finds the nature of pseudosymmetry and estimates the fraction p/N of electrons suffering it.

In recent years more insight into the problem of using triplet relationships was achieved after the contributions by Böhme (1982, 1983), Fan Hai-fu, Yao Jia-xing, Main & Woolfson (1983), Gramlich (1984). A renormalization procedure was combined with suitable probabilistic considerations in order to provide better estimates of triplet invariants. However, some theoretical problems concerning the probabilistic estimation of triplet invariants when pseudotranslational symmetry is present still remained unsolved.

In this paper we describe a probabilistic theory of triplet relationships which explicitly takes into

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0108-7673/87/010014-09S01.50 © 1987 International Union of Crystallography
account pseudotranslational symmetry. More precisely, we will calculate the conditional probability distribution of a phase $\phi_h$ given $\phi_k$, $\phi_{-k}$, $\phi_{h-k}$, ..., when no correlation exists between atomic positions not related by symmetry or by pseudo-translations.

In accordance with the above observations, the first step of the mathematical approach will be the calculations of the joint probability distribution function $P(R_h, R_k, R_{-k} \mid \phi_h, \phi_k, \phi_{h-k})$ by taking into account: (1) the specific algebraic form of the $E$'s, which is strongly dependent on the pseudotranslational symmetry, and (2) the reduced number of primitive random variables. Indeed, now only the $t_p + t_q$ atomic positions constitute the primitive independent random variables. According to paper I we write

$$E_h = \sum_{j=1}^{t_p + t_q} \psi_j(h) g_j(h)$$

where

$$\psi_j(h) = f_j(h) \left[ e_h \left( \alpha_n \sum_p \sum_q \right) \right]^{1/2}.$$  

The normalizing factor in (1) is

$$\langle |F_h^2| \rangle = e_h \left( \alpha_n \sum_p \sum_q \right)$$

where

$$\alpha_n = (n_1 n_2 n_3 \ldots \gamma_n / m)$$

and $\gamma_n$ is the number of times for which the algebraic congruences

$$hR_i u_i = 0 \ (mod \ 1) \quad for \ i = 1, 2, 3, \ldots$$

are simultaneously satisfied when $s$ varies from 1 to $m$. If $\gamma_n = 0$ we say that $F_h$ is a superstructure reflexion: then $\langle |F_h^2| \rangle = e \sum q$. Otherwise $F_h$ is a substructure reflexion. The maximum value of $\gamma$ is $m$: consequently the maximum value of $\alpha$ is $n_1 n_2 n_3 \ldots$.

For $j < t_p$ [see equation (1.4a)],

$$g_j(h) = \sum_{s=1}^{m} \exp 2 \pi i h C_s r_j \left[ \prod_i \left( \sin n_i \pi hR_i u_i \right) \sin \pi hR_i u_i \right] \times \exp 2 \pi i h C_{s+i/2} (n_i - 1) u_i$$

for $t_p < j \leq t_p + t_q$ [see equation (1.4b)]

$$g_j(h) = \sum_{s=1}^{m} \exp 2 \pi i h C_s r_j.$$  

The index $i$ varies over the independent pseudo-translations.

The mathematical model described above may be applied both when a defined substructure exists and when pseudotranslational symmetry does not give rise to a substructure (Cascarono, Giacovazzo & Luić, 1985a). On the other hand, real substructures often do not exactly comply with our model. For example, it may occur that atoms related by pseudotranslational symmetry are not exactly located or are of different nature. Such situations involve a correlation between the superstructure and the substructure not taken into account by our model: dealing with these cases requires the modification of the theoretical background assumed in this paper. The effects of the correlation between superstructure and substructure on triplet estimation will be examined in a further paper. We only show here that our mathematical model provides probabilistic triplet estimations which can be profitably used in direct procedures for the solution of several real structures with superstructure effects.

For the sake of brevity we do not give a full account of our probabilistic approach: the reader is referred to a recent book (Giacovazzo, 1980) for the basic ideas. We give in §§ 2 and 3 only the final formulae for the cs and for the ncs cases respectively. At first sight they may appear rather unexpected. For this reason a short Appendix (Appendix A) will help the reader to justify our theoretical results. It is worthwhile mentioning that they do not hold for those special triplets described by Giacovazzo (1980, pp. 286-287) and by Pontenagel & Krabbendam (1983), for which supplementary algebraic considerations are needed.

2. Centrosymmetric space groups: the conditional probability that $E_h E_k E_{h-k}$ is positive given $R_h R_k R_{h-k}$

Denote by $P(E_h E_k E_{h-k} > 0)$ the conditional probability that the product $E_h E_k E_{h-k}$ is positive given $R_h R_k R_{h-k}$. On the assumption that all the atoms have the same unitary scattering factor we obtain (see Appendix A)

$$P(E_h E_k E_{h-k} > 0) = 0.5 + 0.5 \tanh A_{h,k}$$

where

$$A_{h,k} = R_h R_k R_{h-k} N_{h,k}^{-1/2},$$

$$N_{h,k}^{-1/2} = C_h C_k C_{h-k} \left[ m^{-1}[\sigma_3]_p \sum_{s=1}^{m} \prod_i \tau_{s,i} \right] + [\sigma_3]_q$$

and

$$\tau_{s,i} = \frac{\sin n_i \pi hR_i u_i \sin n_i \pi kR_i u_i}{\sin \pi hR_i u_i \sin \pi kR_i u_i}$$

If $p = 0$ (no pseudotranslation occurs), then $q = N$ and

$$N_{h,k} = [\sigma_3]_p / [\sigma_3]_q.$$  

Thus (2) reduces to the well known Cochran-Woolfson formula.
If all the reflexions $h, k, h-k$ are superstructure reflexions then $(\prod_i \tau_{s,i}) = 0$ for every $s$, and $N_{h-k}$ is given by

$$(N_{h,k})_0 = [\sigma_2]^q/[\sigma_3]^q - q. \quad (4)$$

Thus the reliability of a triplet constituted by superstructure reflexions appears to be inversely proportional to $q^{1/2}$ and not to $N^{1/2}$.

It may be worth mentioning that triplets constituted by superstructure reflexions may not always be found. For example, when a pseudotranslation of order 2 occurs, the superstructure reflexion $h$ satisfies the condition

$$hu \equiv 0 \pmod{1} \quad \text{and} \quad 2hu \equiv 0 \pmod{1}.$$

Thus $hu$ is a semi-integer value. If $h$ and $k$ are superstructure reflexions, $(h-k)u$ is the sum of two semi-integer values, that is to say, $(h-k)$ must be a substructure reflexion.

If only one of $h, k, h-k$ is a substructure reflexion (e.g. the reflexion $h$), then $(\prod_i \tau_{s,i}) = 0$ for every $s$, and $N_{h,h,k}$ is given by

$$(N_{h,k})_1 = (\alpha_h[\sigma_2]_p + [\sigma_2]_q)[\sigma_2]_q/[\sigma_3]_q. \quad (5)$$

$(N_{h,k})_1$ is larger than $(N_{h,k})_0$. In order to have a simple numerical insight, let us assume that all the atoms are of the same type. Then $(N_{h,k})_1 = (\alpha_h + q) \geq (N_{h,k})_0$.

If pseudotranslation symmetry gives rise to a subcell, triplets constituted of two substructure and one superstructure reflexions cannot be found. Indeed, if $h$ and $k$ correspond to the reciprocal lattice of the subcell, $h-k$ will also correspond to points of the same lattice. On the other hand, if pseudotranslational symmetry does not produce a subcell (Casparano, Giacovazzo & Luir, 1985a), 'sub–sub–super' triplets can exist (this case has never been considered in previous literature). As an example, let $h = 417$, $k = 382$ and $h-k = 795$; if $u = a/4$ in $P4$, then $h$ and $k$ are substructure reflexions with $\alpha_h = \alpha_k = 2$ while $h-k$ is a superstructure reflexion.

In general, if $h$ and $k$ are substructure reflexions and $h-k$ is a superstructure reflexion then

$$(N_{h,k})_2 = (\alpha_h[\sigma_2]_p + [\sigma_2]_q)(\alpha_k[\sigma_2]_p + [\sigma_2]_q) \times [\sigma_2]_q/[\sigma_3]_q. \quad (6)$$

It is easy to see that $(N_{h,k})_2 \geq (N_{h,k})_1 \geq (N_{h,k})_0$. If all the atoms are of the same type then

$$(N_{h,k})_2 = (\alpha_h p + q)(\alpha_k p + q)/q,$$

which is larger than $(N_{h,k})_1$ because $(\alpha_h p + q)/q > 1$, unless $p = 0$.

If $h, k, h-k$ are all substructure reflexions then the complete equation (3) has to be calculated, in which the factor $\sum_{i=1}^m (\prod_i \tau_{s,i}/n_i)$ is in general non-vanishing. It should be stressed that $\tau_{s,i}$ is a non-negative quantity.

Indeed: (1) $\sin n_i \pi y/\sin \pi y = 0$ if $y$ is not an integer value [here $y$ is one of $hR_{s,u}, kR_{s,u}, (h-k)R_{s,u}$]; (2) if $n_i$ is odd then $\sin n_i \pi y/\sin \pi y = n_i$ for integral values of $y$; (3) if $n_i$ is even then $\sin n_i \pi y/\sin \pi y$ equals $n_i$ for even values of $y$, and it equals $-n_i$ for odd values of $y$. In both cases $\tau_{s,i}$ is again positive because none or two of $hR_{s,u}, kR_{s,u}, (h-k)R_{s,u}$ can be odd.

It may be written in a way suitable for computer calculations [see equation (A.3)]

$$\sum_{s=1}^m \left( \prod_i \tau_{s,i}/n_i \right) = \beta(n_1^2 n_2^2 n_3^2 \ldots) \quad (7)$$

where $\beta$ is the number of times for which

$$hR_{s,u} = 0 \pmod{1},$$
$$hR_{s,u} = 0 \pmod{1},$$
$$hR_{s,u} = 0 \pmod{1},$$
$$hR_{s,u} = 0 \pmod{1},$$
$$hR_{s,u} = 0 \pmod{1},$$
$$hR_{s,u} = 0 \pmod{1} \ldots$$

are simultaneously satisfied when $s$ varies from 1 to $m$. Obviously, $\beta \leq m$: furthermore, $\beta$ cannot exceed the minimum among $n_h, n_k, n_{h-k}$ (see paper I). In conclusion,

$$(N_{h,k})_3 = \{ (\alpha_h[\sigma_2]_p + [\sigma_2]_q)(\alpha_k[\sigma_2]_p + [\sigma_2]_q) \times (\alpha_{h-k}[\sigma_2]_p + [\sigma_2]_q) \} \times \{(\beta/m)[\sigma_3]_p(n_1^2 n_2^2 n_3^2 \ldots) + [\sigma_3]_q\}^{-2}. \quad (8)$$

It may be shown (see Appendix B) that $(N_{h,k})_3 \leq (N_{h,k})_2$ according to different situations.

The numerical values of $(N_{h,k})_3$ suggest which type of triplet relationships will have a marginal or a central role (see § 4) in direct procedures for phase solution. For equal-atom structures (3) reduces to

$$N_{h,k}^{-1/2} = [(\alpha_h p + q)(\alpha_k p + q)(\alpha_{h-k} p + q)]^{-1/2} \times \left[ (1/m) \sum_{s=1}^m \left( \prod_i \tau_{s,i}/n_i \right) + q \right]. \quad (9)$$

3. Non-centrosymmetric space groups: the conditional probability of $\Phi_{h,k} = \phi_h - \phi_k - \phi_{h-k}$ given $R_h, R_k, R_{h-k}$

Under the same conditions stated in § 2 we obtain for the ncs space groups the relation

$$P(\Phi_{h,k}) = [2\pi I(2A_{h,k})]^{-1} \exp (2A_{h,k} \cos \Phi_{h,k}). \quad (10)$$

Equation (10) is a unimodal von Mises function, with
its maximum at $\Omega_{h,k} = 0$. In order to obtain more insight into the numerical values involved in (2) or (10) we calculate in a few cases some parameters for an equal-atom $P4$ random structure, having $t_p = 5$, $t_q = 15$, $u = a/4$. Then $p = 80$, $q = 60$, $N = 140$. According to paper I the substructure reflexions $hkl$ have $h$ or $k$ congruent to zero modulo 4. If superstructure effects are not taken into account in the normalization process, we would obtain the pseudonormalized structure factors $E'$ and the following expected averages:

$$\langle |E'_h|^2 \rangle_{h=4n} = 1.57$$

$$\langle |E'_h|^2 \rangle_{h=4n,k=4n} = 2.71$$

$$\langle |E'_h|^2 \rangle_{h=-k=0} = 2.71$$

Our normalization program (described in paper I) finds $\langle |E'_h|^2 \rangle_{sub} = 1.76$, from which $p$ and $q$ are estimated to be 83 and 57 respectively.

The true normalized structure factors $E$ can be obtained via (1.22), or, more simply, by

$$E_h = E'_h [\langle \sigma_2 \rangle_N / (\sigma_0 [\sigma_2]_p + [\sigma_2]_q)]^{1/2},$$

(11)

which, in our example, reduces to

$$E_h = E'_h [N / (\sigma_0 p + q)]^{1/2}.$$

In Table 1 the true $N_{h,k}$ values [calculated via (9)] are shown for the various types of triplets; the values calculated by our program are in parentheses (the experimental estimates for $p$ and $q$ have been used).

In Table 2 some pseudonormalized $E'$ and the corresponding normalized structure factors $E$ are shown. The values of $A_{h,k}$ according to Cochrans’s (1955) formula and to our procedure are given for each triplet. The tables show how different the reliability of the various triplets may be according to the two procedures. In particular the value $N = 140$ to be used in Cochrans’s formula is replaced in our procedure by 22, 31, 38, 60, 220, 380, 807 according to the type of triplet. Clearly, triplets constituted by 3, 1 or 0 substructure reflexions may play an important role in the phasing procedures, while triplets constituted by only two substructure reflexions have a marginal role.

Besides space-group symmetry and pseudotranslational symmetry $p$ and $q$ values are also important for defining the specific role of a given type of triplet in the crystal-structure-determination process. Let us consider as an example a random $P4$ structure with $t_p = 15$, $t_q = 5$, $u = a/4$: then $p = 240$, $q = 20$, $N = 260$. In Table 3 the values of $N_{h,k}$ [calculated via (9)] are shown for the various types of triplets (the values calculated by our program in parentheses). From comparison of Table 3 with Table 1 it is easily seen that ‘super–super–super’ triplets are the most important ones. Indeed, the eight triplets with largest values of $A(h,k)$ are all of type ‘super–super–super’ while the largest value of $A(h,k)$ for ‘sub–sub–sub’ is 2.71 (74 in the list).

Two additional points deserve to be stressed. Renormalization of structure factors proposed by Hauptman & Karle (1959) to remove in the phasing procedures problems imposed by systematically strong and weak reflexions does exploit the indirect information contained in the statistics of the structure factors, but on the other hand it ignores the usefulness of knowing the structural regularities causing those statistical effects. In the light of the above results such a procedure appears too drastic and rigid. For example, it reduces too much the reliability of the ‘sub–sub–sub’ triplets and overestimates by different amounts the other types of triplet. According to our theory, the information obtained from the analysis of statistics is used, not only for renormalizing structure factors, but also for evaluating suitable values of $N_{h,k}$ for each type of triplet. For example, for ‘sub–sub–sub’ triplets, $N_{h,k} < N$, so that those triplets are estimated to be more reliable than via the mere normalization process. Support for these conclusions is provided in Appendix C, where the Sayre (1952) equation...
Table 3. Values $N_{h,k}$ for the various types of triplets in a $P4$ randomly generated structure, with $t_p = 15$, $t_q = 5$, $u = a/4$

<table>
<thead>
<tr>
<th>Type of triplet</th>
<th>$N$</th>
<th>$N$ (values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(fnl), (fnl), (fnl)$</td>
<td>33 (33)</td>
<td></td>
</tr>
<tr>
<td>$(ffl), (ffl), (ffl)$</td>
<td>63 (63)</td>
<td></td>
</tr>
<tr>
<td>$(fnl), (fnl), (ffl)$</td>
<td>65 (65)</td>
<td></td>
</tr>
<tr>
<td>$(nnl), (nnl), (nnl)$</td>
<td>20 (21)</td>
<td></td>
</tr>
<tr>
<td>$(nnl), (nnl), (nnt)$</td>
<td>500 (449)</td>
<td></td>
</tr>
<tr>
<td>$(nnl), (nnl), (nil)$</td>
<td>980 (977)</td>
<td></td>
</tr>
<tr>
<td>$(nnl), (fnl), (fnl)$</td>
<td>12 500 (11 738)</td>
<td></td>
</tr>
</tbody>
</table>

For symbols see caption to Table 1.

is briefly discussed and compared with approaches by other authors.

The above remarks are the starting point for a more general proposition: when a priori information is available, it must be used in the normalization process, in the theory aiming at estimating phase relationships, and in the phasing process, otherwise systematic errors or other drawbacks will be produced during the procedure.

The second additional point to stress is that the mathematical approach described above cannot be applied rigorously when $t_p$ or $t_q$ are small numbers (in some structures $t_p = 1$). Situations in which the number of independent random variables is small but direct methods are successful are not infrequent: for example, very small structures or structures partially known.

The usual probabilistic theories also proved to be useful in these cases; therefore we can expect that small values of $t_p$ or $t_q$ are disturbing but not critical parameters for the theory developed in the present paper.

4. The conditional distribution of $\varphi_h$ given $R_h$ and more pairs $\varphi_k, \varphi_{h-k}, R_k, R_{h-k}$

In the cs space groups we obtain

$$P(E_h > 0) = 0.5 + 0.5 \tanh \left[ R_h \sum (N_{h,k})^{1/2} E_k, E_{h-k} \right]$$

and, in ncs space groups,

$$P(\varphi_h) = [2\pi I_0(Q_h)]^{-1} \exp \left[ Q_h \cos (\varphi_h - \theta_h) \right],$$

where

$$Q_h = \left\{ \sum A_{h,k} \cos (\varphi_h + \varphi_{h-k}) \right\}^2$$

$$+ \left\{ \sum A_{h,k} \sin (\varphi_h + \varphi_{h-k}) \right\}^2 \right\}^{1/2},$$

$$\tan \theta_h = \frac{\sum A_{h,k} \sin (\varphi_h + \varphi_{h-k})}{\sum A_{h,k} \cos (\varphi_h + \varphi_{h-k})}.$$  

It is easily seen that the usual algorithms for phase expansion and refinement need only a few modifications for handling superstructure problems.

5. Real structures: possible sources of ambiguity and experimental results

The presence of heavy atoms in a crystal structure is not a factor limiting the effectiveness of the renormalization procedure described in paper I. Indeed, the process depends on the ratios $\Sigma_p/\Sigma_N$ and $\Sigma_q/\Sigma_N$ (scattering powers of the $q$ and $p$ atoms/scattering power of the complete crystal structure) which in principle are statistically estimable with identical accuracy no matter if heavy atoms occur. However, if some heavy atoms are present, the statistical analysis of intensities described in paper I does not provide the species and the number of atoms suffering pseudotranslation, but only the ratio $\Sigma_q/\Sigma_N$ which reduces to $q/N$ only if all atoms are equal. In this case (and only in this case) (3) reduces to (9), which is therefore computable via the statistical analysis of diffraction data.

In general $\Sigma_q/\Sigma_N$ and $q/N$ do not coincide.

In order to give an example, let us suppose that the crystal structure contains $p$ atoms with atomic number $Z_p$ and $q$ atoms with atomic number $Z_q$.

According to (1.13), we write

$$\langle E_h^2 \rangle = (\alpha_h p Z_p^2 + q Z_q^2)/(p Z_p^2 + q Z_q^2).$$

(16)

Since $p = (N - q), (16)$ becomes

$$\frac{q}{N} = \frac{\langle E_h^2 \rangle - \alpha_h}{\langle E_h^2 \rangle - \alpha_h + (Z_q^2/Z_p^2) - \alpha_h + (Z_q^2/Z_p^2)}$$

$$= \frac{\langle E_h^2 \rangle - \alpha_h}{(\langle E_h^2 \rangle - 1)(1 - (Z_q^2/Z_p^2)) + 1 - \alpha_h},$$

(17)

which reduces to equation (1.15) only if $Z_q = Z_p$.

For $p = 4$ atoms with $Z_p = 40$ and $q = 60$ with $Z_q = 6$ the statistical analysis of diffraction data via equation (1.16) should estimate $q/N = 0.25$, so that $p$ and $q$ should be assumed proportional to 48 and 16 respectively, in evident contrast with reality.

The above is a dramatic example in which the scattering power of the $q$ atoms constitutes a small percentage of the total scattering but the number of $q$ atoms is a large percentage of the total number. A converse example may easily be given. The obvious consequence is that $q/N$ or $p/N$ or $p/q$ have always to be interpreted as ratios between scattering powers and not between numbers of atoms.

The situation becomes more complicated when the $p$ atoms as well as the $q$ atoms are not of the same type. Indeed:

(a) If pseudotranslational symmetry relates atoms of different type then the $p$ atoms contribute to both $\Sigma_p$ and $\Sigma_q$ (that is to say, to both substructure and superstructure reflexions). The first contribution
arises from those electrons of the p atoms which do
overlap because of pseudotranslations (the maximum
overlap cannot exceed the lightest atom). The contribu-
tion to \( \Sigma_q \) arises from those electrons of the p atoms
which do not satisfy pseudotranslational symmetry.
Thus, \( \rho_q(r) = \rho(r) - \rho_p(r) \) will contain, besides the q
atoms, also some electron residuals of the p atoms
(see Fig. 1). Then the overall number of atomic peaks
in \( \rho_q(r) \) is larger than \( N - p \). Underestimation of this
effect will produce overestimation of 'super-super-
super' and 'super-super-sub' triplets with respect to
the others.

(b) Statistical underestimation of \( \sigma_2^2 / \sigma_2^2_N \)
is equivalent to partially neglecting information con-
tained in pseudotranslational symmetry and causes
some overestimation of 'sub-sub-sub' triplets with
respect to others. However, overestimation of
\( \sigma_2^2 / \sigma_2^2_N \) is more dangerous (see also Bohme,
1982) because it introduces into the mathematical
model atoms with negative scattering factors (see Fig.
1). In this case, triplets of type 'super-super-super'
are overestimated with respect to 'super-super-sub'
which in their turn are overestimated with respect to
'sub-sub-sub' triplets.

(c) \( \sigma_1^2 \) and \( \sigma_3^2 \) are not accessible via statistical
analysis so that \( N_{b,k} \) is not exactly computable via
(3). Therefore, in the practical procedure, we use the
approximate equation (9) instead of (3).

In spite of the above limitations our approach
works well in several cases. We have applied it to the
five crystal structures described in Table 4. The first
three of them were originally solved via ad hoc

![Fig. 1. \( \rho \) is the unidimensional electron density constituted by triangular 'atoms'. The pseudotranslational symmetry \( u = a/3 \) relates atoms of different type: \( \rho_u \) is the electron density suffering pseudotranslational symmetry, \( \rho_p = p - \rho_p \) is the complementary electron distribution, \( \rho'_q \) is a wrong estimate of \( \rho_p \) (possibly suggested by statistical analysis): in this case \( \rho'_q \) contains 'negative' atoms.]

\begin{table}
\centering
\begin{tabular}{ l c c c c }
Crystal structure & Space group & \( u \) & \( e\% \) \\
\hline
Freieslebenite* & P2_1/a & \( a/2 + b/3 \) & 0.51 \\
Mesolite† & Fdd2 & \( Z = 16 \) & 0.66 \\
Na_2Ca_2Al_5SbS_7 & P2_1/n & \( a + b/2 \) & 0.55 \\
Ni_2S_3 & P1 & \( Z = 2 \) & 0.37 \\
[Ni(C_5H_4)_4][Ni(C_3S_3)_2] & P6_5/mmc & \( Z = 2 \) & 0.44 \\
FeGa & & & \\
Fe_2Ga_2S_5 & & & \\
\hline
\end{tabular}
\caption{Test structures: space group, the main pseudotranslational vector (\( u \)) and the estimated percentages of electrons (\( e\% \)) suffering pseudotranslational symmetry}
\end{table}

methods. Nist can also be routinely solved without
introducing information on pseudotranslational symmetry.
The last one was MULTAN resistant and has
been routinely solved by the present method. In all
cases our procedure revealed for each crystal structure
a large percentage of atoms which, via the usual
Fourier methods, led to the complete structures.

6. Concluding remarks

The mathematical model introduced in paper I has
been applied to the estimation of triplet invariants.
The approach is able to produce for non-centrosym-
metric space groups a unique distribution for the
triplet phases which is of von Mises type and whose
concentration parameter changes according to the
type of triplet and to the pseudotranslational sym-
metry. A mathematical model cannot take into
account every type of pseudotranslational symmetry:
thus in principle our procedure may be successful in
some cases (when the actual crystal structure complies
well with the model) and may be unsuccessful in
others. In spite of this limitation the method described
in this paper seems rather efficient: indeed, it worked
on real crystal structures which do not fully comply
with the mathematical model both because atoms
related by pseudotranslational symmetry are not
equal and because they are not exactly located.

The procedure has been introduced into the SIR
package (Cascarano, Giacovazzo, Burla, Nunzi,
Polidori, Camalli, Spagna & Viterbo, 1985). The
macro-instruction PSEUDO compels the normaliz-
ation program to carry out the statistical analysis of
diffraction intensities, in order to recognize the
pseudotranslational symmetry and to estimate \( p \) and
\( q \) parameters. The information so obtained, together
with renormalized structure factors, is passed to the
\( \Sigma_2 \) routine, which calculates for each triplet the con-
centration parameter \( A_{b,k} \). In its turn this parameter
is used in the CONVERGENCE procedure for origin and enantiomorph definition and in the tangent process.

One of us (ML) is indebted to ICTP (International Centre for Theoretical Physics, Programme for Training and Research in Italian Laboratories, Trieste, Italy) for financial support during a three-month stay at the University of Bari.

APPENDIX A

In accordance with equation (1),

\[ E_{h}E_{k}E_{h+k} = \sum_{j_1=1}^{t_p} \psi_j(h)g_j(h) \sum_{j_2=1}^{t_q} \psi_j(k)g_j(k) \times \sum_{j_3=1}^{t_p+t_q} \psi_j(h+k)g_j(h+k). \]

If no correlation exists among the \( t_p + t_q \) primitive random variables \( r_j \), then

\[ \langle E_{h}E_{k}E_{h+k} \rangle = \sum_{j=1}^{t_p+t_q} \langle \psi_j(h)\psi_j(k)\psi_j(h+k) \rangle \times g_j(h)g_j(k)g_j(h+k). \]  

(A.1)

If we denote

\[ \nu(h, s) = \exp \left\{ 2\pi i h C_s r_j + \frac{1}{2} (n_1 - 1) u_1 + \frac{1}{2} (n_2 - 1) u_2 + \frac{1}{2} (n_3 - 1) u_3 + \ldots \right\}, \]

then

\[ \langle E_{h}E_{k}E_{h+k} \rangle = \sum_{j=1}^{t_p+t_q} \langle \psi_j(h)\psi_j(k)\psi_j(h+k) \rangle \times \nu(h, s) \times \nu(k, s) \times \nu(h+k, s) \]

(A.2)

Non-vanishing contributions to \( \langle E_{h}E_{k}E_{h+k} \rangle \) from the right-hand side of (A.2) occur if

\[ \nu(h, s_1)\nu(k, s_2)\nu(h+k, s_3) \neq 0. \]

Under the conditions specified in § 1, that requires \( s_1 = s_2 = s_3 \). Therefore, (A.2) becomes

\[ \langle E_{h}E_{k}E_{h+k} \rangle = \left[ \sum_{j=1}^{t_p} \psi_j(h)\psi_j(k)\psi_j(h+k) \right] \times \sum_{s_1=1}^{m} \left[ \prod_{i=1}^{n_3} \tau(s, i) \right] \times \sum_{s_2=1}^{m} \psi_j(h)\psi_j(k)\psi_j(h+k), \]

(A.3)

where

\[ \tau(s, i) = S(h, s, i)S(k, s, i)S(h+k, s, i). \]

Since

\[ p = m t_p(n_1, n_2, n_3, \ldots), \quad q = m t_q, \]

then

\[ \langle E_{h}E_{k}E_{h+k} \rangle = \left[ \frac{1}{m} \sum_{j=1}^{p} \psi_j(h)\psi_j(k)\psi_j(h+k) \right] \times \sum_{s_1=1}^{m} \left[ \prod_{i=1}^{n_3} \tau(s, i) \right] \times \sum_{s_2=1}^{m} \psi_j(h)\psi_j(k)\psi_j(h+k), \]

from which (3) is obtained.

APPENDIX B

Suppose all atoms are equal. Then

\[ (N_{h,k})_3 \equiv (N_{h,k})_2 \]

if

\[ (\alpha_{h+k} + q)/((\beta/m)p(n_1^2 n_2^2 n_3^2 \ldots + q)^2) \leq q^{-1}, \]

which is true if

\[ p(p \delta^2 + 2q \delta - \alpha_{h+k} q) \leq 0, \]

(B.1)

where \( \delta = \beta(n_1^2 n_2^2 n_3^2 \ldots)/m. \)

Relation (B.1) may be studied as a function of \( \delta \) (that is, to say, \( p \) and \( q \) are fixed while the space group
and the pseudotranslations are allowed to vary) or as a function of $p$ (the space group and the pseudotranslations are given while $p$ is the variable). In both cases $(N_{h,k})_3 = (N_{h,k})_2$ if $p = 0$.

In the first case, $(B.1)$ is an equality if $\delta = \delta_1$ or $\delta_2$, where

$$\delta_1 = \left(-q - [q(q + \alpha_{h+k} p)]^{1/2}\right)/p,$$

$$\delta_2 = \left(-q + [q(q + \alpha_{h+k} p)]^{1/2}\right)/p.$$  

$\delta_2$ is the unique root allowed for $\delta$ (indeed $\delta > 0$). Therefore $(N_{h,k})_3 > (N_{h,k})_2$ if $\delta < \delta_2$, $(N_{h,k})_3 = (N_{h,k})_2$ if $\delta = \delta_2$. In the second case $(N_{h,k})_3 \neq (N_{h,k})_2$ if $p \neq q(\alpha_{h+k} - 2\delta)/\delta^2$. If $2\delta > \alpha_{h+k}$ then $(N_{h,k})_3 < (N_{h,k})_2$ always.

**APPENDIX C**

Suppose for an equal-atom structure that the electron density $\rho(r)$ may be expressed as the sum of the substructure $\rho_s(r)$, relative to $p$ atoms in the cell, and of $\rho_q(r)$, relative to $q$ atoms not related by pseudotranslations:

$$\rho(r) = \rho_p(r) + \rho_q(r). \quad (C.1)$$

For the sake of simplicity let us deal with the $P1$ case. We write

$$\rho_p(r) = \rho_{p_0}(r) * \sum_{\nu_1=0}^{n_1-1} \delta(r - \nu_1 u_1) * \sum_{\nu_2=0}^{n_2-1} \delta(r - \nu_2 u_2) * \ldots, \quad (C.2)$$

where $\rho_{p_0}(r)$ is the structure corresponding to the $t_p$ independent atoms, * is the symbol of convolution, $u_1, u_2, \ldots$ are the independent pseudotranslations in the cell, and $\delta$ is the Dirac delta function. The Fourier transform of $(C.1)$ gives

$$F_h = T[\rho_p(r)] + T[\rho_q(r)]$$

$$= T[\rho_{p_0}(r)] T \left[ \sum_{\nu_1=0}^{n_1-1} \delta(r - \nu_1 u_1) * \sum_{\nu_2=0}^{n_2-1} \delta(r - \nu_2 u_2) * \ldots \right] + (F_h)_q$$

$$= (F_h)_p \prod_i \left\{ \exp \left[ \frac{2\pi i}{h(n_i-1)} u \right] \sin \frac{n_i \pi u h_i}{\sin \pi u h_i} \right\} + (F_h)_q$$

$$= (F_h)_q + (F_h)_q$$

which agrees with (1).

Squaring of $(C.1)$ according to Sayre (1952) gives

$$F_h = (\theta / V) \left\{ \sum_k (F_k)_p (F_{h-k})_p + \sum_k (F_k)_q (F_{h-k})_q \right\} + 2 \sum_k (F_k)_p (F_{h-k})_q \quad (C.3)$$

where $\theta$ denotes the ratio of the averaged scattering factors to the squared ones. Since $\rho_p$ and $\rho_q$ are supposed to be uncorrelated, in $(C.1)$ it may be assumed that $\rho_p(r) \rho_q(r) = 0$, so that in $(C.3)$ the summation $\sum_k (F_k)_p (F_{h-k})_q$ is expected to be vanishing.

Therefore, $(C.3)$ reduces to

$$F_h = (\theta / V) \left\{ \sum_k (F_k)_p (F_{h-k})_p + \sum_k (F_k)_q (F_{h-k})_q \right\}.$$  

$(C.4)$

In accordance with Jeffery (1964), the values of the superstructure reflexions depend only on $\rho_p$ while substructure reflexions depend both on $\rho_p$ and $\rho_q$. If $F_h$ in $(C.4)$ is a superstructure reflexion, then its value is only fixed by the contribution $\sum_k (F_k)_q (F_{h-k})_q$ and $(C.4)$ reduces to

$$F_h = (\theta / V) \sum_k (F_k)_q (F_{h-k})_q. \quad (C.5)$$

Both $(F_k)_q$ and $(F_{h-k})_q$ are known in practice only when $k$ and $h-k$ correspond to superstructure reflexions. When $k$ or $h-k$ refer to substructure reflexions then $(F_k)_q$ and $(F_{h-k})_q$ are parts of $F_k$ and $F_{h-k}$, unknown but essential for securing Sayre's equation $(C.5)$ to be satisfied. Statistically speaking the average $\langle (F_k)_q (F_{h-k})_q \rangle$ relative to 'super-super' pairs is expected to be nearly equal to the averages relative to 'super-sub' or 'sub-sub' pairs. Consequently, the contributions $F_k F_{h-k}$ relative to 'super-sub' pairs are expected to be more sparsely spread around $F_h$ than the contributions $F_k F_{h-k}$ relative to 'super-super' pairs. In their turn these are expected to be more sparsely spread around $F_h$. If the contributions $F_k F_{h-k}$ relative to 'super-super' pairs are hidden in the known moduli $|F_k|_q, |F_{h-k}|_q$, the contributions $F_k F_{h-k}$ relative to 'super-super' pairs are expected to be more sparsely spread around $F_h$ than the contributions $F_k F_{h-k}$ relative to 'super-super' pairs. That agrees well with our theoretical results according to which

$$(N_{h,k})_3 > (N_{h,k})_2 > (N_{h,k})_1 > (N_{h,k})_0.$$  

From the point of view introduced in this Appendix, the factors $(N_{h,k})_0, (N_{h,k})_1, (N_{h,k})_2$ involved in $(4), (5), (6)$ appear to be nothing but statistical coefficients generated by a procedure aimed at applying a Cochran-like approach to the unknown moduli $|F_{h-k}|_q, |F_k|_q, |F_{h-k}|_q$ hidden in the known moduli $|F_h|_q, |F_k|_q, |F_{h-k}|_q$.

**References**


Figures of Merit in Direct Methods: a New Point of View

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(Received 16 December 1985; accepted 12 May 1986)

Abstract

The probabilistic approach has been extensively used for analysing the statistical meanings of some traditional figures of merit. New figures of merit have also been introduced; some exploit one-phase and two-phase structure seminvariants of the first rank, the expected negative and/or enantiomorph-sensitive triplet invariants, and the expected negative and/or enantiomorph-sensitive quartets. Other figures of merit exploit the distribution of statistical parameters connected with PSI(0) and active triplets. A new combined figure of merit is shown to be a powerful tool for selecting the correct solutions among the various sets output by multisolution methods.

1. Introduction

For the determination of very complex structures by direct methods a large initial set of known phases seems to be a basic requirement. This aim can be achieved by introducing a large number of permutable phases which are used to generate different phase sets. Magic integer sequences (Main, 1977) are often employed for phase permutations: a relatively large number of phase sets are thereby created among which the correct solutions have to be found. Figures of merit (FOM) are usually used to screen the set of solutions, prior to computing Fourier transforms (E map).

In general, FOM's are functions based on quantities which can be expected to have extreme values for the correct solution. The expectation relies on a probabilistic background and/or on algebraic properties. In the SIR program (Nunzi et al., 1984), several low-order structure seminvariants and invariants are estimated by means of representation theory (Giacovazzo, 1977, 1980a). Some of them are actively used for phase expansion and refinement, others are only employed to compute the FOM's. Since one or more FOM's are available for each type of structure seminvariant or invariant, the combined figure of merit CPHASE, based on a variety of FOM's, is expected to be effective in finding the correct solution [see Hašek, Schenk, Kiers & Schagen (1985) for some tests of distribution-fitting methods for centrosymmetric structures].

A probabilistic approach is also introduced which enables us to analyse the statistical meanings of some traditionally widely used FOM's. New effective figures of merit are devised which, combined with CPHASE, give rise to a reliable total combined figure of merit CFOM which is expected to be unity for the correct solutions.

2. The combined figure of merit CPHASE

Overbeek & Schenk (1976) first proposed a FOM based on $\Sigma_i$ relationships. In the SIR program the estimates of the one-phase structure seminvariants of