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A Centrosymmetrical Formula for Triplet Invariants in Dispersive Structures

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Abstract

While probabilistic formulae estimating triplet invariants in non-centrosymmetric dispersive structures are available, equivalent distributions in centrosymmetric dispersive structures are completely unknown. Filling this gap is the main aim of this paper. Some recipes for the use of centrosymmetrical triplets in phasing procedures are also given.

Notation

N number of atoms in the cell.

$f = f' + if''$ general expression for the atomic scattering factor.

$F_{\mathbf{h}} = A_{\mathbf{h}} + iB_{\mathbf{h}} = |F_{\mathbf{h}}| e^{i\varphi_{\mathbf{h}}}$ structure factor with index $\mathbf{h}$: $|F_{\mathbf{h}}|$ is its modulus, $\varphi_{\mathbf{h}}$ its phase.

1. Introduction

Probabilistic treatment of the anomalous-dispersion effect in phasing procedures [see Srinivasan & Parthasarathy (1976) and literature there quoted] is more important in non-centrosymmetric than in centrosymmetric space groups. Accordingly approaches estimating two-phase and three-phase structure invariants are always described in $P1$ (Heinerman, Krabbendam, Kroon & Spek, 1978; Hauptman, 1982; Giacovazzo, 1983).

While in $P1$

$$A_{\mathbf{h}} = \sum_{j=1}^{N} (f_j' \cos 2\pi\mathbf{hr}_j - f_j'' \sin 2\pi\mathbf{hr}_j)$$

$$B_{\mathbf{h}} = \sum_{j=1}^{N} (f_j' \sin 2\pi\mathbf{hr}_j + f_j'' \cos 2\pi\mathbf{hr}_j),$$

in $P\bar{1}$

$$A_{\mathbf{h}} = 2 \sum_{j=1}^{N/2} f_j' \cos 2\pi\mathbf{hr}_j$$

$$B_{\mathbf{h}} = 2 \sum_{j=1}^{N/2} f_j'' \cos 2\pi\mathbf{hr}_j,$$

so that $F_{\mathbf{h}} = F_{-\mathbf{h}}$ always. It may therefore be expected that probabilistic formulae for centrosymmetric space groups will be formally quite different from the corresponding non-centrosymmetric ones. Thus it is of non-negligible interest to derive probabilistic formulae for the estimation of the structure invariants in centrosymmetric space groups. Suitably generalized, these formulae may be used in non-centrosymmetric groups for the estimation of two-phase and three-phase structure invariants constituted by symmetry-restricted phases.

In centrosymmetric crystals the distribution $P(A_{\mathbf{h}}, B_{\mathbf{h}})$ when dispersive atoms are present has been determined by Wilson (1980); the conditional distribution $P(\Phi_{\mathbf{h}} | |F_{\mathbf{h}}|)$ for the two-phase invariant $\Phi_{\mathbf{h}} = \varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}}$ has been provided by Giacovazzo (1987). It is the aim of this paper to develop probabilistic formulae for triplet invariants in centrosymmetric space groups and suggest how they may be used in practical procedures for phase solution.

2. The joint probability distribution function $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h}+\mathbf{k}})$ in $P\bar{1}$

Since $F_{\mathbf{h}} = F_{-\mathbf{h}}$, probabilistic formulae for triplet invariants may be derived *via* the joint probability distribution $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h}+\mathbf{k}})$. Here we introduce the carrying variables u_i, v_i, $i = 1, 2, 3$ associated with A_i and B_i, $i = 1, 2, 3$ respectively, and calculate the characteristic function $C(u_1, u_2, u_3, v_1, v_2, v_3)$ retaining terms up to order $1/\sqrt{N}$. Its Fourier transform gives the required joint probability distribution function

$$\begin{aligned} P(A_1, A_2, A_3, B_1, B_2, B_3) &\simeq 1/(2\pi)^6 \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \exp[-i(u_1A_1 + u_2A_2 \\ &+ u_3A_3 + v_1B_1 + v_2B_2 + v_3B_3)] \\ &\times \exp\{-\tfrac{1}{2}[\alpha_{11}u_1^2 + \alpha_{22}u_2^2 + \alpha_{33}u_3^2 + \beta v_1^2 \\ &+ \beta v_2^2 + \beta v_3^2 + 2\alpha_{14}u_1v_1 + 2\alpha_{25}u_2v_2 + 2\alpha_{36}u_3v_3] \\ &- i[\alpha_{123}u_1u_2u_3 + \alpha_{126}u_1u_2v_3 + \alpha_{135}u_1v_2u_3 \\ &+ \alpha_{234}v_1u_2u_3 + \alpha_{156}u_1v_2v_3 + \alpha_{246}v_1u_2v_3 \\ &+ \alpha_{345}v_1v_2u_3 + \alpha_{456}v_1v_2v_3]\} \, du_1 \cdots dv_3, \end{aligned}$$

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where

$$\alpha_{11}=\sum_{j=1}^{N} f_j'^2(\mathbf{h}),\quad \alpha_{22}=\sum_{j=1}^{N} f_j'^2(\mathbf{k}),\quad \alpha_{33}=\sum_{j=1}^{N} f_j'^2(\mathbf{h}+\mathbf{k}),$$

$$\beta=\sum_{j=1}^{N} f_j''^2,\quad \alpha_{14}=\sum_{j=1}^{N} f_j'(\mathbf{h})f_j'',\quad \alpha_{25}=\sum_{j=1}^{N} f_j'(\mathbf{k})f_j'',$$

$$\alpha_{36}=\sum_{j=1}^{N} f_j'(\mathbf{h}+\mathbf{k})f_j'',\quad \alpha_{123}=\sum_{j=1}^{N} f_j'(\mathbf{h})f_j'(\mathbf{k})f_j'(\mathbf{h}+\mathbf{k}),$$

$$\alpha_{126}=\sum_{j=1}^{N} f_j'(\mathbf{h})f_j'(\mathbf{k})f_j'',\quad \alpha_{135}=\sum_{j=1}^{N} f_j'(\mathbf{h})f_j''f_j'(\mathbf{h}+\mathbf{k}),$$

$$\alpha_{234}=\sum_{j=1}^{N} f_j''f_j'(\mathbf{k})f_j'(\mathbf{h}+\mathbf{k}),\quad \alpha_{156}=\sum_{j=1}^{N} f_j'(\mathbf{h})f_j''^2,$$

$$\alpha_{246}=\sum_{j=1}^{N} f_j''^2f_j'(\mathbf{k}),\qquad \alpha_{345}=\sum_{j=1}^{N} f_j''^2f_j'(\mathbf{h}+\mathbf{k}),$$

$$\alpha_{456}=\sum_{j=1}^{N} f_j''^3.$$

According to the above definitions we do not assume identical unitary scattering curves for the various atoms.

After lengthy calculation the following joint probability distribution (expressed in terms of moduli and phases) is obtained:

$$\begin{aligned}
&P(|F_1|,|F_2|,|F_3|,\varphi_1,\varphi_2,\varphi_3)\\
&\simeq 1/(2\pi)^3|F_1F_2F_3|/(\gamma_1\gamma_2\gamma_3)^{1/2}\\
&\quad\times\exp\left\{-\frac{|F_1|^2}{2}\left(\frac{\beta+\alpha_{11}}{2\gamma_1}\right)-\frac{|F_2|^2}{2}\left(\frac{\beta+\alpha_{22}}{2\gamma_2}\right)\right.\\
&\quad-\frac{|F_3|^2}{2}\left(\frac{\beta+\alpha_{33}}{2\gamma_3}\right)+\frac{|F_1|^2}{2\gamma_1}X_1\cos(2\varphi_1-x_1)\\
&\quad+\frac{|F_2|^2}{2\gamma_2}X_2\cos(2\varphi_2-x_2)+\frac{|F_3|^2}{2\gamma_3}X_3\cos(2\varphi_3-x_3)\\
&\quad+\frac{|F_1F_2F_3|}{\gamma_1\gamma_2\gamma_3}[p_{123}\cos\varphi_1\cos\varphi_2\cos\varphi_3\\
&\quad+p_{126}\cos\varphi_1\cos\varphi_2\sin\varphi_3\\
&\quad+p_{135}\cos\varphi_1\sin\varphi_2\cos\varphi_3\\
&\quad+p_{156}\cos\varphi_1\sin\varphi_2\sin\varphi_3\\
&\quad+p_{234}\sin\varphi_1\cos\varphi_2\cos\varphi_3\\
&\quad+p_{246}\sin\varphi_1\cos\varphi_2\sin\varphi_3\\
&\quad+p_{345}\sin\varphi_1\sin\varphi_2\cos\varphi_3\\
&\quad\left.+p_{456}\sin\varphi_1\sin\varphi_2\sin\varphi_3]\right\},
\end{aligned}\tag{1}$$

where

$$\begin{aligned}
\gamma_1&=(\beta\alpha_{11}-\alpha_{14}^2),\\
\gamma_2&=(\beta\alpha_{22}-\alpha_{25}^2),\\
\gamma_3&=(\beta\alpha_{33}-\alpha_{36}^2),\\
X_1&=[\tfrac{1}{4}(\alpha_{11}-\beta)^2+\alpha_{14}^2]^{1/2},\\
x_1&=\tan^{-1}[2\alpha_{14},(\alpha_{11}-\beta)],\\
X_2&=[\tfrac{1}{4}(\alpha_{22}-\beta)^2+\alpha_{25}^2]^{1/2},\\
x_2&=\tan^{-1}[2\alpha_{25},(\alpha_{22}-\beta)],\\
X_3&=[\tfrac{1}{4}(\alpha_{33}-\beta)^2+\alpha_{36}^2]^{1/2},\\
x_3&=\tan^{-1}[2\alpha_{36},(\alpha_{33}-\beta)].
\end{aligned}$$

The two parameters of $\tan^{-1}$ are proportional to $\sin x_i$ and $\cos x_i$ respectively. Furthermore,

$$\begin{aligned}
p_{123}&=[\beta^3\alpha_{123}-\beta^2(\alpha_{36}\alpha_{126}+\alpha_{25}\alpha_{135}+\alpha_{14}\alpha_{234})\\
&\quad+\beta(\alpha_{14}\alpha_{36}\alpha_{246}+\alpha_{14}\alpha_{25}\alpha_{345}+\alpha_{25}\alpha_{36}\alpha_{156})\\
&\quad-\alpha_{14}\alpha_{25}\alpha_{36}\alpha_{456}],\\
p_{126}&=[\beta^2(\alpha_{33}\alpha_{126}-\alpha_{36}\alpha_{123})+\beta(\alpha_{14}\alpha_{36}\alpha_{234}\\
&\quad-\alpha_{14}\alpha_{33}\alpha_{246}-\alpha_{25}\alpha_{33}\alpha_{156}+\alpha_{25}\alpha_{36}\alpha_{135})\\
&\quad+\alpha_{14}\alpha_{25}\alpha_{33}\alpha_{456}-\alpha_{14}\alpha_{25}\alpha_{36}\alpha_{345}],\\
p_{135}&=[\beta^2(\alpha_{22}\alpha_{135}-\alpha_{25}\alpha_{123})+\beta(\alpha_{14}\alpha_{25}\alpha_{234}\\
&\quad+\alpha_{25}\alpha_{36}\alpha_{126}-\alpha_{22}\alpha_{36}\alpha_{156}-\alpha_{14}\alpha_{22}\alpha_{345})\\
&\quad+\alpha_{14}\alpha_{22}\alpha_{36}\alpha_{456}-\alpha_{14}\alpha_{25}\alpha_{36}\alpha_{246}],\\
p_{156}&=[\beta(\alpha_{22}\alpha_{33}\alpha_{156}-\alpha_{22}\alpha_{36}\alpha_{135}-\alpha_{25}\alpha_{33}\alpha_{126}\\
&\quad+\alpha_{25}\alpha_{36}\alpha_{123})-\alpha_{14}\alpha_{22}\alpha_{33}\alpha_{456}\\
&\quad+\alpha_{14}\alpha_{22}\alpha_{36}\alpha_{345}+\alpha_{14}\alpha_{25}\alpha_{33}\alpha_{246}\\
&\quad-\alpha_{14}\alpha_{25}\alpha_{36}\alpha_{234}],\\
p_{234}&=[\beta^2(\alpha_{11}\alpha_{234}-\alpha_{14}\alpha_{123})+\beta(\alpha_{14}\alpha_{36}\alpha_{126}\\
&\quad-\alpha_{11}\alpha_{36}\alpha_{246}-\alpha_{11}\alpha_{25}\alpha_{345}+\alpha_{14}\alpha_{25}\alpha_{135})\\
&\quad+\alpha_{11}\alpha_{25}\alpha_{36}\alpha_{456}-\alpha_{14}\alpha_{25}\alpha_{36}\alpha_{156}],\\
p_{246}&=[\beta(\alpha_{11}\alpha_{33}\alpha_{246}-\alpha_{11}\alpha_{36}\alpha_{234}-\alpha_{14}\alpha_{33}\alpha_{126}\\
&\quad+\alpha_{14}\alpha_{36}\alpha_{123})+\alpha_{14}\alpha_{25}\alpha_{33}\alpha_{156}-\alpha_{14}\alpha_{25}\alpha_{36}\alpha_{135}\\
&\quad-\alpha_{11}\alpha_{25}\alpha_{33}\alpha_{456}+\alpha_{11}\alpha_{25}\alpha_{36}\alpha_{345}],\\
p_{345}&=[\beta(\alpha_{14}\alpha_{25}\alpha_{123}-\alpha_{14}\alpha_{22}\alpha_{135}-\alpha_{11}\alpha_{25}\alpha_{234}\\
&\quad+\alpha_{11}\alpha_{22}\alpha_{345})+\alpha_{14}\alpha_{22}\alpha_{36}\alpha_{156}-\alpha_{14}\alpha_{25}\alpha_{36}\alpha_{126}\\
&\quad-\alpha_{11}\alpha_{22}\alpha_{36}\alpha_{456}+\alpha_{11}\alpha_{25}\alpha_{36}\alpha_{246}],\\
p_{456}&=[\alpha_{11}\alpha_{22}\alpha_{33}\alpha_{456}-\alpha_{11}\alpha_{22}\alpha_{36}\alpha_{345}\\
&\quad-\alpha_{11}\alpha_{25}\alpha_{33}\alpha_{246}+\alpha_{11}\alpha_{25}\alpha_{36}\alpha_{234}\\
&\quad-\alpha_{14}\alpha_{22}\alpha_{33}\alpha_{156}+\alpha_{14}\alpha_{22}\alpha_{36}\alpha_{135}\\
&\quad+\alpha_{14}\alpha_{25}\alpha_{33}\alpha_{126}-\alpha_{14}\alpha_{25}\alpha_{36}\alpha_{123}].
\end{aligned}$$

If only terms up to order $1/(N)^0$ are included then (1) reduces to the product of the three distributions $P(|F_i|,\varphi_i)$, $i=1,2,3$, provided by Wilson (1980). From (1) the following conditional probability

distribution is obtained:

$$P(\varphi_1, \varphi_2, \varphi_3|R_1, R_2, R_3)$$
$$\simeq \frac{1}{L}\exp\left\{\tfrac{1}{2}\sum_{i=1}^{3}\left[\frac{X_i}{\gamma_i}\sum_i R_i^2\cos(2\varphi_i - x_i)\right]\right.$$
$$+ R_1R_2R_3\frac{(\sum_1\sum_2\sum_3)^{1/2}}{\gamma_1\gamma_2\gamma_3}$$
$$\times[p_{123}\cos\varphi_1\cos\varphi_2\cos\varphi_3$$
$$+ p_{126}\cos\varphi_1\cos\varphi_2\sin\varphi_3$$
$$+ p_{135}\cos\varphi_1\sin\varphi_2\cos\varphi_3$$
$$+ p_{156}\cos\varphi_1\sin\varphi_2\sin\varphi_3$$
$$+ p_{234}\sin\varphi_1\cos\varphi_2\cos\varphi_3$$
$$+ p_{246}\sin\varphi_1\cos\varphi_2\sin\varphi_3$$
$$+ p_{345}\sin\varphi_1\sin\varphi_2\cos\varphi_3$$
$$\left.+ p_{456}\sin\varphi_1\sin\varphi_2\sin\varphi_3]\right\}, \qquad (2)$$

where $\sum_i = (\alpha_{ii} + \beta)$ and $R_i = |F_i|/\sum_i^{1/2}$ are the normalized moduli.

3. The estimation of φ_i given other phases and magnitudes

From (2) the conditional distribution (3) is readily derived:

$$P(\varphi_1|\varphi_2, \varphi_3, R_1, R_2, R_3)$$
$$\simeq (1/L)\exp\{\tfrac{1}{2}(X_1\textstyle\sum_1/\gamma_1)R_1^2\cos(2\varphi_1 - x_1)$$
$$+[(\textstyle\sum_1\sum_2\sum_3)^{1/2}/\gamma_1\gamma_2\gamma_3]$$
$$\times X_{01}R_1R_2R_3\cos(\varphi_1 - x_{01})\}, \qquad (3)$$

where

$$X_{01} = \{[p_{123}\cos\varphi_2\cos\varphi_3 + p_{126}\cos\varphi_2\sin\varphi_3$$
$$+ p_{135}\sin\varphi_2\cos\varphi_3 + p_{156}\sin\varphi_2\sin\varphi_3]^2$$
$$+[p_{234}\cos\varphi_2\cos\varphi_3 + p_{246}\cos\varphi_2\sin\varphi_3$$
$$+ p_{345}\sin\varphi_2\cos\varphi_3 + p_{456}\sin\varphi_2\sin\varphi_3]^2\}^{1/2}$$
$$= (T_{01}^2 + B_{01}^2)^{1/2}$$

and

$$x_{01} = \tan^{-1}[T_{01}, B_{01}].$$

Equation (3) is the product of two exponential functions: the first takes its maximum at $n\pi + x_1/2$, the second at x_{01}. For proteins, (*a*) $x_1/2$ represents a value of a few degrees, while x_{01} often lies around $\pm\pi/2$; (*b*) $\frac{1}{2}X_1/\gamma_1$ is usually much larger than $[(\sum_1\sum_2\sum_3)^{1/2}/\gamma_1\gamma_2\gamma_3]X_{01}$. Thus (3) is often bimodal with mode close to $n\pi + x_1/2$: the estimate will be near 0 or near π according to whether x_{01} is in the quadrants (1, 4) or in the quadrants (2, 3).

For small structures or for very large values of $R_1R_2R_3$, (*a*) $x_1/2$ may be significantly large; (*b*) $[(\sum_1\sum_2\sum_3)^{1/2}/\gamma_1\gamma_2\gamma_3]X_{01}R_1R_2R_3$ is not negligible compared with $\frac{1}{2}(X_1\sum_1/\gamma_1)R_1^2$. Then the modes of (3) are more evenly dispersed in the interval $(0, 2\pi)$.

In order to check (3) 3328 structure factors up to 2 Å resolution have been calculated using the presumed known coordinates of ferredoxin from *Peptococcus aerogenes* (Adman, Sieker & Jensen, 1973) which crystallizes in $P2_12_12_1$ with $M_r \simeq 6000$. The eight iron atoms in the molecule were assumed to be anomalous scatterers with $f' = -1{\cdot}18$ and $f'' = 3{\cdot}20$. In Fig. 1 a typical plot of (3) is shown: some parameters of the distribution are also given.

If several pairs of phases $(\varphi_{\mathbf{k}_j}, \varphi_{\mathbf{h}-\mathbf{k}_j})$ are known then (3) may be generalized as

$$P(\varphi_1|R_1, \{\varphi_2, \varphi_3, R_2R_3\})$$
$$\simeq \frac{1}{L}\exp\left\{\frac{1}{2}\frac{X_1\sum_1}{\gamma_1}R_1^2\cos(2\varphi_1 - x_1)\right.$$
$$\left.+\sum_j\left[\frac{(\sum_1\sum_2\sum_3)^{1/2}}{\gamma_1\gamma_2\gamma_3}X_{01}R_1R_2R_3\right.\right.$$
$$\left.\left.\times\cos(\varphi_1 - x_{01})\right]_j\right\}. \qquad (4)$$

Phase estimates for (3) and (4) may be obtained by numerical methods: in particular the expected value φ_1 is given by

$$\langle\varphi_1\rangle = \tan^{-1}[S, C]$$
$$S = \int_0^{2\pi}\sin\varphi_1 P(\varphi_1)\,d\varphi_1, \quad C = \int_0^{2\pi}\cos\varphi_1 P(\varphi_1)\,d\varphi_1,$$

to which the so-called *circular variance* may be associated, given by

$$V = 1 - R,$$

where $R = (S^2 + C^2)^{1/2}$.

An appropriate transformation of the circular variance is

$$S = \{-2\ln(1 - V)\}^{1/2},$$

which gives a measure somewhat analogous to the ordinary standard deviation on the line.

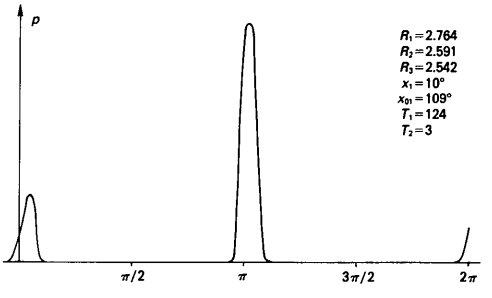

Fig. 1. Plot of equation (3) in the interval $(0, 2\pi)$. The values of $T_1 = \frac{1}{2}X_1\sum_1/\gamma_1$ and of $T_2 = [(\sum_1\sum_2\sum_3)^{1/2}/\gamma_1\gamma_2\gamma_3]X_{01}$ are also given.

Table 1. *Of 68 centrosymmetric reflexions, the 34 with the concentration parameter α (according to non-centrosymmetric formulae) larger than 1·0 are printed*

φ_t and φ_c are true and calculated phase values.
'*' labels wrong indications.

h	k	l	φ_t	φ_c	α
10	0	12	185·0	185·2	17·05
2	0	2	183·0	175·5	8·97
0	18	4	1·0	5·0	7·55
11	0	2	180·0	4·5*	5·82
8	0	12	184·0	184·2	4·53
0	12	12	6·0	4·4	3·90
0	6	17	183·0	184·9	3·79
11	0	4	181·0	185·2	3·54
0	2	4	4·0	3·5	3·00
0	4	6	4·0	183·4*	2·99
0	10	6	358·0	185·0*	2·37
0	18	2	181·0	185·4	2·23
10	14	0	8·0	5·3	2·13
0	14	12	189·0	184·0	1·52
2	7	0	1·0	3·8	1·24
8	1	0	180·0	182·7	1·18
0	14	3	181·0	2·2*	1·09
0	16	10	186·0	186·3	15·49
0	14	2	1·0	6·9	7·74
7	0	14	3·0	4·2	6·16
0	14	4	4·0	4·8	5·45
6	15	0	1·0	4·8	3·90
0	16	1	356·0	3·8	3·86
0	2	3	0·0	1·5	3·71
6	1	0	1·0	2·7	3·48
6	0	18	184·0	184·7	2·99
2	0	4	184·0	182·9	2·50
8	16	0	0·0	5·1	2·29
0	14	10	4·0	4·8	2·20
0	18	0	184·0	171·9	2·11
0	2	18	181·0	6·0*	1·44
0	8	16	181·0	20·8*	1·20
8	0	16	2·0	4·8	1·16
0	2	19	180·0	184·7	1·07

4. Concluding remarks

The limits of (3) and (4) may be described as: (*a*) they hold in $P\bar{1}$: in higher-symmetry space groups they hold only if restricted phases of type $(0, \pi)$ are involved; (*b*) for restricted phases of different type the values of x_1 and x_{01} have to be modified in accordance with space-group symmetry [see equation (10) in Giacovazzo (1987) for the generalized value of x_1].

Equations (3) and (4) are formally quite different from equivalent formulae working in non-centrosymmetrical space groups (Hauptman, 1982; Giacovazzo, 1983). The question arises whether: (*a*) information contained in centrosymmetric triplets is sufficiently large to be useful in practice for protein structure determination; (*b*) non-centrosymmetric formulae are sufficiently accurate to be used also for the estimation of centrosymmetric triplets.

In order to answer both questions 68 reflexions with restricted phase of type $(0, \pi)$ (from ferredoxin calculated data) have been estimated according to (4) by using 290 centrosymmetric triplets only. The same reflexions were also estimated according to non-centrosymmetric formulae. The outcome was practically identical for both types of formulae and is shown in Table 1. This table suggests that information contained in centrosymmetric triplets in dispersive structures is not negligible, and that non-centrosymmetric formulae can be used for estimating centrosymmetric as well as non-centrosymmetric triplets. Tests on real diffraction data have not been attempted; it is easy to foresee a reduced efficiency of the formulae according to the average error magnitude in the experimental data.

References

ADMAN, E. T., SIEKER, L. C. & JENSEN, L. M. (1973). *J. Biol. Chem.* **248**, 3987-3996.
GIACOVAZZO, C. (1983). *Acta Cryst.* A**39**, 585-592.
GIACOVAZZO, C. (1987). *Acta Cryst.* A**43**, 73-75.
HAUPTMAN, H. (1982). *Acta Cryst.* A**38**, 632-641.
HEINERMAN, J. J. L., KRABBENDAM, H., KROON, J. & SPEK, A. L. (1978). *Acta Cryst.* A**34**, 447-450.
SRINIVASAN, R. & PARTHASARATHY, S. (1976). *Some Statistical Applications in X-ray Crystallography*. Oxford: Pergamon Press.
WILSON, A. J. C. (1980). *Acta Cryst.* A**36**, 945-946.

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New Probabilistic Formulas for Finding the Positions of Correctly Oriented Atomic Groups

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Abstract

The probabilistic procedure described by Main [In *Crystallographic Computing Techniques* (1976), edited by F. R. Ahmed, pp. 97-105. Copenhagen: Munksgaard] has been reconsidered. In polar space groups some primitive random variables (atomic positions or shift vectors for molecular fragments) may be conveniently restricted to regions which are smaller than a unit cell. This introduces two new

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