O'KEEFFE, M. (1992). *Acta Cryst.* A**48**, 670–673.
PARISE, J. B. (1984*a*). *J. Chem. Soc. Chem. Commun.* pp. 1449–1450.
PARISE, J. B. (1984*b*). *Acta Cryst.* C**40**, 1641–1642.
PARISE, J. B. (1985*a*). *J. Chem. Soc. Chem. Commun.* pp. 606–607.
PARISE, J. B. (1985*b*). *Zeolites*, edited by B. DRZAJ, S. HOCEVAR & S. PEJOVNIK. *Stud. Surf. Sci. Catal.* **24**, 271–278. Amsterdam: Elsevier.
PLUTH, J. J., SMITH, J. V., BENNETT, J. M. & COHEN, J. P. (1984). *Acta Cryst.* C**40**, 2008–2011.
SIMMEN, A. (1992). PhD thesis No. 9710, Institut für Kristallographie und Petrographie, ETH, Zürich, Switzerland.
SMITH, J. V. (1977). *Am. Mineral.* **62**, 703–709.
SMITH, J. V. (1978). *Am. Mineral.* **63**, 960–969.
SMITH, J. V. (1988). *Chem. Rev.* **88**, 149–182.
SMITH, J. V. & BENNETT, J. M. (1984). *Am. Mineral.* **69**, 104–111.
SMITH, J. V. & DYTRYCH, W. J. (1986). *Z. Kristallogr.* **175**, 31–36.
SMITH, J. V. & RINALDI, F. (1962). *Mineral. Mag.* **33**, 202–212.
STIXRUDE, L. & BUKOWINSKI, M. S. T. (1990). *Am. Mineral.* **75**, 1159–1169.
TREACY, M. M. J., RAO, S. & RIVIN, I. (1992). Paper presented at the Ninth International Zeolite Conference, Montreal, Canada, 5–10 July 1992.
WELLS, A. F. (1977). *Three-Dimensional Nets and Polyhedra.* New York: Wiley-Interscience.
WOOD, I. G. & PRICE, G. D. (1992). *Zeolites*, **12**, 320–327.
YU, L., PANG, W. & LI, L. (1990). *J. Solid State Chem.* **87**, 241–244.

*Acta Cryst.* (1994). A**50**, 325–329

# Strengthening of Quartet Invariant Estimates *via* the Prior Estimation of Triplet Relationships

BY M. C. BURLA

*Dipartimento di Scienze della Terra, Universitá, 06100 Perugia, Italy*

AND G. CASCARANO, C. GIACOVAZZO AND A. GUAGLIARDI

*Instituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche CNR, c/o Dipartimento Geomineralogico, Campus Universitario, 70124 Bari, Italy*

(*Received* 18 *June* 1993; *accepted* 14 *October* 1993)

## Abstract

Formulas for estimating quartet invariants depend on prior information on triplet invariants. If this coincides with the Cochran estimate then the classical quartet formulas [Hauptman (1975). *Acta Cryst.* A**31**, 680–687; Giacovazzo (1976). *Acta Cryst.* A**32**, 91–99, 100–104] are obtained. A mathematical theory is described that improves quartet estimates by exploiting some prior information on triplets. Special emphasis is devoted to the prior estimate of triplet invariants provided by the $P_{10}$ formula.

## Symbols

$N$ = number of atoms in the primitive unit cell. For unequal-atom structures, $N$ is replaced in the formulas by $N_{\rm eq} \simeq \sigma_2^3/\sigma_3^2$, where $\sigma_i = \sum_{j=1}^N z_j^i$. $z_j$ is the atomic number of the $j$th atom.

$E_{\bf h} = R_{\bf h} \exp(i\varphi_{\bf h})$, normalized structure factor of index **h**.

$\varepsilon_i = R_i^2 - 1$

$\Phi = \varphi_{\bf h} + \varphi_{\bf k} + \varphi_{\bf l} + \varphi_{\bf m}$, with ${\bf h} + {\bf k} + {\bf l} + {\bf m} = 0$.

$E_1 = E_{\bf h}$, $E_2 = E_{\bf k}$, $E_3 = E_{\bf l}$, $E_4 = E_{\bf m}$, $E_5 = E_{\bf h+k}$, $E_6 = E_{\bf h+l}$, $E_7 = E_{\bf k+l}$

$G_{ijp} = 2R_iR_jR_p/N^{1/2}$

$G_{ijpq} = 2R_iR_jR_pR_q/N$

$D_1(x) = I_1(x)/I_0(x)$ = ratio of modified Bessel functions of orders one and zero, respectively.

## Introduction

In some recent papers (Giacovazzo, Burla & Cascarano, 1992; Burla, Cascarano & Giacovazzo, 1992; Altomare, Burla, Cascarano, Giacovazzo & Guagliardi, 1993) new attention has been devoted to the practical role of the quartet invariants in direct phasing procedures. A practical recipe was provided: the combined active use of positive estimated quartets and of triplets is not advised. The first reason for this is the well known correlation between positive quartets and positive triplets. The second is the lower accuracy of quartet estimates, which is very remarkable when triplets are estimated *via* the $P_{10}$ formula (Cascarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori, 1984). Since $P_{10}$ estimates triplets *via* their second representation (Giacovazzo, 1977), *i.e.* *via* the special quintets

$$\psi_5 = \varphi_{\bf h} + \varphi_{\bf k} - \varphi_{\bf h+k} + \varphi_{\bf n} - \varphi_{\bf n}, \qquad (1)$$




ISSN 0108-7673 

a possible way of improving the quartet reliability is to use the second representation of the quartets, *i.e.* the sextets

$$\psi_6 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}} + \varphi_{\mathbf{n}} - \varphi_{\mathbf{n}}. \qquad (2)$$

The estimation of $\psi_6$ requires the use of 22 diffraction magnitudes (the second phasing shell), *i.e.*

$$R_1,\ R_2,\ R_3,\ R_4,\ R_5,\ R_6,\ R_7,\ R_{\mathbf{n}},\ R_{\mathbf{h}\pm\mathbf{n}},\ R_{\mathbf{k}\pm\mathbf{n}},$$
$$R_{\mathbf{l}\pm\mathbf{n}},\ R_{\mathbf{m}\pm\mathbf{n}},\ R_{\mathbf{h}+\mathbf{k}\pm\mathbf{n}},\ R_{\mathbf{h}+\mathbf{l}\pm\mathbf{n}},\ R_{\mathbf{k}+\mathbf{l}\pm\mathbf{n}},$$

the first seven of which also belong to the first phasing shell. Since $\mathbf{n}$ is a free vector, several $\psi_6$ sextets have to be estimated and probabilistically combined for more accurate quartet estimations to be obtained. That requires a lot of additional work, certainly too expensive for current direct procedures. The problem is then to find a simple and practicable way for improving quartet estimates without paying too much in terms of computer time. This is the main aim of this paper.

Throughout the paper, we suppose that two types of prior information could be available. The first type involves the prior knowledge of the exact values of some triplet phases. A possible source of such prior information could be, for example, an experiment using multiple diffraction for phase determination (Hümmer, Weckert & Bondza, 1989).

The second type of prior information only requires estimates of triplet phases to be available. Such information could be derived, for example, *via* probabilistic formulas like $P_{10}$ (Cascarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori, 1984) or formulas that exploit isomorphous data or anomalous-dispersion effects. Since probabilistic estimates of triplets *via* $P_{10}$ formula are easy to obtain, we mainly focus our attention on this type of prior information. It is shown that quartet estimates can benefit by $P_{10}$ estimates provided that suitable probabilistic distributions are used. No consideration is taken in this paper of the problem concerning the simultaneous use of triplet and quartet relationships in the phasing process.

## The quartet estimation when some triplet phases are *a priori* known

Let us consider the conditional distribution $P(\varphi_1, \varphi_2, \ldots, \varphi_7|R_1, \ldots, R_7)$ derived by Hauptman (1975):

$$\begin{aligned} P(\varphi_1,\ldots,\varphi_7|R_1,\ldots,R_7) &\simeq (1/S)\exp\{G_{125}\cos\Phi_{125} + G_{136}\cos\Phi_{136} \\ &+ G_{147}\cos\Phi_{147} + G_{237}\cos\Phi_{237} + G_{246}\cos\Phi_{246} \\ &+ G_{345}\cos\Phi_{345} - [G_{1267}\cos\Phi_{1267} + G_{1357}\cos\Phi_{1357} \\ &+ G_{1456}\cos\Phi_{1456} + G_{2356}\cos\Phi_{2356} \\ &+ G_{2457}\cos\Phi_{2457} + G_{3467}\cos\Phi_{3467} \\ &+ 2G_{1234}\cos\Phi]\}, \end{aligned} \qquad (3)$$

where $S$ is a suitable constant and

$$\begin{aligned} &\Phi_{125} = \varphi_1 + \varphi_2 - \varphi_5, && \Phi_{136} = \varphi_1 + \varphi_3 - \varphi_6, \\ &\Phi_{147} = \varphi_1 + \varphi_4 + \varphi_7, && \Phi_{237} = \varphi_2 + \varphi_3 - \varphi_7, \\ &\Phi_{246} = \varphi_2 + \varphi_4 + \varphi_6, && \Phi_{345} = \varphi_3 + \varphi_4 + \varphi_5 \\ &\Phi_{1267} = \varphi_1 - \varphi_2 - \varphi_6 + \varphi_7, && \Phi_{1357} = \varphi_1 - \varphi_3 - \varphi_5 + \varphi_7 \\ &\Phi_{1456} = \varphi_1 - \varphi_4 - \varphi_5 - \varphi_6, && \Phi_{2356} = \varphi_2 - \varphi_3 - \varphi_5 + \varphi_6 \\ &\Phi_{2457} = \varphi_2 - \varphi_4 - \varphi_5 - \varphi_7, && \Phi_{3467} = \varphi_3 - \varphi_4 - \varphi_6 - \varphi_7. \end{aligned}$$

From (3), the conditional distribution $P(\Phi|R_1, \ldots, R_7)$ of $\Phi_{1234}$, given the seven amplitudes, is obtained (Hauptman, 1975):

$$P(\Phi|R_1, \ldots, R_7) \simeq (1/L)\exp(-2G_{1234}\cos\Phi)I_o(Z_5)I_o(Z_6)I_o(Z_7), \qquad (4)$$

where

$$\begin{aligned} Z_5 &= (G_{125}^2 + G_{345}^2 + 2G_{125}G_{245}\cos\Phi)^{1/2}, \\ Z_6 &= (G_{136}^2 + G_{246}^2 + 2G_{136}G_{246}\cos\Phi)^{1/2}, \\ Z_7 &= (G_{237}^2 + G_{147}^2 + 2G_{237}G_{245}\cos\Phi)^{1/2}. \end{aligned}$$

Suppose now that the values of some triplet phases in (3) are *a priori* available: we want to derive the distribution of $\Phi$ under these conditions. A rigorous treatment of the problem requires the *ab initio* derivation of the new distribution

$$P(\varphi_1, \ldots, \varphi_7|R_1, \ldots, R_7, \{\Phi_{ijp}\}).$$

We prefer to use a simpler procedure: to modify (3) so as to meet the new prior information. To see how this is possible, let us suppose that $\Phi_{125}$, $\Phi_{136}$ and $\Phi_{147}$ are known *a priori* [incidentally, it would be absurd to look for thc quartct distribution when the pair ($\Phi_{125}$, $\Phi_{345}$) or ($\Phi_{136}$, $\Phi_{246}$) or ($\Phi_{147}$, $\Phi_{237}$) is known *a priori*; then, $\Phi$ is also known *a priori*]. The distribution (3) may then be written as

$$\begin{aligned} P \simeq (1/S)\exp\{&G_{125}\cos\Phi_{125} + G_{345}\cos(\Phi - \Phi_{125}) \\ &+ G_{136}\cos\Phi_{136} + G_{246}\cos(\Phi - \Phi_{136}) + G_{147}\cos\Phi_{147} \\ &+ G_{237}\cos(\Phi - \Phi_{147}) - [G_{1267}\cos(\Phi - \Phi_{136} - \Phi_{147}) \\ &+ G_{1357}\cos(\Phi - \Phi_{147} - \Phi_{125}) \\ &+ G_{1456}\cos(\Phi - \Phi_{125} - \Phi_{136}) \\ &+ G_{2356}\cos(\Phi - \Phi_{125} - \Phi_{136}) \\ &+ G_{2457}\cos(\Phi_{125} - \Phi_{147}) + G_{3467}\cos(\Phi_{136} - \Phi_{147}) \\ &+ 2G_{1234}\cos\Phi]\}, \end{aligned}$$

from which

$$P(\Phi|R_1, \ldots, R_7, \Phi_{125}, \Phi_{136}, \Phi_{147}) \simeq (1/S)\exp\{G_{345}\cos(\Phi - \Phi_{125})$$

$$+ G_{246}\cos(\Phi-\Phi_{136}) + G_{237}\cos(\Phi-\Phi_{147})$$
$$- G_{1267}\cos(\Phi-\Phi_{136}-\Phi_{147})$$
$$- G_{1357}\cos(\Phi-\Phi_{147}-\Phi_{125})$$
$$- G_{1456}\cos(\Phi-\Phi_{125}-\Phi_{136}) - 2G_{1234}\cos\Phi\}. \quad (5a)$$

This equation may be simplified by neglecting [as suggested by Hauptmann for (4)] the contribution arising from the quartet terms $G_{1267}$, $G_{1357}$ and $G_{1456}$. We obtain:

$$P(\Phi|R_1, \ldots, R_7, \Phi_{125}, \Phi_{136}, \Phi_{147})$$
$$\simeq (1/S)\exp\{G_{345}\cos(\Phi-\Phi_{125})$$
$$+ G_{246}\cos(\Phi-\Phi_{136}) + G_{237}\cos(\Phi-\Phi_{147})$$
$$- 2G_{1234}\cos\Phi\}$$
$$\simeq [2\pi I_o(\alpha)]^{-1}\exp[\alpha\cos(\Phi-\zeta)], \quad (5b)$$

where $\zeta$, the most probable value of $\Phi$, is defined according to $\tan\zeta = T/B$ and

$$T = G_{345}\sin\Phi_{125} + G_{246}\sin\Phi_{136} + G_{237}\sin\Phi_{147},$$
$$B = G_{345}\cos\Phi_{125} + G_{246}\cos\Phi_{136} + G_{237}\cos\Phi_{147} - 2G_{1234}.$$

The reliability parameter of the distribution is

$$\alpha = (T^2 + B^2)^{1/2}.$$

We now show why (5$b$) can improve the estimates provided by (4). Suppose that $R_1, \ldots, R_7$ are large enough. Then, $\Phi$ is expected to be close to zero, by (4). If the prior information $\Phi_{125} \simeq \Phi_{136} \simeq \Phi_{147} \simeq 0$ is used in (5$b$), then $\Phi$ is again estimated close to zero (see Fig. 1 for some numerical examples). If, by prior information, $\Phi_{125} \simeq \Phi_{136} \simeq \Phi_{147} \simeq \pi$, then (5$b$) indicates $\Phi \simeq \pi$, a sounder estimate than $\Phi = 0$. It should also be noticed that if $R_1, \ldots, R_4$ are large and $R_5 \simeq R_6 \simeq R_7 \simeq 0$, then the values of $\Phi_{125}$, $\Phi_{136}$ and $\Phi_{147}$ do not influence the estimation of $\Phi$ (which is always expected to be close to $\pi$).

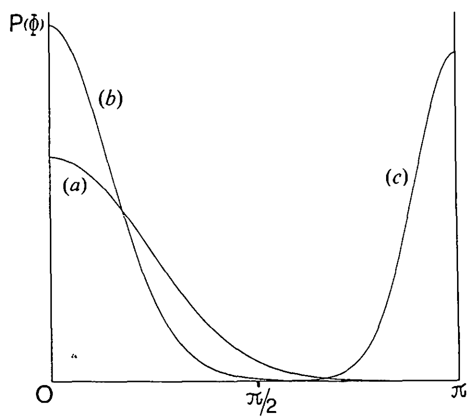


Fig. 1. Quartet phase distributions for $N = 100$, $R_1 = 3.96$, $R_2 = 2.72$, $R_3 = 2.36$, $R_4 = 2.31$, $R_5 = 2.36$, $R_6 = 1.57$ and $R_7 = 2.19$ have been calculated according to: ($a$) Hauptman's (1975) formula, (4); ($b$) (5$b$), with prior information $\Phi_{125} = \Phi_{136} = \Phi_{147} = 2\pi$; ($c$) (5$b$), with prior information $\Phi_{125} = \Phi_{136} = \Phi_{147} = \pi$.

Table 1. *NEWQB – statistical behaviour of the quartets estimated positive by* (4)

| ARG | $nr$ ($nw$) |
|---|---|
| 0.0 | 6711 (1212) |
| 0.4 | 6711 (1212) |
| 0.8 | 2594 (268) |
| 1.2 | 874 (48) |
| 2.0 | 71 (1) |
| 2.8 | 5 (0) |

Table 2. *NEWQB – statistical behaviour of the quartets in Table* 1 *when estimated by* (5$b$)

| ARG | Positive estimated quartets $nr$ ($nw$) | Negative estimated quartets $nr$ ($nw$) |
|---|---|---|
| 0.0 | 5887 (701) | 824 (313) |
| 0.4 | 5376 (514) | 481 (145) |
| 0.8 | 4793 (371) | 260 (62) |
| 1.2 | 3955 (213) | 155 (34) |
| 2.0 | 2637 (32) | 74 (15) |
| 2.8 | 1661 (23) | 40 (6) |
| 4.6 | 573 (0) | 9 (0) |
| 8.0 | 54 (0) | 1 (0) |

An experimental check of the effectiveness of (5$b$) may be made by comparing Tables 1 and 2. In Table 1, (4) is applied to NEWQB experimental data (Grigg, Kemp, Sheldrick & Trotter, 1978). A reliability parameter $\alpha$ is associated with each quartet, in accordance with the procedure described by Altomare, Burla, Cascarano, Giacovazzo & Guagliardi (1993). In Table 1, $nr$ is the number of quartets estimated positive by (4) with $\alpha$ larger than ARG and $nw$ is the number of wrongly estimated quartets. The same 6711 quartets are estimated by means of (5$b$) by using the true values of $\Phi_{125}$, $\Phi_{136}$ and $\Phi_{147}$ as prior information: the results are in Table 2. It should be observed that 824 out of 6711 are estimated negative by (5$b$) and that (5$b$) is much more effective than (4).

## The quartet estimation when some prior triplet estimates are available (Hauptman's formulation)

Let us now suppose that the exact values of $\Phi_{125}$, $\Phi_{136}$ and $\Phi_{147}$ are unknown but their estimates are available from some source. Then, we could replace each $\cos(\Phi-\Phi_{ijl})$ in (5$a$) by its expected value $\cos\Phi\langle\cos\Phi_{ijl}\rangle$ (it is supposed that no information is available about $\sin\Phi_{ijl}$ so we assume that $\langle\sin\Phi_{ijl}\rangle = 0$). If $\Phi_{ijl}$ is supposed to be distributed according to the von Mises distribution

$$P(\Phi_{ijl}) \simeq [2\pi I_o(G^p_{ijl})]^{-1}\exp(G^p_{ijl}\cos\Phi_{ijl}) \quad (6)$$

(the superscript $p$ to the $G$ indicates that it is available from some prior information), then $\langle\cos\Phi_{ijl}\rangle = D_1(G^p_{ijl})$ and (5$a$) becomes

$$\begin{aligned} P(\Phi|R_1, \ldots, R_7, \langle\Phi_{125}\rangle, \langle\Phi_{136}\rangle, \langle\Phi_{147}\rangle) \\ \simeq (1/S')\exp\{[G_{345}D_1(G^p_{125}) \\ + G_{246}D_1(G^p_{136}) + G_{237}D_1(G^p_{147}) \\ - G_{1267}D_1(G^p_{136})D_1(G^p_{147}) \\ - G_{1357}D_1(G^p_{147})D_1(G^p_{125}) \\ - G_{1456}D_1(G^p_{125})D_1(G^p_{136}) - 2G_{1234}]\cos\Phi\}. \quad (7) \end{aligned}$$

If the approximation

$$D_1(x) \simeq x/2 \quad (8)$$

is valid (*i.e.* $G^p_{ijl}$ is not large), we could neglect terms of order $1/N^2$ and replace (7) by

$$\begin{aligned} P(\Phi|R_1, \ldots, R_7, \langle\Phi_{125}\rangle, \langle\Phi_{136}\rangle, \langle\Phi_{147}\rangle) \\ \simeq (1/S')\exp\{[G_{345}D_1(G^p_{125}) + G_{246}D_1(G^p_{136}) \\ + G_{237}D_1(G^p_{147}) - 2G_{1234}]\cos\Phi\}. \quad (9) \end{aligned}$$

The reader might consider the above mathematical procedure rather unusual. It is, however, easy to show that it can provide in a simple way formulas of which the usefulness is well documented. Indeed, if $G^p_{ijl} \equiv G_{ijl}$ (only the Cochran estimates for the $\Phi_{ijl}$'s are available), then (9) is reduced, *via* (8), to the well known quartet formula (Giacovazzo, 1976)

$$\begin{aligned} P(\Phi|R_1, \ldots, R_7) \\ \simeq (1/S)\exp\{G_{1234}(1+\varepsilon_5+\varepsilon_6+\varepsilon_7)\cos\Phi\}. \quad (10) \end{aligned}$$

The procedure described above can be extended further. While, in the preceding section, we noted that it is nonsense to look for the quartet phase distribution when one of the pairs ($\Phi_{125}$, $\Phi_{345}$), ($\Phi_{136}$, $\Phi_{246}$), ($\Phi_{147}$, $\Phi_{237}$) is known *a priori*, in this section, where only estimates of the triplets are supposed to be available, a more relaxed situation is acceptable. As an example, it may be supposed that: ($a$) estimates of all the six triplet phases $\Phi_{ijl}$ in (3) are *a priori* available and ($b$) their distributions comply with (6) and are independent of each other. Then, the probability distribution of the sum $\Phi = \Phi_{125} + \Phi_{345}$ may be approximated by a von Mises distribution (Giacovazzo, Camalli & Spagna, 1989), with concentration parameter $q_5$ given by

$$D_1(q_5) = D_1(G^p_{125})D_1(G^p_{345}).$$

By repeating the same procedure for the pairs ($\Phi_{136}$, $\Phi_{246}$) and ($\Phi_{147}$, $\Phi_{237}$), we obtain

$$\begin{aligned} P(\Phi|R_1, \ldots, R_7, \langle\Phi_{125}\rangle, \langle\Phi_{136}\rangle, \langle\Phi_{147}\rangle, \langle\Phi_{345}\rangle, \langle\Phi_{246}\rangle, \\ \langle\Phi_{237}\rangle) \simeq [2\pi I_o(G)]^{-1}\exp(G\cos\Phi), \quad (11) \end{aligned}$$

where

$$\begin{aligned} G = G_{1234} + (q_5 - G_{1234}) + (q_6 - G_{1234}) + (q_7 - G_{1234}), \\ D_1(q_6) = D_1(G^p_{136})D_1(G^p_{246}) \\ D_1(q_7) = D_1(G^p_{237})D_1(G^p_{147}). \end{aligned}$$

If $G^p_{ijl} \equiv G_{ijl}$ (only Cochran estimates are available for the various $\Phi_{ijl}$), then the distribution (11) coincides with (4) derived by Giacovazzo, Camalli & Spagna (1989).

**Quartet estimation when some prior triplet estimates are available (Giacovazzo's formulation)**

Quartets are frequently estimated *via* the formula (Giacovazzo 1976, 1980)

$$P(\Phi|R_1, \ldots, R_7) \simeq [2\pi I_o(G')]^{-1}\exp(G'\cos\Phi), \quad (12)$$

where

$$G' = G_{1234}(1+\varepsilon_5+\varepsilon_6+\varepsilon_7)/(1+Q) \quad (13)$$

and $Q$ is a scaling term:

$$\begin{aligned} Q = [(\varepsilon_1\varepsilon_2 + \varepsilon_3\varepsilon_4)\varepsilon_5 + (\varepsilon_1\varepsilon_3 + \varepsilon_2\varepsilon_4)\varepsilon_6 \\ + (\varepsilon_1\varepsilon_4 + \varepsilon_2\varepsilon_3)\varepsilon_7]/2N. \end{aligned}$$

For our purposes, (13) may also be written as

$$\begin{aligned} G' = [G_{1234} + (0.5G_{345}G_{125} - G_{1234}) + (0.5G_{246}G_{136} \\ - G_{1234}) + (0.5G_{237}G_{147} - G_{1234})](1+Q)^{-1}. \end{aligned}$$

When some cross reflections are missing in the data set, the value of $G'$ is easily modified. For example, if $R_5$ has not been measured, then the contribution $(0.5G_{345}G_{125} - G_{1234})$ is omitted.

In a recent paper (Altomare, Burla, Cascarano, Giacovazzo & Guagliardi, 1993), it has been shown that: ($a$) for sufficiently large values of $N$, (4) and (12) are equally efficient for estimating positive and negative quartets; ($b$) for small structures, both (4) and (12) are reliable tools for estimating positive quartets while (4) is unreliable for negative quartets. It seems then advisable to introduce the prior information on triplet cosines in Giacovazzo's quartet formulation in order to derive a formula useful over a wide range. If the $\Phi_{ijl}$'s are supposed to be distributed according to (6), then (12) is replaced by

$$\begin{aligned} P(\Phi|R_1, \ldots, R_7, \langle\Phi_{125}\rangle, \langle\Phi_{136}\rangle, \langle\Phi_{147}\rangle, \langle\Phi_{345}\rangle, \langle\Phi_{246}\rangle, \\ \langle\Phi_{237}\rangle) \simeq [2\pi I_o(G'')]^{-1}\exp(G''\cos\Phi), \quad (14) \end{aligned}$$

where

$$\begin{aligned} G'' = [G_{1234} + (0.5G^p_{345}G^p_{125} - G_{1234}) + (0.5G^p_{246}G^p_{136} \\ - G_{1234}) + (0.5G^p_{237}G^p_{147} - G_{1234})](1+Q)^{-1}. \end{aligned}$$

If $G^p_{ijl} = G_{ijl}$ (only Cochran estimates are available for the triplet phases), then $G'' \equiv G'$.

Table 3. *NEWQB – statistical behaviour of the quartets in Table* 1 *when estimated via* (14)

| ARG | Positive estimated quartets *nr* (*nw*) | Negative estimated quartets *nr* (*nw*) |
|---|---|---|
| 0.0 | 5961 (738) | 750 (276) |
| 0.4 | 5380 (525) | 411 (122) |
| 0.8 | 4684 (368) | 219 (62) |
| 1.2 | 3836 (215) | 120 (32) |
| 2.0 | 2439 (71) | 44 (12) |
| 2.8 | 1478 (20) | 17 (4) |
| 4.6 | 382 (0) | |
| 8.0 | 13 (0) | |

## The quartet estimation *via* $P_{10}$ prior information on triplets

In *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) and *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993), triplets can be estimated *via* the $P_{10}$ formula (default choice). $P_{10}$ proved to be more accurate than the traditional Cochran (1955) formula: as an important detail, some triplets are estimated negative by $P_{10}$. Accordingly, a procedure that estimates quartets by using $P_{10}$ triplet estimates as prior information is a no-cost process if *SIR*88 or *SIR*92 is used. The expected result is that quartets with large cross magnitudes could even be estimated negative by (14). The reverse effect cannot be expected; since $P_{10}$ is only applied to triplets with large values of $G_{ijl}$, quartets with small cross magnitudes cannot exploit any $P_{10}$ information.

To check the effectiveness of (14), we have applied it to NEWQB data: the 6711 quartets estimated positive by (4) are processed *via* (14) by using the $P_{10}$ triplet estimates as prior information. The results are shown in Table 3. 750 out of 6711 quartets are now estimated negative by (14) (most of them correctly).

We applied (14) to several crystal structures: tests confirmed that it is more accurate than (4) and (12). For the sake of brevity, we only quote in Table 4 the complete quartet statistics obtained *via* (12) and (14) for the noncentrosymmetric structure AZET (Colens, Declercq, Germain, Putzeys & Van Meerssche, 1974). For example, it may be seen that 178 of 2250 quartets estimated positive by (12) with $G > 1.2$ are wrongly estimated, while only 93 of 2387 quartets estimated positive by (14) with $\mathrm{ARG} > 2.0$ are wrong.

Table 4. *AZET – quartet statistical behaviour when estimated by* (12) *and by* (14)

| ARG | Positive estimated quartets *nr* (*nw*) | Negative estimated quartets *nr* (*nw*) |
|---|---|---|
| Equation (12) | | |
| 0.0 | 16234 (4058) | 3766 (1808) |
| 0.4 | 10291 (1924) | 411 (188) |
| 0.8 | 5575 (769) | 39 (12) |
| 1.2 | 2250 (178) | 5 (1) |
| 1.6 | 533 (23) | |
| 2.0 | 20 (0) | |
| Equation (14) | | |
| 0.0 | 15422 (3578) | 4578 (2197) |
| 0.4 | 9478 (1421) | 738 (289) |
| 0.8 | 6500 (689) | 113 (28) |
| 1.2 | 4650 (339) | 18 (2) |
| 1.6 | 3287 (174) | 2 (0) |
| 2.0 | 2387 (93) | 1 (0) |
| 3.2 | 777 (20) | 1 (0) |
| 5.5 | 87 (0) | |

## Concluding remarks

A mathematical method is described that makes use of some prior information on triplet invariants for a more accurate estimate of quartet invariants. Numerical tests prove that the method works: even quartets with large cross magnitudes can be reliably estimated negative. The efficiency of the method will increase as soon as better techniques for triplet estimation become available.

## References


Altomare, A., Burla, M. C., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *Acta Cryst.* A**49**, 342–346.

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Burla, M. C., Cascarano, G. & Giacovazzo, C. (1992). *Acta Cryst.* A**48**, 906–912.

Cascarano, G., Giacovazzo, C., Camalli, M., Spagna, R., Burla, M. C., Nunzi, A. & Polidori, G. (1984). *Acta Cryst.* A**40**, 278–283.

Cochran, W. (1955). *Acta Cryst.* **8**, 473–478.

Colens, A., Declercq, J. P., Germain, G., Putzeys, J. P. & Van Meerssche, M. (1974). *Cryst. Struct. Commun.* **3**, 119–122.

Giacovazzo, C. (1976). *Acta Cryst.* A**32**, 91–99, 100–104.

Giacovazzo, C. (1977). *Acta Cryst.* A**33**, 527–531, 933–944.

Giacovazzo, C. (1980). *Direct Methods in Crystallography*. London: Academic Press

Giacovazzo, C., Burla, M. C. & Cascarano, G. (1992). *Acta Cryst.* A**48**, 901–906.

Giacovazzo, C., Camalli, M. & Spagna, R. (1989). *Acta Cryst.* A**45**, 141–143.

Grigg, R., Kemp, J., Sheldrick, G. M. & Trotter, J. (1978). *J. Chem. Soc. Chem. Commun.* pp. 109–111.

Hauptman, H. (1975). *Acta Cryst.* A**31**, 680–687.

Hümmer, K., Weckert, E. & Bondza, H. (1989). *Acta Cryst.* A**45**, 182–187.