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Negative Quartet Estimates by Embedding of Triplet and Quintet Invariants

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Abstract

Negative quartet invariants play an important role in direct procedures: they can be actively used in the phasing process or, in a passive way, for selecting the correct solution in multisolution approaches. Unfortunately their average reliability is small. The use of the second representation of the quartets may lead to improved estimates but calculations are expected to be too extensive even for modern computers. The simple and fast process described in this paper provides improved quartet estimates by embedding triplet and quintet estimates. The first applications of the method are satisfactory.

Symbols

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

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

$\varepsilon_i = R_i^2 - 1$.

$\Phi_4 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}}$ with $\mathbf{h} + \mathbf{k} + \mathbf{l} + \mathbf{m} = \mathbf{0}$.

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

$B = 2R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{m}}/N$.

$G_{ijpqr} = 2R_iR_jR_pR_qR_r/[N(N^{1/2})]$.

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

Introduction

We use in this section the following notation:

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

Two formulas are today widely used for estimating quartet invariants Φ_4:

(1) Giacovazzo's (1976, 1980) formula:

$$P(\Phi_4) = [2\pi I_0(G')]^{-1} \exp(G' \cos \Phi_4), \qquad (1)$$

where

$$G' = B(1 + \varepsilon_5 + \varepsilon_6 + \varepsilon_7)/(1 + Q)$$
$$Q = [(\varepsilon_1\varepsilon_2 + \varepsilon_3\varepsilon_4)\varepsilon_5 + (\varepsilon_1\varepsilon_3 + \varepsilon_2\varepsilon_4)\varepsilon_6 + (\varepsilon_1\varepsilon_4 + \varepsilon_2\varepsilon_3)\varepsilon_7]/2N.$$

(2) Hauptman's (1975) formula:

$$P(\Phi_4) = 1/L \exp(-2B \cos \Phi_4) I_0(Z_5) I_0(Z_6) I_0(Z_7), \qquad (2)$$

where

$$Z_5 = [G_{125}^2 + G_{345}^2 + 2G_{125}G_{345} \cos \Phi_4]^{1/2}$$
$$Z_6 = [G_{136}^2 + G_{246}^2 + 2G_{136}G_{246} \cos \Phi_4]^{1/2}$$
$$Z_7 = [G_{237}^2 + G_{147}^2 + 2G_{237}G_{147} \cos \Phi_4]^{1/2}.$$

L is a suitable normalizing constant that may be calculated by numerical methods. Some recent papers (Giacovazzo, Burla & Cascarano, 1992; Burla, Cascarano & Giacovazzo, 1992) addressed the practical role of the quartet invariants in direct procedures. The combined active use of the positive estimated quartets and the triplet invariants was not advised both because of the high correlation between positive estimated quartets and triplets and because of the lower accuracy of the quartet estimates.

More recently (Burla, Cascarano, Giacovazzo & Guagliardi, 1994), the accuracy of the quartet estimates has been improved by exploiting the prior information on triplets, in particular the triplet invariant estimates

provided by the P_{10} formula (Cascarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori, 1984). However, P_{10} is only applied to triplets with large G_{ijp} values; thus, the method is unable to improve the negative quartet reliability. Such quartets are not correlated with active triplets, and therefore introduce supplementary information in the phasing process. Indeed they play an important role in direct procedures both as figures of merit (for picking up the correct solution in a multisolution approach) and as active phase relationships (Sheldrick, 1991). Particularly powerful is the combined active use of negative estimated triplets (*via* the P_{10} formula) and negative estimated quartets (Cascarano, Giacovazzo, Moliterni & Polidori, 1994): such a combination often makes the difference between success and failure.

Any phasing process would benefit from improved negative quartet estimates. However, the use of the second representation of the quartets (*i.e.* special sextets) would be too time consuming even for modern computers. In this paper, a new method is described that estimates quartets by combining triplet and quintet invariants. The procedure is fast and easily transferable to any direct-methods package. The method also involves the original quartet estimates *via* (1) or (2). Since (1) is of simpler use and is reliable even for small structures (Altomare, Burla, Cascarano, Giacovazzo & Guagliardi, 1993), we focus our attention only on the estimates provided by (1).

Strengthening of quartet estimates: the method

Let us consider the quartet invariant

$$\Phi_4 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}} \tag{3}$$

and the triplet invariant

$$\Phi_3 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{q}} - \varphi_{\mathbf{h+q}}. \tag{4}$$

Their difference,

$$\Phi_5 = \Phi_4 - \Phi_3 = \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}} - \varphi_{\mathbf{q}} + \varphi_{\mathbf{h+q}}, \tag{5}$$

is a quintet invariant that may be estimated through different formulas: a semi-empirical one by Van der Putten & Schenk (1977), the formula by Fortier & Hauptman (1977) derived *via* the theory of the joint probability distribution functions, and the formula by Giacovazzo (1977). We refer only to the last method, which combines simplicity with efficiency. If both Φ_5 and Φ_3 are estimated, the last *via* the Cochran (1955) relationship or *via* the P_{10} formula, a back-estimate for Φ_4 arises. Since $\mathbf{q}$ is a free vector for a given Φ_4, several triplets of type (4) can be found. Thus, several quintet–triplet pairs can be used for a given quartet and the back-information on Φ_4 may increase remarkably. Besides triplets (4), triplets like

$$\Phi_3 = \varphi_{\mathbf{k}} + \varphi_{\mathbf{q}} - \varphi_{\mathbf{k+q}}$$
$$\Phi_3 = \varphi_{\mathbf{l}} + \varphi_{\mathbf{q}} - \varphi_{\mathbf{l+q}}$$
$$\Phi_3 = \varphi_{\mathbf{m}} + \varphi_{\mathbf{q}} - \varphi_{\mathbf{m+q}}$$

can also be used, each of which specifies the corresponding quintet involved in the method. Since any quintet depends (in its first representation) on 15 magnitudes, the approach is able to exploit, for each quartet, the information contained in a wide region of reciprocal space. Let us discuss separately the centrosymmetric and the noncentrosymmetric cases.

The noncentrosymmetric case

It is assumed that $P(\Phi_3)$, $P(\Phi_4)$ and $P(\Phi_5)$ are all of the von Mises type:

$$P(\Phi_i) = [2\pi I_0(G_i)]^{-1} \exp(G_i \cos \Phi_i), \quad i = 3, 4, 5. \tag{6}$$

The maximum of the distribution will be in 0 or in π according to whether G is positive or negative. From the jth pair $(\Phi_{3,j}, \Phi_{5,j})$, the following information on Φ_4 can be derived: Φ_4 is a von Mises variable with reliability parameter $G_{4,j}$ defined by the equation (Giacovazzo, Camalli & Spagna, 1989)

$$D_1(G_{4,j}) = D_1(G_{3,j}) D_1(G_{5,j}). \tag{7}$$

Positive values of $G_{3,j}$ and $G_{5,j}$ will generate positive estimated quartets, while negative estimated quartets will be obtained when $G_{3,j}$ and $G_{5,j}$ have opposite signs. The information from the various pairs $(\Phi_{3,j}, \Phi_{5,j})$ may be combined by summation of the various $G_{4,j}$; the final reliability parameter will be

$$\sum_j G_{4,j},$$

to which the intrinsic information arising from (1) must be added. The final reliability parameter is then

$$G_4 = G' + \sum_j G_{4,j}. \tag{8}$$

The centrosymmetric case

It is assumed that the sign probability for Φ_3 and Φ_5 is described by the formula

$$P^+(\Phi_i) \simeq 0.5 + 0.5 \tanh G_i.$$

From the jth pair $(\Phi_{3,j}, \Phi_{5,j})$, the following information on Φ_4 can be derived:

$$P^+(\Phi_{4,j}) = P^+(\Phi_{3,j}) P^+(\Phi_{5,j}) + P^-(\Phi_{3,j}) P^-(\Phi_{5,j}),$$

which can be transformed into $G_{4,j}$ by recalling that $\tanh^{-1}(y) = \frac{1}{2}\ln(1+y)/(1-y)$. Therefore,

$$G_{4,j} = \tfrac{1}{2}[\ln P^+(\Phi_{4,j}) - \ln P^-(\Phi_{4,j})].$$

The information arising from various pairs $(\Phi_{3,j}, \Phi_{5,j})$ may be combined by summing the various $G_{4,j}$, to which the intrinsic information arising from the quartet itself should be added. The final reliability parameter is again given by (8).

While the estimates of the triplet invariants do not require special considerations (they come directly from the P_{10} formula; if P_{10} estimates are not available, the Cochran formula may be used), quintet estimates deserve to be discussed in some detail.

Quintet estimation

Let us consider the quintet (5) and denote:

$$\begin{aligned} E_1 = E_{\mathbf{k}}, \quad E_2 = E_{\mathbf{l}}, \quad E_3 = E_{\mathbf{m}}, \quad E_4 = E_{-\mathbf{q}}, \\ E_5 = E_{\mathbf{h}+\mathbf{q}}, \quad E_6 = E_{\mathbf{k}+\mathbf{l}}, \quad E_7 = E_{\mathbf{h}+\mathbf{l}} \\ E_8 = E_{\mathbf{k}-\mathbf{q}}, \quad E_9 = E_{\mathbf{h}+\mathbf{k}+\mathbf{q}}, \quad E_{10} = E_{\mathbf{h}+\mathbf{k}}, \\ E_{11} = E_{\mathbf{l}-\mathbf{q}}, \quad E_{12} = E_{\mathbf{h}+\mathbf{l}+\mathbf{q}}, \quad E_{13} = E_{\mathbf{m}-\mathbf{q}}, \\ E_{14} = E_{\mathbf{h}+\mathbf{m}+\mathbf{q}}, \quad E_{15} = E_{\mathbf{h}}. \end{aligned} \tag{9}$$

The reliability parameter for the quintets is (Giacovazzo, 1977; Burla, Polidori, Nunzi, Cascarano & Giacovazzo, 1977)

$$G_5 = [G_{12345}/(1 + 6N^{1/2})](A + B)/(1 + C/2N), \tag{10}$$

where

$$A = \sum_{i=6}^{15} \varepsilon_i \tag{11}$$

$$\begin{aligned} B = {} & \varepsilon_6\varepsilon_{13} + \varepsilon_6\varepsilon_{15} + \varepsilon_6\varepsilon_{14} + \varepsilon_7\varepsilon_{11} + \varepsilon_7\varepsilon_{15} + \varepsilon_7\varepsilon_{12} \\ & + \varepsilon_8\varepsilon_{10} + \varepsilon_8\varepsilon_{14} + \varepsilon_8\varepsilon_{12} + \varepsilon_{10}\varepsilon_{15} + \varepsilon_9\varepsilon_{10} \\ & + \varepsilon_{11}\varepsilon_{14} + \varepsilon_9\varepsilon_{11} + \varepsilon_9\varepsilon_{13} + \varepsilon_{12}\varepsilon_{13} \end{aligned} \tag{12}$$

$$\begin{aligned} C = {} & \varepsilon_1\varepsilon_2\varepsilon_6 + \varepsilon_1\varepsilon_3\varepsilon_7 + \varepsilon_1\varepsilon_4\varepsilon_8 + \varepsilon_1\varepsilon_5\varepsilon_9 + \varepsilon_1\varepsilon_{10}\varepsilon_{15} \\ & + \varepsilon_1\varepsilon_{11}\varepsilon_{14} + \varepsilon_1\varepsilon_{12}\varepsilon_{13} + \varepsilon_2\varepsilon_3\varepsilon_{10} + \varepsilon_2\varepsilon_4\varepsilon_{11} \\ & + \varepsilon_2\varepsilon_5\varepsilon_{12} + \varepsilon_2\varepsilon_7\varepsilon_{15} + \varepsilon_2\varepsilon_8\varepsilon_{14} + \varepsilon_2\varepsilon_9\varepsilon_{13} \\ & + \varepsilon_3\varepsilon_4\varepsilon_{13} + \varepsilon_3\varepsilon_5\varepsilon_{14} + \varepsilon_3\varepsilon_6\varepsilon_{15} + \varepsilon_3\varepsilon_8\varepsilon_{12} \\ & + \varepsilon_3\varepsilon_9\varepsilon_{11} + \varepsilon_4\varepsilon_5\varepsilon_{15} + \varepsilon_4\varepsilon_6\varepsilon_{14} + \varepsilon_4\varepsilon_7\varepsilon_{12} \\ & + \varepsilon_4\varepsilon_9\varepsilon_{10} + \varepsilon_5\varepsilon_6\varepsilon_{13} + \varepsilon_5\varepsilon_7\varepsilon_{11} + \varepsilon_5\varepsilon_8\varepsilon_{10}. \end{aligned} \tag{13}$$

C is a scaling constant that is assumed to be equal to zero when it is negative. The quintet is expected to be positive or negative according to whether G_5 is positive or negative.

Negative quintets are obtained by a modified version of *SIR*92 (Altomare, Cascarano, Giacovazzo, Guagliardi, Burla, Polidori & Camalli, 1994) in the following way:

(*a*) A certain number of weak reflections are selected by the program (in the default conditions).

(*b*) Psi-zero triplets are calculated and stored for passive use (Cochran & Douglas, 1957) as well as for active use (Giacovazzo, 1993; Cascarano & Giacovazzo, 1995).

Table 1. *Code name, space group and crystallochemical data for test structures*

Structure code	Space group	Molecular formula	Z
APAPA[1]	$P4_12_12$	$C_{30}H_{37}N_{15}O_{16}P_2 \cdot 6H_2O$	8
GRA4[2]	$P\bar{1}$	$C_{30}H_{22}N_2O_4$	2
MBH2[3]	$P1$	$C_{15}H_{24}O_3$	3
NEWQB[4]	$P\bar{1}$	$C_{24}H_{20}N_2O_5$	4
PGE2[5]	$P1$	$C_{20}H_{32}O_5$	1
QUINOL[6]	$R\bar{3}$	$C_6H_6O_2$	54
SCHWARZ[7]	$P1$	$C_{46}H_{70}O_{27}$	1

References: (1) Suck, Manor & Saenger (1976); (2) Crystallography group of York University (private communication); (3) Hursthouse (unpublished); (4) Grigg, Kemp, Sheldrick & Trotter (1978); (5) DeTitta, Langs, Edmonds & Duax (1980); (6) Wallwork & Powell (1980); (7) Schweizer (unpublished).

Table 2. *Negative estimated quartets and quintets for the centrosymmetric test structures*

n is the number of invariants with reliability parameter larger (in modulus) than a given ARG, nw is the number of wrong estimates

ARG	Quartets n (nw)	Quintets n (nw)
GRA4		
0.4	3212 (508)	352922 (42565)
0.8	1164 (55)	170869 (10336)
2.0	61 (1)	37445 (508)
2.4	36 (0)	24537 (219)
4.5	1 (0)	3092 (7)
7.5		241 (0)
NEWQB		
0.4	512 (145)	18920 (4696)
0.6	68 (13)	3858 (589)
0.8	11 (0)	966 (68)
1.4		38 (0)
QUINOL		
0.4	945 (188)	43191 (8297)
0.6	158 (20)	11993 (1626)
1.0	14 (1)	1677 (204)
1.2	4 (0)	712 (30)
2.4		21 (0)

(*c*) Negative quartets are obtained as a sum of psi-zero triplets and estimated *via* (1). The sum of the two triplets creates a quartet with at least one small cross magnitude: then (1) selects those with negative G' value.

(*d*) Negative quintets are obtained as sums of the negative quartets in (*c*) and of the triplets with large G_{ijp} values stored for active use. Quintet estimates are then obtained *via* (10).

The accuracy of the method here described relies on the quintet reliability. This has been scarcely considered in the literature, probably because of the belief that negative quartets are always much more accurate than negative quintets. But this is not always true. For the test structures quoted in Table 1, we compare in Tables 2 and 3 negative-quintet and negative-quartet reliabilities. It is seen that quintet estimates are always superior to quartet estimates, except for APAPA, which has a very large value of N. For structures of such complexity, quintet reliability is expected to be small. Very likely some

Table 3. *Negative estimated quartets and quintets for the noncentrosymmetric test structures*

n is the number of invariants with reliability parameter larger (in modulus) than a given argument ARG, % is the percentage of invariants with wrong cosine sign estimate, $\langle\Phi\rangle^0$ is the average value of the invariant phases.

	Quartets			Quintets		
ARG	n	%	$\langle\Phi\rangle^0$	n	%	$\langle\Phi\rangle^0$
APAPA						
0.0	1104	59	100	90147	50	90
0.4	36	72	121			
0.8	9	78	125			
MBH2						
0.4	1342	69	113	2370	77	119
0.8	70	80	122	25	84	128
PGE2						
0.4	4000	63	104	42146	72	115
0.8	985	71	113	2879	81	125
1.6	51	78	128	109	94	138
SCHWARZ						
0.4	2117	66	108	9915	74	118
0.8	196	77	122	323	86	130
1.6	3	67	101	1	100	167

improvement could be obtained by making full use of the complete first representation of the quintets, that is by involving in the calculations those supplementary cross reflections that are generated by the existence of special cross terms characterized by a Wilson coefficient $\varepsilon > 1$ (Giacovazzo, 1980, p. 338). This topic is explored in a subsequent paper.

The procedure and its applications

Let us consider the 15 magnitudes in the first representation of Φ_5 as listed in the set (9). Seven of them, R_1, R_2, R_3, R_6, R_7, R_{10} and R_{15}, also belong to the first representation of the quartet (3). Since quartets (3) are constructed in such a way that R_{15} is large and R_6, R_7 and R_{10} are small (these last are the cross magnitudes of Φ_4), the term

$$D = \varepsilon_{15}(\varepsilon_6 + \varepsilon_7 + \varepsilon_{10})$$

occurring in B [see (12)] is strongly negative. This has the following consequences. (*a*) Each quintet $\Phi_{5,j}$ is strongly correlated with the quartet Φ_4. Thus each quintet $\Phi_{5,j}$ is expected to have the same sign as Φ_4. (*b*) The various quintets $\Phi_{5,j}$ are correlated with each other. Indeed, D does not depend on the specific vector $\mathbf{q}$ and will contribute to the estimation of all the $\Phi_{5,j}$'s. Owing to (*a*) and (*b*), G_4 as determined by (8) will probably have the same sign as G', but will be much larger than it because of the strong correlation among the various coefficients $G_{4,j}$.

In order to break this correlation, we omit D from (12) and the term $(\varepsilon_6 + \varepsilon_7 + \varepsilon_{10} + \varepsilon_{15})$ from (11); correspondingly, the scaling term $(\varepsilon_1\varepsilon_2\varepsilon_6 + \varepsilon_1\varepsilon_3\varepsilon_7 + \varepsilon_1\varepsilon_{10}\varepsilon_{15} + \varepsilon_2\varepsilon_3\varepsilon_{10} + \varepsilon_2\varepsilon_7\varepsilon_{15} + \varepsilon_3\varepsilon_6\varepsilon_{15})$ is eliminated from (13). In this way, the estimate of any $\Phi_{5,j}$ will mostly depend on those cross magnitudes that do not coincide with the cross terms of the quartet.

Table 4. *Centrosymmetric test structures*

The quartets estimated negative by (1) and quoted in Table 2 are re-estimated by (8). They split into two subsets, positive and negative estimated quartets. n is the number of quartet invariants with reliability parameter larger (in modulus) than a given argument ARG, nw is the number of wrong estimates.

ARG	Positive estimated quartets n (nw)	Negative estimated quartets n (nw)
GRA4		
0.4	831 (392)	2853 (220)
0.8	698 (309)	2695 (175)
2.0	476 (173)	2363 (91)
4.2	305 (87)	1962 (20)
7.0	212 (54)	1516 (1)
9.0	183 (45)	1204 (0)
NEWQB		
0.4	165 (66)	599 (87)
0.6	114 (41)	376 (41)
0.8	69 (24)	225 (12)
1.4	18 (4)	35 (0)
QUINOL		
0.4	722 (359)	713 (53)
1.0	354 (143)	114 (2)
1.6	202 (66)	18 (0)
2.4	94 (19)	
5.0	14 (0)	

Table 5. *Noncentrosymmetric test structures*

The quartets estimated negative by (1) and quoted in Table 3 are re-estimated by (8). They split into two subsets, positive and negative estimated quartets. n is the number of quartet invariants with reliability parameter (in modulus) larger than a given argument ARG, % is the percentage of invariants with wrong cosine sign estimate, $\langle\Phi\rangle^0$ is the average value of the invariant phases.

	Positive estimated quartets			Negative estimated quintets		
ARG	n	%	$\langle\Phi\rangle^0$	n	%	$\langle\Phi\rangle^0$
APAPA						
0.0	23	48	86	1081	59	100
0.4				7	86	140
MBH2						
0.4	223	57	86	600	83	129
0.8	80	56	86	88	90	138
1.6	11	64	81	3	100	126
PGE2						
0.4	1033	47	94	1738	70	114
0.8	699	48	91	964	75	120
1.6	363	53	87	209	87	134
3.2	116	57	79	13	100	143
SCHWARZ						
0.4	1140	55	85	906	79	124
0.8	739	59	81	218	85	131
1.6	348	62	77	11	91	122
4.4	31	90	45			

Table 6. *Centrosymmetric test structures*

For each structure NPQ quartets are estimated positive *via* (1). When re-estimated *via* (8), some of them are expected negative and are here quoted. Some statistical results are shown.

ARG	Negative estimated quartet *via* (8) *n* (*nw*)
GRA4 (NPQ = 5749)	
0.0	41 (0)
2.0	38 (0)
5.0	36 (0)
NEWQB (NPQ = 1083)	
0.0	180 (60)
0.4	94 (25)
2.0	5 (2)
2.8	1 (0)
5.0	
QUINOL (NPQ = 16958)	
0.0	585 (121)
0.4	191 (33)
2.0	7 (0)

Table 7. *Noncentrosymmetric test structures*

For each structure NPQ quartets are estimated positive *via* (1). When re-estimated *via* (8), some of them are expected negative. Some statistical results are shown.

ARG	Negative estimated quartets *via* (8) *n*	%	$\langle\Phi\rangle^0$
APAPA (NPQ = 20000)			
0.0			
0.4	1161	56	95
MBH2 (NPQ = 1330)			
0.0	109	62	103
0.4	40	63	100
PGE2 (NPQ = 6097)			
0.0	87	49	90
0.8	32	50	96
3.2	1	100	146
SCHWARZ (NPQ = 1728)			
0.0	53	77	118
0.8	12	83	128
1.2	3	100	165

We have then applied to the test structures the method here described: the quartets estimated negative by (1) are re-estimated *via* (8). The results are shown in Table 4 for centrosymmetric structures and in Table 5 for noncentrosymmetric structures. We note two things. (*a*) A percentage of the quartets estimated negative by (1) are estimated positive by (8) with notable accuracy. The new approach is therefore able to pick up positive quartets among the set of quartets having small cross magnitudes. (*b*) The reliability of the quartets estimated negative *via* (8) is higher, and sometimes spectacularly higher, than *via* (1). APAPA is the expected exception.

We wonder now if the method can be applied to quartets estimated positive by (1). We are interested to check if: (*a*) quartets with large cross moduli can be reliably estimated negative by embedding triplet with quintet invariants; (*b*) the positive-quartet reliability can be improved *via* the same method. The results shown in Tables 6 and 7 give a positive answer to both those questions: even for APAPA is possible to select a number of quartets with phases far from 2π.

Concluding remarks

The method here described shows how the prior information contained in a large set of structure-factor moduli may be exploited for the estimation of low-order invariants. For each quartet, triplet estimates derived *via* the second representation are combined with quintet estimates to obtain the estimate of the selected quartet. The attention has been mostly focused on the negative quartets, but some tests have also been made for the positive ones. The reliability of the method is higher than that of the standard formulas by Giacovazzo (1976, 1980) and Hauptman (1975).

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