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The Use of Quintets in Direct Procedures: Some Practical Aspects

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Probabilistic formulae derived for $P\bar{1}$ in the previous paper for general and special types of quintets are tested and slightly modified by suitable empirical factors. The reliability of the new expressions equals that of triplets. The method of complementary invariants is applied to the quintets in order to derive the sign of one and two-phase structure seminvariants.

1. Introduction

In the preceding paper (Giacovazzo, 1977*a*; referred to as I) probabilistic formulae in $P\bar{1}$ for quintet invariants of type:

$$\Phi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}} - \varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}} \quad (1)$$

$$\Phi = \varphi_{2\mathbf{h}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}} \quad (2)$$

$$\Phi = \varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{h}} - \varphi_{\mathbf{h}+\mathbf{l}} \quad (3)$$

were given in terms of the magnitudes of the first phasing shell. The aim of this paper is to explore the reliability of equations (I.5), (I.12) and (I.15) from the following two points of view.

(1) The probability theory used in (I) uses a Gram–Charlier expansion of the characteristic distribution of the magnitudes belonging to the first phasing shell of the quintet invariants. By analogy with what occurred for quartets (Giacovazzo, 1975*a*, 1976) one may expect that probability values for quintets are overestimated. We wish here to modify in an empirical way the theoretical distributions in order to put on an absolute scale (*i.e.* on the same scale as the triplet relationships) the probability levels provided by the theory.

(2) In $P\bar{1}$ (2) and (3) are complementary invariants (Giacovazzo, 1977*b*) of $\varphi_{2\mathbf{h}}$ and $\varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}$ *via* the quartets $\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ and the triplet invariant $\varphi_{\mathbf{l}} + \varphi_{\mathbf{h}} - \varphi_{\mathbf{h}-\mathbf{l}}$ respectively. Thus (2) and (3) may be usefully exploited in order to define $\varphi_{2\mathbf{h}}$ and $\varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}$. The method of complementary invariants for quartets was described in $P\bar{1}$ by Giacovazzo (1975*b*) in order to calculate $\varphi_{2\mathbf{h}}$ by means of the special quartets $\varphi_{2\mathbf{h}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}}$. Here we apply the method to estimate in $P\bar{1}$ one and two-phase seminvariants by means of (2) and (3).

2. General quintets: calculations

Quintets and triplets may be used simultaneously in direct procedures provided that the signs of the triplets and quintets have the same reliability. To check this condition we pay attention to two relevant observations: (*a*) the number of quintets for which all ten cross-magnitudes are in the set of measured reflexions is usually a small percentage of the observable quintets. Therefore a reliability check should be made also for quintets for which not all the cross-magnitudes are in the set. Quintets for which at least five cross-magnitudes are unknown are likely to be unreliable. In order to save computing time we have excluded them from our calculations. (*b*) the number of negative quintets is smaller than the number of positive: the ratio, however, is larger than for quartets. Their use therefore may be relevant in crystal structure solution.

This suggests that we should make separate tests for quintets in which 6, 7, 8, 9 and 10 cross-magnitudes are in the measured set and for negative as well as positive quintets.

As the probability that a triplet has a positive sign is given by:

$$P_+ \simeq 0{\cdot}5 + 0{\cdot}5 \tanh\left(|E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}+\mathbf{k}}| / \sqrt{N}\right),$$

one may compare the reliabilities of triplets and quintets giving the number and percentage of correct ones above the corresponding values of the arguments of the hyperbolic tangent. In order to check (I.5) as a function of structural complexity we have tested five models with $N = 20$, 60, 70, 100, 140, and a real structure ($C_{47}H_{30}N_6O_4Br_2$; Fanfani, Nunzi, Zanazzi & Zanzari, 1974).

The sign probabilities provided by (I.5) proved the more overestimated (compared with those of triplet

Table 1. *Number of relations (n.r.) and percentage of correct relations of triplets and quintets for a 140-atom model structure*

Tanh arg	Triplets n.r.	Triplets %	6 cross-vectors in set: Negative quintets n.r.	Negative quintets %	Positive quintets n.r.	Positive quintets %	7 cross-vectors in set: Negative quintets n.r.	Negative quintets %	Positive quintets n.r.	Positive quintets %	8 cross-vectors in set: Negative quintets n.r.	Negative quintets %	Positive quintets n.r.	Positive quintets %
0·2	613	93	13	69	58	76	37	56	59	74	23	30	30	77
0·4	613	93	1	100	37	78	3	100	41	83	1	100	18	72
0·6	613	93			19	89			29	100	1	100	9	100
0·7	569	93			14	100			22	100			9	100
0·9	392	97			3	100			13	100			4	100
1·0	320	97			1	100			7	100			3	100
1·2	208	98			1	100			2	100				
1·5	95	96												
1·6	64	100												
1·8	31	100												

Tanh arg	9 cross-vectors in set: Negative quintets n.r.	Negative quintets %	Positive quintets n.r.	Positive quintets %	10 cross-vectors in set: Negative quintets n.r.	Negative quintets %	Positive quintets n.r.	Positive quintets %	6–10 cross-vectors in set: Negative quintets n.r.	Negative quintets %	Positive quintets n.r.	Positive quintets %
0·2	6	83	10	90	7	71	10	100	86	55	167	78
0·4	2	100	9	90			5	100	7	100	110	81
0·6	1	100	6	100			5	100	1	100	68	97
0·7			4	100			5	100			54	100
0·9			4	100			2	100			26	100
1·0			1	100							14	100
1·2			1	100							4	100

relationships) the more N decreases. A solution seemed to be to retain the basic probabilistic expression (I.5) and rescale probability values by a suitable empirical factor. Thus we have rescaled the argument of the hyperbolic tangent in (I.5) by dividing it by $(1+6/\sqrt{N})$.

Three further modifications to (I.5) proved satisfactory. (1) The term $D/8N$ was always negligible compared with unity or $C/2N$. We have thus assumed $D=0$. (2) (I.5) has a discontinuity when $1+C/2N+D/8N=0$. The behaviour has no physical meaning and occurs because the Gram–Charlier expansion of the characteristic function has been used for deriving (I.5). Then the probability distribution itself is an asymptotic series cut-off to order $1/N\sqrt{N}$. To avoid large probability values we have assumed $C=0$ when $C<0$. (3) Negative quintets seem more accurately defined than positive ones marked by the same probability value. Thus we have replaced in (I.5) $A+B$ by $A+B-1$.

In Tables 1 and 2 the outcome is shown for the two models with $N=70$, 140, in Table 3 for the real structure. The triplets are found within the group of 250 strongest reflexions, the quintets within the strongest 50. For brevity, the check on our modified form of (I.5) as a function of the number of known cross-magnitudes is shown only for the model structure with $N=140$. For the real structure we have assumed $N=\sigma_2^3/\sigma_3^2$. No advantage has been noted with more sophisticated formulae such as (I.5′).

Tables 1 and 3 suggest that quintet reliability levels are comparable with those of triplets. We have then looked for quintets within the set of 80 strongest reflexions. Even though the quintet reliability is still comparable with that of triplets, some meaningful differences occur. Our modified form of (I.5), in fact, does not hold for a small number of quintets char-

Table 2. *Number of relations (n.r.) and percentage of correct relations of triplets and negative and positive quintets for a 70-atom model structure*

Quintets are found within the 50 strongest reflexions.

Tanh arg	Triplets n.r.	Triplets %	Negative quintets n.r.	Negative quintets %	Positive quintets n.r.	Positive quintets %
0·4	1312	86	105	83	376	81
0·6	1271	87	35	94	246	89
0·8	878	90	16	100	176	91
1·1	318	93	2	100	94	97
1·3	157	97			59	100
1·5	84	99			48	100
1·6	53	100			38	100
2·4	6	100			13	100

Table 3. *Number of relations (n.r.) and percentage of correct relations of triplets and negative and positive quintets for the real structure*

Quintets are found within the 50 strongest reflexions.

Tanh arg	Triplets n.r.	Triplets %	Negative quintets n.r.	Negative quintets %	Positive quintets n.r.	Positive quintets %
0·4	1273	99·3	26	84·6	964	99·7
0·6	1273	99·3	13	100	805	99·9
0·7	1273	99·3	10	100	697	99·9
0·9	1176	99·3	7	100	508	99·8
1·0	1027	99·4	6	100	420	100
1·4	431	100	2	100	151	100
2·0	84	100	1	100	22	100
3·2	6	100			1	100

acterized by large positive values of the argument of the hyperbolic tangent. We give in Table 4 the outcome corresponding to the model with $N=140$: it may be compared with the two last columns of Table 1. For any quintet ten tripoles may be formed, one for every cross-vector, of type:

$$\Phi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}$$
$$\Phi_T=-\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}+\mathbf{k}}$$
$$\Phi_Q=-\varphi_{\mathbf{l}}-\varphi_{\mathbf{m}}+\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}-\varphi_{\mathbf{h}+\mathbf{k}}.$$

Always $\Phi=\Phi_T+\Phi_Q$. If Φ_T is marked by a large value of $\mathrm{ARG}=|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|/\sqrt{N}$, but is really equal to π, the estimate of Φ could be undetermined, especially if a large percentage of cross-magnitudes are not in the set of measurements. Referring to the model with $N=140$, four triplets with ARG > 1·20 are negative (Table 1):

$|E_{7\bar{1}1}E_{\bar{8}2\bar{7}}E_{138}|=2{\cdot}60\times2{\cdot}43\times2{\cdot}94$ ARG = 1·57
$|E_{\bar{2}5\bar{2}}E_{\bar{8}2\bar{7}}E_{10\bar{3}9}|=2{\cdot}60\times2{\cdot}43\times2{\cdot}94$ ARG = 1·57
$|E_{\bar{2}5\bar{2}}E_{1\bar{8}6}E_{138}|=2{\cdot}60\times2{\cdot}42\times2{\cdot}94$ ARG = 1·56
$|E_{9\bar{6}2}E_{\bar{1}59}E_{\bar{8}1\bar{1}\bar{1}}|=2{\cdot}97\times2{\cdot}83\times2{\cdot}19$ ARG = 1·56.

Three of these triplets are involved in five quintets with only seven cross-vectors in the set and are wrongly defined positive by (I. 5). Defining by ARGU the argument of the hyperbolic tangent in our modified form of (I. 5) we have

$E_{11,3,5}E_{17\bar{1}}E_{\bar{11},7,4}E_{7\bar{1}1}E_{\bar{8}2\bar{7}}$ ARGU = 1·17
$E_{11,3,5}E_{10,1,1}E_{\bar{11},7,4}E_{\bar{2}5\bar{2}}E_{\bar{8}2\bar{7}}$ ARGU = 1·50
$E_{8\bar{4}1}E_{\bar{3}10}E_{\bar{4}87}E_{\bar{2}5\bar{2}}E_{1\bar{8}6}$ ARGU = 0·98
$E_{031}E_{17\bar{1}}E_{2\bar{5}2}E_{827}E_{\bar{11},7,9}$ ARGU = 0·91
$E_{11,\bar{2},1}E_{\bar{5}28}E_{2\bar{5}2}E_{\bar{7}11}E_{\bar{1}86}$ ARGU = 0·93.

These considerations suggest limiting the set of the strongest reflexions within which the quintets are to be found, unless a condition is fixed which requires a very large percentage of cross-reflexions in the set of measurements.

3. The sign of $E_{2\mathbf{h}}$ in $P\bar{1}$ *via* the method of quintet complementary invariants

Quintet complementary invariants such as (2) may be estimated in $P\bar{1}$ by means of (I. 12). In accordance with the considerations of §2 we have modified its theoretical expression: (*a*) the argument of the hyperbolic tangent has been divided by $(1+6/\sqrt{N})$; (*b*) we have assumed $D'=0$; (*c*) we have assumed $C'=0$ when $C'<0$.

If the value of (2) is fixed, the sign of $E_{2\mathbf{h}}$ may be derived provided the sign of the quartet $\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ is known. We have estimated the sign of the quartet by means of the probabilistic formulae given by Giacovazzo [1976, equations (11) and (12)] and by Green & Hauptman (1976*a*). We have excluded from our calculations quintet complementary invariants for which one of the following conditions occurs: (1) one of the probability values for the quintet or the corresponding quartet is $>0{\cdot}30$ and $<0{\cdot}70$; (2) the quartet has only one cross-vector in the set of measurements.

Conditions (1) and (2) arise because it seemed preferable to require high probability levels both for quintets and quartets. Considering that the sign of the quartet does not depend on that of the quintet we may write:

$$P^+(E_{2\mathbf{h}})=P_QP_q+(1-P_Q)(1-P_q)$$

where P_Q and P_q are the sign-probability values for the quintet and the quartet respectively.

We note now that the sign of $E_{2\mathbf{h}}$ may be generally fixed by means of more than one quintet complementary invariant (2): in fact **k** and **l** are free vectors which may vary over reciprocal space. A measure of the overall probability that $E_{2\mathbf{h}}$ has a positive sign is given by:

$$P^+(E_{2\mathbf{h}})=\left(1+\frac{\Pi_jP_j^-}{\Pi_jP_j^+}\right)^{-1}, \qquad (4)$$

where $P_j^+(P_j^-)$ is the probability of a positive (negative) sign for $E_{2\mathbf{h}}$ as calculated *via* the jth quintet complementary invariant.

Table 4. *Number of relations (n.r.) and percentage of correct quintet relations for* 70 *and* 140*-atom model structures*

Quintets are found within the 80 strongest reflexions.

	$N=70$				$N=140$			
	Negative quintets		Positive quintets		Negative quintets		Positive quintets	
Tanh arg	n.r.	%	n.r.	%	n.r.	%	n.r.	%
0·4	681	78	2492	82	110	93	1288	89
0·5	336	81	1932	84	28	100	958	90
0·6	170	80	1528	87	8	100	739	91
0·8	62	81	960	91	1	100	378	94
1·1	16	81	506	95			121	98
1·3	4	100	322	98			47	98
1·5	3	100	211	98			15	100
1·6	2	100	174	98			8	100
2·0			92	100			1	100

A last observation is that (4) postulates that each $P_j^{\pm}$ is independent of the others. Thus we expect that (4) will overestimate the sign probability for $E_{2\mathbf{h}}$.

We have checked the method with the models with $N=70$, 140, and the diffraction data of the real structure: the outcome is shown in Tables 5–7; P^+ is given by (4), NQ is the number of quintets which really fix the sign of $E_{2\mathbf{h}}$. The Σ_1 formula fails in three cases: (4) suggests for them the correct negative value only in two cases. Our experience is that quintets with negative values are always more badly estimated than those with positive values of $E_{2\mathbf{h}}$. In conclusion, the procedure seems poor for defining the sign of the one-phase structure seminvariants. This behaviour results because the method requires that quartet and quintet probability theories contemporaneously and with large accuracy recognize the corresponding signs. Further improvements of the quartet and quintet theories will surely be able to make our method more useful.

4. The sign of $E_{\mathbf{h}+\mathbf{k}}$ in $P\bar{1}$ *via* the method of complementary quintet invariants

In accordance with the preceding paragraphs we have used a modified form of (I.15) in order to estimate quintet complementary invariants such as (3). In particular: (*a*) the argument of the hyperbolic tangent has been divided by $(1+6/\sqrt{N})$; (*b*) we have assumed $D''=0$; (*c*) we have assumed $C''=0$ when $C''<0$.

If the sign of (3) is fixed, the sign of $E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}$ may be derived provided the sign of the triplet $\varphi_{\mathbf{l}}+\varphi_{\mathbf{h}}-\varphi_{\mathbf{h}+\mathbf{l}}$ is known. As the probability that a triplet is positive is given by:

$$P_T=0{\cdot}5+0{\cdot}5\tanh\left(|E_{\mathbf{l}}E_{\mathbf{h}}E_{\mathbf{h}+\mathbf{l}}|/\sqrt{N}\right)$$

Table 5. *List of pairs $E_{2\mathbf{h}}$, $E_{\mathbf{h}}$ in the real structure which form quintets $E_{2\mathbf{h}}$, $E_{\mathbf{h}}$, $E_{\mathbf{k}}$, $E_{\mathbf{l}}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ with $|E|>1{\cdot}50$*

2h	$E_{2\mathbf{h}}$	$E_{\mathbf{h}}$	P^+	NQ
2,2̄,12	1·71	−1·97	0·99	21
2,1̄2,2	1·65	1·81	0·99	73
642	1·64	−2·79	0·99	237
26̄0	1·63	−1·55	0·99	78
12,2̄,4̄	1·61	−2·53	0·99	105
44̄2̄	1·52	−2·53	0·99	229
222	−1·51	2·07	0·38	4

Table 6. *List of pairs $E_{2\mathbf{h}}$, $E_{\mathbf{h}}$ in the model with $N=70$ which form quintets $E_{2\mathbf{h}}$, $E_{\mathbf{h}}$, $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ with $|E|>1{\cdot}50$*

2h	$E_{2\mathbf{h}}$	$E_{\mathbf{h}}$	P^+	NQ
24̄2̄	2·48	−1·52	0·99	15
42̄6̄	−2·01	−1·78	0·99	18
40̄4̄	−1·70	1·90	0·29	1
08̄4̄	1·65	−2·07	0·89	5

Table 7. *Outcome for the only $E_{2\mathbf{h}}$ value in the model with $N=140$ which forms quintets $E_{2\mathbf{h}}$, $E_{\mathbf{h}}$, $E_{\mathbf{k}}$, $E_{\mathbf{l}}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ with $|E|>1{\cdot}80$*

2h	$E_{2\mathbf{h}}$	$E_{\mathbf{h}}$	P^+	NQ
482	1·84	−1·92	0·83	3

Table 8. *23 values of P^+ for a model structure in $P\bar{1}$ with $N=70$ atoms in unit cell, arranged in descending order of expected accuracy*

h+k	$E_{\mathbf{h}+\mathbf{k}}$	h−k	$E_{\mathbf{h}-\mathbf{k}}$	P^+	NQ
41̄3	2·23	45̄7	2·08	0·908	4
6̄25	−2·85	6̄61	−1·90	0·879	4
1̄14	2·35	1̄76	1·85	0·870	3
028	2·61	02̄2	2·34	0·869	2
2̄41	−2·29	6̄43	−1·93	0·867	3
5̄52	2·23	5̄16	2·08	0·862	3
2̄42	2·48	2̄8̄6	2·01	0·839	2
066	−2·89	2̄42	2·48	0·211	2
6̄08	−2·62	28̄4	−2·11	0·756	1
34̄6	−2·85	302	−1·90	0·747	2
568	−2·31	722	−2·02	0·744	2
115	2·02	57̄3	−1·95	0·743*	1
7̄21	1·94	76̄3	1·90	0·729	2
58̄1	2·15	54̄7	−2·01	0·291	1
7̄16	−1·98	5̄34	1·92	0·706*	2
14̄1	−2·63	725	−2·08	0·702	1
6̄08	−2·62	6̄42	1·87	0·350	1
24̄2	1·93	2̄02	1·90	0·643	1
28̄4	−2·08	24̄2	1·93	0·364	1
12̄4	−2·47	1̄26	−1·92	0·629	1
023	3·46	645	−3·30	0·375	1
12̄4	−2·47	54̄4	−1·85	0·390*	1
6̄08	−2·62	2̄8̄6	2·01	0·397	1

Table 9. *31 values of P^+ for a model structure in $P\bar{1}$ with $N=140$ atoms in unit cell, arranged in descending order of expected accuracy*

h+k	$E_{\mathbf{h}+\mathbf{k}}$	h−k	$E_{\mathbf{h}-\mathbf{k}}$	P^+	NQ
10,8̄,1	−3·13	84̄1	−3·13	0·992	6
188	2·32	1̄24	2·30	0·982	5
10,2,9	2·32	1̄0,4,3	2·30	0·968	4
8̄81	2·46	2̄89	2·28	0·967	5
1̄0,5,1	−2·43	8̄73	−2·42	0·967	6
120	2·45	7,2,10	2·28	0·964	6
8̄8̄5	2·30	1̄0,4,3	2·30	0·947	2
10,2,9	2·32	8̄8̄5	2·30	0·933	3
10,3̄,9	−2·61	8̄77	−2·60	0·919	3
8̄81	2·46	10,4̄,1	2·45	0·916	1
8̄57	−2·57	8̄35	−2·03	0·910	3
1̄0,7,5	−2·57	8̄57	−2·57	0·890	2
10,4̄,1	2·45	2̄89	2·28	0·884	3
1̄16	−2·57	13̄6	−2·03	0·827	2
425	−3·34	4̄69	−2·20	0·807	3
5̄61	−2·47	1̄23	−2·11	0·805	3
1̄1̄,2,1	−2·67	3̄,2,11	−2·36	0·800	3
313	2·19	1̄53	1·99	0·768	2
3̄39	2·67	7̄39	2·21	0·759	2
6̄,1̄,11	2·98	4̄,3̄,11	2·68	0·691	1
11,7̄,8	2·49	7̄56	2·49	0·685	2
1̄68	−2·71	120	2·45	0·676*	2
809	−2·70	10,4̄,1	2·45	0·674*	2
6̄18	3·06	8̄16	−2·05	0·633*	1
3̄59	3·06	1̄55	−2·05	0·633*	1
727	3·51	5̄27	2·05	0·630	1
10,3̄,9	2·94	8̄35	−2·03	0·370	1
9̄62	2·97	1̄1̄,8̄,2	−2·91*	0·617*	1
138	2·94	13̄6	−2·03	0·383	1
1̄0,0,3	2·25	8̄43	2·16	0·603	1
1̄1̄,5̄,8	2·34	5̄38	−1·97	0·403	1

Table 10. 20 *values of* P^+ *for the real structure arranged in descending order of expected accuracy*

h+k	E_{h+k}	h−k	E_{h-k}	P^+	NQ
026	2·00	$\bar{6}\bar{2}4$	1·87	0·996	6
$\bar{4},\bar{1},10$	1·89	$\bar{1}\bar{0},5,8$	1·87	0·990	5
$\bar{2}03$	−2·60	$\bar{6}09$	1·86	0·021	3
$\bar{6},\bar{4},10$	−1·74	0,0,12	−1·69	0·976	4
$\bar{5}\bar{7}1$	2·13	$1\bar{3}3$	2·09	0·959	4
300	2·38	942	1·90	0·948	2
$\bar{2}03$	−2·60	$\bar{1}\bar{0},2,1$	−1·93	0·932	3
481	−2·06	$2\bar{4}1$	−1·86	0·931	3
$\bar{1},\bar{4},11$	−2·30	$\bar{1}25$	1·79	0·101	3
$\bar{8}37$	−2·16	$4\bar{9}1$	−1·68	0·871	2
$\bar{7}\bar{3}9$	−2·13	$\bar{3}\bar{7}7$	−1·87	0·862	3
$\bar{2}21$	−2·53	$\bar{6}63$	−1·68	0·840	2
$0\bar{2}3$	2·81	$\bar{1}\bar{2},4,1$	2·03	0·831	2
$6\bar{4}2$	−2·04	$\bar{6}\bar{2}4$	1·87	0·180	2
$\bar{7}73$	−2·15	$\bar{7}\bar{3}9$	−2·13	0·819	3
321	−2·79	$\bar{1}63$	−1·66	0·817	1
621	−2·47	$\bar{1}\bar{0},2,1$	−1·93	0·771	1
$6\bar{9}8$	1·74	$\bar{6},\bar{7},12$	1·68	0·771	2
$\bar{6}09$	1·86	$\bar{6}63$	−1·68	0·231	1
$\bar{6}66$	2·29	0,0,12	−1·69	0·273	1

we may write:

$$P^+(E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}) = P_Q P_T + (1-P_Q)(1-P_T).$$

Only quintets for which P_Q^+ or $P_Q^- > 0{\cdot}60$ are used in calculations. Since **l** is a free vector which may vary over reciprocal space, more quintets can contribute to fix the sign of $E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}$. In accordance with §3, an overall sign probability may be obtained by:

$$P^+(E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}) = \left(1+\frac{\Pi_j P_j^-}{\Pi_j P_j^+}\right)^{-1}. \qquad (5)$$

A final observation is that every two-phase seminvariant will be defined on average by a number of useful quintet complementary invariants smaller than those able to fix the sign of $E_{2\mathbf{h}}$. This is because for every two-phase seminvariant the set of quintets is constructed by means of only one free vector.

Tables 8–10 list two-phase seminvariants whose values are determined by means of (5). P^+ is given by (5), NQ is the number of quintets which fix the sign of $E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}$. We have marked by an asterisk the seminvariants for which the method fails. We note that negative seminvariants are recognized with good accuracy in all three structures. Our method seems thus able to strenghthen the sign indications given by a different approach (Giacovazzo, 1974, 1977*c*,*d*; Green & Hauptman, 1976*b*).

Conclusion

Some basic probabilistic formulae for quintets obtained by Giacovazzo (1977*a*) are slightly modified by empirical factors. The experimental tests are satisfactory and suggest the use of quintets in direct procedures for phase solution. In particular, negative quintets with high reliability can be obtained in large symmorphic structures where negative invariants play an important role. Their use is therefore advisable not only to recognize the correct solution in multisolution procedures, but also in the initial stages. Furthermore, our probabilistic approach enables us to obtain, by the complementary invariants method, the signs of one and two-phase seminvariants. In particular, two-phase negative seminvariants are recognized with good accuracy in large structures so that their use in the first stages of direct procedures is advisable. Our conclusion is that quintet relations can assist triplets and quartets to solve the phase problem.

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References

FANFANI, L., NUNZI, A., ZANAZZI, P. F. & ZANZARI, A. R. (1974). *Acta Cryst.* B**30**, 273–281.
GIACOVAZZO, C. (1974). *Acta Cryst.* A**30**, 481–484.
GIACOVAZZO, C. (1975*a*). *Acta Cryst.* A**31**, 252–259.
GIACOVAZZO, C. (1975*b*). *Acta Cryst.* A**31**, 602–609.
GIACOVAZZO, C. (1976). *Acta Cryst.* A**32**, 74–82.
GIACOVAZZO, C. (1977*a*). *Acta Cryst.* A**33**, 944–948.
GIACOVAZZO, C. (1977*b*). Submitted.
GIACOVAZZO, C. (1977*c*). *Acta Cryst.* A**33**, 531–538.
GIACOVAZZO, C. (1977*d*). *Acta Cryst.* A**33**, 539–547.
GREEN, E. A. & HAUPTMAN, H. (1976*a*). *Acta Cryst.* A**32**, 43–45.
GREEN, E. A. & HAUPTMAN, H. (1976*b*). *Acta Cryst.* A**32**, 940–944.