invariant. The formulae obtained are correct up to $1/N^{3/2}$ order and contain some products of normalized structure factors whose signs are *a priori* unknown. The signs of these products are not very critical for the estimate of the sign of $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$, but their magnitudes may affect the scale of the probability levels. Several formulae have been suggested in order to keep on an absolute scale the probability levels provided by the theory (*i.e.* on the same scale as the triplet relationships). In this connexion it seems that some role may be played, for large values of $|E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{h}+\mathbf{l}}|, |E_{\mathbf{k}+\mathbf{l}}|$ and small N, by the terms of order $1/N^2$. The variance of the sign relationships, in fact, is very sensitive to the terms of higher order when N is not too large, and assumes values remarkably different from one. The problem of the scale of the probability levels fortunately does not exist for middle and small $|E_{4,5,6}|$, because the terms of higher order are then negligible.

It would be useful to verify the conditions of validity of the formulae obtained and to test the scale of the probability levels. A positive verification of the theory here described would allow, in the direct procedures for sign determination, the use of quartet as well as triplet relationships on the same scale of reliability. A strong stimulus in this direction is the observation that the theory seems very suitable for identifying the negative invariants $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$. In the field of negative invariants, in fact, the terms of order $1/N^{3/2}$ are negligible in comparison with the terms of order $1/N$. These last terms involve only the magnitudes of the normalized structure factors and are unambiguous.

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On the Reliability of Different Formulations of the Quartets

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Recently derived expressions [Giacovazzo (1975). *Acta Cryst.* A**31**, 252–259] for the reliability of quartets have been tested. For the negative quartets (NQ's) the new expressions lead to an improvement compared with the empirical estimates of the NQ reliability used so far. However, the reliability of all quartets can be better estimated by means of the weights of the empirically derived strengthened quartet relation (SQR).

Introduction

Recently phase relations between four reflexions, quartets, have shown to be very useful for the solution of special problems in direct methods. Strengthened Quartet Relations, referred to as SQR's, can be successfully employed for selecting a good starting set in symbolic-addition procedures and multisolution approaches (Schenk, 1973*a*). Negative quartets, referred to as NQ's (Hauptman, 1974; Schenk, 1974) and their two-dimensional analogues, the Harker–Kasper type relations (Schenk & de Jong, 1973; Schenk, 1973*b*) proved to be very useful to find the correct solution out of a set of $\sum_2$ solutions, particularly in symmorphic space groups.

In these cases the value q of the structure invariant

$$\phi_H+\phi_K+\phi_L+\phi_{-H-K-L}=q \quad (1)$$

is estimated with the magnitudes $|E_{H+K}|$, $|E_{H+L}|$, $|E_{K+L}|$ and the quantity

$$E_4=N^{-1}|E_HE_KE_LE_{-H-K-L}| \,. \quad (2)$$

For NQ's with $q\simeq\pi$, the value of E_4 has to be large and those of $|E_{H+K}|$, $|E_{H+L}|$ and $|E_{K+L}|$ have to be small.

It was empirically shown that for SQR's with $q\simeq 0$ the failure percentage as a function of

$$E_4^* = E_4\left(1+\frac{|E_{H+K}|+|E_{H+L}|+|E_{K+L}|}{E_0}\right) \quad (3)$$

is equal to that of the triplet relations as a function of

$$E_3 = N^{-1/2}|E_H E_K E_{-H-K}| . \quad (4)$$

For centrosymmetric structures Giacovazzo (1975) has recently derived expressions for quartets which contain E_{H+K}, E_{H+L} and E_{K+L} explicitly. These formulae can in principle replace the former formulations of both NQ's and SQR's. The most simple expression is:

$$P_+ = \tfrac{1}{2}+\tfrac{1}{2}\tanh\{E_4(E^2_{H+K}+E^2_{H+L}+E^2_{K+L}-2)\} \quad (5)$$

where P_+ is the probability that the product of signs $s(H)s(K)s(L)s(-H-K-L)=+1$. For small values of $|E_{H+K}|$, $|E_{H+L}|$ and $|E_{K+L}|$ the probability $P_+ \ll 0{\cdot}50$ and for large values $P_+ \gg 0{\cdot}50$. Expression (5) was obtained by approximating

$$P_+ = \tfrac{1}{2}+\tfrac{1}{2}\tanh\{E_4(E^2_{H+K}+E^2_{H+L}+E^2_{K+L}-2 + 6N^{-1/2}E_{H+K}E_{H+L}E_{K+L})\} . \quad (6)$$

The aim of this paper is to explore the usefulness of the expressions (5) and (6) by comparing their reliability with that of the triplets, SQR's and NQ's.

Calculations

As a basis of the comparison of the reliabilities of the different relations, the reliability of the $\sum_2$ relation had been chosen. The probability that a triplet has a positive sign is given by

$$P_+ = \tfrac{1}{2}+\tfrac{1}{2}\tanh E_3 . \quad (7)$$

This expression is similar to expressions (5) and (6). It is known that the SQR's, NQ's and triplets have identical failure percentages as function of E_4^*, E_4 and E_3 respectively (Schenk, 1973*a*, 1974). For them to be useful in practice this should also be the case for the new formulations of the quartets.

The two structures used to test expressions (5) and (6) are the same as were used in the paper on negative quartets (Schenk, 1974). The first is a model structure containing 10 atoms at random positions in the asymmetric unit of space group $P\bar{1}$ ($N=20$). The second is an aza-steroid of 20 atoms in $P\bar{1}$ ($N=40$). For both structures first all quartets are collected down to an E_4 limit value. This group of quartets is then employed to calculate the reliabilities of expressions (5) and (6).

In all tables the number of relations and the percentage of correct ones are given above the corresponding values of the arguments of the hyperbolic tangent. Unless stated otherwise, quartets are only taken into account for which two crossvectors ($H+K$, $H+L$) or one crossvector ($H+K$) are present in the set of measured reflexions, subtracting at the correct positions $(E^2_{K+L}-1)$ and $(E^2_{K+L}+E^2_{H+L}-2)$ respectively (Giacovazzo, 1975).

Negative quartets

One of the important applications of the quartets is the use of NQ's for discrimination between the various $\sum_2$ solutions in symbolic addition (or multisolution) of symmorphic space groups. Therefore we selected those quartets for which the argument A_1 of the hyperbolic tangent of expression (5)

$$A_1 = E_4(E^2_{H+K}+E^2_{H+L}+E^2_{K+L}-2) \quad (8)$$

is negative. For the model structure these are given in Table 1 (column 2), together with the reference triplets (column 1) and weights N_1 given on an empirical basis (column 3):

$N_1 = 2E_4\{1-3^{-1}(|E_{H+K}|+|E_{H+L}|+|E_{K+L}|)\}$ in the case when three crossvectors are present,

$N_1 = 2E_4\{0{\cdot}5-2^{-1}(|E_{H+K}|+|E_{H+L}|)\}$ for two crossvectors, and $N_1=0$ for one crossvector. The latter weights are approximately equal to the weights used in the Negative Quartet Criterion (NQC; Schenk, 1974). In Table 2 the corresponding numbers are given for the aza-steroid.

Table 1. *Total number* (nr) *and percentage of correct relations for triplets and negative quartets* [*expression* (5) *and empirical weights*] *for a* 20-*atom model structure*

	1		2		3	
	Triplets		Negative quartets (5)		Negative quartets (empirical weights)	
E_3 / A_1 / N_1	nr	%	nr	%	nr	%
3·0	8	100				
2·5	28	100				
2·0	94	100				
1·8	162	100	2	100		
1·6	272	100	5	100	1	100
1·4	454	100	21	100	5	100
1·2	764	99·5	44	100	21	100
1·0	1370	98·6	75	100	49	100
0·9	1844	97·6	92	100	71	100
0·8	2531	95·8	116	100	103	100
0·7	3485	93·8	153	100	125	100
0·6			218	97·7	153	98·0
0·5			277	97·5	192	97·4
0·4			332	94·6	229	96·9
0·3			373	93·3	277	93·5
0·2			422	91·5	338	90·5

From the tables it can be concluded that the negativity of a quartet is better predicted by means of expression (5). However, in view of the fact that the differences are rather small, this does not influence former conclusions on the use of negative quartets. The only

Table 2. *Total number and percentage of correct relations for triplets and negative quartets for an aza-steroid*

	1		2		3	
	Triplets		Negative quartets (5)		Negative quartets (empirical weights)	
E_3 A_1 N_1	nr	%	nr	%	nr	%
7·0	8	100				
6·0	21	100				
5·0	61	100				
4·0	143	100				
3·0	353	100	1	100	1	100
2·5	583	99·8	2	100	1	100
2·0	980	99·7	17	100	15	100
1·5	1823	99·2	38	100	40	100
1·4	2101	98·9	51	100	47	100
1·3	2438	98·4	71	98·6	63	98·4
1·2	2888	97·8	98	98·9	81	98·7
1·1	3395	96·9	139	95·0	112	97·3
1·0			165	93·9	124	95·2

difference from the procedure outlined previously for symmorphic space groups (Schenk, 1974) is that instead of using the NQC criterion the discrimination between the various $\sum$ solutions is better achieved by

$$\text{NQC2}=\sum_H \sum_K \sum_L A_1 \times |\pi-(\phi_H+\phi_K+\phi_L+\phi_{-H-K-L})| \quad (9)$$

with $0 \le \phi_H+\phi_K+\phi_L+\phi_{-H-K-L} < 2\pi$.

Test of expression (5)

In Tables 3 and 4 the results of triplets, SQR's and quartets (5), calculated by means of expression (5), are given for the model structure and the aza-steroid respectively. When the results are compared, it must be taken into account that from a certain level of the argument down the quartet lists are not complete, because only quartets with E_4 larger than the limit are used. For instance, for the aza-steroid many of the quartets with $E_4 < 1{\cdot}1$ have $A_1 > 1{\cdot}1$; however these quartets do not appear in the tables. This means that for the smaller arguments the results are overestimations and in cases were all quartets $E_4 > 0$ are collected they will be worse.

From Tables 3 and 4 it can be seen that at the higher levels of the arguments E_3, E_4 and A_1 the reliability of the quartets (5) is appreciably less than that of the triplets and SQR's. The argument of expression (5) can be rewritten as

$$A_1=E_4\{1+(E^2_{H+K}-1)+(E^2_{H+L}-1)+(E^2_{K+L})\}\,. \quad (10)$$

The first term is due to the quartet itself. In the second term $H+K$ suggests that this term is due to the elimination of the phase of $H+K$ from two triplets:

$$\left\{\begin{array}{lll} -H-K & H & K \\ H+K & L & -H-K-L \end{array}\right.$$

Table 3. *Number and percentage of correct relations above variable values of arguments for triplets, empirical SQR's and quartets [expression (5)], for the model structure*

	1		2		3	
	Triplets		SQR's–NQ's		Quartets (5)	
E_3 E_4 A_1	nr	%	nr	%	nr	%
20·0					2	100
15·0					15	100
10·0					94	100
7·5					315	100
5·0					1195	100
4·0			3	100	1966	99·9
3·0	8	100	30	100	3080	99·8
2·5	28	100	97	100	3708	99·7
2·0	94	100	453	100	4483	99·3
1·8	162	100	819	99·9	4618	99·1
1·6	272	100	1562	99·7	4887	98·9
1·4	454	100	2821	99·3	5174	98·7
1·2	764	99·5	4466	98·9	5487	98·2
1·0	1370	98·6	5474	98·3	5788	97·9
0·9	1844	97·6	5598	98·1		
0·8	2531	95·8	5622	98·1		
0·7	3485	93·8	5622	98·1		

Table 4. *Number and percentage of correct relations for triplets, SQR's and quartets (5) for the aza-steroid*

	1		2		3	
	Triplets		SQR's–NQ's		Quartets (5)	
E_3 E_4 A_1	nr	%	nr	%	nr	%
25·0					2671	100
20·0					4217	100
15·0					6698	99·8
10·0					9635	99·7
9·0			5	100	10203	99·7
8·0			28	100	10675	99·7
7·0	8	100	73	100	11183	99·6
6·0	21	100	185	100	11651	99·5
5·0	61	100	454	100	12152	99·4
4·0	143	100	1213	100	12623	99·2
3·0	353	100	3295	100	12994	99·0
2·5	583	99·8	5813	99·8	13199	98·8
2·0	980	99·7	10006	99·5	13405	98·5
1·5	1823	99·2	13114	98·8	13644	98·3
1·4	2101	98·9	13240	98·6		
1·3	2438	98·4	13324	98·6		
1·2	2888	97·8	13339	98·6		
1·1	3395	96·9	13351	98·6		

leading to the same quartet $H, K, L, -H-K-L$. This means that the weight of $E_4(E^2_{H+K}-1)$ of this resulting quartet is less than the weights of either of the triplets. Thus

$$E_4(E^2_{H+K}-1) < N^{-1/2}|E_H E_K E_{H-K}| \quad (11)$$

$$E^2_{H+K}-\frac{E_0 E_{H+K}}{E_L E_{H+K+L}} < 1\,. \quad (12)$$

For the larger values of $|E|$ it will often not be the case that the influence of the three quartets of the second kind is overestimated in expression (5). This may be the reason of the insufficient reliability of this formula.

Reliability of less approximate expressions

Expression (6) contains a correction term

$$6N^{-1/2}E_{H+K}E_{H+L}E_{K+L}$$
$$=6N^{-1/2}|E_{H+K}E_{H+L}E_{K+L}|s(H+K)s(H+L)s(K+L) \quad (13)$$

which can only be calculated if the structure is known. Nevertheless the order of magnitude of (13) is the same as that of the other terms of (6) and consequently this term cannot really be neglected. Of course in order to calculate (13) all three crossvectors have to be measured reflexions.

In Tables 5 and 6 the triplets, the quartets (5) with three crossvectors present, and the quartets calculated by means of expression (6) [referred to as quartets (6)] are given as functions of E_3, A_1 and

Table 5. *Quartets* (5) *and* (6) *with the three crossvectors* $H+K$, $H+L$ *and* $K+L$ *in the set of measured reflexions for the model structure*

Column 4 gives the figures for expression (16).

	1		2		3		4	
	Triplets		Quartets (5)		Quartets (6)		Quartets (16)	
E_3 A_1 A_2	nr	%	nr	%	nr	%	nr	%
25·0					7	100		
20·0			1	100	21	100		
15·0			5	100	66	100		
10·0			36	100	258	100		
7·5			141	100	489	100	2	100
5·0			438	100	858	100	30	100
4·0			674	100	1048	100	106	100
3·0	8	100	949	99·8	1206	99·9	576	100
2·5	28	100	1074	99·7	1276	99·9	1326	100
2·0	94	100	1209	99·5	1339	99·8	2759	99·9
1·8	162	100	1250	99·5	1375	99·7	3467	99·7
1·6	272	100	1303	99·2	1409	99·5	4136	99·5
1·4	454	100	1368	99·0	1436	99·3	4712	99·1
1·2	764	99·5	1431	98·7	1475	99·2	5254	98·7
1·0	1370	98·6	1487	98·5	1516	99·0	5767	98·1
0·9	1844	97·6						
0·8	2531	95·8						
0·7	3485	93·8						

Table 6. *Quartets* (5) *and* (6) *with all crossvectors measured for the aza-steroid*

Column 4 gives the figures for expression (16)

	1		2		3		4	
	Triplets		Quartets (5)		Quartets (6)		Quartets (16)	
E_3 A_1 A_2	nr	%	nr	%	nr	%	nr	%
25·0			1107	100	1844	100	86	100
20·0			1617	100	2264	100	276	100
15·0			2285	99·8	2664	99·9	971	100
10·0			2809	99·7	2996	99·8	3726	100
9·0			2918	99·7	3044	99·7	4975	99·9
8·0			2999	99·7	3097	99·7	6534	99·8
7·0	8	100	3061	99·6	3138	99·6	8248	99·7
6·0	21	100	3124	99·5	3185	99·4	9771	99·7
5·0	61	100	3182	99·3	3220	99·2	11020	99·6
4·0	143	100	3226	99·1	3240	99·2	12010	99·4
3·0	353	100	3257	99·0	3263	99·0	12812	99·2
2·5	583	99·8	3270	98·9	3276	98·9	13101	98·9
2·0	980	99·7	3291	98·8	3294	98·8	13380	98·6
1·5	1823	99·2	3314	98·5	3316	98·5	13709	98·3
1·4	2101	98·9						
1·3	2438	98·4						
1·2	2888	97·8						
1·1	3395	96·9						

$$A_2 = E_4\{E^2_{H+K} + E^2_{H+L} + E^2_{K+L} - 2 + 6N^{-1/2}E_{H+K}E_{H+L}E_{K+L}\} \quad (14)$$

respectively. Table 5 gives the results for the model structure and Table 6 for the aza-steroid.

From the tables it can be concluded that the quartets (6) are slightly better than quartets (5), but the differences are too small to be important for practical procedures. As could be expected, less reliable results are obtained by using

$$A_2^* = E_4\{E^2_{H+K} + E^2_{H+L} + E^2_{K+L} - 2 + 6N^{-1/2}|E_{H+K}E_{H+L}E_{K+L}|\} \quad (15)$$

[*cf.* Giacovazzo, 1975, expression (14)].

Expression (6) was an approximation of

$$P_+ = \tfrac{1}{2} + \tfrac{1}{2}\tanh E_4\{E^2_{H+K} + E^2_{H+L} + E^2_{K+L} - 2 + 6N^{-1/2}E_{H+K}E_{H+L}E_{K+L}\}\{1 - [H_4(E_{H+K}) + H_4(E_{H+L}) + H_4(E_{K+L})](8N)^{-1} + 4[E^2_{H+K} + E^2_{H+L} + E^2_{K+L} - 3]N^{-1} + 60E_{H+K}E_{H+L}E_{K+L}N^{-11/2}\}^{-1} \quad (16)$$

[Giacovazzo, 1975, expression (11)]. In view of the preceding paragraph the reliability of this formula has been tested, with terms containing $E_{H+K}E_{H+L}E_{K+L}$ ignored. The results are given in column 4 of Tables 5 and 6. In the case of the model structure the reliabilities of quartets (16) and triplets are almost equal; for the aza-steroid, however, the large differences in reliability between triplets and quartets still exist.

Concluding remarks

Although the expressions (5) and (6) of Giacovazzo (1975) suggest that they can be used for all quartets, they prove useful only for the negative quartets. The positive new quartets are found to be less reliable than the triplets, whereas the empirically derived Strengthened Quartet Relation (SQR) gives a similar reliability to that of the triplets (Schenk, 1973*a*). Therefore in practical procedures in which triplets and quartets are used simultaneously, SQR's are to be preferred.

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