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An Improved Probabilistic Theory in $P\bar{1}$ of the Invariant $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$

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The probabilistic approach used by the author in a preceding paper [*Acta Cryst.* A**31**, 252–259] for deriving the sign of quartet relations is used to obtain formulae which take terms of order $1/N^2$ into account. Experimental tests show that the overall reliability of the quartets is better estimated by these formulae, but does not reach the reliability of the triplets. Probabilistic formulae are then rescaled by suitable empirical factors. The new expressions lead to an improvement compared both with theoretical formulae and with the empirical [Schenk (1975). *Acta Cryst.* A**31**, 259–263] method: what is more significant, the new quartets are almost always found to be more reliable than triplets.

Introduction

Recently several papers have been devoted to the estimate of the cosine invariant

$$\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})\,.$$

Schenk (1973*a*) compared the reliability of the relation

$$\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}=0$$

as a function of

$$E_4=N^{-1}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}| \times\left\{1+\frac{E_{\mathbf{h}+\mathbf{k}}+E_{\mathbf{h}+\mathbf{l}}+E_{\mathbf{k}+\mathbf{l}}}{E_{000}}\right\}, \quad (1)$$

with that of the $\sum_2$ relationship as a function of

$$E_3=|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}|/\sqrt{N}\,.$$

From a probabilistic point of view Hauptman (1974*a*) derived a negative cosine invariant expression, subject to the condition $|E_{\mathbf{h}+\mathbf{k}}|\simeq|E_{\mathbf{h}+\mathbf{l}}|\simeq|E_{\mathbf{k}+\mathbf{l}}|\simeq 0$:

$$\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})=-\frac{I_1(B)}{I_0(B)}\,,$$

where $B=2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|/N$ and I_1 and I_0 are the modified Bessel functions of order one and zero.

Schenk & de Jong (1973) and Schenk (1973*b*, 1974) proved from semi-empirical observations that negative quartets and quartets of the special type ($\mathbf{h}=\mathbf{k}$) are very useful in finding the correct solution from a set of $\sum_2$ solutions in symmorphic space groups. A probabilistic theory of these special quartets in $P1$ and $P\bar{1}$ was given by Giacovazzo (1974*a*, *b*).

Hauptman (1974*b*) gave in $P1$ a probabilistic theory of the general cosine invariant $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$ subject to no restrictive conditions. This theory leads to an estimate for the value of the cosine which may lie anywhere between -1 and $+1$.

Independently and by a different mathematical approach Giacovazzo (1975*a*) derived in $P\bar{1}$ probabilistic expressions for quartets which can in principle replace former formulations. The reliability of the chief formulae derived in this paper was explored by Schenk (1975) who proved that the new expressions:

(*a*) lead to an improvement compared with the empirical estimate of the reliability of the negative quartets (Schenk, 1974)

(*b*) over-estimate the probability of the strongly defined positive quartets.

The aim of this paper is to improve the theoretical results previously described (Giacovazzo, 1975*a*, referred to as paper I) from two points of view:

1. The probabilistic theory described in paper I leads to expressions correct up to and including terms of order $N^{-3/2}$. It was found that the variance of the sign relationships is sensitive to the terms of higher order when $|E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{h}+\mathbf{l}}|, |E_{\mathbf{k}+\mathbf{l}}|$ are large and N is small. It was explicitly stated that some role may be played in these conditions by the terms of order $1/N^2$. We wish here to estimate the significance of these terms 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. Special quartets ($\mathbf{h}=\mathbf{k}$) have been already treated (Schenk & de Jong, 1973; Schenk, 1973*b*; Giacovazzo, 1974*a*, *b*) solely in order to derive an estimate of the cosine invariant

$$\varphi_{\mathbf{h}+\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}-2\varphi_{\mathbf{h}}=\pi\ .$$

Recently (Giacovazzo, 1975*b*) the distribution functions of special quartets of type $2\mathbf{h},\mathbf{h},\mathbf{k},\mathbf{h}-\mathbf{k}$ have been successfully employed for strengthening the $\sum_1$ relationship. As formulae for general quartets may be inadequate for special quartets, presumably the introduction of special formulae for special quartets will further strengthen the overall theory of quartets.

The mathematical approach

In paper I we introduced, for the seven variates

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

the characteristic function (Giacovazzo, 1975*c*)

$$\begin{aligned}C(u_1,u_2,u_3,\ldots,u_7)&=\exp\{-\tfrac{1}{2}(u_1^2+u_2^2+\ldots+u_7^2)\}\\&\times\{1+S_3/t^{3/2}+(S_4/t^2+S_3^2/2t^3)+(S_5/t^{5/2}+S_3S_4/t^{7/2}\\&+S_3^3/6t^{9/2})+(S_6/t^3+S_4^2/2t^4+S_3S_5/t^4+S_3^2S_4/2t^5\\&+S_3^4/24t^6)+\ldots\}\ ,\end{aligned}\tag{2}$$

where u_i, $i=1,\ldots,7$ are carrying variables associated with E_i, $t=N/2$,

$$S_v=t\sum_{r+s+\ldots+w=v}\frac{\lambda_{rs\ldots w}}{r!s!\ldots w!}(iu_1)^r(iu_2)^s\ldots(iu_7)^w$$

and

$$\lambda_{rs\ldots w}=\frac{K_{rs\ldots w}}{m^{(r+s+\ldots+w)/2}}\ .$$

$K_{rs\ldots w}$ are the cumulants of the distribution and m is the order of the space group. The probability distribution function $P(E_{\mathbf{h}},E_{\mathbf{k}},E_{\mathbf{l}},E_{\mathbf{h}+\mathbf{k}},E_{\mathbf{h}+\mathbf{l}},E_{\mathbf{k}+\mathbf{l}},E_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$ was found by taking the Fourier transform of (2). For the sake of brevity cumulants of order $1/N^2$ (*i.e.* $S_6/t^3+S_4^2/2t^4+S_3S_5/t^4+S_3^2S_4/2t^5+S_3^4/24t^6$) were neglected.

Probabilistic results

Let us denote by P_+ the probability that $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ is positive: in case three cross-vectors are present in the set of measured reflexions we obtained in paper I:

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{N}|E_1E_2E_3E_7|\ .\ (E_4^2+E_5^2+E_6^2-2)\ ,\tag{3}$$

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{N}|E_1E_2E_3E_7|\frac{(E_4^2+E_5^2+E_6^2-2)}{1+4(E_4^2+E_5^2+E_6^2-3)/N},\tag{4}$$

$$\begin{aligned}P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{N}&|E_1E_2E_3E_7|\\&\times[(E_4^2+E_5^2+E_6^2-2)+6E_4E_5E_6/\sqrt{N}]\\&\div\{1-[H_4(E_4)+H_4(E_5)+H_4(E_6)]/8N\\&+4[E_4^2+E_5^2+E_6^2-3]/N+60E_4E_5E_6/N\sqrt{N}\}\ .\end{aligned}\tag{5}$$

In the case when only two cross-vectors are present (*i.e.* E_4 and E_5), we obtained

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{N}|E_1E_2E_3E_7|\ (E_4^2+E_5^2-1)\ ,\tag{6}$$

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{N}|E_1E_2E_3E_7|\frac{(E_4^2+E_5^2-1)}{1+4[E_4^2+E_5^2-2]/N}\ .\tag{7}$$

As the probability distribution is an asymptotic series, (3), (4), (5) and (6), (7) represent various levels of approximation correct to the degree we choose.

In order to verify the sensitivity of the probabilistic formulae to the terms of order higher than $1/N\sqrt{N}$, we calculate the contribution of the cumulants of order $1/N^2$.

In the case when three cross-vectors are present in the set of measurements we obtain

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left\{\frac{1}{N}|E_1E_2E_3E_7|\ .\ \frac{R}{Q}\right\},\tag{8}$$

where

$$\begin{aligned}R&=E_4^2+E_5^2+E_6^2-2+6E_4E_5E_6/\sqrt{N}\\&+[(E_4^2-1)(E_5^2-1)+(E_4^2-1)(E_6^2-1)\\&+(E_5^2-1)(E_6^2-1)]/N-[H_6(E_4)+H_6(E_5)+H_6(E_6)\\&+H_4(E_4)(E_5^2+E_6^2+7)+H_4(E_5)(E_4^2+E_6^2+7)\\&+H_4(E_6)(E_4^2+E_5^2+7)]/8N\ ,\end{aligned}$$

$$\begin{aligned}Q&=1-[H_4(E_4)+H_4(E_5)+H_4(E_6)]/8N\\&+4[E_4^2+E_5^2+E_6^2-3]/N+60E_4E_5E_6/N\sqrt{N}+[H_6(E_4)\\&+H_6(E_5)+H_6(E_6)]/18N^2+9[E_4^2+E_5^2+E_6^2-2]/N^2\\&+[H_8(E_4)+H_8(E_5)+H_8(E_6)+2H_4(E_4)H_4(E_5)\\&+2H_4(E_4)H_4(E_6)+2H_4(E_5)H_4(E_6)]/128N^2\\&+52[(E_4^2-1)(E_5^2-1)+(E_4^2-1)(E_6^2-1)\\&+(E_5^2-1)(E_6^2-1)]/N^2-4[H_4(E_4)+H_4(E_5)\\&+H_4(E_6)]/3N^2\ .\end{aligned}$$

In the case when only two cross-vectors are present (*i.e.* E_4 and E_5) we find

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left\{\frac{1}{N}|E_1E_2E_3E_7|\ .\ \frac{R'}{Q'}\right\},\tag{9}$$

where

$$R' = E_4^2 + E_5^2 - 1 + [(E_4^2 - 1)(E_5^2 - 1)]/N^2 - [H_6(E_4) + H_6(E_5) + H_4(E_4)(E_5^2 + 8) + H_4(E_5)(E_4^2 + 8)]/8N^2,$$

$$Q' = 1 - [H_4(E_4) + H_4(E_5)]/8N + 4(E_4^2 + E_5^2 - 2)/N + [H_6(E_4) + H_6(E_5)]/18N^2 + 9(E_4^2 + E_5^2 - 1)/N^2 + [H_8(E_4) + H_8(E_5) + 2H_4(E_4)H_4(E_5)]/128N^2 + 52(E_4^2 - 1)(E_5^2 - 1)/N^2 - 4[H_4(E_4) + H_4(E_5)]/3N^2.$$

The role of the special quartets

Special quartets of type $\mathbf{2h}, \mathbf{h}, \mathbf{k}, \mathbf{h}-\mathbf{k}$ have been investigated by Giacovazzo (1975*b*) for strengthening $\sum_1$ relationships. Probabilistic considerations led to

$$P_+(E_{2\mathbf{h}}E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}) \simeq \tfrac{1}{2} + \tfrac{1}{2} \tanh \frac{1}{N} |E_{2\mathbf{h}}E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \times \frac{E_{2\mathbf{h}-\mathbf{k}}^2 + E_{\mathbf{h}+\mathbf{k}}^2 - 1}{1 + 4[E_{2\mathbf{h}-\mathbf{k}}^2 + E_{\mathbf{h}+\mathbf{k}}^2 - 1]/N}. \quad (10)$$

As may be noted, the second of the cross-vectors $\mathbf{h}+\mathbf{k}, \mathbf{h}, 2\mathbf{h}-\mathbf{k}$ coincides with a vector which is part of the quartet. Unlike formulae for general quartets, $|E_{\mathbf{h}}|$ is not relevant in (10) for defining the positivity or negativity of the quartets. Let, for example,

$$|E_{2\mathbf{h}}| = |E_{\mathbf{h}}| = |E_{\mathbf{k}}| = |E_{\mathbf{h}-\mathbf{k}}| = 2 \cdot 5\,,$$
$$|E_{2\mathbf{h}-\mathbf{k}}| = |E_{\mathbf{h}+\mathbf{k}}| = 0 \cdot 5\,, \quad N = 40.$$

The application of (10) suggests a negative quartet ($P_+ \simeq 0{\cdot}39$); on the contrary (4) suggested a strongly positive quartet ($P_+ \simeq 0{\cdot}94$). The number of special quartets is a small percentage of the observable quartets: the reliability of the quartet theory, nevertheless, may be improved if special and general quartets are distinguished [see the calculations in Giacovazzo (1975*b*)]. Because of the formal likeness of (7) and (10) we will use hereafter for special quartets the same formulae as for quartets in which one cross-vector is not in the set of measured reflexions.

Calculations

Triplets and quartets may be used simultaneously in the procedures for crystal structures solution on condi-

Table 1. *Number of relations (nr) and percentage of correct relations of triplets and negative quartets for a 20-atom model structure*

The negative quartets are given when only two cross-vectors are within the set of measurements.

Tanh arg.	Triplets		Negative quartets (6)		Negative quartets (9)		Negative quartets (emp. meth.)		Negative quartets (11)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1315	97·9	1400	85·7	2420	81·2	228	96·5	684	91·8
0·6	1314	97·9	257	95·3	601	93·3	16	100	84	95·2
0·8	1213	98·8	32	100	136	91·2			4	100
1·0	995	99·7			25	100				
1·2	765	99·7								
1·4	557	100								
1·6	395	100								

Table 2. *Number of relations (nr) and percentage of correct relations of triplets and negative quartets for a 20-atom model structure*

The negative quartets are given when all three cross-vectors are within the set of measurements.

Tanh arg.	Triplets		Negative quartets (3)		Negative quartets (8)		Negative quartets (emp. meth.)		Negative quartets (12)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1315	97·9	3500	91·2	4952	88·0	3600	92·3	1680	96·9
0·6	1314	97·9	1835	98·0	3719	92·8	1440	98·1	660	99·4
0·8	1213	98·8	784	100	2560	96·1	480	100	284	100
1·0	995	99·7	344	100	1503	98·9	188	100	116	100
1·2	765	99·7	164	100	804	100	92	100	56	100
1·4	557	100	84	100	476	100	32	100	24	100
1·6	395	100	28	100	277	100	20	100	12	100
1·8	268	100	20	100	164	100	4	100		
2·1	144	100	4	100	101	100				
2·4	84	100			28	100				
2·7	50	100			20	100				
3·0	30	100			8	100				
3·5	12	100								

tion that the signs of the triplets and of the quartets have the same reliability. In order to check this condition we pay attention to two relevant observations:

(*a*) the number of quartets for which two cross-vectors alone are in the set of measured reflexions may be a high percentage of the observable quartets.

(*b*) the number of negative quartets is small compared with the number of the positive ones. Their use,

Table 3. *Number of relations (nr) and percentage of correct relations of triplets and positive quartets for a 20-atom model structure*

The positive quartets are given when two cross-vectors alone are within the set of measured reflexions.

Tanh arg.	Triplets		Positive quartets (6)		Positive quartets (9)		Positive quartets (emp. meth.)		Positive quartets (11)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1315	97·9	22043	94·0	20935	95·1	29965	83·6	10911	99·3
0·6	1314	97·9	19295	96·3	17151	97·4	21072	89·0	6908	99·8
0·8	1213	98·8	16941	97·5	13554	98·6	13065	93·2	4421	99·9
1·0	995	99·7	14898	98·6	10586	99·0	7428	96·1	2945	100
1·2	765	99·7	13215	98·9	7934	99·1	4244	98·6	1984	100
1·4	557	100	11866	99·1	5802	99·4	2548	98·9	1399	100
1·6	395	100	10591	99·4	4254	99·6	1501	99·7	922	100
1·8	268	100	9560	99·5	3040	99·6	912	100	615	100
2·1	144	100	7989	99·7	1834	99·8	444	100	356	100
2·4	84	100	6808	99·8	1126	99·6	192	100	213	100
2·7	50	100	5781	99·9	630	100	96	100	140	100
3·0	30	100	4786	99·9	382	100	56	100	68	100
3·5	12	100	3729	100	191	100	16	100	40	100
4·0	1	100	2933	100	48	100			15	100
5·0			1834	100	12	100			8	100
6·0			1154	100						
7·0			679	100						
8·0			416	100						
9·0			260	100						
10·0			188	100						
15·0			28	100						
20·0			8	100						

Table 4. *Number of relations (nr) and percentage of correct relations of triplets and positive quartets for a 20-atom model structure*

The positive quartets are given when all three cross-vectors are within the set of measured reflexions.

Tanh arg.	Triplets		Positive quartets (3)		Positive quartets (8)		Positive quartets (emp. meth.)		Positive quartets (12)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1315	97·9	16604	96·9	17020	96·5	19620	90·9	10272	99·8
0·6	1314	97·9	15156	98·1	15161	98·2	15940	93·7	7168	99·9
0·8	1213	98·8	14016	98·8	12996	98·6	11044	95·9	4976	99·9
1·0	995	99·7	12784	99·2	10733	99·2	7325	97·5	3564	100
1·2	765	99·7	11767	99·5	8512	99·4	4852	98·8	2600	100
1·4	557	100	10900	99·6	6508	99·6	3148	99·5	1923	100
1·6	395	100	9952	99·8	4900	99·7	2108	99·6	1440	100
1·8	268	100	9188	99·8	3740	99·8	1476	100	1092	100
2·1	144	100	7943	99·8	2503	99·7	872	100	688	100
2·4	84	100	7028	99·9	1620	99·5	552	100	451	100
2·7	50	100	6028	99·9	1048	99·2	300	100	324	100
3·0	30	100	5275	99·9	688	99·4	148	100	228	100
3·5	12	100	4288	99·9	348	100	56	100	124	100
4·0	1	100	3520	100	204	100	32	100	72	100
5·0			2388	100	92	100	8	100	36	100
6·0			1652	100	72	100			17	100
7·0			1156	100	48	100			8	100
8·0			792	100	12	100				
9·0			560	100	12	100				
10·0			424	100	8	100				
15·0			88	100						
20·0			36	100						

nevertheless, may be relevant in the procedures for crystal structure solution.

This suggests that we should make separate tests for quartets in which only two cross-vectors are present in the set of measured reflexions, for quartets with three cross-vectors present and for negative quartets as well as positive.

Equations (3)–(7) have already been tested by Schenk (1975). The reliability of these expressions proved very similar to that of the triplets for negative quartets only:

Table 5. *Number of relations (nr) and percentage of correct relations of triplets and negative quartets for a 40-atom model structure*

The negative quartets are given when only two cross-vectors are in the set of measured reflexions.

Tanh arg.	Triplets		Negative quartets (6)		Negative quartets (9)		Negative quartets (emp. meth.)		Negative quartets (11)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1249	92·6	136	88·2	235	89·8	32	100	77	89·5
0·6	1089	94·5	13	100	16	75·0	4	100	8	100
0·8	741	96·2			8	100				
1·0	498	98·8								

Table 6. *Number of relations (nr) and percentage of correct relations of triplets and negative quartets for a 40-atom model structure*

The negative quartets are given when all three cross-vectors are within the set of measurements.

Tanh arg.	Triplets		Negative quartets (3)		Negative quartets (8)		Negative quartets (emp. meth.)		Negative quartets (12)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1249	92·6	972	88·5	1429	85·4	824	90·8	339	95·3
0·6	1089	94·5	227	98·2	580	92·4	140	100	76	100
0·8	741	96·2	56	100	180	97·8	32	100	20	100
1·0	498	98·8	4	100	68	100	4	100		
1·2	344	99·7			20	100				
1·4	223	100			4	100				
1·6	144	100								

Table 7. *Number of relations (nr) and percentage of correct relations of triplets and positive quartets for a 40-atom model structure*

Positive quartets are given when only two cross-vectors are within the set of measurements.

Tanh arg.	Triplets		Positive quartets (6)		Positive quartets (9)		Positive quartets (emp. meth.)		Positive quartets (11)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1249	92·6	14964	90·3	10397	92·8	9813	87·4	4622	98·3
0·6	1089	94·5	11782	92·6	7774	95·1	3519	92·8	2616	99·2
0·8	741	96·2	9367	95·2	5772	96·6	1438	95·8	1613	99·8
1·0	498	98·8	7709	96·1	4218	97·5	636	99·4	1054	100
1·2	344	99·7	6417	96·7	3075	98·2	300	100	737	100
1·4	223	100	5291	97·3	2238	98·7	148	100	519	100
1·6	144	100	4586	98·3	1632	98·8	96	100	363	100
1·8	107	100	3915	98·5	1188	99·3	48	100	268	100
2·1	51	100	3184	98·6	775	100	24	100	179	100
2·4	32	100	2587	99·2	550	100	12	100	139	100
2·7	16	100	2160	99·3	363	100	12	100	100	100
3·0	11	100	1833	99·8	240	100	8	100	64	100
3·5	4	100	1381	100	127	100			23	100
4·0	4	100	1050	100	56	100			23	100
5·0	2	100	666	100	16	100			4	100
6·0			427	100	12	100				
7·0			295	100	4	100				
8·0			190	100						
9·0			160	100						
10·0			120	100						
15·0			24	100						
20·0			4	100						

the reliability of the positive ones was overestimated. For the latter the reliability was better estimated by Schenk by means of empirically derived weights. It seems useful, therefore, to compare the probabilistic results derived here with Schenk's empirical method and the triplet relationships. As the probability that a triplet has a positive sign is given by

$$P_+ \simeq \tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h+k}}|}{\sqrt{N}},$$

Table 8. *Number of relations (nr) and percentage of correct relations of triplets and positive quartets for a 40-atom model structure*

The positive quartets are given when all three cross-vectors are in the set of measurements.

Tanh arg.	Triplets		Positive quartets (3)		Positive quartets (8)		Positive quartets (emp. meth.)		Positive quartets (12)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1249	92·6	11524	90·4	8324	91·4	8465	89·7	4641	98·0
0·6	1089	94·5	9560	93·3	6729	94·8	3608	94·5	2812	98·7
0·8	741	96·2	8116	94·6	5432	96·6	1648	97·1	1760	99·3
1·0	498	98·8	6919	96·2	4296	97·7	840	98·1	1116	100
1·2	344	99·7	5972	97·3	3408	98·6	421	99·0	765	100
1·4	223	100	5156	98·0	2605	98·9	256	100	516	100
1·6	144	100	4561	98·1	1980	99·2	164	100	368	100
1·8	107	100	4072	98·5	1512	99·2	128	100	289	100
2·1	51	100	3328	98·7	1013	99·6	65	100	184	100
2·4	32	100	2793	98·9	724	100	36	100	149	100
2·7	16	100	2340	99·3	480	100	12	100	124	100
3·0	11	100	1980	99·4	340	100	5	100	76	100
3·5	4	100	1461	99·7	185	100	4	100	61	100
4·0	4	100	1116	100	108	100	4	100	45	100
5·0	2	100	668	100	36	100			12	100
6·0			436	100	8	100			4	100
7·0			304	100					4	100
8·0			205	100					4	100
9·0			164	100					4	100
10·0			140	100					4	100
15·0			48	100						
20·0			12	100						

Table 9. *Number of relations (nr) and percentage of correct relations of triplets and negative quartets for a 60-atom model structure*

Negative quartets are given when only two cross-vectors are in the set of measurements.

Tanh arg.	Triplets		Negative quartets (6)		Negative quartets (9)		Negative quartets (emp. meth.)		Negative quartets (11)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1985	90·1	251	79·4	387	83·5	75	94·7	141	85·7
0·6	1897	90·5	32	100	43	100			4	100
0·8	1376	94·2								
1·0	879	96·9								
1·2	573	98·6								
1·4	342	98·5								

Table 10. *Number of relations (nr) and percentage of correct relations of triplets and negative quartets for a 60-atom model structure*

Negative quartets are given when all three cross-vectors are within the set of measurements.

Tanh arg.	Triplets		Negative quartets (3)		Negative quartets (8)		Negative quartets (emp. meth.)		Negative quartets (12)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1985	90·1	1773	84·0	3176	76·7	1433	87·4	711	87·6
0·6	1897	90·5	356	94·4	885	91·0	216	94·4	116	100
0·8	1376	94·2	112	100	248	96·8	64	93·8	36	100
1·0	879	96·9	36	100	80	100	16	100	16	100
1·2	573	98·6	8	100	36	100			4	100
1·4	342	98·5			8	100				
1·6	218	100								

the reliabilities of triplets and quartets may be compared, giving the number and the percentage of the correct ones above the corresponding values of the arguments of the hyperbolic tangent. The number and percentage of the correct relations according to the empirical method are obtained with the weights used by Schenk (1975). In order to check the formulae as a function of the structural complexity we have tested four models with $N=20, 40, 60, 100$: the outcome is shown in Tables 1–17.

The tables suggest that:

(*a*) the estimate of terms of order $1/N^2$ improves the

Table 11. *Number of relations (nr) and percentage of correct relations of triplets and positive quartets for a 60-atom model structure*

Positive quartets are given when only two cross-vectors are within the set of measurements.

Tanh arg.	Triplets		Positive quartets (6)		Positive quartets (9)		Positive quartets (emp. meth.)		Positive quartets (11)	
	nr_r	%	nr	%	nr	%	nr	%	nr	%
0·4	1985	90·1	30232	83·7	28089	84·7	15467	81·5	7163	95·6
0·6	1897	90·5	22506	87·3	19515	88·6	3800	90·1	3447	98·0
0·8	1376	94·2	17087	89·9	13315	91·6	1120	93·9	1880	98·1
1·0	879	96·9	13321	92·1	9591	93·8	344	98·8	971	99·6
1·2	573	98·6	10629	93·9	6840	95·3	96	100	604	99·3
1·4	342	98·5	8647	95·2	4832	96·2	24	100	372	98·9
1·6	218	100	7054	95·7	3347	97·4	12	100	212	100
1·8	137	100	5811	96·2	2436	98·5	4	100	167	100
2·1	70	100	4396	97·1	1552	98·5	4	100	84	100
2·4	33	100	3424	98·0	955	99·6			55	100
2·7	22	100	2664	98·6	592	99·3			27	100
3·0	10	100	2187	98·4	356	100			12	100
3·5	6	100	1443	98·9	148	100			4	100
4·0	3	100	972	99·6	67	100				
5·0			511	99·2	20	100				
6·0			280	98·6	4	100				
7·0			188	100	4	100				
8·0			107	100						
9·0			76	100						
10·0			48	100						
15·0			3	100						
20·0										

Table 12. *Number of relations (nr) and percentage of correct relations of triplets and positive quartets for a 60-atom model structure*

Positive quartets are given when all three cross-vectors are within the set of measurements.

Tanh arg.	Triplets		Positive quartets (3)		Positive quartets (8)		Positive quartets (emp. meth.)		Positive quartets (12)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·4	1985	90·1	27277	84·1	26745	85·0	14615	83·7	8240	95·5
0·6	1897	90·5	21732	87·3	20384	89·1	4504	90·9	4205	98·0
0·8	1376	94·2	17260	89·3	15109	92·1	1576	92·4	2604	98·2
1·0	879	96·9	13740	92·1	11236	94·8	703	96·6	1613	98·3
1·2	573	98·6	11200	94·4	8532	96·1	284	97·2	1084	97·8
1·4	342	98·5	9352	95·0	6220	96·4	128	96·9	684	98·8
1·6	218	100	8025	95·6	4649	97·0	88	100	500	98·4
1·8	137	100	6672	96·5	3584	98·0	29	100	437	98·2
2·1	70	100	5116	97·3	2328	98·1	20	100	284	100
2·4	33	100	4148	98·1	1633	98·3	9	100	217	100
2·7	22	100	3424	98·0	1088	97·4	8	100	153	100
3·0	10	100	2877	98·1	760	98·4			96	100
3·5	6	100	2201	98·4	384	100			72	100
4·0	3	100	1596	98·2	261	100			20	100
5·0			1005	97·6	112	100			4	100
6·0			608	98·7	24	100			4	100
7·0			448	98·2	16	100				
8·0			289	100	8	100				
9·0			240	100	8	100				
10·0			164	100						
15·0			41	100						
20·0			4	100						

reliability of the positive quartets given by (3) and (6). The differences, nevertheless, are not enough to give to the positive quartets reliability levels comparable with those of the triplets. Negative quartets, on the other hand, seem better estimated by (3) and (6).

(*b*) In spite of its limitations, Schenk's empirical method seems preferable to the theoretical probabilistic formulae including terms of order $1/N^2$. We should expect that the inclusion in the probabilistic approach of terms of order higher than $1/N^2$ will improve the reliability of the quartets. The new probabilistic formulae, nevertheless, would become rather difficult to deal with, which would discourage the use of quartets in direct procedures for phase solution. A better approach would be that of saving the basic probabilistic outcome given by (3) and (6) and rescaling probability values by suitable empirical factors. The experimental results shown in Tables 1–17 suggest that

$$P_+ \simeq \tfrac{1}{2} + \tfrac{1}{2} \tanh \frac{1}{N} |E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{l}} E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}| \times \frac{(E^2_{\mathbf{h}+\mathbf{k}} + E^2_{\mathbf{h}+\mathbf{l}} - 1)}{1 + 3 \tanh [(E^2_{\mathbf{h}+\mathbf{k}} + E^2_{\mathbf{h}+\mathbf{l}})/2]}, \quad (11)$$

when two only cross-vectors are in the set of measured reflexions, and

Table 13. *Number of relations (nr) and percentage of correct relations of triplets and positive quartets for a 100-atom model structure*

Tanh arg.	Triplets		Two cross-vectors in measurements: Positive quartets (emp. meth.)		Two cross-vectors in measurements: Positive quartets (11)		Three cross-vectors in measurements: Positive quartets (emp. meth.)		Three cross-vectors in measurements: Positive quartets (12)	
	nr	%	nr	%	nr	%	nr	%	nr	%
0·2	1653	87·1	103301	69·4	32623	87·4	51812	72·6	21573	88·2
0·4	1653	87·1	9319	79·7	9178	95·0	6264	82·4	6822	94·9
0·6	1322	89·5	1072	88·4	3174	97·9	1020	88·6	2570	97·7
0·8	770	93·2	224	94·6	1291	100	172	88·4	1063	99·6
1·0	424	95·0	48	100	628	100	60	80·0	576	99·3
1·2	216	97·2	20	100	276	100	12	66·7	240	100
1·4	123	98·4			136	100	4	100	108	100
1·6	71	100			56	100			52	100
2·0	20	100			16	100			20	100
2·4	4	100			4	100			4	100
2·8	1	100								
3·2										
3·4										
3·8										
4·2										
4·6										

Table 14. *Total numbers of relations (nr) and percentages of correct relations for a 20-atom model structure*

Tanh arg.	Triplets		Quartets (emp. meth.)		Quartets [(11), (12)]	
	nr	%	nr	%	nr	%
0·4	1315	97·9	53413	86·9	23547	99·1
0·6	1314	97·9	38468	91·3	14820	99·8
0·8	1213	98·8	24589	94·6	9685	99·9
1·0	995	99·7	14940	96·8	6625	100
1·2	765	99·7	9188	98·7	4640	100
1·4	557	100	5728	99·2	3346	100
1·6	395	100	3629	99·7	2374	100
1·8	268	100	2392	100	1707	100
2·1	144	100	1316	100	1044	100
2·4	84	100	744	100	664	100
2·7	50	100	396	100	464	100
3·0	30	100	204	100	296	100
3·5	12	100	72	100	164	100
4·0	1	100	32	100	88	100
5·0			8	100	44	100
6·0					16	100
7·0					8	100
8·0						
9·0						
10·0						
15·0						

Table 15. *Total numbers of relations (nr) and percentages of correct relations for a 40-atom model structure*

Tanh arg.	Triplets		Quartets (emp. meth.)		Quartets [(11), (12)]	
	nr	%	nr	%	nr	%
0·4	1249	92·6	19133	88·5	9679	98·0
0·6	1089	94·5	7271	93·8	5512	99·0
0·8	741	96·2	3118	96·5	3393	99·5
1·0	498	98·8	1480	98·6	2170	100
1·2	344	99·7	720	99·4	1502	100
1·4	223	100	404	100	1035	100
1·6	144	100	260	100	731	100
1·8	107	100	176	100	555	100
2·1	51	100	88	100	363	100
2·4	32	100	48	100	288	100
2·7	16	100	24	100	224	100
3·0	11	100	12	100	140	100
3·5	4	100	4	100	84	100
4·0	4	100	4	100	68	100
5·0	2	100			16	100
6·0					4	100
7·0					4	100
8·0					4	100
9·0					4	100
10·0					4	100
15·0						
20·0						

$$P_+ \simeq \tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{1}{N}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}| \times \frac{(E^2_{\mathbf{h}+\mathbf{k}}+E^2_{\mathbf{h}+\mathbf{l}}+E^2_{\mathbf{k}+\mathbf{l}}-2)}{1+3\tanh[(E^2_{\mathbf{h}+\mathbf{k}}+E^2_{\mathbf{h}+\mathbf{l}}+E^2_{\mathbf{k}+\mathbf{l}})/3]}, \quad (12)$$

Table 16. *Total number of relations (nr) and percentages of correct relations for a 60-atom model structure*

Tanh arg.	Triplets		Quartets (emp. meth.)		Quartets [(11), (12)]	
	nr	%	nr	%	nr	%
0·4	1985	90·1	31591	82·8	16255	95·1
0·6	1897	90·5	8520	90·7	7772	98·0
0·8	1376	94·2	2760	93·0	4520	98·1
1·0	879	96·9	1064	97·4	2600	98·8
1·2	573	98·6	380	97·9	1692	98·3
1·4	342	98·5	152	97·4	1056	98·9
1·6	218	100	100	100	712	98·9
1·8	137	100	32	100	604	98·7
2·1	70	100	24	100	368	100
2·4	33	100	8	100	272	100
2·7	22	100	8	100	180	100
3·0	10	100			108	100
3·5	6	100			76	100
4·0	3	100			20	100
5·0					4	100
6·0					4	100
7·0						
8·0						

Table 17. *Total number of relations (nr) and percentage of correct relations of triplets and positive quartets for a 100-atom model structure*

Tanh arg.	Triplets		Positive quartets (emp. meth.)		Positive quartets [(11), (12)]	
	nr	%	nr	%	nr	%
0·2	1653	87·1	168081	70·2	61140	85·7
0·4	1653	87·1	16199	80·8	16280	94·8
0·6	1322	89·5	2128	88·7	5776	97·6
0·8	770	93·2	396	91·9	2354	99·8
1·0	424	95·0	108	88·9	1204	99·7
1·2	216	97·2	32	87·5	516	100
1·4	123	98·4	4	100	244	100
1·6	71	100			108	100
2·0	20	100			36	100
2·4	4	100			8	100
2·8	1	100				
3·2						
3·4						
3·8						
4·2						
4·6						

when all three cross-vectors are present, give a good measure of the reliability of the quartets. As may be observed, the percentages of correct quartet relations calculated by (11) and (12) are almost always better than the same percentages of triplets and of quartet relations obtained by Schenk's method. Furthermore, the quartets in which two cross vectors are in the set of measurements prove to be a large percentage of the available quartets. The new formulae allow their use since they give reliability levels equal to or better than that of the triplets.

Conclusions

The joint probability distribution function $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}}, E_{\mathbf{h}+\mathbf{k}}, E_{\mathbf{h}+\mathbf{l}}, E_{\mathbf{k}+\mathbf{l}}, E_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$ is explored up to the terms of order $1/N^2$. The reliability of quartets is improved, but is not yet comparable with that of triplets.

Some new formulae are proposed which rescale the basic probabilistic laws by suitable empirical factors. The experimental tests are satisfactory: in four model structures the observed reliability of the quartets is almost always higher than that of the triplets. The simplicity of the modified probabilistic formulae suggests their use in practical procedures in which triplets and quartets are used simultaneously.

The new probabilistic expressions are compared with Schenk's (1975) empirical weights. Our probabilistic approach seems to give helpful results in the most difficult structures for which the empirical method may fail.

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