contribution of G to the intensities may be very large. This follows because in the expression (2), the factors which multiply $|G|^2$, $(\mathrm{Re}\, F*G)$ and $(\mathrm{Im}\, F*G)$ all vanish for $\mathbf{u}.\mathbf{R}$ integral, *i.e.* at the reciprocal-lattice points for the unfaulted structure. The peak intensities can be modified by the factors dependent on G only to the extent that the peaks are displaced or extended away from the reciprocal-lattice points into the region for which these multipliers are non-zero. Since both the peak widths and their displacements are roughly proportional to α it is seen that the contribution of G to the peak intensities may also be roughly proportional to α but will be negligibly small except for very large α values.

Hence the 'intuitively obvious' conclusion that the structure amplitudes for the unit cell will be modified from F to $F+\alpha G$ is shown to be false. In the particular case of magnesium fluorogermanate, the existence of faults of the type discussed should not make any appreciable difference to the value of the occupancy factor r for the Ge sites deduced from the structure analysis.

It is seen from equation (2) and Fig. 5 that information regarding the nature of the modification of the structure at the fault planes can, in principle, be obtained from the diffraction pattern but this would involve the careful measurement and interpretation of the intensities of the weak streaks between the main intensity maxima.

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A Probabilistic Theory of the Cosine Invariant $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h+k+l}})$

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A conditional joint probability distribution is derived in order to estimate the values of the cosine invariant $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h+k+l}})$ in terms of the magnitudes of $E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}}, E_{\mathbf{h+k}}, E_{\mathbf{h+l}}, E_{\mathbf{k+l}}, E_{\mathbf{h+k+l}}$. The theory leads to values for the cosines which lie anywhere between -1 and $+1$. Some applications of the quartets in procedures for crystal structure determination are described.

I. Derivation of the theory

I.1 *Introduction*

The significance in direct methods of phase determination of the cosine invariant $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h+k+l}})$ has been stressed in several recent papers.

Starting from semi-empirical observations of Schenk (1973*a*), Hauptman (1974*a*) has developed in $P1$ a probabilistic theory of this cosine invariant which is valid under the assumption that $|E_{\mathbf{h+k}}|, |E_{\mathbf{h+l}}|, |E_{\mathbf{k+l}}|$ are sufficiently small. In particular he derived the negative cosine invariant expression

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

where $B=2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h+k+l}}|/N$. For large values of B this formula gives, in contrast to the estimate for $\cos(\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}-\varphi_{\mathbf{h}_1+\mathbf{h}_2})$,

$$\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h+k+l}}\simeq\pi\,.$$

A more general probabilistic theory of the invariant $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h+k+l}})$, subject to no restrictive conditions, has been given by Hauptman (1974*b*). The theory leads to estimates for the value of the cosine which may lie anywhere between -1 and $+1$. In that paper the joint conditional probability distribution of the pair $\varphi_{\mathbf{k}}, \varphi_{\mathbf{h}_1+\mathbf{k}}$ given $|E_{-\mathbf{h}_3+\mathbf{k}}|, |E_{\mathbf{k}}|, |E_{\mathbf{h}_1+\mathbf{k}}|$ and for fixed $\mathbf{h}_1$ and $\mathbf{h}_3$ was inspected. The vector $\mathbf{k}$ is the sole random variable, which is supposed uniformly distributed over reciprocal space. Hauptman's results seem satisfactory, but the final formulae are rather difficult to deal with.

Independently, Giacovazzo (1975*a*) derived in $P\bar{1}$ probabilistic formulae for $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h+k+l}})$.

In that paper the joint probability distribution

$$P(E_{\mathbf{h}},E_{\mathbf{k}},E_{\mathbf{l}},E_{\mathbf{h}+\mathbf{k}},E_{\mathbf{h}+\mathbf{l}},E_{\mathbf{k}+\mathbf{l}},E_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$$

in which $\mathbf{h},\mathbf{k},\mathbf{l}$ in principle are all uniformly distributed over reciprocal space was inspected. The cosine expression obtained, subject to no restrictive conditions, can assume $+1$ as well as -1 values. It is worth noting that this mathematical approach may be considered as a generalization of that used in $\mathrm{P}\bar{1}$ for quartets of special type ($\mathbf{h}=\mathbf{k}$) (Giacovazzo, 1974*a*).

The aim of this paper is to extend to $P1$ the study of the same probability distribution function used in $P\bar{1}$. The mathematical approach generalizes that used by Giacovazzo (1974*b*) for treating special quartets in $P1$. The present approach, formulated in a general way in a recent monograph (Giacovazzo, 1976*a*), may easily be extended to all space groups. This aspect of the question will be the subject of the following paper.

I.2 *Some preliminary formulae*

We collect here for convenient reference a number of formulae from the theory of Bessel functions. First (Watson, 1958)

$$\frac{1}{\pi}\int_0^\pi \exp(z\cos\varphi)\cos m\varphi \,d\varphi = I_m(z)\,, \qquad (1)$$

$$\int_0^\pi \exp(-z\cos\varphi)\sin m\varphi \,d\varphi = 0\,. \qquad (2)$$

Again

$$\frac{i^m}{\pi}\int_0^\pi \exp(-iz\cos\varphi)\cos m\varphi \,d\varphi = J_m(z)\,, \qquad (3)$$

$$\int_0^\pi \exp(-iz\cos\varphi)\sin m\varphi = 0\,. \qquad (4)$$

$J_m(z)$ is the Bessel function of the first kind of order $m, I_m(z)$ is the corresponding Bessel function of imaginary argument.

Use is also made of the Weber–Sonine integral

$$\int_0^\infty J_\nu(at)\exp(-p^2t^2)t^{\mu-1}dt$$

$$=\frac{\left(\frac{a}{2p}\right)^\nu \Gamma\left(\frac{\nu+\mu}{2}\right)}{2p^\mu\Gamma(\nu+1)}\,{}_1F_1\left(\frac{\nu+\mu}{2};\nu+1;-\frac{a^2}{4p^2}\right), \qquad (5)$$

where Γ represents the gamma function and ${}_1F_1(x;y;z)$ is the generalized hypergeometric function.

I.3 *The joint probability distribution* $P(R_{\mathbf{h}},R_{\mathbf{k}},R_{\mathbf{l}},R_{\mathbf{h}+\mathbf{k}+\mathbf{l}},R_{\mathbf{h}+\mathbf{k}},R_{\mathbf{h}+\mathbf{l}},R_{\mathbf{k}+\mathbf{l}},\varphi_{\mathbf{h}},\varphi_{\mathbf{k}},\varphi_{\mathbf{l}},\ldots,\varphi_{\mathbf{k}+\mathbf{l}})$

Assume that the crystal structure contains N identical atoms per unit cell and that the space group is $P1$. In developing the theory we shall consider the fractional part of $\mathbf{H}\,.\,\mathbf{r}_j$ uniformly distributed in the interval (0,1) if $\mathbf{H}$ is fixed and the atomic coordinates $\mathbf{r}_j$ are uniformly and independently distributed in the interval (0,1). Under these conditions the probability distribution obtained with $\mathbf{H}$ constant and the $\mathbf{r}_j$ as random variables is a very good approximation to the distribution in which the $\mathbf{r}_j$ are held constant and $\mathbf{H}$ is the random variable (Hauptman & Karle, 1953). This observation reveals the difference between the mathematical approach used in this paper and Hauptman's formulation. In Hauptman's theory, in fact, the probability distribution

$$P(|E_{-\mathbf{h}_3+\mathbf{k}}|,|E_{\mathbf{k}}|,|E_{\mathbf{h}_1+\mathbf{k}}|,\varphi_{-\mathbf{h}_3+\mathbf{k}},\varphi_{\mathbf{k}},\varphi_{\mathbf{h}_1+\mathbf{k}})$$

is studied, when the vector $\mathbf{k}$ is the sole random variable uniformly distributed over reciprocal space and $E_{\mathbf{h}_1},E_{\mathbf{h}_2},E_{\mathbf{h}_3}$ are fixed reciprocal vectors satisfying

$$\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0\,.$$

In this paper, on the contrary, the more general joint probability distribution

$$P(|E_{\mathbf{h}}|,|E_{\mathbf{k}}|,|E_{\mathbf{l}}|,|E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|,|E_{\mathbf{h}+\mathbf{k}}|,|E_{\mathbf{h}+\mathbf{k}}|,$$
$$|E_{\mathbf{k}+\mathbf{l}}|,\varphi_{\mathbf{h}},\varphi_{\mathbf{k}},\varphi_{\mathbf{l}},\ldots,\varphi_{\mathbf{k}+\mathbf{l}})$$

is introduced, under the assumption that all $\mathbf{h},\mathbf{k},\mathbf{l},\ldots,\mathbf{k}+\mathbf{l}$ are random variables. As in Hauptman (1974*a*, *b*), excessive overlap in the Patterson function of a real structure, or atoms in fixed special positions, could cause difficulties to the exact validity of the theory.

We introduce the abbreviations

$$\begin{aligned} E_1&=R_1\exp i\varphi_1=A_1+iB_1=E_{\mathbf{h}}\\ E_2&=R_2\exp i\varphi_2=\;\ldots\ldots=E_{\mathbf{k}}\\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\ E_7&=R_7\exp i\varphi_7\;\ldots\ldots\ldots=E_{\mathbf{k}+\mathbf{l}}\,. \end{aligned}$$

By following the generalization of the Klug (1958) theory proposed by Giacovazzo (1976*a*) we derive the characteristic function

$$\begin{aligned} &C(u_1,u_2,\ldots,u_7;\,v_1,v_2,\ldots,v_7)\\ &=\exp\left[-\tfrac{1}{2}\left(\frac{u_1^2}{2}+\ldots+\frac{u_7^2}{2}+\frac{v_1^2}{2}+\ldots+\frac{v_7^2}{2}\right)\right]\\ &\times\left\{1+\frac{S_3}{N^{3/2}}+\left(\frac{S_4}{N^2}+\frac{S_3^2}{2N^3}\right)\right.\\ &\left.+\left(\frac{S_5}{N^{5/2}}+\frac{S_3S_4}{N^{7/2}}+\frac{S_3^3}{6N^{9/2}}\right)+\ldots\right\}, \end{aligned} \qquad (6)$$

where $u_j,v_j,j=1,\ldots,7$ are carrying variables associated respectively with A_j and B_j values,

$$S_\nu=N\sum_{r+s+\ldots+w=\nu}\frac{1}{2^{\nu/2}}\,\frac{\lambda_{rs\ldots w}}{r!s!\ldots w!}(iu_1)^r(iu_2)^s\ldots(iv_7)^w$$

and

$$\lambda_{rs\ldots w}=\frac{K_{rs\ldots w}}{K_{200\ldots}^{r/2}K_{020\ldots}^{s/2}K_{0\ldots2}^{w/2}}\,.$$

$K_{rs\ldots w}$ are the cumulants of the distribution.

The probability distribution is found by taking the Fourier transform of (6). We make in (6) the variable changes:

$$u_j = \sqrt{2}u_j\,, \qquad v_j = \sqrt{2}v_j'\,,$$
$$u_j' = \varrho_j \cos \psi_j\,, \quad v_j' = \varrho_j \sin \psi_j\,,$$
$$A_j = R_j \cos \varphi_j\,, \quad B_j = R_j \sin \varphi_j\,, \quad j = 1, \ldots, 7\,,$$

and obtain

$$P(R_1,\ldots,R_7,\varphi_1,\ldots,\varphi_7) = \frac{1}{(2\pi)^{14}}\int_0^\infty \ldots$$
$$\ldots \int_0^\infty \int_0^{2\pi} \ldots \int_0^{2\pi} \exp\{-i[\sqrt{2}\varrho_1 R_1 \cos(\psi_1-\varphi_1) + \ldots$$
$$+ \sqrt{2}\varrho_7 R_7 \cos(\psi_7-\varphi_7)]\}$$
$$\times \exp\{[-\tfrac{1}{2}(\varrho_1^2+\varrho_2^2+\ldots+\varrho_7^2)]\}\,.\,2^7$$
$$\times \left\{1 + \frac{S_3'}{N^{3/2}} + \left(\frac{S_4'}{N^2} + \frac{S_3'^2}{2N^3}\right)\right.$$
$$\left. + \left(\frac{S_5'}{N^{5/2}} + \frac{S_3'S_4'}{N^{7/2}} + \frac{S_3'^3}{6N^{9/2}}\right) + \ldots\right\}$$
$$\times R_1R_2\ldots R_7\varrho_1\varrho_2\ldots\varrho_7 \mathrm{d}\varrho_1\ldots\mathrm{d}\varrho_7\mathrm{d}\psi_1\ldots\mathrm{d}\psi_7\,, \quad (7)$$

where

$$S_\nu' = N \sum_{r+s+\ldots+w=\nu} \frac{\lambda_{rs\ldots w}}{r!s!\ldots w!}(i)^{r+s+\ldots+w}$$
$$\times(\varrho_1\cos\psi_1)^r(\varrho_2\cos\psi_2)^s\ldots(\varrho_7\sin\psi_7)^w\,.$$

Calculation of the standardized cumulants $\lambda_{rs\ldots w}$ gives

$$S_3'/N^{3/2} = \frac{i^3}{\sqrt{2N}}[\varrho_1\varrho_2\varrho_5\cos(\psi_1+\psi_2-\psi_5)$$
$$+\varrho_1\varrho_3\varrho_6\cos(\psi_1+\psi_3-\psi_6)$$
$$+\varrho_2\varrho_3\varrho_7\cos(\psi_2+\psi_3-\psi_7)$$
$$+\varrho_1\varrho_7\varrho_4\cos(\psi_1+\psi_7-\psi_4)$$
$$+\varrho_2\varrho_6\varrho_4\cos(\psi_2+\psi_6-\psi_4)$$
$$+\varrho_3\varrho_5\varrho_4\cos(\psi_3+\psi_5-\psi_4)]\,,$$

$$S_4'/N^2 = \frac{1}{N}\{-\tfrac{1}{16}(\varrho_1^4+\varrho_2^4+\ldots+\varrho_7^4)$$
$$+\tfrac{1}{2}[\varrho_1\varrho_2\varrho_3\varrho_4\cos(\psi_1+\psi_2+\psi_3-\psi_4)$$
$$+\varrho_1\varrho_2\varrho_6\varrho_7\cos(\psi_1-\psi_2-\psi_6+\psi_7)$$
$$+\varrho_1\varrho_3\varrho_5\varrho_7\cos(\psi_1-\psi_3-\psi_5+\psi_7)$$
$$+\varrho_2\varrho_3\varrho_5\varrho_6\cos(\psi_2-\psi_3-\psi_5+\psi_6)$$
$$+\varrho_1\varrho_4\varrho_5\varrho_6\cos(\psi_1+\psi_4-\psi_5-\psi_6)$$
$$+\varrho_2\varrho_4\varrho_5\varrho_7\cos(\psi_2+\psi_4-\psi_5-\psi_7)$$
$$+\varrho_3\varrho_4\varrho_6\varrho_7\cos(\psi_3+\psi_4-\psi_6-\psi_7)]\}\,.$$

$$S_5'/N^{5/2} = \frac{-i}{8\sqrt{2}}\cdot\frac{1}{N\sqrt{N}}\{\varrho_1^3\varrho_2\varrho_5[\cos(\psi_1+\psi_2-\psi_5)$$
$$+\cos 2\psi_1\cos(\psi_1-\psi_2+\psi_5)]$$
$$+\varrho_1^3\varrho_3\varrho_6[\cos(\psi_1+\psi_3-\psi_6)$$
$$+\cos 2\psi_1\cos(\psi_1-\psi_3+\psi_6)]$$
$$+\varrho_2^3\varrho_3\varrho_7[\cos(\psi_2+\psi_3-\psi_7)$$
$$+\cos 2\psi_2\cos(\psi_2-\psi_3+\psi_7)]$$
$$+\varrho_1^3\varrho_4\varrho_7[\cos(\psi_1-\psi_4+\psi_7)$$
$$+\cos 2\psi_1\cos(\psi_1+\psi_4-\psi_7)]$$
$$+\varrho_2^3\varrho_4\varrho_6[\cos(\psi_2-\psi_4+\psi_6)$$
$$+\cos 2\psi_2\cos(\psi_2+\psi_4-\psi_6)]$$
$$+\varrho_3^3\varrho_4\varrho_5[\cos(\psi_3-\psi_4+\psi_5)$$
$$+\cos 2\psi_3\cos(\psi_3+\psi_4-\psi_5)]+\text{cycl.}\ldots$$
$$-2[\varrho_1^2\varrho_5\varrho_6\varrho_7\cos 2\psi_1\cos(\psi_5+\psi_6-\psi_7)$$
$$+\varrho_2^2\varrho_5\varrho_6\varrho_7\cos 2\psi_2\cos(\psi_5-\psi_6+\psi_7)$$
$$+\varrho_3^2\varrho_5\varrho_6\varrho_7\cos 2\psi_3\cos(-\psi_5+\psi_6+\psi_7)$$
$$+\varrho_4^2\varrho_5\varrho_6\varrho_7\cos 2\psi_4\cos(\psi_5+\psi_6+\psi_7)]\}\,.$$

By repeated application of (3), (4), (5) the desired probability function, correct up to and including terms of order $N^{3/2}$, is finally

$$P(R_1,\ldots,R_7,\varphi_1,\ldots,\varphi_7)$$
$$= \frac{1}{\pi^7}R_1R_2\ldots R_7\exp(-R_1^2-R_2^2-\ldots-R_7^2)$$
$$\times\left\{1+\frac{2}{\sqrt{N}}[R_1R_2R_5\cos(\varphi_1+\varphi_2-\varphi_5)\right.$$
$$+R_1R_3R_6\cos(\varphi_1+\varphi_3-\varphi_6)+R_2R_3R_7\cos(\varphi_2+\varphi_3-\varphi_7)$$
$$+R_1R_4R_7\cos(\varphi_1-\varphi_4+\varphi_7)+R_2R_4R_6\cos(\varphi_2-\varphi_4+\varphi_6)$$
$$+R_3R_4R_5\cos(\varphi_3-\varphi_4+\varphi_5)]$$
$$-\frac{1}{N}[(1-R_1^2)(1-R_2^2)(1-R_5^2)$$
$$-R_1^2R_2^2R_5^2\cos(2\varphi_1+2\varphi_2-2\varphi_5)$$
$$+(1-R_1^2)(1-R_3^2)(1-R_6^2)-R_1^2R_3^2R_6^2\cos(2\varphi_1+2\varphi_3-2\varphi_6)$$
$$+(1-R_2^2)(1-R_3^2)(1-R_7^2)-R_2^2R_3^2R_7^2\cos(2\varphi_2+2\varphi_3-2\varphi_7)$$
$$+(1-R_1^2)(1-R_4^2)(1-R_7^2)-R_1^2R_4^2R_7^2\cos(2\varphi_1-2\varphi_4+2\varphi_7)$$
$$+(1-R_2^2)(1-R_4^2)(1-R_6^2)-R_2^2R_4^2R_6^2\cos(2\varphi_2-2\varphi_4+2\varphi_6)$$
$$+(1-R_3^2)(1-R_4^2)(1-R_5^2)-R_3^2R_4^2R_5^2\cos(2\varphi_3-2\varphi_4+2\varphi_5)]$$
$$-\frac{2}{N}R_1R_2R_3R_4[(1-R_5^2)+(1-R_6^2)+(1-R_7^2)]$$
$$\times\cos(\varphi_1+\varphi_2+\varphi_3-\varphi_4)$$
$$-\frac{2}{N}R_1R_2R_6R_7[(1-R_3^2)+(1-R_4^2)]\cos(\varphi_1-\varphi_2-\varphi_6+\varphi_7)$$
$$-\frac{2}{N}R_1R_3R_5R_7[(1-R_2^2)+(1-R_4^2)]\cos(\varphi_1-\varphi_3-\varphi_5+\varphi_7)$$
$$-\frac{2}{N}R_1R_4R_5R_6[(1-R_2^2)+(1-R_3^2)]\cos(\varphi_1+\varphi_4-\varphi_5-\varphi_6)$$
$$+\ldots$$
$$-\frac{1}{4N}[R_1^4+R_2^4+\ldots+R_7^4-4(R_1^2+R_2^2+\ldots+R_7^2)+14]$$
$$+\frac{2}{N}[R_1R_2R_3R_4\cos(\varphi_1+\varphi_2+\varphi_3-\varphi_4)$$
$$+R_1R_2R_6R_7\cos(\varphi_1-\varphi_2-\varphi_6+\varphi_7)$$
$$+R_1R_3R_5R_7\cos(\varphi_1-\varphi_3-\varphi_5+\varphi_7)$$
$$+R_2R_3R_5R_6\cos(\varphi_2-\varphi_3-\varphi_5+\varphi_6)$$
$$+R_1R_4R_5R_6\cos(\varphi_1+\varphi_4-\varphi_5-\varphi_6)$$
$$+R_2R_4R_5R_7\cos(\varphi_2+\varphi_4-\varphi_5-\varphi_7)$$

$$+R_3R_4R_6R_7\cos(\varphi_3+\varphi_4-\varphi_6-\varphi_7)]$$
$$-\frac{1}{4N\sqrt{N}}[R_1^3R_2R_5\cos(3\varphi_1-\varphi_2+\varphi_5)$$
$$+3R_1(2-R_1^2)R_2R_5\cos(\varphi_1+\varphi_2-\varphi_5)$$
$$+R_1^3R_3R_6\cos(3\varphi_1-\varphi_3+\varphi_6)$$
$$+3R_1(2-R_1^2)R_3R_6\cos(\varphi_1+\varphi_3-\varphi_6)$$
$$+R_2^3R_3R_7\cos(3\varphi_2-\varphi_3+\varphi_7)$$
$$+3R_2(2-R_2^2)R_3R_7\cos(\varphi_2+\varphi_3-\varphi_7)$$
$$+\ldots$$
$$-2R_1^2R_5R_6R_7\cos 2\varphi_1\cos(\varphi_5+\varphi_6-\varphi_7)$$
$$-2R_2^2R_5R_6R_7\cos 2\varphi_2\cos(\varphi_5-\varphi_6+\varphi_7)$$
$$-2R_3^2R_5R_6R_7\cos 2\varphi_3\cos(-\varphi_5+\varphi_6+\varphi_7)$$
$$-2R_4^2R_5R_6R_7\cos 2\varphi_4\cos(\varphi_5+\varphi_6+\varphi_7)]+\ldots\}\,. \quad (8)$$

Some terms not essential to our aim are omitted in (8).

If we define

$$\Phi=\varphi_1+\varphi_2+\varphi_3-\varphi_4\,,$$

we may derive from (8)

$$P(R_1,R_2,\ldots,R_7,\Phi,\varphi_5,\varphi_6,\varphi_7)$$
$$=\int_0^{2\pi}\mathrm{d}\varphi_1\int_0^{2\pi}\mathrm{d}\varphi_2\int_0^{2\pi}\mathrm{d}\varphi_3$$
$$\times P(R_1,\ldots,R_7,\varphi_1,\varphi_2,\varphi_3,\varphi_1+\varphi_2+\varphi_3-\Phi,\varphi_5,\varphi_6,\varphi_7)$$
$$=\frac{8}{\pi^4}R_1R_2\ldots R_7\exp(-R_1^2-\ldots-R_7^2)$$
$$\times\left\{1-\frac{q}{N}+\frac{2}{N}R_1R_2R_3R_4[R_5^2+R_6^2+R_7^2-2]\cos\Phi\right\}, \quad (9)$$

where

$$q=[(1-R_1^2)(1-R_2^2)(1-R_5^2)+(1-R_1^2)(1-R_3^2)(1-R_6^2)$$
$$+(1-R_2^2)(1-R_3^2)(1-R_7^2)+(1-R_1^2)(1-R_4^2)(1-R_7^2)$$
$$+(1-R_2^2)(1-R_4^2)(1-R_6^2)+(1-R_3^2)(1-R_4^2)(1-R_5^2)]$$
$$+\tfrac{1}{4}[R_1^4+R_2^4+\ldots+R_7^4-4(R_1^2+R_2^2+\ldots+R_7^2)+14]\,.$$

Terms containing $\varphi_5,\varphi_6,\varphi_7$ are not present in (9): the marginal probability density $P(R_1,R_2,\ldots,R_7,\Phi)$ is finally given by

$$P(R_1,R_2,\ldots,R_7,\Phi)$$
$$=\frac{64}{\pi}R_1R_2\ldots R_7\exp(-R_1^2-\ldots-R_7^2)$$
$$\times\left\{1-\frac{q}{N}+\frac{2}{N}R_1R_2R_3R_4[R_5^2+R_6^2+R_7^2-2]\cos\Phi\right\}. \quad (10)$$

I.4 *The conditional expected value of* $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h+k+l}})$ *given* $|E_{\mathbf{h}}|,|E_{\mathbf{k}}|,|E_{\mathbf{l}}|,|E_{\mathbf{h+k+l}}|,|E_{\mathbf{h+k}}|,|E_{\mathbf{h+l}}|\,|E_{\mathbf{k+l}}|$

An expected value of considerable importance is the expected value of the cosine invariant $\cos\Phi$ given $R_1,R_2,\ldots,R_7$. The circumstance is the one commonly met in practice in which the magnitudes of the structure factors are known but the phases are not. In order to determine this expected value we derive

$$P(\Phi|R_1,R_2,\ldots,R_7)$$
$$=\frac{1}{2\pi}+\frac{R_1R_2R_3R_4}{\pi N(1-q/N)}[R_5^2+R_6^2+R_7^2-2]\cos\Phi\,. \quad (11)$$

When $R_5^2+R_6^2+R_7^2=2$,

$$P(\Phi|R_1,\ldots,R_7)=\frac{1}{2\pi}: \quad (12)$$

the probability density of Φ is uniform in $(0,2\pi)$.

From (11) we may derive

$$\langle(\cos\Phi|R_1,\ldots,R_7)\rangle=\frac{R_1R_2R_3R_4}{N(1-q/N)}[R_5^2+R_6^2+R_7^2-2]\,, \quad (13)$$

$$V=\langle\cos^2\Phi|R_1,\ldots,R_7\rangle-\cos\langle\Phi|R_1,\ldots,R_7\rangle^2$$
$$=\tfrac{1}{2}-\frac{R_1^2R_2^2R_3^2R_4^2[R_5^2+R_6^2+R_7^2-2]^2}{\pi^2(N-q)^2}\,. \quad (14)$$

Under the conditions in which (12) holds, (14) tells us that the variance joined with $\cos\varphi$ is $\frac{1}{2}$. When N is large enough, $\cos\Phi$ is probably positive when $E_5^2+E_6^2+E_7^2-2>0$, probably negative when $E_5^2+E_6^2+E_7^2<2$. The character of positivity or negativity is strengthened by large values of $|E_1E_2E_3E_4|$. When N is not too large, the mathematical procedure for deriving (13) and (14) presents some inconveniences:

(*a*) for large values of the R's the value of q may equal or approximate N. (13) then has discontinuities or assumes values, very large in modulus, which are positive or negative according to whether N is larger or smaller than q.

(*b*) when q is not very different from N, (14) may be strongly negative.

This aberrant behaviour at small values of N has no physical meaning, and is due to the fact that we have represented the probability distribution as an asymptotic series: the actual values of the expected cosine and variance we obtain are then correct to the degree of approximation we choose. We should expect, therefore, that the inclusion in (8) of terms of higher order than $1/N^{3/2}$ will have the effect of correcting these anomalies. This observation is in accordance with the fact that no aberrant behaviour occurs when N is large.

If we content ourselves with including in the probability density expression the contributions of the terms of order $1/N^2$, we must estimate in (7)

$$\frac{S_6'}{N^3}+\frac{S_4'^2}{2N^4}+\frac{S_3'S_5'}{N^4}+\frac{S_3'^2S_4'}{2N^5}+\frac{S_3'^4}{24N^6}\,. \quad (15)$$

The calculation of the new probability function requires a lengthy application of (1)–(5). Formally, a large number of supplementary terms appear in the expression of the expected value of the cosine invariant.

If we just calculate the contribution of $S_4'^2/2N^4$ we obtain

$$\langle \cos \Phi | R_1, \ldots, R_7 \rangle = \frac{R_1R_2R_3R_4}{N(1-Q/N)} [R_5^2+R_6^2+R_7^2-2+G] \tag{16}$$

where

$$G = -\frac{1}{4N} [(6-6R_1^2+R_1^4)+\ldots+(6-6R_4^2+R_4^4) + (2-4R_5^2+R_5^4)+(2-4R_6^2+R_6^4)+(2-4R_7^2+R_7^4)],$$

$$\begin{aligned} Q = q - \frac{1}{N} \{ & \tfrac{1}{2}(\tfrac{1}{16}R_1^8 - R_1^6 + \tfrac{9}{2}R_1^4 - 6R_1^2 + \tfrac{3}{2}) + \ldots \\ & + \tfrac{1}{2}(\tfrac{1}{16}R_7^8 - R_7^6 + \tfrac{9}{2}R_7^4 - 6R_7^2 + \tfrac{3}{2}) \\ & + \tfrac{1}{16}(2-4R_1^2+R_1^4)[(2-4R_2^2+R_2^4)+(2-4R_3^2+R_3^4) \\ & + \ldots + (2-4R_7^2+R_7^4)] \\ & + \tfrac{1}{16}(2-4R_2^2+R_2^4)[(2-4R_3^2+R_3^4)+\ldots \\ & + (2-4R_7^2+R_7^4)] + \ldots \\ & + \tfrac{1}{16}(2-4R_6^2+R_6^4)(2-4R_7^2+R_7^4) \\ & + (1-R_1^2)(1-R_2^2)(1-R_3^2)(1-R_4^2) \\ & + (1-R_1^2)(1-R_2^2)(1-R_6^2)(1-R_7^2) \\ & + (1-R_1^2)(1-R_3^2)(1-R_5^2)(1-R_7^2) \\ & + (1-R_2^2)(1-R_3^2)(1-R_5^2)(1-R_6^2) \\ & + (1-R_1^2)(1-R_4^2)(1-R_5^2)(1-R_6^2) \\ & + (1-R_2^2)(1-R_4^2)(1-R_5^2)(1-R_7^2) \\ & + (1-R_3^2)(1-R_4^2)(1-R_6^2)(1-R_7^2)\}. \end{aligned}$$

As may be noted, $G<0$ and $Q<q$ for large values of the R's. The estimate of $S_4'^2/2N^4$, therefore, modifies the expected values of $\cos \Phi$ and the variance expression in such a way as to reduce the aberrations in small structures.

We shall not give here the complete expression of the contribution of the terms (15). In fact, if terms of order $1/N^2$ were included in (16), this formula would become rather difficult to deal with, and would discourage the use of quartets in crystal structure solution. A different approach, therefore, will be tried.

I.5 *Expected values of* $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{h+k+l}}\ldots)$ *when the exponential form for the probability density is used*

The possibility of increased accuracy may be elusive when the higher-order terms in the series expansion are discussed, especially if the largest normalized structure factor magnitudes are involved (Karle, 1972). An improvement in the accuracy and interpretation, nevertheless, may be achieved by transforming the series expansion of the joint probability distribution to an exponential form, as from the application of the central-limit theorem (Bertaut, 1960*a*,*b*). In particular the general positivity both of the probability density and of the variance values is assured. Under these assumptions (10) may be rewritten

$$P(R_1, R_2, \ldots, R_7, \Phi) = \frac{64}{\pi} R_1R_2\ldots R_7 \exp(-R_1^2-\ldots-R_7^2) \times \exp \frac{1}{N} \{q+2R_1R_2R_3R_4(R_5^2+R_6^2+R_7^2-2)\cos \Phi\}. \tag{17}$$

From (17) we obtain finally

$$P(\Phi | R_1, R_2, \ldots, R_7) = \frac{1}{2\pi I_0(G)} \exp(G \cos \Phi), \tag{18}$$

where

$$G = \frac{2}{N} R_1R_2R_3R_4(R_5^2+R_6^2+R_7^2-2).$$

We note that (18) has the same algebraic form as the conditional distribution of $\Phi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h+k}}$ given $G=2R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{h}\pm\mathbf{k}}/\sqrt{N}$ (Hauptman, 1972) and of the phase $\Phi=2\varphi_{\mathbf{h}}-\varphi_{\mathbf{h+k}}-\varphi_{\mathbf{h-k}}$ given $G=1/N(2R_{\mathbf{k}}^2-1)R_{\mathbf{h}}^2R_{\mathbf{h+k}}R_{\mathbf{h-k}}$ (Giacovazzo, 1974*a*).

There is no problem in calculating from (18) the following functions (Hauptman, 1972):

$$P(\cos \Phi | G) = \frac{1}{\pi I_0(G)} \exp(G \cos \Phi)/\sin \Phi, \tag{19}$$

$$\langle \cos \Phi | G \rangle = \frac{I_1(G)}{I_0(G)}, \tag{20}$$

$$\mathrm{var}[\cos \Phi | G] = 1 - \frac{I_1(G)}{G I_0(G)} - \frac{I_1^2(G)}{I_0^2(G)}, \tag{21}$$

$$\cos(t\Phi | G) = \frac{I_t(G)}{I_0(G)}. \tag{22}$$

This approach, nevertheless, involves an inconvenience: the quantity q, which may strongly affect in (13) the expected values of the cosine, disappears during the mathematical manipulation which leads from (17) to (18). The effect is small for the cosines strongly defined negative by (13), but may lead to large overestimates for cosines strongly defined positive. A more suitable approach seems to be one which makes use of a suitable empirical function for rescaling the probability levels provided by the theoretical formulae. This procedure has already been successfully used for quartets in $P\bar{1}$. Giacovazzo (1975*b*) showed that the reliability of the relation

$$S(E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h+k+l}}) = +1$$

depends on

$$\frac{N^{-1}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h+k+l}}|(E_{\mathbf{h+k}}^2+E_{\mathbf{h+l}}^2+E_{\mathbf{k+l}}^2-2)}{1+3\tanh[(E_{\mathbf{h+k}}^2+E_{\mathbf{h+l}}^2+E_{\mathbf{k+l}}^2)/3]} \tag{23}$$

in the same way as that of the $\sum_2$ relationship depends on

$$|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h+k}}|/\sqrt{N}.$$

In (23) only the factor $3\tanh[(E^2_{\mathbf{h}+\mathbf{k}}+E^2_{\mathbf{h}+\mathbf{l}}+E^2_{\mathbf{k}+\mathbf{l}})/3]$ was empirically determined.

In accordance with the experimental tests (Giacovazzo, 1976*b*) a G factor suitable for obtaining in $P1$ reliability levels for quartets comparable with that of triplets may be

$$G=\frac{2N^{-1}R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}(R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}+R^2_{\mathbf{k}+\mathbf{l}}-2)}{1+\tanh[(R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}+R^2_{\mathbf{k}+\mathbf{l}})/3]}\,; \quad (24)$$

the factor $1+\tanh[R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}+R^2_{\mathbf{k}+\mathbf{l}})/3]$ has been empirically determined.

I.6 *Marginal distribution functions*

All three cross vectors $\mathbf{h}+\mathbf{k},\mathbf{h}+\mathbf{l},\mathbf{k}+\mathbf{l}$ are not always in the set of measured reflexions. In order to derive useful information even in these less favourable cases, some marginal joint distributions must be considered.

Let us suppose that the reflexion $\mathbf{k}+\mathbf{l}$ is not present. From the marginal distribution $P(R_{\mathbf{h}},R_{\mathbf{k}},\ldots,R_{\mathbf{h}+\mathbf{l}},\varphi_{\mathbf{h}},\varphi_{\mathbf{k}},\ldots,\varphi_{\mathbf{h}+\mathbf{l}})$ we derive again the relationships (18)–(22), but in this case

$$G(\mathbf{h},\mathbf{k},\mathbf{l})=2N^{-1}R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}(R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}-1)\,.$$

In these conditions $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$ is probably positive if $R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}-1>0$. The number of quartets for which two cross vectors alone are in the set of measurement may be a significant percentage of the total number of available quartets. In accordance with Giacovazzo (1976*b*), reliability levels for this kind of quartet comparable with that of the triplets may be achieved assuming

$$G(\mathbf{h},\mathbf{k},\mathbf{l})=\frac{2N^{-1}R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}(R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}-1)}{1+\tanh[(R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}})/2]}\,. \quad (25)$$

If the $\mathbf{h}+\mathbf{l}$ and $\mathbf{k}+\mathbf{l}$ reflexions are not in the set of measured reflexions, inspection of the distribution $P(R_{\mathbf{h}},\ldots,R_{\mathbf{h}+\mathbf{k}},\varphi_{\mathbf{h}},\ldots,\varphi_{\mathbf{h}+\mathbf{k}})$ leads us to derive again (18)–(22); in this case $G(\mathbf{h},\mathbf{k},\mathbf{l})$ equals

$$G''(\mathbf{h},\mathbf{k},\mathbf{l})=2N^{-1}R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\,.\,R^2_{\mathbf{h}+\mathbf{k}}\,.$$

In accordance with results obtained (Giacovazzo, 1975*a*) in $P\overline{1}$, if two of $\mathbf{h}+\mathbf{k},\mathbf{h}+\mathbf{l},\mathbf{k}+\mathbf{l}$ are not in the set of measurements, we cannot define negative cosines.

II. Practical application of the quartets in structure determination

The recent progress in the theory of quartets justifies their greater use in procedures for crystal structure solution. We now give some applications.

II.1 *A tangent formula for quartets*

Let us derive from (8) the marginal probability density

$$P(\varphi_1,\varphi_2,\varphi_3,\varphi_4,R_1,R_2,\ldots,R_7)=\frac{8}{\pi^4}R_1\ldots R_7$$
$$\times\exp(-R_1^2-\ldots R_7^2)\left\{1-\frac{q}{N}+\frac{2}{N}R_1R_2R_3R_4\right.$$
$$\left.\times(R_5^2+R_6^2+R_7^2-2)\cos(\varphi_1+\varphi_2+\varphi_3-\varphi_4)\right\}.$$

It is easy to show that the probability $P(\varphi_1|\varphi_2,\varphi_3,\varphi_4,R_1,\ldots,R_7)$ has the same form as $P(\Phi|R_1,\ldots,R_7)$: in view of the previous arguments we may write

$$P(\varphi_h|\ldots)=\frac{1}{2\pi I_0(G)}\exp[G\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})]\,, \quad (26)$$

where G is defined by (24) [or by (25) if only two cross vectors are present in the set of measurements].

From (26) we obtain

$$\langle\cos\varphi_{\mathbf{h}}\rangle=\frac{I_1(G)}{I_0(G)}\cos(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})\,,$$
$$\langle\sin\varphi_{\mathbf{h}}\rangle=\frac{I_1(G)}{I_0(G)}\sin(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})\,.$$

Given several fixed 'addition triplets' $\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{-\mathbf{h}-\mathbf{k}-\mathbf{l}}$, we multiply the individual probability distributions (26) to obtain the form

$$P(\varphi_h|\ldots)\simeq\prod_{\mathbf{k},\mathbf{l}}P_{\mathbf{k},\mathbf{l}}(\varphi_n|\ldots)$$
$$\simeq A\exp[\sum_{\mathbf{k},\mathbf{l}}G(\mathbf{h},\mathbf{k},\mathbf{l})\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})]$$
$$\simeq[2\pi I_0(\alpha)]^{-1}\exp[\alpha\cos(\varphi_{\mathbf{h}}-\beta)]\,, \quad (27)$$

where

$$\alpha=\{[\sum_{\mathbf{k},\mathbf{l}}G(\mathbf{h},\mathbf{k},\mathbf{l})\cos(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})]^2$$
$$+[\sum_{\mathbf{k},\mathbf{l}}G(\mathbf{h},\mathbf{k},\mathbf{l})\sin(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})]^2\}^{1/2}\,, \quad (28)$$

$$\alpha\cos\beta=\sum_{\mathbf{k},\mathbf{l}}G(\mathbf{h},\mathbf{k},\mathbf{l})\cos(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})\,, \quad (29\cdot1)$$

$$\alpha\sin\beta=\sum_{\mathbf{k},\mathbf{l}}G(\mathbf{h},\mathbf{k},\mathbf{l})\sin(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})\,. \quad (29\cdot2)$$

α estimates the strength of the phase indication.

The variance $\langle(\varphi_{\mathbf{h}}-\langle\varphi_{\mathbf{h}}\rangle)^2\rangle$ is given by

$$\mathrm{Var}=\frac{\pi^2}{3}+[I_0(\alpha)]^{-1}\sum_{n=1}^{\infty}\frac{I_{2n}(\alpha)}{n^2}$$
$$-4[I_0(\alpha)]^{-1}\sum_{n=0}^{\infty}\frac{I_{2n+1}(\alpha)}{(2n+1)^2}\,. \quad (30)$$

A formal treatment of (29) leads to the tangent expression [see Schenk (1973*a*) for a related formula]

$$\tan\beta\simeq\frac{\sum_{\mathbf{k},\mathbf{l}}G(\mathbf{h},\mathbf{k},\mathbf{l})\sin(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})}{\sum_{\mathbf{k},\mathbf{l}}G(\mathbf{h},\mathbf{k},\mathbf{l})\cos(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})}\,, \quad (30)$$

whose nature deserves to be discussed. The usual tangent formula for triplets assigns a value to $\varphi_{\mathbf{h}}$, given an addition pair $\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}$, in accordance with the rule (Karle & Karle, 1966)

$$\sin(\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}-\mathbf{k}})=0\,. \tag{31}$$

Owing to the probability laws, the accepted solution to (31) is

$$\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}-\mathbf{k}}=0\,.$$

Given an 'addition triplet' $\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{-\mathbf{h}-\mathbf{k}-\mathbf{l}}$, we would expect that the tangent formula for quartets assigns to $\varphi_{\mathbf{h}}$ a value in accordance with

$$\sin(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})=0\,;$$

this time, according to the sign of $G(\mathbf{h},\mathbf{k},\mathbf{l})$, the solutions

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

are both possible. In this respect, a more explicit form of (30) is

$$\tan\varphi_{\mathbf{h}}\simeq \frac{\sum_{\mathbf{k},\mathbf{l}}|G(\mathbf{h},\mathbf{k},\mathbf{l})|\sin\{\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}}+[1-S(\mathbf{h},\mathbf{k},\mathbf{l})]\pi/2\}}{\sum_{\mathbf{k},\mathbf{l}}|G(\mathbf{h},\mathbf{k},\mathbf{l})|\cos\{\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}}+[1-S(\mathbf{h},\mathbf{k},\mathbf{l})]\pi/2\}}\,, \tag{32}$$

where $S(\mathbf{h},\mathbf{k},\mathbf{l})$ is the sign of $G(\mathbf{h},\mathbf{k},\mathbf{l})$.

(30) or (32) may be conveniently compared with Simerska's (1956) tangent formula

$$\tan\varphi_{\mathbf{h}}=\frac{\sum_{\mathbf{k},\mathbf{l}}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|\sin(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})}{\sum_{\mathbf{k},\mathbf{l}}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|\cos(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})}\,. \tag{33}$$

(33) may be considered an asymptotic form of (30), since it replaces the actual values of $(R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}+R^2_{\mathbf{k}+\mathbf{l}}-2)$ with the positive normalized value $\langle R^2_{\mathbf{h}+\mathbf{k}}+R^2_{\mathbf{h}+\mathbf{l}}+R^2_{\mathbf{k}+\mathbf{l}}-2\rangle_{\mathbf{k},\mathbf{l}}$.

II.2 *Generalized tangent and Sayre formulae*

Several formulae which involve at the same time triplet and quartet relationships are known. A few have been given for structures which contain two types of atoms. We recall:

$$(a)\ F_{\mathbf{h}}=A\,.\,\frac{1}{V}\sum_{\mathbf{k}}F_{\mathbf{h}}F_{\mathbf{h}+\mathbf{k}}-B\,\frac{1}{V^2}\sum_{\mathbf{k},\mathbf{l}}F_{\mathbf{k}}F_{\mathbf{l}}F_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\,, \tag{34}$$

derived by Woolfson (1958) for centrosymmetric space groups;

$$(b)\ U_{\mathbf{h}}=\left(\frac{1}{n_1}+\frac{1}{n_2}\right)\langle U_{\mathbf{k}}U_{\mathbf{h}-\mathbf{k}}\rangle-\frac{1}{n_1n_2}\langle U_{\mathbf{k}}U_{\mathbf{l}}U_{\mathbf{h}-\mathbf{k}-\mathbf{l}}\rangle\,, \tag{35}$$

obtained by von Eller (1973) by the polynomial method. A,B,n_1,n_2 are positive values here not defined;

$$\begin{aligned}(c)\ \tan\varphi_{\mathbf{h}}=&\{\textstyle\sum_{\mathbf{k}}|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|\sin(\varphi_{\mathbf{h}+\mathbf{k}}-\varphi_{\mathbf{k}})\\&-A\sum_{\mathbf{k},\mathbf{l}}|E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|\sin(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})\}\\&\div\{\textstyle\sum_{\mathbf{k}}|E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|\cos(\varphi_{\mathbf{h}+\mathbf{k}}-\varphi_{\mathbf{k}})\\&-A\sum_{\mathbf{k},\mathbf{l}}|E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|\cos(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})\}\,,\end{aligned} \tag{36}$$

where $A=E_0/2\sum_{\mathbf{k}}E^2_{\mathbf{k}}$, given by Allegra & Colombo (1974) for general structures. (34), (35) and (36) recall a similar formula, given by Hoppe & Gassmann (1968) and used in the 'phase expansion' process (Gassmann & Zechmeister, 1972).

We will show:

(*a*) (34), (35) and (36) are asymptotic relations, which are valid when a large number of triplets and quartets are considered.

(*b*) their meaning is considerably different from the probabilistic Sayre and tangent formulae here stated.

From the conditional probability $P(\varphi_1|R_1,\ldots)$ we obtain

$$\tan\varphi_{\mathbf{h}}=\frac{\sin\beta}{\cos\beta}\,,$$

where

$$\begin{aligned}\sin\beta=Q\,.\,\{&A(\mathbf{h},\mathbf{k})\sin(\varphi_{\mathbf{h}+\mathbf{k}}-\varphi_{\mathbf{k}})\\&+A(\mathbf{h},\mathbf{l})\sin(\varphi_{\mathbf{h}+\mathbf{l}}-\varphi_{\mathbf{l}})\\&+A(\mathbf{h},\mathbf{h}+\mathbf{k}+\mathbf{l})\sin(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}+\mathbf{l}})\\&+G(\mathbf{h},\mathbf{k},\mathbf{l})\sin(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})\\&+G'(\mathbf{h},-\mathbf{k},\mathbf{k}+\mathbf{l})\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}+\mathbf{l}}-\varphi_{\mathbf{k}+\mathbf{l}})\\&+G'(\mathbf{h},-\mathbf{l},\mathbf{k}+\mathbf{l})\sin(\varphi_{\mathbf{l}}+\varphi_{\mathbf{h}+\mathbf{k}}-\varphi_{\mathbf{k}+\mathbf{l}})\\&+G'(\mathbf{h},\mathbf{h}+\mathbf{k}+\mathbf{l},-\mathbf{h}-\mathbf{k})\\&\times\sin(\varphi_{\mathbf{h}+\mathbf{k}}+\varphi_{\mathbf{h}+\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})\}\,,\\ \cos\beta\simeq Q\,.\,\{&A(\mathbf{h},\mathbf{k})\cos(\varphi_{\mathbf{h}+\mathbf{k}}-\varphi_{\mathbf{k}})+\ldots\}\,.\end{aligned}$$

G and G' are defined by (24) and (25) respectively, and

$$A(\mathbf{h},\mathbf{k})=2R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{h}+\mathbf{k}}/\sqrt{N}\,.$$

It is not important in this context to define Q. A further generalization leads to

$$\begin{aligned}\tan\varphi_{\mathbf{h}}=&\{\textstyle\sum_{\mathbf{k}}A(\mathbf{h},\mathbf{k})\sin(\varphi_{\mathbf{h}+\mathbf{k}}-\varphi_{\mathbf{k}})\\&+\sum_{\mathbf{k},\mathbf{l}}G(\mathbf{h},\mathbf{k},\mathbf{l})\sin(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})\}\\&\div\{\textstyle\sum_{\mathbf{k}}A(\mathbf{h},\mathbf{k})\cos(\varphi_{\mathbf{h}+\mathbf{k}}-\varphi_{\mathbf{k}})\\&+\sum_{\mathbf{k},\mathbf{l}}G(\mathbf{h},\mathbf{k},\mathbf{l})\cos(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})\}\,,\end{aligned} \tag{37}$$

which is the required tangent expression.

The reliability of $\varphi_{\mathbf{h}}$ may be estimated by

$$\begin{aligned}\alpha_{\mathbf{h}}=\{[&\sum_{\mathbf{k},\mathbf{l}}A(\mathbf{h},\mathbf{k})\cos(\varphi_{\mathbf{h}+\mathbf{k}}-\varphi_{\mathbf{k}})\\&+G(\mathbf{h},\mathbf{k},\mathbf{l})\cos(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})]^2\\&+[\sum_{\mathbf{k},\mathbf{l}}A(\mathbf{h},\mathbf{k})\sin(\varphi_{\mathbf{h}+\mathbf{k}}-\varphi_{\mathbf{k}})\\&+G(\mathbf{h},\mathbf{k},\mathbf{l})\sin(\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}})]^2\}^{1/2}\,.\end{aligned} \tag{38}$$

Similar considerations are valid in $P\bar{1}$, where (Giacovazzo, 1975*b*)

$$P_+(E_{\mathbf{h}})\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh|E_{\mathbf{h}}|\times\left\{\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}E_{\mathbf{k}}E_{\mathbf{h+k}}+\frac{1}{N}\sum_{\mathbf{k,l}}M(\mathbf{h,k,l})\right\};\quad(39)$$

is

$$M(\mathbf{h,k,l})=\frac{E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h+k+l}}(E^2_{\mathbf{h+k}}+E^2_{\mathbf{h+l}}+E^2_{\mathbf{k+l}}-2)}{1+3\tanh[(E^2_{\mathbf{h+k}}+E^2_{\mathbf{k+l}}+E^2_{\mathbf{k+l}})/3]}$$

if all three cross vectors are in the set of measurements, and

$$M(\mathbf{h,k,l})=\frac{E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h+k+l}}(E^2_{\mathbf{h+k}}+E^2_{\mathbf{h+l}}-1)}{1+3\tanh[(E^2_{\mathbf{h+k}}+E^2_{\mathbf{h+l}})/2]}$$

if the intensities of only two cross-vectors have been measured.

Equations (34), (35) and (36) are derived from the properties of the electron density and of its powers. In fact, when a relationship is given which involves real functions [*i.e.* Patterson and (or) electron density], its Fourier transform gives a property which is valid in reciprocal space. The nature of this last property is asymptotic, inasmuch as summations are required for an infinite number of reflexions. Consequently, if its use involves a limited number of reflexions, the results may be misleading in the same way as

$$\varrho(r)=\frac{1}{V}\sum_{\mathbf{H}}E_{\mathbf{H}}\exp(-2\pi i\,\mathbf{H}.\,\mathbf{r})$$

may fail when the summation involves very few reflexions. The probabilistic approach used here, therefore, is a more powerful device for phase determination.

(37) and (39) are not directly comparable with (34), (35) and (36). Some similarity will be evident if we suppose that:

(*a*) $E_{\mathbf{k}}, E_{\mathbf{l}}, \ldots, E_{\mathbf{k+l}}$ are independent variables.

(*b*) the number of triplets and quartets considered is very large. Under these conditions, in fact, we may replace in (37) and (39) $(|E_{\mathbf{h+k}}|^2+|E_{\mathbf{h+l}}|^2+|E_{\mathbf{k}}+_{\mathbf{l}}|^2-2), (|E_{\mathbf{h+k}}|^2+|E_{\mathbf{h+l}}|^2-1), \ldots,$ by their mean values (~ 1).

The asymptotic expressions of (37) and (39) nevertheless, unlike (34), (35) and (36), add the quartet to the triplet contribution. The difference is due to the fact that (34), (35) and (36) correct in the Sayre equation only the 'squaring effect'. For instance, Allegra & Colombo derived (36) from the condition that the difference between the real and the squared structure must approach zero for the correct phase set as obtained in a multisolution procedure, so that the integral

$$\int_v\left[\frac{\varrho^2(r)}{I_2}-\frac{\varrho(r)}{I_1}\right]^2\mathrm{d}v\,,\qquad(40)$$

where

$$I_n=\int_v\varrho^n(\mathbf{r})\mathrm{d}v$$

must be as small as possible.

In spite of their asymptotic nature, (34), (35) and (36) are of some utility in the procedures for phase determination as they may lead to criteria suitable for finding the correct set of phases in a multisolution procedure (Woolfson, 1961; Allegra & Colombo, 1974).

II.3 *Figures of merit*

The formal similarity between the probabilistic relationships for triplets and quartets allows the use of similar figures of merit for resolving the ambiguities of direct solutions. So, when triplets and quartets are used at the same time for crystal structure solution the correct set of phases should be characterized by the highest values of

$$C=\sum_{\mathbf{h}}\alpha_{\mathbf{h}}\,,$$

$$CC=\sum_{\mathbf{h,k}}A(\mathbf{h,k})\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h+k}})+\sum_{\mathbf{h,k,l}}G(\mathbf{h,k,l})\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h+k+l}});$$

α_h is defined by (38). See Schenk (1973*a*) for related criteria.

For testing the effectiveness of using a particular set of origin- and enantiomorph-fixing reflexions, Germain, Main & Woolfson (1970) proposed in their 'convergence method' the use of the quantity $\langle a^2\rangle^{1/2}$ for each reflexion, calculated in the absence of phase information.

When triplets and quartets are used at the same time

$$\begin{aligned}\langle\alpha^2_{\mathbf{h}}\rangle=&\sum_{\mathbf{k}}A^2(\mathbf{h,k})+\sum_{\mathbf{k,l}}G^2(\mathbf{h,k,l})\\&+2\sum_{\mathbf{k',k'',l}}A(\mathbf{h,k'})\,G(\mathbf{h,k'',l})\frac{I_1[A(\mathbf{h,k'})]}{I_0[A(\mathbf{h,k'})]}\frac{I_1[G(\mathbf{h,k'',l})]}{I_0[G(\mathbf{h,k'',l})]}\\&+2\sum_{\mathbf{k'}\neq\mathbf{k''}}A(\mathbf{h,k'})A(\mathbf{h,k''})\frac{I_1[A(\mathbf{h,k'})]}{I_0[A(\mathbf{h,k'})]}\frac{I_1[A(\mathbf{h,k''})]}{I_0[A(\mathbf{h,k''})]}\\&+2\sum_{\substack{\mathbf{k'}\neq\mathbf{k''}\\\mathbf{l'}\neq\mathbf{l''}}}G(\mathbf{h,k',l'})\,G(\mathbf{h,k'',l''})\frac{I_1[G(\mathbf{h,k',l'})]}{I_0[G(\mathbf{h,k',l'})]}\\&\times\frac{I_1[G(\mathbf{h,k'',l''})]}{I_0[G(\mathbf{h,k'',l''})]}\,.\qquad(41)\end{aligned}$$

Since the value of $\langle\alpha^2_{\mathbf{h}}\rangle$ given by (41) is in general larger than that resulting when triplet relationships alone are used, we would expect that the simultaneous use of quartets and triplets may markedly improve the choice of the origin- and enantiomorph-fixing reflexions as well as the reliability of the new phase indications.

If no self-consistency in the contributors to $\alpha_{\mathbf{h}}$ in (41) can be found, the random expectation values is

$$\langle\alpha^2_{\mathbf{h}}\rangle_{\text{rand}}=\sum_{\mathbf{k}}A^2(\mathbf{h,k})+\sum_{\mathbf{k,l}}G^2(\mathbf{h,k,l})\,.$$

If

$$Z_{\text{exp}}=\sum_{\mathbf{h}}\langle\alpha^2_{\mathbf{h}}\rangle^{1/2}_{\text{exp}};\quad Z_{\text{rand}}=\sum_{\mathbf{h}}\langle\alpha^2_{\mathbf{h}}\rangle^{1/2}_{\text{rand}}\,,$$

an absolute figure of merit M_{abs} may be defined by

$$M_{abs}=\frac{Z-Z_{rand}}{Z_{exp}-Z_{rand}},$$

which should have properties similar to that defined by Germain, Main & Woolfson (1974) when triplet relationships alone are used.

A specific use of the negative cosine invariants $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$ may be made in order to identify the correct solution in centro- and non-centrosymmetric symmorphic space groups.

Semi-empirical figures of merit based on negative general quartets have already been proposed (Schenk, 1974). As they are based on probabilistic relationships, the criteria

$$NQC1=\sum_{\mathbf{h},\mathbf{k},\mathbf{l}} M(\mathbf{h},\mathbf{k},\mathbf{l})S(E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}),$$

$$NQ1=\sum_{\mathbf{h},\mathbf{k},\mathbf{l}} G(\mathbf{h},\mathbf{k},\mathbf{l})\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}),$$

could be more useful for $P\bar{1}$ and $P1$ respectively. NQC1 and NQ1 should be a maximum for the correct structure.

As the available number of general negative quartets may be small, special negative quartets may also be usefully tested. Schenk & de Jong (1973) and Schenk (1973)*b* suggested two criteria, respectively in $P\bar{1}$ and $P1$, based on special quartet ($\mathbf{h}=\mathbf{k}$) relationships

$$\text{HKC}=\sum_{\mathbf{h},\mathbf{k}} \frac{(|U_{\mathbf{h}}|-|U_{\mathbf{k}}|)^2S(\mathbf{h}+\mathbf{k})S(\mathbf{h}-\mathbf{k})}{(1-|U_{\mathbf{h}+\mathbf{k}}|)(1-|U_{\mathbf{h}-\mathbf{k}}|)} \quad (41)$$

$$\text{P1C}=\sum_{\mathbf{h},\mathbf{k}} \frac{(|U_{\mathbf{h}}|-|U_{\mathbf{k}}|)^2}{(1-|U_{\mathbf{h}+\mathbf{k}}|)(1-|U_{\mathbf{h}-\mathbf{k}}|)} \times|\pi-(\varphi_{\mathbf{h}+\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}-2\varphi_{\mathbf{h}})| \quad (42)$$

in which $0\le\varphi_{\mathbf{h}+\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}-2\varphi_{\mathbf{h}}<2\pi$.

The form of (41) and (42) was deduced in conformity with the Harker–Kasper inequalities. Owing to the boundary nature of the inequalities, more useful criteria may be specified in the field of the commonly observed normalized structure factors from probabilistic theories.

In accordance with the probabilistic approach followed by Giacovazzo (1974*a,b*) we suggest for this kind of special quartet the criteria, in $P\bar{1}$ and $P1$ respectively:

$$\text{NSQC1}=\sum_{\mathbf{h},\mathbf{k}} L(\mathbf{h},\mathbf{k})S(\mathbf{h}+\mathbf{k})S(\mathbf{h}-\mathbf{k}), \quad (43)$$

$$\text{NSQ1}=\sum_{\mathbf{h},\mathbf{k}} T(\mathbf{h},\mathbf{k})\cos(\varphi_{\mathbf{h}+\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}-2\varphi_{\mathbf{h}}), \quad (44)$$

where

$$L(\mathbf{h},\mathbf{k})=|E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|(2E^2_{\mathbf{h}}E^2_{\mathbf{k}}-E^2_{\mathbf{h}}-E^2_{\mathbf{k}}),$$
$$T(\mathbf{h},\mathbf{k})=(2R^2_{\mathbf{k}}-1)R_{\mathbf{h}}R_{\mathbf{h}+\mathbf{k}}R_{\mathbf{h}-\mathbf{k}}.$$

III. Conclusions

A probabilistic theory is described which leads to estimates for $\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$. The calculations are performed up to $1/N\sqrt{N}$ order terms. It is recognized that the reliability levels of the phase indications are not on the same scale as that of the triplet cosines. To avoid complications arising from the use of $1/N^2$ order terms, an empirical scaling factor, as suggested by some experimental tests, has been introduced. The proposed formulae are not expensive in computing time and seem to improve the results.

An advantage of the theory is the similarity of the relationships to those valid for triplets. This allows the use of much of the mathematics already used for triplets in procedures for phase determination.

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