On the Theory and Estimation of the Cosine Invariants Cos (φ₁ + φ₃ + φ₄ + φ₅)*

BY HERBERT HAUPTMAN†

Medical Foundation of Buffalo, 73 High Street, Buffalo, New York 14203, U.S.A.

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For fixed h₁, h₂, h₃, subject to h₁ + h₂ + h₃ = 0, and uniformly distributed k, the conditional joint probability distribution of the pair of phases φₖ, φ₃ₖ + k, given |E₃ₖ + k|, |Eₖ|, |E₃ₖ + k| is found. If 1 + m + n + p = 0, this distribution leads, via a suitable sampling technique, to estimates having probabilistic validity for the cosine invariant cos (φ₁ + φ₃ + φ₄ + φ₅) in terms of the seven magnitudes |E₁|, |E₃ₖ|, |E₃ₖ|, |E₃ₖ|, |E₃ₖ|, |E₃ₖ|, |E₃ₖ|.

Introduction

Explicit formulas for the cosine seminvariants cos φ and cos (φ₁ + φ₂), having exact validity under certain conditions, are now known for a number of space groups, and the algebraic techniques for deriving similar formulas in most of the other space groups have been described (Hauptman & Karle, 1953; Weeks & Hauptman, 1970; Hauptman, 1972a, b). Both algebraic and probabilistic methods are available for estimating the value of the cosine invariant cos (φ₁ + φ₃ + φ₄ + φ₅), and it is known for example that the expected value of the latter is

\[ \frac{I_0(A)}{I_0(A)} \]

where \( I_0 \) are modified Bessel functions, \( A = \frac{2}{N}E_1E_2E_3 \), and \( N \) is the number of atoms, assumed identical, in the unit cell. Thus the average value of \( \frac{I_0(A)}{I_0(A)} \) is positive and tends to unity with increasing \( A \); its reliability as an estimate of the value of the cosine also increases with increasing \( A \). Motivated by the Harker-Kasper inequalities, Schenk and de Jong have recently made some semi-empirical observations and applications of cosine quartets \( \cos (φ₁ + φ₂ + φ₃) \) of special type (Schenk & de Jong, 1973; Schenk, 1973a, b, 1974). The theory and estimation of the general cosine invariant, \( \cos (φ₁ + φ₃ + φ₄ + φ₅) \), subject to \( |E₁|, |E₃ₖ|, |E₃ₖ|, |E₃ₖ| \) are large, has also been worked out (Hauptman, 1973, 1974). In the present paper the probabilistic theory of the general cosine invariant \( \cos (φ₁ + φ₃ + φ₄ + φ₅) \) subject to no restrictive conditions is initiated. The theory leads to an estimate for the value of the cosine which, in marked contrast to the estimate for \( \cos (φ₁ + φ₂ + φ₃) \), may lie anywhere between -1 and +1. In particular, if \( B = \frac{2}{N}E₃ₖE₃ₖE₃ₖ \) is sufficiently large and \( |E₁₃ₖ|, |E₃ₖ|, |E₃ₖ| \) are also large, then the estimate is positive and tends to unity with increasing \( |E₁₃ₖ|, |E₃ₖ|, |E₃ₖ| \). If, on the other hand, \( |E₁₃ₖ| \) is sufficiently large and \( |E₃ₖ| \) is also large, then the estimate is negative and tends to -1 with increasing \( B \). The latter result has been recently secured (Hauptman, 1974) so that both the methods and results described here may be regarded as generalizations of this earlier work. Since the values of the cosine invariants, in particular those which are small or negative, are of great significance in direct methods of phase determination, it is anticipated that the results obtained here will have important application in the further development of these procedures.

1.1. Intuitive background*

Let \( \mathbf{l}, \mathbf{m}, \mathbf{n}, \mathbf{p} \), be fixed reciprocal vectors which satisfy

\[ \mathbf{l} + \mathbf{m} + \mathbf{n} + \mathbf{p} = 0, \]  

and assume that \( |E₃ₖ|, |E₃ₖ|, |E₃ₖ| \) are large. Fix the origin by means of

\[ \phi₁ = \phi₃ = \phi₅ = 0. \]  

Suppose next that \( |E₃ₖ|, |E₃ₖ|, |E₃ₖ| \) in view of (1.1) and \( |E₃ₖ| \) are also large. Then it is well known that, under these conditions,

\[ \phi₁ + \phi₃ + \phi₅ \approx 0, \]

\[ \phi₃ + \phi₄ + \phi₅ \approx 0, \]

\[ \phi₅ + \phi₄ + \phi₆ \approx 0. \]

so that, in view of (1.2),

\[ \phi₃ + \phi₄ + \phi₅ \approx 0. \]

It follows similarly, from (1.1), (1.2), (1.6) and the assumed conditions, that

\[ \phi₁ + \phi₂ + \phi₃ \approx 0, \]

\[ \phi₆ + \phi₃ + \phi₄ \approx 0, \]

\[ \phi₄ + \phi₃ + \phi₅ \approx 0. \]

In short, with the origin fixed by means of (1.2),

\[ \phi₃ \approx 0 \]  

or, from (1.2),

\[ \phi₁ + \phi₂ + \phi₃ \approx 0. \]

* The argument presented here is a variant of one suggested by the referee, and due acknowledgement to the referee is made for his suggestion.
However, from (1.1), it follows that the left side of (1.11) is a structure invariant so that its value is independent of the choice of origin. In summary then, if $|E_{1}|, |E_{m}|, |E_{n}|, |E_{p}|, |E_{1+m}|, |E_{1+n}|, |E_{1+p}|$ are all large, the value of the cosine invariant $\cos (\phi_{1} + \phi_{m} + \phi_{n} + \phi_{p})$ is probably positive.

Clearly, however, the cosine invariants must occasionally be negative. In view of the previous argument, it is plausible to suppose that the cosine will be negative precisely in the circumstance that the hypotheses of the preceding paragraph are grossly violated, that is that each of $|E_{1+m}|, |E_{1+n}|, |E_{1+p}|$ is small. While this argument is only heuristic and by no means a rigorous proof, it does serve to motivate the mathematical analysis which follows and throws some light on the more quantitative results given in the sequel.

2. For fixed $\mathbf{h}_{1}$ and $\mathbf{h}_{3}$, the joint conditional probability distribution of the pair, $\varphi_{k}, \varphi_{\mathbf{h}_{1}+\mathbf{k}}$ given $|E_{-\mathbf{h}_{3}+\mathbf{k}}|, |E_{\mathbf{k}}|$, $|E_{\mathbf{h}_{1}+\mathbf{k}}|$

Suppose that a crystal structure in the space group $P 1$ and consisting of $N$ identical point atoms in the unit cell is fixed, and let $\mathbf{h}_{1}, \mathbf{h}_{2}, \mathbf{h}_{3}$ be fixed reciprocal vectors satisfying

$$\mathbf{h}_{1} + \mathbf{h}_{2} + \mathbf{h}_{3} = 0.$$  (2.1)

Introduce the usual abbreviations,

$$E_{j} = E_{\mathbf{h}_{j}}, |E_{j}| = |E_{\mathbf{h}_{j}}|, \varphi_{j} = \varphi_{\mathbf{h}_{j}}, \quad j = 1, 2, 3,$$  (2.2)

$$\varphi = \varphi_{1} + \varphi_{2} + \varphi_{3},$$  (2.3)

where $\varphi_{j}$ is the phase of the normalized structure factor $E_{j}$. Suppose that the vector $\mathbf{k}$ is a random variable which is uniformly distributed over reciprocal space. Then $E_{-\mathbf{h}_{3}+\mathbf{k}}, E_{\mathbf{k}}, E_{\mathbf{h}_{1}+\mathbf{k}}$, as functions of the primitive random variable $\mathbf{k}$, are themselves random variables and the joint probability distribution, correct to terms of order $1/N$, of the respective magnitudes and phases $|E_{-\mathbf{h}_{3}+\mathbf{k}}|, |E_{\mathbf{k}}|, |E_{\mathbf{h}_{1}+\mathbf{k}}|, \varphi_{-\mathbf{h}_{3}+\mathbf{k}}, \varphi_{\mathbf{k}}, \varphi_{\mathbf{h}_{1}+\mathbf{k}}$ is known to be (Tsoucaris, 1970; Hauptman, 1971, 1972b)

$$P(R_{1}, R_{2}, R_{3}; \varphi_{1}, \varphi_{2}, \varphi_{3}) \propto \frac{R_{1} R_{2} R_{3}}{N^{3}} \times \exp \left\{ \frac{1}{4N} \left[ R_{1}^{2} \left( 1 - \frac{|E_{1}|^{2}}{N} \right) + R_{2}^{2} \left( 1 - \frac{|E_{2}|^{2}}{N} \right) \right. \right.$$  (2.4)

$$+ R_{3}^{2} \left( 1 - \frac{|E_{3}|^{2}}{N} \right) \left\} \right.$$  (2.5)

$$\times \exp \left\{ \frac{2}{N^{1/2}} \left[ R_{1}^{2} |E_{2}|^{2} \cos (\varphi_{1} - \varphi_{2} + \varphi_{3}) + R_{2} |E_{1}|^{2} \cos (\varphi_{2} - \varphi_{3} + \varphi_{1}) + R_{3} |E_{1}|^{2} \cos (\varphi_{3} - \varphi_{1} + \varphi_{2}) \right\} \right.$$  (2.6)

$$\times \exp \left\{ \frac{2}{N^{1/2}} \left[ R_{1}^{2} |E_{2}|^{2} + R_{2}^{2} |E_{3}|^{2} + R_{3}^{2} |E_{1}|^{2} \right] \right\},$$  (2.7)

where $R_{1}, R_{2}, R_{3}$ are fixed, non-negative numbers and $\varphi$ is defined by (2.3).

The reader can readily verify, by consulting the references cited if necessary, that (2.4) is a well behaved probability distribution in that it is (essentially) non-negative for all values of the variables $R_{1}, R_{2}, R_{3}$, $\varphi_{1}, \varphi_{2}, \varphi_{3}$ and parameters $|E_{1}|, |E_{2}|, |E_{3}|$, and is suitably normalized.

Suppose next that $R_{1}, R_{2}, R_{3}$ are fixed non-negative numbers and that the vector $\mathbf{k}$ is a random variable which is now uniformly distributed over that region of reciprocal space for which

$$|E_{-\mathbf{h}_{3}+\mathbf{k}}| = R_{1}, \quad |E_{\mathbf{k}}| = R_{2}, \quad |E_{\mathbf{h}_{1}+\mathbf{k}}| = R_{3}.$$  (2.8)

Then the phases $\varphi_{k}, \varphi_{\mathbf{h}_{1}+\mathbf{k}}$, as functions of the primitive random variable $\mathbf{k}$, are themselves random variables. Denote by $P(\varphi_{1}, \varphi_{2}, \varphi_{3} | R_{1}, R_{2}, R_{3})$ the joint conditional probability distribution of the pair $\varphi_{k}, \varphi_{\mathbf{h}_{1}+\mathbf{k}}$ given (2.7). Then $P(\varphi_{1}, \varphi_{2}, \varphi_{3} | R_{1}, R_{2}, R_{3})$ is obtained from (2.4) by fixing $R_{1}, R_{2}, R_{3}$, integrating with respect to $\varphi_{1}$ from 0 to $2\pi$, and multiplying by a suitable normalizing constant. This integration has already been carried out in a different context [Hauptman, 1971, equation (6.6)]. Thus, correct to terms of order $1/N$,

$$P(\varphi_{1}, \varphi_{2}, \varphi_{3} | R_{1}, R_{2}, R_{3}) \propto \frac{1}{K} \exp \left\{ \frac{2}{N^{1/2}} \left[ R_{1} R_{2} |E_{1}| \cos (\varphi_{2} - \varphi_{3} + \varphi_{1}) \right. \right.$$  (2.9)

$$\left. - \frac{2}{AD} R_{2} R_{3} |E_{2}| \cos (\varphi_{2} - \varphi_{3} - \varphi_{2}) \right\} \times \frac{2}{N^{1/2}} \left[ R_{1}^{2} |E_{2}|^{2} + R_{3}^{2} |E_{1}|^{2} \right]$$

$$+ 2 R_{2} R_{3} |E_{2}| \cos (\varphi_{2} - \varphi_{3} - \varphi_{2}) \right\},$$  (2.10)

where $I_{0}$ is the modified Bessel function, $K$ is a normalizing parameter to be determined, and $R_{1}, R_{2}, R_{3}$ are fixed, preassigned, non-negative numbers.

In order to evaluate $K$, one integrates (2.8) with respect to $\varphi_{2}$ and $\varphi_{3}$ between 0 and $2\pi$ and equates the
result to unity. To this end the sum of the two cosines in the exponent of (2.8) is replaced by a single cosine by means of the trigonometric identity

\[ \sum_{i=1}^{n} A_i \cos (\varphi + \alpha_i) = X \cos (\varphi + \xi), \]

(2.9)

where

\[ X = (\sum_{i=1}^{n} A_i A_j \cos (\alpha_i - \alpha_j))^{1/2}, \]

(2.10)

\[ X \cos \xi = \sum_{i=1}^{n} A_i \cos \alpha_i, \]

(2.11)

\[ X \sin \xi = \sum_{i=1}^{n} A_i \sin \alpha_i. \]

(2.12)

Also, with the use of the addition formula for Bessel functions (Watson, 1958, pp. 358, 361), (2.8) finally becomes simply

\[ P(\varphi_2, \varphi_3 | R_1, R_2, R_3) \]

\[ \approx \frac{1}{K} \exp \left\{ \frac{2R_2 R_3 X}{\Delta N^{1/2}} \cos (\varphi_2 - \varphi_3 + \xi) \right\} \]

\[ \times \sum_{\mu = -\infty}^{\infty} I_{\mu} \left( \frac{2R_1 R_3 E_3}{\Delta N^{1/2}} \right) I_{\mu} \left( \frac{2R_1 R_3 E_3}{\Delta N^{1/2}} \right) \]

\[ \times \cos \mu (\varphi_2 + \varphi_3 + \xi), \]

(2.13)

where, from (2.10)–(2.12),

\[ X = \left[ |E_1|^2 - \frac{2|E_1 E_2 E_3|}{N^{1/2}} \cos \varphi + \frac{|E_2 E_3|^2}{N} \right]^{1/2}, \]

(2.14)

\[ X \cos \xi = |E_1| \cos \varphi - \frac{|E_2 E_3|}{N^{1/2}} \cos (\varphi_2 + \varphi_3), \]

(2.15)

\[ X \sin \xi = |E_1| \sin \varphi + \frac{|E_2 E_3|}{N^{1/2}} \sin (\varphi_2 + \varphi_3), \]

(2.16)

and \( \varphi \) is given by (2.3), so that \( X \) and \( \xi \) are independent of \( \varphi_2 \) and \( \varphi_3 \). In view of

\[ \cos \mu (\varphi_2 - \varphi_3 - \varphi_2 - \varphi_3) \]

\[ = \cos \mu (\varphi_2 - \varphi_3 + \xi) \cos \mu (\varphi_2 + \varphi_3 + \xi) + \sin \mu (\varphi_2 - \varphi_3 + \xi) \sin \mu (\varphi_2 + \varphi_3 + \xi), \]

(2.17)

and the integral formulas (Watson, 1958)

\[ \int_{0}^{2\pi} \exp (z \cos \varphi) \cos \mu \varphi \, d\varphi = I_{\mu}(z), \]

(2.18)

\[ \int_{0}^{2\pi} \exp (z \cos \varphi) \sin \mu \varphi \, d\varphi = 0, \]

(2.19)

the integration of (2.13) with respect to \( \varphi_2 \) is readily performed:

\[ \int_{\varphi_2=-\infty}^{\varphi_2=\infty} P(\varphi_2, \varphi_3 | R_1, R_2, R_3) \, d\varphi_2 \]

\[ \approx \int_{\varphi_2=0}^{\varphi_2=2\pi} \frac{2\pi}{2\pi} \sum_{\mu = -\infty}^{\infty} I_{\mu} \left( \frac{2R_1 R_3 E_3}{\Delta N^{1/2}} \right) \]

\[ \times I_{\mu} \left( \frac{2R_1 R_3 E_3}{\Delta N^{1/2}} \right) \]

\[ \times \cos \mu (\varphi_2 + \varphi_3 + \xi), \]

(2.20)

the integrand of which is independent of \( \varphi_3 \). The second integration is therefore immediate and leads to the desired expression for \( K \),

\[ K \approx 4\pi^2 \sum_{\mu = -\infty}^{\infty} \left| \frac{2R_1 R_3 E_3}{\Delta N^{1/2}} \right| I_{\mu} \left( \frac{2R_1 R_3 E_3}{\Delta N^{1/2}} \right) \]

\[ \times \cos \mu (\varphi_2 + \varphi_3 + \xi), \]

(2.21)

where \( X \) and \( \xi \) are given by (2.14)–(2.16).

In order to exhibit the dependence of \( K \) on \( \varphi \) explicitly, one first shows by mathematical induction on \( \mu \), that

\[ \exp \{i\mu (\varphi_2 + \varphi_3 + \xi)\} = \frac{1}{2X^n} \left( |E_1| \exp (i\varphi) - \frac{|E_2 E_3|}{N^{1/2}} \right)^\mu, \]

(2.22)

Then, from (2.22) and (2.14),

\[ \cos \mu (\varphi_2 + \varphi_3 + \xi) = \frac{1}{2} \exp \{i\mu (\varphi_2 + \varphi_3 + \xi)\} \]

\[ + \frac{1}{2} \exp \{-i\mu (\varphi_2 + \varphi_3 + \xi)\} \]

\[ = \frac{1}{2X^n} \left( |E_1| \exp (i\varphi) - \frac{|E_2 E_3|}{N^{1/2}} \right)^\mu \]

\[ \left( |E_1| \exp (-i\varphi) - \frac{|E_2 E_3|}{N^{1/2}} \right)^\mu, \]

(2.23)

Substitution of (2.23) into (2.21) yields

\[ K \approx 2\pi^2 \sum_{\mu = -\infty}^{\infty} \left| \frac{2R_1 R_3 E_3}{\Delta N^{1/2}} \right| I_{\mu} \left( \frac{2R_1 R_3 E_3}{\Delta N^{1/2}} \right) \]

\[ \times I_{\mu} \left( \frac{2R_1 R_3 X}{\Delta N^{1/2}} \right) \left( |E_1| \exp (i\varphi) - \frac{|E_2 E_3|}{N^{1/2}} \right)^\mu \]

\[ \left( |E_1| \exp (-i\varphi) - \frac{|E_2 E_3|}{N^{1/2}} \right)^\mu, \]

(2.24)

an expression for \( K \) in which the dependence on \( \varphi \) is clear.

Another expression for \( K \), independent of \( X \), is obtained by noting that \( I_{\mu} = I_{-\mu} \) so that the cosine function in (2.21) may be replaced by the exponential function and \( K \) becomes
Finally, employing again the addition formula for Bessel Functions, and noting that $I_n(-z) = (-1)^n I_n(z)$,

\[ K \approx 4\pi^2 \sum_{\mu=-\infty}^{\infty} \left( \frac{2R_1R_2|E_3|}{AN^{1/2}} \right)^\mu/2 \times I_{\mu+n} \left( \frac{2R_2R_3X}{AN^{1/2}} \right) \times I_n \left( \frac{2R_1R_3|E_2|}{AN^{1/2}} \right) \times \left( \frac{|E_1| \exp(-ip) - \frac{|E_2E_3|}{N^{1/2}}}{|E_1| \exp(ip) - \frac{|E_2E_3|}{N^{1/2}}} \right) \]  
(2.25)

so that again the dependence of $K$ on $\cos \varphi$ is clear.

### 3. The conditional expected value of $\cos t (\varphi_k + \varphi_{-h_1-k} + \varphi_{-h_2} + \varphi_{-h_3})$, given $|E_{-h_3+k}|, |E_k|, |E_{h_1+k}|$

In this section the conditional expected value of the cosine invariant $\cos t (\varphi_k + \varphi_{-h_1-k} + \varphi_{-h_2} + \varphi_{-h_3})$ is derived. Although only the special case $t = 1$ is important in the applications, the analysis is carried out for arbitrary integral $t$ in order to permit an estimate for the variance, which depends also on the case $t = 2$, to be obtained. The estimate for the variance is needed later (§6).

The conditional expected value of the random variable $\cos t (\varphi_k + \varphi_{-h_1-k} + \varphi_{-h_2} + \varphi_{-h_3})$, given (2.7), is found from (2.13) by means of

\[ \varepsilon \{ \cos t (\varphi_k + \varphi_{-h_1-k} + \varphi_{-h_2} + \varphi_{-h_3}) | R_1, R_2, R_3 \} = \varepsilon \]
\[ = \frac{1}{K} \int_{\varphi_0=0}^{2\pi} \int_{\varphi_3=0}^{2\pi} \cos t (\varphi_0 - \varphi_3 + \xi) \]
\[ \times \exp \left( \frac{2R_2R_3X}{AN^{1/2}} \cos (\varphi_0 - \varphi_3 + \xi) \right) \]
\[ \times \sum_{\mu=-\infty}^{\infty} I_{\mu} \left( \frac{2R_1R_2|E_3|}{AN^{1/2}} \right) \times I_{\mu+n} \left( \frac{2R_2R_3X}{AN^{1/2}} \right) \times \cos \mu (\varphi_0 - \varphi_3 - \varphi_2 - \varphi_3) d\varphi_0 d\varphi_3, \]
(3.1)

where $X, \xi$ and $K$ are given by (2.14)–(2.16) and (2.24)–(2.26). Proceeding as in §2, one finds

\[ F = F_0, \]
(3.2)

where

\[ F_i = F_i \{ |E_1|, |E_3|; R_1, R_2, R_3, \varphi \} = 2\pi^2 \sum_{\mu=-\infty}^{\infty} I_{\mu} \left( \frac{2R_1R_2|E_3|}{AN^{1/2}} \right) \times I_{\mu+n} \left( \frac{2R_2R_3X}{AN^{1/2}} \right) \]
\[ \times \int_{\varphi=0}^{2\pi} \int_{\varphi=0}^{2\pi} \cos t (\varphi_0 - \varphi_3 + \xi) \]
\[ \times \cos \mu (\varphi_0 - \varphi_3 - \varphi_2 - \varphi_3) d\varphi_0 d\varphi_3, \]

so that, from (2.24),

\[ K = F_0. \]
(3.3)
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\[
F_t = 4\pi^2 \sum_{N=0}^{\infty} (-1)^{N+1} N \left( \frac{2R_2 R_3 |E_3|}{AN^{1/2}} \right) \\
\times I_N \left( \frac{2R_2 R_3 |E_3|}{AN^{1/2}} \right) J_{N+1} \left( \frac{2R_2 R_3 |E_3|}{AN^{1/2}} \right) \cos \varphi.
\]  

(3.8)

The conditional expected value of the cosine invariant (3.5) has been derived from the conditional distribution (2.13) in the standard way. The analysis however is rather lengthy and not trivial. It would therefore be desirable, if possible, to bypass the distribution in order to arrive at the expected value. Although initial efforts to derive (3.5) in this way have not yet been successful, the derivation of (3.5) without using the distribution (2.13) would surely be a significant contribution.

4. Suitable sampling of reciprocal space leads to the first estimate for the cosine invariant,\[\cos t (\varphi_1 + \varphi_m + \varphi_n + \varphi_p)\]

Suppose that $l, m, n, p$ are fixed reciprocal vectors which satisfy

\[l + m + n + p = 0 \]  

(4.1)

so that $\varphi_1 + \varphi_m + \varphi_n + \varphi_p$ is a structure invariant. Define reciprocal vectors $h_1, h_2, h_3$ by means of

\[h_1 = -l - m, \quad h_2 = -n, \quad h_3 = -p \]  

(4.2)

so that, in view of (4.1),

\[h_1 + h_2 + h_3 = 0. \]  

(4.3)

Choose a sample of size two from reciprocal space by means of

\[k = 1, \quad k = m. \]  

(4.4)

Then

\[h_1 = -l - m, \quad h_2 = -n, \quad h_3 = -p, \]

\[-h_3 + k = 1 + p, \quad h_1 + k = -m; \]

\[-h_3 + k = m + p, \quad h_3 + k = -l \]  

(4.5)

for the respective members (4.4) of the sample and, in view of (3.5), one obtains an estimate for the expected value of $\cos t (\varphi_1 + \varphi_m + \varphi_n + \varphi_p)$ by means of

\[e \{ \cos t (\varphi_1 - \varphi_2 - \varphi_3) \} = \frac{1}{2} \cos t (\varphi_1 + \varphi_m + \varphi_n + \varphi_p) + \frac{1}{2} \cos t (\varphi_1 + \varphi_2 + \varphi_3) = \cos t (\varphi_1 + \varphi_m + \varphi_n + \varphi_p) \]

\[\simeq \left( \frac{F_t}{F_0} \right)^2 \]  

(4.6)

where $F_t$ is defined by (3.6) or (3.8). The average in (4.6), in view of (4.3), is taken over the two sets of values

\[E_1 = |E_{1+m}||E_n|, \quad E_2 = |E_{1+n}||E_m|, \quad E_3 = |E_{1+p}|, \quad R_1 = |E_{1+m}|, \quad R_2 = |E_{1+n}||E_m|, \quad R_3 = |E_{1+p}||E_m|, \quad R_4 = |E_{1+p}|. \]  

(4.7)

One obtains five other estimates for $\cos t (\varphi_1 + \varphi_m + \varphi_n + \varphi_p)$ by choosing successively

\[h_1 = -l - n, \quad h_2 = -m, \quad h_3 = -p \]  

(4.8)

with sample

\[k = 1, \quad k = n; \]  

(4.9)

\[h_1 = -l - p, \quad h_2 = -m, \quad h_3 = -n \]  

(4.10)

with sample

\[k = 1, \quad k = p; \]  

(4.11)

\[h_1 = -m - n, \quad h_2 = -1, \quad h_3 = -p \]  

(4.12)

with sample

\[k = m, \quad k = n; \]  

(4.13)

\[h_1 = -m - p, \quad h_2 = -1, \quad h_3 = -n \]  

(4.14)

with sample

\[k = m, \quad k = p; \]  

(4.15)

and finally

\[h_1 = -n - p, \quad h_2 = -l, \quad h_3 = -m \]  

(4.16)

with sample

\[k = n, \quad k = p. \]  

(4.17)

Averaging the six expressions like (4.6), one obtains an estimate, based on an overall sample of size twelve, for $\cos t (\varphi_1 + \varphi_m + \varphi_n + \varphi_p)$

\[\cos t (\varphi_1 + \varphi_m + \varphi_n + \varphi_p) \simeq \left( \frac{F_t}{F_0} \right)^2. \]  

(4.18)

in which $F_t$ is defined by (3.6) or (3.8) and the average in (4.18) is, in view of (4.5) and (4.8)-(4.17), taken over the twelve sets of values for $|E_1|, |E_2|, |E_3|, R_1, R_2, R_3, \varphi = \varphi_1 + \varphi_2 + \varphi_3, \Delta$ and $X$ defined by Table 1, (2.6) and (2.14).

Table 1. The twelve sets of values over which the sums in (4.18), (5.5) and (6.1) are taken

<table>
<thead>
<tr>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$E_3$</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$\varphi$</th>
</tr>
</thead>
<tbody>
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<td>$E_{1+m}$</td>
<td>$E_{1+n}$</td>
<td>$E_{1+p}$</td>
<td>$E_{1+m}$</td>
<td>$E_{1+n}$</td>
<td>$E_{1+p}$</td>
<td>$\varphi = \varphi_1 + \varphi_2 + \varphi_3$</td>
</tr>
<tr>
<td>$E_{2+m}$</td>
<td>$E_{2+n}$</td>
<td>$E_{2+p}$</td>
<td>$E_{2+m}$</td>
<td>$E_{2+n}$</td>
<td>$E_{2+p}$</td>
<td>$\varphi = \varphi_1 + \varphi_2 + \varphi_3$</td>
</tr>
<tr>
<td>$E_{3+m}$</td>
<td>$E_{3+n}$</td>
<td>$E_{3+p}$</td>
<td>$E_{3+m}$</td>
<td>$E_{3+n}$</td>
<td>$E_{3+p}$</td>
<td>$\varphi = \varphi_1 + \varphi_2 + \varphi_3$</td>
</tr>
<tr>
<td>$E_{m+n}$</td>
<td>$E_{m+p}$</td>
<td>$E_{m+p}$</td>
<td>$E_{m+n}$</td>
<td>$E_{m+p}$</td>
<td>$E_{m+p}$</td>
<td>$\varphi = \varphi_1 + \varphi_2 + \varphi_3$</td>
</tr>
<tr>
<td>$E_{n+p}$</td>
<td>$E_{n+p}$</td>
<td>$E_{n+p}$</td>
<td>$E_{n+p}$</td>
<td>$E_{n+p}$</td>
<td>$E_{n+p}$</td>
<td>$\varphi = \varphi_1 + \varphi_2 + \varphi_3$</td>
</tr>
</tbody>
</table>
5. The second estimates for the cosine invariant, 
\( \cos t(\varphi_1 + \varphi_m + \varphi_n + \varphi_p) \), dependent on magnitudes only

Owing to the presence of the six unknown invariants \( \varphi \) on the right-hand side of (4.18), this equation is not useful as an estimate for \( \cos t(\varphi_1 + \varphi_m + \varphi_n + \varphi_p) \). Employing the abbreviation

\[
T_v(z) = \frac{I_v(z)}{I_0(z)} ,
\]

a more useful estimate is obtained by replacing \( \cos \varphi \) and \( \varphi \) by their expected values thus,

\[
\bar{C}_v = C_v(IE_1, IE_2, IE_3) = \mathbb{E}\{\cos v(\varphi_1 + \varphi_2 + \varphi_3)\} = \mathbb{E}\{\exp (i\varphi)\}
\]

\[
\approx \frac{1}{2} \left\{ T_v \left( \frac{2|E_1E_2E_3|}{N^{1/2}} \right) - T_v \left( \frac{2|E_1E_2E_3|}{N^{1/2}} \right) \right\}
\]

\[
C_v = \bar{C}_v , \quad \text{if } N \text{ is large},
\]

\[
\bar{\Delta} = \bar{\Delta}(IE_1, IE_2, IE_3)
\]

\[
= \mathbb{E}(\Delta) = 1 - \frac{1}{N} \left( |E_1|^2 + |E_2|^2 + |E_3|^2 \right)
\]

\[
+ \frac{2|E_1E_2E_3|}{N^{3/2}} \bar{C}_1 .
\]

Then, in view of (3.5)-(3.8), (4.18) is replaced by

\[
\cos t(\varphi_1 + \varphi_m + \varphi_n + \varphi_p) \approx \langle \frac{D_t}{D_0} \rangle_{12}
\]

in which the average is taken over the twelve sets of values of \( |E_1|, |E_2|, |E_3| ; R_1, R_2, R_3 \) defined by Table 1 and

\[
D_t = D_t(|E_1|, |E_2|, |E_3| ; R_1, R_2, R_3)
\]

\[
= 4\pi^2 \sum_{\mu=-\infty}^{\infty} Y^{\mu+1} I_{\mu} \left( \frac{2R_1R_2|E_3|}{\Delta N^{1/2}} \right) I_{\mu} \left( \frac{2R_1R_3|E_2|}{\Delta N^{1/2}} \right)
\]

or

\[
D_t = 4\pi^2 \sum_{\mu, \nu=-\infty}^{\infty} (-1)^{\mu+\nu+1} I_{\mu} \left( \frac{2R_1R_2|E_3|}{\Delta N^{1/2}} \right) \times I_{\nu} \left( \frac{2R_1R_3|E_2|}{\Delta N^{1/2}} \right)
\]

\[
\times I_{\mu+\nu+1} \left( \frac{2R_2R_3|E_1|}{\Delta N^{1/2}} \right) C_v
\]

where \( \bar{C}_v \) and \( \bar{\Delta} \) are defined by (5.1)-(5.4) and, in view of (2.14),

\[
Y = \frac{1}{\overline{R}} \left( \frac{|E_1|C_1 - \frac{|E_2E_3|}{N^{1/2}}}{1} \right)
\]

\[
\overline{R} = \left[ \frac{|E_1|^2 - 2|E_2E_3|}{N^{1/2}} \right] C_1 + \frac{|E_2E_3|^2}{N^{1/2}}\right]^{1/2}.
\]

In the applications which have been made so far, (5.6) and (5.7) have led to two values for (5.5) which however have been essentially identical, as was naturally anticipated. Equation (5.6) is a rapidly converging simple infinite sum whereas (5.7) is a double series. In the actual calculations it has been found that the time required to compute (5.6) is less, by about an order of magnitude, than the time required to calculate (5.7). For this reason (5.6) is to be preferred in the applications. However, because of its greater symmetry, (5.7) may prove to be more useful in the further development of the theory.

Although the sample on which the estimate for the cosine invariant (5.5) is based is rather small (size twelve), it appears to be adequate to yield reliable estimates for those cosines which are large and positive and, except for a still unexplained positive scaling parameter, for those cosines which are negative. The estimate is not reliable only when it falls in the middle range (0.0 to 0.7) and this fact appears to be a consequence of the rather large associated variance in this case (§§7 and 8).

6. The third estimates for \( \cos t(\varphi_1 + \varphi_m + \varphi_n + \varphi_p) \), using a weighted average

Instead of (5.5) in which it has been assumed that all contributors to the sums have equal weights, one may employ

\[
\cos t(\varphi_1 + \varphi_m + \varphi_n + \varphi_p) \approx \sum_{i=12} \frac{w_i D_i}{D_0}
\]

where \( D_i \) is again given by (5.6) or (5.7) and the weight \( w_i \) is defined to be the reciprocal of the variance:

\[
\frac{1}{w_i} = V_i(|E_1|, |E_2|, |E_3| ; R_1, R_2, R_3 ; \varphi)
\]

\[
= \text{Var} \{\cos t(\varphi_k + \varphi_{-h_1-k} + \varphi_{-h_2} + \varphi_{-h_3})\}
\]

\[
= \mathbb{E}\{\cos^2 t(\varphi_k + \varphi_{-h_1-k} + \varphi_{-h_2} + \varphi_{-h_3})\}
\]

\[
- \mathbb{E}\{\cos t(\varphi_k + \varphi_{-h_1-k} + \varphi_{-h_2} + \varphi_{-h_3})\}^2
\]

\[
\approx \frac{1}{2} + \frac{1}{2} \mathbb{E}\{\cos 2t(\varphi_k + \varphi_{-h_1-k} + \varphi_{-h_2} + \varphi_{-h_3})\}
\]

\[
= \frac{F_t^2}{F_0^2} \approx \frac{1}{2} + \frac{1}{2} \frac{F_{2t}}{F_0} - \frac{F_t^2}{F_0^2}
\]

\[
\approx \frac{1}{2} + \frac{1}{2} \frac{D_{2t}}{D_0} - \frac{D_t^2}{D_0^2},
\]
so that $w_r$, as given by (6.3), depends only on $|E_i|$, $|E_2|, |E_3|, R_1, R_2, R_3$. As before, the sums in (6.1) are taken over the twelve sets of values of $|E_i|, |E_2|, |E_3|, R_1, R_2, R_3$ defined by Table 1.

7. The applications

An idealized structure consisting of $N=29$ identical point atoms in the space group $P1$ was constructed and normalized structure factors and cosine invariants calculated as shown in Tables 2-4. The structure was designed to simulate an actual crystal structure; in particular it exhibited a great deal of overlap in the Patterson function. As before, $i, m, n, p$ satisfy

$$\mathbf{1} = \mathbf{m} + \mathbf{n} + \mathbf{p} = 0. \quad (7.1)$$

Comparisons between the true values of representative samples of cosines and those calculated by means of (5.5) and (5.6) are shown in Tables 2-4 and the errors briefly summarized in Table 5. The cosines calculated to be most positive are in good agreement with the true values as shown by Tables 2 and 5. Those cosines calculated to be negative correctly identify the cosines which are in fact negative, but Tables 3 and 5 show that

| $i$ | $m$ | $n$ | $p$ | $x$ | $y$ | $z$ | $\cos \theta_1$ | $\cos \theta_2$ | $\cos \theta_3$ | $\cos \theta_4$ | $\cos \theta_5$ | $\cos \theta_6$ | $\cos \theta_7$ | $\cos \theta_8$ | $\cos \theta_9$ | $\cos \theta_{10}$ | $\cos \theta_{11}$ | $\cos \theta_{12}$ |
|-----|-----|-----|-----|-----|-----|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1   | 1   | 0   | 0   | 0   | 0   | 0   | -1.000          | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           |
| 2   | 1   | 0   | 0   | 0   | 0   | 0   | 0.000           | -1.000          | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           |
| 3   | 1   | 0   | 0   | 0   | 0   | 0   | 0.000           | 0.000           | -1.000          | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           |
| 4   | 1   | 0   | 0   | 0   | 0   | 0   | 0.000           | 0.000           | 0.000           | -1.000          | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           |

Table 3. 33 cosines calculated to be negative with $0 < B < 2 - 10$

<table>
<thead>
<tr>
<th>$i$</th>
<th>$m$</th>
<th>$n$</th>
<th>$p$</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
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<th>$\cos \theta_2$</th>
<th>$\cos \theta_3$</th>
<th>$\cos \theta_4$</th>
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<th>$\cos \theta_7$</th>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
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<td>0</td>
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<td>-1.000</td>
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<td>0.000</td>
<td>0.000</td>
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<td>0</td>
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<td>0</td>
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<td>0.000</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Table 4. 25 cosines calculated in the middle range with $0 < B < 2 - 10$

| $i$ | $m$ | $n$ | $p$ | $x$ | $y$ | $z$ | $\cos \theta_1$ | $\cos \theta_2$ | $\cos \theta_3$ | $\cos \theta_4$ | $\cos \theta_5$ | $\cos \theta_6$ | $\cos \theta_7$ | $\cos \theta_8$ | $\cos \theta_9$ | $\cos \theta_{10}$ | $\cos \theta_{11}$ |
|-----|-----|-----|-----|-----|-----|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1   | 1   | 0   | 0   | 0   | 0   | 0   | -1.000          | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           |
| 2   | 1   | 0   | 0   | 0   | 0   | 0   | 0.000           | -1.000          | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           |
| 3   | 1   | 0   | 0   | 0   | 0   | 0   | 0.000           | 0.000           | -1.000          | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           |
| 4   | 1   | 0   | 0   | 0   | 0   | 0   | 0.000           | 0.000           | 0.000           | -1.000          | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           | 0.000           |

Table 5. Cosines calculated to be non-positive with $0 < B < 2 - 10$
Table 5. Average error and average magnitude of the error in calculated cosines taken from Tables 2–4

|          | Average error, \(\langle \Delta \cos \rangle\) | Average magnitude of the error, \(\langle |\Delta \cos| \rangle\) | Number of contributors to the average |
|----------|---------------------------------------------|-------------------------------------------------|-------------------------------------|
| From Table 2 | +0.0129                                    | 0.0661                                          | 35                                   |
| From Table 3 | -0.3620                                    | 0.3894                                          | 33                                   |
| From Table 4 | -0.2982                                    | 0.5271                                          | 25                                   |

quantitative agreement is poor. Nevertheless, because the estimates tend to be consistently too large, i.e. not sufficiently negative, it is clear that rescaling the calculated values by an empirically determined numerical factor will bring the calculated values of these cosines into acceptable agreement with the true values. It is conjectured that the bias shown by Table 3 arises from the excessive overlap in the Patterson function which causes a larger number of extremely negative cosines to occur than predicted by the theory (which assumes no Patterson overlap). A measure of the degree of Patterson overlap is given by comparison of the values of the two parameters,

\[
\langle |E_{kl}|^2 - 1 \rangle_k \simeq 1.3, \quad \langle |E_{kl}|^2 - 1 \rangle_k \simeq 4.6, \quad (7.2)
\]

with the theoretical values of 1 and 2 respectively when no overlap is present (Hauptman, 1964). Finally, Tables 4 and 5 show that those cosines calculated to be in the middle range (0.00 to +0.70) are in poor agreement with the true values, and it is not clear that the initially calculated values can be brought into acceptable agreement with the true values in any simple way. The poor agreement between calculated and true values for these cosines is undoubtedly a consequence, at least in part, of the relatively large associated variance.

8. Concluding remarks

In this paper the probabilistic theory of the cosine invariants \(\cos (\phi_1 + \phi_m + \phi_n + \phi_p)\) has been initiated. The theory leads to estimates for these cosines in terms of the seven magnitudes \(|E_1|, |E_m|, |E_n|, |E_p|, |E_{1+m}|, |E_{1+n}|, |E_{1+p}|\). On the basis of preliminary calculations it appears that the cosines calculated to be most positive serve effectively to identify those cosines which are in fact most positive, those calculated to be negative effectively identify the cosines which are in fact negative, but those calculated to be in the middle range (0.00 to 0.70) are not reliable indicators of the true values.

Further developments along the following lines are suggested: Derive improved distributions which take into account higher-order terms in \(1/N\) and whatever overlap in the Patterson may be present. Derive conditional distributions of two phases from joint probability distributions of four or more structure factors in order to obtain estimates of the cosines dependent on more than seven magnitudes. It is anticipated that more accurate distributions, dependent as well on many magnitudes, will surely lead to improved estimates for the cosine invariants.

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References