

room-temperature values are not in such good agreement; the difference between the two model values is 8–11%. This is not surprising since both models give comparable fits to the 80°K dispersion curves but at 300°K there are so few experimental points that one cannot make the same statement. Consequently one may expect corresponding discrepancies between the eigendata generated by the two models. Calculated values of $\langle U_K^2 \rangle$ for the cesium halides are also shown in Table 2 but shell model results are not available for these crystals, thus no comparison is possible.

In Table 3 the computed B_K values are compared with the values derived from the measurements of the recoilless fraction for the Cs^+ ion in the cesium halides at 4.2°K and for the I^- ion in RbI and CsI at 80°K. The computed values of B_K for the I^- ion agree with the measured values within the experimental error. The computed and measured values for the Cs^+ ion are in agreement to within 3 or 4%. The experimental uncertainties are quoted as being less than 2% in all cases. It is possible that better agreement could be obtained for the Cs^+ ion if the eigendata used in this work were derived using 4.2°K input data in the lattice-dynamical calculations.

The calculated B_K values and those measured by X-ray diffraction for CsCl , CsBr , CsI , and RbCl at 300°K are also shown in Table 3. The computed and measured results agree within the experimental uncertainty for all the ions except for the Cl^- ion in RbCl , the Cs^+ ion in CsCl , and the Br^- ion in RbBr where the difference between the theoretical and experimental values is 10–12%. The computed room-temperature data should not be taken too seriously since no account has been taken of anharmonic effects.

The experimental uncertainty in the X-ray measurements is also generally high.

In conclusion we can say that the computed results based on the DD models are generally in close agreement with the measured results. To obtain better agreement one should include anharmonic effects in the calculations. It would also be desirable to see measurements of B_K made as a function of temperature.

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A Probabilistic Theory in $P\bar{1}$ of the invariant $E_h E_k E_l E_{h+k+l}$

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Some joint probability distributions are studied in order to derive an estimate of the probability that the sign of the invariant $E_h E_k E_l E_{h+k+l}$ is positive. It is shown that this probability depends chiefly on the seven magnitudes $|E_h|$, $|E_k|$, $|E_l|$, $|E_{h+k+l}|$, $|E_{h+k}|$, $|E_{h+l}|$, $|E_{k+l}|$, and may be larger as well as smaller than $\frac{1}{2}$.

Introduction

Schenk (1973a) has derived from semi-empirical observations a useful condition for strengthening the reliability of the relation

$$\varphi_h + \varphi_k + \varphi_l - \varphi_{h+k+l} \approx 0. \quad (1)$$

A weight E_4 which depends on $|E_{h+k}|$, $|E_{h+l}|$, $|E_{k+l}|$, was introduced for (1),

$$E_4 = N^{-1} |E_h E_k E_l E_{h+k+l}| \left\{ 1 + \frac{|E_{h+k}| + |E_{h+l}| + |E_{k+l}|}{E_{000}} \right\}. \quad (2)$$

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

$$\cos(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{-\mathbf{h}-\mathbf{k}-\mathbf{l}}) = -\frac{I_1(B)}{I_0(B)}, \quad (3)$$

with $B = 2N^{-1}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{-\mathbf{h}-\mathbf{k}-\mathbf{l}}|$.

For the special case $\mathbf{h}=\mathbf{k}$ (3) reduces, after re-indexing, to

$$2\varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}+\mathbf{k}} + \varphi_{-\mathbf{h}-\mathbf{k}} = \pi. \quad (4)$$

This relation has been tested in $P\bar{1}$ by Schenk & De Jong (1973), and by Schenk (1973b) in $P1$, on the basis of criteria motivated by the Harker-Kasper inequalities. The general theory of the invariants ($2\varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}+\mathbf{k}} + \varphi_{-\mathbf{h}-\mathbf{k}}$) in $P1$ and $P\bar{1}$ has been given (Giacovazzo, 1974a, b) from joint-probability distribution functions. In a recent paper Schenk (1974) has explored in the space group $P\bar{1}$ the reliability of the negative-quartet relations as a function of B and for different limit values of

$$m = (|E_{\mathbf{h}+\mathbf{k}}| + |E_{\mathbf{h}+\mathbf{l}}| + |E_{\mathbf{k}+\mathbf{l}}|)/3. \quad (5)$$

A probabilistic theory in $P1$ of the cosine invariant $\cos(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{-\mathbf{h}-\mathbf{k}-\mathbf{l}})$ nevertheless has been given more recently by Hauptman (1974b). This theory leads to expected values of the cosine lying between -1 and $+1$. In particular, the estimate of $\cos(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{-\mathbf{h}-\mathbf{k}-\mathbf{l}})$ tends to -1 when B is large and $|E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{h}+\mathbf{l}}|, |E_{\mathbf{k}+\mathbf{l}}|$ are sufficiently small.

In this paper a general probabilistic theory of the invariant $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ will be described in $P\bar{1}$. The mathematical approach follows that used by Giacovazzo (1974a) for deriving the distribution function of ($2\varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}+\mathbf{k}} + \varphi_{-\mathbf{h}-\mathbf{k}}$) in $P\bar{1}$.

The joint probability distribution $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}}, E_{\mathbf{h}+\mathbf{k}}, E_{\mathbf{h}+\mathbf{l}}, E_{\mathbf{k}+\mathbf{l}}, E_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$

For convenience we introduce the abbreviation

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

By generalizing Klug's (1958) mathematical terminology, we derive the characteristic function (Giacovazzo, 1974c)

$$C(u_1, u_2, u_3, \dots, u_7) = \exp\left\{-\frac{1}{2}(u_1^2 + u_2^2 + \dots + u_7^2)\right\} \\ \times \left\{1 + S_3/t^{3/2} + (S_4/t^2 + S_3^2/2t^3) \right. \\ \left. + (S_5/t^{5/2} + S_3S_4/t^{7/2} + S_3^3/6t^{9/2}) \right. \\ \left. + \left(\frac{S_6}{t^3} + \frac{S_4^2}{2t^4} + \frac{S_3S_5}{t^4} + \frac{1}{2}\frac{S_3^2S_4}{t^5} + \frac{1}{24}\frac{S_3^4}{t^6}\right) + \dots\right\} \quad (6)$$

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

$$S_\nu = t \sum_{r+s+\dots+w=\nu} \frac{\lambda_{rs\dots w}}{r!s!\dots w!} (iu_1)^r (iu_2)^s \dots (iu_7)^w$$

and

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

$K_{rs\dots w}$ are the cumulants of the distribution and m is the order of the space group ($m=2$ in $P\bar{1}$). After some calculations we find

$$S_3/t^{3/2} = \frac{1}{\sqrt{N}} \left\{ (iu_1)(iu_2)(iu_4) + (iu_1)(iu_3)(iu_5) \right. \\ \left. + (iu_2)(iu_3)(iu_6) + (iu_1)(iu_6)(iu_7) \right. \\ \left. + (iu_2)(iu_5)(iu_7) + (iu_3)(iu_4)(iu_7) \right\}, \\ S_4/t^2 = \frac{2}{N} \left\{ -\frac{3}{2} \left[\frac{(iu_1)^4}{4!} + \dots + \frac{(iu_7)^4}{4!} \right] \right. \\ \left. + \frac{1}{2} [(iu_1)(iu_2)(iu_3)(iu_7) \right. \\ \left. + (iu_1)(iu_2)(iu_5)(iu_6) + (iu_1)(iu_3)(iu_4)(iu_6) \right. \\ \left. + (iu_2)(iu_3)(iu_4)(iu_5) + (iu_1)(iu_4)(iu_5)(iu_7) \right. \\ \left. + (iu_2)(iu_4)(iu_6)(iu_7) + (iu_3)(iu_5)(iu_6)(iu_7)] \right\}, \\ S_5/t^{5/2} = \frac{1}{2N\sqrt{N}} \left\{ -[(iu_1)^3(iu_2)(iu_4) + (iu_1)(iu_2)^3(iu_4) \right. \\ \left. + (iu_1)(iu_2)(iu_4)^3 \right. \\ \left. + (iu_1)^3(iu_3)(iu_5) + \text{cycl.} \right. \\ \left. + (iu_2)^3(iu_3)(iu_6) + \text{cycl.} \right. \\ \left. + (iu_1)^3(iu_6)(iu_7) + \text{cycl.} \right. \\ \left. + (iu_2)^3(iu_5)(iu_7) + \text{cycl.} \dots \right] \\ \left. + [(iu_1)^2(iu_4)(iu_5)(iu_6) + (iu_2)^2(iu_4)(iu_5)(iu_6) \right. \\ \left. + (iu_3)^2(iu_4)(iu_5)(iu_6) + (iu_4)(iu_5)(iu_6)(iu_7)^2] \right\}.$$

The probability distribution function is found by taking the Fourier transform of (6). We obtain, correct up to and including terms of order $N^{-3/2}$,

$$P(E_1, E_2, \dots, E_7) = \frac{1}{(2\pi)^{7/2}} \exp\left[-\frac{1}{2}(E_1^2 + E_2^2 + \dots + E_7^2)\right] \\ \times \left\{1 + \frac{1}{\sqrt{N}} [E_1E_2E_4 + E_1E_3E_5 \right. \\ \left. + E_2E_3E_6 + E_1E_6E_7 + E_2E_5E_7 + E_3E_4E_7] \right. \\ \left. + \frac{1}{8N} [-H_4(E_1) - \dots - H_4(E_7)] \right\}$$

$$\begin{aligned}
& + 8E_1 E_2 E_3 E_7 + 8E_1 E_2 E_5 E_6 \\
& + 8E_1 E_3 E_4 E_6 + 8E_2 E_3 E_4 E_5 \\
& + 8E_1 E_4 E_5 E_7 + 8E_2 E_4 E_6 E_7 + 8E_3 E_5 E_6 E_7 \\
& + \frac{1}{2N} [(E_1^2 - 1)(E_2^2 - 1)(E_4^2 - 1) \\
& + (E_1^2 - 1)(E_3^2 - 1)(E_5^2 - 1) \\
& + (E_2^2 - 1)(E_3^2 - 1)(E_6^2 - 1) \\
& + (E_1^2 - 1)(E_6^2 - 1)(E_7^2 - 1) \\
& + (E_2^2 - 1)(E_5^2 - 1)(E_7^2 - 1) \\
& + (E_3^2 - 1)(E_4^2 - 1)(E_7^2 - 1) \\
& + 2(E_1^2 - 1)E_2 E_3 E_4 E_5 + 2E_1(E_2^2 - 1)E_3 E_4 E_6 \\
& + 2(E_1^2 - 1)E_2 E_4 E_6 E_7 + 2E_1(E_2^2 - 1)E_4 E_5 E_7 \\
& + 2E_1 E_2 E_3(E_4^2 - 1)E_7 + 2E_1 E_2(E_3^2 - 1)E_5 E_6 \\
& + 2(E_1^2 - 1)E_3 E_5 E_6 E_7 + 2E_1 E_2 E_3(E_5^2 - 1)E_7 \\
& + 2E_1(E_3^2 - 1)E_4 E_5 E_7 + 2E_1 E_2 E_3(E_6^2 - 1)E_7 \\
& + 2(E_2^2 - 1)E_3 E_5 E_6 E_7 + 2E_2(E_3^2 - 1)E_4 E_6 E_7 \\
& + 2E_1 E_2 E_5 E_6(E_7^2 - 1) + 2E_1 E_3 E_4 E_6(E_7^2 - 1) \\
& + 2E_2 E_3 E_4 E_5(E_7^2 - 1)] \\
& + \frac{1}{2N\sqrt{N}} [-H_3(E_1)E_2 E_4 - H_3(E_1)E_3 E_5 \\
& - H_3(E_2)E_3 E_6 - H_3(E_1)E_6 E_7 \\
& - H_3(E_2)E_5 E_7 - H_3(E_3)E_4 E_7 - \text{cycl.} \dots \\
& + E_4 E_5 E_6(E_1^2 + E_2^2 + E_3^2 + E_7^2 - 4)] \\
& + \frac{1}{N\sqrt{N}} [-\frac{1}{8}H_5(E_1)E_2 E_4 - \frac{1}{8}H_5(E_1)E_3 E_5 \\
& - \frac{1}{8}H_4(E_1)E_2 E_3 E_6 - \frac{1}{8}H_5(E_1)E_6 E_7 \\
& - \frac{1}{8}H_4(E_1)E_2 E_5 E_7 - \frac{1}{8}H_4(E_1)E_3 E_4 E_7 \\
& + E_1 H_5(E_2)E_4 + \dots \\
& + \frac{1}{N\sqrt{N}} E_4 E_5 E_6 [(E_1^2 - 1)(E_2^2 - 1) \\
& + (E_1^2 - 1)(E_3^2 - 1) + (E_1^2 - 1)(E_7^2 - 1) \\
& + (E_2^2 - 1)(E_3^2 - 1) + (E_2^2 - 1)(E_7^2 - 1) \\
& + (E_3^2 - 1)(E_7^2 - 1) + 6E_1 E_2 E_3 E_7] \\
& + \frac{1}{6N\sqrt{N}} [H_3(E_1)H_3(E_2)H_3(E_4) \\
& + H_3(E_1)H_3(E_3)H_3(E_5) + \dots \\
& + H_3(E_3)H_3(E_4)H_3(E_7) \\
& + 3H_3(E_1)(E_2^2 - 1)E_3(E_4^2 - 1)E_5 \\
& + 3(E_1^2 - 1)H_3(E_2)E_3(E_4^2 - 1)E_6 \\
& + 3H_3(E_1)(E_2^2 - 1)(E_4^2 - 1)E_6 E_7 \\
& + 3(E_1^2 - 1)H_3(E_2)(E_4^2 - 1)E_5 E_7 \\
& + 3(E_1^2 - 1)(E_2^2 - 1)E_3 H_3(E_4)E_7 + \dots
\end{aligned}$$

$$\begin{aligned}
& + \frac{1}{N\sqrt{N}} E_4 E_5 E_6 \\
& \times [(E_1^2 - 1)(E_2^2 - 1)(E_3^2 - 1) \\
& + (E_1^2 - 1)(E_2^2 - 1)(E_7^2 - 1) \\
& + (E_1^2 - 1)(E_3^2 - 1)(E_7^2 - 1) \\
& + (E_2^2 - 1)(E_3^2 - 1)(E_7^2 - 1) \\
& + E_1 E_2 E_3 H_3(E_7) + E_1 E_2 H_3(E_3)E_7 \\
& + E_1 H_3(E_2)E_3 E_7 + H_3(E_1)E_2 E_3 E_7 + \dots] \}. \quad (7)
\end{aligned}$$

H_ν is the Hermite polynomial of the ν th order defined by

$$H_\nu(x) = (-1)^\nu \exp(\frac{1}{2}x^2) \frac{d^\nu}{dx^\nu} \exp[-\frac{1}{2}x^2].$$

Some terms not essential to our aim are omitted in (7). The conditional joint probability distribution $P(E_1, E_2, E_3, E_7 | E_4, E_5, E_6)$ is defined by

$$\begin{aligned}
& P(E_1, E_2, E_3, E_7 | E_4, E_5, E_6) \\
& = \frac{P(E_1, E_2, E_3, E_4, E_5, E_6, E_7)}{\int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} P(E_1, E_2, E_3, E_4, E_5, E_6, E_7) dE_1 dE_2 dE_3 dE_7} \quad (8)
\end{aligned}$$

The denominator of (8), after some calculation, equals

$$\begin{aligned}
& \frac{1}{(2\pi)^{3/2}} \exp[-\frac{1}{2}(E_4^2 + E_5^2 + E_6^2)] \\
& \times \left\{ 1 - \frac{1}{8N} [H_4(E_4) + H_4(E_5) + H_4(E_6)] \right\}. \quad (9)
\end{aligned}$$

The conditional expected value $\langle E_1 E_2 E_3 E_7 | E_4, E_5, E_6 \rangle$ is defined by

$$\begin{aligned}
& \langle E_1 E_2 E_3 E_7 | E_4, E_5, E_6 \rangle = \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \\
& \times E_1 E_2 E_3 E_7 P(E_1, E_2, E_3, E_7 | E_4, E_5, E_6) dE_1 dE_2 dE_3 dE_7.
\end{aligned}$$

From (8) and (9) we obtain

$$\begin{aligned}
& \langle E_1 E_2 E_3 E_7 | E_4, E_5, E_6 \rangle \\
& = \frac{1}{(2\pi)^2} \left\{ \frac{1}{1 - [H_4(E_4) + H_4(E_5) + H_4(E_6)]/8N} \right\} \\
& \times \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \exp[-\frac{1}{2}(E_1^2 + E_2^2 + E_3^2 + E_7^2)] \\
& \times \frac{1}{N} \left\{ E_1^2 E_2^2 E_3^2 E_7^2 + E_1^2 E_2^2 E_3^2 E_7^2 \right. \\
& \times [(E_4^2 - 1) + (E_5^2 - 1) + (E_6^2 - 1)]
\end{aligned}$$

$$\begin{aligned}
 & + \frac{6}{\sqrt{N}} E_1^2 E_2^2 E_3^2 E_7^2 E_4 E_5 E_6 + \frac{1}{\sqrt{N}} [E_1^2 E_2^2 E_3^2 (E_7^4 - 3E_7^2) \\
 & + E_1^2 E_2^2 (E_3^4 - 3E_3^2) E_7^2 + E_1^2 (E_2^4 - 3E_2^2) E_3^2 E_7^2 \\
 & + (E_1^4 - 3E_1^2) E_2^2 E_3^2 E_7^2] dE_1 dE_2 dE_3 dE_7 \\
 & = \frac{1}{\{1 - [H_4(E_4) + H_4(E_5) + H_4(E_6)]/8N\}} \\
 & \times \frac{1}{N} \left\{ E_4^2 + E_5^2 + E_6^2 - 2 + \frac{6}{\sqrt{N}} E_4 E_5 E_6 \right\}. \quad (10)
 \end{aligned}$$

$$P_+ = \frac{1}{2} + \frac{1}{2} \tanh \left\{ \frac{1}{N} |E_1 E_2 E_3 E_7| \times \frac{E_4^2 + E_5^2 + E_6^2 - 2 + 6E_4 E_5 E_6 / \sqrt{N}}{1 - [H_4(E_4) + H_4(E_5) + H_4(E_6)]/8N + 4[E_4^2 + E_5^2 + E_6^2 - 3]/N + 60E_4 E_5 E_6 / N \sqrt{N}} \right\}. \quad (11)$$

Similarly:

$$\begin{aligned}
 & \langle E_1^2 E_2^2 E_3^2 E_7^2 | E_4, E_5, E_6 \rangle \\
 & = \frac{1}{(2\pi)^2} \times \frac{1}{1 - [H_4(E_4) + H_4(E_5) + H_4(E_6)]/8N} \\
 & \times \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} E_1^2 E_2^2 E_3^2 E_7^2 \\
 & \times \exp [-(E_1^2 + E_2^2 + E_3^2 + E_7^2)/2] \\
 & \times \left\{ 1 - \frac{1}{8N} [H_4(E_1) + \dots + H_4(E_7)] \right. \\
 & + \frac{1}{2N} [H_2(E_1)H_2(E_2)H_2(E_4) \\
 & + H_2(E_1)H_2(E_3)H_2(E_5) + H_2(E_2)H_2(E_3)H_2(E_6) \\
 & + H_2(E_1)H_2(E_6)H_2(E_7) + H_2(E_2)H_2(E_5)H_2(E_7) \\
 & + H_2(E_3)H_2(E_4)H_2(E_7)] \\
 & + \frac{1}{2N\sqrt{N}} [H_2(E_1) + H_2(E_2) \\
 & + H_2(E_3) + H_2(E_7)]E_4 E_5 E_6 \\
 & + \frac{1}{N\sqrt{N}} [H_2(E_1)H_2(E_2) + H_2(E_1)H_2(E_3) \\
 & + H_2(E_1)H_2(E_7) + H_2(E_2)H_2(E_3) \\
 & + H_2(E_2)H_2(E_7) + H_2(E_3)H_2(E_7)]E_4 E_5 E_6 \\
 & + \frac{1}{N\sqrt{N}} [H_2(E_1)H_2(E_2)H_2(E_3) \\
 & + H_2(E_1)H_2(E_2)H_2(E_7) + H_2(E_1)H_2(E_3)H_2(E_7) \\
 & + H_2(E_2)H_2(E_3)H_2(E_7)]E_4 E_5 E_6 \left. \right\} dE_1 dE_2 dE_3 dE_7 \\
 & \simeq \frac{1}{1 - [H_4(E_4) + H_4(E_5) + H_4(E_6)]/8N} \\
 & \times \left\{ 1 - \frac{1}{8N} [H_4(E_4) + H_4(E_5) + H_4(E_6)] \right. \\
 & + \frac{4}{N} [E_4^2 + E_5^2 + E_6^2 - 3] + \frac{60}{N\sqrt{N}} E_4 E_5 E_6 \left. \right\}.
 \end{aligned}$$

We may expand the conditional probability distribution of the random variable $R = E_1 E_2 E_3 E_7$ in a Gram-Charlier series (Cramér, 1951): we obtain

$$P(R|E_4, E_5, E_6) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left[-\frac{(R - \langle R \rangle)^2}{2\sigma^2} \right] + \dots$$

where $\langle R \rangle$ is given by (10), and

$$\sigma^2 = \langle E_1^2 E_2^2 E_3^2 E_7^2 | E_4, E_5, E_6 \rangle - \langle E_1 E_2 E_3 E_7 | E_4, E_5, E_6 \rangle^2.$$

$$\text{As } P_+ = \left(\frac{P_-}{P_+} + 1 \right)^{-1},$$

we find

When N is large enough, (11) tells us that the product $E_1 E_2 E_3 E_7$ is probably positive when $E_4^2 + E_5^2 + E_6^2 - 2 > 0$, probably negative when $E_4^2 + E_5^2 + E_6^2 < 2$. The character of positivity or negativity is strengthened by large values of $|E_1 E_2 E_3 E_7|$.

In order to reduce computing time, a simplified form of (11) may be suggested. In Fig. 1 we have plotted the curves of $H_4(E)$ and $32(E^2 - 1)$. H_4 is slightly negative or positive in the range (0-2.5) and reaches notable values for $|E| > 3$. The contribution of $32(E^2 - 1)$ is always predominant over that of H_4 in the range of the usually observed $|E|$ values, with the exception of the range (0.9-1.1). In this last range, nevertheless, we may safely neglect $[-H_4(E) + 32(E^2 - 1)]/8N$ in comparison with unity.

In conclusion, when all $|E|$ values are in the range (0-3.5), (11) may be approximated without large errors, by

$$\begin{aligned}
 & P_+ \simeq \frac{1}{2} + \frac{1}{2} \tanh \left\{ \frac{1}{N} |E_1 E_2 E_3 E_7| \right. \\
 & \times \left. \frac{E_4^2 + E_5^2 + E_6^2 - 2 + 6E_4 E_5 E_6 / \sqrt{N}}{1 + 4[E_4^2 + E_5^2 + E_6^2 - 3]/N + 60E_4 E_5 E_6 / N \sqrt{N}} \right\}. \quad (12)
 \end{aligned}$$

The role of the product $E_4 E_5 E_6$

We have carried the expansion (7) as far as terms in $1/N^{3/2}$ so that we might gain some insight into the

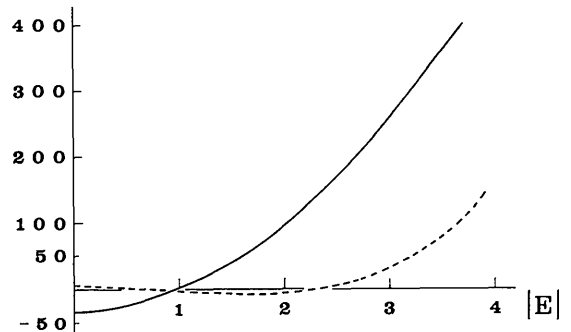


Fig. 1. The full line represents $32H_2(E)$, the broken line $H_4(E)$.

importance of the various terms in practical calculations of P_+ .

It is evident from (11) that, if $|E_{4,5,6}| = |E_4 E_5 E_6|$ is very small, the probability function P_+ reduces to

$$P_+ \simeq \frac{1}{2} + \frac{1}{2} \tanh \frac{1}{N} |E_1 E_2 E_3 E_7| \times \frac{E_4^2 + E_5^2 + E_6^2 - 2}{1 - [H_4(E_4) + H_4(E_5) + H_4(E_6)]/8N + 4[E_4^2 + E_5^2 + E_6^2 - 3]/N} \quad (13)$$

If $|E_{4,5,6}|$ is not small, (13) may be a poor approximation of (11). As the sign of $E_{4,5,6}$ is generally unknown, a comparative study of (11) and (13) is worthwhile. It seems useful, in particular, to look for the conditions in which the sign of $E_{4,5,6}$ is not critical, in order to assign a correct value of P_+ . It would be necessary to this end to compare the values of (11) and (13) in the allowed region of variation of E_4, E_5, E_6 . This is, however, very tedious and we shall not give the calculations here. Useful information, nevertheless, may be derived by a simplified treatment. We shall confine ourselves to the computation of the values $N\langle R \rangle/\sigma^2$, as defined in (11) and (13), in the particular case where $|E_4| = |E_5| = |E_6|$. The results for $N=30$ and $N=60$ are plotted in Figs. 2 and 3: it is a reasonable assumption that the trend of these results may carry over to cases in which E_4, E_5, E_6 adopt any values.

Inspection of Figs. 2 and 3 suggests the following conclusions:

(a) Equation (11) is approximately symmetric in $E_{4,5,6}$ in a range around zero. This range becomes larger as N increases: in particular, when $N=30$ the pseudo-symmetry is verified for $|E_{4,5,6}| < 3.4$, when $N=60$ for $|E_{4,5,6}| < 8$. In other words, in these ranges the value of P_+ is independent of the sign of $E_{4,5,6}$: also (11) is well approximated by (13).

(b) At large values of $|E_{4,5,6}|$ (11) is strongly asymmetric. In particular, for positive values of $E_{4,5,6}$ the probability that the invariant is positive appears overestimated in (13).

(c) Equation (11) presents a discontinuity at negative values of $E_{4,5,6}$. This behaviour has no physical meaning and is due to including in (11) only terms up to $1/N^{3/2}$. In fact, we have represented the probability distribution as an asymptotic series and the actual values of the probability we obtain will be correct to the degree of approximation we choose. We should expect, therefore, that the inclusion in (11) of terms of higher order than $1/N^{3/2}$ will have the effect of enlarging the field in which (13) is pseudo-symmetric. This observation is in accordance with the fact that the discontinuity shifts to higher negative values of $E_{4,5,6}$ as N increases. The above considerations suggest that a useful formula would be

$$P_+ = \frac{1}{2} + \frac{1}{2} \tanh \frac{1}{N} |E_1 E_2 E_3 E_7| \times \frac{E_4^2 + E_5^2 + E_6^2 - 2 + 6|E_4 E_5 E_6|/\sqrt{N}}{1 - [H_4(E_4) + H_4(E_5) + H_4(E_6)]/8N + 4[E_4^2 + E_5^2 + E_6^2 - 3]/N + 60|E_4 E_5 E_6|/N\sqrt{N}} \quad (14)$$

The use of $|E_{4,5,6}|$ instead of $E_{4,5,6}$ would give some difficulty in the region in which $E_4^2 + E_5^2 + E_6^2 \simeq 2$. Although the quartets in this region are generally excluded from the procedures for phase determination,

it seems better for small $|E_{4,5,6}|$ to use (13) instead of (14). (14) seems a better approximation for large values of $|E_{4,5,6}|$ since a large percentage of products $E_4 E_5 E_6$ is positive in this range. This property may be derived from the same distribution function (7): in fact

$$P_+(E_1 E_2 E_3 E_4 E_5 E_6 E_7) \simeq \frac{1}{2} + \frac{1}{2} \tanh \frac{6}{N\sqrt{N}} \frac{|E_1 E_2 E_3 E_4 E_5 E_6 E_7|}{1 + 24/\sqrt{N}} \quad (15)$$

(15) provides the probability that $E_{1,2,\dots,7} = E_1 E_2 \dots E_7$ is positive and shows that, for large $E_{1,2,\dots,7}$ values, $E_{1,2,3,7}$ and $E_{4,5,6}$ have the same sign, which is positive from (11). (15) deserves a final consideration. The set of normalized structure factors E_1, E_2, \dots, E_7 satisfies the property $\sum_{j=1}^7 \mathbf{h}_j = 0$. (15), nevertheless, is not a particular case of the Simerska (1956) formula

$$P_+(E_1 E_2 \dots E_n) = \frac{1}{2} + \frac{1}{2} \tanh \frac{1}{N^{(n-2)/2}} |E_1 E_2 \dots E_n|$$

which would provide in our case a relation of order $N^{-5/2}$. (15) has been derived, in fact, from the product $S_3 S_4$ [the S_j are defined in (6)] which is not zero because both S_3 and S_4 include non-zero standardized cumulants. Cases similar to this are not provided by the Simerska formula, but may often result when phase relationships of high order are used. So, the sole use of the Simerska formula may be misleading in these cases, because it may lead to the neglect of stronger correlations.

The distributions

$$P(E_h, E_k, E_l, E_{h+k}, E_{h+l}, E_{k+l}, E_{h+k+l}, E_{h-k}, \dots)$$

In the preceding sections we have shown that the knowledge of $|E_{h+k}|, |E_{k+l}|, |E_{h+l}|$ may provide a good measure of the probability of the sign of $E_h E_k E_l E_{h+k+l}$. The additional knowledge of $|E_{h-k}|, |E_{h-l}|, |E_{k-l}|$ may contain further information which may be used to assign a more accurate value of P_+ .

To verify this we have studied the distribution

$$P(E_h, E_k, E_l, E_{h+k}, E_{h+l}, E_{k+l}, E_{h+k+l}, E_{h-k}),$$

and have obtained the formula ($E_8 = E_{h-k}$)

$$P_+ = \frac{1}{2} + \frac{1}{2} \tanh |E_1 E_2 E_3 E_7| \frac{\langle R \rangle}{\sigma^2}, \quad (16)$$

where

$$\begin{aligned} \langle R \rangle &= \langle E_1 E_2 E_3 E_7 | E_4, E_5, E_6, E_8 \rangle \\ &= \frac{1}{N} [E_4^2 + E_5^2 + E_6^2 - 2 + E_4 E_8] + \frac{6}{N\sqrt{N}} E_4 E_5 E_6 \\ &\quad + \frac{1}{N\sqrt{N}} [E_4^2 + E_5^2 + E_6^2 + E_8^2 + 2] E_5 E_6 E_8, \\ \sigma^2 &= \langle E_1^2 E_2^2 E_3^2 E_7^2 | E_4, E_5, E_6, E_8 \rangle \\ &= 1 + \frac{1}{\sqrt{N}} E_5 E_6 E_8 - \frac{1}{8N} [H_4(E_4) + H_4(E_5) \end{aligned}$$

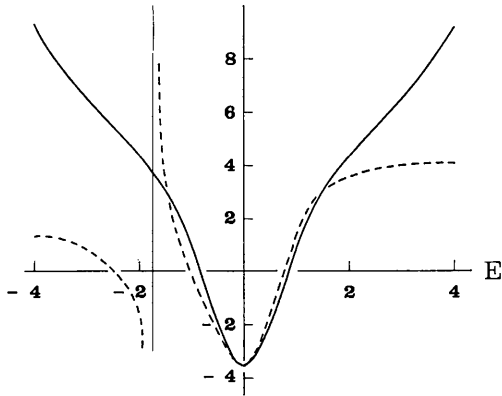


Fig. 2. The full line represents $N\langle R \rangle/\sigma^2$ as defined in (13) in the case in which $|E_{h+k}| = |E_{h+1}| = |E_{k+1}|$ and $N=30$. Under these conditions the broken line is the plot of $N\langle R \rangle/\sigma^2$ as defined in (11).

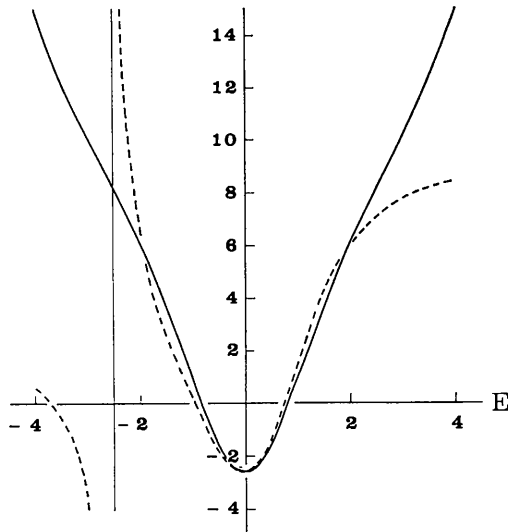


Fig. 3. As in Fig. 2, with $N=60$.

$$\begin{aligned} &+ H_4(E_6) + H_4(E_8)] + \frac{4}{N} [E_4^2 + E_5^2 + E_6^2 - 3 + E_4 E_8] \\ &+ \frac{2}{N} (E_8^2 - 1) + \frac{1}{2N} (E_5^2 - 1)(E_6^2 - 1)(E_8^2 - 1) \\ &- \frac{1}{8N\sqrt{N}} E_5 E_6 E_8 [H_4(E_4) + H_4(E_5) + H_4(E_6) \\ &+ H_4(E_8)] + \frac{E_4 E_5 E_6}{N\sqrt{N}} (56 + 4E_8^2) \\ &+ 4 \frac{E_5 E_6 E_8}{N\sqrt{N}} [E_4^2 + E_5^2 + E_6^2 - 6 + \frac{1}{2}(E_8^2 - 1)] \\ &+ \frac{1}{6N\sqrt{N}} H_3(E_5) H_3(E_6) H_3(E_8) \simeq 1 + \frac{1}{N} E_5 E_6 E_8 \\ &+ \frac{1}{4} [E_4^2 + E_5^2 + E_6^2 - 3 + E_4 E_8 + \frac{1}{2}(E_8^2 - 1)] \\ &+ \frac{1}{2N} (E_5^2 - 1)(E_6^2 - 1)(E_8^2 - 1) \\ &+ \frac{E_4 E_5 E_6}{N\sqrt{N}} (56 + 4E_8^2) \\ &+ 4 \frac{E_4 E_5 E_6}{N\sqrt{N}} [E_4^2 + E_5^2 + E_6^2 - 6 + \frac{1}{2}(E_8^2 - 1)] \\ &+ \frac{1}{6N\sqrt{N}} H_3(E_5) H_3(E_6) H_3(E_8). \end{aligned}$$

The reader will be able to derive an approximate formula for the case in which $|E_{h-k}|, |E_{h-1}|, |E_{k-1}|$ are all known. (16) tells us that the value of P_+ depends on the signs of the products $E_{4,5,6}$ and $E_{5,6,8}$. These signs are *a priori* unknown but, statistically, are prevalently positive. To show the general character of (16) we have plotted in Fig. 4 the values of $N\langle R \rangle/\sigma^2$ in the range (0-4) for $N=30,60$ (full lines). For the sake of simplicity we have supposed $|E_4| = |E_5| = |E_6| = |E_8|$, which may be a rough approximation of real cases. The curves reveal no marked deviations compared with the analogous curves calculated for (11) (broken lines). In particular the probability levels in (11) and (16) are reasonably close. We can conclude that the sign of $E_h E_k E_l E_{h+k+l}$ depends strongly on $|E_{h+k}|, |E_{h+1}|, |E_{k+1}|$, while the dependence on $E_{h-k}, E_{h-1}, E_{k-1}$ seems weak. These normalized structure factors, therefore, may be neglected in the direct procedures which use quartet relationships without compromising the accuracy of the results.

Reduced distribution function

Not all $|E_j|$ factors, $j=1, \dots, 7$ are necessarily known. In this part of paper, therefore, we wish to consider some simplified distributions in which only six or five E_j factors are present in the set of measured reflexions. It is expected, in these cases, that some useful information may be derived (Schenk, 1974).

Let us suppose that only two of the three reflexions $h+k, h+l, k+l$ are present in the set. By the same

mathematical approach described above we derive, from the marginal distribution function

$$P(E_h, E_k, E_l, E_{h+k}, E_{h+1}, E_{h+k+1}),$$

the relationship

$$P'_+ \simeq \frac{1}{2} + \frac{1}{2} \tanh \frac{1}{N} |E_h E_k E_l E_{h+k+1}| \times \frac{(E_{h+k}^2 + E_{h+1}^2 - 1)}{1 + 4[E_{h+k}^2 + E_{h+1}^2 - 2]/N}. \quad (17)$$

Equation (17), correct up to $N^{-3/2}$ order, tells us that $E_h E_k E_l E_{h+k+1}$ is probably positive if $E_{h+k}^2 + E_{h+1}^2 > 1$, probably negative otherwise. We note explicitly that, if $E_{h+k}^2 + E_{h+1}^2 > 2$, the knowledge of $|E_{k+1}|$ cannot transform a quartet defined positive by (17) into one defined negative by (14). If only one of the three reflexions $h+k, h+1, k+1$ is present in the set, from the marginal distribution $P(E_h, E_k, E_l, E_{h+k}, E_{h+k+1})$, we obtain

$$P''_+ \simeq \frac{1}{2} + \frac{1}{2} \tanh \frac{1}{N} |E_h E_k E_l E_{h+k+1}| \times \frac{1}{1 + 4(E_{h+k}^2 - 1)/N} \cdot E_{h+k}^2. \quad (18)$$

(18) may be useful to strengthen the positivity of the quartet $E_h E_k E_l E_{h+k+1}$ if $|E_{h+k}|$ is large: one cannot however derive, from the additional knowledge of the single $|E_{h+k}|$, a condition for defining a negative quartet. (18) seems, therefore, less reliable than (11) and (17).

It should perhaps be emphasized that the probability levels in (17) and (18) are not on the same scale as in (11): from an algebraic point of view the contribution of order $1/N\sqrt{N}$ in (17) and (18) equals zero. This fact could involve an overestimate of the sign probability when $|E_{h+k}|$ and $|E_{h+1}|$ in (17) or $|E_{h+k}|$ in (18) are very large. As in the automatic procedures for phase determination one may use (11) as well as (17) or (18), the situation appears to contrast with the principles usually adopted for proper weighting. We have plotted in Fig. 5 (full lines) the values of $N\langle R \rangle/\sigma^2$, as defined in (17) and (18), in the range (2-4) and for $N=30$. For the sake of simplicity we have supposed $|E_{h+k}| = |E_{h+1}|$ in (17). As we can see (17) and (18) really provide an overestimate of P_+ for large $|E_{h+k}|$ and $|E_{h+1}|$: this property is enhanced in (17). To overcome this difficulty one could suggest for quartets strongly defined positive, the formulae

$$P'_+ \simeq \frac{1}{2} + \frac{1}{2} \tanh \frac{1}{N} |E_h E_k E_l E_{h+k+1}| \times \frac{(E_{h+k}^2 + E_{h+1}^2 - 1 + 4 \cdot 8 |E_{h+k} E_{h+1}|/\sqrt{N})}{1 + 4[E_{h+k}^2 + E_{h+1}^2 - 2]/N + 48 |E_{h+k} E_{h+1}|/N\sqrt{N}}, \quad (19)$$

$$P''_+ \simeq \frac{1}{2} + \frac{1}{2} \tanh \frac{1}{N} |E_h E_k E_l E_{h+k+1}| \times \frac{E_{h+k}^2 + 3 \cdot 8 |E_{h+k}|/\sqrt{N}}{1 + 4(E_{h+k}^2 - 1)/N + 38 |E_{h+k}|/N\sqrt{N}}. \quad (20)$$

(19) and (20) are derivable from (14) by assigning in the terms of order $1/N\sqrt{N}$ the expectation value 0.8 to the unknown normalized structure factor. It is easy to show that (19) and (20) agree with (11) more than (17) and (18).

Concluding remarks

In this paper has been described in $P\bar{I}$ a probabilistic theory of the invariant $E_h E_k E_l E_{h+k+1}$. The theory leads to estimates of the invariant which may be positive or negative according to the values of $|E_{h+k}|, |E_{h+1}|, |E_{k+1}|$. On the other hand, the values of $|E_{h-k}|, |E_{h-1}|, |E_{k-1}|$ only weakly affect the sign of the

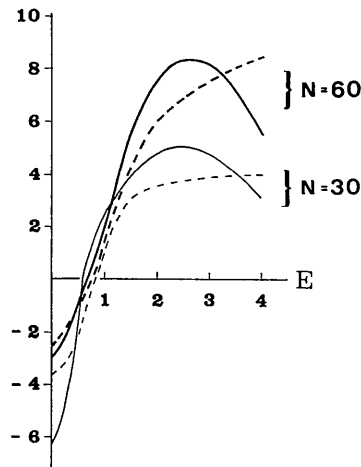


Fig. 4. Full lines and broken lines represent respectively the values of $N\langle R \rangle/\sigma^2$ as defined in (16) and in (11) in the case in which $|E_{h+k}| = |E_{h+1}| = \dots$.

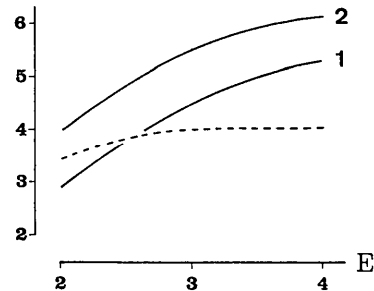


Fig. 5. Full lines 1 and 2 represent respectively $N\langle R \rangle/\sigma^2$ as defined in (18) and (17) when $N=30$. It has been supposed in (17) that $|E_{h+k}| = |E_{h+1}|$. The function $N\langle R \rangle/\sigma^2$ as defined in (11) is plotted as the broken line.

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

It would be useful to verify the conditions of validity of the formulae obtained and to test the scale of the probability levels. A positive verification of the theory here described would allow, in the direct procedures for sign determination, the use of quartet as well as triplet relationships on the same scale of reliability. A strong stimulus in this direction is the observation that the theory seems very suitable for identifying the

negative invariants $E_h E_k E_l E_{h+k+l}$. In the field of negative invariants, in fact, the terms of order $1/N^{3/2}$ are negligible in comparison with the terms of order $1/N$. These last terms involve only the magnitudes of the normalized structure factors and are unambiguous.

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On the Reliability of Different Formulations of the Quartets

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Recently derived expressions [Giacovazzo (1975). *Acta Cryst.* **A31**, 252–259] for the reliability of quartets have been tested. For the negative quartets (NQ's) the new expressions lead to an improvement compared with the empirical estimates of the NQ reliability used so far. However, the reliability of all quartets can be better estimated by means of the weights of the empirically derived strengthened quartet relation (SQR).

Introduction

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

proved to be very useful to find the correct solution out of a set of \sum_2 solutions, particularly in symmorphic space groups.

In these cases the value q of the structure invariant

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

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

$$E_4 = N^{-1} |E_H E_K E_L E_{-H-K-L}| \quad (2)$$

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