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The Joint Probability Distribution Applied to a Weak Sign Relationship in Non-Centrosymmetric Space Groups

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The probability distribution of the phase $\Phi=2\varphi_{\mathbf{h}}-\varphi_{\mathbf{h-k}}-\varphi_{\mathbf{h+k}}$ is found in $P1$. It is shown that for strong $|E_{\mathbf{h}}|$, $|E_{\mathbf{h+k}}|$, $|E_{\mathbf{h-k}}|$ and weak $|E_{\mathbf{k}}|$ structure factors, Φ is distributed around π.

1. Introduction

As is well known (Woolfson, 1961; Schenk & de Jong, 1973), from the Harker–Kasper inequalities for $P\bar{1}$,

$$(U_{\mathbf{h}}+U_{\mathbf{k}})^2\le(1+U_{\mathbf{h+k}})(1+U_{\mathbf{h-k}}),$$
$$(U_{\mathbf{h}}-U_{\mathbf{k}})^2\le(1-U_{\mathbf{h+k}})(1-U_{\mathbf{h-k}}). \qquad (1)$$

When $|U_{\mathbf{h}}|$, $|U_{\mathbf{h+k}}|$, $|U_{\mathbf{h-k}}|$ are sufficiently large and $U_{\mathbf{k}}=0$ then

$$U^2_{\mathbf{h}}>(1-|U_{\mathbf{h+k}}|)(1-|U_{\mathbf{h-k}}|),$$

and it follows that the sign relation $S(\mathbf{h+k})\simeq -S(\mathbf{h-k})$ must hold. Giacovazzo (1974*a*) has worked out a probability density function for this relationship by the mathematical device of the joint probability distribution.

In a recent short communication Schenk (1973), by a geometrical interpretation of the Harker–Kasper inequalities, suggested for non-centrosymmetric structures the relationship

$$\varphi_{\mathbf{h+k}}+\varphi_{\mathbf{h-k}}-2\varphi_{\mathbf{h}}\simeq\pi \qquad (2)$$

for strong structure factors **h**, **h+k**, **h−k** and weak **k**. This relationship can be derived from the Karle–Hauptman determinant,*

$$\begin{vmatrix} 1 & U_{\mathbf{h}} & U_{\mathbf{k}} & U_{\mathbf{h+k}} \\ U_{-\mathbf{h}} & 1 & U_{-\mathbf{h+k}} & U_{\mathbf{k}} \\ U_{-\mathbf{k}} & U_{\mathbf{h-k}} & 1 & U_{\mathbf{h}} \\ U_{-\mathbf{h-k}} & U_{-\mathbf{k}} & U_{-\mathbf{h}} & 1 \end{vmatrix}\ge 0.$$

Making $U_{\mathbf{k}}=0$ gives

$$1-2|U_{\mathbf{h}}|^2-|U_{\mathbf{h+k}}|^2-|U_{\mathbf{h-k}}|^2+|U_{\mathbf{h}}|^4+|U_{\mathbf{h+k}}|^2|U_{\mathbf{h-k}}|^2$$
$$-2|U_{\mathbf{h}}|^2|U_{\mathbf{h+k}}|\,|U_{\mathbf{h-k}}|\cos(2\varphi_{\mathbf{h}}-\varphi_{\mathbf{h-k}}-\varphi_{\mathbf{h+k}})\ge 0.$$

If the U's are sufficiently large then the cosine term must be negative and relationship (2) is therefore justified.

The aim of this paper is to determine the probability law for (2) for space group $P1$ by means of the joint probability distribution.

* Referee's suggestion.

2. Preliminary formulae

For convenience a number of formulae occurring in the theory of Bessel functions, which are used in the analysis, are given below. From Watson (1948) the following integral formulae can be found.

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

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

$$\int_0^\infty \exp(-pt^2)J_m(at)t^{m+1}\mathrm{d}t=\frac{a^m}{(2p)^{m+1}}\times\exp(-a^2/4p)\,, \qquad (5)$$

where $J_m(z)$ is the Bessel function of the first kind of order m. Also used are the relations obtained from (5) by successive differentiation of both sides with respect to p.

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

We introduce the abbreviation $E_1=R_1\exp i\varphi_1=E_{\mathbf{h}}$; $E_2=R_2\exp i\varphi_2=E_{\mathbf{k}}$; $E_3=R_3\exp i\varphi_3=E_{\mathbf{h-k}}$; $E_4=R_4\exp i\varphi_4=E_{\mathbf{h+k}}$. By generalizing Klug's (1958) mathematical terminology, we derive the characteristic function (Giacovazzo, 1974*b*)

$$C(u_1,u_2,u_3,u_4;v_1,\ldots,v_4)$$
$$\times\exp\left[-\tfrac{1}{2}\left(\frac{u_1^2}{2}+\ldots+\frac{u_4^2}{2}+\frac{v_1^2}{2}+\ldots+\frac{v_4^2}{2}\right)\right]$$
$$\times\left\{1+\frac{1}{N^{3/2}}S_3+\frac{1}{N^2}S_4+\frac{1}{2N^3}S_3^2+\ldots\right\},$$

where u_i,v_i, $i=1,\ldots,4$ are carrying variables associated respectively with A_i and B_i values ($E_i=A_i+iB_i$),

$$S_v=N\sum_{r+s+\ldots+w=v}\frac{1}{2^{v/2}}\frac{\lambda_{rs\ldots w}}{r!s!\ldots w!}\times(iu_1)^r(iu_2)^s\ldots(iv_4)^w,$$

and

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

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

The probability distribution function is found by taking the Fourier transform of (6): after two variable changes in (6),

$$u_i=\sqrt{2}u_i',\ \ v_i=\sqrt{2}v_i',\ \ i=1,\ldots,4,$$

and

$$u_i'=\varrho_i\cos\psi_i;\ \ v_i'=\varrho_i\sin\psi_i;\ \ A_i=R_i\cos\varphi_i,$$
$$B_i=R_i\sin\varphi_i,\ \ i=1,\ldots,4,$$

we obtain

$$\begin{aligned}P(R_1,\ldots,R_4,\varphi_1,\ldots,\varphi_4)&=\frac{R_1R_2R_3R_4}{(2\pi)^8}\\ &\times\int_0^\infty\ldots\int_0^\infty\int_0^{2\pi}\ldots\int_0^{2\pi}\exp\{-i[\sqrt{2}\varrho_1R_1\cos(\psi_1-\varphi_1)\\ &+\ldots+\sqrt{2}\varrho_4R_4\cos(\psi_4-\varphi_4)\}\exp[-\tfrac{1}{2}(\varrho_1^2\\ &+\varrho_2^2+\ldots+\varrho_4^2)]2^4.\Big\{1+\frac{1}{N^{3/2}}S_3'+\frac{1}{N^2}S_4'\\ &+\frac{1}{2N^3}S_3'^2+\ldots\Big\}\varrho_1\varrho_2\varrho_3\varrho_4\mathrm{d}\varrho_1\ldots\mathrm{d}\varrho_4\mathrm{d}\psi_1\ldots\mathrm{d}\psi_4,\end{aligned}\quad(7)$$

where

$$S_v'=N\sum_{r+s+\ldots+w=v}\frac{\lambda_{rs\ldots w}}{r!s!\ldots w!}(i)^{r+s+\ldots+w}$$
$$+(\varrho_1\cos\psi_1)^r(\varrho_2\cos\psi_2)^s\ldots(\varrho_4\sin\psi_4)^w.$$

Calculation for $P1$ of the standardized cumulants $\lambda_{rs\ldots w}$ gives the following expressions:

$$\begin{aligned}\frac{S_3'}{N^{3/2}}&=\frac{i^3}{\sqrt{2N}}[\varrho_1\varrho_2\varrho_3\cos(\psi_1-\psi_2-\psi_3)\\ &\qquad+\varrho_1\varrho_2\varrho_4\cos(\psi_1+\psi_2-\psi_4)],\\ \frac{S_4'}{N^2}&=\frac{1}{N}\{-\tfrac{1}{16}(\varrho_1^4+\varrho_2^4+\varrho_3^4+\varrho_4^4)\\ &+\tfrac{1}{4}[\varrho_1^2\varrho_3\varrho_4\cos2\psi_1\cos(\psi_3+\psi_4)\\ &+\varrho_2^2\varrho_3\varrho_4\cos2\psi_2\cos(\psi_3-\psi_4)]\\ &+\tfrac{1}{4}[\varrho_1^2\varrho_3\varrho_4\sin2\psi_1\sin(\psi_3+\psi_4)\\ &-\varrho_2^2\varrho_3\varrho_4\sin2\psi_2\sin(\psi_3-\psi_4)]\}.\end{aligned}$$

The integral contribution of $S_3'/N^{3/2}$ in (7) is

$$\begin{aligned}&\frac{2^4}{(2\pi)^8}\frac{i^3}{\sqrt{2N}}R_1R_2R_3R_4\\ &\times\int_0^\infty\ldots\int_0^\infty\int_0^{2\pi}\ldots\int_0^{2\pi}\exp\{-i\sqrt{2}\\ &\times[\varrho_1R_1\cos(\psi_1-\varphi_1)+\ldots\varrho_4R_4\cos(\psi_4-\varphi_4)]\}\\ &\times\exp[-\tfrac{1}{2}(\varrho_1^2+\ldots+\varrho_4^2)]\varrho_1\varrho_2\varrho_3\varrho_4\\ &\times[\varrho_1\varrho_2\varrho_3\cos(\psi_1-\psi_2-\psi_3)\\ &+\varrho_1\varrho_2\varrho_4\cos(\psi_1+\psi_2-\psi_4)]\mathrm{d}\varrho_1\mathrm{d}\varrho_2\ldots\mathrm{d}\psi_4,\end{aligned}$$

which equals, after the application of the equations (3), (4) and (5) (Karle & Hauptman, 1958)

$$\begin{aligned}&\frac{2}{\pi^4\sqrt{N}}R_1R_2R_3R_4\exp(-R_1^2-\ldots-R_4^2)\{R_1R_2R_3\\ &\times\cos(\varphi_1-\varphi_2-\varphi_3)+R_1R_2R_4\cos(\varphi_1+\varphi_2-\varphi_4)\}.\end{aligned}$$

The integral contribution of $S_3'^2/2N^3$ in (7) equals

$$\begin{aligned}&-\frac{R_1R_2R_3R_4}{(2\pi)^8}\frac{2^4}{4N}\Big\{\int_0^\infty\ldots\int_0^\infty\exp[-\tfrac{1}{2}(\varrho_1^2+\ldots+\varrho_4^2)]\\ &\times\varrho_1^3\varrho_2^3\varrho_3^3\varrho_4\mathrm{d}\varrho_1\ldots\mathrm{d}\varrho_4\\ &\times\int_0^{2\pi}\ldots\int_0^{2\pi}\exp-i[\sqrt{2}\varrho_1R_1\cos(\psi_1-\varphi_1)+\ldots\\ &+\sqrt{2}\varrho_4R_4\cos(\psi_4-\varphi_4)]\cos^2(\psi_1-\psi_2-\psi_3)\\ &\times\mathrm{d}\psi_1\ldots\mathrm{d}\psi_4+\text{anag.}\\ &+2\int_0^\infty\ldots\int_0^\infty\exp[-\tfrac{1}{2}(\varrho_1^2+\ldots+\varrho_4^2)]\\ &\times\varrho_1^3\varrho_2^3\varrho_3^2\varrho_4^2\mathrm{d}\varrho_1\ldots\mathrm{d}\varrho_4\\ &\times\int_0^{2\pi}\ldots\int_0^{2\pi}\exp-i[\sqrt{2}\varrho_1R_1\cos(\psi_1-\varphi_1)+\ldots\\ &+\sqrt{2}\varrho_4R_4\cos(\psi_4-\varphi_4)]\cos(\psi_1-\psi_2-\psi_3)\\ &\times\cos(\psi_1+\psi_2-\psi_4)\mathrm{d}\psi_1\ldots\mathrm{d}\psi_4\Big\}.\end{aligned}$$

After some calculation, this expression becomes

$$\begin{aligned}&-\frac{1}{N\pi^4}R_1R_2R_3R_4\exp(-R_1^2-\ldots-R_4^2)\\ &\times\{(1-R_1^2)(1-R_2^2)(1-R_3^2)\\ &-R_1^2R_2^2R_3^2\cos(2\varphi_12\varphi_2-2\varphi_3)\\ &+(1-R_1^2)(1-R_2^2)(1-R_4^2)\\ &-R_1^2R_2^2R_4^2\cos(2\varphi_1+2\varphi_2-2\varphi_4)\\ &+2(1-R_2^2)R_1^2R_3R_4\cos(2\varphi_1-\varphi_3-\varphi_4)\\ &+2(1-R_1^2)R_2^2R_3R_4\cos(2\varphi_2+\varphi_3-\varphi_4)\}.\end{aligned}$$

After a lengthy analysis, we obtain, by repeated application of (3), (4) and (5), the integral contribution in (7) of S_4'/N^2, which is

$$\begin{aligned}&\frac{1}{N\pi^4}R_1R_2R_3R_4\exp(-R_1^2-\ldots-R_4^2)\\ &\times[-\tfrac{1}{4}(R_1^4+\ldots+R_4^4)+R_1^2+R_2^2+R_3^2+R_4^2\\ &-2+R_1^2R_3R_4\cos2\varphi_1\cos(\varphi_3+\varphi_4)\\ &+R_2^2R_3R_4\cos2\varphi_2\cos(\varphi_3-\varphi_4)\\ &+R_1^2R_3R_4\sin2\varphi_1\sin(\varphi_3+\varphi_4)\\ &-R_2^2R_3R_4\sin2\varphi_2\sin(\varphi_3-\varphi_4)]\\ &=\frac{1}{N\pi^4}R_1R_2R_3R_4\exp(-R_1^2-\ldots-R_4^2)\end{aligned}$$

$$\times[-\tfrac{1}{4}(R_1^4+\ldots+R_4^4)+R_1^2+R_2^2+R_3^2+R_4^2 -2+R_1^2R_3R_4\cos(2\varphi_1-\varphi_3-\varphi_4) +R_2^2R_3R_4\cos(2\varphi_2+\varphi_3-\varphi_4)]\,.$$

Finally we obtain the desired probability distribution, correct up to and including terms of order N^{-1},

$$P(R_1,R_2,R_3,R_4,\varphi_1,\varphi_2,\varphi_3,\varphi_4) = \frac{1}{\pi^4}R_1R_2R_3R_4\exp[-R_1^2-R_2^2-R_3^2-R_4^2] \times\Big\{1+\frac{2}{\sqrt{N}}[R_1R_2R_3\cos(\varphi_1-\varphi_2-\varphi_3) +R_1R_2R_4\cos(\varphi_1+\varphi_2-\varphi_4)] +\frac{1}{N}[q+R_1^2R_2^2R_3^2\cos 2(\varphi_1-\varphi_2-\varphi_3) +R_1^2R_2^2R_4^2\cos 2(\varphi_1+\varphi_2-\varphi_4) +(2R_2^2-1)R_1^2R_3R_4\cos(2\varphi_1-\varphi_3-\varphi_4) +(2R_1^2-1)R_2^2R_3R_4\cos(2\varphi_2+\varphi_3-\varphi_4)]\Big\},$$

where

$$q=-4+3R_1^2+3R_2^2+2R_3^2+2R_4^2-2R_1^2R_2^2-R_2^2R_3^2 -R_1^2R_3^2-R_2^2R_4^2-R_1^2R_4^2+R_1^2R_2^2R_3^2+R_1^2R_2^2R_4^2 -\tfrac{1}{4}(R_1^4+R_2^4+R_3^4+R_4^4)\,.$$

The marginal probability density

$$P(R_1,R_2,R_3,R_4,\varphi_1,\varphi_3,\varphi_4) =\int_{-\pi}^{\pi}P(R_1,R_2,R_3,R_4,\varphi_1,\varphi_2,\varphi_3,\varphi_4)\mathrm{d}\varphi_2$$

is easily derived from (8): we obtain, by transforming in exponential form (Bertaut, 1960*a*,*b*; Karle, 1972),

$$P(R_1,R_2,R_3,R_4,\varphi_1,\varphi_3,\varphi_4) =\frac{2}{\pi^3}R_1R_2R_3R_4\exp[-R_1^2-R_2^2-R_3^2-R_4^2] \times\exp\frac{1}{N}\{q+(2R_2^2-1)R_1^2R_3R_4\cos(2\varphi_1-\varphi_3-\varphi_4)\}. \quad (9)$$

From (9) the conditional probability density $P(\Phi|R_1,R_2,R_3,R_4)$, where $\Phi=2\varphi_1-\varphi_3-\varphi_4$, is easily derived: we obtain

$$P(\Phi|R_1,R_2,R_3,R_4)=\frac{1}{2\pi I_0(S)}\exp(S\cos\Phi)\,, \quad (10)$$

where

$$S=\frac{1}{N}(2R_2^2-1)R_1^2R_3R_4\,.$$

We note explicitly that the relation (10) has the same algebraic form which corresponds to the conditional distribution of $\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}$ given

$$A=2/\sqrt{N}\,|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|$$

[Hauptman, 1972, equation (6.3)]. However, unlike A, S can be negative. If S is positive, the maximum value of P is for $\Phi=0$; for negative values of S, P attains its greatest value when $\Phi=\pi$.

There is no problem in calculating the following functions:

$$P(\cos\Phi|S)=\exp(S\cos\Phi)/[\pi I_0(S)\sin\Phi], \quad (11)$$

$$\langle\cos\Phi|S\rangle=\int_{-\pi}^{\pi}\cos\Phi P(\Phi|R_1,R_2,R_3,R_4)\mathrm{d}\Phi =I_1(S)/I_0(S), \quad (12)$$

$$\mathrm{var}[\cos\Phi|S]=1-\frac{I_1(S)}{SI_0(S)}-\frac{I_1^2(S)}{I_0^2(S)}.$$

Equations (10), (11) and (12) justify, from the point of view of the joint probability distribution, equation (2) proposed by Schenk (1973).

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