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On the Conditional Probability of Quintets

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A new expression for the conditional probability distribution of quintet structure invariants is given, which in exponential approximation reduces to the exponential expression of Hauptman & Fortier [*Acta Cryst.* (1977), A**33**, 575–580]. In a practical example the expression gave promising results.

Introduction

Several expressions for the conditional probability distributions (c.p.d.) of quartet and quintet structure invariants have been reported, some of which have a purely exponential form while others contain Bessel functions as well.

For quartets the theory is well established. For the magnitudes of the reflexions H, K, L, $H+K+L$, $H+K$, $H+L$, $K+L$ Hauptman (1975) derived the expression

$$P(|\varphi_4|)=L\exp(-4E_4\cos\varphi_4)I_0(2N^{-1/2}|E_{H+K}|Z_{HK})\times I_0(2N^{-1/2}|E_{H+L}|Z_{HL})I_0(2N^{-1/2}|E_{K+L}|Z_{KL}) \quad (1)$$

in which L is a suitable normalizing constant,

$$E_4=N^{-1}|E_HE_KE_LE_{H+K+L}|\,,$$
$$\varphi_4=\varphi_H+\varphi_K+\varphi_L+\varphi_{-H-K-L}\,,$$

I_0 is a modified Bessel function and

$$Z_{HK}=(E_H^2E_K^2+E_L^2E_{H+K+L}^2+2NE_4\cos\varphi_4)^{1/2}\,.$$

Dependent on the seven $|E|$ values a maximum value of $P(|\varphi_4|)$ corresponds to a phase $|\varphi_4|$ anywhere in the range $0\le|\varphi_4|\le\pi$.

A second expression for the c.p.d. of quartets is derived by Giacovazzo (1976):

$$P(|\varphi_4|)=L'\exp[-2E_4(2-E_{H+K}^2-E_{H+L}^2-E_{K+L}^2)\cos\varphi_4] \quad (2)$$

in which L' is a suitable normalizing constant. This formula has maxima for $\varphi_4=0$ or π only.

Making use of

$$I_0(z)\simeq\exp\left(\frac{z^2}{4}\right), \quad (3)$$

which is valid for small values of z, Heinerman (1976) (see also Giacovazzo, 1977) has shown that (2) is an approximation of (1). Test results (Schenk, 1977) show that (1) leads to phase estimates with smaller errors than (2) does.

For the estimation of phases

$$|\varphi_5|=|\varphi_H+\varphi_K+\varphi_L+\varphi_M+\varphi_{-H-K-L-M}|$$

of quintet relations several procedures and expressions have been described (Schenk, 1975; Schenk & van der Putten, 1976; Krabbendam, 1976; van der Putten & Schenk, 1976; Hauptman & Fortier, 1977).

Among the purely exponential expressions the one of Hauptman & Fortier (1977) looks the most promising.

$$P(|\varphi_5|)=C\exp[(\sum_{15\text{ terms}}E_{H+K}^2E_{L+M}^2-2\sum_{10\text{ terms}}E_{H+K}^2+6)2E_5\cos\varphi_5]\,. \quad (4)$$

Here C is a suitable normalizing constant, the sums are taken over all combinations of the 10 cross-reflexions $H+K$ *etc.* and

$$E_5=N^{-3/2}|E_HE_KE_LE_ME_{H+K+L+M}|\,.$$

Like its quartet analogue (2) this formula gives values for $|\varphi_5|$ of 0 and π only.

The mixed exponential–Bessel formulae for quintets reported so far are proposed on the basis of the purely exponential expressions. It was stated by Hauptman & Fortier (1977) that: 'it is therefore plausible to assume that the correct functional form for $P_{5|15}$ is an exponential multiplied by ten Bessel functions'. Under this assumption and employing (3) they transformed (4) into

$$P(|\varphi_5|)=C'\exp(12E_5\cos\varphi_5)\prod_{10\ \text{terms}} I_0(2E_{H+K}X_{HK}) \quad (5)$$

in which C' is a suitable normalizing constant and (Fortier & Hauptman, 1977)

$$X_{HK}=N^{-3/4}[4^{-1}E_H^2E_K^2(E_{L+M}^2+E_{H+K+M}^2+E_{H+K+L}^2-4)^2+N^{3/2}E_5(E_{L+M}^2+E_{H+K+M}^2+E_{H+K+L}^2-4)\cos\varphi_5+E_L^2E_M^2E_{H+K+L+M}^2]^{1/2}.$$

By the exponential approximation (3) the Bessel expression (5) reduces to the pure exponential form (4). The object of this paper is to indicate that there are many Bessel-type equations which reduce to the same exponential expression (4). The one which describes $P|\varphi_5|$ best for practical purposes can be selected experimentally, as will be shown.

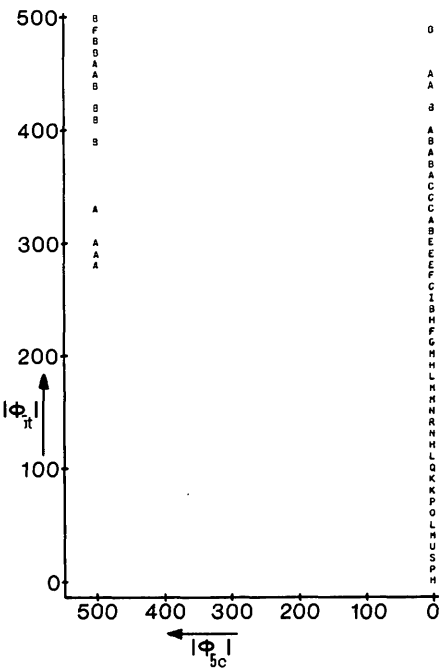

Fig. 1. Graph of $|\varphi_{5(\text{true})}|$ against $|\varphi_{5(\text{calc})}|$ in millicycles (1000 millicycles $=2\pi$) calculated with (4). The number of quintets with the same $|\varphi_{5(\text{true})}|$ and $|\varphi_{5(\text{calc})}|$ are represented by capital letters: *A* means 1, *B* 2, *C* 3 *etc.*

Exponential Bessel expressions for the c.p.d. of quintets

In Fig. 1 the phases $|\varphi_5|$ predicted by means of (4) are plotted against the true phases $|\varphi_5|$ for 400 quintets with $E_5>0{\cdot}35$ for a real 30-atom $P1$ structure. Although only phases of 0 and π can be predicted, the results are promising.

In Fig. 2 a comparable plot is given for predictions by the exponential Bessel equation (5) of Hauptman & Fortier (1977), from which it can be seen that the predicted phases do not reproduce the true phases at all.

Many expressions of the general form

$$P(|\varphi_5|)=C\exp(A\cos\varphi_5)\prod_{10\ \text{terms}} I_0(B) \qquad (6)$$

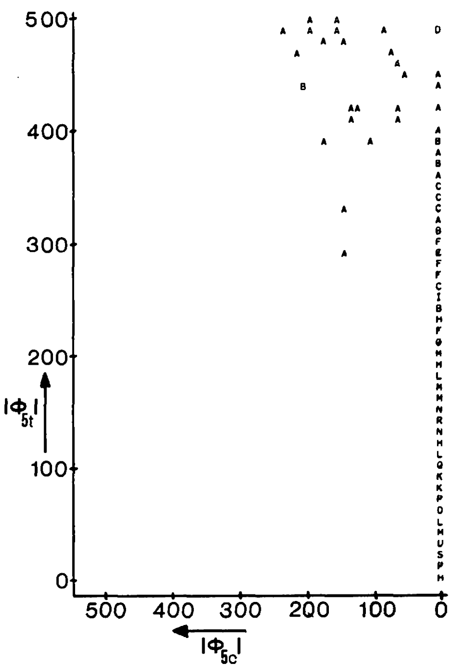

Fig. 2. Graph of $|\varphi_{5(\text{true})}|$ against $|\varphi_{5(\text{calc})}|$ calculated with (5).

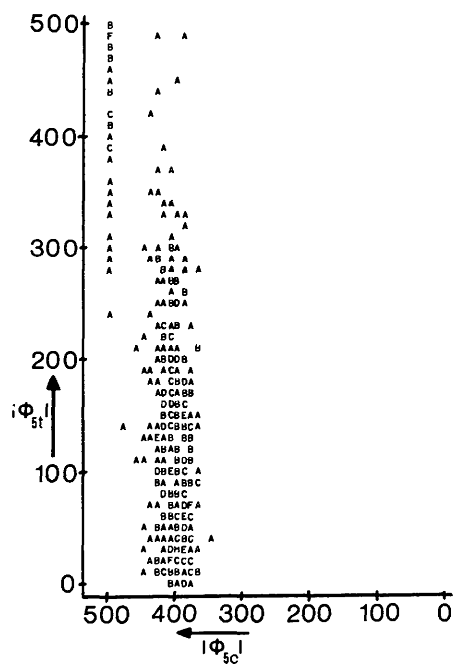

Fig. 3. Graph of $|\varphi_{5(\text{true})}|$ against $|\varphi_{5(\text{calc})}|$ calculated with (7).

can be formulated which all reduce to (4) by the exponential approximation (3) of the Bessel functions. We have made calculations with about 15 of them and produced plots comparable with Figs. 1 and 2.

All expressions but one do not reproduce the true phases, an example of which is given by

$$P(|\varphi_5|)=C\exp\left[\left(6-2\sum_{10\text{ terms}}E^2_{H+K}\right)2E_5\cos\varphi_5\right]\times\prod_{10\text{ terms}}I_0(2E_{H+K}Y_{HK})\quad(7)$$

in which

$$Y_{HK}=N^{-3/4}[4^{-1}E^2_HE^2_K(E^2_{L+M}+E^2_{H+K+M}+E^2_{H+K+L})^2+N^{3/2}E_5(E^2_{L+M}+E^2_{H+K+M}+E^2_{H+K+L})\cos\varphi_5+E^2_LE^2_ME^2_{H+K+L+M}]^{1/2}.$$

The plot of the phases $|\varphi_5|$, predicted with (7), against the true phases is given in Fig. 3, and again the predicted phases do not reproduce the true phases, although the plot is quite different from Fig. 2.

The only expression for the c.p.d. with good test results is given by

$$P(|\varphi_5|)=C\exp\left[\left(6-\sum_{10\text{ terms}}E^2_{H+K}\right)2E_5\cos\varphi_5\right]\times\prod_{10\text{ terms}}I_0(2E_{H+K}Y_{HK})\quad(8)$$

in which C is a suitable normalizing constant and

$$Y_{HK}=N^{-3/4}[4^{-1}E^2_HE^2_K(E^2_{L+M}+E^2_{H+K+M}+E^2_{H+K+L}-2)^2+N^{3/2}E_5(E^2_{L+M}+E^2_{H+K+M}+E^2_{H+K+L}-2)\cos\varphi_5+E^2_LE^2_ME^2_{H+K+L+M}]^{1/2}.$$

It is striking that in the Y_{HK} expressions terms related to the quartet formula (2) are present.

The plot of the test results of this equation is given in Fig. 4, and it can be seen that true phases are well estimated by the predicted phases. The mean difference $\langle||\varphi_{5(\text{true})}|-|\varphi_{5(\text{calc})}||\rangle=68$ millicycles, which is smaller than the same quantities for our empirical method (79 millicycles, Schenk & van der Putten, 1977) and our earlier proposed expression (88 millicycles, van der Putten & Schenk, 1976):

$$P(|\varphi_5|)=C\exp(-18E_5\cos\varphi_5)\times\prod_{10\text{ terms}}I_0(2N^{-3/4}|E_{H+K}|Y_{HK})$$

in which

$$Y_{HK}=[E_LE_ME_{H+K+L+M}(E^2_H+E^2_K+2|E_HE_K|\cos\varphi_5)]^{1/2}.$$

It might well be that (8) is the Bessel counterpart of the exponential formula (4), but the only way to ascertain this would be the derivation of the Bessel–exponential expression for quintets as Hauptman (1975) has done for quartets. Until this is done (8) seems good enough for practical purposes.

Note added in proof: In the finally published version of Hauptman & Fortier (1977) expression (5) has been replaced by two related formulae. Test results give similar graphs to those shown in Fig. 2.

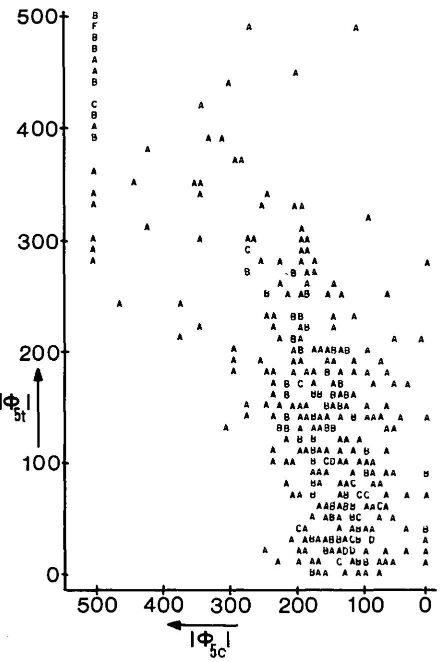

Fig. 4. Graph of $|\varphi_{5(\text{true})}|$ against $|\varphi_{5(\text{calc})}|$ calculated with (8).

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