– *symmetry class* $\bar{4}3m$

$(h+k,l)$ or $(h+l,k)$ or $(k+l,h) \equiv 0 \bmod (2,2)$

$(h,k,l) \equiv 0 \bmod (0,2,2)$ or $(2,0,2)$ or $(2,2,0)$

$(h \pm k \pm l) \equiv 0 \bmod (0)$.

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Quintets in $P\bar{1}$ and Related Phase Relationships: a Probabilistic Approach

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A probabilistic theory is described which is able to estimate in $P\bar{1}$ the signs of the quintet invariants. An investigation is carried out on the use of special quintets in order to estimate one and two-phase seminvariants by means of the complementary-invariants method.

1.1. Introduction

Let $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$, $\mathbf{h}_4$, $\mathbf{h}_5$ be reciprocal vectors for which

$$\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3+\mathbf{h}_4+\mathbf{h}_5=0.$$

Then the linear combination of phases

$$\varphi=\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3}+\varphi_{\mathbf{h}_4}+\varphi_{\mathbf{h}_5} \quad (1)$$

is a structure invariant. The theory of representations (Giacovazzo, 1977) states that φ may be evaluated in $P1$ or $P\bar{1}$ *via* its first phasing shell by means of the 15 magnitudes

$$E_{m_1\mathbf{h}_1+\ldots m_5\mathbf{h}_5} \quad (m_p=0,1). \quad (2)$$

Schenk (1975) spoke of quintets at the Tenth International Congress of Crystallography. The main result presented was a linear trend of φ *versus* the sum of the cross-magnitudes. At the Buffalo Symposium on Direct Methods more detailed analysis was presented by Schenk (1976) by a semi-empirical method and by Fortier & Hauptman (1976) with the theory of the joint probability distribution functions. More recently, Fortier & Hauptman (1977) described a probabilistic approach in $P\bar{1}$ which is able to predict the sign of a quintet by means of a formula which involves a summation over 1024 contributions. This paper describes a probabilistic approach to quintets in $P\bar{1}$ which leads to formulae more tractable than Fortier & Hauptman's. Special quintets are also studied which may allow good estimates of one and two-phase structure seminvariants.

1.2. The mathematical approach

The method to be described requires the derivation of a variety of conditional probability distributions. If we denote by $P(E_1, E_2, \ldots, E_n)$ the joint probability function of n normalized structure factors, its characteristic function may be expanded in a Gram–Charlier series:

$$\begin{aligned}C(u_1,\ldots,u_n)=&\exp\left[-\tfrac{1}{2}(u_1^2+\ldots+u_n^2)\right]\\&\times[1+S_3/t^{3/2}+(S_4/t^2+S_3^2/2t^3)\\&+(S_5/t^{5/2}+S_3S_4/t^{7/2}+S_3^3/6t^{9/2})+\ldots],\end{aligned} \quad (3)$$

where u_i, $i=1,\ldots,n$ are carrying variables associated with E_i, t is the number of independent atoms in the unit cell,

$$S_v=t\sum_{r+s+\ldots+w=v}\frac{\lambda_{rs\ldots w}}{r!s!\ldots w!}(iu_1)^r(iu_2)^s\ldots(iu_n)^w,$$

and

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

$K_{rs\ldots w}$ are the cumulants of the distribution and m is the order of the space group. $P(E_1, E_2, \ldots, E_n)$ is the Fourier transform of (3).

This method is simpler than that followed by Fortier & Hauptman (1976), who use the exponential form of the characteristic function to calculate the probability density function. Since this function would be too intractable to be useful in applications, it is expanded in a Taylor series. Thus in both methods the probability density functions have the form of a series expansion, but their algebraic expressions are not identical because of the different mathematical approaches.

Because of the lengthy calculations, only the conclusive formulae derived in this paper will be quoted. An account of the approach may be found in Giacovazzo (1976*a*).

1.3. The sign of a quintet *via* its first phasing shell

Let φ, as given by (1), be a quintet. The 15 reflexions contained in the first phasing shell of φ are

$$\begin{aligned} &E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}}, E_{\mathbf{m}}, E_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}},\\ &E_{\mathbf{h}+\mathbf{k}}, E_{\mathbf{h}+\mathbf{l}}, E_{\mathbf{h}+\mathbf{m}}, E_{\mathbf{k}+\mathbf{l}+\mathbf{m}}, E_{\mathbf{k}+\mathbf{l}},\\ &E_{\mathbf{k}+\mathbf{m}}, E_{\mathbf{h}+\mathbf{l}+\mathbf{m}}, E_{\mathbf{l}+\mathbf{m}}, E_{\mathbf{h}+\mathbf{k}+\mathbf{m}}, E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}. \end{aligned} \tag{4}$$

Let us denote

$$E_1=E_{\mathbf{h}};\ E_2=E_{\mathbf{k}};\ \ldots;\ E_{15}=E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}.$$

By means of the mathematical approach described in § 1.2 we have studied the joint probability distribution function of the reflexions (4). Denoting by P_+ the probability that the sign of $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{m}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}$ is positive, we have

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{E_{1\ldots5}}{N\sqrt{N}}\left(\frac{1+A+B}{1+C/2N+D/8N}\right)\right], \tag{5}$$

where

$$E_{1\ldots5}=|E_1E_2E_3E_4E_5|,$$

$$A=\sum_{6\,i}^{15}\varepsilon_i,$$

$$\begin{aligned} B=&\varepsilon_6\varepsilon_{13}+\varepsilon_6\varepsilon_{15}+\varepsilon_6\varepsilon_{14}+\varepsilon_7\varepsilon_{11}+\varepsilon_7\varepsilon_{15}+\varepsilon_7\varepsilon_{12}\\ &+\varepsilon_8\varepsilon_{10}+\varepsilon_8\varepsilon_{14}+\varepsilon_8\varepsilon_{12}+\varepsilon_{10}\varepsilon_{15}+\varepsilon_{10}\varepsilon_9+\varepsilon_{11}\varepsilon_{14}\\ &+\varepsilon_{11}\varepsilon_9+\varepsilon_{13}\varepsilon_9+\varepsilon_{13}\varepsilon_{12}, \end{aligned}$$

$$\begin{aligned} C=&\varepsilon_1\varepsilon_2\varepsilon_6+\varepsilon_1\varepsilon_3\varepsilon_7+\varepsilon_1\varepsilon_4\varepsilon_8+\varepsilon_1\varepsilon_5\varepsilon_9+\varepsilon_1\varepsilon_{10}\varepsilon_{15}\\ &+\varepsilon_1\varepsilon_{11}\varepsilon_{14}+\varepsilon_1\varepsilon_{13}\varepsilon_{12}+\varepsilon_2\varepsilon_3\varepsilon_{10}+\varepsilon_2\varepsilon_4\varepsilon_{11}\\ &+\varepsilon_2\varepsilon_5\varepsilon_{12}+\varepsilon_2\varepsilon_7\varepsilon_{15}+\varepsilon_2\varepsilon_8\varepsilon_{14}+\varepsilon_2\varepsilon_{13}\varepsilon_9+\varepsilon_3\varepsilon_4\varepsilon_{13}\\ &+\varepsilon_3\varepsilon_5\varepsilon_{14}+\varepsilon_3\varepsilon_6\varepsilon_{15}+\varepsilon_3\varepsilon_8\varepsilon_{12}+\varepsilon_3\varepsilon_{11}\varepsilon_9+\varepsilon_4\varepsilon_5\varepsilon_{15}\\ &+\varepsilon_4\varepsilon_6\varepsilon_{14}+\varepsilon_4\varepsilon_7\varepsilon_{12}+\varepsilon_4\varepsilon_{10}\varepsilon_9+\varepsilon_5\varepsilon_6\varepsilon_{13}+\varepsilon_5\varepsilon_7\varepsilon_{11}\\ &+\varepsilon_5\varepsilon_8\varepsilon_{10}, \end{aligned}$$

$$D=\sum_{1\,i}^{15}H_4(E_i),$$

$$\varepsilon_i=(E_i^2-1).$$

$H_4(x)$ is the Hermite polynomial of order four given by

$$H_4(x)=x^4-6x^2+3.$$

Equation (5) tells us that the sign of a quintet depends on an intricate interrelationship among the cross-magnitudes. The character of positivity or negativity is strengthened by large values of $E_{1\ldots5}$.

Equation (5) may be generalized to structures with unequal atoms (see Fortier & Hauptman, 1976, for a related expression) by means of

$$P_+\simeq0{\cdot}5+0{\cdot}5\tanh\left[E_{1,\ldots,5}\times\left(\frac{1}{\alpha}+\frac{A}{\beta}+\frac{B}{\gamma}\right)\Bigg/\left(1+\frac{C}{2\alpha^{2/3}}+\frac{D}{8\delta}\right)\right], \tag{5'}$$

where

$$\begin{aligned} \alpha&=\sigma_2^{9/2}/\sigma_3^3,\\ \beta&=\sigma_2^{9/2}/\sigma_3(3\sigma_3^2-\sigma_2\sigma_4),\\ \gamma&=\sigma_2^{9/2}/(15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5),\\ \delta&=\sigma_2^2/\sigma_4,\\ \sigma_n&=\sum_{1\,j}^{N}f_j^n. \end{aligned}$$

Practical aspects of (5) and experimental results are described in the following paper.

1.4. A comparison with triplet and quartet theories

The sign of a triplet is always probably positive:

$$P_+(E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}})\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left(\frac{|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|}{\sqrt{N}}\right).$$

The sign of a quartet, according to the relation (Giacovazzo, 1975*a*)

$$P_+(E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}})\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{1}{N}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|\times\frac{E^2_{\mathbf{h}+\mathbf{k}}+E^2_{\mathbf{h}+\mathbf{l}}+E^2_{\mathbf{k}+\mathbf{l}}-2}{1+4(E^2_{\mathbf{h}+\mathbf{k}}+E^2_{\mathbf{h}+\mathbf{l}}+E^2_{\mathbf{k}+\mathbf{l}}-3)/N}\right],$$

depends on the values of the cross-magnitudes.

From (5) we can expect that the percentage of negative quintets will in general be larger than that of triplets and quartets in the same structure. In fact, the mean values of triplets, quartets and quintets under the hypothesis that the cross-vectors are independent variables over reciprocal space, are respectively

$$\begin{aligned} &\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}\rangle\simeq1/\sqrt{N},\\ &\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\rangle\simeq1/N,\\ &\langle E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{m}}E_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}\rangle\simeq1/N\sqrt{N}. \end{aligned} \tag{6}$$

Equation (6) tell us that the mean positivities of the triplets and quartets are of order $1/\sqrt{N}$ and $1/N$ respectively, whereas the mean positivity of the quintets is of order $1/N\sqrt{N}$. This property, as we show in the Appendix, can be of use in crystal structure solution.

1.5. The marginal probability $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}}, E_{\mathbf{m}}, E_{\mathbf{h+k+l+m}})$

If instead of 15 magnitudes, one has only the five magnitudes $E_{\mathbf{h}}$, $E_{\mathbf{k}}$, $E_{\mathbf{l}}$, $E_{\mathbf{m}}$, $E_{\mathbf{h+k+l+m}}$, the final sign relationship, correct up to and including terms of order $1/N\sqrt{N}$, is

$$P_+ \simeq \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\frac{E_{1\ldots5}}{N\sqrt{N}}\right). \quad (7)$$

(7) is a particular case of the Simerska (1956) formula and may be compared with (5) to illustrate the dramatic change which may take place when 5 magnitudes are given instead of 15. According to (7) in fact the sign of a quintet is always probably positive.

1.6. The marginal probability densities $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}}, E_{\mathbf{m}}, E_{\mathbf{h+k+l+m}}, \ldots)$

The number of quintets for which all ten cross-vectors are in the set of measured reflexions may be a small percentage of the observable quintets. So it might be useful to use in direct procedures quintets for which merely nine, eight, seven, ... cross-vectors are in the set. The marginal probability densities

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

are able to provide suitable formulae. One may show that the probability values may be derived from (5) by equating to zero the terms ε_i corresponding to the magnitudes $|E_i|$ which are not in the set of measurements. In this connexion we note that marginal probability densities of the same order are not equally efficacious (in the statistical sense) for estimating the sign of a quintet. Let us suppose, for example, that $|E_{\mathbf{h+k}}|$ and $|E_{\mathbf{h+l}}|$ are not in the set. Then the factors A, B, C, D in (5) will contain 8, 9, 8, 13 terms respectively. The same situation does not occur when $|E_{\mathbf{h+k}}|$ and $|E_{\mathbf{h+k+l}}|$ are unknown. In this case A, B, C, D contain 8, 10, 9, 13 terms respectively. Of course the latter situation is, in general, more favourable than the former for giving a sign to a quintet invariant.

2.1. Special quintets

When $\mathbf{m} = -\mathbf{l}$ the quintet invariant $\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}} - \varphi_{\mathbf{h+k+l+m}}$ reduces to

$$\varphi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h+k}},$$

and the 15 reflexions (4) reduce to 10:

$$E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h+k}}, E_{\mathbf{l}}, E_{\mathbf{h}\pm\mathbf{l}}, E_{\mathbf{k}\pm\mathbf{l}}, E_{\mathbf{h+k}\pm\mathbf{l}}. \quad (8)$$

In accordance with the theory of representations

$$\psi_2 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h+k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{l}}$$

is an element of the second representation of φ and the magnitudes (8) are its phasing magnitudes.

When $\mathbf{m} = \mathbf{l}$ the quintet invariant reduces to

$$\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + 2\varphi_{\mathbf{l}} - \varphi_{\mathbf{h+k+2l}}. \quad (9)$$

In $P\bar{1}$ (9) coincides with the three-phase seminvariant

$$\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h+k+2l}}. \quad (10)$$

In accordance with the theory of representations, (9) is an element of the first representation of (10).

These types of special quintets can play an important role in procedures for phase assignment: they will be studied in subsequent papers. In this section we deal only with special quintets which enable us to estimate in $P\bar{1}$ one and two-phase seminvariants. The method will be that of complementary invariants, whose background is described by Giacovazzo (1977). We note furthermore that formulae for general quintets may be inadequate for special quintets. Thus the introduction of special formulae for special quintets will further strengthen the overall theory of quintets.

2.2. The sign of $E_{2\mathbf{h}}$

If $\mathbf{m} = -2\mathbf{h}$, the quintet invariant $\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}} - \varphi_{\mathbf{h+k+l+m}}$ reduces in $P\bar{1}$ to

$$\varphi_{2\mathbf{h}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{h+k+l}}. \quad (11)$$

A distinctive feature of (11) is that it contains the quartet $\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{h+k+l}}$. Under the assumption that the sign of the quartet is known, the sign of the quintet fixes that of $E_{2\mathbf{h}}$. The method is a further generalization of that described by Giacovazzo (1975*b*). There, special quartets $\varphi_{2\mathbf{h}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h+k}}$ were used in order to derive the sign of $E_{2\mathbf{h}}$.

We note that one of the cross-vectors of (11) (*i.e.* $\mathbf{h}$) coincides with a basis-vector; thus the sign of (11) may be derived from only 14 phasing magnitudes. From the distribution

$$P(E_{2\mathbf{h}}, E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}}, E_{\mathbf{h+k+l}}, E_{2\mathbf{h+k}}, E_{2\mathbf{h+l}}, E_{-\mathbf{h+k}}, E_{-\mathbf{h+l}}, E_{\mathbf{k+l}}, E_{\mathbf{h+k}}, E_{\mathbf{h+l}}, E_{-\mathbf{h+k+l}}, E_{2\mathbf{h+k+l}})$$

we obtain for (11) the sign probability:

$$P_+ \simeq \tfrac{1}{2} + \tfrac{1}{2}\tanh\left[\frac{E_{1\ldots5}}{N\sqrt{N}}\left(\frac{1+A'+B'}{1+C'/2N+D'/8N}\right)\right], \quad (12)$$

where

$$E_{1\ldots5} = |E_1E_2E_3E_4E_5|,$$

$$A' = \sum_{6}^{14} \varepsilon_i,$$

$$\begin{aligned} B' = {} & \varepsilon_6\varepsilon_9 + \varepsilon_6\varepsilon_{11} + \varepsilon_6\varepsilon_{14} \\ & + \varepsilon_7\varepsilon_8 + \varepsilon_7\varepsilon_{12} + \varepsilon_7\varepsilon_{14} \\ & + \varepsilon_8\varepsilon_{11} + \varepsilon_8\varepsilon_{13} + \varepsilon_9\varepsilon_{12} \\ & + \varepsilon_9\varepsilon_{13} + \varepsilon_{10}\varepsilon_{13} + \varepsilon_{10}\varepsilon_{14}, \end{aligned}$$

$$\begin{aligned} C' = {} & \varepsilon_1 H_4(E_2)/4 + \varepsilon_1\varepsilon_3\varepsilon_6 + \varepsilon_1\varepsilon_4\varepsilon_7 \\ & + \varepsilon_1\varepsilon_5\varepsilon_{13} + \varepsilon_1\varepsilon_8\varepsilon_{11} + \varepsilon_1\varepsilon_9\varepsilon_{12} \\ & + \varepsilon_1\varepsilon_{10}\varepsilon_{14} + \varepsilon_2\varepsilon_3\varepsilon_8 + \varepsilon_2\varepsilon_3\varepsilon_{11} \end{aligned}$$

$$+\varepsilon_2\varepsilon_4\varepsilon_9+\varepsilon_2\varepsilon_4\varepsilon_{12}+\varepsilon_2\varepsilon_5\varepsilon_{10}$$
$$+\varepsilon_2\varepsilon_5\varepsilon_{14}+\varepsilon_2\varepsilon_6\varepsilon_{11}+\varepsilon_2\varepsilon_7\varepsilon_{12}$$
$$+\varepsilon_2\varepsilon_{10}\varepsilon_{13}+\varepsilon_3\varepsilon_4\varepsilon_{10}+\varepsilon_3\varepsilon_5\varepsilon_{12}$$
$$+\varepsilon_3\varepsilon_7\varepsilon_{14}+\varepsilon_3\varepsilon_9\varepsilon_{13}+\varepsilon_4\varepsilon_5\varepsilon_{11}$$
$$+\varepsilon_4\varepsilon_6\varepsilon_{14}+\varepsilon_4\varepsilon_8\varepsilon_{13}+\varepsilon_5\varepsilon_6\varepsilon_9$$
$$+\varepsilon_5\varepsilon_7\varepsilon_8+\varepsilon_8\varepsilon_{10}\varepsilon_{12}+\varepsilon_9\varepsilon_{10}\varepsilon_{11}$$
$$+\varepsilon_{11}\varepsilon_{12}\varepsilon_{14},$$

$$D'=-\sum_{1\,i}^{14} H_4(E_i).$$

The order of the indices follows that of the E's in the distribution. A great advantage of the approach is that, for a given $E_{2\mathbf{h}}$, $\mathbf{k}$ and $\mathbf{l}$ are free vectors which may vary over reciprocal space. Thus a large number of quintets may be exploited in order to make reliable the estimation of the sign of $E_{2\mathbf{h}}$. Practical aspects of the approach and experimental results are described in the following paper.

2.3. The sign of the two-phase seminvariants

Let $\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}$ be a structure seminvariant in $P\bar{1}$. By denoting

$$\mathbf{h}=\mathbf{H}+\mathbf{K},\ \mathbf{k}=\mathbf{H}-\mathbf{K},$$

the structure invariant $\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}-\varphi_{\mathbf{h}+\mathbf{k}-\mathbf{l}+\mathbf{m}}$ may be written

$$\varphi_{\mathbf{H}+\mathbf{K}}+\varphi_{\mathbf{H}-\mathbf{K}}-\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}-\varphi_{2\mathbf{H}-\mathbf{l}+\mathbf{m}}. \tag{13}$$

The value of $\varphi_{\mathbf{H}+\mathbf{K}}+\varphi_{\mathbf{H}-\mathbf{K}}$ is fixed if (13) and the three-phase seminvariant $\varphi_{\mathbf{l}}-\varphi_{\mathbf{m}}+\varphi_{2\mathbf{H}-\mathbf{l}+\mathbf{m}}$ are known. A large number of quintets may occur to make reliable the estimation of $\varphi_{\mathbf{H}+\mathbf{K}}+\varphi_{\mathbf{H}-\mathbf{K}}$ since $\mathbf{l}$ and $\mathbf{m}$ are free vectors.

A simpler procedure for estimating $\varphi_{\mathbf{H}+\mathbf{K}}+\varphi_{\mathbf{H}-\mathbf{K}}$ is that of putting in (13) $\mathbf{m}=-\mathbf{H}$. (13) reduces then to

$$\varphi_{\mathbf{H}+\mathbf{K}}+\varphi_{\mathbf{H}-\mathbf{K}}-\varphi_{\mathbf{H}}-\varphi_{\mathbf{l}}-\varphi_{\mathbf{H}-\mathbf{l}}. \tag{14}$$

Under the assumption that the sign of the triplet invariant $\varphi_{\mathbf{H}}-\varphi_{\mathbf{l}}-\varphi_{\mathbf{H}-\mathbf{l}}$ is known, the sign of (14) fixes that of $\varphi_{\mathbf{H}+\mathbf{K}}+\varphi_{\mathbf{H}-\mathbf{K}}$. Several quintets may occur to fix the value of $\varphi_{\mathbf{H}+\mathbf{K}}+\varphi_{\mathbf{H}-\mathbf{K}}$, since $\mathbf{l}$ is a free vector. The value of (14) depends on the eight cross-vectors

$$2\mathbf{H},\mathbf{K},\mathbf{H}+\mathbf{K}-\mathbf{l},\mathbf{K}+\mathbf{l},\mathbf{H}-\mathbf{K}-\mathbf{l},-\mathbf{K}+\mathbf{l},\mathbf{H}+\mathbf{l},-2\mathbf{H}+\mathbf{l}.$$

We have thus studied the distribution

$$P(E_{\mathbf{h}+\mathbf{k}},E_{\mathbf{h}-\mathbf{k}},E_{\mathbf{h}},E_{\mathbf{l}},E_{\mathbf{h}-\mathbf{l}},E_{2\mathbf{h}},E_{\mathbf{k}},E_{\mathbf{h}+\mathbf{k}-\mathbf{l}},E_{\mathbf{k}+\mathbf{l}},E_{\mathbf{h}-\mathbf{k}-\mathbf{l}},E_{\mathbf{k}-\mathbf{l}},E_{\mathbf{h}+\mathbf{l}},E_{2\mathbf{h}-\mathbf{l}})$$

and obtained for (14) the sign probability

$$P_+\simeq\tfrac{1}{2}+\tfrac{1}{2}\tanh\left[E_{1\ldots5}\left(\frac{1+A''+B''}{1+C''/2N+D''/8N}\right)\right], \tag{15}$$

where

$$A''=\sum_{6\,i}^{13}\varepsilon_i,$$

$$B''=\varepsilon_6\varepsilon_{12}+\varepsilon_6\varepsilon_{13}+\varepsilon_7\varepsilon_8+\varepsilon_7\varepsilon_9$$
$$+\varepsilon_7\varepsilon_{10}+\varepsilon_7\varepsilon_{11}+\varepsilon_8\varepsilon_{11}+\varepsilon_8\varepsilon_{13}$$
$$+\varepsilon_9\varepsilon_{10}+\varepsilon_9\varepsilon_{12}+\varepsilon_{10}\varepsilon_{13}+\varepsilon_{11}\varepsilon_{12},$$

$$C''=\varepsilon_1\varepsilon_2\varepsilon_6+\varepsilon_1\varepsilon_3\varepsilon_7+\varepsilon_1\varepsilon_4\varepsilon_8$$
$$+\varepsilon_1\varepsilon_5\varepsilon_9+\varepsilon_1\varepsilon_{10}\varepsilon_{13}+\varepsilon_1\varepsilon_{11}\varepsilon_{12}$$
$$+\varepsilon_2\varepsilon_3\varepsilon_7+\varepsilon_2\varepsilon_4\varepsilon_{10}+\varepsilon_2\varepsilon_5\varepsilon_{11}$$
$$+\varepsilon_2\varepsilon_8\varepsilon_{13}+\varepsilon_2\varepsilon_9\varepsilon_{12}+\varepsilon_3\varepsilon_4\varepsilon_5$$
$$+\varepsilon_3\varepsilon_4\varepsilon_{12}+\varepsilon_3\varepsilon_5\varepsilon_{13}+\varepsilon_3\varepsilon_8\varepsilon_{11}$$
$$+\varepsilon_3\varepsilon_9\varepsilon_{10}+\varepsilon_6H_4(E_3)/4+\varepsilon_4\varepsilon_6\varepsilon_{13}$$
$$+\varepsilon_4\varepsilon_7\varepsilon_{11}+\varepsilon_4\varepsilon_7\varepsilon_9+\varepsilon_5\varepsilon_6\varepsilon_{12}$$
$$+\varepsilon_5\varepsilon_7\varepsilon_{10}+\varepsilon_5\varepsilon_7\varepsilon_8,$$

$$D''=-\sum_{1\,i}^{13} H_4(E_i).$$

The order of the indices follows that of the E's in the distribution. Practical aspects of the formula and experimental results are described in the following paper.

Conclusions

We have obtained a formula which is able to calculate in $P\bar{1}$ the sign probability for quintet invariants. We anticipate that the formula holds in all centrosymmetric space groups when all cross-reflexions are of general type. When special cross-reflexions occur, algebraic considerations similar to that described by Giacovazzo (1976*b*) will be needed.

Special quintets which enable one to estimate one and two-phase seminvariants in $P\bar{1}$ are described and the corresponding sign probabilities are obtained. The method pursued is that of complementary invariants, whose background has been recently described by Giacovazzo (1977).

APPENDIX

About quartets and quintets

The quartet

$$q=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$$

exploits three (not independent) tripoles

$$q_1=q$$
$$t_1=-\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}+\mathbf{k}}$$
$$t_2=-\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}}+\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}},$$

$$q_1=q$$
$$t_3=-\varphi_{\mathbf{h}}-\varphi_{\mathbf{l}}+\varphi_{\mathbf{h}+\mathbf{l}}$$
$$t_4=-\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{l}}+\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}},$$

$$q_1=q$$
$$t_5=-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}}+\varphi_{\mathbf{k}+\mathbf{l}}$$
$$t_6=-\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}+\mathbf{l}}+\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}.$$

One obtains $-q=t_1+t_2=t_3+t_4=t_5+t_6$. Thus the expected value of a quartet estimates three sums of two triplets. Let us now suppose that all the reflexions involved in the tripoles have magnitudes larger than E_t, where E_t is the minimum value of $|E|$ chosen for carrying out phase determination by means of triplets. If E_t is large enough (*i.e.* $>1{\cdot}3$) and the probabilistic theories of triplets and quartets hold, then

$$q\simeq t_1\simeq t_2\simeq\ldots\simeq t_6\simeq 0.$$

In this case it is claimed that 'quartets contain the same information as triplets'. As we have just seen this is not quite true because the expected value of a quartet estimates sums of two triplets.

Let us now suppose all $|E|$'s are larger than E_t, except $|E_{\mathbf{h}+\mathbf{l}}|$ and $|E_{\mathbf{k}+\mathbf{l}}|$ which are near zero. In this case t_1 and t_2 are the only triplets which are estimated in the direct procedure. In particular, if $\varphi_{\mathbf{h}}\simeq\varphi_{\mathbf{k}}\simeq\varphi_{\mathbf{l}}\simeq 0$, triplet theory gives $\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\simeq 0$. Under the same conditions from probabilistic quartet theories (Hauptman, 1975*a*,*b*; Giacovazzo, 1975*a*, 1976*c*) one obtains $q\simeq\pi/2$ (or π in centrosymmetric space groups). In particular, if $\varphi_{\mathbf{h}}=\varphi_{\mathbf{k}}=\varphi_{\mathbf{l}}\simeq 0$, then $\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\simeq\pi/2$ (or π). This dramatic change occurs chiefly because quartet theory is able to exploit information not used by triplet theory (*i.e.* $|E_{\mathbf{h}+\mathbf{l}}|$ and $|E_{\mathbf{k}+\mathbf{l}}|$ are small).

If all $|E|$'s are larger than E_t, except $|E_{\mathbf{h}+\mathbf{k}}|$, $|E_{\mathbf{h}+\mathbf{l}}|$, $|E_{\mathbf{k}+\mathbf{l}}|$ which are near zero, no triplet appearing in the tripoles is estimated in the direct procedure. However, quartet theory enables us to estimate $q\simeq\pi$. The importance of these quartets is too well known to be described here.

The quintet

$$Q=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}$$

may be considered as arising from multipoles of type

$$\begin{aligned}Q_1&=Q\\ t_1&=-\varphi_{\mathbf{h}}-\varphi_{\mathbf{l}}+\varphi_{\mathbf{h}+\mathbf{l}}\\ t_2&=-\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{l}}+\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\\ t_3&=-\varphi_{\mathbf{m}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}+\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}\end{aligned}\qquad(A.1)$$

or of type

$$\begin{aligned}Q_1&=Q\\ q_1&=-\varphi_{\mathbf{h}}-\varphi_{\mathbf{k}}-\varphi_{\mathbf{l}}+\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\\ t_3&=-\varphi_{\mathbf{m}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}+\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}.\end{aligned}\qquad(A.2)$$

Ten tripoles such as (*A*.2) may be contructed for each quintet, one for every cross-vector of the quintet. Since every quartet is equivalent to three triplets, 30 quadrupoles of type (*A*.1) may be contructed for every quintet. In conclusion, the expected value of a quintet estimates sums of three triplets (or of a quartet plus triplet).

Let us now suppose that all the basis and the cross-magnitudes of the quintet are larger than E_t. If the probabilistic theories of triplets and quintets hold, then

$$-Q=t_1+t_2+t_3=t_1\simeq t_2\ldots\simeq 0.$$

In this case it is claimed that 'quintets contain the same information as triplets', even though we have just shown this is not true in principle.

If not all the $|E|$'s are larger than E_t, then a quintet is estimated from a set of experimental data not wholly exploited by triplets. If we suppose that in (*A*.2) $|E_{\mathbf{h}}|$, $|E_{\mathbf{k}}|$, $|E_{\mathbf{l}}|$, $|E_{\mathbf{m}}|$, $|E_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}|$ are large and $|E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|$ is near zero, quartets like q_1 are not calculated in a direct procedure using quartets. It should be noted that such quartets are expected to assume any value between 0 and 2π. Thus, a percentage of negative relationships are to be expected for quintets larger than for triplets and quartets.

In conclusion, information given by quintets is in general different from that given by triplets and quartets both because of the different meaning of the relationships and of the extension of experimental data accessible for each phase relationship.

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