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Phase Determination from the Karle–Hauptman Determinant. II. Connexion between Inequalities and Probabilities*

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The probabilistic properties of a Karle–Hauptman determinant are investigated, with particular reference to the case where all elements are assumed to be known except one. In previous papers it has been shown that the matrix associated with a Karle–Hauptman determinant can be interpreted as a covariance matrix, and also that the probability law associated with *one unknown element* is a complex Gaussian law centred at the expected value given by the regression-plane equation. These results are now extended to the case where several structure factors are unknown. Furthermore, the connexion between inequalities, the Sayre–Hughes equation and probability relations is discussed. It appears that the Karle–Hauptman inequality defines the allowed domain as a hyperellipsoid, the centre of which corresponds to the most probable set of structure-factor phases. Factors concerned in the selection of a determinant suitable for efficient phase determination are given.

I. General scope

The aim of this paper is the development of useful mathematical relations for phase determination, in which are *simultaneously* included a large number of structure factors.

In a previous paper (Tsoucaris, 1970, referred to hereafter as paper I; see also Tsoucaris, 1969; de Rango, Tsoucaris & Zelwer, 1969), it has been shown that the central-limit theorem leads to a very restrictive connexion, *in the statistical sense*, between structure factors included in a Karle–Hauptman determinant, the m-dimensional Laplace–Gauss distribution and, as a consequence, the 'maximum determinant rule'.

In this paper we report further results to the probabilistic properties of a Karle–Hauptman determinant.

I. 1. *Probability law for one structure factor included in the determinant or regression-plane equation* (§II)

If it is assumed that all elements of a Δ_{m+1} determinant (as defined in Table 1) are known *except one*, denoted by $E_q = E_{m+1,q}$, the probability law associated with this unknown element is a Gaussian law centred at the *expected value*:

$$\bar{E}_q = -\frac{1}{D_{qq}} \sum_p D_{pq} E_p \,. \qquad (1)$$

The right-hand side includes, of course, only the remaining known elements; D_{pq} and D_{qq} are minors of D_m defined in § II. 1.

A proof of this equation was first given by de Rango (1969) and quoted by Tsoucaris in the above references. In the present paper the distribution of

$$X_q = E_q - \bar{E}_q \qquad (2)$$

Table 1. *Definition of determinant* Δ_{m+1} *whose minor* D_m *is indicated by dotted lines*

All elements of D_m are assumed known in modulus and phase. The last row (or column) includes the unknown elements of Δ_{m+1}. The shorter notations used in the text correspond to: $U_{pq} = U_{\mathbf{H}_p - \mathbf{H}_q}$; $E_q = E_{\mathbf{L}-\mathbf{H}_q}$.

$$\Delta_{m+1} = \frac{1}{N} \begin{vmatrix} 1 & \dots & U_{-\mathbf{H}_p} & \dots & U_{-\mathbf{H}_q} & E_{-\mathbf{L}} \\ \vdots & & \vdots & & \vdots & \vdots \\ U_{\mathbf{H}_p} & \dots & 1 & \dots & U_{\mathbf{H}_p-\mathbf{H}_q} & E_{-\mathbf{L}+\mathbf{H}_p} \\ \vdots & & \vdots & & \vdots & \vdots \\ U_{\mathbf{H}_q} & \dots & U_{\mathbf{H}_q-\mathbf{H}_p} & \dots & 1 & E_{-\mathbf{L}+\mathbf{H}_q} \\ \vdots & & \vdots & & \vdots & \vdots \\ E_{\mathbf{L}} & \dots & E_{\mathbf{L}-\mathbf{H}_p} & \dots & E_{\mathbf{L}-\mathbf{H}_q} & N \end{vmatrix}$$

will be extensively studied, both from theoretical and practical points of view. Also a generalization will be given for the case of $m-s$ ($s<m$) unknown structure factors which is, again, an $(m-s)$ dimensional Laplace–Gauss distribution.

Furthermore, the expected values relative to a given structure factor but obtained from different determinants can be averaged to provide a more precise evaluation of the unknown phase.

I. 2. *Connexion between inequalities and probabilities* (§III)

A strictly correct probability theory should yield a zero value for the probability density of all sets of structure factors which do not fulfil the inequality $\Delta_{m+1} \geq 0$. This requirement is not fulfilled for a Gaussian distribution which falls off to zero only for infinite values of $|E|$'s. Of course, this is due to the approximations inherent in the central-limit theorem, especially to the requirement that the number of atoms $N \to \infty$. However, there exists a very simple connexion

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between inequalities and probabilities in the case of $(m-s)$ $(1 \le s \le m)$ structure factors considered variable, all others being assumed as known and fixed. These $(m-s)$ variables span an $(m-s)$ dimensional space. It will be proved that:

The inequality $\Delta_{m+1} \ge 0$ defines the allowed domain in the $(m-s)$-dimensional space, as a hyper-ellipsoid, the centre of which corresponds to the most probable set of structure factors.

In the special case, $m-s=1$, the statement amounts to a simple one: for the centrosymmetric structures, the allowed domain reduces itself to a segment of a straight line; for the acentric case, the allowed domain for a given modulus is an arc of a circle and the most probable phase is given by the middle of this allowed arc.

Besides its theoretical interest, this statement provides a useful tool to improve practically the available theoretical formulae, as is described in §IV.

As the theory developed in this section involves probabilities, inequalities and also the Sayre–Hughes equations (Sayre, 1952; Hughes, 1953) we develop briefly the most useful results concerning X_q by using a uniform notation. Let us recall first the definitions of $U_{\mathbf{H}}$ and $E_{\mathbf{H}}$:

$$U_{\mathbf{H}} = \sum_{j=1}^{N} n_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j); \quad E_{\mathbf{H}} = \sum_{j=1}^{N} g_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j)$$

where N is the number of atoms in the unit cell, n_j is the unitary atomic scattering factor with:

$$\sum_{j=1}^{N} n_j = 1; \quad g_j = n_j \Big/ \sqrt{\sum_j n_j^2};$$

$\mathbf{r}_j$ is the vector which defines the position of the jth atom in the unit cell. When all atoms are equal we have:

$$E_{\mathbf{H}} = \sqrt{N} U_{\mathbf{H}} .$$

For unequal atoms the square root of N has to be replaced by E_{000}.

(*a*) *Inequalities: Karle–Hauptman determinant*

Let us choose arbitrarily m vectors in the reciprocal space denoted by $\mathbf{H}_q$, $(q=1, \ldots m)$, and consider the differences:

$$(\mathbf{H}_p - \mathbf{H}_q) \quad p,q = 1, \ldots m .$$

The corresponding structure factors $U_{\mathbf{H}_p - \mathbf{H}_q} = U_{pq}$ form a square matrix of order m. It is well known that the determinant D_m of this matrix has the property of being non-negative (Karle & Hauptman, 1950):

$$D_m = \det(U_{\mathbf{H}_p - \mathbf{H}_q}) \ge 0; \quad \text{(for any } m\text{)} . \qquad (3)$$

A strictly equivalent form of this inequality is given by (24):

$$\boxed{|X_q| \le \sqrt{N} \cdot r} \quad m \le N+1$$

where r involves minors of D_m defined in §III. 2 [equation (25*a*)].

(*b*) *Sayre–Hughes equalities and correlation coefficients between m structure factors*

Let us choose two fixed vectors $\mathbf{H}_p$ and $\mathbf{H}_q$ and a random vector $\mathbf{L}$. The correlation coefficient r_{pq} between two structure factors:

$$E_p = E_{\mathbf{L}-\mathbf{H}_p} \quad \text{and} \quad E_q = E_{\mathbf{L}-\mathbf{H}_q} ,$$

is defined by the Hermitian product:

$$r_{pq} = \overline{E_{\mathbf{L}-\mathbf{H}_p} \cdot E^*_{\mathbf{L}-\mathbf{H}_q}}^{\mathbf{L}} = U_{\mathbf{H}_q - \mathbf{H}_p} = U_{qp} . \qquad (4)$$

This equation is exactly the Sayre–Hughes equation written with a different notation. Next, let us choose m fixed vectors and consider the m^2 equations (4), obtained for $p,q=1, \ldots m$; we notice that the right-hand sides of these equations are the elements of a Karle–Hauptman determinant D_m.

Moreover, if we edge this determinant with a row whose elements are the m structure factors E_q appearing in (4), and the corresponding column with elements E_q^*, we obtain again a Karle–Hauptman determinant denoted by Δ_{m+1} (Table 1). The D_m and Δ_{m+1} determinants play an essential role in the theory of probabilities.

Although both D_m and Δ_{m+1} are Karle–Hauptman determinants, we adopt a distinct notation in order to emphasize that their meaning in probability theory is essentially different. D_m is the determinant of the covariance matrix denoted by [U], and therefore, includes only known and fixed structure factors; on the contrary, Δ_{m+1} includes also in the last column and row the m random (unknown) variables. Once the correlation coefficients are defined, one can use the central limit theorem to obtain the Laplace–Gauss functions and the results given in the next section. These are classical formulas conveniently expressed in crystallographic notation. However, a fact proper to this crystallographic problem must be underlined:

the correlation coefficients U_{qp} and the random variables E_q are of the same nature, in the physical sense;

that is to say, they all are structure factors. The distinction comes exclusively from the fact that E_q are considered as unknown whereas U_{qp} are considered as known.

(*c*) *Probabilities*

First, let us notice that the matrix, whose determinant is Δ_{m+1}, is positive-definite. In order to exploit practically inequality (3), we should calculate the value of Δ_{m+1} for all possible combinations of phases. According to (3), all sets of phases which lead to a negative value of Δ_{m+1} are to be rejected. In other words, the correct solution is to be found among those sets corresponding to a positive (or null) value of Δ_{m+1} (Fig. 1).

Unfortunately the criterion of positivity of Δ_{m+1} (and of the eigenvalues) is not restrictive enough: generally too large a number of allowed sets remains to make such a method alone sufficient to solve the structure directly (except for a simple structure).

However, the probability theories lead to a new result which further restricts the allowed range of phases: let us consider both determinants D_m and Δ_{m+1}; it has been shown that:

Among all sets of phases which are compatible with inequalities, the most probable one is that which leads to a maximum value of Δ_{m+1}.

Thus, 'the maximum-determinant rule' allows the *simultaneous* determination, *in the statistical sense*, of a large number of phases. The proof of this rule involves the central-limit theorem and as a consequence the m-dimensional Laplace–Gauss distribution (7). From this distribution (7), one obtains immediately the one-dimensional distribution of one unknown element, say E_q, all other elements of Δ_{m+1} being known. The mean value $\bar{E}_q$ given by equation (1) defines in probability theory the 'regression-plane equation' or the regression equation. Equivalently, we can write from (1) and (2):

$$\boxed{[X_q]_{\text{most probable}}=0}\,.$$

This statistical relation becomes a strict equality when: $m=N+1$ or $m=N$ [r is given by equation (25)]

$$\boxed{X_q=0} \text{ for } m=N+1; \quad \boxed{|X_q|=r} \text{ for } m=N\,.$$

I. 3. *Criterion for the selection of a determinant suitable for efficient phase determination* (§IV)

'Intuitively' one would expect that 'a good' determinant is one which includes a great number of large-modulus E's (§III); this is certainly true, but information theory provides a precise criterion (de Rango, 1969). Assuming that all elements of D_m are known, the efficiency in determining the phases of the unknown elements of the last row of Δ_{m+1} depends solely on the value of D_m:

The smaller the value of D_m, *the higher the efficiency of probability formulae in phase determination.*

This statement, whose proof and implications will be discussed in §IV, is directly connected with an important property of a Karle–Hauptman determinant: the content of the allowed region is proportional to D_m.

II. Probability theory: regression law

The aim of this section is to investigate the distribution law of one structure factor included in a Karle–Hauptman determinant under the condition that all others are known and fixed. In probability theory such a distribution is called a conditional probability distribution.

In paper I, the 'joint probability distribution' of m structure factors $(E_1 \ldots E_m)$ has been considered.* Here, the notion of 'conditional probability distribution' is more restrictive in the sense that not only are all elements of D_m known but also all elements of the last column of Δ_{m+1}, except one, namely E_q.

II. 1. *Most probable value of* E_q *and regression plane equation*

It will be shown below that the most probable value for E_q denoted by $\bar{E}_q$ is given by:

$$\bar{E}_q=-\frac{1}{D_{qq}}\sum_{\substack{p=1\\p\neq q}}^{m} D_{pq}E_p; \quad m\leq N+1\,. \qquad (1a)$$

The expressions D_{qq} and D_{pq} are elements of the matrix $[\mathrm{U}]^{-1}$ defined by:

$$D_{qq}=\frac{\delta^{qq}_{m-1}}{D_m}\,; \quad D_{pq}=(-1)^{p+q}\frac{\delta^{qp}_{m-1}}{D_m}\,.$$

The δ^{qq}_{m-1} and δ^{qp}_{m-1} are minors of D_m with the following notation: the order of the determinant will be subscripted and the indices of the rows and columns suppressed in D_m will be indicated on the upper right as follows:

$$\delta^{qp}_{m-1} = {}_{q}\overset{p}{\square}\,; \quad \delta^{qq}_{m-1} = {}_{q}\overset{q}{\square}$$

δ^{qq}_{m-1} is a principal minor of D_m where the qth row and column are suppressed; δ^{qp}_{m-1} is obtained from D_m by suppressing the qth row and the pth column.

II. 2. *Conditional probability law of the unknown structure factor* E_q

The distribution law of this structure factor E_q deduced from the general relations of probability theory is:†

* In paper I, this law has been improperly called 'conditional probability'.

† $\bar{E}_q$ denotes the expected value of E_q whereas E_q^* denotes the complex conjugate of E_q.

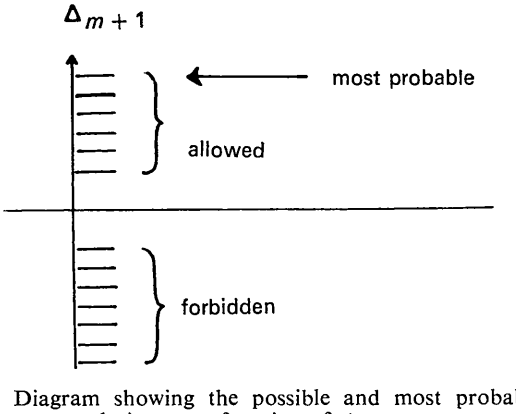


Fig. 1. Diagram showing the possible and most probable solutions as a function of Δ_{m+1}.

$$p(E_q/[\mathbf{U}], E_1 \ldots E_m) = \frac{1}{\sqrt{2\pi}\sigma_q} \exp\left(-\frac{(E_q-\bar{E}_q)^2}{2\sigma_q^2}\right)$$

centrosymmetric case (5*a*)

$$p(E_q/[\mathbf{U}], E_1 \ldots E_m) = \frac{1}{\pi\sigma_q^2} \exp\left(-\frac{|E_q-\bar{E}_q|^2}{\sigma_q^2}\right)$$

non-centrosymmetric case (5*b*)

with $\bar{E}_q$ defined by equation (1*a*) and σ_q^2 given by:

$$\sigma_q^2 = \frac{1}{D_{qq}} . \qquad (6)$$

In other words, the value of X_q is a centred Gaussian variable with a variance σ_q^2 and equation (1*a*) defines what is called in statistics the 'regression plane'.

We outline the proof of (1) and (5): the joint probability law of the m-dimensional random variable $\mathbf{E}$ $(E_1 \ldots E_m)$ is a multidimensional Laplace–Gauss law* (Tsoucaris, 1969, 1970, equation 8).

$$p(E_1 \ldots E_q \ldots E_m/[\mathbf{U}]) = \frac{1}{(2\pi)^{m/2} D_m^{1/2}} \exp(-\tfrac{1}{2}Q_m);$$

centrosymmetric case (7*a*)

$$p(E_1 \ldots E_q \ldots E_m/[\mathbf{U}]) = \frac{1}{\pi^m D_m} \exp(-Q_m);$$

non-centrosymmetric case (7*b*)

with

$$Q_m = N\frac{D_m - \Delta_{m+1}}{D_m} = \sum_{p,q} E_p E_q^* D_{pq} = \mathbf{E}[\mathbf{U}]^{-1}\mathbf{E}^+ . \qquad (8)$$

By deriving Q_m with respect to one random variable one immediately obtains equation (1). The Gaussian character of E_q [equation (5)] is a consequence of the central-limit theorem which is stated here in crystallographic terms (Appendices I and II):

If m random variables $(E_1 \ldots E_m)$ are themselves a sum of N random variables, *i.e.* the N atomic contributions x_{jq}:

$$E_q = E_{\mathbf{L}-\mathbf{H}_q} = \sum_{j=1}^{N} x_{jq} = \sum_{j=1}^{N} g_j \exp\left[2\pi i(\mathbf{L}-\mathbf{H}_q)\,.\,\mathbf{r}_j\right],$$

the correlation coefficients being known and fixed, as given by (4), and if $N \to \infty$, then, the m variables follow a Laplace–Gauss distribution; any subset of $(m-s)$, $(1 \le s \le m)$ also follows a Laplace–Gauss distribution. For $s = m-1$, the distribution is reduced to the familiar Gaussian distribution, centred at the expected value given by equation (1*a*). In simple words, the distribution laws 5(*a*) and 5(*b*) state that a one-dimensional (real or complex) section of the m-dimensional Laplace–Gauss distribution is a Gaussian distribution (Fortet, 1965).

* According to classical notation, the expression to the left of the bar on the left-hand side of (7) contains random variables (unknown); the expressions to the right of the bar are assumed known and fixed. [U] means: 'all structure factors included in matrix [U] whose determinant is D_m'.

Remark: The Hermitian form Q_m is a random variable whose probability law is the χ^2 distribution with m 'degrees of freedom'.

II. 3. *Assessment of the probability associated with the unknown phase*

Since the modulus of E_q is known, the probability law (5) leads us to a probability law for the phase (or sign) of E_q.

(*a*) *Centrosymmetric case*

The probability that the signs of E_q and $\bar{E}_q$ are identical is given by the expression:

$$P_0(E_q) = \tfrac{1}{2} + \tfrac{1}{2}\,\mathrm{th}\left(\frac{1}{\sigma_q^2}|\bar{E}_q E_q|\right) . \qquad (9)$$

In the special case $m=2$, we obtain Woolfson's well known formula with a correction coefficient $[1/(1-U_{\mathbf{H}}^2)]$:

$$P_+(E_{\mathbf{K}-\mathbf{H}}) = \tfrac{1}{2} + \tfrac{1}{2}\,\mathrm{th}\left(\frac{[|E_{\mathbf{K}-\mathbf{H}}|E_{-\mathbf{H}}E_{\mathbf{K}}]}{\sqrt{N(1-U_{\mathbf{H}}^2)}}\right) . \qquad (9a)$$

(*b*) *Non-centrosymmetric case*

The probability law for the phase difference ε_q can be derived immediately from expression (5*b*):

$$p(\varepsilon_q) = \frac{\exp(A_q \cos\varepsilon_q)}{2\pi I_0(A_q)} \qquad (10)$$

where

$$\varepsilon_q = \phi(E_q) - \phi(\bar{E}_q); \quad A_q = 2|\bar{E}_q E_q|/\sigma_q^2 .$$

Then, the conditional probability that $\cos\varepsilon_q > x$, given A_q, is defined by the function:

$$P(x) = \int_x^1 \frac{\exp A_q x}{\pi I_0(A_q)\sqrt{1-x^2}}\,\mathrm{d}x \quad \text{if} \quad |x| < 1 . \qquad (11)$$

For practical applications a useful weighting factor derived from the distribution (10) is given by:

$$W_q = \int_{-\pi}^{+\pi} \cos\varepsilon_q p(\varepsilon_q)\mathrm{d}\varepsilon_q = I_1(A_q)/I_0(A_q) . \qquad (12)$$

In the special case $m=2$, the expression (11) gives again a well known formula† (Cochran, 1955; Hauptman, 1969), since we have:

$$E_q = E_{\mathbf{K}-\mathbf{H}}$$
$$\bar{E}_q = E_{\mathbf{K}} U_{\mathbf{H}}^*$$
$$\sigma_q^2 = \frac{1}{D_{qq}} = 1 - |U_{\mathbf{H}}|^2$$
$$A_q = \frac{2|E_{\mathbf{K}-\mathbf{H}}E_{\mathbf{K}}U_{\mathbf{H}}^*|}{1-|U_{\mathbf{H}}|^2}$$
$$\Delta_3 = \frac{1}{N}\begin{vmatrix} 1 & U_{\mathbf{H}}^* & \vdots & E_{\mathbf{K}}^* \\ U_{\mathbf{H}} & 1 & \vdots & E_{\mathbf{K}-\mathbf{H}}^* \\ \cdots & \cdots & \cdots & \\ E_{\mathbf{K}} & E_{\mathbf{K}-\mathbf{H}} & & N \end{vmatrix} .$$

† However the factor $(1-|U_{\mathbf{H}}|^2)$ does not appear in Cochran's original formula. Its importance has been emphasized in Paper I (Fig. 1).

The distribution (10) becomes more restrictive when the order m increases, as is pointed out in Fig. 2 where are plotted the curves corresponding to the cases $m=2$ (curve *a*) and $m=29$ (curve *b*) for one element ($E_q=1{\cdot}12$) of a determinant of isoniazide (Tsoucaris & Marsh, 1964).

Remark: All the above formulae remain valid if the phase of a structure factor $\phi(E_q)$ is replaced by the phase of the structure invariant:

$$\phi(T_q)=\phi(E_1^*)+\phi(U_{q1})+\phi(E_q)$$

as will be indicated in a forthcoming paper (Rango, Tsoucaris, Zelwer & Sarrazin, 1974, referred to as Paper III).

II. 4. *Generalization of the regression-plane formula*

When any number s ($s<m$) of structure factors E_p of the last row are known, the distribution of the $(m-s)$ unknown E's can be derived from the m-dimensional law (7) (Fortet, 1965):

$$p(E_{s+1},\ldots E_m/[\mathbf{U}],\,E_1\ldots E_s)=\frac{(D'_{m-s})^{1/2}}{(2\pi)^{(m-s)/2}}\times\exp\left(-\tfrac{1}{2}Q'_{m-s}\right)\text{ centrosymmetric case}\quad(13a)$$

$$p(E_{s+1},\ldots E_m/[\mathbf{U}],\,E_1\ldots E_s)=\frac{D'_{m-s}}{\pi^{m-s}}\times\exp\left(-Q'_{m-s}\right)\text{ non-centrosymmetric case}\quad(13b)$$

with:

$$Q'_{m-s}=\mathbf{X}[\mathbf{U}]^{-1}_{m-s}\mathbf{X}^+.\qquad(14)$$

The Hermitian form Q'_{m-s} is deduced from Q'_m according to the following scheme:

$$\begin{bmatrix}[\mathbf{U}]_s^{-1} & \mathbf{T}^+\\ \mathbf{T} & [\mathbf{U}]^{-1}_{m-s}\end{bmatrix}\quad\begin{bmatrix}(\mathbf{E})_s^+\\ \mathbf{X}^+\end{bmatrix}$$
$$[(\mathbf{E})_s \quad \mathbf{X}]$$

$[\mathbf{U}]^{-1}_{m-s}$ denotes the matrix whose determinant is D'_{m-s}, derived from the matrix $[\mathbf{U}]^{-1}$ by suppressing the s rows and columns corresponding to known elements. The $(m-s)$ elements X_q of the vector X are defined as follows:

$$X_q=E_q-(\bar{E}_q)_s;\quad(\bar{E}_q)_s=-\sum_{r=s+1}^{m}D'_{rq}\alpha_r;\qquad\alpha_r=\sum_{\substack{p=1\\p\neq q}}^{s}D_{pr}E_p\qquad(15)$$

in which D'_{rq} is the element of the inverse matrix of $[\mathbf{U}]^{-1}_{m-s}$ and α_r is defined by the linear combination of the product of known structure factors and elements of the matrix $\mathbf{T}$.

This law will be further examined in a forthcoming paper.

II. 5. *Case of several determinants*

In the course of practical applications, it often happens that the same structure factor, denoted E_q, appears in several determinants.

In this case, it would be tempting to evaluate an average value by summing over all $\bar{E}_q$'s obtained by these determinants (each of them being labelled by the index i). In performing this average, it is implicitly assumed that the terms are independent of each other

$$E_q\simeq\langle\bar{E}_q\rangle_i\,.\qquad(16)$$

It might be better to weight each term by the corresponding inverse variance:

$$E_q=\frac{1}{\sum_{i=1}^{n}\omega_i}\sum_{i=1}^{n}\omega_i(\bar{E}_q)_i;\quad\omega_i=\frac{1}{(\sigma_q^2)_i}=(D_{qq})_i\,.\qquad(17)$$

These expressions are a convenient way of taking into account the 'redundancies' which occur in the course of practical crystallographic structure analysis by the determinant method. By redundancy is meant the fact that the same structure factor E_q, or a symmetry-related structure factor, appears several times in different $\Delta_{m+1}(\mathbf{L})$ determinants. A more sophisticated way of treating redundancies is given in paper III.

The number of $\Delta_{m+1}(\mathbf{L})$ defined from a given determinant D_m could be very large since $\mathbf{L}$ can sweep all observed reciprocal space. However, for each $\Delta_{m+1}(\mathbf{L})$ all structure factors $E_{\mathbf{L}-\mathbf{H}_q}$ are not observed; also, it is convenient to delete the rows and columns corresponding to the structure factors $E_{\mathbf{L}-\mathbf{H}_q}$ whose moduli are out of reach of the experiment.

This procedure leads to the consideration of a group of different D_r determinants ($r\leq m$) issued from the same D_m rather than only one determinant. For instance, in the case of Jamine (Karle & Karle, 1964) the practical application of formula (1) (de Rango, 1969; Paper III) has been performed by considering a large number of different D_r determinants ($10\leq r\leq 18$) issued from the given determinant D_{18}. Of course, not all $\Delta_{r+1}(\mathbf{L})$ are to be considered; (the total number of ob-

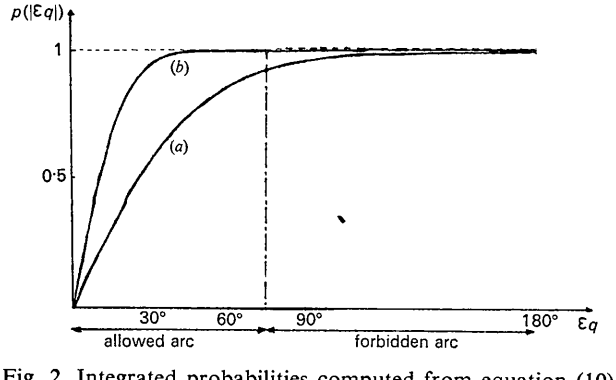


Fig. 2. Integrated probabilities computed from equation (10) for one structure invariant corresponding to one element of an order 30 Karle–Hauptman determinant of isoniazide ($|E_q|=1{\cdot}12$) in case $m=2$ ($A_q=2{\cdot}6$) curve (*a*) and $m=29$ ($A_q=13{\cdot}6$), curve (*b*). The correct values of $|\varepsilon_q|$ are respectively 50 and 6°. In the case $m=29$, the values of $|\varepsilon_q|>74°$ are forbidden by inequalities whereas in the case $m=2$ all values are allowed.

served structure factors in the Jamine data is 1831) only some hundred of them are necessary to perform the determination of the structure.

In the non-centrosymmetric case, the complex expression (16) amounts to one equation for moduli and another for the tangent of the phase:

$$\tan \varphi(E_q) = \frac{\sum_{i=1}^{n} |\bar{E}_q|_i \sin \varphi(\bar{E}_q)_i}{\sum_{i=1}^{n} |\bar{E}_q|_i \cos \varphi(\bar{E}_q)_i} . \qquad (18)$$

In a recent paper, Karle (1971) has examined the relation between E_q and the right-hand side of (18), assuming that E_q is proportional to the average estimation in equation (11), he then indicates that algebraic analysis involving expansions of the determinants and use of the structure factors expression should verify this assumption.

However, for high-order and small-value determinants (say $m=20$ for $N=50$ to 100) a reasonably accurate value of E_q can be obtained even with one term in (16). An idea of the agreement for an actual structure will be given in Paper III. On the contrary, the results we have obtained both in centrosymmetric and non-centrosymmetric cases, indicate that for low-order determinants, it is likely that a very large number of terms should be included to obtain an accurate value of E_q.

III. Connexion between inequalities and probabilities

III. 1. *m-Dimensional case*

In this section we consider the m-dimensional probability law (7) as well as the conditional probability laws (5) and (13).

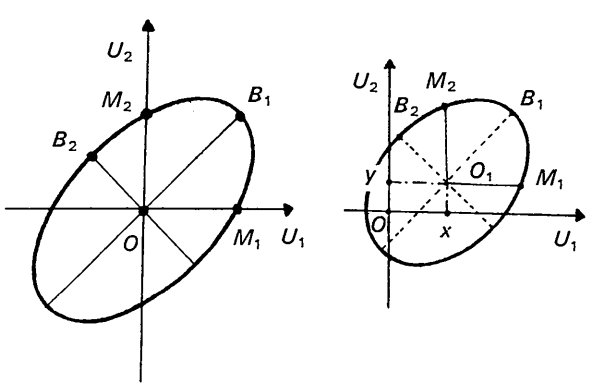


Fig. 3. Boundary ellipses in two special cases (*a*) $m=2$. The ellipses surface is: $S_1=\pi\lambda_1\lambda_2=\pi D_2=\pi(1-U_{\mathbf{H}}^2)$; the ellipse axes are: $OB_1=\lambda_1=1+U_{\mathbf{H}}$, $OB_2=\lambda_2=1-U_{\mathbf{H}}$; the coordinate axis intersections are: $OM_1=OM_2=\sigma=\sqrt{1-U_{\mathbf{H}}^2}$. (*b*) $m=3$, $s=1$. The ellipse surface is: $S_2=\pi D_3(1-U_{\mathbf{H}}^2)$; the ellipse centre coordinates are: $Ox=U_{\mathbf{K}}U_3$, $Oy=U_{\mathbf{K}-\mathbf{H}}U_3$;

$$O_1M_1=\sigma_1=\sqrt{\frac{1}{1-U_{\mathbf{K}-\mathbf{H}}^2}}\ ,\quad O_1M_2=\sigma_2=\sqrt{\frac{1}{1-U_{\mathbf{K}}^2}}\ .$$

Let us consider the determinant Δ_{m+1} as a function of m variables (real or complex) included in the last row (or column):

$$\Delta_{m+1}(E_1 \ldots E_m) \geq 0 .$$

In the non-centrosymmetric case, the m-dimensional complex function is, in fact, a special $2m$-dimensional real function of variables $A_1 \ldots A_m$, $B_1 \ldots B_m$; A_m and B_m being the real and imaginary parts of E_m. For simplicity, we will refer to an m-dimensional function whether the function is real or complex.

In all cases, the limiting equation $\Delta_{m+1}=0$ defines the inequality boundary which separates the m-dimensional space into allowed and forbidden regions.

From the theory developed or recalled in this paper, and summarized by the following formulae:

$$p(E_1 \ldots E_m) = K' \exp \frac{N}{D_m} \cdot \Delta_{m+1} \qquad (19a)$$

$$\text{if } \Delta_{m+1} \geq 0 \qquad (20a)$$

or, equivalently:

$$p(E_1 \ldots E_m) = K \exp(-Q_m) \qquad (19b)$$

if

$$0 \leq Q_m \leq N , \qquad (20b)$$

it is clear that both the equiprobability surfaces [equation (19*a*)] and the inequality boundary (20*a*) are determined by the relation:

$$\Delta_{m+1}(E_1 \ldots E_m) = \text{constant} . \qquad (21a)$$

Alternatively the same results can be equivalently expressed in terms of the Hermitian form:

$$\frac{Q_m(E_1 \ldots E_m)}{N} = 1 - \frac{\Delta_{m+1}(E_1 \ldots E_m)}{D_m} = \text{constant.} \qquad (21b)$$

The Q_m $(E_1 \ldots E_m)$ expressions have the advantage of providing a clear geometrical image, as described below.

(*a*) *Region allowed by inequalities*

The boundary surface is a hyperellipsoid denoted by f_0 and defined by the equation:

$$\frac{1}{N} Q_m(E_1 \ldots E_m) = 1 . \qquad (22)$$

In the real case, we point out two geometrical properties of the allowed region f_0, which will be used in §IV (in the complex case, a similar geometrical construction can be imagined):

(1) The content of f_0 is proportional to D_m (independent of Δ_{m+1}), the content of f_0 is given in the real case by Kendall (1961):

$$V = \frac{2}{m} D_m \frac{\pi^{m/2}}{\Gamma(m/2)} . \qquad (23)$$

(2) The proper axes of a hyperellipsoid Q_m are proportional to the eigenvalues of the matrix [U]. Moreover, the coordinates of the intersections between the inequality boundary and the axes of the bases of the

variables $(E_1 \ldots E_m)$ are proportional to the corresponding standard deviations $(\sigma_1 \ldots \sigma_m)$ given by equation (6) (Fig. 3).

Equiprobability surfaces

The equiprobability surfaces coincide with hyperellipsoids homothetic to the hyperellipsoid f_0. The probability density has the highest value at the centre of the hyperellipsoid which coincides with the origin $(E_1=0, \ldots E_m=0)$.

It should be noted that equation (19) does not describe correctly the probability density near the boundaries. This is a consequence of the fact that the central limit theorem, which is the basis of equation (19) is only an approximation. A strict probability theory should yield a zero probability density in the forbidden region, whereas in equation (19) the probability steadily decreases from the centre, is equal to Ke^{-N} at the inequality boundary and becomes zero only at infinite distance.

For $m=1$, in the non-centrosymmetric case, the boundary hyperellipsoid reduces to the familiar complex circle:

$$|E_1|^2 = A_1^2 + B_1^2 \leq N .$$

Fig. 3(*a*) formally corresponds to the centrosymmetric case with $m=2$ (variables: $U_1 = E_K/\sqrt{N}$, $U_2 = E_{K-H}/\sqrt{N}$). The surface of the allowed region is: $V = \pi D_2$.

For $m \geq 3$ the hyperellipsoid can have any orientation with respect to the coordinate axes $(U_1 \ldots U_m)$ whereas for $m=2$ the axes are at 45° to the coordinate axes.

Let us examine now the case where s structure factors of the last column are known and fixed, the remaining being considered as variables. It follows from equations (14) and (15) that the maximum probability is obtained for:

$$E_q = (\bar{E}_q)_s ; \quad q = s+1, \ldots m .$$

The set of $(\bar{E}_q)_s$ defines the centre of a hyperellipsoid. Therefore, we can state:

For any set of $(m-s)$ structure factors included in one row or column of a determinant Δ_{m+1}, *the allowed region is a hyperellipsoid. The most probable set of values is that which corresponds to the centre of the allowed hyperellipsoid.* Fig. 3(*b*) corresponds to the centrosymmetric case with $m=3$, $s=1$; (variables U_1, U_2, with $U_3 = E_3/\sqrt{N}$ as fixed value) the volume of the allowed hyperellipsoid, which is reduced to an ellipse, is: $V = \pi D_3(1-U_3^2)$.

III. 2. *Regression-plane equation* (*special non-centrosymmetric case*: $s=m-1$)

(*a*) *Inequalities and expected values*

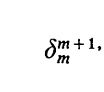
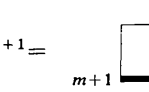
Karle & Hauptman (1950) have shown that X_q is limited in modulus by a constant r:

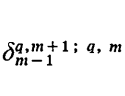
$$|X_q| = \sqrt{N}|U_q - \delta_q| \leq \sqrt{N} \, . \, r . \qquad (24)$$

This inequality is strictly equivalent to the familiar inequality $D_{m+1} \geq 0$. In relation (24) r is a real positive number defined as follows:

$$r^2 = \frac{\delta_m^{m+1,\,m+1}\,\delta_m^{qq}}{|\delta_{m-1}^{q,m+1;q,m+1}|^2} . \qquad (25a)$$

$\delta_m^{m+1,\,m+1}$, δ_m^{qq} and $\delta_{m-1}^{q,m+1;\,q,m+1}$ are obtained from a determinant D_{m+1} as explained in §II. 1 (the last collumn and row of D_{m+1} include U's);

$\delta_m^{m+1,\,m+1} =$  ; $\delta_m^{qq} =$ 

$\delta_{m-1}^{q,m+1;\,q,\,m+1} =$ 

δ_q has been expressed in the original paper of Karle & Hauptman (1950), equation (25), from a minor of the initial determinant† denoted by δ. A comparison between the determinant δ_q, developed along one column, and $\bar{U}_q$, given by equation (1), shows immediately that:

$$\boxed{\delta_q = \bar{U}_q} . \qquad (26)$$

The coincidence is not fortuitous; it expresses an important property in crystal-structure analysis which can be stated as follows:

The expected phase $\varphi(\bar{U}_q)$ of a structure factor included in a Karle–Hauptman determinant given all other structure factors, is given by the middle of the interval allowed by inequalities for this structure factor.

This statement is a special case of the conclusion given above for the general multivariate case.

We will show that in equation (24) not only has δ_q a probability meaning given by equation (26), but r can also be connected with probability theory.

Let us write the expression r^2 as follows:

$$r^2 = \frac{\delta_m^{m+1,\,m+1}}{\delta_{m-1}^{q,m+1;q,\,m+1}} \cdot \frac{\delta_m^{q,q}}{\delta_{m-1}^{q,m+1;\,q,\,m+1}} . \qquad (25b)$$

We recognize in the first factor the expression for the variance σ_q^2 already given in equation (6). The second factor also has the meaning of a variance, but it corresponds to a different set of random variables, although Δ_{m+1} is still the same, as shown below.

Let us consider, for simplicity, that the unknown factor is $E_{m+1,1}$ and the m-dimensional law is now:

$$p(E_{1,2}, \ldots E_{1,q}, \ldots E_{1,m}, E_{1,m+1}) .$$

In other words, starting from the matrix of Table 1, we have to interchange the first and last rows and then the first and last columns. After this interchange, the

† In the Karle–Hauptman original paper the initial determinant was D_m. But here, in connexion with probability theory, we consider U_q as an element of D_{m+1}.

structure factor $E_{m+1,1}$ is replaced by its conjugate $E_{1,m+1}$ in Δ_{m+1}.

Now, from the general m-dimensional law, we can deduce a new conditional probability law where D_m is replaced by $\delta_m^{1,1}$, and σ_1 by σ_1':

$$(\sigma_1')^2 = \frac{\delta_m^{1,1}}{\delta_{m-1}^{1,m+1;\ 1,m+1}} .$$

The δ's are minors defined from the initial D_{m+1} *before* the interchange described above. For any structure factor E_q the same result is obtained after an obvious interchange between the qth and first row (and column).

Finally r, for a given q and m, can be written as:

$$r^2 = (\sigma_q \,.\, \sigma_q')^2 . \qquad (25c)$$

In other words, the radius of the allowed circle is equal to the geometrical mean of the variances associated with the two ways of expresssing a conditional probability law for one structure factor included in Δ_{m+1}.

(*b*) *Strict equalities*

In the following special cases inequality (24) becomes strict equality

$m=N$:

$$|U_q - \bar{U}_q| = r; \quad (U_q = U_{N+1,q} \text{ belongs to } D_{N+1}) . \qquad (27)$$

$m=N+1$: The relation (24) is still an equality but with $r=0$

$$|U_q - \bar{U}_q| = 0 \quad \text{or} \quad U_q = \bar{U}_q . \qquad (28)$$

This equation can be written in the following form:

$$U_q = -\frac{1}{\delta_N^{qq;\ N+2,N+2}} \sum_{\substack{p=1 \\ p\neq q}}^{N+1} (-1)^{p+q} \delta_N^{qp;\ N+2,N+2} U_p . \qquad (29)$$

The structure factors U_q are elements of the last row and column of a Karle–Hauptman determinant of order $N+2$ and the δ's are determinants as defined previously:

$$\delta_N^{qq;\ N+2,\ N+2} = \begin{matrix} & & & & q & N+2 \\ & & & & \square & \square \\ N+2 & q & & & & \end{matrix}$$

$$\delta_N^{qp;\ N+2,\ N+2} = \begin{matrix} & & & p & N+2 \\ & & & \square & \square \\ N+2 & q & & & \end{matrix} .$$

We notice that although $D_{N+1}=D_{N+2}=0$, only minors of order N, not generally null, are involved in (29). This equation is valid for atoms of any atomic number.

III. 3. *Discussion*

In the general case, the principal trends of the connexion between inequality and probabilities theories are:

– all equiprobability surfaces, defined by equation (21*b*) and having physical sense, are hyperellipsoids included within 'the inequality boundary hyperellipsoid'

– the most probable set of phases corresponds to the centre of the allowed hyperellipsoid in the case of equation (14).

In the special non-centrosymmetric case, $s=m-1$, the boundary hyperellipsoid is reduced (in complex space) to an allowed circle, first given by Hauptman & Karle (1950); the radius r of this circle is recalled by equation (25), the most probable value, at the centre of the circle, is given by equation (26). The difference X_q between $\bar{E}_q$ and the actual value of E_q depends on r. From the theory developed in this paper, it appears that X_q enters several relations with different meanings as summarized in Table 2; equivalent relations involving an order-$(m+1)$ determinant, the elements of which are assumed known except one, are also given.

Table 2. *Summary of the mathematical properties of Karle–Hauptman determinants*

Relations involving the determinant	Relations involving expression (2)	Meaning	Restrictions
$D_{m+1}\geq 0$	$\lvert X_q\rvert \leq r \,.\, \sqrt{N}$	Inequalities	$m\leq N$
D_{m+1} is max. for the most probable phase	$\lvert X_q\rvert$ most probable phase $=0$	Statistics	$m<N$
$D_{N+1}=0$	$\lvert X_q\rvert = r \,.\, \sqrt{N}$	Strict equalities	$m=N$
$D_{N+2}=0$	$\lvert X_q\rvert = 0$		$m=N+1$

For practical purposes, useful information can be provided with the approximate equation $X_q=0$, although it is strict only for $m=N+1$. The inequalities are useful only if r is small as shown in Fig. 4, where the calculation was done with the coordinates of isoniazide: the order-30 determinant can be very restrictive for phases whereas the Δ_3 is not at all. But, even if r is not small enough to restrict phases sufficiently, probability theory can still provide useful information (in the example of Fig. 4, the correct values of $|\varepsilon_q|$ are very small: 1 and 6°).

Indeed, the approximate equation $X_q=0$ has been used for practical purposes even for $m \ll N$ and has provided the basis of procedures for direct determination of phases as will be pointed out in Paper III.

IV. Efficiency of the probability laws for phase determination

We consider the efficiency for phase determination of the general probability laws as well as that of the regression law (5). These distributions are characterized by the variance–covariance matrix [U] whose determinant is D_m.

The criterion of the highest efficiency we are seeking has been derived from a combination of information

theory and probability theory (Renyi, 1966). It states that:

The information quantity which can be extracted from any Δ_{m+1} about any set $(E_1 \ldots E_m)$ depends solely on the value of D_m: *the D_m of smallest value provides the largest information obtainable about the phases of any set* $(E_1 \ldots E_m)$; (de Rango, 1969). Here, the notion of information has a precise mathematical meaning (Shannon & Weaver, 1949).

In order to examine the physical meaning of the above mathematical statement, we will use a geometrical construction. This geometrical image is based upon the fact that the equiprobability surfaces steadily decrease from the centre of the allowed region, where $p(E_1 \ldots E_m)$ is maximum, to the outer boundary, where $p(E_1 \ldots E_m)$ should be zero.

Clearly, *the steeper the decrease, the more efficient the probability laws.* Therefore, the decrease of probability depends on:

– the value of $p(E_1 \ldots E_m)$ at the origin, which is inversely proportional to the square root of D_m,

– the distance from the centre of the hyperellipsoid to the outer boundary (zero probability) which decreases in average as D_m decreases; however, this distance is a function of the particular geometrical form of the hyperellipsoid for a given direction (see §III).

Both factors are most favourable for the lowest value of D_m, in agreement with the mathematical statement. Also, the geometrical construction of §III shows that the criterion for highest efficiency, *i.e.* a small value of D_m, still applies for the phase determination of the last row of Δ_{m+1} by using only inequalities.

The m-dimensional Laplace–Gauss law is based on the hypothesis that there exists no rational relationship between atomic coordinates. If such a relationship occurs and if the structure contains special trends (for instance several atoms lie in the same plane), then the probability law and the criterion of the highest efficiency are not strictly valid in the statistical sense, but, of course, the inequalities remain valid.

In a forthcoming paper, both theories, inequalities and probabilities, will be used in practical structure determination.

APPENDIX I
m-Dimensional Laplace–Gauss law
Centrosymmetric case

Assuming that the elements of the variance–covariance matrix [**U**] are given, the aim of this section is the evaluation of the conditional joint probability of the m-dimensional random variable $(E_1 \ldots E_m)$. Let us set

$$q=1,\ldots m; \quad E_q=\sum_{j=1}^{N/S} \mathbf{x}_{jq} \tag{I.1}$$

where

$$x_{jq}=\sum_{s=1}^{S} g_j \exp\left[2\pi i(\mathbf{L}-\mathbf{H}_q)\,.\,\mathbf{r}_{js}\right]$$

is the contribution to E_q of the S atoms at $\mathbf{r}_{js}$ related to the jth independent atom by the crystal symmetry. The system of m equations,

$$\begin{cases} E_1 = x_{11}+\ldots x_{j1}+\ldots x_{n1} \\ \quad\cdot\quad\cdot\quad\ldots\quad\ldots \\ E_q = x_{1q}+\ldots x_{jq}+\ldots x_{nq} \\ \quad\cdot\quad\cdot\quad\ldots\quad\ldots \\ E_m = x_{1m}+\ldots x_{jm}+\ldots x_{nm} \end{cases} \tag{I.2}$$

where $n=N/S$, can be condensed into one vector equation:

$$\mathbf{E}=\sum_{j=1}^{n} \mathbf{x}_j \tag{I.3}$$

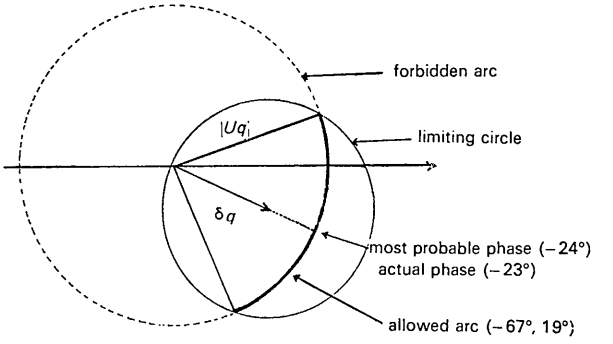
by using the vectors:

$$\mathbf{E}=(E_1 \ldots E_m) \quad \mathbf{x}_j=(x_{j1} \ldots x_{jm})\,.$$

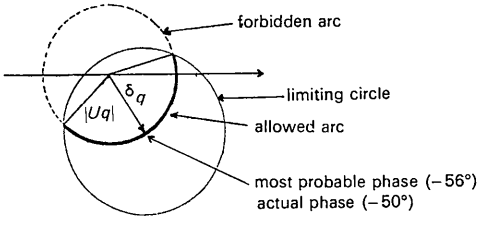
Consequently, for a given q the random variables $x_{1q} \ldots x_{nq}$ are mutually independent. In simpler terms: columns in system (2) are mutually independent, but the random variables along each column (**x**'s and **E**'s) are linked to each other through the given variance–covariance matrix [**U**].

Let us denote by $p_1(\mathbf{x}) \ldots p_n(\mathbf{x})$ the probability law for each of the n variables $\mathbf{x}_1 \ldots \mathbf{x}_n$. As a result of the independence of atoms the probability law $p(\mathbf{E})$ is given by the convolution product:

$$p(\mathbf{E})=p_1(\mathbf{x})*p_2(\mathbf{x})*\ldots p_n(\mathbf{x})\,. \tag{I.4}$$



(*a*)



(*b*)

Fig. 4. Limitation on the phase of two structure factors, elements of Δ_{30} for isoniazide arising from inequalities (24). The correct values are located very near the middle of the allowed arc. For Δ_3 all values are allowed since there is no intersection between the two circles.

The characteristic function is:

$$C(\mathbf{u})=\int_{v_E} p(\mathbf{E})\exp(2\pi i\mathbf{u}\,.\,\mathbf{E})\mathrm{d}v_E=\prod_j C_j(\mathbf{u}) \quad \text{(I.5)}$$

where $\mathbf{u}=(u_1\ldots u_m)$ is an m-dimensional vector expressed in a reciprocal-space reference system such that the scalar product is:

$$\mathbf{u}\,.\,\mathbf{E}=\sum_{q=1}^{m} u_q E_q\,.$$

The second characteristic function $K(\mathbf{u})$ is defined by:

$$K(\mathbf{u})=\log[C(\mathbf{u})]=\sum_j K_j(\mathbf{u})=\sum_j \log[C_j(\mathbf{u})]\,. \quad \text{(I.6)}$$

Let us expand $C_j(\mathbf{u})$ as a Maclaurin series:*

$$C_j(\mathbf{u})=\int_{v_x} p_j(\mathbf{x})\left(\sum_{k=0}^{\infty}\frac{(2\pi i\mathbf{u}\,.\,\mathbf{x}_j)^k}{k!}\right)\mathrm{d}v_x\,. \quad \text{(I.7)}$$

The meaning of the kth term is obviously: 'average value of $(2\pi i\mathbf{u}\,.\,\mathbf{x})^k/k!$'

$$C_j(\mathbf{u})=\sum_{k=0}^{\infty}\frac{1}{k!}\overline{(2\pi i\mathbf{u}\,.\,\mathbf{x}_j)^k}^{L}=1-2\pi^2\overline{(\mathbf{u}\,.\,\mathbf{x}_j)^2}^{L}+\ldots\,. \quad \text{(I.8)}$$

Up to $k=2$, these averages have very simple expressions;
for $k\geq 3$ they are negligible if $n\to\infty$.

$$\text{For } k=0 \quad \int_{v_u} p_j(\mathbf{x})\mathrm{d}v_u=1\,.$$

If we assume that no atoms are in special positions, it follows that:

$$\text{for } k=1 \quad \overline{(\mathbf{u}\,.\,\mathbf{x}_j)}=\sum_{q=1}^{m} u_q\overline{x_{jq}}=0\,.$$

Therefore,

$$K(\mathbf{u})=\sum_j K_j(\mathbf{u})=-2\pi^2\sum_j\overline{(\mathbf{u}\,.\,\mathbf{x}_j)^2}+\ldots\,. \quad \text{(I.9}a\text{)}$$

By summing over j and inverting the order of the summations, we obtain:

$$\sum_{j=1}^{n}\overline{(\mathbf{u}\,.\,\mathbf{x}_j)^2}=\sum_{p=1}^{n}\sum_{q=1}^{m}u_p u_q\sum_j x_{jp}x_{jq}=\mathbf{u}^+[\mathbf{U}]\mathbf{u}\,, \quad \text{(I.10)}$$

where $\mathbf{u}$ is a column vector, $\mathbf{u}^+$ a line vector, $[\mathbf{U}]$ the variance–covariance matrix. The proof of the basic equality:

$$\sum_j\overline{x_{jp}x_{jq}}=\overline{E_pE_q}=U_{\mathbf{H}_q-\mathbf{H}_p}=U_{qp} \quad \text{(I.11)}$$

is obtained by replacing E_p and E_q in the product (E_p,E_q) by their defining equations (I.1), because the 'cross atom' terms $(i\neq j)$ vanish as a consequence of the mutual independence of atoms.

Alternative proof of (I.11)

Les us recall the meaning of x_{jp} and x_{jq} [equation (1)] as the contribution of S (equal) atoms to, respectively, $E_{\mathbf{H}_p}$ and $E_{\mathbf{H}_q}$. Then by applying the Sayres–Hughes equations to these partial structure factors, we can write immediately:

$$\overline{x_{jp}x_{jq}}=g_j^2\sum_{s=1}^{S}\exp[(2\pi i\mathbf{H}_q-\mathbf{H}_p)\,.\,\mathbf{r}_{js}]$$

and

$$\sum_j\overline{x_{jp}x_{jq}}=U_{\mathbf{H}_q-\mathbf{H}_p}=U_{qp}\,.$$

We recognize in the right-hand side of equation (I.10) a quadratic form which is 'definite-non-negative' because $[\mathbf{U}]$ is a definite-non-negative matrix.

Terms $k\geq 3$

Recalling that $g_j=(N)^{-1/2}$, we write:

$$x_{jq}=\frac{1}{\sqrt{N}}\sum_{s=1}^{S}\exp[2\pi i(\mathbf{L}-\mathbf{H}_q)\,.\,\mathbf{r}_{sj}]=\frac{1}{\sqrt{N}}\,t_{jq}\,.$$

Let us evaluate r:

$$r=\frac{\overline{(\mathbf{u}\,.\,\mathbf{x}_j)^k}}{\overline{(\mathbf{u}\,.\,\mathbf{x}_j)^2}}=\left(\frac{1}{N}\right)^{k/2-1}\frac{\overline{(\sum_q u_q t_{jq})^k}}{\overline{(\sum_q u_q t_{jq})^2}}\,.$$

The ratio on the right-hand side is a function of the u's independent of N. Therefore $r\to 0$ as $N\to\infty$ (for odd values of k, r is strictly null).

Coming back to (I.9a), we write:

$$K(\mathbf{u})=-2\pi^2(\mathbf{u}^+[\mathbf{U}]\mathbf{u}) \quad \text{(I.9}b\text{)}$$

$$C(\mathbf{u})=\exp[K(\mathbf{u})]=\exp\{-2\pi^2(\mathbf{u}^+[\mathbf{U}]^{-1}\mathbf{u})\}\,. \quad \text{(I.12}$$

This is an m-dimensional Laplace–Gauss function and $p(\mathbf{E})$ is derived by a classical Fourier transformation.

$$p(\mathbf{E})=\frac{1}{(2\pi)^{m/2}(D_m)^{1/2}}\exp\{-\tfrac{1}{2}(\mathbf{E}\,[\mathbf{U}]^{-1}\mathbf{E}^+)\} \quad \text{(I.13)}$$

where D_m is the determinant of the variance–covariance matrix $[\mathbf{U}]$; $[\mathbf{U}]^{-1}$ is the inverse matrix of $[\mathbf{U}]$.

If we denote by D_{pq} the elements of the inverse matrix, the quadratic form in the exponent is expressed by:

$$\mathbf{E}[\mathbf{U}^{-1}]\mathbf{E}^+=\sum_{p=1}^{m}\sum_{q=1}^{m}D_{pq}E_pE_q=N\frac{D_m-\Delta_{m+1}}{D_m}\,. \quad \text{(I.14)}$$

APPENDIX II

m-Dimensional Laplace–Gauss law Non-centrosymmetric case

Let us set:

$$E_{\mathbf{L}-\mathbf{H}_q}=E_q=A_q+iB_q=\sum_{j=1}^{n}g_j\sum_{s=1}^{S}\exp[2\pi i\times(\mathbf{L}-\mathbf{H}_q)\mathbf{r}_{js}] \quad \text{(II.1)}$$

where

$$A_q=\sum_{j=1}^{n}x_{jq};\quad x_{jq}=g_j\sum_{s=1}^{S}\cos 2\pi(\mathbf{L}-\mathbf{H}_q)\mathbf{r}_{js} \quad \text{(II.2)}$$

$$B_q=\sum_{j=1}^{n}y_{jq};\quad y_{jq}=g_j\sum_{s=1}^{S}\sin 2\pi(\mathbf{L}-\mathbf{H}_q)\mathbf{r}_{js}\,.$$

* The index j is suppressed when it enters as an integration variable.

Again, following the classical notation in probability theory, we consider the m-dimensional row vector $\mathbf{E}$ with complex coordinates:

$$\mathbf{E}(E_1 \dots E_m) = \sum_{j=1}^{S} \mathbf{Z}_j \quad \text{with } \mathbf{Z}_j = \mathbf{x}_j + i\mathbf{y}_j \qquad \text{(II.3)}$$

and the m-dimensional vectors $\mathbf{A}$, $\mathbf{B}$ with real coordinates:

$$\mathbf{A}(A_1 \dots A_m), \quad \mathbf{B}(B_1 \dots B_m) .$$

By definition, the probability law for the m-dimensional random variables $(E_1 \dots E_m)$ is identical to the probability law for the $2m$-dimensional real variables: $(A_1 B_1, \dots A_m, B_m)$:

$$p(\mathbf{E}) = p(\mathbf{A},\mathbf{B}) .$$

The calculation will be performed in real $2m$-dimensional (Euclidian) space, but in the last step, the introduction of complex vectors in m-dimensional Hilbert space will lead to an expression which is formally very similar to equation (I.13).

We give the development of the theory following closely the development in the real case. The hypothesis of the mutual independence of atoms, leads to the fundamental equation:

$$p(\mathbf{A},\mathbf{B}) = p_1(\mathbf{x},\mathbf{y}) * \dots * p_n(\mathbf{x},\mathbf{y}) . \qquad \text{(II.4)}$$

The characteristic function is:

$$C(\mathbf{u},\mathbf{t}) = \int_{v_{\mathbf{A},\mathbf{B}}} p(\mathbf{A},\mathbf{B}) \exp\left[2\pi i(\mathbf{A}\,.\,\mathbf{u} + \mathbf{B}\,.\,\mathbf{t})\right] \mathrm{d}v_{\mathbf{A},\mathbf{B}} = \prod_j C_j(\mathbf{u},\mathbf{t}) . \qquad \text{(II.5)}$$

The second characteristic function is:

$$K(\mathbf{u},\mathbf{t}) = \log C(\mathbf{u},\mathbf{t}) = \sum_j K_j(\mathbf{u},\mathbf{t}) . \qquad \text{(II.6)}$$

The development in Maclaurin series leads to:

$$C_j(\mathbf{u},\mathbf{t}) = \int_{v_{\mathbf{x},\mathbf{y}}} p_j(\mathbf{x},\mathbf{y}) \sum_{k=0}^{\infty} \frac{([2\pi i(\mathbf{u}\,.\,\mathbf{x} + \mathbf{t}\,.\,\mathbf{y})]^k)}{k!} \mathrm{d}v_{\mathbf{x},\mathbf{y}} \qquad \text{(II.7)}$$

$$C_j(\mathbf{u},\mathbf{t}) = \sum_{k=0}^{\infty} \frac{1}{k!} \overline{[2\pi i(\mathbf{u}\,.\,\mathbf{x} + \mathbf{t}\,.\,\mathbf{y})]^k}^{\,\mathrm{L}} \qquad \text{(II.8)}$$

$$K(\mathbf{u},\mathbf{t}) = \sum_j K_j(\mathbf{u},\mathbf{t}) = -2\pi^2 \sum_j \overline{(\mathbf{u}\,.\,\mathbf{x} + \mathbf{t}\,.\,\mathbf{y})^2} . \qquad \text{(II.9)}$$

Let us define now the complex vector:

$$\mathbf{w} = \mathbf{u} + i\mathbf{t} .$$

We prove next that:

$$\sum_j \overline{(\mathbf{u}\,.\,\mathbf{x}_j + \mathbf{t}\,.\,\mathbf{y}_j)^2} = \tfrac{1}{2}\mathbf{w}^+[\mathbf{U}]\mathbf{w} . \qquad \text{(II.10)}$$

The development of the left-hand side gives, after elementary manipulations:

$$\sum_j \overline{(\mathbf{u}\,.\,\mathbf{x}_j + \mathbf{t}\,.\,\mathbf{y}_j)^2} = \sum_{p=1}^{m}\sum_{q=1}^{m} u_p u_q \Big(\sum_j \overline{x_{jp}x_{jq}}\Big) + t_p t_q \Big(\sum_j \overline{y_{jp}y_{jq}}\Big) + u_p t_q \Big(\sum_j \overline{x_{jp}y_{jq}}\Big) + u_q t_p \Big(\sum_j \overline{y_{jp}x_{jq}}\Big) . \qquad \text{(II.10}a\text{)}$$

Following a reasoning similar to that in the real case, it is not difficult to prove that:

$$\sum_j x_{jp}x_{jq} = \sum_j y_{jp}y_{jq} = \tfrac{1}{2}a_{qp}$$
$$\sum_j x_{jp}y_{jq} = -\sum_j y_{jp}x_{jq} = -\tfrac{1}{2}b_{qp} \qquad \text{(II.11)}$$

where

$$U_{qp} = a_{qp} + ib_{qp} .$$

By introducing (II.11) in (II.10a) we arrive at (II.10). The proof that terms in (II.8) with $k=3$ are negligible as $n \to \infty$ is similar to that of the real case. We arrive then at:

$$C(\mathbf{u}\,.\,\mathbf{t}) = \exp\left[K(\mathbf{u}\,.\,\mathbf{t})\right] = \exp\left\{-\pi^2(\mathbf{w}^+[\mathbf{U}]\mathbf{w}\right) . \qquad \text{(II.12)}$$

By Fourier inversion we obtain finally:

$$p(\mathbf{E}) = p(\mathbf{A},\mathbf{B}) = \frac{1}{\pi^m D_m} \exp\left(-\mathbf{E}[\mathbf{U}]^{-1}\mathbf{E}^+\right) . \qquad \text{(II.13)}$$

As in the centrosymmetric case, the Hermitian form in the exponent of equation (II.13) is expressed by:

$$\mathbf{E}[\mathbf{U}]^{-1}\mathbf{E}^+ = \sum_{p=1}^{m}\sum_{q=1}^{m} D_{pq}E_pE_q^* = N\frac{D_m - \Delta_{m+1}}{D_m} . \qquad \text{(II.14)}$$

Remark: in equations (II.12) and (II.13) functions $C(\mathbf{u},\mathbf{t})$ and $p(\mathbf{A},\mathbf{B})$ are *real-valued* functions of *real variables* since the Hermitian forms $\mathbf{w}^+[\mathbf{U}]\mathbf{w}$ and $\mathbf{E}[\mathbf{U}]^{-1}\mathbf{E}^+$ are real. Therefore the expression:

$$p(\mathbf{E}) = p(E_1 \dots E_m)$$

is a condensed way of writing:

$$p(\mathbf{E}) = p(\mathbf{A},\mathbf{B}) = p(A_1, B_1, \dots A_m, B_m) ,$$

and we consider $\mathbf{E}$ as a $2m$-dimensional Laplacian real random variable. The corresponding variance–covariance matrix is a real symmetric matrix constituted by the four sub-matrices:

$$[\mathbf{U}_{XX}], [\mathbf{U}_{YX}], [\mathbf{U}_{XY}], [\mathbf{U}_{YY}]$$

which satisfy the conditions (Fortet, 1961):

$[\mathbf{U}_{XX}]$ and $[\mathbf{U}_{YY}]$ are symmetric and $[\mathbf{U}_{XY}] = -[\mathbf{U}_{YX}]$
$[\mathbf{U}]_{XX} + [\mathbf{U}]_{YY} = \tfrac{1}{2}([\mathbf{U}]^* + [\mathbf{U}])$
$[\mathbf{U}]_{YX} - [\mathbf{U}]_{XY} = \tfrac{1}{2}([\mathbf{U}]^* - [\mathbf{U}])$.

But, as a consequence of (II.11), we have:

$$[\mathbf{U}]_{XX} = [\mathbf{U}]_{YY} = \tfrac{1}{4}([\mathbf{U}] + [\mathbf{U}]^*)$$
$$[\mathbf{U}]_{YX} = -[\mathbf{U}]_{XY} = \tfrac{1}{4}([\mathbf{U}]^* - [\mathbf{U}]) .$$

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Magnetic Symmetry Groups and Their Representation by Stereographic Projections

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Using the theory of representation analysis [Bertaut, E. F. (1968). *Acta Cryst.* A**24**, 217–231] and with the aid of some newly introduced symmetry symbols we present the stereographic projections for all the magnetic symmetry groups. These groups are useful in studying the properties of magnetically ordered crystals.

Introduction

The aim of the present paper is to use the information contained in several related papers (Bertaut, 1968; Boyle, 1969; Krishnamurti & Gopalakrishnamurty, 1969) to construct and present the stereographic projections of all the magnetic point groups. The stereograms for all these groups have been given by Koptsick (1966) in a rather inconvenient and unattractive fashion using red and black colours. We show here by introducing some new symmetry symbols, which are really extensions of the well known ordinary point-group symmetry symbols, that the construction of the stereographic projections for all the magnetic symmetry groups becomes relatively simple. Furthermore the method emphasizes the idea of antisymmetry in a very instructive manner. In the next section we shall briefly introduce the idea of antisymmetry and outline the method used by Bertaut (1968), Boyle (1969) and Krishnamurti & Gopalakrishnamurti (1969) to construct the magnetic symmetry groups.

Antisymmetry and representation theory

In recent years neutron diffraction studies have revealed that all macroscopic properties of magnetic crystals should be characterized by one of the magnetic groups or Shubnikov groups (Shubnikov, 1951; Shubnikov & Belov, 1964; Tavger & Zaitsev, 1956; Opechowski & Guccione, 1965). This is because the 32 ordinary crystallographic point groups merely describe the possible point symmetry of the mean charge-density function $\varrho(\mathbf{r})$ of the crystal in the equilibrium state. In magnetic crystals however, besides $\varrho(\mathbf{r})$ there may also be present a non-vanishing time-averaged distribution of current density $J(\mathbf{r})$ and spin density $S(\mathbf{r})$, or in other words a total magnetic moment density $\mu(\mathbf{r})=J(\mathbf{r})+S(\mathbf{r})$. Now the symmetry of $\mu(\mathbf{r})$ is characterized by a special symmetry transformation which involves the reversal of the vector direction (Tavger & Zaitsev, 1956; Dimmock & Wheeler, 1962*a*,*b*; Wigner, 1959). This specific operation of vector reversal, which is not present in the ordinary crystallographic point groups, is incorporated in magnetic groups by means of a new antisymmetry operator R which simply reverses the sign of magnetic moment at each point in space but does not act on the space coordinates. Shubnikov (1951) introduced the idea of antisymmetry by studying the symmetry groups of the polyhedra with coloured faces and derived 122 coloured groups. These groups have now been shown to be isomorphic with the magnetic groups and are therefore appropriate for describing ordered magnetic crystals. The Shubnikov antisymmetry operator may be thought of as a colour-changing operator (*i.e.* changing black $\leftrightarrow$ white) if the lattice points are thought of as having two possible