spectively. Analogously, the third and fourth rows give the covariants for those groups in which $\varepsilon\tau$ transforms like x_3 or x_4, without or with parity labels.

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The Joint Probability Distribution of the Structure Factors in a Karle–Hauptman Matrix*

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Abstract

The joint probability distribution of *all* structure factors $E_{\mathbf{h}_i-\mathbf{h}_j}$ $(i,j=0,\ldots,m)$ in an $(m+1)\times(m+1)$ Karle–Hauptman matrix is derived for structures in the space group $P1$.

Introduction

The joint probability distribution of the normalized structure factors $E_{\mathbf{h}_0-\mathbf{h}_m}$, $E_{\mathbf{h}_1-\mathbf{h}_m}$, ... and $E_{\mathbf{h}_{m-1}-\mathbf{h}_m}$ where $\mathbf{h}_0,\ldots,\mathbf{h}_{m-1}$ are fixed and $\mathbf{h}_m$ is the primitive random variable leads *via* the conditional joint probability distribution of the phases $\varphi_{\mathbf{h}_0-\mathbf{h}_m},\ldots,\varphi_{\mathbf{h}_{m-1}-\mathbf{h}_m}$ to the maximum-determinant rule for phase determination: the most probable values for the phases $\varphi_{\mathbf{h}_0-\mathbf{h}_m}$, $\ldots,\varphi_{\mathbf{h}_{m-1}-\mathbf{h}_m}$ are those for which the determinant of the Karle–Hauptman matrix (Karle & Hauptman, 1950) with last column $E_{\mathbf{h}_0-\mathbf{h}_m},\ldots,E_{\mathbf{h}_{m-1}-\mathbf{h}_m},E_0$ takes on its maximum value (de Rango, 1969; Tsoucaris, 1970). The distribution of only one structure factor, say $E_{\mathbf{h}_0-\mathbf{h}_m}$, is obtained by fixing the magnitudes and phases of $E_{\mathbf{h}_1-\mathbf{h}_m},\ldots,E_{\mathbf{h}_{m-1}-\mathbf{h}_m}$. The maximum of this distribution gives the most probable value for $E_{\mathbf{h}_0-\mathbf{h}_m}$, expressed in (i) the $E_{\mathbf{h}_i-\mathbf{h}_m}$ $(i=1,\ldots,m-1)$ and (ii) the remaining structure factors in the Karle–Hauptman matrix (de Rango, 1969; Tsoucaris, 1970). From a probabilistic point of view the structure factors (i) and (ii) are of a different nature since for (i) the $E_{\mathbf{h}_i-\mathbf{h}_m}$ are fixed but the reciprocal-lattice vectors $\mathbf{h}_i-\mathbf{h}_m$ are not, while for (ii) the reciprocal-lattice vectors are fixed.

We shall show that it is possible to treat all structure factors in the same way. For structures in space group $P1$ we shall derive the joint probability distribution of *all* structure factors $E_{\mathbf{h}_i-\mathbf{h}_j}$ in a Karle–Hauptman matrix, where all $\mathbf{h}_i$, $\mathbf{h}_j$ are primitive random variables. Two different routes will be followed. The first is straightforward and does not resort to any previous work on determinants. The second involves conditional joint probability distributions and shows both the similarities and differences from the earlier probability calculations that led to the maximum-determinant rule.

As will be shown in the following paper the joint probability distribution of all structure factors in a Karle–Hauptman matrix leads to new functions whose maxima correspond with the most probable values for structure-factor phases.

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Notation

N: number of atoms in the unit cell

Z_j: atomic number of atom j

$$\sigma_n \equiv \sum_{j=1}^{N} Z_j^n$$

$$E_{\mathbf{h}} \equiv \sum_{j=1}^{N} \frac{Z_j}{\sigma_2^{1/2}} \exp(2\pi i \mathbf{h}.\mathbf{r}_j)$$

$$\prod^{m}{}' \equiv \prod_{\substack{i_1=0\\ i_1<i_2}}^{m} \prod_{i_2=0}^{m}$$

$$\sum^{m}{}' \equiv \sum_{\substack{i_1=0\\ i_1<i_2}}^{m} \sum_{i_2=0}^{m}$$

$$\sum^{m}{}'' \equiv \sum_{i_1=0}^{m} \sum_{\substack{i_2=0\\ i_1<i_2<i_3}}^{m} \sum_{i_3=0}^{m}$$

$$\sum^{m}{}''' \equiv \sum_{i_1=0}^{m} \sum_{\substack{i_2=0\\ i_1<i_2<i_3<i_4}}^{m} \sum_{i_3=0}^{m} \sum_{i_4=0}^{m} .$$

The joint probability distribution

First method

Denote by $P(R_{lm}; \Phi_{lm})$ the joint probability distribution of the magnitudes and phases of $E_{\mathbf{h}_0-\mathbf{h}_1}$, $E_{\mathbf{h}_0-\mathbf{h}_2}$, $E_{\mathbf{h}_1-\mathbf{h}_2}$, $E_{\mathbf{h}_0-\mathbf{h}_3}$, $E_{\mathbf{h}_1-\mathbf{h}_3}$, $E_{\mathbf{h}_2-\mathbf{h}_3}$, ..., $E_{\mathbf{h}_0-\mathbf{h}_m}$, $E_{\mathbf{h}_1-\mathbf{h}_m}$, ..., $E_{\mathbf{h}_{m-1}-\mathbf{h}_m}$, where $\mathbf{h}_0, \ldots, \mathbf{h}_m$ are the primitive random variables. Then, analogous to Karle & Hauptman (1958),

$$P(R_{lm}; \Phi_{lm}) = \frac{\prod^{m}{}' R_{i_1 i_2}}{(2\pi)^{m(m+1)}} \int_0^{\infty} \int_0^{2\pi} \cdots$$
$$\cdots \int_0^{\infty} \int_0^{2\pi} \exp\left[-i \sum^{m}{}' R_{i_1 i_2} y_{i_1 i_2} \cos(\alpha_{i_1 i_2} - \Phi_{i_1 i_2})\right]$$
$$\times \prod_{j=1}^{N} q_j(y_{lm}; \alpha_{lm}) \prod^{m}{}' y_{i_1 i_2} \mathrm{d}y_{i_1 i_2} \mathrm{d}\alpha_{i_1 i_2}, \tag{1}$$

in which

$$q_j(y_{lm}; \alpha_{lm}) = \left\langle \prod^{m}{}' \exp\left\{ i \frac{Z_j}{\sigma_2^{1/2}} y_{i_1 i_2} \right.\right.$$
$$\left.\left. \times \cos[2\pi(\mathbf{h}_{i_1} - \mathbf{h}_{i_2}).\mathbf{r}_j - \alpha_{i_1 i_2}] \right\} \right\rangle_{\mathbf{h}_i\text{'s}}. \tag{2}$$

The R_{ij} and Φ_{ij} are the variables corresponding to the magnitudes and phases of the $E_{\mathbf{h}_i-\mathbf{h}_j}$; the y_{ij} and α_{ij} are the corresponding variables of the characteristic function.

The exponentials in (2) are expanded into Bessel functions, the averages of the individual terms are calculated and the Bessel functions are written as ascending series of $(Z_j/\sigma_2^{1/2}) y_{i_1 i_2}$. The result is

$$q_j(y_{lm}; \alpha_{lm}) = 1 - \frac{1}{4} \frac{Z_j^2}{\sigma_2} \sum^{m}{}' y_{i_1 i_2}^2$$
$$- i \frac{1}{4} \frac{Z_j^3}{\sigma_2^{3/2}} \sum^{m}{}'' y_{i_1 i_2} y_{i_2 i_3} y_{i_1 i_3} \cos(\alpha_{i_1 i_2} + \alpha_{i_2 i_3} - \alpha_{i_1 i_3})$$
$$+ \frac{1}{8} \frac{Z_j^4}{\sigma_2^2} \sum^{m}{}''' [y_{i_1 i_2} y_{i_2 i_3} y_{i_3 i_4} y_{i_1 i_4}$$
$$\times \cos(\alpha_{i_1 i_2} + \alpha_{i_2 i_3} + \alpha_{i_3 i_4} - \alpha_{i_1 i_4}) + y_{i_1 i_2} y_{i_2 i_4} y_{i_3 i_4} y_{i_1 i_3}$$
$$\times \cos(\alpha_{i_1 i_2} + \alpha_{i_2 i_4} - \alpha_{i_3 i_4} - \alpha_{i_1 i_3}) + y_{i_1 i_3} y_{i_2 i_3} y_{i_2 i_4} y_{i_1 i_4}$$
$$\times \cos(\alpha_{i_1 i_3} - \alpha_{i_2 i_3} + \alpha_{i_2 i_4} - \alpha_{i_1 i_4})] + O'\left(\frac{1}{N^2}\right), \tag{3}$$

where $O'(1/N^2)$ denotes terms of order $1/N^2$ and higher in which the terms of order $1/N^2$ are independent of the $\alpha_{i_1 i_2}$. The exponential form of (3) $\{1 + x = e^x[1 + O(x^2)]\}$ is used to calculate $\prod q_j$. We obtain

$$\prod_{j=1}^{N} q_j(y_{lm}; \alpha_{lm}) =$$
$$\exp\left\{ -\frac{1}{4} \sum^{m}{}' y_{i_1 i_2}^2 - i \frac{1}{4} \frac{\sigma_3}{\sigma_2^{3/2}} \sum^{m}{}'' y_{i_1 i_2} y_{i_2 i_3} y_{i_1 i_3} \right.$$
$$\times \cos(\alpha_{i_1 i_2} + \alpha_{i_2 i_3} - \alpha_{i_1 i_3}) + \frac{1}{8} \frac{\sigma_4}{\sigma_2^2} \sum^{m}{}''' [y_{i_1 i_2} y_{i_2 i_3}$$
$$\times y_{i_3 i_4} y_{i_1 i_4} \cos(\alpha_{i_1 i_2} + \alpha_{i_2 i_3} + \alpha_{i_3 i_4} - \alpha_{i_1 i_4})$$
$$\left. + \text{two terms}] \right\} \left[1 + O'\left(\frac{1}{N}\right) \right]. \tag{4}$$

Next the integrations in (1) are performed. We collect all terms that depend on α_{01} and y_{01}, and employ the sum of cosines formula

$$\sum_i x_i \cos(\alpha + \beta_i) = A \cos(\alpha + \varepsilon), \tag{5}$$

where A and ε do not depend on α, and

$$A = \left[\sum_{i_1} \sum_{i_2} x_{i_1} x_{i_2} \cos(\beta_{i_1} - \beta_{i_2}) \right]^{1/2}. \tag{6}$$

For the calculation of the integrations with respect to α_{01} and y_{01} we use [Watson (1966), p. 20 formula (5) and p. 393 formula (1)]

$$\int_0^{\infty}\int_0^{2\pi} \exp\left(-\tfrac{1}{4}y^2 - iay\cos\alpha\right) y\,\mathrm{d}y\,\mathrm{d}\alpha = 4\pi \exp(-a^2). \tag{7}$$

The same procedure is applied to $\alpha_{02}, y_{02}, \alpha_{12}, y_{12}, \alpha_{03}, y_{03}, \alpha_{13}, y_{13}, \alpha_{23}, y_{23}, \ldots, \alpha_{0m}, y_{0m}, \alpha_{1m}, y_{1m}, \ldots$ and α_{m-1m}, y_{m-1m} respectively. [In fact this procedure is first applied to the α, y up to and including α_{23}, y_{23}. Then a formula for $P(R_{lm}; \Phi_{lm})$ in which the integrations with respect to the α, y up to and including α_{n-1n}, y_{n-1n} have been performed suggests itself. Next this formula is proved by mathematical induction.] The result of these calculations is

$$P(R_{lm}; \Phi_{lm}) = \frac{\prod'^{\,m} R_{i_1 i_2}}{\pi^{m(m+1)/2}} \exp\Bigg[-\sum^{m}{}' R^2_{i_1 i_2} + 2\frac{\sigma_3}{\sigma_2^{3/2}} \sum^{m}{}'' T_{i_1 i_2 i_3} - 2\frac{\sigma_3^2}{\sigma_2^3} \sum^{m}{}''' (Q_{i_1 i_2 i_3 i_4} + Q_{i_1 i_2 i_4 i_3} + Q_{i_1 i_3 i_2 i_4})\Bigg]\left[1 + O'\left(\frac{1}{N}\right)\right], \tag{8}$$

in which

$$T_{i_1 i_2 i_3} = R_{i_1 i_2} R_{i_2 i_3} R_{i_1 i_3} \cos(\Phi_{i_1 i_2} + \Phi_{i_2 i_3} - \Phi_{i_1 i_3}), \tag{9}$$

$$Q_{i_1 i_2 i_3 i_4} = R_{i_1 i_2} R_{i_2 i_3} R_{i_3 i_4} R_{i_1 i_4} \times \cos(\Phi_{i_1 i_2} + \Phi_{i_2 i_3} + \Phi_{i_3 i_4} - \Phi_{i_1 i_4}), \tag{10a}$$

$$Q_{i_1 i_2 i_4 i_3} = R_{i_1 i_2} R_{i_2 i_4} R_{i_3 i_4} R_{i_1 i_3} \times \cos(\Phi_{i_1 i_2} + \Phi_{i_2 i_4} - \Phi_{i_3 i_4} - \Phi_{i_1 i_3}), \tag{10b}$$

$$Q_{i_1 i_3 i_2 i_4} = R_{i_1 i_3} R_{i_2 i_3} R_{i_2 i_4} R_{i_1 i_4} \times \cos(\Phi_{i_1 i_3} - \Phi_{i_2 i_3} + \Phi_{i_2 i_4} - \Phi_{i_1 i_4}), \tag{10c}$$

and $O'(1/N)$ represents terms of order $1/N$ and higher in which the terms of order $1/N$ are independent of the phases. These higher order terms may contain sums of five phases and more.

Second method

Denote by $P(X_{lm}|X_{lm-1})$ the joint probability distribution of $E_{\mathbf{h}_0-\mathbf{h}_m}, E_{\mathbf{h}_1-\mathbf{h}_m}, \ldots, E_{\mathbf{h}_{m-1}-\mathbf{h}_m}$, where $\mathbf{h}_0, \ldots, \mathbf{h}_m$, are the primitive random variables and $E_{\mathbf{h}_0-\mathbf{h}_1}, E_{\mathbf{h}_0-\mathbf{h}_2}, E_{\mathbf{h}_1-\mathbf{h}_2}, E_{\mathbf{h}_0-\mathbf{h}_3}, E_{\mathbf{h}_1-\mathbf{h}_3}, E_{\mathbf{h}_2-\mathbf{h}_3}, \ldots, E_{\mathbf{h}_0-\mathbf{h}_{m-1}}, E_{\mathbf{h}_1-\mathbf{h}_{m-1}}, \ldots, E_{\mathbf{h}_{m-2}-\mathbf{h}_{m-1}}$ are given. The calculation of this conditional joint probability distribution appears to be only slightly different from the calculation of the joint probability distribution of $E_{\mathbf{h}_0-\mathbf{h}_m}, E_{\mathbf{h}_1-\mathbf{h}_m}, \ldots, E_{\mathbf{h}_{m-1}-\mathbf{h}_m}$, where $\mathbf{h}_0, \ldots, \mathbf{h}_{m-1}$ are fixed and $\mathbf{h}_m$ is the primitive random variable (for the latter see Heinerman, 1975). Up to and including those terms of order $1/N$ that depend on the phases of the structure factors the expressions for these joint probability distributions are the same if the structure consists of equal atoms. The result for $P(X_{lm}|X_{lm-1})$ reads

$$P(X_{lm}|X_{lm-1}) = \frac{1}{\pi^m U_{m-1}} \exp(-\mathbf{X}_m^{\dagger} \mathbf{U}_{m-1}^{-1} \mathbf{X}_m) \times \left[1 + O'\left(\frac{1}{N}\right)\right], \tag{11}$$

where $\mathbf{X}_m$ is a column vector with components $X_{0m}, X_{1m}, \ldots, X_{m-1m}$; $\mathbf{X}_m^{\dagger}$ is a row vector with components that are the complex conjugates of those of $\mathbf{X}_m$; $\mathbf{U}_{m-1}^{-1}$ and U_{m-1} are the inverse and determinant of $\mathbf{U}_{m-1}$ respectively – for $\mathbf{U}_{m-1}$‡ see Fig. 1 – and $O'(1/N)$ denotes terms of order $1/N$ and higher in which the terms of order $1/N$ are independent of the phases. In deriving (11) use is made of the fact that $\mathbf{U}_{m-1}$ is positive-definite. The joint probability distribution $P(X_{lm})$ of the structure factors $E_{\mathbf{h}_0-\mathbf{h}_1}, E_{\mathbf{h}_0-\mathbf{h}_2}, E_{\mathbf{h}_1-\mathbf{h}_2}, E_{\mathbf{h}_0-\mathbf{h}_3}, E_{\mathbf{h}_1-\mathbf{h}_3}, E_{\mathbf{h}_2-\mathbf{h}_3}, \ldots, E_{\mathbf{h}_0-\mathbf{h}_m}, E_{\mathbf{h}_1-\mathbf{h}_m}, \ldots, E_{\mathbf{h}_{m-1}-\mathbf{h}_m}$ equals a product of conditional probability distributions:

$$P(X_{lm}) = P(X_{lm}|X_{lm-1})\,P(X_{lm}|X_{lm-2}) \ldots P(X_{01}). \tag{12}$$

‡ The elements of $\mathbf{U}_{m-1}$ arise from terms

$$\left\langle \sum_{j=1}^{N} \frac{Z_j^2}{\sigma_2} \exp[2\pi i(\mathbf{h}_p - \mathbf{h}_q).\mathbf{r}_j] | X_{pq} \right\rangle_{\mathbf{h}_p, \mathbf{h}_q}$$

in the characteristic function of $P(X_{lm}|X_{lm-1})$. To calculate these terms use is made of the 'least-squares' estimation

$$\sum_{j=1}^{N} \frac{Z_j^2}{\sigma_2} \exp[2\pi i(\mathbf{h}_p - \mathbf{h}_q).\mathbf{r}_j] \simeq \frac{\sigma_3}{\sigma_2^{3/2}} X_{pq},$$

which is exact for equal-atom structures.

$$\begin{matrix} 1 & \frac{\sigma_3}{\sigma_2^{3/2}} X_{01} & \frac{\sigma_3}{\sigma_2^{3/2}} X_{02} & \cdots & \frac{\sigma_3}{\sigma_2^{3/2}} X_{0m-1} \\ \frac{\sigma_3}{\sigma_2^{3/2}} X_{01}^{*} & 1 & \frac{\sigma_3}{\sigma_2^{3/2}} X_{12} & & \vdots \\ \frac{\sigma_3}{\sigma_2^{3/2}} X_{02}^{*} & \frac{\sigma_3}{\sigma_2^{3/2}} X_{12}^{*} & 1 & & \vdots \\ \vdots & & & \ddots & \vdots \\ \frac{\sigma_3}{\sigma_2^{3/2}} X_{0m-1}^{*} & \cdots & \cdots & \cdots & 1 \end{matrix}$$

Fig. 1. The matrix $\mathbf{U}_{m-1}$. The X^*'s are the complex conjugates of the X's. For the case when the structure consists of equal atoms $\mathbf{U}_{m-1}$ is a Karle–Hauptman matrix.

From (11) and (12) it is found that

$$P(X_{lm}) = \frac{1}{\pi^{m(m+1)/2} \prod_{n=1}^{m} U_{n-1}} \exp\left(-\sum_{n=1}^{m} \mathbf{X}_n^\dagger \mathbf{U}_{n-1}^{-1} \mathbf{X}_n\right) \times \left[1 + O'\left(\frac{1}{N}\right)\right]. \tag{13}$$

Next, employing

$$-\mathbf{X}_n^\dagger \mathbf{U}_{n-1}^{-1} \mathbf{X}_n = \frac{\sigma_2^3}{\sigma_3^2}\left(\frac{U_n}{U_{n-1}} - 1\right) \tag{14}$$

[*cf.* Tsoucaris (1970), equation (9)] and

$$\begin{aligned} U_n = 1 &- \frac{\sigma_3^2}{\sigma_2^3} \sum^{n}{}' \, |X_{i_1 i_2}|^2 \\ &+ \frac{\sigma_3^3}{\sigma_2^{9/2}} \sum^{n}{}'' \, (X_{i_1 i_2} X_{i_2 i_3} X^*_{i_1 i_3} + X^*_{i_1 i_2} X^*_{i_2 i_3} X_{i_1 i_3}) \\ &- \frac{\sigma_3^4}{\sigma_2^6} \sum^{n}{}''' \, (X_{i_1 i_2} X_{i_2 i_3} X_{i_3 i_4} X^*_{i_1 i_4} \\ &+ X^*_{i_1 i_2} X^*_{i_2 i_3} X^*_{i_3 i_4} X_{i_1 i_4} + X_{i_1 i_2} X_{i_2 i_4} X^*_{i_3 i_4} X^*_{i_1 i_3} \\ &+ X^*_{i_1 i_2} X^*_{i_2 i_4} X_{i_3 i_4} X_{i_1 i_3} + X_{i_1 i_3} X^*_{i_2 i_3} X_{i_2 i_4} X^*_{i_1 i_4} \\ &+ X^*_{i_1 i_3} X_{i_2 i_3} X^*_{i_2 i_4} X_{i_1 i_4}) + O'\left(\frac{1}{N^2}\right), \ddagger \end{aligned} \tag{15}$$

where X^* denotes the complex conjugate of X, we obtain

$$\begin{aligned} P(X_{lm}) = \frac{1}{\pi^{m(m+1)/2}} \exp\Big[&- \sum^{m}{}' \, |X_{i_1 i_2}|^2 \\ &+ \frac{\sigma_3}{\sigma_2^{3/2}} \sum^{m}{}'' \, (X_{i_1 i_2} X_{i_2 i_3} X^*_{i_1 i_3} + X^*_{i_1 i_2} X^*_{i_2 i_3} X_{i_1 i_3}) \\ &- \frac{\sigma_3^2}{\sigma_2^3} \sum^{m}{}''' \, (X_{i_1 i_2} X_{i_2 i_3} X_{i_3 i_4} X^*_{i_1 i_4} \\ &+ X^*_{i_1 i_2} X^*_{i_2 i_3} X^*_{i_3 i_4} X_{i_1 i_4} + X_{i_1 i_2} X_{i_2 i_4} X^*_{i_3 i_4} X^*_{i_1 i_3} \\ &+ X^*_{i_1 i_2} X^*_{i_2 i_4} X_{i_3 i_4} X_{i_1 i_3} + X_{i_1 i_3} X^*_{i_2 i_3} X_{i_2 i_4} X^*_{i_1 i_4} \\ &+ X^*_{i_1 i_3} X_{i_2 i_3} X^*_{i_2 i_4} X_{i_1 i_4})\Big] \left[1 + O'\left(\frac{1}{N}\right)\right]. \end{aligned} \tag{16}$$

It can readily be seen that the transformation $X = R \exp(i\Phi)$ (which implies $\mathrm{d}X = R\,\mathrm{d}R\,\mathrm{d}\Phi$) in (16) leads to (8). From (15) it follows that correct up to and including those terms of order $1/N$ that depend on the phases the exponential in (16) can be written as $\exp[(\sigma_2^3/\sigma_3^2)(U_m - 1)]$. This means that to our degree of approximation $P(X_{lm})$ solely depends on the determinant U_m.

‡ Quintets and higher-order structure invariants are contained in $O'(1/N^2)$.

Discussion

The joint probability distribution of all structure factors in a Karle–Hauptman matrix has been calculated up to and including those terms of order $1/N$ that depend on the phases. The exponent of this distribution contains squares of structure-factor magnitudes, triple products and quartets. For large values of N and when $m \ll N$, which has been assumed throughout our calculations [in the calculations of de Rango (1969) and Tsoucaris (1970) it was implicitly assumed that $m \ll N$; *cf.* Heinerman (1975)], these terms constitute the most important part in the evaluation of a Karle–Hauptman determinant. Therefore our joint probability distribution resembles that of de Rango (1969) and Tsoucaris (1970) in the sense that it will lead to a function of the phases which is closely related to a Karle–Hauptman determinant. The relation between our calculations and those of de Rango and Tsoucaris is best seen in our second method where we use conditional joint probability distributions of the structure factors in the last columns of Karle–Hauptman matrices.

In our joint probability distribution all structure factors $E_{\mathbf{h}_i-\mathbf{h}_j}$ ($i, j = 0, \ldots, m$ $i \neq j$) are variables. This permits the integration with respect to an arbitrary number of phases $\varphi_{\mathbf{h}_i-\mathbf{h}_j}$ and an arbitrary number of structure factors $E_{\mathbf{h}_i-\mathbf{h}_j}$ (*i.e.* magnitudes and phases) leading to a function which depends on a restricted set of phases (see following paper). This does not hold for the joint probability distribution in which only $\mathbf{h}_m$ is a primitive random variable. For the latter the structure factors $E_{\mathbf{h}_i-\mathbf{h}_m}$ ($i = 0, \ldots, m-1$) of the last column of a Karle–Hauptman matrix are variables, but the remaining structure factors are not. In our calculations all reciprocal-lattice vectors are primitive random variables and all structure factors as functions of the reciprocal-lattice vectors are variables.

Finally another remark should be made about the primitive random variables. In the approach adopted in this paper we considered the structure as fixed. It was also assumed that certain conditions with regard to the atomic position vectors (not specified here) are fulfilled. A second approach is to consider the reciprocal-lattice vectors as fixed and the atomic position vectors as the primitive random variables. However, if it is assumed that the reciprocal-lattice vectors fulfil certain conditions the second approach leads to the same result as the first. For examples of precise formulations of the conditions with regard to the atomic position vectors in the first approach and the reciprocal-lattice vectors in the second see Heinerman (1977*a*; 1977*b*, ch. IV) and Heinerman, Krabbendam & Kroon (1977). As discussed earlier (Heinerman, 1977*a*) the approach in which the atomic position vectors are the primitive random variables opens the possibility of including structural information.

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Conditional Phase Probability Distributions of Structure Factors in a Karle–Hauptman Matrix*

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Abstract

From the joint probability distribution of all structure factors in a Karle–Hauptman matrix new phase probability distributions are obtained. These calculations lead to a reformulation of the maximum-determinant rule for phase determination. In addition a new function is derived whose maximum corresponds to the most probable values for the phases of an arbitrary subset of the structure factors in a Karle–Hauptman matrix. This function accounts for the interaction among phases in a Karle–Hauptman matrix through triple products and quartets simultaneously.

Introduction

The maximum-determinant rule for phase determination (de Rango, 1969; Tsoucaris, 1970) has been derived from the joint probability distribution of the normalized structure factors $E_{\mathbf{h}_0-\mathbf{h}_m}$, $E_{\mathbf{h}_1-\mathbf{h}_m}$, ... and $E_{\mathbf{h}_{m-1}-\mathbf{h}_m}$ where $\mathbf{h}_0, \ldots, \mathbf{h}_{m-1}$ are fixed and $\mathbf{h}_m$ is the primitive random variable. Since the $\mathbf{h}_i$ ($i = 0, \ldots, m-1$) are fixed the $E_{\mathbf{h}_i-\mathbf{h}_j}$ ($i, j = 0, \ldots, m-1$), which enter into the joint probability distribution of $E_{\mathbf{h}_i-\mathbf{h}_m}$ ($i = 0, \ldots, m-1$), are also fixed. Therefore their magnitudes and phases should be known before the maximum-determinant rule can be applied. In practice, if some of the $E_{\mathbf{h}_i-\mathbf{h}_j}$ are unknown, they are set equal to zero (Castellano, Podjarny & Navaza, 1973; de Rango, Mauguen & Tsoucaris, 1975; Podjarny, Yonath & Traub, 1976).

The present paper gives the derivation of a new function whose maximum, by analogy with the maximum-determinant rule, corresponds to the most probable values for structure-factor phases, but which does not require knowledge of all $E_{\mathbf{h}_i-\mathbf{h}_j}$ ($i, j = 0, \ldots, m-1$). The basis of all our calculations is the result of the preceding paper, *viz* the joint probability distribution of all structure factors in a Karle–Hauptman matrix (Karle & Hauptman, 1950) for structures in space group $P1$. With this distribution we shall perform the following calculations. (i) By fixing the magnitudes of the structure factors we obtain a function of phases which is closely related to the phase-dependent terms that appear in the evaluation of a Karle–Hauptman determinant. (ii) Integrations with respect to an arbitrary set of phases are performed; next the magnitudes of the structure factors are fixed. This leads to a function of phases which is related to that in (i) but which depends only on an arbitrary subset of the phases in a Karle–Hauptman matrix. (iii) In addition to the integrations in (ii) we perform the integrations with respect to the structure-factor magnitudes that correspond to an arbitrary subset of the phases for which the integrations have been performed; next, the remaining magnitudes are fixed. This leads to a function of phases

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