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Probabilistic Connexion between One Phase Invariant and Moduli of All Structure Factors

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Recalling the 'conditional joint probability law' of m normalized structure factors [Tsoucaris (1969), *C.R. Acad. Sci. Paris, Sér. B*, **268**, 875; (1970). *Acta Cryst.* A**26**, 492] the conditional probability density is established for three moduli, assuming that the structure invariant α is known. Then, using the Bayes theorem, in order to 'invert' the role of random variables and known parameters, the probability density of α is obtained under the condition that the moduli are fixed. By the application of the axiom of joint probabilities for vectors running over all reciprocal lattice points located within the observable Ewald sphere, the expression for one phase invariant α is derived as a function of all observed moduli $p(\alpha|\text{all moduli})$.

Introduction - statement of the problem

The introduction of the probability concept into crystallography (Wilson, 1948; Karle & Hauptman, 1953) gave rise to an interesting new field in statistics: indeed, diffraction techniques yield a sample of several thousands of measurements connected by probability relations.

In this paper we wish to show how 'conditional joint probability theory' (Tsoucaris, 1969, 1970; De Rango, Tsoucaris & Zelwer, 1969) enables us to obtain information about one phase by using the whole set of observed moduli.

We recall first that the conditional joint probability law of m normalized structure factors $(E_1 \ldots E_p \ldots E_m)$ is an m dimensional Laplace–Gauss law involving the definite positive Hermitian form Q_m (in non-centrosymetric space groups: equation (8) of Tsoucaris, 1970),

$$p(E_1 \ldots E_m | U_{pq}) = \frac{1}{(2\pi)^m D_m^{1/2}} \exp(-Q_m) . \qquad (1)$$

The complex structure factors involved in equation (1) are defined by the following reciprocal lattice vectors:

$\mathbf{H}_p$ $p = 1 \ldots m$: fixed vectors.
$U_{pq} = U_{\mathbf{H}_p - \mathbf{H}_q}$: unitary structure factors, elements of matrix [U] where values are assumed fixed and known in both amplitude and phase.
$\mathbf{L}$: primitive random vector running uniformly over all reciprocal lattice points.
$E_1 = A_1 + iB_1 = E_{\mathbf{L}-\mathbf{H}_p}$: (derived) random variables.

The Hermitian form Q_m is defined by equation (9*b*) of Tsoucaris (1970)

$$Q_m = E^H [U^{-1}] \mathbf{E} = \sum_{p=1}^{m} \sum_{q=1}^{m} E_p E_q^* D_{pq} = N \frac{D_{m-1} - D_m}{D_m} \qquad (2)$$

$\mathbf{E}$: m-dimensional column vector $(E_1 \ldots E_m)$.
$\mathbf{E}^H$: Hermitian tranpose of $\mathbf{E}$ (E_p^*: conjugate of E_p).
D_{pq}: elements of the inverse matrix $[U]^{-1}$.
N: total number of atoms in the unit cell (we assume, for simplicity, that all atoms are identical, but the results can be generalized).
D_{m+1}: Karle–Hauptman determinant obtained by adding an $(m+1)$th column and row (elements: $E_{\mathbf{L}-\mathbf{H}_p}/\sqrt{N}$) to the determinant D_m.

The vertical bar on the left-hand side of equation (1) expresses the fact that we are looking for the joint probability density of m structure factors $E_1 \ldots E_m$ under the condition that all structure factors $U_p \ldots$ (elements of matrix [U]) are fixed and known.

In a previous paper (Tsoucaris, 1970), it has been shown that the 'cosine invariant' formula of Karle & Hauptman (1957) could be obtained from the probability theory concerning the D_4 determinant; moreover it has been suggested that the use of the *probability theory could provide more information* about phases than that conveyed by the averaging formulas of Karle & Hauptman.

In this paper, we shall apply the above probability law for $m = 3$.

After a convenient change of notation: $\mathbf{H}_1 = 0$, $\mathbf{H}_2 = H$, $\mathbf{H}_3 = K$, $E_1 = E_L$, $E_2 = E_{L-H}$, $E_3 = E_{L-K}$, we write:

$$D_{m+1} = D_4 = \frac{1}{N} \times \begin{vmatrix} 1 & U_H & U_K & E_L \\ U_{-H} & 1 & U_{K-H} & E_{L-H} \\ U_{-K} & U_{H-K} & 1 & E_{L-K} \\ E_{-L} & E_{H-L} & E_{K-L} & N \end{vmatrix}$$

and, for the probability density:

$$p(E_1, E_2, E_3 | U_H, U_K, U_{H-K}) = (2\pi)^{-3} D_3^{-1/2} \exp(-Q_3) . \qquad (3)$$

Also, it has been proved that the above expression does

not depend on the individual phases φ_H, φ_K, φ_{K-H}, but solely on the value of the structure invariant α,

$$\alpha=\varphi_{-H}+\varphi_K+\varphi_{H-K}\,.$$

In order to emphasize the dependence of the probability distribution on the value of α, we will use the notation of equation (3*a*) instead of that of equation (3) [strictly, one should write: $p(E_1,E_2,E_3|H,K)$].

$$p(E_1,E_2,E_3|\alpha)=(2\pi)^{-3}D_3^{-1/2}\exp(-Q_3)\,. \qquad (3a)$$

The present problem consists in obtaining the probability density of α, under the condition that all observed moduli are known:

$$p(\alpha|\text{ all moduli})\quad\text{[see equation (7)]}.$$

This can be performed in two steps:

I. We assume for the moment that, conversely, α is known, and we establish the conditional probability density for three moduli:

$$p(R_1,R_2,R_3|\alpha)\quad\text{[see equation (5)]}$$

with the following notation:

$$E_1=R_1\,e^{i\varphi 1}$$
$$E_2=R_2\,e^{i\varphi 2}$$
$$E_3=R_3\,e^{i\varphi 3}.$$

II. Next, we use the Bayes theorem, in order to 'invert' the role of random variables and known parameters; we obtain thus the probability density of α, under the condition that the three moduli R_1, R_2, R_3 (depending on vector **L**) are known

$$p(\alpha|R_1,R_2,R_3)\,.\quad\text{[see equation (6)]}$$

Finally from this last expression, we obtain immediately the desired probability density $p(\alpha|$ all moduli); this is given by the final expression (7).

I. The joint probability density of the moduli

The change of variable (polar coordinates instead o Cartesian coordinates).

$$(A_1,B_1)\rightarrow(R_1,\varphi_1)\ \textit{etc.}$$

yields a Jacobian: $R_1\,.\,R_2\,.\,R_3$. Thus, in order to obtain the probability density of the moduli, we have to integrate over the three phases:

$$p(R_1,R_2,R_3)|\alpha)$$
$$=\int_{\varphi 1=0}^{2\pi}\int_{\varphi 2=0}^{2\pi}\int_{\varphi 3=0}^{2\pi}R_1R_2R_3\,.\,p(E_1,E_2,E_3|\alpha)\mathrm{d}\varphi_1\mathrm{d}\varphi_2\mathrm{d}\varphi_3. \qquad (4)$$

The integration (Messager, 1972) is outlined in the Appendix. The final result is:

$$p(R_1,R_2,R_3|\alpha)$$
$$=R_1R_2R_3D_3^{-1/2}\exp(-D_{11}R_1^2-D_{22}R_2^2-D_{33}R_3^2)$$
$$\times[I_{0(x)}I_{0(y)}I_{0(z)}+2\sum_{r=1}^{\infty}(-1)^2I_{r(x)}I_{r(y)}I_{r(z)}\cos r\gamma \qquad (5)$$

where $I_r(x)$ is a modified Bessel function of order r, and

$$x=2R_2R_3|D_{32}|\quad y=2R_1R_3|D_{13}|\quad z=2R_1R_2|D_{12}|. \qquad (5a)$$

$|D_{12}|$ *etc.*, are the moduli of minors of determinant D_3,

$$|D_{23}|=D_3^{-1}(|U_H|^2|U_K|^2+|U_{K-H}|^2$$
$$-2|U_HU_KU_{K-H}|\cos\alpha)^{1/2}, \qquad (5b)$$

$$\gamma=\alpha-\tan^{-1}a-\tan^{-1}b-\tan^{-1}c, \qquad 5c)$$

$$a=\frac{|U_HU_K|\sin\alpha}{|U_HU_K|\cos\alpha-|U_{K-H}|} \qquad (5d)$$

(b and c are symmetrically obtained by permutation of the subscripts H, K, $K-H$).

II. The probability density of the structure invariant $p(\alpha|R_1,R_2,R_3)$

Equation (5) expresses the joint probability law of the moduli R_1, R_2, R_3 under the condition that α is fixed.

Conversely, one can obtain probabilistic information on α, under the condition that R_1, R_2, R_3 are fixed, by using the fundamental theorem of conditional joint probabilities, also called Bayes theorem. In a more concise notation we use the three dimensional column vector $\mathbf{R}_L$: (R_1,R_2,R_3).

Then, this theorem states that for two random variables $\mathbf{R}_L$ and α, we have:

$$p(\mathbf{R}_L|\alpha)\,.\,p(\alpha)=p(\mathbf{R}_L,\alpha)=p(\alpha|\mathbf{R}_L)\,.\,p(\mathbf{R}_L) \qquad (6)$$

$$p(\alpha|\mathbf{R}_L)=p(\mathbf{R}_L|\alpha)\,.\,p(\alpha)/p(\mathbf{R}_L), \qquad (6a)$$

where the denominator depends solely on R_1, R_2, R_3 and can be considered as a constant with respect to α:

$$K'=1/P(\mathbf{R}_L)\,.$$

Therefore:

$$p(\alpha|\mathbf{R}_L)=K'p(\alpha)\,.\,p(\mathbf{R}_L|\alpha) \qquad (6b)$$

where $p(\alpha)$ is the *a priori* probability density of α, *i.e.* assuming that we only know the values of the moduli $|U_H|$, $|U_K|$, $|U_{K-H}|$ having no information about the moduli R_1, R_2, R_3. This expression is already known (Cochran, 1955; Hauptman, Fisher, Hancock & Norton; Cooper, Norton & Hauptman, 1969):

$$p(\alpha)=\frac{\exp(A\cos\alpha)}{2\pi I_0(A)},$$
$$A=2N^{-1/2}\,|E_HE_KE_{H-K}|\,.$$

We can now apply the axiom of joint probabilities for vector **L** running over all reciprocal lattice points:

$$p(\alpha|\mathbf{R}_{L1}\ldots\mathbf{R}_{Lj}\ldots\mathbf{R}_{Ln})=Kp(\alpha)\prod_{j=1}^{n}p(R_{Lj}|\alpha) \qquad (7)$$

where Π denotes the n-fold product over j, comprising all vectors $\mathbf{L}_j$ for which the three corresponding moduli

$$R_1=|E_1|\quad R_2=|E_2|\quad R_3=|E_3|$$

are located within the observable Ewald sphere. Therefore, equation (7) is the desired expression of

$$p(\alpha|\text{ all moduli}).$$

Remark: In the above formula we assume that the $\mathbf{R}_L$'s are mutually independent. This is, of course, only an approximation.

Equation (7) is remarkable in the sense that it represents a probability expression of one phase invariant α as a function of all observed moduli. The practical use of (7) has been examined by Sarrazin (1971). Detailed results will be published later.

Equation (7) can also be connected with an attempt to obtain α from the probability density of Z (Tsoucaris, 1970; Hauptman, Messager, Speck & Vitterbo, 1970):

$$Z=(|E_{\mathbf{L}}|^2-1)\,(|E_{\mathbf{L}-\mathbf{H}}|^2-1)\,(|E_{\mathbf{L}-\mathbf{K}}|^2-1)\,.$$

It may be of interest to suggest that more information about the phases can be obtained, in a similar way, if one is able to perform the general integration (for $m>4$) of equation (1) over the m phases $\varphi_1 \ldots \varphi_m$. Further work is under preparation along these lines.

This work is a further development of ideas worked out during a workshop on direct methods organized by the Centre Européen de Calcul Atomique et Moléculaire (C.E.C.A.M.) in Orsay, France (September–October 1970). The authors are indebted to H. Hauptman for helpful discussions.

APPENDIX

First we write Q_3 as:

$$\begin{aligned}Q_3=&D_{11}|E_1|^2+D_{22}|E_2|^2+D_{33}|E_3|^2\\&+[D_{21}E_2E_1^*+D_{12}E_2^*E_1]+E_3[D_{31}E_1^*+D_{32}E_2^*]\\&+E_3^*[D_{13}E_1+D_{23}E_2]\,.\end{aligned}$$

Let us set:

$$B=|B|\,e^{i\beta}=D_{31}E_1^*+D_{32}E_2^*$$

$$D_{pq}=|D_{pq}|\exp(ix_{pq})\,,\quad p,q=1,2,3\,.$$

By introducing Q_3 in (4), we obtain:

$$\begin{aligned}&p(R_1,R_2,R_3)\\&=(2\pi)^{-3}D_3^{-1/2}\exp[-(D_{11}R_1^2+D_{22}R_2^2+D_{33}R_3^2)]\\&\times\int_{\phi_1}\int_{\phi_2}\exp[-2R_1R_2|D_{12}|\cos(\varphi_2-\varphi_1+x_{21})\mathrm{d}\varphi_1\mathrm{d}\varphi_2\\&\times\int_{\phi_3}\exp[-2R_3|B|\cos(\varphi_3+\beta)\mathrm{d}\varphi_3\,.\end{aligned}$$

The integration over φ_3 immediately yields

$$2\pi I_0(2R_3|B|)\,.$$

Next, the above expression is expanded by using the known formula

$$I_{0(\sqrt{x^2+y^2-2xy\cos\theta})}=I_{0(x)}I_{0(y)}+2\sum_{r=1}^{\infty}(-1)^rI_{r(x)}I_{r(y)}\cos r\theta$$

and recalling that

$$2R_3|B|=[x^2+y^2-2xy\cos(\pi+\varphi_2-\varphi_1+x_{31}+x_{23})]^{1/2}.$$

The integration over φ_2 is performed, by using the formula

$$\int_0^{2\pi}\cos ru\,.\,e^{-z\cos u}\mathrm{d}u=2\pi I_{r(-z)}\,.$$

Then, the integration on φ_1 is trivial, and we obtain finally equation (7).

We notice, that γ can be expressed in a simple way in terms of the phases x_{12} *etc.* of the minors D_{12} *etc.*:

$$\gamma=x_{12}+x_{23}+x_{31}\,.$$

Note: When this work was completed the authors learned that Hauptman [1971; equation (6.25)] has independently derived an expression nearly identical to equation (5) (to the order $N^{-1/2}$). A lengthy calculation has shown that the definition of angle γ [equation (5*c*) of this paper] and angle η (equations 6.23 and 6.24 of Hauptman's paper) are strictly equivalent. Finally, the only difference concerns the factor $D_3^{-1/2}$ in equation (5), whereas a factor D_3^{-1} (denoted by Δ) appears in Hauptman's paper. It seems that equation (5) is the correct expression to the order $N^{-1/2}$.

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