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Integration of Patterson Information into Direct Methods. IV. The Use of Interatomic Triangles

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(*Received* 10 *November* 1993; *accepted* 15 *February* 1994)

Abstract

A probabilistic approach is described that is able to estimate triplet phase invariants when prior information on interatomic vectors and interatomic triangles is available. The conclusive formula is compared with the vector-interaction formula derived by Hauptman & Karle [*Acta Cryst.* (1962), **15**, 547–550] and with a probabilistic formula obtained *via* maximum-entropy methods.

Symbols and abbreviations

The papers by Giacovazzo (1991) and Altomare, Cascarano & Giacovazzo (1992*a*,*b*) are referred to as papers I, II and III, respectively. Symbols and abbreviations are the same as those used in these papers.

Introduction

In paper I of this series, the standard method of joint probability distribution functions was modified in order to exploit the information provided by a Patterson map. If interatomic vectors $\mathbf{u}_{j_1 j_2} = \mathbf{r}_{j_1} - \mathbf{r}_{j_2}$ are known *a priori*, the symmetry-independent atomic positional vectors cannot be considered as random variables uniformly distributed in the asymmetric unit (indeed, $\mathbf{r}_{j_1}$ is completely determined in terms of $\mathbf{r}_{j_2}$ and $\mathbf{u}_{j_1 j_2}$). The theory provided triplet invariant estimates different from those provided by standard methods. The formula requires prior information both on the coordinates of the peaks and on the scattering factors of the atoms with mutual distance $\mathbf{u}$. Since this second type of information is usually unavailable (for example because of peak overlapping), in paper II the formula was modified to depend on $\mathbf{u}$ and on the corresponding Patterson peak intensity. Some applications were also described.

In paper III, the theory was extended to introduce the information contained in Harker sections.

The main aim of this paper is to describe a probabilistic approach for triplet invariant estimation that is able to exploit the information contained in the interatomic triangles. This type of information includes prior knowledge of interatomic vectors and also takes into account correlation among different interatomic vectors. The problem is correlated with the double Patterson function (Sayre, 1953; Kroon & Krabbendam, 1970) and a first answer was found in an algebraic expression derived by Hauptman & Karle (1962) for the calculation of triplet phases

ISSN 0108-7673

from the Patterson function. More recently, the derivation of an exponential joint probability distribution of structure factors with maximum entropy and irreducible cluster integrals (Kronenburg, Peschar & Schenk, 1991) led to a probabilistic formula (Kronenburg, 1992).

In the present paper, our final formula is compared with corresponding expressions by Hauptman & Karle (1962) and Kronenburg (1992).

The probabilistic approach

When some interatomic vectors are known *a priori* (see § 6 of paper II), the average value of $|F_{\mathbf{h}}|^2$ is

$$\langle |F_{\mathbf{h}}|^2|\{\mathbf{u}\}\rangle = \varepsilon_{\mathbf{h}}\Big(\sum\nolimits_N(\mathbf{h}) + 2\sum_{\mathbf{u}}\Big\{\sum_{s=1}^{m}\cos 2\pi\mathbf{h}\mathbf{R}_s\mathbf{u} \times \Big[\sum\nolimits'_{j_1,j_2} f_{j_1}(\mathbf{h})f_{j_2}(\mathbf{h})\Big]\Big\}\Big). \quad (1)$$

Let us now suppose that, besides $\mathbf{u}_{j_1j_2}$, $\mathbf{u}_{j_1j_3}$ (and consequently $\mathbf{u}_{j_2j_3}$) is also simultaneously known; then, an interatomic triangle is known. It is immediately seen from (1) that this prior information cannot change the expected value of $|F_{\mathbf{h}}|^2$. In other words,

$$\langle |F_{\mathbf{h}}|^2|\{\mathbf{u}_{j_1j_2},\mathbf{u}_{j_1j_3},\mathbf{u}_{j_2j_3}\}\rangle \equiv \langle |F_{\mathbf{h}}|^2|\{\mathbf{u}\}\rangle.$$

Therefore, the normalized structure factor $E_{\mathbf{h}}$ calculated by taking into account the prior information on $\{\mathbf{u}_{j_1j_2},\mathbf{u}_{j_1j_3},\mathbf{u}_{j_2j_3}\}$ is again defined by

$$|E_{\mathbf{h}}|^2 = |F_{\mathbf{h}}|^2/\langle |F_{\mathbf{h}}|^2|\{\mathbf{u}\}\rangle$$

or, according to equation (16) of paper II,

$$|E_{\mathbf{h}}| = |E'_{\mathbf{h}}|\Big/\Big[1+\sum_{\mathbf{u}}(2I'_{\mathbf{u}}\alpha_{\mathbf{h}})\Big]^{1/2},$$

where $|E'_{\mathbf{h}}|$ is the normalized structure factor calculated in the absence of Patterson information, $I'_{\mathbf{u}} = I_{\mathbf{u}}/(j_{\mathbf{u}}I_o)$, I_o and $I_{\mathbf{u}}$ are the Patterson peak heights at the origin and at $\mathbf{u}$, respectively, $j_{\mathbf{u}}$ is the ratio between the order of the space group and the peak multiplicity and

$$\alpha_{\mathbf{h}} = \sum_{s=1}^{m}\cos 2\pi\mathbf{h}\mathbf{R}_s\mathbf{u}.$$

The conditional probability of Φ, given $|E_{\mathbf{h}_1}|$, $|E_{\mathbf{h}_2}|$, $|E_{\mathbf{h}_3}|$ and a set of interatomic triangles $\{\mathbf{u}_{j_1j_2},\mathbf{u}_{j_1j_3},\mathbf{u}_{j_2j_3}\}$ is given by

$$P(\Phi|E_{\mathbf{h}_1}|,|E_{\mathbf{h}_2}|,|E_{\mathbf{h}_3}|,\{\mathbf{u}_{j_1j_2},\mathbf{u}_{j_1j_3},\mathbf{u}_{j_2j_3}\}) \simeq [2\pi I_o(G)]^{-1}\exp[G\cos(\Phi-g)],$$

where

$$G\exp(ig) = 2\langle F_{\mathbf{h}_1}F_{\mathbf{h}_2}F_{\mathbf{h}_3}|\{\mathbf{u}_{j_1j_2},\mathbf{u}_{j_1j_3},\mathbf{u}_{j_2j_3}\}\rangle \times [\langle |F_{\mathbf{h}_1}|^2|\{\mathbf{u}\}\rangle\langle |F_{\mathbf{h}_2}|^2|\{\mathbf{u}\}\rangle\langle |F_{\mathbf{h}_3}|^2|\{\mathbf{u}\}\rangle]^{-1/2} \times |E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}| \quad (2)$$

Since the averages $\langle |F_{\mathbf{h}_i}|^2|\{\mathbf{u}\}\rangle$, $i=1, 2, 3$, are defined by (1), we only need to estimate

$$\langle F_{\mathbf{h}_1}F_{\mathbf{h}_2}F_{\mathbf{h}_3}|\{\mathbf{u}_{j_1j_2},\mathbf{u}_{j_1j_3},\mathbf{u}_{j_2j_3}\}\rangle = \Big\langle \sum_{j_1,j_2,j_3=1}^{t} f_{j_1}(\mathbf{h}_1)f_{j_2}(\mathbf{h}_2)f_{j_3}(\mathbf{h}_3) \times \sum_{s_1,s_2,s_3=1}^{m}\exp 2\pi i[\mathbf{h}_1(\mathbf{C}_{s_1}\mathbf{r}_{j_1}-\mathbf{C}_{s_3}\mathbf{r}_{j_3}) + \mathbf{h}_2(\mathbf{C}_{s_2}\mathbf{r}_{j_2}-\mathbf{C}_{s_3}\mathbf{r}_{j_3})]\Big\rangle.$$

Let $\mathbf{C}_\nu$ and $\mathbf{C}_\mu$ be two symmetry operators for which $\mathbf{C}_{s_1} = \mathbf{C}_{s_3}\mathbf{C}_\nu$ and $\mathbf{C}_{s_2} = \mathbf{C}_{s_3}\mathbf{C}_\mu$. Then,

$$\begin{aligned}\mathbf{C}_{s_1}\mathbf{r}_{j_1}-\mathbf{C}_{s_3}\mathbf{r}_{j_3} &= \mathbf{R}_{s_3}(\mathbf{C}_\nu\mathbf{r}_{j_1}-\mathbf{r}_{j_3}),\\ \mathbf{C}_{s_2}\mathbf{r}_{j_2}-\mathbf{C}_{s_3}\mathbf{r}_{j_3} &= \mathbf{R}_{s_3}(\mathbf{C}_\mu\mathbf{r}_{j_2}-\mathbf{r}_{j_3})\end{aligned} \quad (3)$$

and

$$\langle F_{\mathbf{h}_1}F_{\mathbf{h}_2}F_{\mathbf{h}_3}|\{\mathbf{u}_{j_1j_2},\mathbf{u}_{j_1j_3},\mathbf{u}_{j_2j_3}\}\rangle = \Big\langle \sum_{j_1,j_2,j_3=1}^{t} f_{j_1}(\mathbf{h}_1)f_{j_2}(\mathbf{h}_2)f_{j_3}(\mathbf{h}_3) \times \sum_{s=1}^{m}\exp 2\pi i[\mathbf{h}_1\mathbf{R}_s\mathbf{u}_{j_1j_3}-\mathbf{h}_2\mathbf{R}_s\mathbf{u}_{j_3j_2}]\Big\rangle, \quad (4)$$

where $\mathbf{R}_s$ stands for $\mathbf{R}_{s_3}$ and $\mathbf{u}_{j_1j_3} = \mathbf{C}_\nu\mathbf{r}_{j_1}-\mathbf{r}_{j_3}$ and $\mathbf{u}_{j_2j_3} = \mathbf{C}_\mu\mathbf{r}_{j_2}-\mathbf{r}_{j_3}$ are the generic interatomic vectors including the effects of $\mathbf{C}_\nu$ and $\mathbf{C}_\mu$.

The right-hand side of (4) contains three terms:

(*a*) The term corresponding to the case $j_1=j_2=j_3$ (the so-called Cochran term), equal to $\sum_3(\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3)$.

(*b*) The term arising from the prior information on the existence of the vectors $\{\mathbf{u}\}$ and corresponding to the special cases $j_1=j_3$, $j_2=j_3$, $j_1=j_2$. This term was calculated in paper I and denoted $M\exp(i\theta)$.

(*c*) The term arising from the known correlation among the vectors $\{\mathbf{u}\}$ and corresponding to the case $j_1\neq j_2\neq j_3$. It may be observed that the Patterson function is centrosymmetric and that the vectors $\mathbf{u}_{j_1j_2}$, $\mathbf{u}_{j_1j_3}$ and $\mathbf{u}_{j_2j_3}$ must play a symmetrical role in (4). Accordingly, the contribution of this third term may be explicitly written by the symmetrized formula

$$\begin{aligned}\sum_{j_1\neq j_2\neq j_3} & f_{j_1}(\mathbf{h}_1)f_{j_2}(\mathbf{h}_2)f_{j_3}(\mathbf{h}_3)\\ &\times\sum_{s=1}^{m}[\cos 2\pi(\mathbf{h}_1\mathbf{R}_s\mathbf{u}_{j_1j_2}-\mathbf{h}_2\mathbf{R}_s\mathbf{u}_{j_2j_3})\\ &+\cos 2\pi(\mathbf{h}_1\mathbf{R}_s\mathbf{u}_{j_2j_3}-\mathbf{h}_2\mathbf{R}_s\mathbf{u}_{j_1j_2})\\ &+\cos 2\pi(\mathbf{h}_3\mathbf{R}_s\mathbf{u}_{j_1j_2}-\mathbf{h}_2\mathbf{R}_s\mathbf{u}_{j_2j_3})\\ &+\cos 2\pi(\mathbf{h}_3\mathbf{R}_s\mathbf{u}_{j_1j_2}-\mathbf{h}_1\mathbf{R}_s\mathbf{u}_{j_2j_3})\\ &+\cos 2\pi(\mathbf{h}_3\mathbf{R}_s\mathbf{u}_{j_2j_3}-\mathbf{h}_1\mathbf{R}_s\mathbf{u}_{j_1j_2})\\ &+\cos 2\pi(\mathbf{h}_3\mathbf{R}_s\mathbf{u}_{j_2j_3}-\mathbf{h}_2\mathbf{R}_s\mathbf{u}_{j_1j_2})].\end{aligned} \quad (5)$$

Let us now denote the above contribution by the simplified symbol

$$\sum_{\mathbf{u}_1,\mathbf{u}_2} f_{j_1}(\mathbf{h}_1) f_{j_2}(\mathbf{h}_2) f_{j_3}(\mathbf{h}_3) \beta_{\mathbf{u}_1,\mathbf{u}_2},$$

where $\mathbf{u}_1$ and $\mathbf{u}_2$ are vectors of type $\mathbf{u}_{ij}$ and $\mathbf{u}_{jk}$, respectively. Since (Hauptman & Karle, 1962)

$$\begin{aligned} &f_{j_1}(\mathbf{h}_1) f_{j_2}(\mathbf{h}_2) f_{j_3}(\mathbf{h}_3) / [\textstyle\sum_N(\mathbf{h}_1) \sum_N(\mathbf{h}_2) \sum_N(\mathbf{h}_3)]^{1/2} \\ &\simeq Z_{j_1} Z_{j_2} Z_{j_3} / (\sigma_2)^{3/2} \\ &= [(Z_{j_1} Z_{j_2}/\sigma_2)(Z_{j_1} Z_{j_3}/\sigma_2)(Z_{j_2} Z_{j_3}/\sigma_2)]^{1/2}, \end{aligned}$$

the contribution (5) may be written in terms of Patterson peak heights $I'_{\mathbf{u}}$, provided there is no overlap of Patterson peaks. After some calculations, we obtain

$$\begin{aligned} &P(\Phi | |E_{\mathbf{h}_1}|, |E_{\mathbf{h}_2}|, |E_{\mathbf{h}_3}|, \{\mathbf{u}_1, \mathbf{u}_2\}) \\ &\quad \simeq [2\pi I_o(G)]^{-1} \exp(G \cos \Phi), \end{aligned} \tag{6}$$

where

$$\begin{aligned} G = {} & 2|E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_3}| N^{-1/2} \\ & \times \left[1 + \sum_{\mathbf{u}} I'_{\mathbf{u}} \left(\sum_{i=1}^{3} \alpha_i \right) + \sum_{\mathbf{u}_1,\mathbf{u}_2} I'_{\mathbf{u}_1,\mathbf{u}_2} \beta_{\mathbf{u}_1,\mathbf{u}_2} \right] \\ & \times \left\{ \prod_{i=1}^{3} \varepsilon_{\mathbf{h}_i} \left[1 + \sum_{\mathbf{u}} (2 I'_{\mathbf{u}} \alpha_i) \right] \right\}^{-1/2} \end{aligned} \tag{7}$$

where $I'_{\mathbf{u}_1,\mathbf{u}_2} = [I'(\mathbf{u}_{12}) I'(\mathbf{u}_{13}) I'(\mathbf{u}_{23})]^{1/2}$.

According to whether G is positive or negative, Φ is expected to be close to 0 or π, respectively. Equation (7) is clearly an extension of equation (11) of paper III.

A comparison with the Hauptman & Karle (1962) vector-interaction formula

In our notation, the vector-interaction formula may be written as

$$\begin{aligned} |E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_3}| \cos \Phi \simeq {} & N^{-1/2} (|E_{\mathbf{h}_1}|^2 + |E_{\mathbf{h}_2}|^2 + |E_{\mathbf{h}_3}|^2 - 2) \\ & + \sum_{\mathbf{u}_1,\mathbf{u}_2} I'_{\mathbf{u}_1,\mathbf{u}_2} \beta_{\mathbf{u}_1,\mathbf{u}_2}. \end{aligned} \tag{8}$$

The link between (6) and (8) may be described as follows.

(*a*) Equation (8) is an algebraic relationship, therefore cosine values out of the permitted range $(-1, +1)$ can frequently be obtained. Owing to its probabilistic nature, the distribution (6) provides an expected value of $\cos\Phi$ that is always in the interval $(-1, +1)$.

(*b*) Equation (8) is asymptotic; indeed it is only valid when all the interatomic vectors of the structure are taken into account. In this case, the term

$$\sum_{\mathbf{u}} I'_{\mathbf{u}} \left(\sum_{i=1}^{3} \alpha_i \right) = \sum_{i=1}^{3} \sum_{\mathbf{u}} I'_{\mathbf{u}} \sum_{s=1}^{m} \cos 2\pi \mathbf{h}_i \mathbf{R}_s \mathbf{u}$$

in (7) closely approximates

$$\begin{aligned} &(|E_{\mathbf{h}_1}|^2 - 1) + (|E_{\mathbf{h}_2}|^2 - 1) + (|E_{\mathbf{h}_3}|^2 - 1) \\ &\quad = \sum_{i=1}^{3} \sum_{j_1 \neq j_2} (Z_{j_1} Z_{j_2}/\sigma_2) \sum_{s=1}^{m} \cos 2\pi \mathbf{h}_i \mathbf{R}_s \mathbf{u}_{j_1, j_2} \end{aligned}$$

and (7) reduces to

$$G = 2\left[(E^2_{\mathbf{h}_1} + E^2_{\mathbf{h}_2} + E^2_{\mathbf{h}_3} - 2) + \sum_{\mathbf{u}_1,\mathbf{u}_2} I'_{\mathbf{u}_1,\mathbf{u}_2} \beta_{\mathbf{u}_1,\mathbf{u}_2} \right] N^{-1/2}.$$

Unlike (8), the distribution (6) is able to exploit the information contained in any subset of interatomic vectors and interatomic triangles.

A comparison with the Kronenburg formula

In our notation, the Kronenburg exponential distribution may be written as

$$\begin{aligned} &P(\Phi | |E_{\mathbf{h}_1}|, |E_{\mathbf{h}_2}|, |E_{\mathbf{h}_3}|, \{\mathbf{u}_1, \mathbf{u}_2\}) \\ &\quad \simeq [2\pi I_o(G)]^{-1} \exp G \left[1 + \sum_{j_1 \neq j_2 \neq j_3} f_{j_1} f_{j_2} f_{j_3} \beta_{\mathbf{u}_1,\mathbf{u}_2} \right]. \end{aligned} \tag{9}$$

Comparison of (9) with (6) suggests two things. (*a*) In (9), renormalization of structure factors (taking into account the prior information on Patterson peaks) is not performed. (*b*) The three terms for $j_1 = j_2 \neq j_3$, $j_2 = j_3 \neq j_1$ and $j_1 = j_3 \neq j_2$ are not considered (they cancel out in the Kronenburg derivation). Since their contribution is expected to be positive, we expect for (9) some tendency to overestimate the number of negative triplets.

Applications

Crystal structures with few heavy atoms are the best candidates for an efficient application of (6). We focused our attention onto two centrosymmetric structures:

(*a*) CUPP ($Cu_2Br_2P_4C_{88}H_{68}$, space group $P2_1/n$, $Z = 4$; Camalli, Caruso & Venanzi, 1985);

(*b*) AGI ($Ag_2I_2P_4C_{64}H_{56}$, space group $P2_1/c$, $Z = 4$; Camalli, Caruso & Venanzi, 1986).

The results are presented in Table 1. *SIR*92 (Altomare, Cascarano, Giacovazzo, Guagliardi, Burla, Polidori & Camalli, 1994) selected for CUPP 8000 triplet invariants among the 499 largest $|E|$: 26 triplets are really negative. The reliability parameter G was calculated by including in $\beta_{\mathbf{u}_1,\mathbf{u}_2}$ all the 56 interatomic triangles corresponding to Cu atoms [fraction of scattering power (f.s.p.) equal to 0.21]. The calculations were then repeated by including in $\beta_{\mathbf{u}_1,\mathbf{u}_2}$ the 56 interatomic triangles corresponding to Br atoms (f.s.p. = 0.30). These tests suggest that (6) can remarkably improve Cochran estimates only if the interatomic triangles used in the calculations involve a relevant percentage of the electron density. The expected tendency of the Kronenburg formula

Table 1. *Comparison of estimated positive and negative triplets according to our formula and to the Kronenburg formula*

nr and nw are the numbers of estimated triplets and of wrongly estimated triplets, respectively; f.s.p. is the fraction of scattering power corresponding to the atoms involved in the triangles.

	Our formula [(6)]				Kronenburg formula			
	Positive triplets		Negative triplets		Positive triplets		Negative triplets	
	nr	nw	nr	nw	nr	nw	nr	nw
(*a*) CUPP ($Cu_2Br_2P_4C_{88}H_{68}$)								
56 Cu-atom triangles f.s.p. = 0.21	7904	20	96	90	7256	18	744	736
56 Br-atom triangles f.s.p. = 0.30	7976	2	24	0	7898	2	102	78
(*b*) AGI ($Ag_2I_2P_4C_{64}H_{56}$)								
56 Ag-atom triangles f.s.p. = 0.33	7915	12	85	82	7489	6	511	502
56 I-atom triangles f.s.p. = 0.42	7945	8	55	48	7688	4	312	301
560 Ag + I-atom triangles f.s.p. = 0.75	7988	3	12	0	7965	0	35	20

to overestimate triplet negativity is also supported. These conclusions are confirmed by the following additional test.

For AGI, 8000 triplet invariants among the 486 largest $|E|$ were selected by *SIR*92: 15 triplets are really negative. The value of G was calculated by including in $\beta_{\mathbf{u}_1,\mathbf{u}_2}$ all the 56 interatomic triangles corresponding to Ag atoms (f.s.p. = 0.33); calculations were then repeated by including iodine triangles (f.s.p. = 0.42). At the end, we calculated G by including in $\beta_{\mathbf{u}_1,\mathbf{u}_2}$ all the 560 interatomic triangles corresponding to I and Ag atoms (f.s.p. = 0.75).

Concluding remarks

A probabilistic approach has been described that is able to take into account prior information on interatomic triangles that may be available after inspection of a Patterson map. The procedure generalizes the so-called vector-interaction formula of Hauptman & Karle (1962) and provides a final formula different from a previous probabilistic expression derived by Kronenburg (1992). The three methods are compared: our probabilistic approach overcomes some theoretical limitations of the algebraic method and improves triplet estimates provided by the Kronenburg formula. Practical tests show also that our triplet estimates are markedly better than Cochran–Woolfson estimates, provided the electron density involved in the interatomic triangles is a non-negligible percentage of the total electron density.

Thanks are due to Miss C. Chiarella for technical support.

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Acta Cryst. (1994). A**50**, 588–595

Asymmetric Tilt Boundaries in Polycrystalline Nickel

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(*Received* 30 *July* 1993; *accepted* 14 *March* 1994)

Abstract

A large sample population of grain-boundary geometries in annealed polycrystalline nickel has been collected and analysed. The data include all five degrees of freedom, that is, the grain misorientation plus the crystallographic orientation of the boundary plane. The most significant category of boundaries on the basis of those geometries that could give rise to 'special' properties were symmetric and