HAUPTMAN, H., FISHER, J., HANCOCK, H. & NORTON, D. A. (1969). *Acta Cryst.* B25, 811-814.
KŘÍŽ, V. (1982). *Optimizations Method for Determination of Arguments of Structure Factors.* FzU ČSAV, Czechoslovakia.
LUENBERGER, D. G. (1973). *Introduction to Linear and Nonlinear Programming.* Reading, MA: Addison-Wesley.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
PODLAHA, J., PODLAHOVÁ, J. & SYMERSKÝ, J. (1987). *Acta Cryst.* C43, 1949-1951.
SHELDRICK, G. M. (1982). *Testing Structures for Direct Methods.* Univ. of Cambridge, England.
SYMERSKÝ, J., BLÁHA, K. & JEČNÝ, J. (1988). *Acta Cryst.* C44, 148-150.
SYMERSKÝ, J., BLÁHA, K. & LANGER, V. (1987*a*). *Acta Cryst.* C43, 303-306.
SYMERSKÝ, J., BLÁHA, K. & LANGER, V. (1987*b*). *Acta Cryst.* C43, 490-493.
SYMERSKÝ, J., HUML, K. & PETŘÍČEK, V. (1987). *Acta Cryst.* C43, 1603-1607.
SYMERSKÝ, J. & KŘÍŽ, V. (1989). *J. Appl. Cryst.* In the press.
WOOLFSON, M. M. (1976). In *Crystallographic Computing Techniques*, edited by F. R. AHMED, pp. 85-96. Munksgaard: Copenhagen.
WRIGHT, H. (1983). *A Random Approach to Crystal Structure Determination.* Department of Physics, Univ. of York, England.
YAO, J. (1981). *Acta Cryst.* A37, 642-644.

Acta Cryst. (1989). A45, 463-468

New Methods for Deriving Joint Probability Distributions of Structure Factors. II. Strengthening the Triplet Relationship in *P*1

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Abstract

Two methods are discussed in detail. In the first method the triplet relationship is treated using the first neighborhood, and the quartet relationship using its second neighborhood. For the triplet relationship it is found that the reliability

$$\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}}\simeq 0$$

is enhanced when

$$R_{\mathbf{h}}\simeq R_{\mathbf{k}}\simeq R_{\mathbf{h}+\mathbf{k}}$$

and large. This conclusion is drawn from formula (16) giving the conditional probability of $\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}}$ using an asymptotic development up to and including terms of order $N^{-1/2}$. For the quartet relationship it is found that the reliability that

$$\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\simeq \pi$$

given $R_{\mathbf{h}+\mathbf{k}}\simeq R_{\mathbf{h}+\mathbf{l}}\simeq R_{\mathbf{k}+\mathbf{l}}\simeq 0$ is diminished when

$$R_{\mathbf{h}}\simeq R_{\mathbf{k}}\simeq R_{\mathbf{l}}\simeq R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$$

and large. This conclusion is drawn from formula (19) using similar calculations for the triplet relationship. A heuristic theoretical discussion of this last result trying to explain this difference with the usual theories is given. In the second method the triplet relationship is treated using its *first* neighborhood. These calculations have been done using a 'normal' asymptotic development up to and including terms of order $N^{-1/2}$. As a result a formula (28) is obtained that is (at least theoretically) able to predict negative cosine values. A third method that is proposed where one uses the ideas of Patterson superposition will be discussed in detail in a forthcoming paper.

Introduction

Let us consider an equal-atom structure with space group *P*1. For N atoms with respective position vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ the normalized structure factor $E_{\mathbf{h}}$ for the reciprocal-lattice vector $\mathbf{h}$ becomes

$$E_{\mathbf{h}}=N^{-1/2}\sum_{j=1}^{N}\exp(2\pi i\mathbf{h}\,.\,\mathbf{r}_j).$$

For deriving joint probability distributions of structure factors we shall consider the atomic vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ as random vectors and this leads us to consider the random variable

$$\hat{E}_{\mathbf{h}}=N^{-1/2}\sum_{j=1}^{N}\exp(2\pi i\mathbf{h}\,.\,\mathbf{x}_j) \qquad (1)$$

where the $\mathbf{x}_j$ are random variables that range over the possible positions of the atomic position vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$. Usually one considers the $\mathbf{x}_j$ to be mutually independent and one imposes each $\mathbf{x}_j$ to range uniformly over the unit cell. Another approach (Brosius, 1985) is to observe that all $\mathbf{x}_i-\mathbf{x}_j$ only have to range over the set of all Patterson vectors. In order to impose this latter condition one can use two methods: (1)

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one can analyse the Patterson map and search for all Patterson vectors, or (2) one can use the density function

$$f(\mathbf{x}_r-\mathbf{x}_s)=\sum_{\mathbf{q}}[(R_{\mathbf{q}}^2-1)/(N-1)] \times\exp[2\pi i\mathbf{q}\,.\,(\mathbf{x}_r-\mathbf{x}_s)] \qquad (2)$$

where $\sum_{\mathbf{q}}$ stands for a finite sum [we sum over a sufficient number of $\mathbf{q}$ values so that we may neglect the negative ripples of $f(\mathbf{x}_r-\mathbf{x}_s)$]. The first method is also equivalent to using a density function similar to expression (21) of Brosius (1985); since we cannot give an analytical expression for it we shall not consider this method any further.

Instead of (2) one could also use a density

$$h(\mathbf{x}_r-\mathbf{x}_s)\propto f(\mathbf{x}_r-\mathbf{x}_s)^2, \qquad (2a)$$

that is

$$h(\mathbf{x}_r-\mathbf{x}_s)=\sum_{\mathbf{q}}C_{\mathbf{q}}\exp[2\pi i\mathbf{q}\,.\,(\mathbf{x}_r-\mathbf{x}_s)] \qquad (2b)$$

where

$$C_{\mathbf{q}}=\frac{\langle(R_{\mathbf{l}+\mathbf{q}}^2-1)(R_{\mathbf{l}}^2-1)\rangle_{\mathbf{l}}}{\langle(R_{\mathbf{l}}^2-1)^2\rangle_{\mathbf{l}}}. \qquad (2c)$$

In general, however, one expects (Hauptman, 1964) that

$$C_{\mathbf{q}}=(R_{\mathbf{q}}^2-1)/(N-1). \qquad (2d)$$

For this reason we prefer to use $f(\mathbf{x}_r-\mathbf{x}_s)$ instead of $h(\mathbf{x}_r-\mathbf{x}_s)$. Finally, notice that the moments calculated in § *A* below do not depend on our assumption that the sum in (2) is taken to be finite. For a rigorous construction of the associated probability density we refer to Brosius (1985).

In this paper we shall use $f(\mathbf{x}_r-\mathbf{x}_s)$ given by (2), but notice that (in the case of Patterson overlap) $f(\mathbf{x}_r-\mathbf{x}_s)$ is a density function that puts different weights on the Patterson vectors. As we have already noticed in Brosius (1985) the total density function

$$K\prod_{r}\prod_{r<s}f(\mathbf{x}_r-\mathbf{x}_s), \qquad (3)$$

where K is a suitable normalization constant, is not practical; moreover we also cannot use the asymptotic development technique for calculating the joint distribution of several structure factors if we use the density function (3). For all these reasons we must simplify expression (3). We propose three main methods for doing this:

(*A*) we use the density function

$$\prod_{j=2}^{N}f(\mathbf{x}_j-\mathbf{x}_1) \qquad (4)$$

and we let $\mathbf{x}_1$ range uniformly over the unit cell;

(*B*) we divide the total structure into several groups of approximately equal atoms and for every group of atoms we use a simplified version of (3);

(*C*) we use the idea of Patterson superposition to construct the total density function; *e.g.* one might consider a total density function of the form

$$K_1\left[\prod_{j=3}^{N}f(\mathbf{x}_j-\mathbf{x}_1)f(\mathbf{x}_j-\mathbf{x}_2)\right]f(\mathbf{x}_1-\mathbf{x}_2), \qquad (5)$$

where K_1 is a suitable normalization constant.

In order to keep this paper within a reasonable length we shall discuss here only the first two methods for the first neighborhood of the triplet invariant; we shall discuss the third method in a forthcoming paper. We think that the formulas we obtain from these two methods (*A*) and (*B*) have a lot of theoretical importance. Whether they are an improvement of older formulas should be decided after practical tests have been done.

A. The density function $\prod_{j=2}^{N}f(\mathbf{x}_j-\mathbf{x}_1)$

This is the simplest density function that we may consider. It is equivalent to putting the origin in $\mathbf{x}_1$ and writing $\hat{E}_{\mathbf{h}}$ as

$$\hat{E}_{\mathbf{h}}=N^{-1/2}\exp(-2\pi i\mathbf{h}\,.\,\mathbf{x}_1) + N^{-1/2}\sum_{j=2}^{N}\exp[-2\pi i\mathbf{h}\,.\,(\mathbf{u}_j+\mathbf{x}_1)] \qquad (6)$$

where we let $\mathbf{x}_1$ range uniformly over the unit cell and where we use

$$\prod_{j=2}^{N}f(\mathbf{u}_j)$$

as a density function for the vectors $\mathbf{u}_j$. One can easily verify the relations

$$\langle\hat{E}_{\mathbf{h}}\rangle=0;\ \langle\hat{E}_{\mathbf{h}}\exp(-2\pi i\mathbf{h}\,.\,\mathbf{x}_1)\rangle=N^{-1/2}R_{\mathbf{h}}^2$$
$$\langle|\hat{E}_{\mathbf{h}}\exp(-2\pi i\mathbf{h}\,.\,\mathbf{x}_1)-N^{-1/2}R_{\mathbf{h}}^2|^2\rangle \qquad (7)$$
$$=1-[N(N-1)]^{-1}(R_{\mathbf{h}}^2-1)^2.$$

The last relation tells us that $\varphi_{\mathbf{h}}$ probably behaves as $2\pi\mathbf{h}\,.\,\mathbf{x}_1$ when $R_{\mathbf{h}}$ is great. Of course this is the basic reason why $\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}}\simeq 0$ for large $R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{h}+\mathbf{k}}$ values. In order to see how probable the relation $\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}}\simeq 0$ is, we must calculate the joint probability distribution of $\hat{E}_{\mathbf{h}}$, $\hat{E}_{\mathbf{k}}$ and $\hat{E}_{\mathbf{h}+\mathbf{k}}$.

We think that it is necessary to give some details of the derivation. To this end let us put

$$E_{\mathbf{h}}=R_1\,e^{i\varphi_1},\quad E_{\mathbf{k}}=R_2e^{i\varphi_2}\quad\text{and}\quad E_{\mathbf{h}+\mathbf{k}}=R_3\,e^{i\varphi_3}. \qquad (8)$$

The joint probability distribution $P(R_1, R_2, R_3, \varphi_1,$

φ_2, φ_3) can then be written

$$P(R_1, R_2, R_3, \varphi_1, \varphi_2, \varphi_3)$$
$$= (1/2\pi)^6 R_1 R_2 R_3 \int_0^\infty \rho_1 \, d\rho_1 \ldots \int_0^\infty \rho_3 \, d\rho_3$$
$$\times \int_0^{2\pi} d\theta_1 \ldots \int_0^{2\pi} d\theta_3 \exp\{-i\rho_1 R_1 \cos(\varphi_1 - \theta_1)$$
$$+ \cdots - i\rho_3 R_3 \cos(\varphi_3 - \theta_3)\}$$
$$\times \Phi(\rho_1, \rho_2, \rho_3, \theta_1, \theta_2, \theta_3), \tag{9}$$

where

$$\Phi(\rho_1, \rho_2, \rho_3, \theta_1, \theta_2, \theta_3)$$
$$= \int d\mathbf{x}_1 \{\exp[i(\rho_1 N^{-1/2}) \cos\theta_1' + \cdots$$
$$+ i(\rho_3 N^{-1/2}) \cos\theta_3']$$
$$\times \Phi(\rho_1, \rho_2, \rho_3, \theta_1', \theta_2', \theta_3')^{N-1}\}, \tag{10}$$

where we have put

$$\theta_1' = \theta_1 - 2\pi \mathbf{h} \cdot \mathbf{x}_1, \quad \theta_2' = \theta_2 - 2\pi \mathbf{k} \cdot \mathbf{x}_1,$$
$$\theta_3' = \theta_3 - 2\pi(\mathbf{h}+\mathbf{k}) \cdot \mathbf{x}_1,$$
$$\Phi(\rho_1, \rho_2, \rho_3, \theta_1', \theta_2', \theta_3')$$
$$= \int d\mathbf{u} f(\mathbf{u}) \exp\{i(\rho_1 N^{-1/2}) \cos(2\pi \mathbf{h} \cdot \mathbf{u} - \theta_1')$$
$$+ \cdots + i(\rho_3 N^{-1/2}) \cos[2\pi(\mathbf{h}+\mathbf{k}) \cdot \mathbf{u} - \theta_3']\}. \tag{11}$$

Developing

$$\Phi(\rho_1, \ldots, \theta_3')^{N-1} = \exp[(N-1) \ln \Phi(\rho_1, \ldots, \theta_3')]$$

asymptotically one gets after putting

$$\varphi_1' = \varphi_1 - 2\pi \mathbf{h} \cdot \mathbf{x}_1, \ldots, \varphi_3' = \varphi_3 - 2\pi(\mathbf{h}+\mathbf{k}) \cdot \mathbf{x}_1:$$

$$P(R_1, \ldots, \varphi_3)$$
$$= \frac{R_1 R_2 R_3}{(2\pi)^6} \int d\mathbf{x}_1 \int_0^\infty \rho_1 \, d\rho_1 \ldots \int_0^\infty \rho_3 d\rho_3$$
$$\times \int_0^{2\pi} d\theta_1' \ldots \int_0^{2\pi} d\theta_3'$$
$$\times \exp\{-i\rho_1 R_1 \cos(\varphi_1' - \theta_1')$$
$$- \ldots - i\rho_3 R_3 \cos(\varphi_3' - \theta_3')\}$$
$$\times \exp\left\{ i\rho_1 (R_{\mathbf{h}} N^{-1/2}) \cos\theta_1' + \cdots \right.$$
$$+ i\rho_3 (R_{\mathbf{h}+\mathbf{k}} N^{-1/2}) \cos\theta_3'$$
$$- \frac{1}{4}\frac{N-1}{N}\rho_1^2 - \frac{1}{4}\frac{N-1}{N}\rho_2^2 - \frac{1}{4}\frac{N-1}{N}\rho_3^2$$
$$\left. - \frac{i}{N^{1/2}} \rho_1 \rho_2 \rho_3 \cos(\theta_1' + \theta_2' - \theta_3') + O\left(\frac{1}{N}\right)\right\}. \tag{12}$$

In order to calculate this integral, we define

$$D_1 \exp(i\psi_1) = R_1 \exp(i\varphi_1) - (R_{\mathbf{h}}^2 N^{-1/2})$$
$$\times \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_1), \ldots$$
$$D_3 \exp(i\psi_3) = R_3 \exp(i\varphi_3) - (R_{\mathbf{h}+\mathbf{k}}^2 N^{-1/2}) \tag{13}$$
$$\times \exp[2\pi i(\mathbf{h}+\mathbf{k}) \cdot \mathbf{x}_1]$$
$$\psi_1' = \psi_1 - 2\pi \mathbf{h} \cdot \mathbf{x}_1, \ldots, \psi_3' = \psi_3 - 2\pi(\mathbf{h}+\mathbf{k}) \cdot \mathbf{x}_1.$$

We then obtain

$$P(R_1, \ldots, \varphi_3) \propto \int d\mathbf{x}_1 \exp\{-D_1^2 - D_2^2 - D_3^2$$
$$+ 2N^{-1/2} D_1 D_2 D_3 \cos(\psi_1' + \psi_2' - \psi_3')$$
$$+ O(1/N)\}. \tag{14}$$

Using the relations in (13) we then get

$$P(R_1, \ldots, \varphi_3)$$
$$\propto \int d\mathbf{x}_1 \exp\{-R_1^2 - R_2^2 - R_3^2 + 2R_1 R_{\mathbf{h}}^2 N^{-1/2} \cos\varphi_1'$$
$$+ 2R_2 R_{\mathbf{k}}^2 N^{-1/2} \cos\varphi_2' + 2R_3 R_{\mathbf{h}+\mathbf{k}}^2 N^{-1/2} \cos\varphi_3'$$
$$+ 2N^{-1/2} R_1 R_2 R_3 \cos(\varphi_1 + \varphi_2 - \varphi_3)$$
$$+ O(1/N^{-1/2})\}. \tag{15}$$

Let us denote by $P(\varphi | R_1 = R_{\mathbf{h}}, \ldots, R_3 = R_{\mathbf{h}+\mathbf{k}})$ the conditional distribution of $\varphi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}}$ given $\hat{R}_1 = R_{\mathbf{h}}, \ldots, \hat{R}_3 = R_{\mathbf{h}+\mathbf{k}}$. Then we obtain

$$P(\varphi | R_1 = R_{\mathbf{h}}, \ldots, R_3 = R_{\mathbf{h}+\mathbf{k}})$$
$$\propto [1 + 2\alpha_1(2R_{\mathbf{h}}^3 N^{-1/2}) \alpha_1(2R_{\mathbf{k}}^3 N^{-1/2})$$
$$\times \alpha_1(2R_{\mathbf{h}+\mathbf{k}}^3 N^{-1/2}) \cos\varphi + \text{h.o.t.}]$$
$$\times \exp(2R_{\mathbf{h}} R_{\mathbf{k}} R_{\mathbf{h}+\mathbf{k}} N^{-1/2} \cos\varphi) \tag{16}$$

where $\alpha_n(x) = I_n(x)/I_0(x)$ and where $I_n(x)$ denotes the modified Bessel function of order n. The higher-order terms (h.o.t.) in (16) have been neglected, which is reasonable for moderately high R values. If at least one of the values $2N^{-1/2}R_{\mathbf{h}}^3$, $2N^{-1/2}R_{\mathbf{k}}^3$, $2N^{-1/2}R_{\mathbf{h}+\mathbf{k}}^3$ is low, formula (14) reduces to the well known Cochran & Woolfson (1955) relation. This remark shows that formula (16) predicts that among the triplets ($\mathbf{h}$, $\mathbf{k}$, $\mathbf{h}+\mathbf{k}$) with the same (large) $R_{\mathbf{h}} R_{\mathbf{k}} R_{\mathbf{h}+\mathbf{k}}$ values, the relation $\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}} \simeq 0$ is *more* reliable for those triplets for which $R_{\mathbf{h}}$, $R_{\mathbf{k}}$, $R_{\mathbf{h}+\mathbf{k}}$ are almost equal than for those for which $R_{\mathbf{h}}$, $R_{\mathbf{k}}$, $R_{\mathbf{h}+\mathbf{k}}$ are strongly different. Clearly, formula (16) may be approximated well by

$$P(\varphi | R_1 = R_{\mathbf{h}}, \ldots, R_3 = R_{\mathbf{h}+\mathbf{k}})$$
$$\propto \exp[(X + 2R_{\mathbf{h}} R_{\mathbf{k}} R_{\mathbf{h}+\mathbf{k}} N^{-1/2}) \cos\varphi], \tag{17}$$

where X is the unique root of the transcendental equation

$$\alpha_1(X) = \alpha_1(2R_{\mathbf{h}}^3 N^{-1/2}) \alpha_1(2R_{\mathbf{k}}^3 N^{-1/2})$$
$$\times \alpha_1(2R_{\mathbf{h}+\mathbf{k}}^3 N^{-1/2}). \tag{18}$$

This may seem a bit strange at first glance, but

consider the following reasoning. Let

$$1+2a\cos\varphi+2b\cos 2\varphi+2c\cos 3\varphi+\ldots$$

be a probability density function in φ.

In our case b, c *etc.* are negligible with respect to a (this is true for moderately high R values). This may tempt us to write the above density function in a form proportional to

$$\exp(X\cos\varphi).$$

We would then obtain

$$\alpha_1(X)=a.$$

It may now be interesting to consider the quartet invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ for which the cross terms $R_{\mathbf{h}+\mathbf{k}}$, $R_{\mathbf{h}+\mathbf{l}}$, $R_{\mathbf{k}+\mathbf{l}}$ of its second neighborhood are almost 0. Similar calculations to the one performed before would then give for the conditional distribution $P_{\text{cond}}(\varphi|R_{\mathbf{h}+\mathbf{k}}\simeq 0,\ R_{\mathbf{h}+\mathbf{l}}\simeq 0,\ R_{\mathbf{k}+\mathbf{l}}\simeq 0)$ of $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ given $R_{\mathbf{h}+\mathbf{k}}\simeq 0$, $R_{\mathbf{h}+\mathbf{l}}\simeq 0$, $R_{\mathbf{k}+\mathbf{l}}\simeq 0$,

$$P_{\text{cond}}(\varphi\,|\,R_{\mathbf{h}+\mathbf{k}}\simeq 0,\ldots,R_{\mathbf{k}+\mathbf{l}}\simeq 0)\propto\exp\{[X-(4/N)R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}]\cos\varphi\}\qquad(19)$$

where X is the unique root of the equation

$$\alpha_1(X)=\alpha_1(2R_{\mathbf{h}}^3N^{-1/2})\alpha_1(2R_{\mathbf{k}}^3N^{-1/2})\times\alpha_1(2R_{\mathbf{l}}^3N^{-1/2})\alpha_1(2R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}^3)N^{-1/2}.\qquad(20)$$

This shows that the relation $\varphi=\pi$ would be less reliable for 'moderately high' $R_{\mathbf{h}}\simeq R_{\mathbf{k}}\simeq R_{\mathbf{l}}\simeq R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ values.

If at least one of the values $2N^{-1/2}R_{\mathbf{h}}^3$, $2N^{-1/2}R_{\mathbf{k}}^3$, $2N^{-1/2}R_{\mathbf{l}}^3$, $2N^{-1/2}R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}^3$ is low, formula (19) coincides with well known older formulas (Hauptman, 1975; Giacovazzo, 1977; Schenk, 1974).

For very high values of $R_{\mathbf{h}}$, $R_{\mathbf{k}}$, $R_{\mathbf{l}}$ and $R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ one should calculate the joint distribution more carefully since correlation terms of higher order do play a role.

It is also instructive to consider the determinant

$$\Delta_4=\begin{vmatrix}1 & A_{\mathbf{h}} & A_{\mathbf{h}+\mathbf{k}} & A_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\\ A_{\mathbf{h}} & 1 & A_{\mathbf{k}} & A_{\mathbf{k}+\mathbf{l}}\\ A_{\mathbf{h}+\mathbf{k}} & A_{+\mathbf{k}} & 1 & A_{\mathbf{l}}\\ A_{\mathbf{h}+\mathbf{k}+\mathbf{l}} & A_{+\mathbf{k}+\mathbf{l}} & A_{\mathbf{l}} & 1\end{vmatrix}$$

where $A_{\mathbf{q}}=(R_{\mathbf{q}}^2-1)/(N-1)$. In the same way as for Karle–Hauptman determinants, see, for example, Messager & Tsoucaris (1972), one has $\Delta_4\geq 0$. Putting $A=A_{\mathbf{h}}=A_{\mathbf{k}}=A_{\mathbf{l}}=A_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ and $A_{\mathbf{h}+\mathbf{k}}=A_{\mathbf{k}+\mathbf{l}}=0$ in Δ_4 one finds that $\Delta_4<0$ for large A values.

This might be an indication that it would be more improbable to have large and equal $R_{\mathbf{h}}$, $R_{\mathbf{k}}$, $R_{\mathbf{l}}$ and $R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ values when $R_{\mathbf{h}+\mathbf{k}}\simeq R_{\mathbf{h}+\mathbf{l}}\simeq R_{\mathbf{k}+\mathbf{l}}\simeq 0$ than otherwise. For quintets and higher invariants a lot of correlation terms will have to be taken into account.

B. The density function $g(\mathbf{x}_1,\ldots,\mathbf{x}_m)\ldots g(\mathbf{x}_{N-m+1},\ldots,\mathbf{x}_N)$

Let m be an integer number that divides N; we divide the total structure (of N atoms) into substructures of m atoms. To put it more precisely we arrange the set $\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N$ of all atomic random variables in the subsets

$$\{\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_m\},\{\mathbf{x}_{m+1},\ldots,\mathbf{x}_{2m}\},\ldots,\{\mathbf{x}_{N-m+1},\ldots,\mathbf{x}_N\}.$$

For the subset $\{\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_m\}$ we use the density function $g(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_m)$ defined by

$$g(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_m)=\frac{K_m^{-1}}{m!}\sum f(\mathbf{x}_{i_1}-\mathbf{x}_{i_2})\times f(\mathbf{x}_{i_2}-\mathbf{x}_{i_3})\ldots f(\mathbf{x}_{i_m}-\mathbf{x}_{i_1})\qquad(21)$$

where K_m is a normalization constant [we find that $K_m=(N-1)^{-m}\sum_{\mathbf{q}}(R_{\mathbf{q}}^2-1)^m$] and where the sum in (21) denotes a sum over all permutations $(i_1,i_2,\ldots,i_m)$ of the integers $1,2,\ldots,m$. For instance, for $m=4$ one would have

$$\begin{aligned}g(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\mathbf{x}_4)&=(K_4^{-1}/3)f(\mathbf{x}_1-\mathbf{x}_2)f(\mathbf{x}_2-\mathbf{x}_3)f(\mathbf{x}_3-\mathbf{x}_4)f(\mathbf{x}_4-\mathbf{x}_1)\\&\quad+f(\mathbf{x}_1-\mathbf{x}_2)f(\mathbf{x}_2-\mathbf{x}_4)f(\mathbf{x}_4-\mathbf{x}_3)f(\mathbf{x}_3-\mathbf{x}_1)\\&\quad+f(\mathbf{x}_1-\mathbf{x}_4)f(\mathbf{x}_4-\mathbf{x}_2)f(\mathbf{x}_2-\mathbf{x}_3)f(\mathbf{x}_3-\mathbf{x}_1)\end{aligned}\qquad(22)$$

with

$$K_4=(N-1)^{-4}\sum_{\mathbf{q}}(R_{\mathbf{q}}^2-1)^4.$$

The above density function can be represented by a 'sum' of three diagrams as shown in Fig. 1. Hence the three diagrams in Fig. 1 will give a contribution when $\mathbf{x}_1-\mathbf{x}_2$, $\mathbf{x}_1-\mathbf{x}_3$, $\mathbf{x}_1-\mathbf{x}_4$, $\mathbf{x}_2-\mathbf{x}_3$, $\mathbf{x}_2-\mathbf{x}_4$ and $\mathbf{x}_3-\mathbf{x}_4$ are all Patterson vectors and only the first diagram will give a contribution when $\mathbf{x}_1-\mathbf{x}_2$, $\mathbf{x}_2-\mathbf{x}_3$, $\mathbf{x}_3-\mathbf{x}_4$, and $\mathbf{x}_4-\mathbf{x}_1$ are Patterson vectors whereas $\mathbf{x}_1-\mathbf{x}_3$ and (or) $\mathbf{x}_2-\mathbf{x}_4$ are not Patterson vectors.

For general m the total density function $h(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ can now be written

$$h(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)=g(\mathbf{x}_1,\ldots,\mathbf{x}_m)g(\mathbf{x}_{m+1},\ldots,\mathbf{x}_{2m})\times\ldots g(\mathbf{x}_{N-m+1},\ldots,\mathbf{x}_N).\qquad(23)$$

This form for $h(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ indicates that we can use an asymptotic development for the characteristic

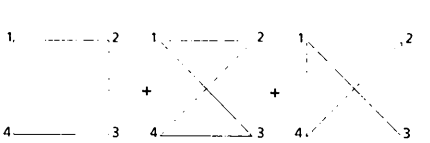

Fig. 1. Diagrammatic representation of the three components of the density function of equation (22).

function if N/m is high enough. We shall now use this density function to calculate the joint distribution of the first neighborhood of a triplet invariant. To this end let us put

$$E_{\mathbf{h}} = R_1 e^{i\varphi_1}, \quad E_{\mathbf{k}} = R_2 e^{i\varphi_2}, \quad E_{\mathbf{h}+\mathbf{k}} = R_3 e^{i\varphi_3}.$$

We then get for the joint probability distribution $P(R_1, R_2, R_3, \varphi_1, \varphi_2, \varphi_3)$

$$\begin{aligned} P(R_1, R_2, R_3, \varphi_1, \varphi_2, \varphi_3) &= \frac{R_1 R_2 R_3}{(2\pi)^6} \int_0^\infty \rho_1 \mathrm{d}\rho_1 \ldots \int_0^\infty \rho_3 \mathrm{d}\rho_3 \\ &\times \int_0^{2\pi} \mathrm{d}\theta_1 \ldots \int_0^{2\pi} \mathrm{d}\theta_3 \\ &\times \exp\{-i\rho_1 R_1 \cos(\varphi_1 - \theta_1) + \ldots \\ &- i\rho_3 R_3 \cos(\varphi_3 - \theta_3)\} \\ &\times \Phi(\rho_1, \rho_2, \rho_3, \theta_1, \theta_2, \theta_3)^{N/m} \end{aligned} \tag{24}$$

where

$$\begin{aligned} \Phi(\rho_1, \ldots, \theta_3) &= \int \mathrm{d}\mathbf{x}_1 \ldots \mathrm{d}\mathbf{x}_m g(\mathbf{x}_1, \ldots, \mathbf{x}_m) \\ &\times \exp\{i\rho_1 N^{-1/2} \sum_{j=1}^{m} \cos(2\pi \mathbf{h} \cdot \mathbf{x}_j - \theta_1) \\ &+ \ldots + i\rho_3 N^{-1/2} \sum_{j=1}^{m} \cos(2\pi \mathbf{h} \cdot \mathbf{x}_j - \theta_3)\}. \end{aligned} \tag{25}$$

Let us define

$$\begin{aligned} \mu(\mathbf{h}) &= \langle \cos 2\pi \mathbf{h} \cdot (\mathbf{x}_1 - \mathbf{x}_2) \rangle \\ &= \int \mathrm{d}\mathbf{x}_1 \ldots \mathrm{d}\mathbf{x}_m g(\mathbf{x}_1, \ldots, \mathbf{x}_m) \cos[2\pi \mathbf{h} \cdot (\mathbf{x}_1 - \mathbf{x}_2)] \\ &= \frac{1}{(m-1)} \sum_{s=1}^{m-1} \frac{\langle (R_{\mathbf{q}}^2 - 1)^{m-s} (R_{\mathbf{q}+\mathbf{h}}^2 - 1)^s \rangle_{\mathbf{q}}}{\langle (R_{\mathbf{q}}^2 - 1)^m \rangle_{\mathbf{q}}} \end{aligned}$$

$$\begin{aligned} \mu(\mathbf{h}, \mathbf{k}) &= \langle \cos 2\pi [\mathbf{h} \cdot (\mathbf{x}_1 - \mathbf{x}_3) + \mathbf{k} \cdot (\mathbf{x}_2 - \mathbf{x}_3)] \rangle \\ &= [(m-1)(m-2)]^{-1} \\ &\times \Bigg\{ \sum_{s=1}^{m-2} \sum_{r=1}^{m-(s+1)} \langle (R_{\mathbf{q}}^2 - 1)^{m-s-r} (R_{\mathbf{q}+\mathbf{h}}^2 - 1)^s \\ &\times (R_{\mathbf{q}+\mathbf{h}+\mathbf{k}}^2 - 1)^r \rangle_{\mathbf{q}} [\langle (R_{\mathbf{q}}^2 - 1)^m \rangle_{\mathbf{q}}]^{-1} \\ &+ \sum_{s=2}^{m-1} \sum_{r=1}^{s-1} \langle (R_{\mathbf{q}}^2 - 1)^{m-s} (R_{\mathbf{q}+\mathbf{h}}^2 - 1)^r \\ &\times (R_{\mathbf{q}-\mathbf{k}}^2 - 1)^{s-r} \rangle_{\mathbf{q}} [\langle (R_{\mathbf{q}}^2 - 1)^m \rangle_{\mathbf{q}}]^{-1} \Bigg\}. \end{aligned} \tag{26}$$

We then obtain

$$\begin{aligned} \Phi(\rho_1, \ldots, \theta_3) = 1 &- (m/4N)\rho_1^2 [1 + (m-1)\mu(\mathbf{h})] + \ldots \\ &- (m/4N)\rho_3^2 [1 + (m-1)\mu(\mathbf{h}+\mathbf{k})] \\ &- (im/4N^{3/2})\rho_1 \rho_2 \rho_3 \cos(\theta_1 + \theta_2 - \theta_3) \\ &\times [1 + (m-1)\mu(\mathbf{h}) + (m-1)\mu(\mathbf{k}) \\ &+ (m-1)\mu(\mathbf{h}+\mathbf{k}) \\ &+ (m-1)(m-2)\mu(\mathbf{h}, \mathbf{k})] \\ &+ O(m/N^2). \end{aligned} \tag{27}$$

'Classical' asymptotic development of $\Phi(\rho_1, \ldots, \theta_3)^{N/m}$ then gives for the conditional distribution $P(\varphi | R_1 = R_{\mathbf{h}}, \quad R_2 = R_{\mathbf{k}}, \quad R_3 = R_{\mathbf{h}+\mathbf{k}})$ of $\varphi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}}$ given $R_1 = R_{\mathbf{h}}, \ldots, R_3 = R_{\mathbf{h}+\mathbf{k}}$ the following formula:

$$\begin{aligned} &P(\varphi | R_1 = R_{\mathbf{h}}, \ldots, R_3 = R_{\mathbf{h}+\mathbf{k}}) \\ &\propto \exp[2R_{\mathbf{h}} R_{\mathbf{k}} R_{\mathbf{h}+\mathbf{k}} (B_{\mathbf{h}} B_{\mathbf{k}} B_{\mathbf{h}+\mathbf{k}} N)^{-1/2} A_{\mathbf{h},\mathbf{k}} \cos\varphi] \end{aligned} \tag{28}$$

where

$$\begin{aligned} A_{\mathbf{h},\mathbf{k}} &= 1 + (m-1)[\mu(\mathbf{h}) + \mu(\mathbf{k}) + \mu(\mathbf{h}+\mathbf{k})] \\ &\quad + (m-1)(m-2)\mu(\mathbf{h}, \mathbf{k}) \\ B_{\mathbf{h}}^2 &= 1 + (m-1)\mu(\mathbf{h}), \ldots, \\ B_{\mathbf{h}+\mathbf{k}}^2 &= 1 + (m-1)\mu(\mathbf{h}+\mathbf{k}). \end{aligned} \tag{29}$$

For $m \simeq N^{1/2}$, formula (28) should in principle be able to indicate negative cosines. Notice also that all the terms occurring in $\mu(\mathbf{h}, \mathbf{k})$ [(26)] are of the same form of the most important term of the $B_{3,0}$ formula (Hauptman, 1964): so in the absence of 'chance interactions' (Hauptman, 1964) we may expect

$$\mu(\mathbf{h}, \mathbf{k}) \simeq N^{-3/2} R_{\mathbf{h}} R_{\mathbf{k}} R_{\mathbf{h}+\mathbf{k}} \cos(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}})$$

and

$$\mu(\mathbf{h}) \simeq (N-1)^{-1}(R_{\mathbf{h}}^2 - 1).$$

In that case $A_{\mathbf{h},\mathbf{k}}$ becomes

$$\begin{aligned} A_{\mathbf{h},\mathbf{k}} \simeq 1 &+ N^{-1/2}[R_{\mathbf{h}}^2 + R_{\mathbf{k}}^2 + R_{\mathbf{h}+\mathbf{k}}^2 - 3 \\ &+ R_{\mathbf{h}} R_{\mathbf{k}} R_{\mathbf{h}+\mathbf{k}} \cos\varphi] \end{aligned}$$

so if $\cos\varphi \simeq -1$ and $R_{\mathbf{h}} R_{\mathbf{k}} R_{\mathbf{h}+\mathbf{k}}$ is large, $A_{\mathbf{h},\mathbf{k}} \simeq 0$ or even $A_{\mathbf{h},\mathbf{k}} < 0$. Notice that not all averages $\langle \ldots \rangle_{\mathbf{q}}$ occurring in $\mu(\mathbf{h}, \mathbf{k})$ are different. To see this, let us write symbolically

$$\langle \mathbf{q}^r (\mathbf{q}+\mathbf{h})^s (\mathbf{q}+\mathbf{h}+\mathbf{k})^t \rangle_{\mathbf{q}}$$

for $\langle (R_{\mathbf{q}}^2 - 1)^r (R_{\mathbf{q}+\mathbf{h}}^2 - 1)^s (R_{\mathbf{q}+\mathbf{h}+\mathbf{k}} - 1)^t \rangle_{\mathbf{q}}$. Then, after using such substitutions as $\mathbf{m} = \mathbf{q}+\mathbf{h}$ or $\mathbf{m} = \mathbf{q}+\mathbf{h}+\mathbf{k}$ or $\mathbf{m} = -\mathbf{q}$ *etc.*, we get

$$\langle \mathbf{q}^r (\mathbf{q}+\mathbf{h})^s (\mathbf{q}+\mathbf{h}+\mathbf{k})^t \rangle_{\mathbf{q}} = \langle \mathbf{q}^s (\mathbf{q}+\mathbf{h})^r (\mathbf{q}-\mathbf{k})^t \rangle_{\mathbf{q}}.$$

Concluding remarks

We expect that method *A* will work best for invariants like quintets and higher, since then a lot of correlation terms of order $N^{-3/2}$ can be taken into account. Method *B* is expected to work fine for large *m* values ($m \simeq N^{-1/2}$). We think that a combination of method *A* and method *B* will give still better results, since then the correlation terms that normally appear in method *A* will be boosted. We shall explore this in a forthcoming paper.

Finally, let us notice that one can also use another approach for calculating triplet phase invariants; in this approach one considers the atomic position vectors to be fixed and the structure factors to be random variables of the reciprocal-lattice vectors. For more on this we refer to Hauptman (1985) and Gilmore & Hauptman (1985).

References

BROSIUS, J. (1985). *Acta Cryst.* A**41**, 613-617.
COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1-12.
GIACOVAZZO, C. (1977). *Acta Cryst.* A**32**, 91-99.
GILMORE, C. J. & HAUPTMAN, H. (1985). *Acta Cryst.* A**41**, 457-462.
HAUPTMAN, H. (1964). *Acta Cryst.* **17**, 1421-1433.
HAUPTMAN, H. (1975). *Acta Cryst.* A**31**, 91-99.
HAUPTMAN, H. (1985). *Acta Cryst.* A**41**, 454-457.
MESSAGER, J. C. & TSOUCARIS, G. (1972). *Acta Cryst.* A**28**, 482-484.
SCHENK, H. (1974). *Acta Cryst.* A**30**, 477-482.

Acta Cryst. (1989). A**45**, 468-471

A Statistical Interpretation for the $B_{3,0}$ formula in $P1$

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Abstract

A model is discussed that is able to give a statistical interpretation for the $B_{3,0}$ formula of Karle & Hauptman [*Acta Cryst.* (1957), **10**, 515-524] for the space group $P1$. The main idea is to use a suitable probability measure for the interatomic position vectors and to 'linearize' the triplet phase invariant. As a result of the model a statistical formula is given using a 'first neighborhood' of random variables.

Introduction

The $B_{3,0}$ formula of Karle & Hauptman (1957) for $P1$ [and Hauptman & Karle (1958) for $P\bar{1}$] is well known among 'direct-methods' crystallographers. It gives the value of the cosine of a triplet phase invariant when the structure consists of equal atoms and if no 'chance interactions' (Hauptman, 1964) occur. Unfortunately, when the number of atoms increases, the number of these chance interactions (or 'near chance interactions' since we have only a finite number of E_k values at our disposal) increases also, thereby violating the strict validity of the $B_{3,0}$ formula. A lot of research has been undertaken to modify the $B_{3,0}$ formula (*e.g.* Hauptman, 1964; Hauptman, Fisher, Hancock & Norton, 1969; Karle, 1970; Fisher, Hancock & Hauptman, 1970). All these approaches tried to calculate the exact value of the cosine invariant rather than giving a statistical interpretation of it.

A first (and up to now the only known) attempt to give a statistical interpretation of the $B_{3,0}$ formula was given by Giacovazzo (1977). The work of Vaughan (1958, 1959) should however also be mentioned for other formulas than the $B_{3,0}$ formula. In our opinion there are many serious objections to Giacovazzo's approach. A more detailed discussion of Giacovazzo's paper will appear as a short comment (Brosius, 1989).

Our approach will be entirely different. It is based on the observation (Brosius, 1978) that the $B_{3,0}$ formula comes mainly from the average of $\exp\{2\pi i[\mathbf{h}.(\mathbf{x}_i-\mathbf{x}_l)+\mathbf{k}.(\mathbf{x}_j-\mathbf{x}_l)]\}$ with a suitably chosen density function for $\mathbf{x}_i$, $\mathbf{x}_j$ and $\mathbf{x}_l$. This forces us to 'linearize' the random variable $E_{\mathbf{h}}E_{\mathbf{k}}E_{-(\mathbf{h}+\mathbf{k})}$. In order to control the wrong results caused by this linearization we also use three control variables that are $N^{1/2}R_{\mathbf{h}}^2$, $N^{1/2}R_{\mathbf{k}}^2$ and $N^{1/2}R_{\mathbf{h}+\mathbf{k}}^2$. Together with $E_{\mathbf{h}}E_{\mathbf{k}}E_{-(\mathbf{h}+\mathbf{k})}$ we shall consider it as the first neighborhood (a term first used by Hauptman) of our triplet $E_{\mathbf{h}}E_{\mathbf{k}}E_{-(\mathbf{h}+\mathbf{k})}$.

We would like to mention some recent papers concerning the calculation of the triplet phase invariant where one also uses real averages over reciprocal space (or part of it), namely Hauptman (1985) and Gilmore & Hauptman (1985).

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