Acta Cryst. (1977). A33, 107–109

The Derivation of Joint Probability Distributions of Structure Factors for Space Group $P\bar{1}$ from the Corresponding Distributions for Space Group $P1$

BY J. J. L. HEINERMAN

Laboratorium voor Structuurchemie, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands

(*Received* 24 *June* 1976; *accepted* 24 *July* 1976)

A general procedure is given to obtain joint probability distributions of structure factors for structures in space group $P\bar{1}$ from the corresponding distributions for structures in space group $P1$. Some examples are given.

Introduction

Joint probability distributions of structure factors for structures in centrosymmetric space groups and those for structures in non-centrosymmetric space groups have always been derived separately. In both cases first the primitive random variables are specified, then the characteristic function is calculated and next, from the Fourier transform, the probability distribution is obtained. We shall show that once a probability distribution for $P1$ has been calculated, it is simple to calculate the corresponding distribution for $P\bar{1}$.

The procedure

For equal-atom structures the normalized structure factor is given by

$$E_{\mathbf{h}} = A_{\mathbf{h}} + iB_{\mathbf{h}}, \tag{1a}$$

where

$$A_{\mathbf{h}} = \sum_{j=1}^{N} N^{-1/2} \cos 2\pi \mathbf{h} \,.\, \mathbf{r}_j, \tag{1b}$$

$$B_{\mathbf{h}} = \sum_{j=1}^{N} N^{-1/2} \sin 2\pi \mathbf{h} \,.\, \mathbf{r}_j \tag{1c}$$

and N is the number of atoms in the unit cell. For structures in $P1$, denote by $P_1(X_1,\ldots,X_n; Y_1,\ldots,Y_n)$ the joint probability distribution of the real parts $A_{\mathbf{h}_1},\ldots,A_{\mathbf{h}_n}$ and the imaginary parts $B_{\mathbf{h}_1},\ldots,B_{\mathbf{h}_n}$ of the normalized structure factors $E_{\mathbf{h}_1},\ldots,E_{\mathbf{h}_n}$. Then $P_1(X_1,\ldots,X_n; Y_1,\ldots,Y_n)\mathrm{d}X_1\ldots\mathrm{d}X_n\mathrm{d}Y_1\ldots\mathrm{d}Y_n$ is the joint probability that $X_1 < A_{\mathbf{h}_1} < X_1 + \mathrm{d}X_1, \ldots, X_n < A_{\mathbf{h}_n} < X_n + \mathrm{d}X_n$, $Y_1 < B_{\mathbf{h}_1} < Y_1 + \mathrm{d}Y_1, \ldots, Y_n < B_{\mathbf{h}_n} < Y_n + \mathrm{d}Y_n$.

From a structure in $P1$, we construct a structure in $P\bar{1}$ by adding to each atom j with position vector $\mathbf{r}_j$ an atom $N+j$ with position vector $\mathbf{r}_{N+j} = -\mathbf{r}_j$. The normalized structure factor for such a $P\bar{1}$ structure, containing $2N$ atoms in the unit cell, is

$$E_{\mathbf{h}} = \sum_{j=1}^{2N} (2N)^{-1/2} \cos 2\pi \mathbf{h} \,.\, \mathbf{r}_j = \sqrt{2} A_{\mathbf{h}}, \tag{2}$$

where $A_{\mathbf{h}}$ is the real part of the normalized structure factor of the $P1$ structure. For structures in $P\bar{1}$, denote by $P_{\bar{1}}(S_1,\ldots,S_n)$ the joint probability distribution of the structure factors $E_{\mathbf{h}_1},\ldots,E_{\mathbf{h}_n}$. Then $P_1(S_1,\ldots,S_n)\mathrm{d}S_1\ldots\mathrm{d}S_n$ is the joint probability that $S_1 < E_{\mathbf{h}_1} < S_1 + \mathrm{d}S_1, \ldots, S_n < E_{\mathbf{h}_n} < S_n + \mathrm{d}S_n$. This probability can be obtained from $P_1(X_1,\ldots,X_n; Y_1,\ldots,Y_n)\mathrm{d}X_1\ldots\mathrm{d}X_n\mathrm{d}Y_1\ldots\mathrm{d}Y_n$. First we integrate with respect to $Y_1,\ldots,Y_n$,

$$P_1(X_1,\ldots,X_n)\mathrm{d}X_1\ldots\mathrm{d}X_n = \int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty} P_1(X_1,\ldots,X_n; Y_1,\ldots,Y_n) \times \mathrm{d}X_1\ldots\mathrm{d}X_n\mathrm{d}Y_1\ldots\mathrm{d}Y_n, \tag{3}$$

and next, according to (2), we replace the X_i by $S_i/\sqrt{2}$,

$$P_{\bar{1}}(S_1,\ldots,S_n)\mathrm{d}S_1\ldots\mathrm{d}S_n = 2^{-n/2} P_1\left(\frac{S_1}{\sqrt{2}},\ldots,\frac{S_n}{\sqrt{2}}\right)\mathrm{d}S_1\ldots\mathrm{d}S_n. \tag{4}$$

$P_{\bar{1}}(S_1,\ldots,S_n)$ may depend on N, which is half the number of atoms in the unit cell. In the following examples N in $P_{\bar{1}}(S_1,\ldots,S_n)$ will be replaced by $N/2$; then N denotes the total number of atoms in the unit cell.

Examples

(*a*) The joint probability distribution of the real and imaginary part of one structure factor has been calculated by Wilson (1949). For normalized structure factors as given by (1) this distribution is

$$P_1(X, Y) = \pi^{-1} \exp(-X^2 - Y^2). \tag{5}$$

The probability distribution of the real part is obtained by integrating with respect to Y,

$$P_1(X) = \pi^{-1} \exp(-X^2) \int_{-\infty}^{\infty} \exp(-Y^2)\mathrm{d}Y = \pi^{-1/2} \exp(-X^2). \tag{6}$$

Next, employing (4), we obtain the probability distribution of one normalized structure factor for a $P\bar{1}$ structure,

$$P_{\bar{1}}(S)=(2\pi)^{-1/2}\exp(-\tfrac{1}{2}S^2), \tag{7}$$

in agreement with a result of Wilson (1949).

(*b*) As a second example we consider the joint probability distribution of three structure factors $E_{\mathbf{h}_1}, E_{\mathbf{h}_2}, E_{\mathbf{h}_3}$, with $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=\mathbf{0}$. The joint probability distribution $P_1(R_1,R_2,R_3;\Phi_1,\Phi_2,\Phi_3)$ of the magnitudes and the phases of $E_{\mathbf{h}_1}$, $E_{\mathbf{h}_2}$ and $E_{\mathbf{h}_3}$, correct up to and including terms of order $N^{-1/2}$, is given by

$$P_1(R_1,R_2,R_3;\Phi_1,\Phi_2,\Phi_3)=\frac{R_1R_2R_3}{\pi^3}\exp[-R_1^2-R_2^2-R_3^2+2N^{-1/2}R_1R_2R_3\cos(\Phi_1+\Phi_2+\Phi_3)] \tag{8}$$

[Heinerman (1977*a*), formula (21) with $Q_{123}=N^{-1/2}$ and $q_{123}=0$]. Using the transformation

$$R_v\cos\Phi_v=X_v,\quad R_v\sin\Phi_v=Y_v, \tag{9a}$$

for which

$$R_v\mathrm{d}R_v\mathrm{d}\Phi_v=\mathrm{d}X_v\mathrm{d}Y_v, \tag{9b}$$

we find

$$P_1(X_1,X_2,X_3;Y_1,Y_2,Y_3)=\pi^{-3}\exp[-X_1^2-X_2^2-X_3^2-Y_1^2-Y_2^2-Y_3^2+2N^{-1/2}(X_1X_2X_3-X_1Y_2Y_3-Y_1X_2Y_3-Y_1Y_2X_3)]. \tag{10}$$

Integrating with respect to Y_1 gives, correct up to and including terms of order $N^{-1/2}$,

$$P_1(X_1,X_2,X_3;Y_2,Y_3)=\pi^{-5/2}\exp[-X_1^2-X_2^2-X_3^2-Y_2^2-Y_3^2+2N^{-1/2}(X_1X_2X_3-X_1Y_2Y_3)]. \tag{11}$$

The integrations with respect to Y_2 and Y_3 are performed in the same way and lead to

$$P_1(X_1,X_2,X_3)=\pi^{-3/2}\exp(-X_1^2-X_2^2-X_3^2+2N^{-1/2}X_1X_2X_3). \tag{12}$$

Next we employ (4) and replace N by $N/2$. The resulting joint probability distribution of three structure factors in $P\bar{1}$, correct up to and including terms of order $N^{-1/2}$, is

$$P_{\bar{1}}(S_1,S_2,S_3)=(2\pi)^{-3/2}\exp[-\tfrac{1}{2}(S_1^2+S_2^2+S_3^2)+N^{-1/2}S_1S_2S_3], \tag{13}$$

from which the well known sign probability of a triple product (Cochran & Woolfson, 1955) can be obtained.

(*c*) A more complicated case is the joint probability distribution of the seven structure factors $E_{\mathbf{h}}$, $E_{\mathbf{k}}$, $E_{\mathbf{l}}$, $E_{\mathbf{m}}$, $E_{\mathbf{h}+\mathbf{k}}$, $E_{\mathbf{k}+\mathbf{l}}$, $E_{\mathbf{l}+\mathbf{h}}$, with $\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}=\mathbf{0}$ [space group $P1$: Giacovazzo (1976); Hauptman (1975); for a comparison of their results see Heinerman (1977*b*); space group $P\bar{1}$: Giacovazzo (1975); Green & Hauptman (1976)]. Here we use Hauptman's (1975) formula for the joint probability distribution of the magnitudes and the phases of the seven structure factors:

$$\begin{aligned}
&P_1(R_1,R_2,R_3,R_4,R_{12},R_{23},R_{31};\Phi_1,\Phi_2,\Phi_3,\Phi_4,\Phi_{12},\Phi_{23},\Phi_{31})\\
&=\frac{R_1R_2R_3R_4R_{12}R_{23}R_{31}}{\pi^7}\exp\{-R_1^2-R_2^2-R_3^2-R_4^2-R_{12}^2-R_{23}^2-R_{31}^2\\
&+2N^{-1/2}[R_1R_2R_{12}\cos(\Phi_1+\Phi_2-\Phi_{12})+R_3R_4R_{12}\cos(\Phi_3+\Phi_4+\Phi_{12})+R_2R_3R_{23}\cos(\Phi_2+\Phi_3-\Phi_{23})\\
&+R_1R_4R_{23}\cos(\Phi_1+\Phi_4+\Phi_{23})+R_1R_3R_{31}\cos(\Phi_1+\Phi_3-\Phi_{31})+R_2R_4R_{31}\cos(\Phi_2+\Phi_4+\Phi_{31})]\\
&-2N^{-1}[R_1R_3R_{12}R_{23}^2\cos(\Phi_1-\Phi_3-\Phi_{12}+\Phi_{23})+R_2R_4R_{12}R_{23}\cos(\Phi_2-\Phi_4-\Phi_{12}-\Phi_{23})\\
&+R_1R_2R_{23}R_{31}\cos(\Phi_1-\Phi_2+\Phi_{23}-\Phi_{31})+R_3R_4R_{23}R_{31}\cos(\Phi_3-\Phi_4-\Phi_{23}-\Phi_{31})\\
&+R_2R_3R_{31}R_{12}\cos(\Phi_2-\Phi_3+\Phi_{31}-\Phi_{12})+R_1R_4R_{31}R_{12}\cos(\Phi_1-\Phi_4-\Phi_{31}-\Phi_{12})\\
&+2R_1R_2R_3R_4\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4)]\},
\end{aligned} \tag{14}$$

which is correct up to and including those terms of order N^{-1} that depend on the phases. Using the same transformation as in the preceding example we find

$$\begin{aligned}
&P_1(X_1,X_2,X_3,X_4,X_{12},X_{23},X_{31};Y_1,Y_2,Y_3,Y_4,Y_{12},Y_{23},Y_{31})\\
&=\pi^{-7}\exp\{-X_1^2-X_2^2-X_3^2-X_4^2-X_{12}^2-X_{23}^2-X_{31}^2-Y_1^2-Y_2^2-Y_3^2-Y_4^2-Y_{12}^2-Y_{23}^2-Y_{31}^2\\
&+2N^{-1/2}[X_1X_2X_{12}+X_3X_4X_{12}+X_2X_3X_{23}+X_1X_4X_{23}+X_1X_3X_{31}+X_2X_4X_{31}\\
&+F(X_1,X_2,X_3,X_4,X_{12},X_{23},X_{31};Y_1,Y_2,Y_3,Y_4,Y_{12},Y_{23},Y_{31})]\\
&-2N^{-1}[X_1X_3X_{12}X_{23}+X_2X_4X_{12}X_{23}+X_1X_2X_{23}X_{31}+X_3X_4X_{23}X_{31}+X_2X_3X_{31}X_{12}\\
&+X_1X_4X_{31}X_{12}+2X_1X_2X_3X_4+G(X_1,X_2,X_3,X_4,X_{12},X_{23},X_{31};Y_1,Y_2,Y_3,Y_4,Y_{12},Y_{23},Y_{31})]\},
\end{aligned} \tag{15}$$

where F and G are sums of products of three and four variables respectively, with all variables to the power one. The products of three variables are of the form XYY, while there are no two terms that contain the same combination of Y's, and those of four variables are of the form $XXYY$ or $YYYY$. Let us consider the integration with respect to Y_1. Denote by $Y_1 f$ the terms in F depending on Y_1 and by $Y_1 g$ the terms in G depending on Y_1. The integration with respect to Y_1 gives

$$\int_{-\infty}^{\infty} \exp\left[-Y_1^2+2N^{-1/2}Y_1(f-N^{-1/2}g)\right]\mathrm{d}Y_1 = \pi^{1/2}\exp\left(N^{-1}f^2\right)\left[1+O(N^{-3/2})\right]. \quad (16)$$

The terms in f^2 can be divided into two groups: (*a*) terms of the form $XXYY$ depending on two different Y's; these terms are of the same class as the remaining terms of G; (*b*) terms of the form X^2Y^2; these terms are independent of the signs of the X's and are neglected [they belong to the same class as the terms of order N^{-1} not depending on the phases, which have been neglected in (14)]. Continuing in this way for the other integrations it is seen that $P_1(X_1,X_2,X_3,X_4,X_{12},X_{23},X_{31})$ is obtained from (15) by leaving out the terms depending on the Y's and by multiplying by $\pi^{7/2}$. Next, employing (4) and replacing N by $N/2$ we obtain

$$\begin{aligned}
&P_{\bar{1}}(S_1,S_2,S_3,S_4,S_{12},S_{23},S_{31})\\
&=(2\pi)^{-7/2}\exp\left[-\tfrac{1}{2}(S_1^2+S_2^2+S_3^2+S_4^2+S_{12}^2+S_{23}^2+S_{31}^2)\right.\\
&+N^{-1/2}(S_1S_2S_{12}+S_3S_4S_{12}+S_2S_3S_{23}\\
&+S_1S_4S_{23}+S_1S_3S_{31}+S_2S_4S_{31})\\
&-N^{-1}(S_1S_3S_{12}S_{23}+S_2S_4S_{12}S_{23}\\
&+S_1S_2S_{23}S_{31}+S_3S_4S_{23}S_{31}+S_2S_3S_{31}S_{12}\\
&\left.+S_1S_4S_{31}S_{12}+2S_1S_2S_3S_4)\right], \quad (17)
\end{aligned}$$

which is correct up to and including those terms of order N^{-1} that depend on the signs of the S's. This formula is identical with the one derived by Green & Hauptman (1976).

Concluding remarks

A general procedure has been given to obtain joint probability distributions of structure factors for structures in $P\bar{1}$ from those for structures in $P1$. Some examples, of increasing complexity, have been given. It is stressed that this procedure leads to $P\bar{1}$ distributions with the same probabilistic background as the $P1$ distributions from which they are derived.

The idea of considering a $P\bar{1}$ structure as the sum of two $P1$ structures which led to the procedure described in this paper was suggested by Dr J. Kroon. The author thanks Drs J. Kroon and H. Krabbendam and Professor A. F. Peerdeman for stimulating discussions and critical reading of the manuscript.

References

COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1–12.
GIACOVAZZO, C. (1975). *Acta Cryst.* A**31**, 252–259.
GIACOVAZZO, C. (1976). *Acta Cryst.* A**32**, 91–99.
GIACOVAZZO, C. (1977). *Acta Cryst.* A**33**, 50–54.
GREEN, E. A. & HAUPTMAN, H. (1976). *Acta Cryst.* A**32**, 43–45.
HAUPTMAN, H. (1975). *Acta Cryst.* A**31**, 671–679.
HEINERMAN, J. J. L. (1977*a*). *Acta Cryst.* A**33**, 100–106.
HEINERMAN, J. J. L. (1977*b*). Submitted to *Acta Cryst.* A, but see footnote to Giacovazzo (1977).
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318–321.

Acta Cryst. (1977). A**33**, 109–113

Approximations for the Calculation of High-Resolution Electron-Microscope Images of Thin Films

BY P. L. FEJES*

Department of Physics, Arizona State University, Tempe, Arizona 85281, *USA*

(*Received* 13 *February* 1976; *accepted* 25 *July* 1976)

Phase-grating calculations were carried out to calculate lattice images from thin crystals. A method for including the effect of chromatic aberration in these calculations is shown and the results are compared with experimental images. The improved agreement of calculations with experiment when chromatic aberration is taken into account is shown.

Introduction

By high-resolution electron microscopy it is possible to observe images of crystal structures with a resolution of about 3 Å. This type of imaging is being carried out in the study of a number of compounds having large unit cells such that features inside the unit cells can easily be identified. Complex oxide structures as well as many mineral structures have been studied. For a review of this work see for example Allpress & Sanders (1973), Buseck & Iijima (1974) and Cowley & Iijima (1976).

* Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, 1 Berlin 33, Faradayweg 4–6, Germany (BRD).