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The Probability Distribution of the Magnitude of a Structure Factor. II. The Non-centrosymmetric Crystal

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The general formula for the compound probability distribution of the real and imaginary parts of the structure factor is derived for all rigid non-centrosymmetric crystals as a function of the indices h, k, l. The probability distribution for the magnitude of the structure factor is then readily found. The distributions and the averages of any power of $|F|$ corresponding to a particular space group may be obtained from the general formula by means of routine mathematical computations. The analysis includes the case that the crystal contains atoms in special positions as well as in general positions. Illustrative examples are worked out in detail.

Introduction

In the preceding paper (Karle & Hauptman, 1953), hereafter described as I, the probability distributions of the structure factors for centrosymmetric crystals were obtained. This paper is devoted to the derivation of the probability distribution for the magnitude of the structure factor for the non-centrosymmetric crystal. The probability distribution of the phase of the structure factor for any crystal will be given in subsequent papers. As in the case of the centrosymmetric crystal, the distributions for each space group may be computed from the general formula to any desired accuracy by means of routine mathematical calculations.

In paper I the probability distribution for the structure factor coincided with that for the real part of the structure factor. In the present paper, the previous method is generalized to yield the compound or joint probability distribution of the real and imaginary parts of the structure factor. From this joint distribution, it is possible to derive both the distribution for the magnitude and for the phase. For those values of h, k, l for which either the real or imaginary part of the structure factor is identically zero, the methods of I apply.

Joint distribution

We treat first the case in which the crystal has atoms only in general positions. The structure factor is defined by

$$F = X+iY\,, \tag{1}$$

where

$$X = \sum_{j=1}^{N/n} f_j\xi(x_j, y_j, z_j),\quad Y = \sum_{j=1}^{N/n} f_j\eta(x_j, y_j, z_j)\,, \tag{2}$$

n is the symmetry number, f_j is the atomic scattering factor, N is the number of atoms in the unit cell, and $\xi_j = \xi(x_j, y_j, z_j)$ and $\eta_j = \eta(x_j, y_j, z_j)$ are known trigonometric functions of h, k, l and the atomic coordinates which are determined by the space group. If the x_j, y_j, z_j are uniformly and independently distributed in the interval (0, 1), then the compound probability that ξ_j lie in the interval $(\alpha, \alpha+d\alpha)$ and that η_j lie in the interval $(\beta, \beta+d\beta)$ is denoted by the function $p(\alpha, \beta)d\alpha d\beta$. This function will be derived in the Appendix. It is now possible to find the probability $Q(A, B)$ that X be less than A and that Y be less than B. We have

$$Q(A, B) = \int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty} p(\xi_1, \eta_1)\ldots p(\xi_{N/n}, \eta_{N/n})\times T(\xi_1, \eta_1, \ldots, \xi_{N/n}, \eta_{N/n})\, d\xi_1\, d\eta_1 \ldots d\xi_{N/n}d\eta_{N/n}\,, \tag{3}$$

where

$$\begin{aligned} T(\xi_1, \eta_1, \ldots, \xi_{N/n}, \eta_{N/n}) &= \left\{\frac{1}{2}-\frac{1}{\pi}\int_0^\infty \frac{\sin[(X-A)x]}{x}dx\right\}\times \left\{\frac{1}{2}-\frac{1}{\pi}\int_0^\infty \frac{\sin[(Y-B)y]}{y}dy\right\} \\ &= 1 \text{ if } X<A \text{ and } Y<B\,, \\ &= 0 \text{ if } X>A \text{ or } Y>B\,. \end{aligned} \tag{4}$$

By differentiating successively with respect to A and with respect to B, we obtain

$$\frac{\partial^2 Q(A, B)}{\partial A\partial B} = P_{XY}(A, B) = \frac{1}{\pi^2}\int_0^\infty\int_0^\infty dx\,dy\int_{-\infty}^{\infty}\ldots \int_{-\infty}^{\infty} p(\xi_1, \eta_1)\ldots p(\xi_{N/n}, \eta_{N/n}) \cos[(X-A)x]\times \cos[(Y-B)y]\, d\xi_1\, d\eta_1 \ldots d\xi_{N/n}d\eta_{N/n}\,, \tag{5}$$

where $P(A, B)dAdB$ is the compound probability that X lie between A and $A+dA$ and that Y lie between B and $B+dB$. The probability distribution of $R = (X^2+Y^2)^{\frac{1}{2}}$ cannot be obtained directly from those for X and Y separately as found in the previous paper because X and Y are not independently distributed. In order to evaluate (5), the following definitions are introduced:

$$A_0 = B_0 = 0,\ A_k = \sum_{j=1}^{k} f_j \xi_j,\ B_k = \sum_{j=1}^{k} f_j \eta_j, \quad k = 1, 2, \ldots, N/n . \quad (6)$$

Therefore

$$A_k = A_{k-1}+f_k\xi_k,\ B_k = B_{k-1}+f_k\eta_k \quad (7)$$

and

$$A_{N/n} = X,\ B_{N/n} = Y . \quad (8)$$

A typical operation in the evaluation of (5) is

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p(\xi_k, \eta_k)\cos[(A_k-A)x]\cos[(B_k-B)y]\,d\xi_k d\eta_k = \quad (9)$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p(\xi_k, \eta_k)\,\{\cos[(A_{k-1}-A)x]\cos(f_k\xi_k x) - \sin[(A_{k-1}-A)x]\sin(f_k\xi_k x)\} \times \{\cos[(B_{k-1}-B)y]\cos(f_k\eta_k y) - \sin[(B_{k-1}-B)y]\sin(f_k\eta_k y)\}\,d\xi_k d\eta_k . \quad (10)$$

As seen from the Appendix, $p(\xi_k, \eta_k)$ is an even function of both ξ_k and η_k so that (10) reduces to

$$\cos[(A_{k-1}-A)x]\cos[(B_{k-1}-B)y]\,q(f_k x, f_k y) , \quad (11)$$

where

$$q(f_k x, f_k y) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p(\xi_k, \eta_k)\cos(f_k\xi_k x)\cos(f_k\eta_k y)\,d\xi_k d\eta_k . \quad (12)$$

By repeated application of this result we obtain from (5) the desired compound probability function,

$$P_{XY}(A, B) = \frac{1}{\pi^2}\int_0^{\infty}\int_0^{\infty}\cos Ax\cos By \prod_{k=1}^{N/n} q(f_k x, f_k y)\,dx\,dy , \quad (13)$$

which may be compared with equation (2) of I.

The expansion of both cosines in (12) yields

$$q(f_k x, f_k y) = 1-\frac{1}{2!}f_k^2x^2m_{20}-\frac{1}{2!}f_k^2y^2m_{02} +\frac{1}{4!}f_k^4x^4m_{40}+\frac{1}{2!2!}f_k^4x^2y^2m_{22}+\frac{1}{4!}f_k^4y^4m_{04} -\frac{1}{6!}f_k^6x^6m_{60}-\frac{1}{4!2!}f_k^6x^4y^2m_{42} -\frac{1}{2!4!}f_k^6x^2y^4m_{24}-\frac{1}{6!}f_k^6y^6m_{06}+\ldots , \quad (14)$$

where

$$m_{ij} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\xi_k^i\eta_k^j p(\xi_k, \eta_k)\,d\xi_k d\eta_k . \quad (15)$$

As may be verified from $p(\xi_k, \eta_k)$ given in the Appendix, or from the meaning of a moment as an expected value or average, (15) becomes

$$m_{ij} = \int_0^1\int_0^1\int_0^1 \xi^i\eta^j\,dx\,dy\,dz , \quad (16)$$

and the subscript k has been omitted in (16) since ξ_k and η_k as functions of x_k, y_k, z_k are independent of k. It is seen that the function $P_{XY}(A, B)$ is expressible in terms of the moments m_{ij}, which in turn are readily computed from (16) once ξ and η are given as functions of x, y, z. The problem which remains is to derive the probability distribution for the magnitude, R, of the structure factor from (13) and to express it in the more useful form of a rapidly converging infinite series.

We seek the function $P_{R\theta}(c, \varphi)$ such that $P_{R\theta}(c, \varphi)dc\,d\varphi$ is the compound probability that R lie between c and $c+dc$ and that θ, the phase angle, lie between φ and $\varphi+d\varphi$, where

$$R = \sqrt{(X^2+Y^2)},\quad \theta = \tan^{-1}Y/X , \quad (17)$$

or

$$X = R\cos\theta,\quad Y = R\sin\theta . \quad (18)$$

Since

$$dXdY = \begin{vmatrix} \cos\theta & \sin\theta \\ -R\sin\theta & R\cos\theta \end{vmatrix} dRd\theta = RdRd\theta , \quad (19)$$

R will lie in the interval $(c, c+dc)$ and θ will lie in the interval $(\varphi, \varphi+d\varphi)$ if and only if the point (X, Y) lies in the elementary area $cdcd\varphi$ at the point $(c\cos\varphi, c\sin\varphi)$. The probability of the latter event is, however, $P_{XY}(c\cos\varphi, c\sin\varphi)cdcd\varphi$, so that

$$P_{R\theta}(c, \varphi) = cP_{XY}(c\cos\varphi,\ c\sin\varphi) \quad (20)$$

and is readily found from (13). The probability $P_R(c)dc$ that R lie between c and $c+dc$ is obtained from (20) by means of

$$P_R(c) = c\int_0^{2\pi} P_{XY}(c\cos\varphi,\ c\sin\varphi)\,d\varphi \quad (21)$$

(Uspensky, 1937, p. 246).

The series for $P_{XY}(A, B)$ may be obtained from (13) and (14) by a method used previously (Hauptman & Karle, 1952, p. 50) and is found to be

$$P_{XY}(A, B) = \frac{1}{\pi^2}\int_0^{\infty}\int_0^{\infty}\cos(Ax)\cos(By)\prod_{k=1}^{N/n} q(f_k x, f_k y)\,dx\,dy$$

$$= \frac{\exp\left(-\frac{A^2}{4\sqrt{(\Sigma a_{k20})}}-\frac{B^2}{4\sqrt{(\Sigma a_{k02})}}\right)}{4\pi\sqrt{\Sigma a_{k20}\Sigma a_{k02}}} \times \left\{1-\left[\frac{(12(\Sigma a_{k20})^2-12A^2\Sigma a_{k20}+A^4)\Sigma(\frac{1}{2}a_{k20}^2-a_{k40})}{2^4(\Sigma a_{k20})^4} + \frac{(2\Sigma a_{k20}-A^2)(2\Sigma a_{k02}-B^2)\Sigma(a_{k20}a_{k02}-a_{k22})}{2^4(\Sigma a_{k20})^2(\Sigma a_{k02})^2} + \frac{(12(\Sigma a_{k02})^2-12B^2\Sigma a_{k02}+B^4)\Sigma(\frac{1}{2}a_{k02}^2-a_{k04})}{2^4(\Sigma a_{k02})^4}\right]\right.$$

$$
\begin{aligned}
&-\left[\frac{(120(\Sigma a_{k20})^3-180A^2(\Sigma a_{k20})^2+30A^4\Sigma a_{k20}-A^6)\Sigma(\frac{1}{3}a_{k20}^3-a_{k20}a_{k40}+a_{k60})}{2^6(\Sigma a_{k20})^6}\right.\\
&+\frac{(12(\Sigma a_{k20})^2-12A^2\Sigma a_{k20}+A^4)(2\Sigma a_{k02}-B^2)\Sigma(a_{k20}^2a_{k02}-a_{k20}a_{k22}-a_{k02}a_{k40}+a_{k42})}{2^6(\Sigma a_{k20})^4(\Sigma a_{k02})^2}\\
&+\frac{(12(\Sigma a_{k02})^2-12B^2\Sigma a_{k02}+B^4)(2\Sigma a_{k20}-A^2)\Sigma(a_{k02}^2a_{k20}-a_{k02}a_{k22}-a_{k20}a_{k04}+a_{k24})}{2^6(\Sigma a_{k20})^2(\Sigma a_{k02})^4}\\
&\left.+\frac{(120(\Sigma a_{k02})^3-180B^2(\Sigma a_{k02})^2+30B^4\Sigma a_{k02}-B^6)\Sigma(\frac{1}{3}a_{k02}^3-a_{k02}a_{k04}+a_{k06})}{2^6(\Sigma a_{k02})^6}\right]-\ldots\Bigg\}, \qquad (22)
\end{aligned}
$$

where

$$a_{kij}=\frac{m_{ij}f_k^{i+j}}{i!\,j!} \qquad (23)$$

and all summations in (22) extend from $k=1$ to N/n. The substitution of (22) into (21) gives the desired series for the probability distribution of the magnitude of the structure factor for any non-centrosymmetric crystal. A survey of the space groups indicates that $m_{20}=m_{02}$ for all space groups and all h, k, l for which neither m_{20} nor m_{02} is zero. The latter case has already been treated in I. In any event, (21) always applies and may be evaluated in terms of Bessel functions. In the case that $m_{20}=m_{02}=m_2$, (21) reduces to

$$
\begin{aligned}
P_R(c)=\frac{nc\exp(-nc^2/2m_2\sigma_2)}{m_2\sigma_2}&\left\{1-\frac{n\sigma_4}{2\times4m_2^2\sigma_2^2}(8m_2^2-M_4)\left(1-\frac{nc^2}{m_2\sigma_2}+\frac{n^2c^4}{8m_2^2\sigma_2^2}\right)\right.\\
&-\frac{n^2\sigma_6}{2\times4\times6m_2^3\sigma_2^3}(96m_2^3-18m_2M_4+M_6)\left(1-\frac{3nc^2}{2m_2\sigma_2}+\frac{3n^2c^4}{8m_2^2\sigma_2^2}-\frac{n^3c^6}{48m_2^3\sigma_2^3}\right)\\
&-\frac{n^3\sigma_8(2304m_2^4-576m_2^2M_4+32m_2M_6-M_8+P_8)-n^2\sigma_4^2(1152m_2^4-288m_2^2M_4+P_8)}{2\times4\times6\times8m_2^4\sigma_2^4}\times\\
&\left.\left(1-\frac{2nc^2}{m_2\sigma_2}+\frac{3n^2c^4}{4m_2^2\sigma_2^2}-\frac{n^3c^6}{12m_2^3\sigma_2^3}+\frac{n^4c^8}{384m_2^4\sigma_2^4}\right)-\ldots\right\}, \qquad (24)
\end{aligned}
$$

Table 1. *Moments for the space groups P1, P2, P222, having atoms in general positions only*

Space group		n	m_2	m_{40} or m_{04}	m_{22}	m_{60} or m_{06}	m_{42} or m_{24}	m_{80} or m_{08}	m_{62} or m_{26}	m_{44}
$P1$		1	$\frac{1}{2}$	$\frac{3}{8}$	$\frac{1}{8}$	$\frac{5}{16}$	$\frac{1}{16}$	$\frac{35}{128}$	$\frac{5}{128}$	$\frac{3}{128}$
$P2$	$k\neq0$, $h=l=0$	1	$\frac{1}{2}$	$\frac{3}{8}$	$\frac{1}{8}$	$\frac{5}{16}$	$\frac{1}{16}$	$\frac{35}{128}$	$\frac{5}{128}$	$\frac{3}{128}$
	$k\neq0$, $h^2+l^2\neq0$	2	1	$\frac{9}{4}$	$\frac{3}{4}$	$\frac{25}{4}$	$\frac{5}{4}$	$\left(\frac{35}{8}\right)^2$	$\frac{175}{64}$	$\frac{105}{64}$
$P222$	$hkl\neq0$	4	2	$\frac{3^3}{2}$	4	5^3	1	$\frac{35^3}{2^7}$	$\frac{5^3}{2^5}$	$\frac{3^3}{2^5}$

Table 2. *Averages of the powers of* $|F|$ *derived from the moments of Table* 1

Space group		$\langle\lvert F\rvert\rangle$	$\langle\lvert F\rvert^2\rangle$	$\langle\lvert F\rvert^4\rangle$	$\langle\lvert F\rvert^6\rangle$
$P1$		$\frac{1}{2}(\pi\sigma_2)^{\frac{1}{2}}\left(1+\frac{\sigma_4}{16\sigma_2^2}+\frac{\sigma_6}{24\sigma_2^3}\ldots\right)$	σ_2	$2\sigma_2^2-\sigma_4$	$6\sigma_2^3-9\sigma_2\sigma_4+4\sigma_6$
$P2$	$k\neq0$	$\frac{1}{2}(\pi\sigma_2)^{\frac{1}{2}}\left(1+\frac{\sigma_4}{16\sigma_2^2}+\frac{\sigma_6}{24\sigma_2^3}\ldots\right)$	σ_2	$2\sigma_2^2-\sigma_4$	$6\sigma_2^3-9\sigma_2\sigma_4+4\sigma_6$
$P222$	$hkl\neq0$	$\frac{1}{2}(\pi\sigma_2)^{\frac{1}{2}}\left(1-\frac{3\sigma_4}{64\sigma_2^2}-\frac{59\sigma_6}{96\sigma_2^3}\ldots\right)$	σ_2	$2\sigma_2^2+\frac{3}{4}\sigma_4$	$6\sigma_2^3+\frac{27}{4}\sigma_2\sigma_4-59\sigma_6$

where
$$M_4 = m_{40}+2m_{22}+m_{04}\,, \tag{25}$$
$$M_6 = m_{60}+3m_{42}+3m_{24}+m_{06}\,, \tag{26}$$
$$M_8 = m_{80}+4m_{62}+6m_{44}+4m_{26}+m_{08}\,, \tag{27}$$
$$P_8 = 35m_{40}^2+108m_{22}^2+35m_{04}^2+60m_{40}m_{22} +6m_{40}m_{04}+60m_{04}m_{22}\,, \tag{28}$$
and $\sigma_k = \sum_{j=1}^{N} f_j^k = n\sum_{j=1}^{N/n} f_j^k$.

Average value of $|F|^p$

The average value of $|F|^p$ can be immediately obtained from the probability distribution (24) by means of the integral formula
$$\int_0^\infty x^p \exp\,[-ax^2]\,dx = \frac{\Gamma\left(\frac{p+1}{2}\right)}{2a^{\frac{p+1}{2}}}\,, \tag{29}$$
where $p > -1$. We find from (24) that
$$\langle|F|^p\rangle = \int_0^\infty c^p P_R(c)dc = \Gamma\left(\frac{p+2}{2}\right)\left(\frac{2m_2\sigma_2}{n}\right)^{p/2} \times$$
$$\left\{1-\frac{n\sigma_4(8m_2^2-M_4)}{2^2\times 4^2 m_2^2\sigma_2^2}\,p(p-2)+\frac{n^2\sigma_6(96m_2^3-18m_2M_4+M_6)}{2^2\times 4^2\times 6^2 m_2^3\sigma_2^3}\,p(p-2)(p-4)\,-\right.$$
$$\left.\frac{n^3\sigma_8(2304m_2^4-576m_2^2M_4+32m_2M_6-M_8+P_8)-n^2\sigma_4^2(1152m_2^4-288m_2^2M_4+P_8)}{2^2\times 4^2\times 6^2\times 8^2 m_2^4\sigma_2^4}\,p(p-2)(p-4)(p-6)+\ldots\right\}\,, \tag{30}$$
a formula which should be compared with the analogous formula (23) of I. Equation (30) gives the average value of $|F|^p$ for all values of $p > -1$. It should be noted that if p is an even integer, the series (30) terminates.

Examples

The application of (24) is illustrated by deriving the probability distributions of the structure factor magnitudes for three space groups, $P1$, $P2$, $P222$:

$$P1:\quad \left.\begin{aligned} \xi &= \cos 2\pi(hx+ky+lz)\,, \\ \eta &= \sin 2\pi(hx+ky+lz)\,. \end{aligned}\right\} \tag{31}$$

$$P2:\quad \left.\begin{aligned} \xi &= 2\cos 2\pi(hx+lz)\cos 2\pi ky\,, \\ \eta &= 2\cos 2\pi(hx+lz)\sin 2\pi ky\,. \end{aligned}\right\} \tag{32}$$

$$P222:\quad \left.\begin{aligned} \xi &= 4\cos 2\pi hx\cos 2\pi ky\cos 2\pi lz\,, \\ \eta &= -4\sin 2\pi hx\sin 2\pi ky\sin 2\pi lz\,. \end{aligned}\right\} \tag{33}$$

The moments are readily found from (16) and are exhibited in Table 1. The case $k = 0$ for space group $P2$ and the case $hkl = 0$ for space group $P222$ may be treated by the method of the centrosymmetric crystal (I), since the imaginary part of the structure factor is zero, and are therefore not considered here. It is to be noted that for the space groups in Table 1, it so happens that $m_{ij} = m_{ji}$, but this property is not shared by all the space groups. It is of some interest to note that the first two rows of Table 1 are identical, while the moments of the third row lead to a distribution which is identical with that derived from the moments in the first two rows. In general, however, different space groups lead to different distributions. The h, k, l triples within a space group fall into different families, and the distributions of the magnitudes associated with the triples belonging to the same family are identical. Substitution into (24) yields immediately the desired probability distributions. The averages of several powers of $|F|$ for these space groups are obtained from (30) and are listed in Table 2. When the moments m_{ij} for the space group $P1$ are substituted into (24) we obtain equation (10) of Hauptman and Karle (1952), which was derived in a different manner.

Special positions

So far, this paper has been concerned with crystals having atoms only in general positions. However, the methods developed apply equally well to crystals having atoms in special positions in addition to those in general positions. Equations (2) are replaced by the more general
$$X = \sum_{j=1}^{t} f_j\xi_j,\quad Y = \sum_{j=1}^{t} f_j\eta_j,\quad t = \sum_{j=1}^{v} N_i/n_i\,, \tag{34}$$
where v is the total number of types of positions (special and general) exclusive of the fixed special positions, N_i is the number of atoms in each type of position, and n_i is the number of equivalent atoms in the corresponding type. While N_i depends upon the particular crystal specimen, v and n_i depend only on the space group. The functions ξ_j maintain the same form for each fixed value of i, and the functions η_j maintain the same form for each fixed value of i, i.e. for values of j corresponding to a fixed type of position and, together with v and n_i, are known for each space group. The probability that ξ_j lie between α and $\alpha+d\alpha$ and that η_j lie between β and $\beta+d\beta$ now depends on j and is denoted by $p_j(\alpha,\beta)d\alpha d\beta$ where $p_j(\alpha,\beta)$ is derived in the Appendix. However, as before, only the moments
$$m_{kij} = \int_{-\infty}^{\infty}\alpha^i\beta^i p_k(\alpha,\beta)\,d\alpha d\beta = \int_0^1\int_0^1\int_0^1 \xi_k^i\eta_k^j\,dxdydz \tag{35}$$
are needed. If $q_k(f_kx, f_ky)$ is defined as follows,
$$q_k(f_kx, f_ky) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_k(\alpha,\beta)\cos(f_kx\alpha)\cos(f_ky\beta)\,d\alpha d\beta\,, \tag{36}$$

then, denoting as before, by $P_{XY}(A, B)dAdB$ the probability that X lie in the interval $A, A+dA$ and that Y lie in the interval $B, B+dB$, we find that

$$P_{XY}(A, B) = \frac{1}{\pi^2}\int_0^\infty\int_0^\infty \cos(Ax)\cdot\cos(By)\prod_{k=1}^{t} q_k(f_k x, f_k y)\,dx\,dy\ . \quad (37)$$

Replacing A and B by $c\cos\varphi$ and $c\sin\varphi$ respectively, and multiplying by c, we obtain

$$P_{R\theta}(c, \varphi) = cP_{XY}(c\cos\varphi,\ c\sin\varphi)\ , \quad (38)$$

where $P_{R\theta}(c, \varphi)dcd\varphi$ is the probability that the magnitude R lie in the interval $c, c+dc$ and that the phase θ lie in the interval $\varphi, \varphi+d\varphi$. Then the desired probability distribution $P_R(c)$ is given by

$$P_R(c) = \int_0^{2\pi} P_{R\theta}(c, \varphi)d\varphi\ , \quad (39)$$

By methods already explained, this function may be written in terms of a series which is a generalization of (24)

$$P_R(c) = \frac{c\exp(-c^2/2\Sigma f_k^2 m_{k2})}{\Sigma f_k^2 m_{k2}}\left\{1 - \frac{\Sigma f_k^4(8m_{k2}^2-(m_{k40}+2m_{k22}+m_{k04})}{2\times4(\Sigma f_k^2 m_{k2})^2}\left(1-\frac{c^2}{\Sigma f_k^2 m_{k2}}+\frac{c^4}{8(\Sigma f_k^2 m_{k2})^2}\right)\right.$$
$$-\frac{\Sigma f_k^6(96m_{k2}^3-18m_{k2}(m_{k40}+2m_{k22}+m_{k04})+(m_{k60}+3m_{k42}+3m_{k24}+m_{k06}))}{2\times4\times6(\Sigma f_k^2 m_{k2})^3}\times$$
$$\left.\left(1-\frac{3c^2}{2\Sigma f_k^2 m_{k2}}+\frac{3c^4}{8(\Sigma f_k^2 m_{k2})^2}-\frac{c^6}{8(\Sigma f_k^2 m_{k2})^3}\right)-\ldots\right\}\ , \quad (40)$$

where k ranges from 1 to t and $m_{k2} = m_{k20} = m_{k02}$.

The remaining problem concerns the case that the crystal also contains atoms in fixed special positions. If we denote by $f' = f'(h, k, l)$ and by $g' = g'(h, k, l)$ the contributions to the real part X and the imaginary part Y of the structure factor of the atoms in fixed special positions, $P_{XY}(A, B)$ is obtained from (22) by replacing A by $A-f'$ and B by $B-g'$, giving

$$P_{XY}(A, B) = \frac{\exp\left(-\frac{(A-f')^2}{4\Sigma a_{k20}}-\frac{(B-g')^2}{4\Sigma a_{k02}}\right)}{4\pi\sqrt{(\Sigma a_{k20}\Sigma a_{k02})}}\times$$
$$\left\{1-\left[\frac{(12(\Sigma a_{k20})^2-12(A-f')^2(\Sigma a_{k20})+(A-f')^4)\Sigma(\frac{1}{2}a_{k20}^2-a_{k40})}{2^4(\Sigma a_{k20})^4}\right.\right.$$
$$+\frac{(2\Sigma a_{k20}-(A-f')^2)(2\Sigma a_{k02}-(B-g')^2)\Sigma(a_{k20}a_{k02}-a_{k22})}{2^4(\Sigma a_{k20})^2(\Sigma a_{k02})^2}$$
$$\left.\left.+\frac{(12(\Sigma a_{k02})^2-12(B-g')^2(\Sigma a_{k02})+(B-g')^4)\Sigma(\frac{1}{2}a_{k02}^2-a_{k04})}{2^4(\Sigma a_{k02})^4}\right]-\ldots\right\}\ . \quad (41)$$

Then, denoting by $P_{R\theta}(c, \varphi)dcd\varphi$ the probability that R lie between c and $c+dc$ and that θ lie between φ and $\varphi+d\varphi$, we obtain from (41),

$$P_{R\theta}(c, \varphi) = \frac{c\exp\left(-\frac{(c\cos\varphi-f')^2+(c\sin\varphi-g')^2}{2\Sigma f_k^2 m_{k2}}\right)}{2\pi\Sigma f_k^2 m_{k2}}\times$$
$$\left\{1-\left[\frac{(3(\Sigma f_k^2 m_{k2})^2-6(c\cos\varphi-f')^2\Sigma f_k^2 m_{k2}+(c\cos\varphi-f')^4)\Sigma f_k^4(3m_{k2}^2-m_{k40})}{4!(\Sigma f_k^2 m_{k2})^4}\right.\right.$$
$$+\frac{(\Sigma f_k^2 m_{k2}-(c\cos\varphi-f')^2)(\Sigma f_k^2 m_{k2}-(c\sin\varphi-g')^2)\Sigma f_k^4(m_{k2}^2-m_{k22})}{2!\,2!\,(\Sigma f_k^2 m_{k2})^4}$$
$$\left.\left.+\frac{(3(\Sigma f_k^2 m_{k2})^2-6(c\sin\varphi-g')^2\Sigma f_k^2 m_{k2}+(c\sin\varphi-g')^4)\Sigma f_k^4(3m_{k2}^2-m_{k04})}{4!(\Sigma f_k^2 m_{k2})^4}\right]-\ldots\right\}\ . \quad (42)$$

By means of the following integral formulas,

$$\int_0^{2\pi} e^{z\cos\theta}\cos n\theta d\theta = 2\pi I_n(z)\ , \quad (43)$$

$$\int_0^{2\pi} e^{z\cos\theta}\sin^{2n}\theta d\theta = \frac{2\Gamma(\frac{1}{2})\Gamma(n+\frac{1}{2})}{(\frac{1}{2}z)^n}I_n(z)\ , \quad (44)$$

where $I_n(z)$ is the Bessel function of imaginary argument, $P_R(c)$ may be obtained. Owing to the complexity of the final results, only the first term in the series is given here. However, merely routine calculations are required to obtain as many terms as desired. We get*

$$P_R(c) = \frac{c \exp\left(-\dfrac{c^2+f'^2+g'^2}{2\Sigma f_k^2 m_{k2}}\right) I_0\left(\dfrac{c\sqrt{(f'^2+g'^2)}}{\Sigma f_k^2 m_{k2}}\right)}{\Sigma f_k^2 m_{k2}} . \quad (45)$$

Further simplification may be realized if the Maclaurin expansions of the Bessel functions are used, but we omit this development since it involves elementary mathematical manipulations.

Concluding remarks

From (20) we obtain

$$P_\theta(\varphi) = \int_0^\infty c P_{XY}(c \cos\varphi,\ c \sin\varphi)\,dc\,, \quad (46)$$

where $P_\theta(\varphi)d\varphi$ is the probability that the phase angle lie in the interval $(\varphi, \varphi+d\varphi)$. Equation (46) can be generalized to yield the probability distribution of the phase angle as a consequence of a set of observed magnitudes. Thus the concept of the joint or compound probability distribution forms the basis for a direct attack on the phase problem, and will be the subject of subsequent papers.

APPENDIX

An explicit expression for the function $p(c_\xi, c_\eta)dc_\xi dc_\eta$, the compound probability that ξ lie between c_ξ and $c_\xi+dc_\xi$ and that η lie between c_η and $c_\eta+dc_\eta$, may be derived as in I by making use of the discontinuous integral (4) to find the probability $r(c_\xi, c_\eta)$ that ξ be less than c_ξ and that η be less than c_η. We obtain

$$r(c_\xi, c_\eta) = \int_0^1\int_0^1\int_0^1 \left[\frac{1}{2} - \frac{1}{\pi}\int_0^\infty \frac{\sin[(\xi-c_\xi)u]}{u}du\right] \times \left[\frac{1}{2} - \frac{1}{\pi}\int_0^\infty \frac{\sin[(\eta-c_\eta)v]}{v}dv\right] dxdydz\,, \quad (47)$$

where ξ and η are functions of x, y, z, h, k, l and

$$p(c_\xi, c_\eta) = \partial^2 r(c_\xi, c_\eta)/\partial c_\xi \partial c_\eta\,.$$

Evaluation of (47) gives

$$p(c_\xi, c_\eta) = \frac{1}{2\pi}\left\{\int_0^1\int_0^1\int_0^1 \frac{\exp\left(-\dfrac{c_\xi^2}{2\xi^2}-\dfrac{c_\eta^2}{2\eta^2}\right)}{\xi\eta} - \frac{1}{4}\int_0^1\int_0^1\int_0^1 \frac{\exp\left(-\dfrac{c_\xi^2}{2\xi^2}-\dfrac{c_\eta^2}{2\eta^2}\right)}{\xi\eta}\left(1-\frac{2c_\xi^2}{\xi^2}+\frac{c_\xi^4}{3\xi^4}\right) - \frac{1}{4}\int_0^1\int_0^1\int_0^1 \frac{\exp\left(-\dfrac{c_\xi^2}{2\xi^2}-\dfrac{c_\eta^2}{2\eta^2}\right)}{\xi\eta}\left(1-\frac{2c_\eta^2}{\eta^2}+\frac{c_\eta^4}{3\eta^4}\right) + \frac{1}{16}\int_0^1\int_0^1\int_0^1 \frac{\exp\left(-\dfrac{c_\xi^2}{2\xi^2}-\dfrac{c_\eta^2}{2\eta^2}\right)}{\xi\eta} \times \left(1-\frac{2c_\xi^2}{\xi^2}+\frac{c_\xi^4}{3\xi^4}\right)\left(1-\frac{2c_\eta^2}{\eta^2}+\frac{c_\eta^4}{3\eta^4}\right) + \ldots\right\}. \quad (48)$$

The various moments m_{ij} given by (15) and required for (22) and (24) are readily found to reduce to (16).

* The average of any power of $|F|$ may be obtained from (45) in the usual way, e.g. $\langle|F|^2\rangle = f'^2+g'^2+2\Sigma f_k^2 m_{k2}$.

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