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The Probability Distribution of the Magnitude of a Structure Factor. I. The Centrosymmetric Crystal

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The general formula for the probability distribution of the structure factor is derived for all rigid centrosymmetric crystals as a function of the indices h, k, l. 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 a recent paper (Hauptman & Karle, 1952), probability distributions for the magnitudes of the structure factors and for interatomic vectors were obtained for asymmetric and centrosymmetric crystals having no other symmetry elements. Wilson (1949) had previously obtained approximate distributions for the magnitudes of the structure factors valid for heavily populated unit cells. He also studied the effect of symmetry properties on these distributions (Wilson, 1950). The present series of papers concerns a detailed study of the effect of the various symmetry elements of crystals on the probability distributions for the magnitudes and for the phases of the structure factors. These distributions lead in an obvious way to improved methods for identifying the space group, adjusting observed intensities to an absolute scale, and removing the effect of vibrational motion.

In the development of the probability distributions, it should be emphasized that there are two conceptually distinct distributions. The first distribution arises by fixing the h, k, l indices and allowing the atoms in the crystal to range uniformly throughout the unit cell but subject to the conditions imposed by symmetry. This is the distribution obtained from the theoretical considerations to follow. In the second distribution, the positions of the atoms are fixed and the set of structure-factor magnitudes is obtained by allowing the h, k, l to range uniformly over the integers. This is the distribution of the observed structure-factor magnitudes corrected for vibrational motion. As recognized by Wilson, it is of great importance that these two distributions are identical except for differences which occasionally arise when there are atoms in certain special positions in the unit cell. Actually, for any space group, the h, k, l triples fall into different classes, and a different distribution corresponds to each class. A single distribution for any space group can be obtained from these by means of a suitable weighted average, the weights depending upon the h, k, l whose corresponding intensities have been observed. This single distribution is the one to be compared with the distribution of the observed structure-factor magnitudes. Where feasible (i.e. if the number of observed intensities is sufficiently large), the distributions associated with the separate classes may be compared with the corresponding distributions of the observed magnitudes.

In the previous paper (Hauptman & Karle, 1952) the results were obtained by a development of the problem of the random walk. It did not appear feasible to adapt this method for general treatment of the symmetry problem. Instead, a direct analytic method was used to obtain the desired distributions.

In this paper, the general form of all distributions is obtained for centrosymmetric crystals and from this it is shown how the particular distribution corresponding to each space group can be found. The probability distributions for the structure factors will be seen to be expressible in terms of the moments of the individual terms of the summation defining the structure factor. The particular distributions for each space group may thus be found to any desired accuracy by means of routine mathematical computations.

Probability distribution

We treat first the case in which the crystal contains atoms only in general positions. The structure factor for the centrosymmetric crystal is given by

$$F = \sum_{j=1}^{N/n} f_j \xi(x_j, y_j, z_j) \; , \qquad (1)$$

where n is the symmetry number, f_j is the atomic scattering factor, N is the number of atoms in the unit cell and $\xi(x_j, y_j, z_j)$ is some known trigonometric function of h, k, l and the atomic coordinates which is determined by the space group. The probability that $\xi_j = \xi(x_j, y_j, z_j)$ lie between c and $c+dc$ is given by $p(c)dc$, where $p(c)$ is a function which can be determined on the basis that the atoms in the unit cell are uniformly distributed. We make use of the property that $p(c)$ is an even function which vanishes when the magnitude of c exceeds some positive number, b. Denote by $P(A)dA$ the probability that F lie between A and $A+dA$. We next derive the general result that

$$P(A) = \frac{1}{\pi}\int_0^\infty \cos Ax \prod_{k=1}^{N/n} q(f_k x)\,dx\,, \tag{2}$$

where

$$q(f_k x) = \int_{-\infty}^{\infty} p(c)\cos(f_k xc)\,dc = 2\int_0^\infty p(c)\cos(f_k xc)\,dc\,. \tag{3}$$

We write

$$A_k = \sum_{j=1}^{k} f_j \xi_j\,, \quad k = 1, 2, \ldots, N/n\,. \tag{4}$$

Then

$$A_0 = 0,\quad A_{N/n} = F,\quad A_k = A_{k-1}+f_k\xi_k\,,\quad k = 1, 2, \ldots, N/n. \tag{5}$$

The probability, $Q(c)$, that F be less than c is

$$Q(c) = \int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty} p(\xi_1)\ldots p(\xi_{N/n})T(\xi_1, \ldots, \xi_{N/n})\,d\xi_1\ldots d\xi_{N/n}\,, \tag{6}$$

where

$$T(\xi_1, \ldots, \xi_{N/n}) = 0 \quad \text{if} \quad F > c\,, \tag{7}$$

$$T(\xi_1, \ldots, \xi_{N/n}) = 1 \quad \text{if} \quad F < c\,. \tag{8}$$

We choose for T the discontinuous function

$$T(\xi_1, \ldots, \xi_{N/n}) = \frac{1}{2}-\frac{1}{\pi}\int_0^\infty \frac{\sin[(F-c)x]}{x}\,dx \tag{9}$$

so that (7) and (8) are satisfied. Then

$$Q(c) = \int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty}\left(\frac{1}{2}-\frac{1}{\pi}\int_0^\infty \frac{\sin[(F-c)x]}{x}\,dx\right)\times p(\xi_1)\ldots p(\xi_{N/n})\,d\xi_1\ldots d\xi_{N/n} \tag{10}$$

$$= \frac{1}{2}-\frac{1}{\pi}\int_0^\infty \frac{dx}{x}\int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty} p(\xi_1)\ldots p(\xi_{N/n})\times \sin[(F-c)x]\,d\xi_1\ldots d\xi_{N/n}\,. \tag{11}$$

But, from (5),

$$\int_{-\infty}^{\infty} p(\xi_k)\sin[(A_k-c)x]\,d\xi_k = \int_{-\infty}^{\infty} p(\xi_k)\sin[(A_{k-1}+f_k\xi_k-c)x]\,d\xi_k \tag{12}$$

$$= \int_{-\infty}^{\infty} p(\xi_k)\sin[(A_{k-1}-c)x]\cos(f_k\xi_k x)\,d\xi_k \tag{13}$$

$$= \sin[(A_{k-1}-c)x]\,q(f_k x)\,. \tag{14}$$

Repeated application of (14) enables us to replace (11) by

$$Q(c) = \frac{1}{2}+\frac{1}{\pi}\int_0^\infty \frac{\sin(cx)}{x}\prod_{k=1}^{N/n} q(f_k x)\,dx\,. \tag{15}$$

In order to obtain $P(A)$, (15) is differentiated with respect to c, and c replaced by A, yielding (2).

From (3), $q(f_k x)$ may be expressed in the form of a series

$$q(f_k x) = a_{k0}-a_{k2}x^2+a_{k4}x^4-\ldots\,, \tag{16}$$

where

$$a_{kj} = \frac{f_k^j}{j!}m_j\,, \tag{17}$$

and

$$m_j = \int_{-\infty}^{\infty} c^j p(c)\,dc \tag{18}$$

is the jth moment of $p(c)$. Consequently, in order to find $q(f_k x)$, it is not necessary to determine the function $p(c)$. Instead, we need only determine the jth moment of $p(c)$ for even values of j. Evidently the jth moment of $p(c)$ is the expected (or average) value of ξ^j and is therefore given by*

$$m_j = \int_0^1\int_0^1\int_0^1 [\xi(x, y, z)]^j\,dx\,dy\,dz\,. \tag{19}$$

From (16) and (17), (2) may be reduced by the method employed in equations (3)–(10) of the previous paper (Hauptman & Karle, 1952):

$$\begin{aligned}
P(A) = \sqrt{\left(\frac{n}{2\pi m_2\sigma_2}\right)}\cdot\exp\left(-\frac{A^2 n}{2m_2\sigma_2}\right)\Bigg\{1&-\frac{n\sigma_4(3m_2^2-m_4)}{2\times 4m_2^2\sigma_2^2}\left(1-2\cdot\frac{nA^2}{m_2\sigma_2}+\frac{1}{3}\cdot\frac{n^2A^4}{m_2^2\sigma_2^2}\right)\\
&-\frac{n^2\sigma_6(30m_2^3-15m_2m_4+m_6)}{2\times 4\times 6m_2^3\sigma_2^3}\left(1-3\cdot\frac{nA^2}{m_2\sigma_2}+\frac{n^2A^4}{m_2^2\sigma_2^2}-\frac{1}{15}\cdot\frac{n^3A^6}{m_2^3\sigma_2^3}\right)\\
&-\frac{n^3\sigma_8(630m_2^4-420m_2^2m_4+28m_2m_6+35m_4^2-m_8)-35n^2\sigma_4^2(3m_2^2-m_4)^2}{2\times 4\times 6\times 8m_2^4\sigma_2^4}\times\\
&\left(1-4\cdot\frac{nA^2}{m_2\sigma_2}+2\cdot\frac{n^2A^4}{m_2^2\sigma_2^2}-\frac{4}{15}\cdot\frac{n^3A^6}{m_2^3\sigma_2^3}+\frac{1}{105}\cdot\frac{n^4A^8}{m_2^4\sigma_2^4}\right)\\
&-\frac{n^4\sigma_{10}(22680m_2^5-18900m_2^3m_4+1260m_2^2m_6-45m_2m_8+3150m_2m_4^2-210m_4m_6+m_{10})-210n^3\sigma_4\sigma_6(3m_2^2-m_4)(30m_2^3-15m_2m_4+m_6)}{2\times 4\times 6\times 8\times 10m_2^5\sigma_2^5}\\
&\times\left(1-5\cdot\frac{nA^2}{m_2\sigma_2}+\frac{10}{3}\cdot\frac{n^2A^4}{m_2^2\sigma_2^2}-\frac{2}{3}\cdot\frac{n^3A^6}{m_2^3\sigma_2^3}+\frac{1}{21}\cdot\frac{n^4A^8}{m_2^4\sigma_2^4}-\frac{1}{945}\cdot\frac{n^5A^{10}}{m_2^5\sigma_2^5}\right)-\ldots\Bigg\}\,,
\end{aligned} \tag{20}$$

* A short derivation of the function $p(c)$ is given in the Appendix, and (19) is readily derived from it.

where $\sigma_k = \sum_{j=1}^{N} f_j^k = n \sum_{j=1}^{N/n} f_j^k$. Since $P(A)$ is an even function of A, the probability distribution of the magnitude of the structure factor is obtained by replacing $P(A)$ by $2\,P(A)$.

Formula (20) is also applicable to the structure factor for a noncentrosymmetric crystal whose real or imaginary part is identically zero in x, y, z.

Average value of $|F|^p$

The average value of $|F|^p$ can be immediately obtained from the probability distribution (20) by evaluating the integral

$$\int_{-\infty}^{\infty} |A|^p P(A) dA = 2 \int_0^{\infty} A^p P(A) dA \,. \tag{21}$$

Since

$$\int_0^{\infty} x^p \exp\,[-ax^2]\, dx = \frac{\Gamma\left(\frac{p+1}{2}\right)}{2a^{\frac{p+1}{2}}} \,, \tag{22}$$

where $p > -1$ and $\Gamma\left(\frac{p+1}{2}\right)$ is the gamma function, (21) becomes the rapidly converging series

$$\langle |F|^p \rangle = \frac{1}{\sqrt{\pi}} \Gamma\left(\frac{p+1}{2}\right) \left(\frac{2m_2\sigma_2}{n}\right)^{p/2} \left\{ 1 - \frac{n\sigma_4(3m_2^2-m_4)}{4!\,m_2^2\sigma_2^2} p(p-2) + \frac{n^2\sigma_6(30m_2^3-15m_2m_4+m_6)}{6!\,m_2^3\sigma_2^3} p(p-2)(p-4) \right.$$
$$\left. - \frac{n^3\sigma_8(630m_2^4-420m_2^2m_4+28m_2m_6-m_8+35m_4^2)-35n^2\sigma_4^2(3m_2^2-m_4)^2}{8!\,m_2^4\sigma_2^4} p(p-2)(p-4)(p-6) + \ldots \right\} . \tag{23}$$

Equation (23) 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 (23) terminates.

Adjustment of data

It is assumed that the intensities R^2 have already been adjusted for vibrational motion and to an absolute scale, so that the average values of $nR^2/m_2\sigma_2$ are unity, where each average is taken over a set of values of h, k, l corresponding to some specified s interval. In order to improve the magnitudes still further, minor adjustments may be made which will bring the actual distribution of the magnitudes into agreement with the theoretical distribution, (20). This may be done in several ways; either by use of the averages, (23), or the complete distribution (20). As an example of the latter method, the magnitudes, R, are arranged in increasing order. Small but statistically significant fractions of the total number of magnitudes are then selected, thus dividing the magnitude range into intervals. The theoretical range of values of the magnitudes in each such interval can be computed from (20), and the R values may then be adjusted by interpolation to coincide with the computed ranges.

Examples

The application of (20) is illustrated by deriving the probability distribution of the structure factors for three space groups, $P\bar{1}$, $P2/m$ and $Ibam$:

$$P\bar{1}: \quad \xi = 2\cos 2\pi(hx+ky+lz) \,. \tag{24}$$

$$P2/m: \xi = 4\cos 2\pi(hx+lz)\cos 2\pi ky \,. \tag{25}$$

$$Ibam: \xi = 16\cos^2 \frac{2\pi(h+k+l)}{4} \cos 2\pi(hx-\tfrac{1}{4}l) \times \cos 2\pi(ky+\tfrac{1}{4}l)\cos 2\pi lz \,. \tag{26}$$

By means of (19) the moments in Table 1 are readily computed. Substitution of these values into (20) yields the probability distributions for the structure factors. It is of interest to note that the two sets of moments in rows 1 and 3 lead to identical distributions. 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 a particular family are identical. The various averages given in Table 2 are readily computed from Table 1 and (23). Table 2 shows that for many space groups these averages are not closely approximated by the first term in the series. In fact, for the higher averages, the major contribution may come from terms other than the first.

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. Equation (1) is replaced by the more general

$$F = \sum_{j=1}^{t} f_j \xi_j \,, \qquad t = \sum_{i=1}^{v} N_i/n_i \,, \tag{27}$$

where v is the total number of types of positions (special and general), exclusive of those atoms in 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, 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 c and $c+dc$ now depends on j and is given by $p_j(c)dc$, where $p_j(c)$ is

Table 1. *Moments for the space groups $P\bar{1}$, $P2/m$, $Ibam$ having atoms in general positions only*

Space group		n	m_2	m_4	m_6	m_8
$P\bar{1}$		2	$2^2(\frac{1}{2})$	$2^4\left(\frac{1\times3}{2\times4}\right)$	$2^6\left(\frac{1\times3\times5}{2\times4\times6}\right)$	$2^8\left(\frac{1\times3\times5\times7}{2\times4\times6\times8}\right)$
$P2/m$	$k = 0$ or $h = l = 0$	4	$4^2(\frac{1}{2})$	$4^4\left(\frac{1\times3}{2\times4}\right)$	$4^6\left(\frac{1\times3\times5}{2\times4\times6}\right)$	$4^8\left(\frac{1\times3\times5\times7}{2\times4\times6\times8}\right)$
	$k \neq 0$ and $h^2+l^2 \neq 0$	4	$4^2(\frac{1}{2})^2$	$4^4\left(\frac{1\times3}{2\times4}\right)^2$	$4^6\left(\frac{1\times3\times5}{2\times4\times6}\right)^2$	$4^8\left(\frac{1\times3\times5\times7}{2\times4\times6\times8}\right)^2$
$Ibam$	$h = k = 0$, l even; or $h = l = 0$, k even; or $k = l = 0$, h even	16	$16^2(\frac{1}{2})$	$16^4\left(\frac{1\times3}{2\times4}\right)$	$16^6\left(\frac{1\times3\times5}{2\times4\times6}\right)$	$16^8\left(\frac{1\times3\times5\times7}{2\times4\times6\times8}\right)$
	$h = 0$, $kl \neq 0$, k, l even; or $k = 0$, $hl \neq 0$, h, l even; or $l = 0$, $hk \neq 0$, $h+k$ even	16	$16^2(\frac{1}{2})^2$	$16^4\left(\frac{1\times3}{2\times4}\right)^2$	$16^6\left(\frac{1\times3\times5}{2\times4\times6}\right)^2$	$16^8\left(\frac{1\times3\times5\times7}{2\times4\times6\times8}\right)^2$
	$hkl \neq 0$ and $h+k+l$ even	16	$16^2(\frac{1}{2})^3$	$16^4\left(\frac{1\times3}{2\times4}\right)^3$	$16^6\left(\frac{1\times3\times5}{2\times4\times6}\right)^3$	$16^8\left(\frac{1\times3\times5\times7}{2\times4\times6\times8}\right)^3$

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

(Note that $\sigma_k = n\sum_{j=1}^{N/n} f_j^k$)

Space group		$\langle\lvert F\rvert\rangle$	$\langle\lvert F\rvert^2\rangle$	$\langle\lvert F\rvert^4\rangle$	$\langle\lvert F\rvert^6\rangle$
$P\bar{1}$		$\left(\frac{2\sigma_2}{\pi}\right)^{\frac{1}{2}}\left(1+\frac{\sigma_4}{8\sigma_2^2}+\frac{\sigma_6'}{6\sigma_2^3}+\ldots\right)$	σ_2	$3\sigma_2^2-3\sigma_4$	$15\sigma_2^3-45\sigma_2\sigma_4+40\sigma_6$
$P2/m$	$k = 0$ or $h = l = 0$	$2\left(\frac{\sigma_2}{\pi}\right)^{\frac{1}{2}}\left(1+\frac{\sigma_4}{4\sigma_2^2}+\frac{2\sigma_6}{3\sigma_2^3}+\ldots\right)$	$2\sigma_2$	$12\sigma_2^2-24\sigma_4$	$120\sigma_2^3-720\sigma_2\sigma_4+1280\sigma_6$
	$k \neq 0$ and $h^2+l^2 \neq 0$	$\left(\frac{2\sigma_2}{\pi}\right)^{\frac{1}{2}}\left(1+\frac{\sigma_4}{8\sigma_2^2}+\frac{\sigma_6}{6\sigma_2^3}+\ldots\right)$	σ_2	$3\sigma_2^2-3\sigma_4$	$15\sigma_2^3-45\sigma_2\sigma_4+40\sigma_6$
$Ibam$	$h = k = 0$, l even; or $h = l = 0$, k even; or $k = l = 0$, h even	$4\left(\frac{\sigma_2}{\pi}\right)^{\frac{1}{2}}\left(1+\frac{\sigma_4}{\sigma_2^2}+\frac{32\sigma_6}{3\sigma_2^3}+\ldots\right)$	$8\sigma_2$	$192\sigma_2^2-1536\sigma_4$	$7680\sigma_2^3-184320\sigma_2\sigma_4+1310720\sigma_6$
	$h = 0$, $kl \neq 0$, k, l even; or $k = 0$, $hl \neq 0$, h, l even; or $l = 0$, $hk \neq 0$, $h+k$ even	$2\left(\frac{2\sigma_2}{\pi}\right)^{\frac{1}{2}}\left(1+\frac{\sigma_4}{2\sigma_2^2}+\frac{8\sigma_6}{3\sigma_2^3}+\ldots\right)$	$4\sigma_2$	$48\sigma_2^2-192\sigma_4$	$960\sigma_2^3-11520\sigma_2\sigma_4+40960\sigma_6$
	$hkl \neq 0$ and $h+k+l$ even	$2\left(\frac{\sigma_2}{\pi}\right)^{\frac{1}{2}}\left(1-\frac{\sigma_4}{4\sigma_2^2}-\frac{16\sigma_6}{3\sigma_2^3}-\ldots\right)$	$2\sigma_2$	$12\sigma_2^2+24\sigma_4$	$120\sigma_2^3+720\sigma_2\sigma_4-10240\sigma_6$

derived in the Appendix. However, as before, only the moments

$$m_{jk} = \int_{-\infty}^{\infty} c^k p_j(c)\,dc = \int_0^1\int_0^1\int_0^1 \xi_j^k\,dx\,dy\,dz \qquad (28)$$

are needed. If $q_j(f_jx)$ is defined as follows:

$$q_j(f_jx) = \int_{-\infty}^{\infty} p_j(c)\cos(f_jxc)\,dc\,, \qquad (29)$$

then the desired probability distribution $P(A)$ is given by

$$P(A) = \frac{1}{\pi}\int_0^{\infty}\cos(Ax)\prod_{j=1}^{t} q_j(f_jx)\,dx\,. \qquad (30)$$

By methods already explained, this function may be written in terms of a series which is a generalization of (20)

$$P(A) = \frac{\exp\left(-\frac{A^2}{2\Sigma f_j^2 m_{j2}}\right)}{\sqrt{(2\pi\Sigma f_j^2 m_{j2})}}\left\{1-\frac{\Sigma f_j^4(3m_{j2}^2-m_{j4})}{2\times4(\Sigma f_j^2 m_{j2})^2}\left(1-2\cdot\frac{A^2}{\Sigma f_j^2 m_{j2}}+\frac{1}{3}\cdot\frac{A^4}{(\Sigma f_j^2 m_{j2})^2}\right)\right.$$

$$\left.-\frac{\Sigma f_j^6(30m_{j2}^3-15m_{j2}m_{j4}+m_{j6})}{2\times4\times6(\Sigma f_j^2 m_{j2})^3}\left(1-3\cdot\frac{A^2}{\Sigma f_j^2 m_{j2}}+\frac{A^4}{(\Sigma f_j^2 m_{j2})^2}-\frac{1}{15}\cdot\frac{A^6}{(\Sigma f_j^2 m_{j2})^3}\right)\right.$$

$$-\frac{\Sigma f_j^8(630m_{j2}^4-420m_{j2}^2m_{j4}+28m_{j2}m_{j6}-m_{j8}+35m_{j4}^2)-35(\Sigma f_j^4(3m_{j2}^2-m_{j4})^2)^2}{2\times4\times6\times8(\Sigma f_j^2m_{j2})^4}\times$$
$$\left(1-4\cdot\frac{A^2}{\Sigma f_j^2m_{j2}}+2\cdot\frac{A^4}{(\Sigma f_j^2m_{j2})^2}-\frac{4}{15}\cdot\frac{A^6}{(\Sigma f_j^2m_{j2})^3}+\frac{1}{105}\cdot\frac{A^8}{(\Sigma f_j^2m_{j2})^4}\right)-\ldots\Bigg\}\,, \qquad (31)$$

where j ranges from 1 to t.

The remaining problem concerns the case that the crystal also contains atoms in fixed special positions. If we denote by $f'=f'(h,k,l)$, the contribution to the structure factor of the atoms in fixed special positions, $P_{f'}(A)$ is obtained from (31) by replacing A by $A-f'$, giving

$$P_{f'}(A)=P(A-f')=\frac{\exp\left(-\frac{(A-f')^2}{2\Sigma f_j^2m_{j2}}\right)}{\sqrt{(2\pi\Sigma f_j^2m_{j2})}}\times$$
$$\Bigg\{1-\frac{\Sigma f_j^4(3m_{j2}^2-m_{j4})}{2\times4(\Sigma f_j^2m_{j2})^2}\left(1-2\frac{(A-f')^2}{\Sigma f_j^2m_{j2}}+\frac{1}{3}\frac{(A-f')^4}{(\Sigma f_j^2m_{j2})^2}\right)$$
$$-\frac{\Sigma f_j^6(30m_{j2}^3-15m_{j2}m_{j4}+m_{j6})}{2\times4\times6(\Sigma f_j^2m_{j2})^3}\times$$
$$\left(1-3\frac{(A-f')^2}{\Sigma f_j^2m_{j2}}+\frac{(A-f')^4}{(\Sigma f_j^2m_{j2})^2}-\frac{1}{15}\frac{(A-f')^6}{(\Sigma f_j^2m_{j2})^3}\right)-\ldots\Bigg\}\,, \qquad (32)$$

where $P_{f'}(A)$ is the probability distribution for F.

The structure factor magnitude, $|F|$, will lie between A and $A+dA$, where $A\geq0$, if and only if the structure factor F lies either between A and $A+dA$ or between $-A$ and $-A-dA$. Therefore, the probability that $|F|$ lie in the interval $(A, A+dA)$ is given by $M(A)dA$ where,

$$M(A)=P(A+f')+P(A-f')\,. \qquad (33)$$

When the moments m_{jk} for the space group $P\bar{1}$ are substituted into (33), we obtain (71) of our previous paper (Hauptman & Karle, 1952) which was there derived from a completely different point of view.

The average values of $|F|^k$ are readily obtained from (33).* It should be emphasized that these averages are obtained by fixing h, k, l and then allowing the atoms to range uniformly throughout the unit cell. As pointed out previously (Hauptman & Karle, 1952, p. 57), this is in general equivalent to the statement that the expected value of the ratio of the observed $|F|^k$ to the theoretical average of $|F|^k$ is unity. More precisely, this is true if for each atom not in a fixed special position no relation $m_1x+m_2y+m_3z=m_0$ exists where the m_i's are integers, not all zero (Weyl, 1915–16, p. 319; Perron, 1921, pp. 143–157).

* E.g. $\langle|F|^2\rangle=f'^2+\sum_{j=1}^{t}f_j^2m_{j2}$.

APPENDIX

An explicit expression for the function $p(c)dc$, the probability that ξ lie between c and $c+dc$, may be derived by making use of the discontinuous function (9) to find the probability, $r(c)$, that ξ be less than c. We obtain

$$r(c)=\frac{1}{2}-\frac{1}{\pi}\int_0^1\int_0^1\int_0^1\int_{t=0}^{\infty}\frac{\sin[(\xi-c)t]}{t}\,dt\,dx\,dy\,dz\,, \qquad (34)$$

where ξ is a function of x, y, z, h, k, l and $p(c)=dr/dc$. Evaluation of (34) gives

$$p(c)=\frac{1}{\sqrt{(2\pi)}}\Bigg\{\int_0^1\int_0^1\int_0^1\frac{\exp(-c^2/2\xi^2)}{\xi}\,dx\,dy\,dz$$
$$-\frac{1}{4}\int_0^1\int_0^1\int_0^1\frac{\exp(-c^2/2\xi^2)}{\xi}\left(1-\frac{2c^2}{\xi^2}+\frac{c^4}{3\xi^4}\right)dx\,dy\,dz$$
$$-\frac{1}{3}\int_0^1\int_0^1\int_0^1\frac{\exp(-c^2/2\xi^2)}{\xi}\times$$
$$\left(1-\frac{3c^2}{\xi^2}+\frac{c^4}{\xi^4}-\frac{c^6}{15\xi^6}\right)dx\,dy\,dz-\ldots\Bigg\}\,. \qquad (35)$$

The various moments m_j given by (18) and required for (20) are readily found to reduce to (19).

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