maining 60 components are connected by the following relations:

$111=222=333$
$121=131=212=232=313=323$
$123=132=213=231=312=321$
$155=166=244-266=344=355$
$441=552=663$
$442=443=551=553=661=662$
$112=113=221=223=331=332$
$122=133=211=233=311=322$
$144=255=366$
$414=525=636$
$424=434=515=535=616=626$
$456=465=546=564=645=654$

If $R_{abc}=R_{bac}$ (126 components) these 12 independent components reduce to 9 in agreement with Bhagavantam's result (Bhagavantam & Suryanarayana, 1949). To obtain the independent components of the tensor N one must start from those of $R_{abc} \neq R_{bac}$: they are 111, 112, 122, 123, 414, 424, owing to the possibility of interchanging at random the last four indices. The results obtained by Dr Mason for the tensor N are incorrect.

Correspondence with Dr Mason on this matter is acknowledged.

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Crystal-Structure Determination by Means of a Statistical Distribution of Interatomic Vectors

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The structure-factor equations are interpreted as coupled, closed-vector polygons. This interpretation permits the application of the random-walk problem to yield the probability distribution of the structure factors and of the co-ordinate differences between specified pairs of atomic centers in the case of rigid crystals. In practice the intensities must be corrected for vibrational motion. All crystals may be treated with the probability formula for the general asymmetric case, and the symmetry which exists in the crystal will automatically be obtained. Probability distributions which make use of an *a priori* knowledge of the crystal symmetry may also be obtained, and the case of the centrosymmetric crystal is worked out in detail. The relationship between the probability distribution for the interatomic vectors and the Patterson synthesis is derived.

A mathematical analysis (Hauptman & Karle, 1950*a*, *b*; Karle & Hauptman, 1951) of the crystal-structure problem shows that the atomic co-ordinates are generally greatly overdetermined by the observed X-ray intensities, provided the atomic scattering factors are known. This calls for a procedure which leads from the experimental data directly to the atomic co-ordinates. In this paper a statistical method will be described which appears to make efficient use of the observed intensities and the known atomic scattering factors.

From the geometric point of view, the structure-factor equations may be regarded as a system of coupled, closed-vector polygons, the sides of each of which are the magnitude of the structure factor and the atomic scattering factors for the corresponding angle. The coupling arises from the fact that the external angles of the polygons are linear functions of the atomic co-ordinates whose coefficients are the Miller indices.

Owing to the fact that the algebra indicates a great redundancy in the X-ray data, a statistical treatment of the vector polygons suggests itself. In this method the absolutely rigid coupling among vector polygons, as required by the geometric construction, is replaced by a less stringent coupling which uses more than the algebraic minimum of data and results in a great simplification of the mathematics. At first the relationships among the polygons are ignored. This means that the angles of the polygons are no longer exactly determined but are defined by probability distributions instead. Additional information in the form of redundant X-ray data is then introduced which compensates for the coupling relationships originally discarded. Each vector polygon yields a relatively flat probability distribution for the atomic co-ordinates. When a large number of these are combined, however, the resulting probability distribution becomes quite sharp.

Statistical concepts

The statistical treatment of the crystal-structure problem is a development of the problem of the random walk (Pearson, 1906; Kluyver, 1906; Rayleigh, 1919). This problem concerns the derivation of the probability distribution for the distance between the first and final points in a walk consisting of N steps, each step of known length but randomly oriented in the same plane. Thus, if all sides but one of a plane polygon are known, and if these are oriented at random, the solution of the problem of the random walk yields the probability distribution of the length of the last side. However, given the length of the last side, the other sides are no longer oriented at random. Instead, the angles of the polygon have definite probability distributions.*

This is exactly the development of the random-walk problem which is needed for the crystal-structure problem since the last side of the vector polygon is the known magnitude of the structure factor, obtained directly from experiment, and the resulting probability distributions for the angles of the polygon give the probability distributions for the atomic co-ordinates.

The program to be followed in this paper will be to give the mathematical results of the random-walk problem, since these are needed for deriving the probability distributions for the angles. The relationship between the crystal-structure problem and the random walk is then shown, and the probability distributions for the atomic co-ordinates in a general asymmetric crystal are obtained. The centrosymmetric crystal is treated next and, finally, some examples of the application of the statistical method are given.

Probability distribution of $|F|$

The structure factors, F_{hkl}, are given by

$$F_{hkl}=\sum_{j=1}^{N} f_j(h,k,l)\exp\left[-2\pi i(hx_j+ky_j+lz_j)\right], \quad (1)$$

where the $f_j(h, k, l)$ are the atomic scattering factors at the appropriate angle and the x_j, y_j, z_j are the co-ordinates of the N atoms in the unit cell. A single equation may be considered as a closed vector polygon (Fig. 1).

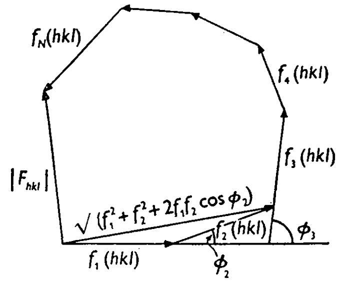

Fig. 1. Vector polygon interpretation of structure-factor equation. Direction of $f_1(hkl)$ is arbitrary and is taken as reference. $\phi_j=-2\pi(hx_j+ky_j+lz_j)$.

Before any information is available it is assumed that all positions of the atoms in the unit cell are equally probable. The relationship between the structure-factor equations and the random walk derives from the fact that the sides of the polygon of Fig. 1 will be randomly oriented if the atoms in the unit cell are randomly distributed. More precisely, *if x, y, z are chance variables, and x is uniformly distributed in the interval* (0, 1), *but occurs with zero probability elsewhere, then the fractional part* of $hx+ky+lz$ is also uniformly distributed in the interval* (0, 1) *provided that h is an integer.*† It should be noted that if no one of h, k, l is an integer, the fractional part of $hx+ky+lz$ will, in general, not be uniformly distributed in the interval (0, 1) even if each of x, y and z is uniformly distributed in the interval (0, 1). Fortunately, in the application to crystal structures, h, k, l are integers.

The problem of the random walk has been solved by Kluyver (1906), who showed that the probability that the distance between the initial and final points of the random walk be less than R is

$$R\int_0^\infty J_1(Rx)\,J_0(f_1x)\,J_0(f_2x)\ldots J_0(f_Nx)\,dx, \quad (2)$$

where $f_1, f_2, \ldots, f_N$ are the lengths of the N steps (atomic structure factors) and J_0, J_1 are Bessel functions.

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* An extreme example of this occurs if the last side is equal to the sum of all the other sides. Then the external angles of the polygon are all fixed and are equal to zero, except the angles at the first and final points which are equal to π.

* The fractional part of the number A means $A-[A]$, where $[A]$ is the greatest integer not exceeding A. Random or uniform distribution means that all values are equally probable.

† We omit the proof.

Following Rayleigh (1919), we obtain the probability that this distance lies between R and $R+dR$ by differentiating (2) with respect to R, giving—since

$$J_1(y)+y\frac{dJ_1}{dy}=yJ_0(y)\text{—}$$

$$Q(R)\,dR=R\,dR\int_0^\infty xJ_0(Rx)\,J_0(f_1x)\,J_0(f_2x)\dots J_0(f_Nx)\,dx. \tag{3}$$

A great simplification of (3) is obtained from the series expansion of the integral, the first term of which appears to be adequate for $N\geqslant 7$ (compare Pearson (1906) for the case $f_1=f_2=\dots=f_N$). From the expansion (Watson, 1945, p. 40)

$$\log J_0(f_jx) =\log\left(1-\frac{f_j^2x^2}{2^2(1\,!)^2}+\frac{f_j^4x^4}{2^4(2\,!)^2}-\frac{f_j^6x^6}{2^6(3\,!)^2}+\frac{f_j^8x^8}{2^8(4\,!)^2}-\dots\right), \tag{4}$$

we obtain, by expanding the logarithm and adding,

$$\log\left[J_0(f_1x)\,J_0(f_2x)\dots J_0(f_Nx)\right] =-\frac{x^2\sigma_2}{4}-\frac{x^4\sigma_4}{64}-\frac{x^6\sigma_6}{576}-\frac{11x^8\sigma_8}{49152}-\dots, \tag{5}$$

where
$$\sigma_n=\sum_{j=1}^{N}f_j^n. \tag{6}$$

From (5), and the series expansion for the exponential, we obtain

$$J_0(f_1x)\,J_0(f_2x)\dots J_0(f_Nx)=\exp\left[-\tfrac{1}{4}x^2\sigma_2\right] \times\left[1-\frac{x^4\sigma_4}{64}-\frac{x^6\sigma_6}{576}-x^8\left(\frac{11\sigma_8}{49152}-\frac{\sigma_4^2}{8192}\right)-\dots\right]. \tag{7}$$

From the formula (Watson, 1945, p. 393)

$$\int_0^\infty xJ_0\,(Rx)\exp[-px^2]\,dx=\frac{1}{2p}\exp\left[-R^2/4p\right], \tag{8}$$

successive differentiations with respect to p yield the values of

$$\int_0^\infty x^{2h+1}J_0(Rx)\exp\left[-px^2\right]dx \quad (h=1,2,\dots) \tag{9}$$

which are needed when (7) is substituted into (3). On identifying R with $|F_{hkl}|$, we obtain for the probability distribution for a particular $|F_{hkl}|$, when the atoms are assumed to be distributed at random,

$$\begin{aligned}Q(R)=\frac{2R}{\sigma_2}\exp\left[-R^2/\sigma_2\right]\Bigg\{1&-\frac{\sigma_4}{2\sigma_2^2}\left(1-\frac{2R^2}{\sigma_2}+\frac{R^4}{2\sigma_2^2}\right)\\ &-\frac{2\sigma_6}{3\sigma_2^3}\left(1-\frac{3R^2}{\sigma_2}+\frac{3R^4}{2\sigma_2^2}-\frac{R^6}{6\sigma_2^3}\right)-\frac{(11\sigma_8-6\sigma_4^2)}{8\sigma_2^4}\\ &\times\left(1-\frac{4R^2}{\sigma_2}+\frac{3R^4}{\sigma_2^2}-\frac{2R^6}{3\sigma_2^3}+\frac{R^8}{24\sigma_2^4}\right)-\frac{(57\sigma_{10}-50\sigma_4\sigma_6)}{15\sigma_2^5}\\ &\times\left(1-\frac{5R^2}{\sigma_2}+\frac{5R^4}{\sigma_2^2}-\frac{5R^6}{3\sigma_2^3}+\frac{5R^8}{24\sigma_2^4}-\frac{R^{10}}{120\sigma_2^5}\right)-\dots\Bigg\}.\end{aligned} \tag{10}$$

The first term of (10) has been obtained by Wilson (1949).

Probability distribution of x_j, y_j, z_j

Before the observation $|F_{hkl}|=R_{hkl}$ is made, it is assumed that all positions of the atoms in the unit cell are equally probable, i.e. all values of the angles $\phi_2, \phi_3, \dots, \phi_N$ of Fig. 1 are equally probable. Equations (3) and (10) then give the probability distribution of R_{hkl}. If now R_{hkl} is observed to have a certain fixed value, then all values of each of the angles $\phi_2, \phi_3, \dots, \phi_N$ can no longer be considered to be equally probable. Instead, a probability distribution is to be associated with each angle. It is now shown how this distribution can be found.

The following definitions are made:

(A) is the probability that R lies between R and $R+dR$, assuming that each of $\phi_2, \phi_3, \dots, \phi_N$ is uniformly distributed.

(B) is the *a priori* probability that ϕ_2 lies between ϕ_2 and $\phi_2+d\phi_2$.

(A, B) is the probability that, for fixed ϕ_2 and uniformly distributed ϕ_3, $\phi_4, \dots, \phi_N$, R lies between R and $R+dR$.

(B, A) is the probability that, for fixed R and uniformly distributed ϕ_3, $\phi_4, \dots, \phi_N$, subject to the constraints of the system, ϕ_2 lies between ϕ_2 and $\phi_2+d\phi_2$.

(AB) is the probability that both ϕ_2 lies between ϕ_2 and $\phi_2+d\phi_2$ and R lies between R and $R+dR$, assuming that ϕ_3, $\phi_4, \dots, \phi_N$ are uniformly distributed.

By the theorem of compound probabilities (Uspensky, 1937, p. 31)

$$(AB)=(A)\,(B,A)=(B)\,(A,B), \tag{11}$$

giving
$$(B,A)=\frac{(B)\,(A,B)}{(A)}. \tag{12}$$

Evidently
$$(B)=d\phi_2/2\pi, \tag{13}$$

while (A) is equal to (3). Using (3) with fixed ϕ_2 gives

$$(A,B)=R\int_0^\infty xJ_0(Rx)\,J_0(x\sqrt{[f_1^2+f_2^2+2f_1f_2\cos\phi_2]}) \times J_0(f_3x)\dots J_0(f_Nx)\,dx. \tag{14}$$

From (12) we now find the probability distribution for ϕ_2 after the observation R has been made:

$$M(\phi_2)=\frac{(B,A)}{d\phi_2} =\frac{\displaystyle\int_0^\infty xJ_0(Rx)\,J_0(x\sqrt{[f_1^2+f_2^2+2f_1f_2\cos\phi_2]})\times J_0(f_3x)\dots J_0(f_Nx)\,dx}{\displaystyle 2\pi\int_0^\infty xJ_0(Rx)\,J_0(f_1x)\,J_0(f_2x)\dots J_0(f_Nx)\,dx}. \tag{15}$$

The substitution of the first term of (10) into (15) yields

$$M(\phi_2)\sim\frac{\exp\left(\dfrac{R^2}{\sigma_2}\dfrac{B_2\cos\phi_2}{1+B_2\cos\phi_2}\right)}{2\pi(1+B_2\cos\phi_2)}, \tag{16}$$

where
$$B_2=2f_1f_2/\sigma_2. \tag{17}$$

In general ϕ_2 may be replaced by ϕ_j and B_2 by

$$B_j = 2f_1 f_j/\sigma_2.$$

It is now possible to translate the probability distribution for ϕ_j into a probability distribution for x_j, y_j, z_j, using

$$\phi_j = -2\pi(hx_j + ky_j + lz_j). \tag{18}$$

One dimension

For the case of one dimension, we obtain from (16) and (18), the probability distribution for x_j, the co-ordinate of the jth atom relative to the first,

$$N(x_j) = \frac{\exp\left(\dfrac{R_h^2}{\sigma_2}\,\dfrac{B_j\cos 2\pi hx_j}{1+B_j\cos 2\pi hx_j}\right)}{1+B_j\cos 2\pi hx_j} \quad (h=1, 2, \ldots), \tag{19}$$

as a consequence of a particular observation R_h. It is to be expected that the distributions (19), while quite flat, will usually have maxima in the neighbourhood of the true value of x_j. Therefore, in order to obtain the probability distribution function on the basis of all the observed R_h's, it seems plausible to multiply together all the distributions (19). It is reasonable to expect that deviations from the correct maximum in these curves will tend to compensate one another if enough factors (19) are used, and the product will have a sharp maximum at the correct value of x_j. It is possible to give the following justification for this procedure if we assume that the value of each R_h is independent of the value of any other R_h. This assumption is equivalent to ignoring the rigid coupling between the vector polygons, as explained above.

From the previous definitions for (A), (A, B), etc., and the replacement of A by A_i, R by R_i $(i=1, 2, \ldots)$ and ϕ_j by x_j, we have (Jeffreys, 1948, p. 29)

$$(B, A_1A_2) = (B, A_2)\,(A_1, A_2B)/(A_1, A_2), \tag{20}$$

$$(B, A_1A_2) = (B, A_1)\,(A_2, A_1B)/(A_2, A_1), \tag{21}$$

where, for example, $(B,\ A_1A_2)$ means the probability that x_j lies between x_j and x_j+dx_j, given that both R_1 and R_2 have been observed. The product of (20) and (21) is

$$(B, A_1A_2)^2 = \frac{[(B, A_1)\,(B, A_2)]\,[(A_1, A_2B)\,(A_2, A_1B)]}{(A_1, A_2)\,(A_2, A_1)}. \tag{22}$$

Similarly,

$$(B, A_1A_2A_3)^3 = \frac{\begin{array}{l}[(B, A_1)\,(B, A_2)\,(B, A_3)]\\ \quad\times[(A_1A_2, A_3B)\,(A_1A_3, A_2B)\,(A_2A_3, A_1B)]\end{array}}{(A_1, A_2A_3)\,(A_2, A_1A_3)\,(A_3, A_1A_2)}, \tag{23}$$

and so forth. In view of the assumed independence of A_1, A_2 and A_3, we have, for example,

$$(A_1A_2, A_3B) = (A_1A_2, B) = (A_1, B)\,(A_2, B), \tag{24}$$

and from (11)

$$(A_1A_2, A_3B) = \frac{(A_1)\,(B, A_1)}{(B)}\,\frac{(A_2)\,(B, A_2)}{(B)}. \tag{25}$$

Similarly,

$$(A_1A_3, A_2B) = \frac{(A_1)\,(B, A_1)}{(B)}\,\frac{(A_3)\,(B, A_3)}{(B)} \tag{26}$$

and

$$(A_2A_3, A_1B) = \frac{(A_2)\,(B, A_2)}{(B)}\,\frac{(A_3)\,(B, A_3)}{(B)}. \tag{27}$$

The substitution of (25), (26) and (27) into (23) gives

$$(B, A_1A_2A_3) = \frac{(B, A_1)\,(B, A_2)\,(B, A_3)\,(A_1)^{\frac{1}{3}}\,(A_2)^{\frac{1}{3}}\,(A_3)^{\frac{1}{3}}}{(B)^2}. \tag{28}$$

Relation (28) may be generalized to give

$$(B, A_1A_2\ldots A_n) = \frac{(B, A_1)\,(B, A_2)\ldots(B, A_n)\,(A_1)^{1/n}\,(A_2)^{1/n}\ldots(A_n)^{1/n}}{(B)^{n-1}}. \tag{29}$$

Since $(B, A_1A_2 \ldots A_n)$ is the probability that x_j lies between x_j and x_j+dx_j after the observations R_1, $R_2, \ldots, R_n$ have been made, and (B, A_i) is the probability that x_j lies between x_j and x_j+dx_j on the basis of the single observation R_i, and since the remaining factors $(A_i)^{1/n}$ and (B) occurring in (29) are independent of x_j, we are therefore permitted to multiply the distributions (19) in order to obtain the probability distribution for x_j. We get

$$P(x_j) = K_1 \prod_h \frac{\exp\left(\dfrac{R_h^2}{\sigma_2}\,\dfrac{B_j\cos 2\pi hx_j}{1+B_j\cos 2\pi hx_j}\right)}{1+B_j\cos 2\pi hx_j}, \tag{30}$$

where K_1 is the normalization factor. The maxima of (30) determine the possible values of x_j, the co-ordinate of the jth atom with respect to the first atom.

Two dimensions

The two-dimensional problem is now treated and will be seen to clarify considerably the more complicated three-dimensional case. We wish to find the probability distribution function $P(x, y)$, where $P(x, y)\,dxdy$ is the probability that the point x, y lie in the elementary area $dA = dxdy$. This probability must be related to the known probability that the quantity $hx+ky$ be in an interval of length $d\phi/2\pi$. This relationship may be found since, for fixed ϕ, the interval $d\phi$ generates an area in the x, y plane over which the probability distribution is constant.

Let h, k, ϕ $(0 \leqslant \phi < 2\pi)$ and $d\phi > 0$ be fixed. The regions $d\rho_\nu$ (Fig. 2) consist of all points x', y' which satisfy

$$-2\pi(hx'+ky') = 2\pi\nu + \phi_0 = \phi_\nu \quad (\nu = 0, \pm 1, \pm 2, \ldots), \tag{31}$$

$$0 \leqslant x' < 1, \quad 0 \leqslant y' < 1, \tag{32}$$

as ϕ_0 ranges through the interval ϕ, $\phi+d\phi$. Then the point (x, y) lies in the region $d\rho$ defined by

$$d\rho=\sum_{\nu} d\rho_{\nu}, \tag{33}$$

if the fractional part of $\phi'/2\pi=-(hx+ky)$ lies in the interval $(\phi/2\pi,\ (\phi+d\phi)/2\pi)$, but not otherwise. It follows then that the probability that the point (x, y) lies in the region $d\rho$ is given by

$$M(\phi)\,d\phi, \tag{34}$$

where $M(\phi)$ is defined by (16). The probability that (x, y) lies in the region $d\rho_{\nu}$ is

$$\frac{d\rho_{\nu}}{d\rho}M(\phi)\,d\phi, \tag{35}$$

where $d\rho_{\nu}$ and $d\rho$ denote the areas of the corresponding regions. Finally, the probability that (x, y) lies in the elementary area dA is given by

$$\frac{dA}{d\rho_{\nu}}\frac{d\rho_{\nu}}{d\rho}M(\phi)\,d\phi=\frac{d\phi}{d\rho}\,M(2\pi(hx+ky))\,dx\,dy. \tag{36}$$

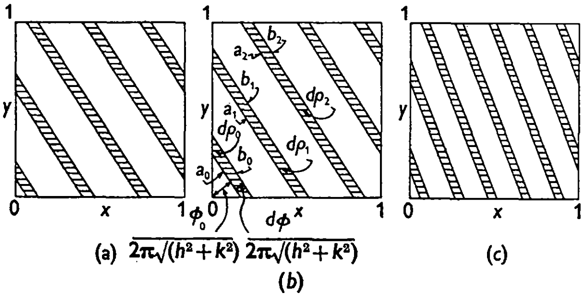


Fig. 2. The regions $d\rho_{\nu}$ in the unit square. Each region $d\rho_{\nu}$ defines a ϕ_{ν} interval by means of (31), where the x', y' range through the points of $d\rho_{\nu}$. The shaded areas $\sum_{\nu} d\rho_{\nu}$ are seen to be the same in (a), (b) and (c) illustrating their independence of ϕ_0, h and k.

It is next shown that

$$d\rho=d\phi/2\pi. \tag{37}$$

From Fig. 2 it is found that for any fixed ϕ_0, $0\leqslant\phi_0<2\pi$, the sum of the lines defined by

$$-2\pi(hx+ky)=2\pi\nu+\phi_0=\phi_{\nu}\quad(\nu=0,\ \pm1,\ \pm2,\ldots), \tag{38}$$

where $0\leqslant x<1$, $0\leqslant y<1$, is

$$\sum_{\nu} a_{\nu}=\sqrt{(h^2+k^2)}, \tag{39}$$

which is seen to be independent of ϕ_0. Similarly, the sum of the lines defined by

$$-2\pi(hx+ky)=2\pi\nu+\phi_0+d\phi=\phi_{\nu}+d\phi\quad(\nu=0,\ \pm1,\pm2,\ldots), \tag{40}$$

where $0\leqslant x<1$, $0\leqslant y<1$, is

$$\sum_{\nu} b_{\nu}=\sqrt{(h^2+k^2)}. \tag{41}$$

Since the altitude of each trapezoid $d\rho_{\nu}$ is

$$d\phi/2\pi\sqrt{(h^2+k^2)}, \tag{42}$$

the total area $d\rho$ is given by

$$d\rho=\tfrac{1}{2}\sum_{\nu}(a_{\nu}+b_{\nu})\,d\phi/2\pi\sqrt{(h^2+k^2)}=d\phi/2\pi. \tag{43}$$

From (16) and (36) it follows that the probability distribution for the co-ordinates of the jth atom with respect to the first in two dimensions on the basis of a single observation R_{hk} is given by

$$N(x_j,y_j)=2\pi M(2\pi(hx_j+ky_j))\,\frac{\exp\left(\dfrac{R^2_{hk}}{\sigma_2}\dfrac{B_j\cos2\pi(hx_j+ky_j)}{1+B_j\cos2\pi(hx_j+ky_j)}\right)}{1+B_j\cos2\pi(hx_j+ky_j)}. \tag{44}$$

From the analysis in (20)–(29), where B is now redefined to apply to the two-dimensional problem, we find that the probability distribution function for the co-ordinates of the jth atom with respect to the first on the basis of a set of observations R_{hk} is

$$P(x_j,y_j)=K_2\prod_{h,k}\frac{\exp\left(\dfrac{R^2_{hk}}{\sigma_2}\dfrac{B_j\cos2\pi(hx_j+ky_j)}{1+B_j\cos2\pi(hx_j+ky_j)}\right)}{1+B_j\cos2\pi(hx_j+ky_j)}, \tag{45}$$

where K_2 is the normalization constant.

Three dimensions

We wish to find the probability, $P(x, y, z)\,dx\,dy\,dz$, that the co-ordinates of the jth atomic center with respect to the first lie in the volume element $dx\,dy\,dz$ at the point x, y, z. As in the two-dimensional case, we define the regions $d\rho_{\mu}$ (Fig. 3) as those points x', y', z' which satisfy

$$-2\pi(hx'+ky'+lz')=2\pi\mu+\phi_0=\phi_{\mu}\quad(\mu=0,\ \pm1,\ \pm2,\ldots), \tag{46}$$

$$0\leqslant x'<1,\quad 0\leqslant y'<1,\quad 0\leqslant z'<1, \tag{47}$$

as ϕ_0 ranges through the interval ϕ, $\phi+d\phi$ and h, k, l, ϕ $(0\leqslant\phi<2\pi)$ and $d\phi>0$ are fixed. By following the same argument as in (33)–(36), we obtain the probability that the point (x, y, z) lie in the elementary volume $dV=dx\,dy\,dz$:

$$\frac{dV}{d\rho_{\mu}}\frac{d\rho_{\mu}}{d\rho}M(\phi)\,d\phi=\frac{d\phi}{d\rho}\,M(2\pi(hx+ky+lz))\,dx\,dy\,dz. \tag{48}$$

It may be shown that the total volume $d\rho=\sum_{\mu} d\rho_{\mu}$ is given by

$$d\rho=d\phi/2\pi. \tag{49}$$

In analogy with the two-dimensional case, we find that for any fixed ϕ_0, $0\leqslant\phi_0<2\pi$, the sum of the areas defined by

$$-2\pi(hx+ky+lz)=2\pi\mu+\phi_0=\phi_{\mu}\quad(\mu=0,\ \pm1,\ \pm2,\ldots), \tag{50}$$

where $0\leqslant x<1$, $0\leqslant y<1$, $0\leqslant z<1$, is*

$$\sum_{\mu} A_{\mu}=\sqrt{(h^2+k^2+l^2)}, \tag{51}$$

and is independent of ϕ_0. Likewise the sum of the areas defined by

$$-2\pi(hx+ky+lz)=2\pi\mu+\phi_0+\tfrac{1}{2}d\phi=\phi_{\mu}+\tfrac{1}{2}d\phi\quad(\mu=0,\ \pm1,\ \pm2,\ldots) \tag{52}$$

---

* The details of the derivation of (51) have been omitted.

or

$$-2\pi(hx+ky+lz)=2\pi\mu+\phi_0+d\phi=\phi_\mu+d\phi \qquad (\mu=0,\ \pm1,\ \pm2,\ \ldots) \qquad (53)$$

is given by
$$\sum_\mu M_\mu=\surd(h^2+k^2+l^2) \qquad (54)$$
or
$$\sum_\mu B_\mu=\surd(h^2+k^2+l^2) \qquad (55)$$
respectively. Since the altitude of each prismoid $d\rho_\mu$ is
$$d\phi/2\pi\surd(h^2+k^2+l^2), \qquad (56)$$
the total volume $d\rho$ is given by
$$d\rho=\sum_\mu d\rho_\mu=\tfrac{1}{6}\sum_\mu(A_\mu+4M_\mu+B_\mu)\,d\phi/2\pi\surd(h^2+k^2+l^2)$$
$$=d\phi/2\pi, \qquad (57)$$
and is independent of ϕ_0. From (48) and the previous arguments for combining the results of the individual measurements (20)–(29), we obtain the probability distribution function for the co-ordinate differences between the *i*th and *j*th atoms on the basis of a set of observations R_{hkl}.

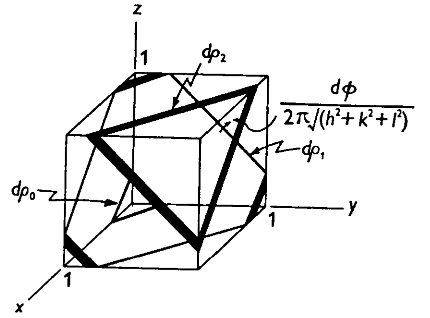


Fig. 3. The regions $d\rho_\mu$ in the unit cube. Each region $d\rho_\mu$ defines a ϕ_μ interval by means of (46), where the x', y', z' range through the points of $d\rho_\mu$.

$$P(x_{ij},y_{ij},z_{ij})$$
$$=K_3\prod_{h,k,l}\frac{\exp\left(\dfrac{R^2_{hkl}}{\sigma_2}\dfrac{B_{ij}\cos2\pi(hx_{ij}+ky_{ij}+lz_{ij})}{1+B_{ij}\cos2\pi(hx_{ij}+ky_{ij}+lz_{ij})}\right)}{1+B_{ij}\cos2\pi(hx_{ij}+ky_{ij}+lz_{ij})}, \qquad (58)$$
$$x_{ij}=x_i-x_j,\quad y_{ij}=y_i-y_j,\quad z_{ij}=z_i-z_j,$$
where
$$\sigma_2=\sigma_2(h,k,l)=\sum_{j=1}^{N}f_j^2(h,k,l) \qquad (59)$$
and
$$B_{ij}=B_{ij}(h,k,l)=2f_i(h,k,l)f_j(h,k,l)/\sigma_2, \qquad (60)$$
and R^2_{hkl} is the measured X-ray intensity, $|F_{khl}|^2$.

Center of symmetry

The presence of symmetry in the unit cell implies that the angles of Fig. 1 are not all independent, and therefore the sides of the vector polygon are not all randomly oriented. The distributions of $|F_{hkl}|$ and of the atomic co-ordinates are now different from those derived from the random walk. The effect of a symmetry center is now discussed.

A typical vector polygon for the case of a center of symmetry is shown in Fig. 4 (*a*) and (*b*), where the origin has been taken at the center of symmetry.

We make the definitions

$$f'_{hkl}=\sum_{\mu,\nu,\rho}f_{\mu\nu\rho}(h,k,l)\exp[-2\pi i(h\mu+k\nu+l\rho)]$$
$$=\sum_{\mu,\nu,\rho}f_{\mu\nu\rho}\cos2\pi(h\mu+k\nu+l\rho)\quad(\mu,\nu,\rho=0,\tfrac{1}{2}), \qquad (61)$$
$$s_n=\sum_{\mu,\nu,\rho}f^n_{\mu\nu\rho},\quad \mu,\nu,\rho=0,\tfrac{1}{2} \qquad (62)$$
$$x\exp(i\theta)=\sum_{j=1}^{N/2}f_j\exp[-2\pi i(hx_j+ky_j+lz_j)],\quad(x\geqslant0), \qquad (63)$$
$$r_{hkl}=2x\,|\cos\theta\,|, \qquad (64)$$

where the $f_{\mu\nu\rho}$ are the atomic scattering factors (some or all of which may be zero) of the atoms in the eight special positions, N is the number of atoms per unit cell in *general* positions, x_j, y_j, z_j are the co-ordinates of the $\tfrac{1}{2}N$ atoms in general positions in the asymmetric group, and the f_j are their scattering factors. It is seen from Fig. 4 (*b*) that the probability that the resultant r_{hkl} be less than R is the same as the probability that $x<\tfrac{1}{2}R\,|\sec\theta\,|$, since
$$x=\tfrac{1}{2}r_{hkl}\,|\sec\theta\,|. \qquad (65)$$

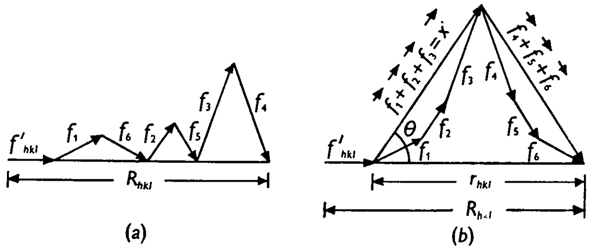
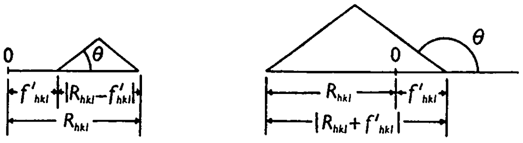


Fig. 4. The vector polygon for the case of a center of symmetry. The quantity f'_{hkl} represents the contribution of the atoms in special positions to the structure factor, F_{hkl}.

The problem is split into two random walks, as indicated in Fig. 4 (*b*), and we obtain from (2) the probability that, for any θ, $r_{hkl}<R$, namely,
$$\tfrac{1}{2}R\,|\sec\theta\,|\int_0^\infty J_1(\tfrac{1}{2}Rx\,|\sec\theta\,|)\,J_0(f_1x)\ldots J_0(f_{\frac{1}{2}N}x)\,dx. \qquad (66)$$
As before, differentiation with respect to R yields the probability that r_{hkl} lie between R and $R+dR$:
$$\tfrac{1}{4}R\sec^2\theta\int_0^\infty xJ_0(\tfrac{1}{2}Rx\,|\sec\theta\,|)\,J_0(f_1x)\ldots J_0(f_{\frac{1}{2}N}x)\,dx\,dR. \qquad (67)$$
In order to find the probability distribution for $R_{hkl}=|F_{hkl}|$ we distinguish the four cases
$$f'_{hkl}\gtrless0,\quad R_{hkl}\gtrless|f'_{hkl}|.$$
The case $f'_{hkl}>0$, $R_{hkl}>|f'_{hkl}|$ is illustrated in Fig. 5. There are two mutually exclusive and exhaustive

possibilities: either $F_{hkl} \geqslant 0$ (Fig. 5(*a*)) or $F_{hkl} < 0$ (Fig. 5(*b*)). Since all directions for the resultant of the random walk are equally probable, the probability that θ lie in the interval θ, $\theta + d\theta$ is $d\theta/2\pi$. In the first case (Fig. 5(*a*)) $-\frac{1}{2}\pi < \theta < \frac{1}{2}\pi$ and R_{hkl} lies in the interval R, $R+dR$ if, and only if, $|R_{hkl} - f'_{hkl}|$ lies in the interval $|R-f'|$, $|R+dR-f'|$, where $f' = f'_{hkl}$. In the second case (Fig. 5(*b*)) $\frac{1}{2}\pi < \theta < \frac{3}{2}\pi$, and R_{hkl} lies in the interval R, $R+dR$ if, and only if, $|R_{hkl} + f'_{hkl}|$ lies in the interval $|R+f'|$, $|R+dR+f'|$. The three remaining cases are treated in the same way,* and we conclude that the probability that R_{hkl} lie in the interval R, $R+dR$ is $Q(R)dR$, where

$$Q(R) = \frac{|R-f'|}{4\pi} \int_0^{\frac{1}{2}\pi} \sec^2\theta \int_0^\infty x J_0(\tfrac{1}{2}|R-f'|\, x \sec\theta) \times J_0(f_1 x) \ldots J_0(f_{\frac{1}{2}N} x)\, dx\, d\theta + \frac{|R+f'|}{4\pi} \int_0^{\frac{1}{2}\pi} \sec^2\theta \int_0^\infty x J_0(\tfrac{1}{2}|R+f'|\, x\sec\theta) \times J_0(f_1 x) \ldots J_0(f_{\frac{1}{2}N} x)\, dx\, d\theta. \quad (68)$$



(*a*) (*b*)

Fig. 5. The definition of the contribution from atoms in general positions to R_{hkl} used in the derivation of (68) for the case $f'_{hkl} > 0$, $R_{hkl} > |f'_{hkl}|$, (*a*) $F_{hkl} \geqslant 0$, (*b*) $F_{hkl} < 0$.

The Bessel function expansion (10) and the formulas for

$$\int_0^{\frac{1}{2}\pi} \exp(-q\sec^2\theta)\sec^{2n}\theta\, d\theta \quad (n = 1, 2, \ldots) \cdot \quad (69)$$

obtained by differentiating

$$\int_0^{\frac{1}{2}\pi} \exp(-q\sec^2\theta)\sec^2\theta\, d\theta = \tfrac{1}{2} e^{-q} \sqrt{\left(\frac{\pi}{q}\right)} \quad (70)$$

successively with respect to q, permit (68) to be replaced by

$$\begin{aligned} Q(R) = {} & \frac{\exp\left(-\dfrac{(R-f')^2}{2(\sigma_2-s_2)}\right)}{\sqrt{[2\pi(\sigma_2-s_2)]}} \left\{1 - \frac{3(\sigma_4-s_4)}{8(\sigma_2-s_2)^2}\right. \\ & \times \left(1 - \frac{2(R-f')^2}{\sigma_2-s_2} + \frac{(R-f')^4}{3(\sigma_2-s_2)^2}\right) - \frac{5(\sigma_6-s_6)}{6(\sigma_2-s_2)^3} \\ & \left. \times \left(1 - \frac{3(R-f')^2}{\sigma_2-s_2} + \frac{(R-f')^4}{(\sigma_2-s_2)^2} - \frac{(R-f')^6}{15(\sigma_2-s_2)^3}\right) - \ldots\right\} \\ & + \frac{\exp\left(-\dfrac{(R+f')^2}{2(\sigma_2-s_2)}\right)}{\sqrt{[2\pi(\sigma_2-s_2)]}} \left\{1 - \frac{3(\sigma_4-s_4)}{8(\sigma_2-s_2)^2}\right. \\ & \times \left(1 - \frac{2(R+f')^2}{\sigma_2-s_2} + \frac{(R+f')^4}{3(\sigma_2-s_2)^2}\right) - \frac{5(\sigma_6-s_6)}{6(\sigma_2-s_2)^3} \\ & \left. \times \left(1 - \frac{3(R+f')^2}{\sigma_2-s_2} + \frac{(R+f')^4}{(\sigma_2-s_2)^2} - \frac{(R+f')^6}{15(\sigma_2-s_2)^3}\right) - \ldots\right\}, \end{aligned} \quad (71)$$

where, as before, σ_n is the sum of the nth powers of all the f's:

$$\sigma_n = s_n + 2\sum_{j=1}^{\frac{1}{2}N} f_j^n. \quad (72)$$

Proceeding exactly as in the derivation of (15), we obtain the probability distribution for

$$\phi_j = -2\pi(hx_j + ky_j + lz_j)$$

after the observation $R = R_{hkl}$ has been made:

$$\begin{aligned} M(\phi_j) = \frac{1}{8\pi^2 Q(R)} \Bigg\{ & |R - (f' + 2f_j\cos\phi_j)| \\ & \times \int_0^{\frac{1}{2}\pi} \sec^2\theta \int_0^\infty x J_0(\tfrac{1}{2}|R-(f'+2f_j\cos\phi_j)|\, x\sec\theta) \\ & \times \prod_{\substack{i \neq j \\ 1}}^{\frac{1}{2}N} J_0(f_i x)\, dx\, d\theta + |R + (f' + 2f_j\cos\phi_j)| \\ & \times \int_0^{\frac{1}{2}\pi} \sec^2\theta \int_0^\infty x J_0(\tfrac{1}{2}|R+(f'+2f_j\cos\phi_j)|\, x\sec\theta) \\ & \times \prod_{\substack{i \neq j \\ 1}}^{\frac{1}{2}N} J_0(f_i x)\, dx\, d\theta \Bigg\}. \end{aligned} \quad (73)$$

If only the first term in each of the series of the expansion (71) is retained (73) reduces to

$$M(\phi_j) \sim \frac{\exp\left\{-\dfrac{1}{1-\dfrac{2f_j^2}{\sigma_2-s_2}}\left(\dfrac{(R^2+f'^2)f_j^2}{(\sigma_2-s_2)^2} + \dfrac{2f_j\cos\phi_j(f'+f_j\cos\phi_j)}{\sigma_2-s_2}\right)\right\}}{2\pi\sqrt{\left(1-\dfrac{2f_j^2}{\sigma_2-s_2}\right)}} \, \frac{\cosh\left\{\dfrac{R(f'+2f_j\cos\phi_j)/(\sigma_2-s_2)}{\left(1-\dfrac{2f_j^2}{\sigma_2-s_2}\right)}\right\}}{\cosh\dfrac{Rf'}{(\sigma_2-s_2)}}. \quad (74)$$

On the basis of previous arguments the probability distribution for the x, y, z co-ordinates of the jth atom, with reference to the center of symmetry, as a consequence of all the measurements R_{hkl} is

$$\begin{aligned} P(x_j, y_j, z_j) = K \prod_{h,k,l} & \frac{\exp\left\{-\dfrac{1}{1-2C_j}\left[C_j\left(\dfrac{R_{hkl}^2}{\sigma_2-s_2}+D\right) + 2\sqrt{(C_j)}\cos 2\pi(hx_j+ky_j+lz_j)\left(\sqrt{(D)}+\sqrt{(C_j)}\cos 2\pi(hx_j+ky_j+lz_j)\right)\right]\right\}}{\sqrt{(1-2C_j)}} \\ & \times \frac{\cosh\left(\dfrac{R_{hkl}}{\sqrt{(\sigma_2-s_2)}} \, \dfrac{\sqrt{(D)}+2\sqrt{(C_j)}\cos 2\pi(hx_j+ky_j+lz_j)}{(1-2C_j)}\right)}{\cosh\dfrac{R_{hkl}\sqrt{(D)}}{\sqrt{(\sigma_2-s_2)}}}, \end{aligned} \quad (75)$$

---

* The limiting cases in which one or both of $f'_{hkl} = 0$, $R_{hkl} = |f'_{hkl}|$ holds are readily treated in a similar way.

where

$$C_j = C_j(h,k,l) = \frac{f_j^2}{\sigma_2 - s_2}$$

$$\left(\begin{array}{l} j=1,2,\ldots,\tfrac{1}{2}N, \text{ including only} \\ \text{atoms in general positions} \end{array}\right), \quad (76)$$

$$D = D(h,k,l) = \frac{f'^2}{\sigma_2 - s_2}, \quad (77)$$

and K is a normalization constant.

In case there are no atoms in special positions, $f' = s_2 = 0$, $D = 0$ and (75) reduces to

$$P(x_j, y_j, z_j) = K \prod_{h,k,l} \frac{\exp\left\{-\frac{C_j}{1-2C_j}\left(\frac{R_{hkl}^2}{\sigma_2} + 2\cos^2 2\pi(hx_j+ky_j+lz_j)\right)\right\} \cosh\left(\frac{R_{hkl}}{\sqrt{\sigma_2}} \frac{2\sqrt{(C_j)}\cos 2\pi(hx_j+ky_j+lz_j)}{1-2C_j}\right)}{\sqrt{(1-2C_j)}}. \quad (78)$$

Equation (78) may be used when there are no atoms in special positions or for cases in which they may be neglected. When atoms in special positions must be taken into consideration, (75) may be used if these special positions are known.

Other symmetry elements also cause deviations from the random walk which may be treated in a manner similar to that for the center of symmetry. The characteristic effect of a symmetry element is that no longer are all the sides of the vector polygon randomly oriented. For example, in the case of a four-fold axis, the directions of three of the sides determine that of the fourth. The value of making use of symmetry information will ultimately be determined by the balance between the relative complexity of the procedure and the relative efficiency of the formulas for each space group. It should be noted that the formula for the general asymmetric case may always be used and any symmetry characteristics in the unit cell will automatically be obtained.

Computational tests

The foregoing mathematical analysis indicates that if sufficient data are used, formula (58) should provide an accurate evaluation of the difference between pairs of atomic co-ordinates. It is known that $3(N-1)$ independent R_{hkl} are required to determine the co-ordinate differences in the strict algebraic sense, and it is consequently of interest to estimate how many R_{hkl} are required in (58) to determine these differences for some special problems.

A one-dimensional test was performed ($k, l = 0$) with (58) using twelve atoms in which the $f_j(h)$ were considered independent of the scattering angle. From assumed values for the $f_j(h)$ and the atomic positions, fifty R_h were computed constituting $4\frac{1}{2}$ times the algebraic minimum required. Formula (58) was then applied using these R_h, and the distance between a pair of atoms (spaced at one radian) was computed. The result is shown in Fig. 6, giving a sharp peak at one radian as expected. The auxiliary peaks which occur correspond to other distances from which the R_h were computed. Since (58) is seen to be a continuous function of B_{ij}, those distances corresponding to atom pairs with B_{ij} close to the one of interest will appear as minor maxima. With sufficient data these auxiliary maxima should be eliminated, leaving only the maxima corresponding to the actual B_{ij} used in (58).

A three-dimensional test was also made using the data of Table 1. Since there are twelve atoms, $3 \times 11 = 33$ independent magnitudes, R_{hkl}, are needed to determine the co-ordinate differences between any pair of atoms. Eighty-seven magnitudes R_{hkl} were computed using the following values of h, k, l:

$$h, k = 0, \pm 1, \pm 2; \quad l = 0, \pm 1, \pm 2, \pm 3.$$

With these values of R_{hkl}, equation (58) was used to obtain the co-ordinate differences between the first and third atoms listed in Table 1 for each of the five sets of values of h, k, l listed in Table 2.

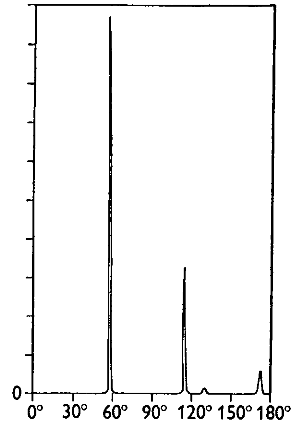


Fig. 6. Probability distribution for one-dimensional example showing prominent maximum at one radian. Unit length is represented by 2π radians.

Table 1. *Atom factors and co-ordinates for three-dimensional tests*

i	f_i	x_i	y_i	z_i
1	0·14	0·00	0·00	0·00
2	0·14	0·43	0·81	0·13
3	0·11	0·74	0·56	0·29
4	0·11	0·31	0·52	0·94
5	0·11	0·68	0·47	0·14
6	0·10	0·85	0·46	0·94
7	0·08	0·41	0·07	0·69
8	0·07	0·26	0·79	0·46
9	0·06	0·52	0·95	0·39
10	0·05	0·91	0·64	0·51
11	0·02	0·16	0·23	0·73
12	0·01	0·32	0·37	0·88

Table 2. *Amount of data for three-dimensional tests*

Case	Values of h, k, l	No. of R_{hkl}
I	$h, k, l = 0, \pm 1$	13
II	$h, k = 0, \pm 1$; $l = 0, \pm 1, \pm 2$	22
III	$h = 0, \pm 1$; $k, l = 0, \pm 1, \pm 2$	37
IV	$h, k, l = 0, \pm 1, \pm 2$	62
V	$h, k = 0, \pm 1, \pm 2$; $l = 0, \pm 1, \pm 2, \pm 3$	87

The first two atoms in Table 1 are of the same type characterized by the scattering factor f_a and the next three are of the same type characterized by f_b. In computing the co-ordinate differences between an atom of type *a* and one of type *b* from (58), all six possible sets of co-ordinate differences should be obtained simultaneously. Owing to the great length of the calculations, (58) was computed at four of the co-ordinate differences between atoms *a* and *b* which were used in computing the R_{hkl} and at eight other points chosen at random (Table 3). The probability function was also computed in the regions of the remaining two points near which maxima were expected (Table 4).

Table 3. *Values of probability function* (58) *at specified points corresponding to the various cases listed in Table* 2

				Case				
	x	*y*	*z*	I	II	III	IV	V
Co-ordinate differences between atoms	0·31	0·75	0·16	1·322	1·452	3·245	7·082	32·37
	0·31	0·52	0·94	2·171	2·753	9·160	52·67	256·0
	0·68	0·47	0·14	2·892	3·601	26·42	65·48	74·16
	0·88	0·71	0·81	0·9393	1·674	1·112	5·640	42·45
Background points	0	0	0	0·3236	0·1033	0·06643	0·06139	0·06859
	0	0	0·5	0·5626	0·1796	0·01445	0·004627	0·0001525
	0	0·5	0	0·5996	1·095	0·7041	0·004535	0·001098
	0	0·5	0·5	0·7492	1·368	0·1100	0·001162	0·0001767
	0·5	0	0	0·8608	0·6636	0·3305	0·3055	3·158
	0·5	0	0·5	0·8933	0·6888	1·173	0·3758	0·001338
	0·5	0·5	0	1·687	1·343	0·6687	0·004307	0·0006226
	0·5	0·5	0·5	0·5490	0·4368	0·7441	0·007856	0·002001

Table 4. *Values of the probability function* (58) *at points in the neighborhood of two interatomic spacings for case V of Table* 2

x	*y*	*z*	*P*
0·23	0·64	−0·01	82·39
0·27	0·64	−0·01	60·52
0·23	0·68	−0·01	19·49
0·23	0·64	0·03	52·12
0·25	0·66	0·01	43·58
0·23	0·68	0·03	19·49
0·27	0·64	0·03	28·70
0·27	0·68	−0·01	12·10
0·27	0·68	0·03	9·738
0·72	0·54	0·27	1·423
0·76	0·54	0·27	6·810
0 72	0·58	0·27	0·7362
0·72	0·54	0·31	0·7595
0·74	0·56	0·29	1·494
0·72	0·58	0·31	0·4563
0·76	0·54	0·31	2·315
0·76	0·58	0·27	2·783
0·76	0·58	0·31	1·258

The main feature of Table 3 is that, for case V, the order of magnitude of the function at the expected maxima is more than 10^4 times as great as its value at true background points. The values of 0·06859 and 3·158 at the background points (0, 0, 0) and (0·5, 0, 0) respectively, are due to the presence of interatomic distances, in the vicinity of these points, which are not related to the atom pair *a*, *b*. The results in Table 3 are quite satisfactory, especially in view of the fact that only $2\frac{1}{2}$ times the algebraic minimum of data was used in the computations (ref. Table 2). With more data it is expected that the value of the maxima for a specific atom pair will increase relative to the background and to those minor maxima corresponding to other atomic pairs. The progressive sharpening of the probability distribution is apparent from inspection of the cases listed in Table 3.

In Table 4 the values of (58) are tabulated for case V at points in the neighborhood of the two remaining anticipated maxima. It is seen that the values are again large relative to the values of the background as listed in Table 3. A comparison with Table 1 shows that the maxima in Table 4 are displaced somewhat from the anticipated values, but these discrepancies should decrease as the number of data increases. The relatively small maximum in the neighborhood of 0·74, 0·56, 0·29 is a measure of the statistical fluctuations which may occur when so few values of the *h*, *k*, *l* are used (Table 2). Usually, there is much more information available. It is worth noting that approximate values of the atomic parameters may be obtained with relatively few data using the statistical method. If desired, these values may then be improved by well-known methods of successive approximation.

There are many more tests of interest which should be made when automatic computing facilities become available.* They are, to mention a few: (1) the effect of uncertainties in the data; (2) the effect of uncertainties in the tabulated atomic scattering factors; (3) the number of data required to place the atoms accurately. Systematic errors in the observed intensities may be largely removed by adjusting the data to an absolute scale (Wilson, 1949). It is also to be expected that random errors in the data as well as the atomic scattering factors will tend to compensate one another if the data are sufficiently extensive.

From (10) and (71), the distributions for *R* in the asymmetric and centrosymmetric cases, the averages

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* We are expecting that the high-speed computing facilities (the SEAC) at the National Bureau of Standards will be made available to us in the near future.

of any power of R may be readily obtained. It is found, for example, that in the asymmetric case

$$\left\langle R/\tfrac{1}{2}\sqrt{(\pi\sigma_2)}\left[1+\frac{\sigma_4}{16\sigma_2^2}+\frac{\sigma_6}{24\sigma_2^3}+\frac{5(11\sigma_8-6\sigma_4^2)}{1024\sigma_2^4}+\dots\right]\right\rangle=1, \quad (79)$$

$$\langle R^2/\sigma_2\rangle=1, \quad (80)$$

$$\langle R^4/(2\sigma_2^2-\sigma_4)\rangle=1, \quad (81)$$

$$\langle R^6/(6\sigma_2^3-9\sigma_2\sigma_4+4\sigma_6)\rangle=1. \quad (82)$$

For the centrosymmetric case,*

$$\langle R^2/(\sigma_2-s_2+f'^2)\rangle=1, \quad (83)$$

$$\langle R^4/[3(\sigma_2-s_2)^2-3(\sigma_4-s_4)+6f'^2(\sigma_2-s_2)+f'^4]\rangle=1. \quad (84)$$

The possibility of using these formulas for placing intensity data on an absolute scale and for distinguishing between asymmetric and centrosymmetric crystals is apparent and has been pointed out by Wilson (1949).

It should be noted that the averages in (79)–(84) are obtained by allowing the atoms in general positions to range uniformly throughout the unit cell. In general, this is equivalent to fixing the co-ordinates and then taking the average by allowing the h, k, l to range through all integer values provided that for each atom no relation $m_1x+m_2y+m_3z=m$ exists where the m's are integers not all zero (Weyl, 1915–16, p. 319; Perron, 1921, pp. 143–57).† Numerical tests have shown that the average over h, k, l often gives the same results as (79)–(84), even though all the atoms have all rational co-ordinates. The reason for this is not understood at present.

Additional procedures for analysis

As in the case of the computation of the Patterson synthesis, the contribution of Harker (1936), which employs crystal symmetry to determine regions containing maxima, may be applied to formula (58). This will serve to locate the equilibrium values for the interatomic vectors.

Once the co-ordinate differences between a pair of atoms have been found by the statistical or any other method, then the angle ϕ_{12}, for example, between f_1 and f_2 in Fig. 7 is known. It is now possible to compute the magnitude of the third side

$$f_{12}=(f_1^2+f_2^2+2f_1f_2\cos\phi_{12})^{\frac{1}{2}} \quad (85)$$

and its direction. Similarly, it is possible to compute the magnitude and direction of the vector f_{34} of Fig. 7 if ϕ_{34} is known. For ψ_{12} and ψ_{34} we have

$$\psi_{12}=\psi_{12}(h,k,l)=\arcsin\{(f_2/f_{12})\sin\phi_{12}\}, \quad (86)$$

$$\psi_{34}=\psi_{34}(h,k,l)=\arcsin\{(f_4/f_{34})\sin\phi_{34}\}, \quad (87)$$

where f_{12}, f_{34}, ϕ_{12} and ϕ_{34} are known as functions of h, k, l and the co-ordinate differences. If now in the vector polygon of Fig. 1 we replace $\mathbf{f}_1$ and $\mathbf{f}_2$ by $\mathbf{f}_{12}$, and $\mathbf{f}_3$ and $\mathbf{f}_4$ by $\mathbf{f}_{34}$, then the probability distribution of $\phi_{12,34}$, the angle between $\mathbf{f}_{12}$ and $\mathbf{f}_{34}$, may be found from (16). Since the angle ϕ_{13} between $\mathbf{f}_1$ and $\mathbf{f}_3$ is given by

$$\phi_{13}=\phi_{12,34}+\psi_{12}-\psi_{34}, \quad (88)$$

where ψ_{12} and ψ_{34} are now known from (86) and (87), the probability distribution of ϕ_{13} on the basis of a single observation may be found. By multiplying the distributions from all the observations, we obtain the probability distribution of the co-ordinate differences between the first and third atoms on the basis of all the data.

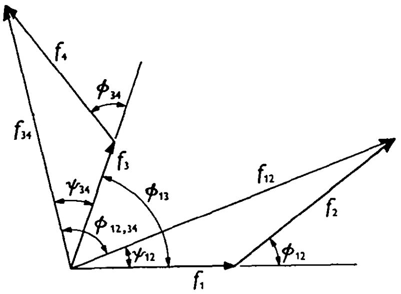

Fig. 7. The definition of ϕ_{13} in terms of the angles ψ_{12}, ψ_{34} and $\phi_{12,34}$.

One application of the procedure just described is in the determination of the co-ordinate differences between a pair of atoms in a crystal whose unit cell contains a large number of like atoms. The direct application of (58) yields a distribution having many maxima some of which may not be resolved. Since, in general, relatively few atoms f_1 can be combined with atoms f_2 to yield f_{12} and relatively few pairs f_3 and f_4 will combine to yield f_{34}, the probability distribution for the co-ordinate differences between the first and third atoms will have relatively few maxima. A simpler application, once ϕ_{12} and f_{12} have been determined, would be to use (58) with f_{12} instead of f_1 and f_2 in order to obtain ϕ_{34}.

The method also permits the ambiguities which arise (e.g. if (x, y, z) is a maximum of (58) then so is $(1-x, 1-y, 1-z)$) to be resolved. For example, once the co-ordinate differences between the first and second atoms are decided upon (i.e. ϕ_{12} is selected) the above procedure, with f_3 replacing f_{34}, yields only those angles ϕ_{13} consistent with the choice of ϕ_{12}. In this manner, only the structures consistent with the observed data will be obtained. These include the ambiguities of Patterson (1944).

The method for making use of known parameters to aid in finding other co-ordinate differences may be varied in any number of ways to suit the particular problem.

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* If (83) and (84) are averaged over h, k, l for the atoms in special positions, we obtain, since $\langle f'^2\rangle=s_2$, $\langle f'^4\rangle=3s_2{}^2-2s_4$, the result that $\langle R^2/\sigma_2\rangle=1$ and $\langle R^4/(3\sigma_2{}^2-3\sigma_4+s_4)\rangle=1$.

† The averages over h, k, l depend only on the atoms constituting the crystal and are independent of the positions of the atoms in the unit cell provided only that for each atom no relation $m_1x+m_2y+m_3z=m$ exists where the m's are integers not all zero.

Electron distributions

Once the atoms are located in a crystal, there remains the problem of determining the electron distribution about these atoms. An analysis will now be given which shows that the phases of the structure factors are mainly determined by the positions of the atomic centers and are relatively insensitive to small changes in the electron distribution. This permits an accurate evaluation of the phases from the results of the statistical procedure and the tabulated atomic scattering factors. These phases may be used in conjunction with the observed intensities, corrected for vibrational motion, to obtain an improved electron distribution by means of the Fourier series. The analysis also shows that the shape of the electron distribution is mainly dependent upon the magnitudes of the structure factors rather than their phases.

From the definition of the structure factor, we have

$$F_{\mathbf{h}} = R_{\mathbf{h}} \exp[i\phi_{\mathbf{h}}] = \sum_{j=1}^{N} f_{\mathbf{h}j} \exp[-2\pi i \mathbf{h}\,.\,\mathbf{r}_j] \tag{89}$$

$$= \sum_{j=1}^{N} f_{\mathbf{h}j} \cos 2\pi \mathbf{h}\,.\,\mathbf{r}_j - i \sum_{j=1}^{N} f_{\mathbf{h}j} \sin 2\pi \mathbf{h}\,.\,\mathbf{r}_j, \tag{90}$$

$$R_{\mathbf{h}}^2 = \left(\sum_{j=1}^{N} f_{\mathbf{h}j} \cos 2\pi \mathbf{h}\,.\,\mathbf{r}_j \right)^2 + \left(\sum_{j=1}^{N} f_{\mathbf{h}j} \sin 2\pi \mathbf{h}\,.\,\mathbf{r}_j \right)^2, \tag{91}$$

$$R_{\mathbf{h}} dR_{\mathbf{h}} = \sum_{j=1}^{N} f_{\mathbf{h}j} df_{\mathbf{h}j} + \sum_{\substack{i<j\\1}}^{N} \cos 2\pi \mathbf{h}\,.\,(\mathbf{r}_i - \mathbf{r}_j)\,(f_{\mathbf{h}i} df_{\mathbf{h}j} + f_{\mathbf{h}j} df_{\mathbf{h}i})$$
$$- 2\pi \sum_{\substack{i<j\\1}}^{N} f_{\mathbf{h}i} f_{\mathbf{h}j} \sin 2\pi \mathbf{h}\,.\,(\mathbf{r}_i - \mathbf{r}_j)\,[\mathbf{h}\,.\,(d\mathbf{r}_i - d\mathbf{r}_j)]. \tag{92}$$

For random positions of the atoms the average of each term in the second and third sums of (92) is zero, so that these sums approximate to zero and we have

$$R_{\mathbf{h}} dR_{\mathbf{h}} \sim \sum_{j=1}^{N} f_{\mathbf{h}j} df_{\mathbf{h}j}. \tag{93}$$

While in any given crystal (93) is not exactly true and in special cases may be in significant error, as a general rule (93) shows that the uncertainty in the magnitude of the structure factor is mainly dependent upon the uncertainties in the atom-scattering factors and is largely independent of the uncertainties in the atomic positions.

From the relation

$$\tan \phi_{\mathbf{h}} = -\frac{\sum_{j=1}^{N} f_{\mathbf{h}j} \sin 2\pi \mathbf{h}\,.\,\mathbf{r}_j}{\sum_{j=1}^{N} f_{\mathbf{h}j} \cos 2\pi \mathbf{h}\,.\,\mathbf{r}_j}, \tag{94}$$

we have

$$-R_{\mathbf{h}}^2 d\phi_{\mathbf{h}} = \sum_{\substack{i<j\\1}}^{N} \sin 2\pi \mathbf{h}\,.\,(\mathbf{r}_i - \mathbf{r}_j)\,(f_{\mathbf{h}j} df_{\mathbf{h}i} - f_{\mathbf{h}i} df_{\mathbf{h}j})$$
$$+ 2\pi \sum_{j=1}^{N} f_{\mathbf{h}j}^2\, \mathbf{h}\,.\,d\mathbf{r}_j + 2\pi \sum_{\substack{i<j\\1}}^{N} f_{\mathbf{h}i} f_{\mathbf{h}j} \cos 2\pi \mathbf{h}\,.\,(\mathbf{r}_i - \mathbf{r}_j)$$
$$\times [\mathbf{h}\,.\,(d\mathbf{r}_i + d\mathbf{r}_j)], \tag{95}$$

and therefore, as before,

$$R_{\mathbf{h}}^2 d\phi_{\mathbf{h}} \sim -2\pi \sum_{j=1}^{N} f_{\mathbf{h}j}^2\, \mathbf{h}\,.\,d\mathbf{r}_j. \tag{96}$$

Again, as in the case of (93), we may conclude as a general rule that the uncertainty in the phase of a structure factor is largely dependent upon the uncertainties in the atomic positions, whereas it is relatively independent of the uncertainties in the atomic scattering factors.

Since the atomic positions are known from the statistical method, the phases may be accurately computed from (89) using tabulated atomic scattering factors. The electron distribution may then be found from the Fourier series

$$\rho(\mathbf{r}) = \sum_{\mathbf{h}} R_{\mathbf{h}} \exp[i(\phi_{\mathbf{h}} + 2\pi \mathbf{h}\,.\,\mathbf{r})], \tag{97}$$

where the $R_{\mathbf{h}}$ are the observed magnitudes corrected for vibrational motion. It is seen from (97) that

$$d\rho(\mathbf{r}) = \sum_{\mathbf{h}} \exp[i(\phi_{\mathbf{h}} + 2\pi \mathbf{h}\,.\,\mathbf{r})]\,(dR_{\mathbf{h}} + iR_{\mathbf{h}} d\phi_{\mathbf{h}}), \tag{98}$$

and substituting (96) gives

$$d\rho(\mathbf{r}) \sim \sum_{\mathbf{h}} \exp[i(\phi_{\mathbf{h}} + 2\pi \mathbf{h}\,.\,\mathbf{r})]$$
$$\times \left(dR_{\mathbf{h}} - 2\pi i \sum_{j=1}^{N} f_{\mathbf{h}j}^2\, \mathbf{h}\,.\,d\mathbf{r}_j / R_{\mathbf{h}} \right). \tag{99}$$

For negligible error in the atomic positions, $d\mathbf{r}_j$, the error in $\rho(\mathbf{r})$, depends solely on the experimental errors in the magnitudes $dR_{\mathbf{h}}$.

Relation to the Patterson synthesis

The problem of determining the differences between the co-ordinates of pairs of atoms in a crystal purely from X-ray data without knowledge of the phases of the Fourier coefficients was solved by Patterson (1934). It was immediately obvious that these vector differences obtained from the Patterson synthesis would lead to a unique arrangement of the atoms in a crystal (except for Patterson ambiguities (Patterson, 1944)). The main difference between the Patterson synthesis and the statistical computation is that the latter gives the probability distribution for the co-ordinate differences between the *point centers* of atom pairs, and detailed use is made of the known atom scattering factors. As a consequence, the maxima of (58) are well resolved. In addition, formula (58) permits the computation of the distribution for specific pairs of atoms and incidentally eliminates the peak at the origin for pairs of distinct atoms. An entirely new class of distribution formulas, of which the centrosymmetric case (75) is an example, can be expected for the various space groups. The following analysis shows the mathematical relationship between (58) and the Patterson synthesis.

If we multiply (58) over all possible combinations of i and j, the resulting function will have maxima at all points x, y, z representing co-ordinate differences of any pair of atoms (not merely the ith and jth atoms):

$$\prod_{\substack{i,j\\1}}^{N} P(x,y,z) = \prod_{\substack{i,j\\1}}^{N} \prod_{h,k,l} \frac{\exp\left(\dfrac{R^2_{hkl}}{\sigma_2}\dfrac{B_{ij}\cos 2\pi(hx+ky+lz)}{1+B_{ij}\cos 2\pi(hx+ky+lz)}\right)}{1+B_{ij}\cos 2\pi(hx+ky+lz)}. \quad (100)$$

Replacing $1+B_{ij}\cos 2\pi(hx+ky+lz)$ by its average value, namely, unity, gives

$$\prod_{\substack{i,j\\1}}^{N} P(x,y,z) \sim \exp\left\{\sum_{h,k,l} \frac{R^2_{hkl}}{\sigma_2}\cos 2\pi(hx+ky+lz) \sum_{\substack{i,j\\1}}^{N} B_{ij}\right\}. \quad (101)$$

Making the assumption that

$$f_i(h,k,l) = k_i f(h,k,l), \quad (102)$$

where k_i is almost independent of h, k, l, gives

$$\sigma_2 = \sum_{i=1}^{N} f_i^2 = f^2 \sum_{i=1}^{N} k_i^2, \quad (103)$$

$$B_{ij} = \frac{2f_i f_j}{\sigma_2} = \frac{2k_i k_j}{\sum\limits_{i=1}^{N} k_i^2}, \quad (104)$$

$$\sum_{\substack{i,j\\1}}^{N} B_{ij} = \frac{2\left(\sum\limits_{i=1}^{N} k_i\right)^2}{\sum\limits_{i=1}^{N} k_i^2} = B, \quad (105)$$

and the dependence of B on h, k, l is seen to be negligible even though k_i may vary somewhat with h, k, l. Therefore (101) becomes

$$\prod_{\substack{i,j\\1}}^{N} P(x,y,z) \sim \exp\left(B \sum_{h,k,l} \frac{R^2_{hkl}}{\sigma_2}\cos 2\pi(hx+ky+lz)\right), \quad (106)$$

the maxima of which coincide with those of the 'sharpened' Patterson series in the exponent.

The same analysis applied to (58) as it stands yields

$$P(x,y,z) \sim \exp\left(\sum_{h,k,l} \frac{R^2_{hkl}}{\sigma_2}\frac{B_{ij}\cos 2\pi(hx+ky+lz)}{1+B_{ij}\cos 2\pi(hx+ky+lz)}\right), \quad (107)$$

or

$$P(x,y,z) \sim \exp\left(\sum_{h,k,l} B_{ij}\frac{R^2_{hkl}}{\sigma_2}\cos 2\pi(hx+ky+lz)\right), \quad (108)$$

the exponents of which are modifications of the Patterson series.

Future tests will show whether the approximations involved are good enough to permit the use of (107) or (108) instead of (58) for the evaluation of the relative co-ordinates of selected pairs of atoms. It appears unlikely that (108) will be accurate enough for this purpose, although (107) may.

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