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The Theory of Sign Relations Between Structure Factors

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All the known sign relationships for the space group $P\bar{1}$ are reviewed and the value of each for sign determination is critically assessed.

The first relationships considered are those which give sign indications directly from intensities. The probability of deriving the sign of $U_{2\mathbf{h}}$ from the magnitude of $U_{\mathbf{h}}$ is calculated and it is shown that no other 'signs from intensities' relationship is stronger than this one. The probability of the truth of the normal sign relationship $s(\mathbf{h}) = s(\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ is next derived and it is pointed out that the sign of $U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$ is the probable sign of the **h**th Fourier coefficient of the *squared* structure. The slight limitations on sign determination imposed by this fact are defined. Other sections are devoted to the combination of probabilities, to less important sign relationships, and to the determination of signs from intensities for the space group $P2_1/a$.

In the light of the results found the claim of Hauptman & Karle to have solved the phase problem is examined. It is concluded that, while their individual probability expressions are correct within certain limits, they have misinterpreted these results.

1. Introduction

It would be fair to say that the subject with which this paper is concerned is in a confused state at the present time. We are therefore including in this introduction a paragraph outlining the scope of previous publications.

The inequalities derived by Harker & Kasper (1948) can be used to show that when the unitary structure factors $U_{\mathbf{h}}$, $U_{\mathbf{h}'}$ and $U_{\mathbf{h}+\mathbf{h}'}$ are sufficiently large, their signs are necessarily related by

$$s(\mathbf{h}) = s(\mathbf{h}')s(\mathbf{h}+\mathbf{h}') \; . \qquad (1\cdot1)$$

One of Sayre's (1952) results has been used by Cochran (1952) to estimate the probability that (1·1) is true in the general case, but only a qualitative result was obtained. Zachariasen (1952) considered the probability of the truth of the relation

$$s(\mathbf{h}) = \overline{s(\mathbf{h}')s(\mathbf{h}+\mathbf{h}')}^{h'}, \qquad (1\cdot2)$$

but it has since been shown that the correct form of (1·2) is

$$s(\mathbf{h}) = s\{\overline{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}^{h'}\} \; . \qquad (1\cdot3)$$

This relation is certainly true when the average is taken over all values of $\mathbf{h}'$, and the atoms of the structure are all equal to one another. It is still probably true in other circumstances (Cochran, 1953; Hughes, 1953), but these authors did not derive a quantitative expression for the probability. Relation (1·1) is of course a special case of (1·3). In an important recent publication, Hauptman & Karle (1953), have derived expressions for the probability of the truth of (1·1) and (1·3), and for a number of new relations of the same general kind, including some for which the sign of a structure factor is related to the magnitudes of others only. The claim that these results form the basis of a general solution of the phase problem has been disputed (Vand & Pepinsky, 1953, 1954; Cochran & Woolfson, 1954), and reasserted (Hauptman & Karle, 1954). Vand & Pepinsky (1953) have recalculated some of the probabilities by a much simpler method, obtaining results which are to a first approximation the same as those of Hauptman & Karle (1953). Woolfson (1954) has obtained an expression for the probability of the truth of (1·1) which differs from that obtained by Vand & Pepinsky (1953), but agrees with that given by Kitaigorodski (1953, 1954) for the special case of equal atoms.

The conclusions which we reach in the present paper are:

(i) The probabilities found by Hauptman & Karle are correct as a first approximation, but their interpretation of these results is incorrect.

(ii) Vand & Pepinsky have made incorrect assumptions in the course of their derivations, but have nevertheless obtained the correct expression for the probability in some special cases, but not in others. The same appears to be true of the work of Kitaigorodski.

(iii) Woolfson's (1954) result is correct only when the atoms are equal.

We have recalculated the various probabilities and have also found a number of new results. We conclude that there is, as yet, no routine solution of the phase problem.

2. Notation

N is the number of atoms per unit cell.

$\mathbf{r}_j$ specifies the coordinates of the jth atom.

$n_j = f_j \Big/ \sum_{j=1}^{N} f_j$, is taken to be constant and equal to that fraction of the total number of electrons which is associated with the jth atom.

$\varepsilon_m = \sum_{j=1}^{N} n_j^m$. (When the atoms are equal, $\varepsilon_m = N^{1-m}$.)

$\mathbf{h}$ specifies the reciprocal lattice point (hkl).

$F_{\mathbf{h}} = 2 \sum_{j=1}^{\frac{1}{2}N} f_j \cos 2\pi \mathbf{h} \cdot \mathbf{r}_j$ defines a structure factor.

$U_{\mathbf{h}} = 2 \sum_{j=1}^{\frac{1}{2}N} n_j \cos 2\pi \mathbf{h} \cdot \mathbf{r}_j$ is a unitary structure factor.

$E_{\mathbf{h}} = U_{\mathbf{h}} / \sqrt{(\overline{U^2})} = U_{\mathbf{h}} / \varepsilon_2^{\frac{1}{2}}$ is a normalized structure factor.

$V_{\mathbf{h}} = 2 \sum_{j=1}^{\frac{1}{2}N} n_j^2 \cos 2\pi \mathbf{h} \cdot \mathbf{r}_j$.

$D_{\mathbf{h}} = \overline{(E_{\mathbf{h}'}^2 - 1)(E_{\mathbf{h}+\mathbf{h}'}^2 - 1)}^{\mathbf{h}'}$, the average being over an infinite range of values of $\mathbf{h}'$.

c_j is an abbreviation for $\cos 2\pi \mathbf{h} \cdot \mathbf{r}_j$.

σ^2 is an abbreviation for $\varepsilon_4 - \varepsilon_3^2/\varepsilon_2$.

$Z_{\mathbf{h},\mathbf{h}'}$ is an abbreviation for $U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}$.

$s(X)$ denotes the sign of a function X. Since $s(F_{\mathbf{h}}) = s(U_{\mathbf{h}}) = s(E_{\mathbf{h}})$, $s(\mathbf{h})$ is used for them all.

$P(X)dX$ is the probability that a function has a value between X and $X+dX$. For certain probability distributions ψ, θ and μ are used instead of P.

$P_+(X)$ is the probability that $s(X)$ is positive. $P_-(X) = 1 - P_+(X)$.

$\overline{X_{\mathbf{h}}}^{\mathbf{h}}$ is the average of X over a range of values of $\mathbf{h}$.

$\langle X \rangle$ is the expected value of X.

$\varphi(x)$ is the probability integral $(2\pi)^{-\frac{1}{2}} \int_0^x \exp(-\frac{1}{2}t^2) dt$.

3. Relations between the sign of a structure factor and the intensities

3·1. *Some general results*

In §§ 3 and 4 we shall confine our attention to the space group $P\bar{1}$. The results given in § 3·1 are used in later sections; detailed derivations are given in Appendix I. The first problem is to find the average contribution of an atom to a unitary structure factor $U_{\mathbf{h}}$ of fixed magnitude and sign. In the averaging process we can imagine the atoms to be moved around at random, and the contribution of the jth atom to a structure factor of fixed index to be recorded whenever $U_{\mathbf{h}}$ has a definite value. The same results would be achieved by keeping the atoms fixed, and recording the contribution of the jth atom to every unitary structure factor which has this definite value, irrespective of its index (see Hauptman & Karle, 1953, appendix). The contribution of the jth atom to a unitary structure factor is $2n_j \cos 2\pi \mathbf{h} \cdot \mathbf{r}_j = 2n_j c_j$, say. The mean value of c_j is zero, and there is a certain distribution of values of c_j in the range -1 to $+1$. When $U_{\mathbf{h}}$ is fixed in magnitude and sign, $\overline{c_j}^{\mathbf{h}} \neq 0$ and the distribution is changed. Let the new probability distribution be $\psi(c_j)$. It is shown in Appendix I that

$$\psi(c_j) = \frac{1}{2\pi}(1 + n_j^2/\varepsilon_2)(1 - c_j^2)^{-\frac{1}{2}} \times \exp\left(-\frac{n_j^2 U_{\mathbf{h}}^2}{\varepsilon_2^2}\right) \exp\left[\frac{2}{\varepsilon_2}\left(1 + \frac{2n_j^2}{\varepsilon_2}\right)(n_j U_{\mathbf{h}} c_j - n_j^2 c_j^2)\right]. \quad (3\cdot1)$$

The first four moments of this distribution are found to be

$$\overline{c_j}^{\mathbf{h}} = \frac{n_j}{\varepsilon_2} U_{\mathbf{h}}, \quad (3\cdot2)$$

$$\overline{c_j^2}^{\mathbf{h}} = \tfrac{1}{2} + \frac{n_j^2}{4\varepsilon_2^2}(U_{\mathbf{h}}^2 - \varepsilon_2), \quad (3\cdot3)$$

$$\overline{c_j^3}^{\mathbf{h}} = \left(\frac{3n_j}{4\varepsilon_2} + \frac{n_j^3}{\varepsilon_2^2}\right) U_{\mathbf{h}} - \frac{n_j^3}{3\varepsilon_2^3} U_{\mathbf{h}}^3, \quad (3\cdot4)$$

$$\overline{c_j^4}^{\mathbf{h}} = \tfrac{3}{8} + \frac{n_j^2}{4\varepsilon_2^2}(U_{\mathbf{h}}^2 - \varepsilon_2). \quad (3\cdot5)$$

For values of c_j chosen at random there are corresponding averages of $0, \frac{1}{2}, 0$, and $\frac{3}{8}$ respectively; the extra terms result from the specification that $U_{\mathbf{h}}$ is to remain fixed.

3·2. *The distribution of values of $U_{2\mathbf{h}}$ for a fixed value of $U_{\mathbf{h}}$*

We write

$$U_{2\mathbf{h}} = \sum_{j=1}^{\frac{1}{2}N} \xi_j,$$

where

$$\xi_j = 2n_j \cos 4\pi \mathbf{h} \cdot \mathbf{r}_j = 2n_j(2c_j^2 - 1). \quad (3\cdot6)$$

Thus

$$\overline{\xi_j}^{\mathbf{h}} = 4n_j\left(\overline{c_j^2}^{\mathbf{h}} - \tfrac{1}{2}\right) = \frac{n_j^3}{\varepsilon_2^2}(U_{\mathbf{h}}^2 - \varepsilon_2), \quad (3\cdot7)$$

from (3·3).

The variance of ξ_j is given by

$$\overline{\xi_j^2}^{\mathbf{h}} - \left(\overline{\xi_j}^{\mathbf{h}}\right)^2.$$

The first term is of order N^{-2}, the second is of order N^{-4} and will be neglected. Using (3·3) and (3·5) we then find that

$$\overline{\xi^2}^{\mathbf{h}} \simeq 2n^2.$$

If we now invoke the central limit theorem in exactly the same way as was done by Woolfson (1954) in a similar derivation, we find that $U_{2\mathbf{h}}$ is normally distributed about

$$\sum_{j=1}^{\frac{1}{2}N} \frac{n_j^3}{\varepsilon_2^2}(U_{\mathbf{h}}^2 - \varepsilon_2) = \frac{\varepsilon_3}{2\varepsilon_2^2}(U_{\mathbf{h}}^2 - \varepsilon_2)$$

with variance

$$\sum_{j=1}^{\frac{1}{2}N} 2n_j^2 = \varepsilon_2.$$

The distribution of values of $U_{2\mathbf{h}}$ can therefore be described by

$$P(U_{2\mathbf{h}}) = (2\pi\varepsilon_2)^{-\frac{1}{2}} \exp\left[-\frac{1}{2\varepsilon_2}\left\{U_{2\mathbf{h}}-\frac{\varepsilon_3}{2\varepsilon_2^2}(U_{\mathbf{h}}^2-\varepsilon_2)\right\}^2\right]. \quad (3\cdot8).$$

The probability that $U_{2\mathbf{h}}$ has a positive sign, divided by the probability that it is negative, is therefore

$$\frac{P_+(U_{2\mathbf{h}})}{P_-(U_{2\mathbf{h}})} = \frac{\exp\left[-\frac{1}{2\varepsilon_2}\left\{|U_{2\mathbf{h}}|-\frac{\varepsilon_3}{2\varepsilon_2^2}(U_{\mathbf{h}}^2-\varepsilon_2)\right\}^2\right]}{\exp\left[-\frac{1}{2\varepsilon_2}\left\{|U_{2\mathbf{h}}|+\frac{\varepsilon_3}{2\varepsilon_2^2}(U_{\mathbf{h}}^2-\varepsilon_2)\right\}^2\right]}$$

$$= \exp\left[\frac{\varepsilon_3}{\varepsilon_2^3}|U_{2\mathbf{h}}|(U_{\mathbf{h}}^2-\varepsilon_2)\right]. \quad (3\cdot9)$$

Since $P_+(U_{2\mathbf{h}})+P_-(U_{2\mathbf{h}}) = 1$,

$$P_+(U_{2\mathbf{h}}) = \left[1+\exp\left\{-\frac{\varepsilon_3}{\varepsilon_2^3}|U_{2\mathbf{h}}|(U_{\mathbf{h}}^2-\varepsilon_2)\right\}\right]^{-1}$$

$$= \tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{\varepsilon_3}{2\varepsilon_2^3}|U_{2\mathbf{h}}|(U_{\mathbf{h}}^2-\varepsilon_2)\right]. \quad (3\cdot10)$$

When this result is expanded as a power series as far as the first power, and is expressed in terms of normalized structure factors, one finds

$$P_+(U_{2\mathbf{h}}) = \tfrac{1}{2}+\frac{\sum_{j=1}^{N} n_j^3\,|E_{2\mathbf{h}}|(E_{\mathbf{h}}^2-1)}{4N^{\frac{1}{2}}\left(\sum_{j=1}^{N} n_j^2\right)^{\frac{3}{2}}}. \quad (3\cdot11)$$

Equation (3·11) is exactly the result given by Hauptman & Karle (1953, p. 40). The result (3·10) is more accurate, and satisfies the condition $0 \leqslant P \leqslant 1$, which any probability must do. This result has already been obtained by Vand & Pepinsky (1953) for the special case of equal atoms (for which $\varepsilon_3 = N\varepsilon_2^3$). Since their derivation leads them to assume that, for a fixed value of $U_{\mathbf{h}}$, $U_{2\mathbf{h}}$ is distributed about $NU_{\mathbf{h}}^2-1$ (compare our $\frac{1}{2}(U_{\mathbf{h}}^2-1/N)$) with variance 2 (compare our $1/N$), it is clear that they obtain the correct result for $P_+(U_{2\mathbf{h}})$ only by a cancellation of errors.

3·3. *The distribution function* $P(U_{\mathbf{h}}, U_{2\mathbf{h}})$.

Vand & Pepinsky (1953, Part III) have described a method whereby the distribution of values of $U_{\mathbf{h}}$ and $U_{2\mathbf{h}}$ for a random distribution of atoms in the unit cell can be obtained when N is not too great. Formula (3·14) of Hauptman & Karle (1953) might also be used, but the series does not converge rapidly. The results given in § 3·2 can be used to calculate the limiting form of this distribution for large N. Let $P(U_{\mathbf{h}}, U_{2\mathbf{h}})dU_{\mathbf{h}}dU_{2\mathbf{h}}$ be the probability that $U_{\mathbf{h}}$ and $U_{2\mathbf{h}}$ simultaneously lie within the indicated limits. For simplicity we take the atoms to be equal. The probability that $U_{\mathbf{h}}$ lies in the range $dU_{\mathbf{h}}$ is approximately

$$P(U_{\mathbf{h}})dU_{\mathbf{h}} = (N/2\pi)^{\frac{1}{2}} \exp\left(-\tfrac{1}{2}NU_{\mathbf{h}}^2\right)dU_{\mathbf{h}},$$

while for fixed $U_{\mathbf{h}}$, $P(U_{2\mathbf{h}})dU_{2\mathbf{h}}$ is given by (3·8) with $\varepsilon_2 = 1/N$ and $\varepsilon_3 = \varepsilon_2^2$, since the atoms are equal. Combining these results,

$$P(U_{\mathbf{h}}, U_{2\mathbf{h}}) = (N/2\pi)\exp\left[-\tfrac{1}{2}N(U_{\mathbf{h}}^2+\{U_{2\mathbf{h}}-\tfrac{1}{2}(U_{\mathbf{h}}^2-1/N)\}^2)\right]. \quad (3\cdot12)$$

Curves of constant probability are shown in Fig. 1.

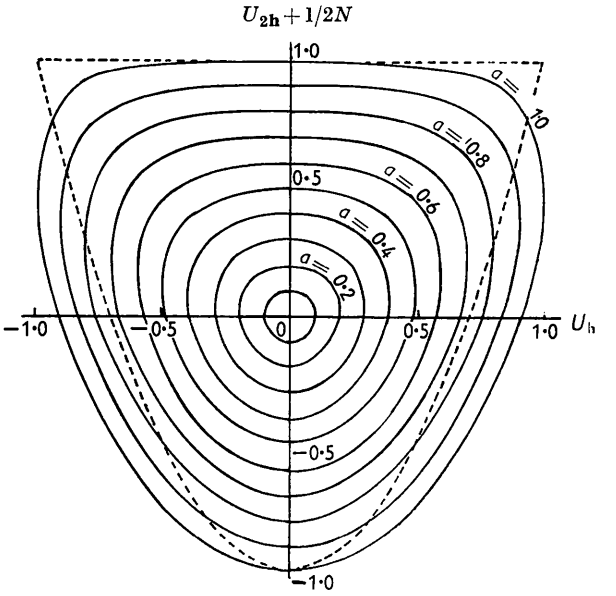

Fig. 1. The curves show where the quantity

$$a^2 = U_{\mathbf{h}}^2+(U_{2\mathbf{h}}+1/2N-\tfrac{1}{2}U_{\mathbf{h}}^2)^2$$

assumes the values $a^2 = 0\cdot1^2, 0\cdot2^2, \ldots$.

Since the vertical ordinate has been taken as $U_{2\mathbf{h}}+1/2N$, the value of $P(U_{\mathbf{h}}U_{2\mathbf{h}})$ can be read off from this chart as $(N/2\pi)\exp(-\frac{1}{2}Na^2)$.

The broken line shows where the final contour should be when $N = \infty$, as its position is determined by the inequality $U_{\mathbf{h}}^2 \leqslant \frac{1}{2}+\frac{1}{2}U_{2\mathbf{h}}$.

There is already qualitative agreement with the Fig. 2 of Vand & Pepinsky, which is accurate for $N = 10$. Our formula, of course, cannot reproduce the 'forbidden region' required by the inequality $U_{\mathbf{h}}^2 \leqslant \frac{1}{2}(1+U_{2\mathbf{h}})$; it merely gives a very small probability for any point in this region.

3·4. *Other relations between* $U_{2\mathbf{h}}$ *and the intensities*

Realizing that a reliable indication of the sign of $U_{2\mathbf{h}}$ cannot be obtained from the value of $U_{\mathbf{h}}^2$, Hauptman & Karle (1953, p. 47) have derived the relation

$$s(2\mathbf{h}) = s\left(\sum_{\mathbf{h}'}(E_{\mathbf{h}'}^2-1)(E_{\mathbf{h}+\mathbf{h}'}^2-1)\right). \quad (3\cdot13)$$

In a later note (Hauptman & Karle, 1954) they particularly stress the value of this result.

Let

$$D_{\mathbf{h}} = \overline{(E_{\mathbf{h}'}^2-1)(E_{\mathbf{h}+\mathbf{h}'}^2-1)}^{\mathbf{h}'},$$

where the average is over an infinite range of $\mathbf{h}'$.

When the atoms are equal to one another it may be shown by a lengthy derivation (which we omit, in view of the results given in Table 3·1 below) that the probability that $U_{2\mathbf{h}}$ and $D_{\mathbf{h}}$ have the same sign, $P_+(U_{2\mathbf{h}}D_{\mathbf{h}})$, is given by

$$\frac{P_+(U_{2\mathbf{h}}D_{\mathbf{h}})}{P_-(U_{2\mathbf{h}}D_{\mathbf{h}})} = \exp\left[\tfrac{1}{2}|U_{2\mathbf{h}}||NU_{\mathbf{h}}^2-1|\right].$$

From (3·8) it can be shown that

$$\frac{P_+\{U_{2\mathbf{h}}(U_{\mathbf{h}}^2-1/N)\}}{P_-\{U_{2\mathbf{h}}(U_{\mathbf{h}}^2-1/N)\}} = \exp\left[|U_{2\mathbf{h}}||NU_{\mathbf{h}}^2-1|\right].$$

The sign indication given by $D_{\mathbf{h}}$ is thus less reliable than that given by $(U_{\mathbf{h}}^2-1/N)$. The conditions under which $D_{\mathbf{h}}$ will give a correct sign indication for a structure containing equal atoms and whose Patterson function is composed of resolved peaks are shown in Table 3·1, which is based on the correct result

$$U_{2\mathbf{h}} = N\left\{2\left(U_{\mathbf{h}}^2-\frac{1}{N}\right)-D_{\mathbf{h}}\right\} \quad \text{(see Cochran, 1954).}$$

There is no instance where $D_{\mathbf{h}}$ gives a better result than $(U_{\mathbf{h}}^2-1/N)$. Nevertheless, the equation (3·32) of Hauptman & Karle (1953), which in our notation is

$$P_+(U_{2\mathbf{h}}) = \tfrac{1}{2}+\frac{1}{8N^{3/2}}|E_{2\mathbf{h}}|(E_{\mathbf{h}'}^2-1)(E_{\mathbf{h}+\mathbf{h}'}^2-1)\,,$$

is correct within the limitations which their analysis imposes. If values of $U_{2\mathbf{h}}$, of $(E_{\mathbf{h}'}^2-1)$ and of $(E_{\mathbf{h}+\mathbf{h}'}^2-1)$ are chosen at random, there is always a probability, slightly greater than $\frac{1}{2}$, that $U_{2\mathbf{h}}(E_{\mathbf{h}'}^2-1)(E_{\mathbf{h}+\mathbf{h}'}^2-1)$ will be positive. This does *not* require that $U_{2\mathbf{h}}\overline{(E_{\mathbf{h}'}^2-1)(E_{\mathbf{h}+\mathbf{h}'}^2-1)}^{h'}$ should certainly be positive, as Hauptman & Karle believe, but merely that $\overline{U_{2\mathbf{h}}(E_{\mathbf{h}'}^2-1)(E_{\mathbf{h}+\mathbf{h}'}^2-1)}^{h,h'}$ should certainly be positive (which it is, being equal to $1/N^2$ when the atoms are equal). Whereas the former result, if it had been correct, would have been invaluable for sign determination, the second is quite useless. The method of obtaining joint probability distributions by imagining the atoms to roam throughout the unit cell, subject for example to the condition that $U_{2\mathbf{h}}$ is to remain fixed in magnitude and sign, must be used with caution. In the case we are considering the distribution (A) with which we are concerned in practice is that of values of $(E_{\mathbf{h}'}^2-1)(E_{\mathbf{h}+\mathbf{h}'}^2-1)$ when $U_{2\mathbf{h}}$ is fixed in magnitude, sign and index. The distribution (B) given by the theory of Hauptman & Karle is the average of all such distributions (A) over all $\mathbf{h}$ for which $U_{2\mathbf{h}}$ has a fixed value, and for this distribution (B) it is quite correct that $U_{2\mathbf{h}}\overline{(E_{\mathbf{h}'}^2-1)(E_{\mathbf{h}+\mathbf{h}'}^2-1)}^{h'}$ is certainly positive. By failing to distinguish between these two distributions Hauptman & Karle have been led to the incorrect conclusion that $s(2\mathbf{h}) = s(D_{\mathbf{h}})$.

3·5. *The correlation of other structure factors with* $U_{\mathbf{h}}$

From (3·4) it may be shown that, for a fixed value of $U_{\mathbf{h}}$, the expected value of $U_{3\mathbf{h}}$ is

$$\langle U_{3\mathbf{h}}\rangle = (4\varepsilon_3/\varepsilon_2^3)(U_{\mathbf{h}}\varepsilon_2-U_{\mathbf{h}}^3/3)\,.$$

A derivation similar to that given in § 3·2 then shows that there is a definite, but small, probability that when $|U_{\mathbf{h}}|$ and $|U_{3\mathbf{h}}|$ are large, $s(3\mathbf{h}) = s(\mathbf{h})$. From (3·5) we find that $\langle U_{4\mathbf{h}}\rangle = 0$, but this is incorrect and comes about because terms of order N^{-2} were neglected in the derivation. From the general result

$$\overline{U_{\mathbf{h}}^m U_{m\mathbf{h}}}^h = \varepsilon_{m+1} \quad \text{(see Appendix II)}$$

we see that there is always a correlation between $U_{\mathbf{h}}$ and structure factors of multiple indices. Beyond $U_{2\mathbf{h}}$ it becomes too small to be useful for sign determination.

4. Relations between the sign of a structure factor and other structure factors

4·1. *The distribution of values of* $U_{\mathbf{h}}U_{\mathbf{h}+\mathbf{h}'}$

In § 4 our object is to find exact expressions for the probability that relation (1·1) or relation (1·3) is true. To do this, it is necessary to consider the distribution of values of $U_{\mathbf{h}}U_{\mathbf{h}+\mathbf{h}'}$ for a fixed value of $U_{\mathbf{h}}$. The situation differs from that considered in § 3·2, since, for a fixed value of $U_{\mathbf{h}}$, with $\mathbf{h}$ also fixed, there is already a distribution of values of $U_{\mathbf{h}}U_{\mathbf{h}+\mathbf{h}'}$, since the range of h' is unlimited. The exact form of this distribution is not specified when only $U_{\mathbf{h}}$ is given, but an expected distribution can be found, and this

Table 3·1

Conditions		Conclusions
$U_{2\mathbf{h}} > 0$	$U_{2\mathbf{h}} < 0$	
$U_{\mathbf{h}}^2 > \frac{1}{N}+\frac{U_{2\mathbf{h}}}{2N}$	$U_{\mathbf{h}}^2 < \frac{1}{N}-\frac{\lvert U_{2\mathbf{h}}\rvert}{2N}$	$s\left(U_{\mathbf{h}}^2-\frac{1}{N}\right) = s(2\mathbf{h}) = s(D_{2\mathbf{h}})$
$\frac{1}{N}+\frac{U_{2\mathbf{h}}}{2N} > U_{\mathbf{h}}^2 > \frac{1}{N}$	$\frac{1}{N}-\frac{\lvert U_{2\mathbf{h}}\rvert}{2N} < U_{\mathbf{h}}^2 < \frac{1}{N}$	$s\left(U_{\mathbf{h}}^2-\frac{1}{N}\right) = s(2\mathbf{h}) \neq s(D_{2\mathbf{h}})$
$U_{\mathbf{h}}^2 < \frac{1}{N}$	$U_{\mathbf{h}}^2 > \frac{1}{N}$	$s\left(U_{\mathbf{h}}^2-\frac{1}{N}\right) \neq s(2\mathbf{h}) \neq s(D_{2\mathbf{h}})$

is all that is required for the application of the probability theory. It is shown in Appendix III that

$$\theta(Z_{\mathbf{h},\mathbf{h}'}) = (\pi\varepsilon_2)^{-1} \times \exp\left(\frac{V_{\mathbf{h}}U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}{\varepsilon_2^2}\right) K_0\left\{\frac{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}{\varepsilon_2}\left(1+\frac{V_{\mathbf{h}}^2}{\varepsilon_2^2}\right)^{\frac{1}{2}}\right\}, \quad (4\cdot1)$$

where $\theta(Z_{\mathbf{h},\mathbf{h}'})dZ_{\mathbf{h},\mathbf{h}'}$ is the probability that $U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$ lies between $Z_{\mathbf{h},\mathbf{h}'}$ and $(Z+dZ)_{\mathbf{h},\mathbf{h}'}$. $K_0(x)$ is a zero-order Bessel function of the third kind, and is an even function of x. The distribution (4·1) is shown graphically in Fig. 2. It is very different from the normal distribution which Vand & Pepinsky (1953, p. 71)

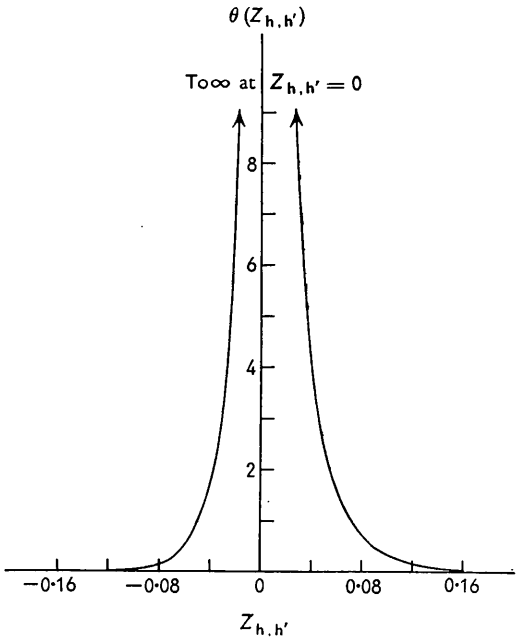

Fig. 2. The expected distribution of values of $U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$ $(= Z_{\mathbf{h},\mathbf{h}'})$ for the case where there are 40 equal atoms per unit cell and $U_{\mathbf{h}} = +0{\cdot}25$.

have assumed in a corresponding derivation. The first moment of the distribution (4·1) is, by definition, $\overline{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}^{h'}$. On evaluation from (4·1) it is found to be $V_{\mathbf{h}}$. This result,

$$V_{\mathbf{h}} = \overline{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}^{h'}, \quad (4\cdot2)$$

can be confirmed directly without the use of probability concepts (see Appendix II). When the atoms are equal it reduces to the known result

$$U_{\mathbf{h}} = N\overline{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}^{h'}. \quad (4\cdot3)$$

4·2. *Relations between $U_{\mathbf{h}}$ and $V_{\mathbf{h}}$*

Before any use can be made of (4·1) it is necessary to consider in more detail the relation between $U_{\mathbf{h}}$ and $V_{\mathbf{h}}$. When the atoms are equal $V_{\mathbf{h}} = U_{\mathbf{h}}/N$; when they are unequal the two are still closely correlated. As an approximation, take

$$V_{\mathbf{h}} \simeq K U_{\mathbf{h}}.$$

The 'least squares' value of K, which makes

$$\overline{(V_{\mathbf{h}} - KU_{\mathbf{h}})^2}^h$$

a minimum, is then given by

$$\overline{U_{\mathbf{h}}V_{\mathbf{h}}}^h = K\overline{U_{\mathbf{h}}^2}^h. \quad (4\cdot4)$$

Using the value of the left-hand side of (4·4) given in Appendix II we find $K = \varepsilon_3/\varepsilon_2$. The equation

$$V_{\mathbf{h}} = \overline{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}^{h'} \simeq \frac{\varepsilon_3}{\varepsilon_2}U_{\mathbf{h}} \quad (4\cdot5)$$

is a statistical form of Sayre's equation, valid when the atoms are unequal, but true only in the sense that it leads to a minimum value of

$$\sum_{\mathbf{h}}\left(V_{\mathbf{h}} - \frac{\varepsilon_3}{\varepsilon_2}U_{\mathbf{h}}\right)^2.$$

Furthermore, when $U_{\mathbf{h}}$ is fixed in magnitude and sign, we have

$$\langle V_{\mathbf{h}}\rangle = 2\sum_{j=1}^{\frac{1}{2}N} n_j^2\bar{c}_j^h = \frac{\varepsilon_3}{\varepsilon_2}U_{\mathbf{h}},$$

from (3·2). The variance (for which we write σ^2) of the distribution of $V_{\mathbf{h}}$, which will be approximately Gaussian about its mean value, is given by

$$\sigma^2 = \overline{\left(2\sum_{j=1}^{\frac{1}{2}N}\left(n_j^2 - \frac{\varepsilon_3}{\varepsilon_2}n_j\right)c_j\right]^2}^h.$$

Using (3·3), and making reasonable approximations, reduces this to

$$\sigma^2 = \varepsilon_4 - \varepsilon_3^2/\varepsilon_2, \quad (4\cdot6)$$

so that, given $U_{\mathbf{h}}$,

$$P(V_{\mathbf{h}}) = (2\pi\sigma^2)^{-\frac{1}{2}}\exp\left[-\frac{1}{2\sigma^2}\left(V_{\mathbf{h}} - \frac{\varepsilon_3}{\varepsilon_2}U_{\mathbf{h}}\right)^2\right]. \quad (4\cdot7)$$

From (4·7) it may be deduced in the usual way that, given $|U_{\mathbf{h}}|$ and $V_{\mathbf{h}}$,

$$P_+(U_{\mathbf{h}}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\frac{\varepsilon_3}{\varepsilon_2\varepsilon_4 - \varepsilon_3^2}|U_{\mathbf{h}}|V_{\mathbf{h}}\right), \quad (4\cdot8)$$

a result to which reference will be made later.

4·3. *The probability that $s(\mathbf{h}) = s(\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$*

When we are given only the value of $|U_{\mathbf{h}}|$ there are two possible forms of the distribution (4·1) which are *a priori* equally likely, the first having $V_{\mathbf{h}}$ positive and therefore being positive skew-symmetric, and the second being negative skew-symmetric. On the first hypothesis, the probability of obtaining a certain definite value of $U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$ is proportional to

$$\exp\left[\frac{+|V_{\mathbf{h}}|U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}{\varepsilon_2^2}\right]K_0\left[\frac{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}{\varepsilon_2}\left(1+\frac{V_{\mathbf{h}}^2}{\varepsilon_2^2}\right)^{\frac{1}{2}}\right], \quad (4\cdot9)$$

while on the second it is proportional to

$$\exp\left[\frac{-|V_{\mathbf{h}}|U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}{\varepsilon_2^2}\right]K_0\left[\frac{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}{\varepsilon_2}\left(1+\frac{V_{\mathbf{h}}^2}{\varepsilon_2^2}\right)^{\frac{1}{2}}\right]. \quad (4\cdot10)$$

It follows that

$$\frac{P_+(V_\mathbf{h})}{P_-(V_\mathbf{h})} = \frac{\text{expression (4·9)}}{\text{expression (4·10)}} = \exp\left[\frac{2|V_\mathbf{h}|U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}{\varepsilon_2^2}\right]. \quad (4·11)$$

Hence

$$P_+(V_\mathbf{h}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh\left(\frac{1}{\varepsilon_2^2}|V_\mathbf{h}|U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}\right). \quad (4·12)$$

When the atoms are equal, $P_+(V_\mathbf{h}) = P_+(U_\mathbf{h})$, $\varepsilon_2^2 = N^{-2}$, $|V_\mathbf{h}| = |U_\mathbf{h}|/N$ and (4·12) reduces to the result found by a less general derivation (Woolfson, 1954). When the atoms are unequal it does not appear to be possible to derive $P_+(U_\mathbf{h})$, as distinct from $P_+(V_\mathbf{h})$, from (4·1). The following derivation follows the lines of that already given by Woolfson (1954). For a fixed value of $U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$ the expected value of $U_\mathbf{h}$ is

$$\langle U_\mathbf{h}\rangle = \frac{\varepsilon_3}{\varepsilon_2^2}U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'} \quad (4·13)$$

(see Appendix III).

The distribution of $U_\mathbf{h}$ about this average value will be approximately Gaussian with variance ε_2. Thus, given $U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$,

$$P(U_\mathbf{h}) = (2\pi\varepsilon_2)^{-\frac{1}{2}}\exp\left[-\frac{1}{2\varepsilon_2}\left(U_\mathbf{h}-\frac{\varepsilon_3}{\varepsilon_2^2}U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}\right)^2\right], \quad (4·14)$$

from which it follows that

$$P_+(U_\mathbf{h}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh\left(\frac{\varepsilon_3}{\varepsilon_2^3}|U_\mathbf{h}|U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}\right), \quad (4·15)$$

which is the required result. On expressing (4·15) in terms of normalized structure factors and expanding tanh as far as the first power, one obtains exactly the expression given by Hauptman & Karle (1953, equation (3·30)). From (4·15) it follows that the general expression giving the probability of the truth of the sign relation (1·1) is

$$P_+(U_\mathbf{h}U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh\left(\frac{\varepsilon_3}{\varepsilon_2^3}|U_\mathbf{h}U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}|\right). \quad (4·16)$$

The result (4·16) shows that when the unitary structure factors are well outside the range where Harker–Kasper inequalities apply, the probability of the truth of relation (1·1) is independent of $|U_{\mathbf{h}-\mathbf{h}'}|$. This conclusion differs from that of Vand & Pepinsky (1953, p. 74), whose derivation we have already criticized.

4·4. *The probability that* $s(\mathbf{h}) = s(\sum_{\mathbf{h}'} U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'})$

In the previous section we considered the probability that an indication of $s(\mathbf{h})$ obtained as $s(U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'})$ was correct. Suppose that two sign indications are available from the values of $U_{\mathbf{h}_1}U_{\mathbf{h}+\mathbf{h}_1}$ and of $U_{\mathbf{h}_2}U_{\mathbf{h}+\mathbf{h}_2}$. If $V_\mathbf{h}$ is positive, the probability of obtaining these two values, which is equal to the product of the probabilities of obtaining them separately, is proportional to

$$\exp\left[\frac{+|V_\mathbf{h}|U_{\mathbf{h}_1}U_{\mathbf{h}+\mathbf{h}_1}}{\varepsilon_2^2}\right]K_0\left[\frac{U_{\mathbf{h}_1}U_{\mathbf{h}+\mathbf{h}_1}}{\varepsilon_2}\left(1+\frac{V_\mathbf{h}^2}{\varepsilon_2^2}\right)^{\frac{1}{2}}\right] \times \exp\left[\frac{+|V_\mathbf{h}|U_{\mathbf{h}_2}U_{\mathbf{h}+\mathbf{h}_2}}{\varepsilon_2^2}\right]K_0\left[\frac{U_{\mathbf{h}_2}U_{\mathbf{h}+\mathbf{h}_2}}{\varepsilon_2}\left(1+\frac{V_\mathbf{h}^2}{\varepsilon_2^2}\right)^{\frac{1}{2}}\right],$$

while if $V_\mathbf{h}$ is negative, the probability is proportional to the same expression with $-|V_\mathbf{h}|$ replacing $+|V_\mathbf{h}|$. Therefore

$$\frac{P_+(V_\mathbf{h})}{P_-(V_\mathbf{h})} = \exp\left[\frac{2}{\varepsilon_2^2}|V_\mathbf{h}|(U_{\mathbf{h}_1}U_{\mathbf{h}+\mathbf{h}_1}+U_{\mathbf{h}_2}U_{\mathbf{h}+\mathbf{h}_2})\right]. \quad (4·17)$$

A more rigorous derivation, making use of Baye's theorem (Uspensky, 1937) leads to the same conclusion. Equation (4·17) is easily extended to the case where any number of sign indications are available: the only effect is to replace $U_{\mathbf{h}_1}U_{\mathbf{h}+\mathbf{h}_1}+U_{\mathbf{h}_2}U_{\mathbf{h}+\mathbf{h}_2}$ by $\sum_{\mathbf{h}'} U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$, so that in general

$$P_+(V_\mathbf{h}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh\left(\frac{1}{\varepsilon_2^2}|V_\mathbf{h}|\sum_{\mathbf{h}'}U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}\right). \quad (4·18)$$

As the number of terms in the summation increases, we find, therefore, with a probability tending to certainty, that

$$s(V_\mathbf{h}) = s\left(\sum_{\mathbf{h}'}U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}\right), \quad (4·19)$$

a result which agrees with the (non-statistical) relation

$$V_\mathbf{h} = \overline{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}^{\mathbf{h}'}.$$

When the atoms are equal, (4·18) reduces to

$$P_+(U_\mathbf{h}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh\left(N|U_\mathbf{h}|\sum_{\mathbf{h}'}U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}\right). \quad (4·20)$$

If in (4·18) we replace the unknown $|V_\mathbf{h}|$ by its expected value $(\varepsilon_3/\varepsilon_2)|U_\mathbf{h}|$, and expand tanh retaining only one term, equation (3·36) of Hauptman & Karle (1953) is obtained. In this instance the approximation is particularly inadequate as there is no limit to the argument of tanh. Furthermore, Hauptman & Karle express their result as $P_+(U_\mathbf{h})$ and not as $P_+(V_\mathbf{h})$. This leads them to the conclusion that as the summation over $\mathbf{h}'$ is extended more widely, one finds with certainty that relation (1·3) is true, a result which is strictly correct only when the atoms are equal. In other words, their analysis makes no distinction between $s(\mathbf{h})$ and $s(V_\mathbf{h})$, for reasons similar to those we set out at the end of § 3·4.

In the case where the atoms are unequal, and a number of values of $U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$ are given, we have not been able to derive rigorously an expression for $P_+(U_\mathbf{h})$. The following derivation does, however, lead to a result consistent with others which have already been obtained. Suppose that m different values of $U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$, corresponding to m different values of $\mathbf{h}'$, are given. As suggested by earlier results, we *assume* that

$$\langle U_{\mathbf{h}} \rangle = k \sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'} . \quad (4\cdot21)$$

The best value of k is then given by the least-squares solution,

$$\overline{U_{\mathbf{h}} \sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}}^{\mathbf{h},\mathbf{h}'} = k \overline{\left(\sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}\right)^2}^{\mathbf{h},\mathbf{h}'} . \quad (4\cdot22)$$

The left-hand side of this equation reduces to $m\varepsilon_3$ (see Appendix II). The right-hand side can be shown to reduce to $k(m\varepsilon_2^2+(m^2-m)\varepsilon_4)$ (we omit the proof which is exact but lengthy). Therefore,

$$k = \frac{\varepsilon_3}{\varepsilon_2^2+(m-1)\varepsilon_4} . \quad (4\cdot23)$$

We now further assume that $U_{\mathbf{h}}$ has a Gaussian distribution about the expected value and that the variance, for which we write ϱ^2, can be obtained from

$$\varrho^2 = \overline{(U_{\mathbf{h}} - k \sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'})^2}^{\mathbf{h},\mathbf{h}'} .$$

This leads readily to

$$\varrho^2 = \frac{\varepsilon_2^3+(m-1)\varepsilon_2\varepsilon_4-m\varepsilon_3^2}{\varepsilon_2^2+(m-1)\varepsilon_4} . \quad (4\cdot24)$$

Thus, given m values of $U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}$,

$$P(U_{\mathbf{h}}) = (2\pi\varrho^2)^{-\frac{1}{2}} \exp\left[-\frac{1}{2\varrho^2}(U_{\mathbf{h}} - k \sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'})^2\right] , \quad (4\cdot25)$$

where ϱ^2 and k are given by (4·24) and (4·23) respectively. It follows from (4·25) that

$$P_+(U_{\mathbf{h}}) = \tfrac{1}{2}+\tfrac{1}{2} \tanh\left(\frac{\varepsilon_3}{\varepsilon_2^3+(m-1)\varepsilon_2\varepsilon_4-m\varepsilon_3^2} |U_{\mathbf{h}}| \sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}\right) . \quad (4\cdot26)$$

The probability of the truth of the sign relation (1·3) is therefore

$$P_+(U_{\mathbf{h}} \sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}) = \tfrac{1}{2}+\tfrac{1}{2} \tanh\left(\frac{\varepsilon_3}{\varepsilon_2^3+(m-1)\varepsilon_2\varepsilon_4-m\varepsilon_3^2} |U_{\mathbf{h}} \sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}|\right) . \quad (4\cdot27)$$

The derivation of (4·26) is not rigorous. We have confidence in its correctness, however, because it passes four non-trivial tests:

(i) When $P_+(V_{\mathbf{h}})$ is derived by a similar route, we obtain (4·18) which we derived earlier by a comparatively exact calculation.

(ii) When only one value of $U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}$ is given, $m = 1$. Equation (4·26) then reduces to (4·15).

(iii) When a very large number of values of $U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}$ are given, $\sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}$ tends to $m\overline{U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}}^{\mathbf{h}'} = mV_{\mathbf{h}}$, and (4·26) becomes identical with (4·8).

(iv) When the atoms are equal (4·26) reduces to (4·20) for all values of m.

We note from (4·27) that as m, the number of terms in the summation, increases indefinitely, the probability that relation (1·3) is true does not tend to unity, but to a maximum of

$$P_+(U_{\mathbf{h}}V_{\mathbf{h}}) = \tfrac{1}{2}+\tfrac{1}{2} \tanh\left(\frac{\varepsilon_3}{\varepsilon_2\varepsilon_4-\varepsilon_3^2} |U_{\mathbf{h}}V_{\mathbf{h}}|\right) . \quad (4\cdot28)$$

The actual value of $P_+(U_{\mathbf{h}}V_{\mathbf{h}})$ for a particular structure factor cannot be calculated unless both $|U_{\mathbf{h}}|$ and $|V_{\mathbf{h}}|$ are known. However, the average value of this probability can be calculated, and will apply to a group of structure factors all of which have the same $|U_{\mathbf{h}}|$. This average probability is simply the *a priori* probability (that is, before anything is known about values of $U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}$) that $U_{\mathbf{h}}$ and $V_{\mathbf{h}}$ are alike in sign. From (4·8) it is given by

$$P_+(U_{\mathbf{h}}V_{\mathbf{h}}) = \tfrac{1}{2}+(2\pi\sigma^2)^{-\frac{1}{2}} \int_0^{(\varepsilon_3/\varepsilon_2)U_{\mathbf{h}}} \exp\left(-\frac{V_{\mathbf{h}}^2}{2\sigma^2}\right) dV_{\mathbf{h}} .$$

Writing $\varphi(x) = (2\pi)^{-\frac{1}{2}} \int_0^x \exp(-\frac{1}{2}t^2)\,dt$, a function which is tabulated by Uspensky (1937), we find

$$P_+(U_{\mathbf{h}}V_{\mathbf{h}}) = \tfrac{1}{2}+\varphi\left(\frac{U_{\mathbf{h}}\varepsilon_3}{\varepsilon_2^{\frac{1}{2}}(\varepsilon_2\varepsilon_4-\varepsilon_3^2)^{\frac{1}{2}}}\right) = \tfrac{1}{2}+\varphi\left(\frac{E_{\mathbf{h}}\varepsilon_3}{(\varepsilon_2\varepsilon_4-\varepsilon_3^2)^{\frac{1}{2}}}\right) . \quad (4\cdot29)$$

The value of the factor φ will differ appreciably from $\frac{1}{2}$ only for rather small structure factors. For example, Table 4·1 gives some values for a structure which contains atoms of relative weights two and one in the proportion 1:8.

Table 4·1

$\|E_{\mathbf{h}}\|$	0	0·1	0·25	0·5	0·75	1·0	2·0
φ	0	0·11	0·26	0·42	0·48	0·498	0·5
$P_+(U_{\mathbf{h}}V_{\mathbf{h}})$	0·5	0·61	0·76	0·92	0·98	0·998	1·0

It is apparent that in this case, (1·3) *can* be used to find $s(\mathbf{h})$ with almost complete certainty for any $U_{\mathbf{h}}$ whose magnitude is not much less than the r.m.s. value. For small structure factors, however, (1·3) gives $s(\mathbf{h})$ with a probability not much in excess of $\frac{1}{2}$. When the atoms are equal, $\varphi = \frac{1}{2}$ and (1·3) is valid for all structure factors, as is shown, of course, by Sayre's equation.

4·5. *The number of sign-determining relations*

The other sign-determining formulae given by Hauptman & Karle (1953) for space group $P\bar{1}$ can be derived from those we have already considered, and are not really independent of them. To simplify the discussion, we assume that the atoms are equal. Corresponding to their equation (3·31), which is, in our notation,

$$P_+(U_{2\mathbf{h}+\mathbf{h}'}) = \tfrac{1}{2}+(1/4N)|E_{2\mathbf{h}+\mathbf{h}'}|(E_{\mathbf{h}}^2-1)E_{\mathbf{h}'} \quad (4\cdot30)$$

we find

$$\tfrac{1}{2}+\tfrac{1}{2}\tanh\left\{\tfrac{1}{2}N|U_{2\mathbf{h}+\mathbf{h}'}|\left(U_{\mathbf{h}}^2-\frac{1}{N}\right)U_{\mathbf{h}'}\right\}. \quad (4\cdot31)$$

The proof of this result will merely be indicated. It follows from the fact that, given $U_{\mathbf{h}}^2$ and $U_{\mathbf{h}'}$,

$$\langle U_{2\mathbf{h}+\mathbf{h}'}\rangle = \tfrac{1}{2}\left(U_{\mathbf{h}}^2-\frac{1}{N}\right)U_{\mathbf{h}'}, \quad (4\cdot32)$$

as can be found in the usual way. This result is, however, not really additional to those we have already found, for, given $U_{\mathbf{h}}^2$, $\langle U_{2\mathbf{h}}\rangle = \tfrac{1}{2}(U_{\mathbf{h}}^2-1/N)$ (see § 3·2), and, given $\langle U_{2\mathbf{h}}\rangle$ and $U_{\mathbf{h}'}$, $\langle U_{2\mathbf{h}+\mathbf{h}'}\rangle = \langle U_{2\mathbf{h}}\rangle U_{\mathbf{h}'}$ (see for example, Appendix III), from which (4·32) follows. There is however no reason why one should use $\langle U_{2\mathbf{h}}\rangle$ when one already *knows* $|U_{2\mathbf{h}}|$ and its probable sign. In other words one should use

$$s(2\mathbf{h}) = s(U_{\mathbf{h}}^2-1/N)$$

with probability given by (3·10) followed by

$$s(2\mathbf{h}+\mathbf{h}') = s(2\mathbf{h})s(\mathbf{h}')$$

with probability given by (4·15) rather than

$$s(2\mathbf{h}+\mathbf{h}') = s\{(U_{\mathbf{h}}^2-1/N)U_{\mathbf{h}'}\}$$

with probability given by (4·31).

To take a numerical example, suppose $N = 40$, $|U_{\mathbf{h}}| = |U_{\mathbf{h}'}| = |U_{2\mathbf{h}}| = |U_{2\mathbf{h}+\mathbf{h}'}| = 0{\cdot}3$ and $s(\mathbf{h}')$ is positive. Then $P_+(U_{2\mathbf{h}+\mathbf{h}'})$ is 0·63 by the first route, and 0·56 by the second. The former is to be preferred, since it takes into account the known value of $|U_{2\mathbf{h}+\mathbf{h}'}|$, while the latter does not. Similar remarks apply with added force to the formulae (3·33), (3·34) and (3·35) (Hauptman & Karle, 1953).

We conclude that the relations

$$s(2\mathbf{h}) = s(U_{\mathbf{h}}^2-\varepsilon_2)$$

and

$$s(\mathbf{h}) = s\left(\overline{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}^{h'}\right)$$

are the *only* sign-determining relations for space group $P\bar{1}$.

5. Sign-determining formulae for other space groups

5·1. *General discussion*

We shall not attempt a detailed study of the formulae which apply to other space groups, but some indication of their nature can readily be found. For example, for space group $P2_1/a$ Hauptman & Karle (1953) have derived a result which, in our notation, is

$$P_+(U_{2h,0,2l}) = \tfrac{1}{2}+\frac{\varepsilon_3|E_{2h,0,2l}|}{2\sqrt{2}\,.\,(\varepsilon_2)^{3/2}}\sum_k(-1)^{h+k}(E_{hkl}^2-1)\,. \quad (5\cdot1)$$

We find that

$$P_+(V_{2h,0,2l}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{1}{\varepsilon_2^2}|V_{2h,0,2l}|\sum_k(-1)^{h+k}(U_{hkl}^2-\varepsilon_2)\right]. \quad (5\cdot2)$$

The result (5·2) leads to the conclusion that

$$s(V_{2h,0,2l}) = s\{\sum_k(-1)^{h+k}(E_{hkl}^2-1)\} \quad (5\cdot3)$$

with a probability tending to certainty when the range of values of k is sufficiently great. This can be confirmed by a simple physical argument. Vand & Pepinsky (1953) have pointed out that $\overline{(-1)^{h+k}(E_{hkl}^2-1)}$ is the Fourier coefficient of a 'sharpened' Patterson–Harker section. The peak in this function which corresponds to the jth atom has weight proportional to n_j^2, as has the peak in the function whose Fourier coefficient is $V_{2h,0,2l}$. From the identity of these functions one can derive the result

$$V_{2h,0,2l} = \varepsilon_2^{\,k}\overline{(-1)^{h+k}(E_{hkl}^2-1)}^{k}, \quad (5\cdot4)$$

which holds when k covers an infinite range. This confirms the conclusion reached from the probability expression.

Since it is only for the smaller structure factors that one need distinguish $s(2h,0,2l)$ from $s(V_{2h,0,2l})$, our conclusion is in practice no different from that of Hauptman & Karle as far as (5·3) is concerned. The only other useful sign-determining relations for this space group are (1·1) and (1·3) for which probabilities are as for space group $P\bar{1}$. The added symmetry gives relation (1·1) greater scope however; for example, since $s(hkl) = (-1)^{h+k}s(h\bar{k}l)$, two structure factors of known sign can be used to obtain sign indications for four more, as compared with only two more in space group $P\bar{1}$.

Similar remarks apply to other centrosymmetric space groups, and in particular the 'signs from intensities' formulae of Hauptman & Karle always give $s(V_{\mathbf{h}})$, and have a simple explanation in terms of the Patterson function. The formulae given by Woolfson (1954) are apparently an exception to this rule.

6. Discussion

The results which we have found in the foregoing sections show that the only fundamental sign relations for space group $P\bar{1}$ are that, with calculable probabilities,

$$s(2\mathbf{h}) = s(U_{\mathbf{h}}^2-\varepsilon_2), \quad (6\cdot1)$$

$$s(\mathbf{h}) = s(\mathbf{h}')s(\mathbf{h}+\mathbf{h}'), \quad (6\cdot2)$$

and

$$s(\mathbf{h}) = s\{\overline{U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}}^{h'}\}. \quad (6\cdot3)$$

Of these the first was found by Hauptman & Karle (1953), but the other two have been known for some time and their properties and limitations have been discussed in the literature. For space groups of higher symmetry the formulae which replace (6·1) give the

same information as may be found from a Patterson–Harker section; for some purposes they give it in a more convenient form.

The analyses of Hauptman & Karle are formally correct, potentially more so than those of this paper, since they treat the distribution of structure factors as a random-walk problem, and take account of the variation in the relative values of scattering factors. However, their final results are expressed to a very poor approximation, and, as we have indicated, each is usually the first two terms of the series expansions of the expressions which we give. Furthermore, by losing sight of the physical background of the problem, Hauptman & Karle have wrongly interpreted their results, and it is clear that their discovery of (6·1) and rediscovery of (6·3) leaves the phase problem much as it was. Their claim to have solved this problem was apparently strengthened by the determination of the structure of colemanite, $CaB_3O_4(OH)_3.H_2O$ (Christ, Clark & Evans, 1954), in which their method was used exclusively. We shall use this structure as an example for the application of the formulae which we have derived.

Since the atoms of colemanite are unequal we must first consider the probability that $s(\mathbf{h}) = s(V_\mathbf{h})$.

Taking $n_{Ca}:n_O:n_B$ as 5:1·6:1 we find from (4·29) that

$$P_+(U_\mathbf{h}V_\mathbf{h}) = \tfrac{1}{2}+\varphi(1\cdot92E_\mathbf{h}) . \qquad (6\cdot4)$$

Values for this probability are given in Table 6·1.

Table 6·1

$\lvert E_\mathbf{h}\rvert$	0·5	1·0	1·5	2·0	2·5	3·0
$P_+(U_\mathbf{h}V_\mathbf{h})$	0·83	0·97	1·00	1·00	1·00	1·00

For structure factors with $|E_\mathbf{h}| \geqslant 1\cdot0$ it is practically certain that $s(\mathbf{h}) = s(V_\mathbf{h})$ and there will be few failures of the relation as long as $|E_\mathbf{h}| \geqslant 0\cdot5$. The colemanite structure has space group $P2_1/a$, and its Patterson–Harker section will be dominated by the Ca–Ca peaks which should be $5^2 \div 1\cdot6^2 = 10$ times greater than any others. Even if the section contains a few 'non-Harker' peaks it is clear that the signs determined from

$$s(V_{2h,0,2l}) = s\{\sum_k (-1)^{h+k}(E^2_{hkl}-1)\} \qquad (6\cdot5)$$

will be correct for almost all structure factors to which the calcium atom makes an appreciable contribution. We would estimate that, even allowing for the influence of 'non-Harker' peaks, (6·5) would correctly determine the signs of about 98% of the $(2h,0,2l)$ structure factors with $|E_\mathbf{h}| \geqslant 0\cdot5$. It is worth noting at this point that somewhat better results could have been achieved by evaluating the Patterson–Harker section and deducing the signs of most of the $(2h,0,2l)$ *and* of the $(2h,0,l)$ structure factors from the position of the calcium atom. It is also worth emphasizing, as Vand & Pepinsky (1953) have already done, that while (6·5) can give no more information than is contained in a Patterson–Harker section, it may actually give less, as in this case.

We have shown that of the other formulae which were used to determine the structure of colemanite, none is independent of, or more powerful than (6·1), (6·2) and (6·3). On substituting the appropriate colemanite constants, equation (4·15) gives

$$P_+(U_\mathbf{h}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh(0\cdot24|E_\mathbf{h}|E_{\mathbf{h}'}E_{\mathbf{h}+\mathbf{h}'}) . \qquad (6\cdot6)$$

Table 6·2 shows the probability that $s(\mathbf{h})$ is positive when $s(\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ is positive. Values of $|E| > 3$ will be very rare.

Table 6·2

$E_\mathbf{h}E_{\mathbf{h}'}E_{\mathbf{h}+\mathbf{h}'}$	3×3×3	2×2×2	2×2×1	2×1×1	1×1×1
$P_+(U_\mathbf{h})$	1·00	0·98	0·87	0·72	0·62

It is seen that the situation is very favourable for the application of (6·2) and sign indications will almost certainly be correct when the largest $|E|$'s are used. For the smaller $|E|$'s the more powerful relation (6·3) may then be used and signs should be determined with a high degree of probability even down to $|E|$'s of about 0·5, this lower limit of $|E|$ being set by (6·4). The sign-determining relations are greatly strengthened by the presence of a heavy atom. For example, if all the atoms (except hydrogen) were equal in colemanite, (6·6) would become

$$P_+(U_\mathbf{h}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh(0\cdot14|E_\mathbf{h}|E_{\mathbf{h}'}E_{\mathbf{h}+\mathbf{h}'})$$

and the probabilities given in Table 6·2 would be 1·00, 0·91, 0·75, 0·64 and 0·58 respectively. The increase of $P_+(U_\mathbf{h}V_\mathbf{h})$ to 1·00 from the values given in Table 6·1 does very little to redress this less favourable situation.

Our conclusion is, in short, that the successful determination of the structure of colemanite depended for its outcome on known methods which were unwittingly given a heavy mathematical disguise and applied in a most complicated fashion which offered no advantages.

We would now like to comment on the validity of the formulae which we obtain. These are reasonably exact but they do not apply when N is small or when the structure factors are large enough to be related by inequalities. Certain other assumptions of the probability theory should be borne in mind. When we say that $s(\mathbf{h})$ is given by (6·3), with probability given by (4·26), we are assuming that the values of $U_{\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$ are random selections from an infinitely large population. This is not so in practice, but it seems likely that the necessary conditions are well enough satisfied if the range of data available is sufficient to resolve the atoms in a Fourier synthesis. Again, our theory assumes that successive values of $(-1)^{h+k}(E^2_{hkl}-1)$ used in (5·2) are taken at random from an infinite range of values of k. In practice the

range of k is very limited and the systematic error thereby introduced can be correlated with the existence of non-Harker peaks in the Patterson–Harker section. What has just been said demonstrates the value of considering the physical interpretation of the various probability relations. The failure of Hauptman & Karle to distinguish between $s(D_{\mathbf{h}})$ and $s(2\mathbf{h})$ and also between $s(V_{\mathbf{h}})$ and $s(\mathbf{h})$ would not have arisen had they been aware of the physical basis of their results.

Although we have been critical of the results of other workers in this field, we wish to acknowledge that without the ideas, results and stimulus provided by their publications this paper could not have been written. We also wish to express our thanks to Dr A. S. Douglas for some assistance with the mathematics. One of us (M. M. W.) gratefully acknowledges the financial assistance of the Department of Scientific and Industrial Research.

APPENDIX I

The unitary structure factor $U_{\mathbf{h}}$ is given by

$$U_{\mathbf{h}} = 2\sum_{j=1}^{\frac{1}{2}N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j .$$

It is proposed to find the probability that $\cos 2\pi\mathbf{h}\cdot\mathbf{r}_1$ lies between c_1 and c_1+dc_1 when $U_{\mathbf{h}}$ has a given value.

Let us consider that the structure is formed by a random selection of the $\mathbf{r}_j$'s. Then the probability that $\cos 2\pi\mathbf{h}\cdot\mathbf{r}_1$ lies between c_1 and c_1+dc_1 is

$$dc_1/2\pi(1-c_1^2)^{\frac{1}{2}} . \qquad \text{(A. 1)}$$

The probability that the remaining $(N-2)\mathbf{r}_j$'s (for which $j \neq 1$) will be such that

$$2\sum_{j=2}^{\frac{1}{2}N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j$$

lies between

$$U_{\mathbf{h}}-2n_1c_1 \quad \text{and} \quad U_{\mathbf{h}}-2n_1(c_1+dc_1)$$

is

$$[2\pi(\varepsilon_2-2n_1^2)]^{-\frac{1}{2}} \times \exp\left[-(U_{\mathbf{h}}-2n_1c_1)^2/2(\varepsilon_2-2n_1^2)\right]2n_1dc_1 . \qquad \text{(A. 2)}$$

The latter result may be deduced from the distribution of structure factors given by Wilson (1949).

When the above two conditions are satisfied, $U_{\mathbf{h}}$ lies between $U_{\mathbf{h}}$ and $U_{\mathbf{h}}+2n_1dc_1$ and the probability of this is

$$(2\pi\varepsilon_2)^{-\frac{1}{2}} \exp\left(-U_{\mathbf{h}}^2/2\varepsilon_2\right)2n_1dc_1 . \qquad \text{(A. 3)}$$

For a *fixed* value of $U_{\mathbf{h}}$ the probability that $\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j$ lies between c_1 and c_1+dc_1, $\psi(c_1)dc_1$, is the product of the probabilities given by (A. 1) and (A. 2) divided by the probability given by (A. 3). Generalizing this result for the jth atom we have

$$\psi(c_j) = \frac{1}{2\pi(1-c_j^2)^{\frac{1}{2}}}\left(\frac{\varepsilon_2}{\varepsilon_2-2n_j^2}\right)^{\frac{1}{2}} \exp\left[\frac{U_{\mathbf{h}}^2}{2\varepsilon_2}-\frac{(U_{\mathbf{h}}-2n_jc_j)^2}{2(\varepsilon_2-2n_j^2)}\right].$$

If $n_j^4/\varepsilon_2^2 \ll 1$ then

$$\frac{1}{\varepsilon_2-2n_j^2} = \frac{1}{\varepsilon_2}\left(1-\frac{2n_j^2}{\varepsilon_2}\right)^{-1} = \frac{1}{\varepsilon_2}+\frac{2n_j^2}{\varepsilon_2^2}$$

and

$$(1+2n_j^2/\varepsilon_2)^{\frac{1}{2}} = 1+n_j^2/\varepsilon_2 ,$$

whence we find that

$$\psi(c_j) = \frac{1}{2\pi(1-c_j^2)^{\frac{1}{2}}}\left(1+\frac{n_j^2}{\varepsilon_2}\right)\exp\left(-\frac{n_j^2U_{\mathbf{h}}^2}{\varepsilon_2^2}\right) \times \exp\left[\frac{2}{\varepsilon_2}\left(1+\frac{2n_j^2}{\varepsilon_2}\right)(n_jc_jU_{\mathbf{h}}-n_j^2c_j^2)\right], \qquad \text{(A. 4)}$$

which is the required result.

The exponential terms of (A. 4) may be expanded as a power series, and terms of order N^{-2} may be ignored. Since $\overline{U_{\mathbf{h}}^2}^h = N^{-1}$ for equal atoms, then terms of order $U_{\mathbf{h}}^4$ and $U_{\mathbf{h}}^2/N$ fall into this category. Expanding and rearranging terms, we have

$$\psi(c_j) = \frac{1}{2\pi(1-c_j^2)^{\frac{1}{2}}}\left\{1-\frac{n_j^2}{\varepsilon_2^2}(U_{\mathbf{h}}^2-\varepsilon_2)\right\} \times\left\{1+\left(\frac{2n_jU_{\mathbf{h}}}{\varepsilon_2}+\frac{4n_j^3U_{\mathbf{h}}}{\varepsilon_2^2}\right)c_j+\left(\frac{2n_j^2U_{\mathbf{h}}^2}{\varepsilon_2^2}-\frac{2n_j^2}{\varepsilon_2}\right)c_j^2 +\left(\frac{4n_j^3U_{\mathbf{h}}^3}{3\varepsilon_2^3}-\frac{4n_j^3U_{\mathbf{h}}}{\varepsilon_2^2}\right)c_j^3\right\} . \qquad \text{(A. 5)}$$

The pth moment of this distribution $\overline{c_j^p}$ is easily calculable for any p from

$$\overline{c_j^p} = \int_{\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j=0}^{2\pi} \psi(c_j)c_j^p\,dc_j$$

when the expanded form (A. 5) is used. The first few moments are given in § 3·2.

APPENDIX II

(i) To prove that $\overline{U_{\mathbf{h}}^m U_{m\mathbf{h}}}^h = \varepsilon_{m+1}$.

For $m = 0$ and $m = 1$ well known results are obtained. For $m = 2$ it is required to prove that

$$\overline{U_{\mathbf{h}}^2 U_{2\mathbf{h}}}^h = \varepsilon_3 .$$

Now

$$U_{\mathbf{h}}^2U_{2\mathbf{h}} = 8\left(\sum_{j=1}^{\frac{1}{2}N} n_j\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j\right)^2\left(\sum_{j=1}^{\frac{1}{2}N} n_j\cos 4\pi\mathbf{h}\cdot\mathbf{r}_j\right).$$

The term $n_j^2\cos^2 2\pi\mathbf{h}\cdot\mathbf{r}_j$ which appears on expanding the first bracket can be put as $\frac{1}{2}n_j^2(\cos 4\pi\mathbf{h}\cdot\mathbf{r}_j+1)$. On multiplying this particular term by $n_j\cos 4\pi\mathbf{h}\cdot\mathbf{r}_j$ from the second bracket, a term $\frac{1}{2}n_j^3\cos^2 4\pi\mathbf{h}\cdot\mathbf{r}_j$ appears. All other terms involve products of cosines, and therefore vanish when an average over an infinite range of $\mathbf{h}$ is made. That is,

$$\overline{U_{\mathbf{h}}^2 U_{2\mathbf{h}}}^{h} = 8\sum_{j=1}^{\frac{1}{2}N} \tfrac{1}{2} n_j^3 \overline{\cos^2 4\pi\mathbf{h}\cdot\mathbf{r}_j}^{h} = 2\sum_{j=1}^{\frac{1}{2}N} n_j^3 = \varepsilon_3 . \qquad \text{(A. 6)}$$

The proof for other values of m is similar. The result for $m = 2$ can also be found by noting that $\overline{U_{\mathbf{h}}^2 U_{2\mathbf{h}}}^{h}$ measures the degree of correlation between the function whose Fourier coefficient is $U_{\mathbf{h}}^2$ and that whose coefficient is $U_{2\mathbf{h}}$. This alternative derivation will not be given; it does, however, show that the result (A. 6) is true as soon as the range of values of $\mathbf{h}$ is great enough to give the Patterson function whose coefficient is $U_{\mathbf{h}}^2$, as a set of resolved peaks.

(ii) To prove that $V_{\mathbf{h}} = \overline{U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}}^{h'}$.

We write

$$U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'} = 4\left(\sum_{j=1}^{\frac{1}{2}N} n_j \cos 2\pi\mathbf{h}'\cdot\mathbf{r}_j\right) \times \left(\sum_{j=1}^{\frac{1}{2}N} n_j (\cos 2\pi\mathbf{h}\cdot\mathbf{r}_j \cos 2\pi\mathbf{h}'\cdot\mathbf{r}_j - \sin 2\pi\mathbf{h}\cdot\mathbf{r}_j \sin 2\pi\mathbf{h}'\cdot\mathbf{r}_j)\right) .$$

On multiplying out and averaging over all $\mathbf{h}'$, the only term which does not vanish gives

$$\overline{U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}}^{h'} = 4\sum_{j=1}^{\frac{1}{2}N} n_j^2 \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j \overline{\cos^2 2\pi\mathbf{h}'\cdot\mathbf{r}_j}^{h'} = V_{\mathbf{h}} . \qquad \text{(A. 7)}$$

(iii) To prove $\overline{U_{\mathbf{h}} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}}^{h,h'} = \varepsilon_3$.

Taking the average over $\mathbf{h}'$ first,

$$U_{\mathbf{h}} \overline{U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}}^{h'} = U_{\mathbf{h}} V_{\mathbf{h}} , \quad \text{from (A. 7) above.}$$

Thus

$$\overline{U_{\mathbf{h}} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}}^{h,h'} = \overline{U_{\mathbf{h}} V_{\mathbf{h}}}^{h} .$$

But

$$U_{\mathbf{h}} V_{\mathbf{h}} = 4\left(\sum_{j=1}^{\frac{1}{2}N} n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j\right)\left(\sum_{j=1}^{\frac{1}{2}N} n_j^2 \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j\right) ,$$

so that

$$\overline{U_{\mathbf{h}} V_{\mathbf{h}}}^{h} = 4\sum_{j=1}^{\frac{1}{2}N} n_j^3 \overline{\cos^2 2\pi\mathbf{h}\cdot\mathbf{r}_j}^{h} = \varepsilon_3 ,$$

which is the required result.

Another derivation can be given which shows that the results $V_{\mathbf{h}} = \overline{U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}}^{h'}$ and $\overline{U_{\mathbf{h}} V_{\mathbf{h}}}^{h} = \varepsilon_3$ are true as soon as the values of $\mathbf{h}$ cover a range such that the function whose Fourier coefficient is $U_{\mathbf{h}}$ consists of a set of resolved peaks.

APPENDIX III

The unitary structure factor $U_{\mathbf{h}+\mathbf{h}'}$ may be written as

$$U_{\mathbf{h}+\mathbf{h}'} = \sum_{j=1}^{\frac{1}{2}N} \xi_j + \sum_{j=1}^{\frac{1}{2}N} \eta_j ,$$

where

$$\xi_j = 2n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j \cos 2\pi\mathbf{h}'\cdot\mathbf{r}_j$$

and

$$\eta_j = -2n_j \sin 2\pi\mathbf{h}\cdot\mathbf{r}_j \sin 2\pi\mathbf{h}'\cdot\mathbf{r}_j .$$

If $U_{\mathbf{h}}$ is fixed in value and index, and $U_{\mathbf{h}'}$ is of fixed value, then

$$\overline{\xi}_j = \overline{2n_j \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j \cos 2\pi\mathbf{h}'\cdot\mathbf{r}_j}^{h'} = (2n_j^2/\varepsilon_2) U_{\mathbf{h}'} \cos 2\pi\mathbf{h}\cdot\mathbf{r}_j ,$$

where the mean value of $\cos 2\pi\mathbf{h}'\cdot\mathbf{r}_j$ is given by (3·2). The variance of ξ_j is $\alpha_j^2 = \overline{\xi_j^2} - (\overline{\xi_j})^2$, but $(\overline{\xi_j})^2$ (of order N^{-4}) may be ignored in comparison to $\overline{\xi_j^2}$ (of order N^{-2}). Then

$$\alpha_j^2 = \overline{4n_j^2 \cos^2 2\pi\mathbf{h}\cdot\mathbf{r}_j \cos^2 2\pi\mathbf{h}'\cdot\mathbf{r}_j}^{h'} = 2n_j^2 \cos^2 2\pi\mathbf{h}\cdot\mathbf{r}_j .$$

Similarly we find that η_j has mean value $\overline{\eta_j} = 0$ and variance $\beta_j^2 = 2n_j^2 \sin^2 2\pi\mathbf{h}\cdot\mathbf{r}_j$.

If the variables ξ_j and η_j are assumed to be independent, then the application of the central-limit theorem shows that $U_{\mathbf{h}+\mathbf{h}'}$ has a Gaussian distribution about a mean value

$$\sum_{j=1}^{\frac{1}{2}N} \overline{\xi}_j + \sum_{j=1}^{\frac{1}{2}N} \overline{\eta}_j = V_{\mathbf{h}} U_{\mathbf{h}'}/\varepsilon_2$$

with variance

$$\sum_{j=1}^{\frac{1}{2}N} \alpha_j^2 + \sum_{j=1}^{\frac{1}{2}N} \beta_j^2 = \varepsilon_2 .$$

The probability that $U_{\mathbf{h}+\mathbf{h}'}$ lies between $U_{\mathbf{h}+\mathbf{h}'}$ and $U_{\mathbf{h}+\mathbf{h}'} + dU_{\mathbf{h}+\mathbf{h}'}$ is thus

$$\mu(U_{\mathbf{h}+\mathbf{h}'}) dU_{\mathbf{h}+\mathbf{h}'} = (2\pi\varepsilon_2)^{-\frac{1}{2}} \times \exp\left[-\frac{(U_{\mathbf{h}+\mathbf{h}'} - V_{\mathbf{h}} U_{\mathbf{h}'}/\varepsilon_2)^2}{2\varepsilon_2}\right] dU_{\mathbf{h}+\mathbf{h}'} . \qquad \text{(A. 8)}$$

(If the distribution is found when $\mathbf{h}$ is variable but $U_{\mathbf{h}}$ fixed in magnitude, the distribution of $U_{\mathbf{h}+\mathbf{h}'}$ is given by (A. 8) with $V_{\mathbf{h}}$ replaced by its expected value, $(\varepsilon_3/\varepsilon_2)U_{\mathbf{h}}$. Under these conditions an incorrect value of $\overline{U_{\mathbf{h}+\mathbf{h}'}}$, $U_{\mathbf{h}} U_{\mathbf{h}'}$, was found by Woolfson (1954); the true value of $\overline{U_{\mathbf{h}+\mathbf{h}'}}$ is $(\varepsilon_3/\varepsilon_2^2) U_{\mathbf{h}} U_{\mathbf{h}'}$ which equals $U_{\mathbf{h}} U_{\mathbf{h}'}$ only for the case of equal atoms.)

Since we now wish to find the distribution of $U_{\mathbf{h}+\mathbf{h}'} U_{\mathbf{h}'}$ for a fixed $\mathbf{h}$, we may consider the problem in the following two stages:

(*a*) $U_{\mathbf{h}'}$ may take all possible values and will have a distribution function

$$P(U_{\mathbf{h}'}) = (2\pi\varepsilon_2)^{-\frac{1}{2}} \exp(-U_{\mathbf{h}'}^2/2\varepsilon_2) .$$

(*b*) For each $U_{\mathbf{h}'}$ the associated $U_{\mathbf{h}+\mathbf{h}'}$ will have a value governed by the distribution function (A. 8).

If the product $U_{\mathbf{h}+\mathbf{h}'} U_{\mathbf{h}'}$ has a value between $Z_{\mathbf{h},\mathbf{h}'}$ and $Z_{\mathbf{h},\mathbf{h}'} + dZ_{\mathbf{h},\mathbf{h}'}$ and $U_{\mathbf{h}'}$ has a value between y and $y + dy$ then $U_{\mathbf{h}+\mathbf{h}'}$ has a value between $Z_{\mathbf{h},\mathbf{h}'}/y$ and $(Z_{\mathbf{h},\mathbf{h}'} + dZ_{\mathbf{h},\mathbf{h}'})/y$. The total probability of a value of $U_{\mathbf{h}+\mathbf{h}'} U_{\mathbf{h}'}$ between $Z_{\mathbf{h},\mathbf{h}'}$ and $Z_{\mathbf{h},\mathbf{h}'} + dZ_{\mathbf{h},\mathbf{h}'}$ is therefore

$$\theta(Z_{\mathbf{h},\mathbf{h}'})dZ_{\mathbf{h},\mathbf{h}'}$$
$$= 2\int_{y=0}^{\infty}\frac{1}{y}P(y)\mu\left(\frac{Z_{\mathbf{h},\mathbf{h}'}}{y}\right)dy\,dZ_{\mathbf{h},\mathbf{h}'}$$
$$= (\pi\varepsilon_2)^{-1}\int_{y=0}^{\infty}\frac{1}{y}\exp\left(-\frac{y^2}{2\varepsilon_2}\right)$$
$$\times\exp\left[-\frac{(Z_{\mathbf{h},\mathbf{h}'}/y - V_{\mathbf{h}}y/\varepsilon_2)^2}{2\varepsilon_2}\right]dy\,dZ_{\mathbf{h},\mathbf{h}'}$$
$$= (\pi\varepsilon_2)^{-1}\exp\left(\frac{Z_{\mathbf{h},\mathbf{h}'}V_{\mathbf{h}}}{\varepsilon_2^2}\right)$$
$$\times\int_{y=0}^{\infty}\frac{1}{y}\exp\left[-\frac{1}{2\varepsilon_2}\left\{y^2\left(1+\frac{V_{\mathbf{h}}^2}{\varepsilon_2^2}\right)+\frac{Z_{\mathbf{h},\mathbf{h}'}^2}{y^2}\right\}\right]dy\,dZ_{\mathbf{h},\mathbf{h}'}$$
$$= (\pi\varepsilon_2)^{-1}\exp\left(\frac{Z_{\mathbf{h},\mathbf{h}'}V_{\mathbf{h}}}{\varepsilon_2^2}\right)K_0\left[\frac{Z_{\mathbf{h},\mathbf{h}'}}{\varepsilon_2}\left(1+\frac{V_{\mathbf{h}}^2}{\varepsilon_2^2}\right)^{\frac{1}{2}}\right]dZ_{\mathbf{h},\mathbf{h}'},$$

where $K_0(x)$ is a zero-order Bessel function of the third kind (Watson, 1922, p. 123).

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Some Observations on the Probability Distribution of X-ray Intensities

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Wilson's theory for the probability distribution of X-ray intensities applies only when the unit cell contains a number of atoms of similar scattering power. Consideration is given to the way the distribution is modified when the intensities are dominated by a single atom in the unit of pattern of the structure.

1. Introduction

A theoretical investigation of the probability distribution of reflected X-ray intensities (Wilson, 1949) has been developed (Howells, Phillips & Rogers, 1950) to give a simple method of distinguishing between centrosymmetrical and non-centrosymmetrical structures. If each intensity is expressed as a fraction, z, of the local average intensity, then the fractions, $N(z)$, of the reflexions whose intensities are less than or equal to z are

$$_1N(z) = 1-\exp(-z)$$

for a non-centrosymmetrical structure

and

$$_{\bar{1}}N(z) = \text{erf}\,(\tfrac{1}{2}z)^{\frac{1}{2}}$$

for a centrosymmetrical structure.

The functions $_1N(z)$ and $_{\bar{1}}N(z)$ are plotted in Fig. 1.

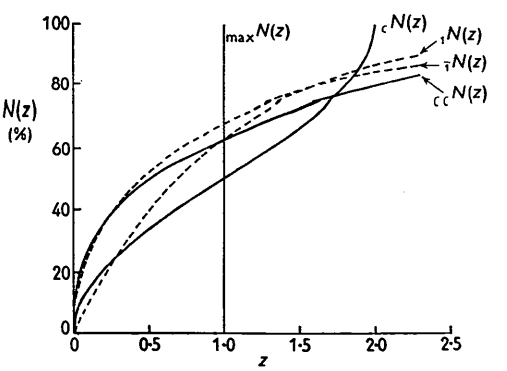

Fig. 1. Comparison of the functions $_1N(z)$, $_{\bar{1}}N(z)$, $_{\max}N(z)$, $_cN(z)$ and $_{cc}N(z)$.