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A New Theory for Sign Determination

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A new probability distribution for the structure factor signs in centrosymmetrical crystals is proposed and discussed; it is related as follows to the probability distributions previously given by Hauptman & Karle and Bertaut. If $P(A_1A_2 \cdots A_m)$ is the joint elementary probability that the A_i normalized values of the observed structure factors are comprised between A_i and A_i+dA_i, the proposed joint probability distribution of the s_i-signs is of the kind $P(s_1s_2 \cdots s_m)=K \, . \exp\,[H \, . \, P(A_1A_2 \cdots A_m)]$, where both K and H are proper constant values; a useful substitution proves to be $A_i=s_i|A_i|$, since the moduli of A_i are experimentally known. The proposed probability distribution is also related to the sign probability distributions of structure factor products (Kitaigorodskii, Woolfson, Cochran & Woolfson) in the sense that it is to be regarded as a generalization of them.

From the above expression the probability $P(s_i^+)$ that the sign of A_i is positive is derived; it contains many new contributions with respect to the previously known expressions. Another way of application of the proposed joint probability distribution is then discussed: it allows the derivation of the most probable set of signs of any number whatever of properly selected reflexions.

1. Introduction

The problem of the direct solution of a crystal structure by inequality or probability relations among phases has received very deep consideration in the last two decades. We will particularly recall here the important contribution made by Hauptman & Karle (1953) in which, for the first time, the phase probability relations between all the structure factors were jointly considered. The theory put forward by these authors includes the results previously attained by Harker & Kasper, and gives rise to some new probability contributions for the signs of the structure factors in a centrosymmetrical crystal, which take into account the magnitudes of other structure factors only. Subsequently Bertaut (1955), by an elegant mathematical procedure, gave a general expression to the joint probability distribution of structure factors and atomic coordinates in a centrosymmetrical crystal; it may be utilized either to deduce the results given by Hauptman & Karle or to derive information about the most probable distribution of atoms. Both Hauptman & Karle and Bertaut obtain probability relations between structure factor signs from a completely general probability distribution of structure factor values.

A different approach is adopted by, among others, Kitaigorodskii (1953, 1954), Woolfson (1954) and Cochran & Woolfson (1955). It is substantially based upon the derivation of probability distributions of some structure factor products, measuring the probability that the corresponding products between observed quantities are positive.

In § 3 a new probability distribution of structure factor signs will be given, which may be considered as a generalization of the last approach outlined above. The final expression of the sign probability distribution [see equation (10)] shows some resemblance to the expression (III-1) given by Bertaut (1955), in the sense that all the terms contained in the summation reported in the latter expression have their correspondent in (10); nevertheless, the mathematical dependence of the total probability on these terms is different because, while it is of a linear type in Bertaut's expression, it becomes of an exponential type in (10).

In § 4 some considerations about the above result are discussed, while in § 5 some general relationships are derived both for obtaining the sign probability of a single structure factor [expressions (16) and (18)] and for obtaining the most probable signs of a limited set of structure factors [expressions (23) and (25)]. Examples of application of the above formulae are being studied in our laboratory.

2. Notation

The following symbols are largely derived from the notation of Bertaut (1955, 1958):

n is the number of atoms per unit cell;

$\mathbf{x}_j$ is a vector specifying the position of the jth atom inside the cell;

H, **K**, **L** ... are vectors in reciprocal space. They specify different reciprocal lattice nodes (hkl);

F_H is the observed structure factor corresponding to the **H** reciprocal vector;

$\varphi_j(H)=f_j(H)/\sqrt{\sum_1^n f_j^2(H)}$ is a normalized atomic factor, $f_j(H)$ being the corresponding atomic factor;

if $\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_n)$ is a given function of the atomic coordinates, $\bar{\Phi}$ means the corresponding average value over the whole domain of the $\mathbf{x}_j$ variables;

$E_H(\mathbf{x}_1, \mathbf{x}_2 \ldots \mathbf{x}_n) = 2 \sum_{j=1}^{n/2} \varphi_j(H) \cos 2\pi\mathbf{H} \,.\, \mathbf{x}_j$ is a *calculated* structure factor, in normalized form. Its average squared value is unity: $\overline{E_H^2} = 1$;

$\xi_j(H)$ is the product $\varphi_j(H) \cos 2\pi\mathbf{H} \,.\, \mathbf{x}_j$;

A_H is an *observed* (or *observable*) structure factor in normalized form. It represents a value that the E_H function may assume;

the relation between A_H and F_H is: $A_H = F_H / \sqrt{\overline{\sum_{j=1}^{n} f_j^2}}$;

$\delta(x)$ is the Dirac function, which is defined as having zero value for $x \neq 0$, and an infinite value for $x = 0$, so that: $\int_{-\infty}^{+\infty} \delta(x)\, dx = 1$;

s_H is the sign of A_H: $A_H = s_H |A_H|$.

In this paper the ($H, K, L \ldots$) indices of structure factors will be frequently substituted by numerical indices ($i, j, l \ldots$) which refer to their progressive numbers in a given order.

3. A new probability distribution of the structure factor signs

Bertaut (1955, expression I-6) has given the following expression to the joint probability distribution of structure factors and atomic coordinates in centrosymmetrical structures:

$$P(A_1, A_2 \ldots A_m; \mathbf{x}_1, \mathbf{x}_2 \ldots \mathbf{x}_n) = \delta(A_1 - E_1) \,.\, \delta(A_2 - E_2) \ldots \delta(A_m - E_m) \qquad (1)$$

where

$$P(A_1 A_2 \ldots A_m; \mathbf{x}_1, \mathbf{x}_2 \ldots \mathbf{x}_n) dA_1 dA_2 \ldots dA_m d\mathbf{x}_1 d\mathbf{x}_2 \ldots d\mathbf{x}_n$$

is the elementary joint probability that the n vectors lie between $\mathbf{x}_j$ and $\mathbf{x}_j + d\mathbf{x}_j$, and the m values A_j take values comprised between A_j and $A_j + dA_j$.

By expressing the $\delta(x)$ function in a suitable mathematical form, then expanding in series and integrating over the space coordinates, Bertaut (1955, expression III-1) has arrived at the following expression for the probability distribution of the m structure factors, which is substantially similar to the results previously obtained by Hauptman & Karle (1953):

$$\begin{aligned} P(A_1, A_2 \ldots A_m) = (\sqrt{2\pi})^{-m} \,.\, \exp[-\tfrac{1}{2}(A_1^2 + \ldots + A_m^2)] \{1 + \sum_{k \neq l}{}_1 \tfrac{1}{2} A_k (A_1^2 - 1) \overline{E_k (E_l^2 - 1)} \\ + \sum_{k \neq l \neq m}{}_2 A_k A_l A_m \overline{E_k E_l E_m} + \sum_{k \neq l \neq m}{}_3 \tfrac{1}{2} A_k A_l (A_m^2 - 1) \\ \overline{E_k E_l (E_m^2 - 1)} + \ldots\}. \qquad (2) \end{aligned}$$

In all the centrosymmetrical space groups the terms contained in Σ_1 are different from zero when $\mathbf{H}(E_k) = 2\mathbf{H}(E_1)$; the terms in Σ_2 when $\mathbf{H}(E_k) \pm \mathbf{H}(E_1) \pm \mathbf{H}(E_m) = 0$, and so on. Depending upon the symmetry of the various space groups, other linear relationships may hold among the indices of the structure factors contained in a non-zero term of (2).

Using (2), and referring for sake of simplicity to the centrosymmetrical space group $P\bar{1}$, the probability of having a positive sign for the general structure factor with reciprocal vector $\mathbf{H}$ is:

$$\begin{aligned} P(A_H^+) = \tfrac{1}{2} + \tfrac{1}{2} \{\tfrac{1}{2} |A_H| (A_{H/2}^2 - 1) \overline{E_H (E_{H/2}^2 - 1)} \\ + |A_H| \sum_{K(\neq H)} A_K A_{H+K} \overline{E_H E_K E_{H+K}} + \ldots\}. \qquad (3) \end{aligned}$$

Moreover, remembering the definition (1) of the joint probability distribution, we see that, given a set of m moduli $|A_i|$, all the sets of corresponding signs which are not compatible with a given distribution of atomic coordinates have zero probability, so that the corresponding expression (2) must be zero. Let us assume that only the real atomic distribution may give rise to the observed moduli $|A_i|$; in other words, let us assume that no structure exists which is related by homometry to the real one. The summation in brackets in (2) may be written in the following way, putting into evidence the structure factor signs:

$$\begin{aligned} S\{s_i\} = 1 + \sum_{k \neq l}{}_1 \tfrac{1}{2} s_k |A_k| (A_l^2 - 1) \overline{E_k (E_l^2 - 1)} \\ + \sum_{k \neq l \neq m}{}_2 s_k s_l s_m |A_k A_l A_m| \overline{E_k E_l E_m} \\ + \sum_{k \neq l \neq m}{}_3 \tfrac{1}{2} s_k s_l |A_k A_l| (A_m^2 - 1) \overline{E_k E_l (E_m^2 - 1)} + \ldots \\ = 1 + \sum_{k}{}_1 s_k a_k + \sum_{k \neq l \neq m}{}_2 s_k s_l s_m a_{klm} + \sum_{k \neq l}{}_3 s_k s_l a_{kl} + \ldots \qquad (4) \end{aligned}$$

where[*]

$$\begin{aligned} a_k &= \tfrac{1}{2} |A_k| \sum_{l(\neq k)} (A_l^2 - 1) \overline{E_k (E_l^2 - 1)} \\ a_{klm} &= |A_k A_l A_m| \overline{E_k E_l E_m} \\ a_{kl} &= \tfrac{1}{2} |A_k A_l| \sum_{m(\neq k \neq l)} (A_m^2 - 1) \overline{E_k E_l (E_m^2 - 1)}\,. \qquad (4') \end{aligned}$$

For what precedes, (4) must have a non-zero (positive) value only when the set of signs $\{s_i\}$ coincides with the correct set. This allows us to state the following theorem:

Theorem I: *Apart from the possible existence of homometric structures, the correct signs* ($s_1, s_2 \ldots s_m$) *of m structure factors under consideration may be obtained by maximizing the summation* $S\{s_i\}$ (see (4)) *over all the possible sets of signs.*

Now let us consider the other class of sign probability relationships, namely those derived from the probability distributions of structure factor products. In

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[*] Considering the last expression given in (4) for $S\{s_j\}$ it should be remembered that other terms are comprised in a_k, a_{klm}, $a_{kl} \ldots$ which are not indicated above. For instance, other terms to be included in a_k are (see Bertaut, 1955): $a_k' = \tfrac{1}{4} |A_k| \sum_{l \neq m(\neq k)} (A_l{}^2 - 1)(A_m{}^2 - 1) \overline{E_k (E_l{}^2 - 1)(E_m{}^2 - 1)}$. However, for sake of simplicity, in the following we shall always neglect such terms, confining ourselves to the expressions of a_k, a_{klm}, a_{kl} given in (4').

particular, Woolfson (1954) and Cochran & Woolfson (1955) have derived the following expression for the probability $P(s_H^+)$ that the sign of the A_H structure factor is positive (space group $P\bar{1}$), when the atomic weights are more or less the same and the number of independent atoms is sufficiently large:

$$P(s_H^+) = \tfrac{1}{2}+\tfrac{1}{2}\,\mathrm{Th}a_H = \frac{\exp a_H}{\exp a_H + \exp(-a_H)} \qquad (5)$$

where a_H may be either:

$$a_H^{(1)} = \tfrac{1}{2}|A_H|(A_{H/2}^2-1)\overline{E_H(E_{H/2}^2-1)}\,, \quad \text{or:}$$

$$a_H^{(2)} = |A_H| \sum_{K(\neq H)} A_K A_{H+K} \overline{E_H E_K E_{H+K}}\,. \qquad (5')$$

By developing in series $\mathrm{Th}x = x - x^3/3 + \ldots$ and stopping at the first term, we may see some analogy between the expressions (3) and (5). An advantage given by (5) is that it always gives probability values comprised between 0 and 1, while in general (3) does not, at least if the series is not pushed too far.

Now the question arises: may the two different forms of the expression (5), given (5'), be related among themselves? We will first remember that (5) is derived from probability distributions of the kind:

$$P(s_H^+) = K \exp a_H\,, \qquad (6)$$

where K is a normalizing factor, which is evaluated by imposing the condition: $P(s_H^+)+P(s_H^-)=1$. Indicating by K_1 and K_2 the normalization factors corresponding to $a_H^{(1)}$ and to $a_H^{(2)}$ respectively, we may write:

$$P_1(s_H^+) = K_1 \exp a_H^{(1)}\,; \quad P_2(s_H^+) = K_2 \exp a_H^{(2)}\,. \qquad (7)$$

But, *since there must be only one probability distribution for the sign of A_H*, the unique way of reconciling the expressions (7) is to write:

$$P(s_H^+) = K' \exp a_H^{(1)}\,.\,\exp a_H^{(2)} = K' \exp(a_H^{(1)}+a_H^{(2)}) \quad (8)$$

where K' is a new normalization factor, whose value is:

$$\{\exp(a_H^{(1)}+a_H^{(2)}) + \exp(-a_H^{(1)}-a_H^{(2)})\}^{-1}\,.$$

Therefore (8) reduces to:

$$\begin{aligned} P(s_H^+) &= \tfrac{1}{2}+\tfrac{1}{2}\mathrm{Th}\,(a_H^{(1)}+a_H^{(2)}) = \tfrac{1}{2}+ \\ &+ \tfrac{1}{2}\mathrm{Th}\,\{\tfrac{1}{2}|A_H|\,(A_{H/2}^2-1)\,\overline{E_H(E_{H/2}^2-1)} + \\ &+ |A_H| \sum_{K(\neq H)} A_K A_{H+K} \overline{E_H E_K E_{H+K}}\}\,. \end{aligned} \qquad (9)$$

Comparison of expressions (3) and (9) shows an interesting analogy between them. Namely, the argument of Th in (9) coincides with the first terms of the expression in brackets in (3). Since in deriving (9) we have not exhausted all possible sign probability relations which are contained in (3) – for instance we have not taken into account the sign probability distributions of the products contained in Σ_3 [see (2)] – we will try to find a more general sign probability distribution, from which (9) could be derived as a particular case.

The probability relationship (3) is derived from the more general expression (2) in which all the observed structure factors are considered jointly; it regards both the signs and the amplitudes of the structure factors. However, the more general distribution from which (9) is to be derived should regard only *the signs* of the structure factors, not their amplitudes, in much the same way as (5), from which (9) has been derived, regards only the sign of A_H (this last statement may be proved as shown in Appendix I). Therefore, developing the analogy between (3) and (9), and remembering (2), we propose the following expression for the joint probability distribution of the signs $(s_1, s_2 \ldots s_m)$ of m structure factors under consideration $(A_i = s_i|A_i|)$:

$$\begin{aligned} P(s_1, s_2 \ldots s_m) = P\{s_i\} = K\,.\,\exp\{1 \\ + \sum_{k\neq l}{}_1\, \tfrac{1}{2}s_k\,|A_k|\,(A_l^2-1)\,\overline{E_k\,(E_l^2-1)} \\ + \sum_{k\neq l\neq m}{}_2\, s_k s_l s_m\,|A_k A_l A_m|\,\overline{E_k E_l E_m} \\ + \sum_{k\neq l\neq m}{}_3\, \tfrac{1}{2}s_k s_l\,|A_k A_l|\,(A_m^2-1)\,\overline{E_k E_l\,(E_m^2-1)} + \ldots\} \\ = K\,.\,\exp S\{s_i\}\,. \quad \text{[compare expression (4)]} \end{aligned} \qquad (10)$$

The normalization constant K may be evaluated by imposing the condition that the sum of the probabilities $P\{s_i\}$ over all the possible sets of signs is equal to unity:

$$\sum_{\{s_i\}} P\{s_i\} = 1\,; \quad K = [\sum_{\{s_i\}} \exp S\{s_i\}]^{-1}\,. \qquad (11)$$

From the above, it is clear that the expression (10) has been introduced on semi-empirical grounds. In the next section we will discuss two arguments that strongly support the reliability of (10).

4. Two considerations on formula (10)

Let us first consider the argument of the exponential in (10). The general form of the argument is expressed by [see Bertaut, 1955 (I-18)]:

$$\begin{aligned} X(p_1, \ldots p_m) = \frac{1}{p_1! \ldots p_m!} \\ \times Hp_1(A_1) \ldots Hp_m(A_m)\overline{Hp_1(E_1) \ldots Hp_m(E_m)} \end{aligned} \qquad (12)$$

where $Hp(z)$ is the Hermite polynomial of pth order [see Appendix II, (II-1) and (II-2)], with p an integral number. We have shown in Appendix II that, under the hypotheses that the number of independent atoms is sufficiently large, and that their weights are approximately equal, the following gaussian probability distribution applies:

$$\begin{aligned} P[Hp_1(A_1) \ldots Hp_m(A_m)] = \frac{1}{\sqrt{2\pi}\,D} \times \exp\Big[-\tfrac{1}{2} \\ \frac{\{Hp_1(A_1) \ldots Hp_m(A_m) - \overline{Hp_1(E_1) \ldots Hp_m(E_m)}\}^2}{D^2}\Big] \end{aligned} \qquad (13)$$

where D^2 (mean square deviation) $= p_1!p_2! \ldots p_m!$

Following the same lines discussed in Appendix I, it follows from (13), remembering (12), that:

$$P_{p_1 \ldots p_m}(s_1 \ldots s_m) = K_{p_1 \ldots p_m} \cdot \exp\{X(p_1 \ldots p_m)\} \,. \tag{14}$$

Now, under the above hypotheses, by the general criterion of multiplying probabilities, we get from the above [expression (15)]:

$$\begin{aligned} P(s_1 \ldots s_m) &= \prod_{p_1 \ldots p_m = 0,\infty} P_{p_1 \ldots p_m}(s_1 \ldots s_m) \\ &= K \,.\, \exp\{ \sum_{p_1 \ldots p_m = 0,\infty} X(p_1 \ldots p_m)\} \\ &= K \,.\, \exp\{S(s_1 \ldots s_m)\} \end{aligned} \tag{15}$$

so that we have in this way obtained expression (10).

There is still another consideration which further supports the reliability of (10), and seems to remove any condition for its general validity. We have already shown, in discussing expression (4) (see page 950) that $S\{s_i\}$ is different from zero, apart from particular cases, only when $\{s_i\}$ coincides with the real set of signs. In Appendix III we have proved that in such a case $S\{s_i\}$ is at least of the order of 2^m, where m is the number of structure factors under consideration. This means that, even when m is very small (3 or 4), the probability $P\{s_i\}$ of the real set of signs is practically 1, and zero otherwise. This seems to be a strong argument not only for the *approximate* validity of (10), but even for its *exact* validity; in fact the above conclusions are not limited by any condition about the number or the weights of the atoms, in much the same way as expressions (1)–(3) are not subjected to these limitations.

In the following section we will discuss two distinct possibilities of applying the probability relationship (10).

5. General applications of formula (10)

(*a*) We will here give a general expression for the probability $P(s_i^+)$ that the sign s_i is positive, some of the other signs being known, but not necessarily. Let us first write down the following relationship:

$$\begin{aligned} P(s_i^+) &= \tfrac{1}{2}[P(s_i^+)+P(s_i^-)] + \tfrac{1}{2}[P(s_i^+)-P(s_i^-)] \\ &= \tfrac{1}{2} + \tfrac{1}{2}[P(s_i^+)-P(s_i^-)] \end{aligned} \tag{16}$$

since $P(s_i^+)+P(s_i^-)$ must always be unity. We will evaluate $P(s_i^+)-P(s_i^-)$ in the following way, supposing the signs $s_1, s_2 \ldots s_p$ to be known *a priori* ($i>p$):

$$\begin{aligned} P(s_i^+)-P(s_i^-) &= \\ = \sum\sum_{s_{p+1}, \ldots s_{i-1}, s_{i+1} \ldots s_m = +,-} \ldots \sum \ldots \sum \, [P\,(s_1, s_2 \ldots s_{i-1}, +, \; & s_{i+1} \ldots s_m) - P(s_1, s_2 \ldots s_{i-1}, -, \\ & s_{i+1}, \ldots s_m)] \,. \end{aligned} \tag{17}$$

Remembering from (10) that $a_{ikl \ldots t}$ is the coefficient of the sign product $(s_i s_k s_l \ldots s_t)$, and introducing the notation $\alpha_{ikl \ldots t} = \mathrm{Th}(a_{ikl \ldots t})$, we have shown in Appendix IV that (17) reduces to [expression (18)]:

$$P(s_i^+) - P(s_j^-) = \frac{\begin{aligned} &(\alpha_i + \sum_{j(\neq i)} \alpha_j\alpha_{ij} + \sum_{j\neq k(\neq i)} \alpha_j\alpha_k\alpha_{ijk} + \sum_{j\neq k(\neq i)} \alpha_{jk}\alpha_{ijk} + \sum_{j\neq k(\neq i)} \alpha_j\alpha_{jk}\alpha_{ik} + \ldots) + \\ &+ (\sum_{j(\neq i)} s_j\alpha_j\alpha_i + \sum_{j(\neq i)} s_j\alpha_{ij} + \sum_{j\neq k(\neq i)} s_js_k\alpha_{ijk} + \sum_{j\neq k(\neq i)} s_j\alpha_k\alpha_{ijk} + \ldots)\end{aligned}}{\begin{aligned} &(1 + \sum_{j\neq k} \alpha_j\alpha_k\alpha_{jk} + \sum_{j\neq k\neq l} \alpha_{jk}\alpha_{kl}\alpha_{jl} + \sum_{j\neq k\neq l} \alpha_j\alpha_{kl}\alpha_{jkl} + \ldots) + \\ &+ (\sum_{j} s_j\alpha_j + \sum_{\neq k\neq l} s_js_ks_l\alpha_{jkl} + \sum_{j\neq k} s_js_k\alpha_{jk} + \sum_{j\neq k} s_j\alpha_k\alpha_{jk} + \ldots)\end{aligned}} \tag{18}$$

Both the numerator and the denominator of (18) have been divided into two parts by parentheses; in the first part there are terms not depending on any known sign, the opposite in the second part. Every product in the numerator has the following property: every index ($j, k \ldots$) which appears both in the α's and in the s's appears an even number of times, except the index i, which refers to the structure factor whose sign is wanted. In the denominator all the indices appear an even number of times in any product: the denominator may therefore be derived by summing up all possible products of α's and s's which possess this property. Of course in all the summations the indices applied to the signs must run only from 1 to p, while the other indices run from 1 to m.

The various products which appear both in the numerator and in the denominator of (18) may be given a simple probabilistic interpretation. If we consider, as an approximation of zero order, only the first term in both sides of the fraction, we obtain, remembering (16):

$$\begin{aligned} P_0(s_i^+) &= \tfrac{1}{2} + \tfrac{1}{2}\alpha_i = \tfrac{1}{2} + \tfrac{1}{2}\mathrm{Th}a_i \\ &= \tfrac{1}{2} + \tfrac{1}{2}\mathrm{Th}\{\tfrac{1}{2}|A_H|\overline{(A^2_{H/2}-1)E_H(E^2_{H/2}-1)}\} \end{aligned} \tag{19}$$

apart from terms of higher order which should be comprised in a_i (see footnote page 950). In (19) we have assumed that we are dealing with the space group $P\bar{1}$ and also that the ith structure factor corresponds to the reciprocal vector **H**. We have thus derived from (18) one of the expressions (5).

Let us go on to examine the meaning of the next terms in the numerator of (18), for instance $\sum_{j(\neq i)} \alpha_j\alpha_{ij}$.

From (19) it follows that α_j is equal to $\{P_0(s_j^+) - P_0(s_j^-)\}$, when no other sign relationship is considered: we will therefore call α_j the *zero-order contribution* to the sign of A_j. In a completely analogous way α_{ij} is the zero-order contribution to the sign of the product $A_i \,.\, A_j$.

Indicating by $P_{ji}(s_i^{\pm})$ the probability of having a positive or negative sign for A_i derivable from joint consideration of the probable signs of A_j and A_i, the following relationships apply:

$$P_{ji}(s_i^+) = P_0(s_j^+)\,.\,P_0(s_is_j^+) + P_0(s_j^-)\,.\,P_0(s_is_j^-)$$
$$P_{ji}(s_i^-) = P_0(s_j^+)\,.\,P_0(s_is_j^-) + P_0(s_j^-)\,.\,P_0(s_is_j^+)\,, \qquad (20)$$

whence, subtracting the corresponding sides of these two equations:

$$P_{ji}(s_i^+) - P_{ji}(s_i^-)$$
$$= [P_0(s_j^+) - P_0(s_j^-)]\ [P_0(s_is_j^+) - P_0(s_is_j^-)] = \alpha_j\,.\,\alpha_{ij}\,. \qquad (21)$$

From equation (21) it clearly follows that $\Sigma\alpha_j\alpha_{ij}$ represents the probability contribution to the sign of A_i derived from the zero-order contributions to the signs of the other structure factors and their products in pairs. An analogous conclusion may be drawn from examination of the other products which appear in the numerator of (18), while the denominator must be considered as a normalization factor. We wish to emphasize the fact that formula (18) represents the first case in which the probability distribution of a structure factor sign is expressed as a function of the sign probabilities of the other structure factors. *We think that expression* (18) *may be rightly denominated a joint sign probability.*

Every product appearing in the denominator of (18) is probably positive, as it could be seen from considerations analogous to those reported above. We may also deduce that the larger the relative weight of the positive terms, the greater is the self-consistency of the whole set of zero-order contributions to the signs; therefore, the larger should be the probability of solving the structure on purely statistical grounds, as a rule.

At the very beginning of every structural study of a centrosymmetric crystal, no sign is known apart from the arbitrary signs of the structure factors of three *odd* reflexions (*i.e.* whose reciprocal vector **H** has no rational correspondent **H**/2) linearly independent modulo 2, that specify the choice of the origin of the unit cell. In such a case, it is not difficult to see that only the first expression inside parentheses gives a non-zero contribution to the denominator of (18) – for instance, the sum $\Sigma s_j\alpha_j$ must be zero in all its terms, because α_j is necessarily zero if the jth reflexion is *odd* – while, in the numerator, the first expression inside parentheses gives a contribution to the *even* reflexions, and the second expression to the *odd* reflexions only. This seems to be quite logical, because the sign of every *even* reflexion must be independent of the choice of the origin (therefore of the choice of the arbitrary signs), while the signs of the *odd* reflexions depend entirely on this choice. Of course, this is no more the case when new signs are known, and they are introduced into (18). As an example, we will write in the following the explicit expression of $P(s_H^+)$ for the space group $P\bar{1}$, when **H** is an even reciprocal vector [see (16) and (18)]:

$$P(s_H^+) = \tfrac{1}{2} + \tfrac{1}{2}\,\frac{\mathrm{Th}\{\tfrac{1}{2}|A_H|(A^2_{H/2}-1)\overline{E_H(E^2_{H/2}-1)}\} + \sum\limits_{K(\neq H)}\mathrm{Th}\{\tfrac{1}{2}|A_K|(A^2_{K/2}-1)\overline{E_K(E^2_{K/2}-1)}\}\times}{1 + \sum\limits_{K\neq L}\mathrm{Th}\{\tfrac{1}{2}|A_K|(A^2_{K/2}-1)\overline{E_K(E^2_{K/2}-1)}\}\,.\,\mathrm{Th}\{\tfrac{1}{2}|A_L|(A^2_{L/2}-1)\overline{E_L(E^2_{L/2}-1)}\}\times}$$
$$\frac{\times\,\mathrm{Th}\{\tfrac{1}{2}|A_HA_K|(A^2_{(H+K)/2}-1)\,\overline{E_HE_K(E^2_{(H+K)/2}-1)}\} + \ldots}{\times\,\mathrm{Th}\{\tfrac{1}{2}|A_KA_L|(A^2_{(K+L)/2}-1)\,\overline{E_KE_L(E^2_{(K+L)/2}-1)}\} + \ldots} \qquad (22)$$

We may now add the following conclusion to the preceding matter. Starting from the expression (10) for the joint probability distribution of all the signs, we have obtained the expression (18) for the probable sign of a single structure factor. Careful examination of (18) has proved not only that it is fully self-consistent, but also that it gives new contributions to the sign probabilities, which have never been given before, at least in an explicit form. We think that this affords strong support for the total correctness of the theory.

(*b*) It is well known that, in some cases, applying probability treatments to the structure factor signs in a centrosymmetrical structure, different sets of signs give rise to high contributions to the total probability $P(A_1 \ldots A_m)$ [see expression (2)], if only the first terms are considered. The choice between these sets must be generally made on examining them separately from a truly structural viewpoint; for instance, the presence or absence of atoms in some special positions, or more generally the indications derivable from Fourier syntheses, built up with all the probable sets, are criteria frequently employed in the choice of the correct set of signs (see *e.g.* Karle & Karle, 1964).

In the following, we will discuss a mathematical treatment based on the present theory, which should allow the most probable set (or sets) of signs to be obtained. This method, which may be interpreted as an alternative way of utilizing the probability distribution (10), is based on the same idea already expressed in Theorem I (page 950), the maximization with respect to the sets of signs being carried out on the $P(s_1s_2 \ldots s_m)$ function.

Maximization of (10) over all the 2m possible sets of signs may be of prohibitive length even with the aid of a large computer, if m, or the number of reflexions taken into consideration, is of the order of 20 or greater [$2^{20} > 1$ million (!)]. Nevertheless, we will show a procedure which allows the variation of only a small number p of signs, properly selected among the strongest structure factors, with the utilization of the partial sign probabilities which refer also to the other structure factors whose moduli are known. Once these p signs are known, it will be easy to derive a large number of other structure factor signs [for instance by application of (18)].

The mathematical procedure is outlined in Appendix IV. We give in the following the expression (IV, 8) in explicit form:

$$\mathrm{Max}\,P(s_1s_2 \ldots s_p)$$
$$= \mathrm{Max}\{\Sigma s_j\alpha_j + \Sigma s_js_ks_l\alpha_{jkl} + \Sigma s_js_k\alpha_{jk}$$
$$+ \Sigma s_j\alpha_k\alpha_{jk} + \Sigma s_js_k\alpha_l\alpha_{jkl}$$
$$+ \Sigma s_j\alpha_k\alpha_l\alpha_{jkl} + \ldots\}\,, \qquad (23)$$

where $P(s_1 \dots s_p)$ is the sum of the probabilities of the set of signs $(s_1 \dots s_p)$ given by (10) over all possible sets of the remaining signs. In the summations indicated in (23) the indices which are applied to the signs run only from 1 to p, while the other indices run from 1 to m, m being the total number of available moduli of structure factors; moreover, in any summation the indices expressed by different letters must always assume different values. It may be seen that every index appears an even number of times in every product; $a_{ijk} \dots$ are the quantities already defined in (4'); $\alpha_{ijk} \dots = \mathrm{Th}(a_{ijk} \dots)$.

An important particular case is that in which only the contributions of the Sayre terms, which are generally very important, are considered. This means that from the series under brackets in the probability relationship (10), we retain only the summation Σ_2; moreover, referring for simplicity to the space group $P\bar{1}$:

$$a_{ijk} = A_H A_K A_{H+K} \overline{E_H E_K E_{H+K}} \qquad (24)$$

having assumed that:

$$A_i \equiv A_H;\ A_j \equiv A_K;\ A_k \equiv A_{H+K}\,.$$

In this case expression (23) reduces to:

$$\begin{aligned} \mathrm{Max}P(s_1, s_2 \dots s_p) = \\ = \mathrm{Max}\{\Sigma s_i s_j s_k \alpha_{ijk} + \Sigma s_i s_j \alpha_{ikl} \alpha_{jkl}{}^{*} \\ + \Sigma s_i s_j s_k s_l \alpha_{ijn} \alpha_{kln}{}^{*} + \Sigma s_i s_j s_k s_l s_m s_n \alpha_{ijk} \alpha_{lmn} \\ + \Sigma s_i s_j s_k \alpha_{inr} \alpha_{jrs} \alpha_{kns} \\ + \Sigma s_i s_j s_k s_l s_m s_n \alpha_{ijt} \alpha_{klr} \alpha_{mns} \alpha_{trs} + \dots\}\,. \qquad (25) \end{aligned}$$

With the aid of an Olivetti 6001 computer we have applied formula (25) to a two-dimensional projection having *pgg* symmetry [(100) projection in the space group $P2_1/c$, with four molecules in the unit cell] of crystalline *trans-anti-trans-anti-trans*-perhydrotriphenylene ($C_{18}H_{30}$) obtained by complete hydrogenation of triphenylene (Fig. 1).

The number of signs which could be permuted in all possible ways was $p = 10$; only the reflexions with $|A| > 1{\cdot}8$ were considered, so that m was equal to 26. From the $2^{10} = 1024$ values of the $P(s_1 s_2 \dots s_{10})$ function, two values were sharply greater than the others, and equal between themselves. Since the projection had been previously solved by other methods, we recognized that the real set of signs corresponded to one of the two maximum values.

All the formulae given in this paper are now in course of practical application to this structure and to other examples in our laboratory.

APPENDIX I

The expressions (5) may be derived from the nearly gaussian statistical distribution of the structure factor products, for example:

$$\begin{aligned} P[A_H(A_{H/2}^2 - 1)] &= \frac{1}{\sqrt{2\pi}\,D} \\ &\times \exp\left[-\tfrac{1}{2}\frac{\{A_H(A_{H/2}^2 - 1) - \overline{E_H(E_{H/2}^2 - 1)}\}^2}{D^2}\right] \\ &= \frac{1}{\sqrt{4\pi}} \exp\left[-\frac{A_H^2(A_{H/2}^2 - 1)^2 + \overline{E_H(E_{H/2}^2 - 1)^2}}{4}\right] \\ &\times \exp[\tfrac{1}{2}A_H(A_{H/2}^2 - 1)\overline{E_H(E_{H/2}^2 - 1)}]\,, \qquad \text{(I-1)} \end{aligned}$$

in which P represents the probability distribution of the product $[A_H\,.\,(A_{H/2}^2 - 1)]$ and D^2 is the corresponding mean square deviation when the atoms are allowed to move freely throughout the unit cell. If the atoms have similar weights and their number is sufficiently large it follows that $D^2 \simeq 2$ (see also Appendix II). In the last member of (I-1) only the second exponential depends on the sign of A_H; therefore:

$$\begin{aligned} &P(\text{sign of } A_H) \\ &\quad = K\,.\,\exp[\tfrac{1}{2}A_H(A_{H/2}^2 - 1)\overline{E_H(E_{H/2}^2 - 1)}] \qquad \text{(I-2)} \end{aligned}$$

The expressions (5) are of the same type as (I-2); now, (I-2) does not suggest anything about the distribution of the *values* A_H and $A_{H/2}$, since it has lost the first exponential in the last member of (I-1). Therefore, both (5) and (I-2) are to be interpreted merely as *sign* probability distributions, the moduli of A_H and $A_{H/2}$ being known.

APPENDIX II

We will prove in the following the validity of expression (13) under the hypotheses that the number of the independent atoms is large and that their weights are approximately the same.

Let us first recall the algebraic form of the Hermite polynomials of the lowest orders:

$$\begin{aligned} &H_0(z) = 1;\quad H_1(z) = z;\quad H_2(z) = z^2 - 1; \\ &\quad H_3(z) = z^3 - 3z;\quad H_4(z) = z^4 - 6z^2 + 3;\ \dots \qquad \text{(II-1)} \end{aligned}$$

More generally:

$$H_p(z) = (-1)^p \exp\frac{z^2}{2}\,.\,\frac{d^p}{dz^p}\left(\exp -\frac{z^2}{2}\right). \qquad \text{(II-2)}$$

Confining our attention to the space group $P\bar{1}$, the general expression of $E_H(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_n)$ is:

$$\begin{aligned} &E_H(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_n) \\ &\quad = 2\sum_{i=1}^{n/2} \varphi_i(H) \cos 2\pi\mathbf{H}\,.\,\mathbf{x}_i = 2\sum_{i=1}^{n/2} \xi_i(H). \qquad \text{(II-3)} \end{aligned}$$

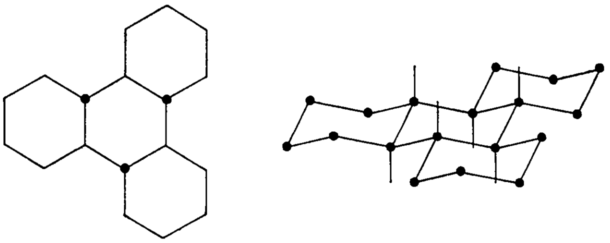

Fig. 1. Side and perspective view of *trans-anti-trans-anti-trans*-perhydrotriphenylene.

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[*] *Note added in proof.* – It is interesting to note, that these terms correspond to the coincidences of the first and of the second kind respectively, according to de Vries (1965).

The product $H_{p1}(E_H)H_{p2}(E_K)H_{p3}(E_L) \ldots$ may then be expressed as a proper summation of terms of the kind:

$$\eta_{i_1 i_2 i_3 \ldots i_t} = 2^t \xi_{i_1}(H_1)\xi_{i_2}(H_2)\xi_{i_3}(H_3) \ldots \xi_{i_t}(H_t)\,, \quad \text{(II-4)}$$

where H_1, H_2, H_3 may correspond either to H, or to K, or to $L \ldots$ If every term of the above kind may be considered as statistically independent of the others, then the central-limit theorem (Cramér, 1946) may be applied: it states that the sum of a large number, N, of independent variables η_j with mean value $\bar{\eta}_j$ and mean square deviation α_j^2, is normally distributed about $\sum_{j=1}^{N} \bar{\eta}_j$ with mean square deviation $D^2 = \sum_{j=1}^{N} \alpha_j^2$.

We have limited ourselves to the consideration of two of the simplest products of the kind $H_{p1}(E_H)H_{p2}(E_K)H_{p3}(E_L) \ldots$ with a non-zero average value, because we are interested only in them. We have proved that, if the atoms have similar weights, the total covariance of $\eta_{i_1 i_2 \ldots}$ is in these cases of the order of $1/n$, and therefore negligible for large n (number of atoms in the cell). By induction, we have assumed that the hypothesis of independence among $\eta_{i_1 i_2 \ldots}$ may be held for every product of the above kind, and also for every space group, under the same conditions of similar weights for all the atoms and of large n. We will report in the following only the results of our calculations.

The mean square deviation $D^2(\Sigma\eta_i)$ of every sum of functions $\eta_i(\mathbf{x}_1 \ldots \mathbf{x}_n)$ of the n variables under consideration is given by:

$$D^2(\Sigma\eta_i) = \overline{(\Sigma\eta_i)^2} - (\overline{\Sigma\eta_i})^2 = \Sigma(\overline{\eta_i^2} - \bar{\eta}_i^2) + 2\sum_{i<j}\sum \overline{\eta_i\eta_j}$$
$$= D_0^2(\Sigma\eta_i) + \mathrm{Cov}(\eta_i\eta_j)\,. \quad \text{(II-5)}$$

In the third member of (II-5) we have expressed $D^2(\Sigma\eta_i)$ as the sum of $D_0^2(\Sigma\eta_i)$, which is the mean square deviation of $\Sigma\eta_i$ when the separate terms are independent, and of the total covariance between these terms. We have evaluated both D^2 and D_0^2 for the following products:

$$(\mathrm{I}) = H_1(E_H)\,.\,H_2(E_{H/2}) = E_H(E_{H/2}^2 - 1);$$
$$(\mathrm{II}) = H_1(E_H)H_1(E_K)H_1(E_{H+K}) = E_H E_K E_{H+K} \quad \text{(II-6)}$$

thus obtaining:

$$D^2(\mathrm{I}) = 2 + 5(\sum_{i=1}^{n} \varphi_i^3)^2 - 3\sum_{i=1}^{n} \varphi_i^4 - 11\sum_{i=1}^{n} \varphi_i^6$$
$$D_0^2(\mathrm{I}) = 2 + (\sum_{i=1}^{n} \varphi_i^3)^2 - 3\sum_{i=1}^{n} \varphi_i^4 - 3\sum_{i=1}^{n} \varphi_i^6\,. \quad \text{(II-7)}$$

Total covariance $= D^2(\mathrm{I}) - D_0^2(\mathrm{I}) = 4(\Sigma\varphi_i^3)^2 - 8\Sigma\varphi_i^6 =$ (for n identical atoms) $\frac{4}{n}\left(1 - \frac{2}{n}\right)$;

$$D^2(\mathrm{II}) = 1 + 3(\sum_{i=1}^{n} \varphi_i^3)^2 - 7\sum_{i=1}^{n} \varphi_i^6$$
$$D^2(\mathrm{II}) = 1 \qquad - \sum_{i=1}^{n} \varphi_i^6\,. \quad \text{(II-8)}$$

Total covariance $= 3(\Sigma\varphi_i^3)^2 - 6\Sigma\varphi_i^6 =$ (for n identical atoms) $\frac{3}{n}\left(1 - \frac{2}{n}\right)$.

Therefore, the total covariance is of the order of $1/n$ in both cases. As a conclusion, we may assume that, under the hypotheses stated at the beginning of this Appendix, the central limit theorem holds for every product of the type $H_{p1}(E_1)\,.\,H_{p2}(E_2) \ldots H_{p_m}(E_m)$ which will be therefore assumed to be normally distributed around its mean value.

To evaluate now the mean square deviation of the above products, let us first recall the following results (see Bertaut, 1955), valid for every space group:

$$\overline{E_H^{2m}} = 1\cdot3\cdot5 \ldots (2m-1) + O(n^{-1}); \quad \overline{E_H^{2m+1}} = 0 \quad \text{(II-9)}$$

where $O(n^{-1})$ means terms of the order of magnitude of n^{-1}.

Remembering (II-1), (II-2) and (II-9) we may easily recognize that $\overline{H_{p1}(E_i)}$ is zero or of the order of magnitude of n^{-1}, while:

$$\overline{H_{pi}^2(E_i)} = p_i! + R(n^{-1})(p_i > 0)\,. \quad \text{(II-10)}$$

Considering now the mean value $\overline{E_H^{2m}E_K^{2n} \ldots E_L^{2r}}$ and neglecting terms in n^{-1}, it can be shown that:

$$\overline{E_H^{2m}\,.\,E_K^{2n} \ldots E_L^{2r}} = \overline{E_H^{2m}}\,.\,\overline{E_K^{2n}} \ldots \overline{E_L^{2r}}\,. \quad \text{(II-11)}$$

This allows us to write, with the same approximations, remembering that $H_p^2(z)$ is a polynomial containing only even powers of z:

$$\overline{H_{p1}^2(E_1)H_{p2}^2(E_2) \ldots H_{pm}^2(E_m)} = \overline{H_{p1}^2(E_1)}$$
$$\times\,\overline{H_{p2}^2(E_2)} \ldots \overline{H_{pm}^2(E_m)} \simeq p_1!p_2! \ldots p_m! \quad \text{(II-12)}$$

The largest mean value of $H_{p1}(E_1) \ldots H_{p_m}(E_m)$ is of the order of $n^{-\frac{1}{2}}$, and is reached in the case of the third-order products $E_H\,.\,(E_{H/2}^2 - 1)$ and $E_H E_K E_{H+K}$. We may therefore conclude that:

$$D^2[H_{p1}(E_1)H_{p2}(E_2) \ldots H_{p_m}(E_m)]$$
$$= \overline{H_{p1}^2(E_1)H_{p2}^2(E_2) \ldots H_{pm}^2(E_m)}$$
$$- \overline{H_{p1}(E_1)H_{p2}(E_2) \ldots H_{p_m}(E_m)} \simeq p_1!p_2! \ldots p_m! \quad \text{(II-13)}$$

We may point our here that formulae (II-7) and (II-8) are special cases of (II-13), since:

$$D^2[H_1(E_H)\,.\,H_2(E_{H/2})] = D^2[E_H\,.\,(E_{H/2}^2 - 1)]$$
$$\simeq 2(=1!\,2!) \quad \text{(II-14)}$$
$$D^2[H_1(E_H)\,.\,H_1(E_K)\,.\,H_1(E_{H+K})]$$
$$= D^2(E_H E_K E_{H+K}) \simeq 1(=1!\,1!\,1!)\,. \quad \text{(II-15)}$$

From all the above, on the assumption of neglecting terms in n^{-1}, we have proved expression (13), in which the observed set of structure factors has been substituted for the general set of calculated structure factors.

APPENDIX III

We will prove in the following that the quantity $S\{s_i\}$ [see (4)] is at least of the order of 2^m, where m is the number of structure factors under consideration, if $\{s_i\}$ corresponds to the correct set of signs.

Let us start by writing the expression (2) in the following way:

$$P(A_1, A_2 \ldots A_m) = (\sqrt{2\pi})^{-m} \exp\left[-\tfrac{1}{2}(A_1^2 + \ldots + A_m^2)\right] \times S(s_1, s_2 \ldots s_m; |A_1|, |A_2|, \ldots |A_m|) \,. \tag{III-1}$$

In (III-1) we have explicitly indicated the dependence of S on both the moduli and the signs of the structure factors. Bertaut (1955) has shown that the above mathematical form of $P(A_1 A_2 \ldots A_m)$ is normalized in the domain of the A_i variables, *i.e.*:

$$\iint \ldots \int_{-\infty}^{+\infty} P(A_1, A_2 \ldots A_m) dA_1 dA_2 \ldots dA_m = 1 \,. \tag{III-2}$$

Let us now remember that:

$$\iint \ldots \int_{-\infty}^{+\infty} (\sqrt{2\pi})^{-m} \times \exp\left[-\tfrac{1}{2}(A_1^2 + \ldots + A_m^2)\right] dA_1 \ldots dA_m = 1 \,. \tag{III-3}$$

Comparison of expressions (III-1), (III-2) and (III-3) shows that the average value of $S(s_1, \ldots s_m; |A_1| \ldots |A_m|)$ over the distribution function $(\sqrt{2\pi})^{-m} \exp[-\frac{1}{2}(A_1^2 + \ldots + A_m^2)]$ is equal to 1.

First, let us assume that the average value of S for any distribution of $|A_i|$ is constant, and therefore equal to unity everywhere. Since there are 2^m sign distributions for every set of $|A_i|$, we may write:

$$\sum_{s_1, s_2 \ldots s_m = +,-} S(s_1 \ldots s_m; |A_1| \ldots |A_m|) = 2^m \,. \tag{III-4}$$

Neglecting the cases of possible homometry, we have already seen (see page 950) that S is in general different from zero only for one set of signs, for a given set of $|A_i|$. This means that, indicating by $(\bar{s}_1, \bar{s}_2 \ldots \bar{s}_m)$ the set of signs which is consistent with a possible distribution of atoms inside the unit cell:

$$S(\bar{s}_1, \bar{s}_2 \ldots \bar{s}_m; |A_1| \ldots |A_m|) = 2^m \,. \tag{III-5}$$

However, it is certainly not correct to assume that S is constant throughout all possible distributions of $|A_i|$. In fact, it is intuitive that there may be many hypothetical distributions of $|A_i|$ which do not correspond to any atomic distribution; in these cases S will be zero for any set of signs. But since the average value of S over all the sign and moduli distributions must be unity, the following conclusion may be drawn: the value given by (III-5) is a lower limit for S, when both signs and moduli of A_i correspond to the real structure.

APPENDIX IV

Let us first write down the following identity:

$$\exp(s_a \,.\, a) = \mathrm{Ch}a + s_a \,\mathrm{Sh}a = \mathrm{Ch}a(1 + s_a \mathrm{Th}a) \tag{IV-1}$$

where s_a is a sign, or a number which may assume the two values $+1$ or -1. Remembering (IV-1) and the notation $\alpha_{ij \ldots 1} = \mathrm{Th}(a_{ij \ldots 1})$, expression (10) may be written in the following way:

$$\begin{aligned} P(s_1, s_2 \ldots s_m) &= K \,.\, e \,.\, [\Pi \exp(s_i a_i)] \times [\Pi \exp(s_i s_j s_k a_{ijk})][\Pi \exp(s_i s_j a_{ij})] \ldots \\ &= K \,.\, e \,.\, [\Pi \,\mathrm{Ch}a_i][\Pi \,\mathrm{Ch}a_{ijk}][\Pi \,\mathrm{Ch}a_{ij}] \ldots [\Pi(1 + s_i \alpha_i)] \\ &\quad \times [\Pi(1 + s_i s_j s_k \alpha_{ijk})][\Pi(1 + s_i s_j \alpha_{ij})] \ldots \end{aligned} \tag{IV-2}$$

Indicating by $\bar{K}$ (which must necessarily be >0) the total product of all the factors that do not depend on the signs, in the last member of (IV-2), and developing the other products, we have:

$$P(s_1, s_2 \ldots s_m) = \bar{K}\Big\{1 + \Sigma s_i \alpha_i + \sum_{i \neq j \neq k} s_i s_j s_k \alpha_{ijk} + \sum_{i \neq j} s_i s_j \alpha_{ij} + \sum_{i \neq j} s_i s_j \alpha_i \alpha_j + \sum_{i \neq j} s_i s_j s_k \alpha_i \alpha_{jk} + \ldots\Big\} \,. \tag{IV-3}$$

Now let us evaluate the sum of the above probabilities, considering separately the two cases $(s_i = +1)$ and $(s_i = -1)$, over all the permutations of the other signs except $(s_1 s_2 \ldots s_p)$ $(p < i)$ that will be held fixed. We shall thus obtain the total probability $P_p(s_i^\pm)$ of A_i being positive or negative, when the first p signs are fixed. The result may be expressed in the following form:

$$\begin{aligned} P_p(s_i^\pm) &= \sum\sum \ldots \sum_{(s_{p+1} \ldots s_{i-1}, s_{i+1} \ldots s_m = +,-)} P(s_1, s_2 \ldots s_{i-1}, \pm, s_{i+1}, \ldots s_m) = 2^{m-p-1} \bar{K}(\pm A_1 \pm A_2(s_1 \ldots s_p) \\ &\quad + B_1 + B_2(s_1 \ldots s_p)] \,, \end{aligned} \tag{IV-4}$$

where A_1 and B_1 do not depend on the signs $(s_1 s_2 \ldots s_p)$. The explicit forms of A_1, A_2, B_1 and B_2 are:

$$\begin{aligned} A_1 &= \alpha_i + \Sigma \alpha_j \alpha_{ij} + \Sigma \alpha_j \alpha_k \alpha_{ijk} + \Sigma \alpha_{jk} \alpha_{ijk} + \Sigma \alpha_j \alpha_{jk} \alpha_{ik} + \ldots \\ A_2 &= \Sigma s_j \alpha_i \alpha_j + \Sigma s_j \alpha_{ij} + \Sigma s_j s_k \alpha_{ijk} + \Sigma s_j \alpha_k \alpha_{ijk} + \ldots \\ B_1 &= 1 + \Sigma \alpha_j \alpha_k \alpha_{jk} + \Sigma \alpha_{jk} \alpha_{kl} \alpha_{jl} + \Sigma \alpha_j \alpha_{kl} \alpha_{jkl} + \ldots \\ B_2 &= \Sigma s_j \alpha_j + \Sigma s_j s_k s_l \alpha_{jkl} + \Sigma s_j s_k \alpha_{jk} + \Sigma s_j \alpha_k \alpha_{jk} + \ldots \end{aligned} \tag{IV-5}$$

In all the summations reported in (IV-5) it is tacitly assumed that two different indices can never be given identical numbers. Moreover, the indices which are attributed to the signs may vary only from 1 to p, while the i index is fixed (it corresponds to the structure factor under investigation). The other indices run from 1 to m.

From (IV-4) we may evaluate $P_p(s_i^+) - P_p(s_i^-)$, by determining $\bar{K}$ so that $P_p(s_i^+) + P_p(s_i^-) = 1$. We obtain:

$$P_p(s_i^+) - P_p(s_i^-) = \frac{A_1 + A_2(s_1, s_2 \ldots s_p)}{B_1 + B_2(s_1, s_2 \ldots s_p)} \,. \tag{IV-6}$$

(IV-6) is reported in explicit form in expression (18) $[P_p(s_i) \to P(s_i)]$.

Without specifying the value of $\bar{K}$, the expression of $P_p(s_i^+) + P_p(s_i^-)$, from (IV-4), is:

$$P_r(s_i^+) + P_r(s_i^-) = 2^{m-p} \,.\, \bar{K} \,.\, \{B_1 + B_2(s_1 \ldots s_p)\} \tag{IV-7}$$

We have thus obtained the total probability pertaining to the set $(s_1 \ldots s_p)$ over all the permutations of the other signs. Maximization of (IV-7) over all the possible values of $(s_1 \ldots s_p)$, assuming $\bar{K}$ to have a fixed value, will give the most probable set of these signs. (IV-7) gives rise to expression (23); in fact, since B_1 does not depend on any sign, it clearly follows that:

$$\text{Max } P(s_1 \ldots s_p) = \text{Max } B_2(s_1 \ldots s_p) \,. \quad \text{(IV-8)}$$

Remembering the last equation in (IV-5), we may easily see that (23) and (IV-8) are equivalent.

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Intrinsic and Systematic Multiple Diffraction

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The geometric conditions under which intrinsic multiple diffraction can occur have been examined for the single-crystal orienter technique in the equatorial plane, and for the precession camera technique. The conditions for the single-crystal orienter are the same that have already been found for normal beam and equi-inclination techniques by Zachariasen, and in part by Fankuchen and co-workers. If a crystal is oriented with a symmetry axis parallel to, or a symmetry plane normal to, the rotation axis (φ axis) then intrinsic multiple diffraction will occur. The consequences of the conditions are different, however. For the normal beam and equi-inclination cases reflections on nonzero layer lines will be recorded under conditions of double and triple diffraction, respectively, and the situation is both intrinsic and systematic. For the single-crystal orienter the situation is intrinsic but not always systematic. Depending both on the crystal symmetry and the indices of the reflections the multiplicities may be triple, quintuple, septuple, 11-fold, or 15-fold. For the precession camera the situation is not intrinsic. However, if a crystal is again oriented with a symmetry axis parallel to, or a symmetry plane normal to, the rotation axis (in this case the spindle axis) a systematic case can be created. If the precession angle $\bar{\mu}$ is set at $\bar{\mu} = \cos^{-1}(d^*/2)$, where d^* is the reciprocal lattice spacing from the zero level to an upper level, then all reflections on the zero level are recorded under conditions of triple diffraction. The possibilities for nonsystematic cases with the precession camera are more interesting. The conditions for multiple diffraction of selected groups of zero level reflections can be created or avoided at will by the choice of $\bar{\mu}$, regardless of crystal symmetry or crystal orientation. In principle this should permit direct observation of the effects of multiple diffraction on intensities.

Zachariasen (1965) has recently emphasized that most intensity measurements reported in the literature, and used for structure determination, have been made under conditions of multiple diffraction. For normal beam techniques (rotating crystal, oscillating crystal, or Weissenberg) all reflections on nonzero layer lines are obtained under conditions of double diffraction if a crystal is oriented with a symmetry axis parallel to, or a symmetry plane normal to, the rotation axis*. For the equi-inclination Weissenberg technique all reflections on nonzero layer lines are obtained under conditions of triple diffraction if a crystal is oriented as above.† Zachariasen also illustrated two special cases where certain zero layer line reflections are subject to triple or quintuple diffraction when a fourfold or sixfold symmetry axis is normal to the rotation axis. In addition Zachariasen solved the intensity equations for double, triple, and quintuple diffraction for a plane,

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* Depending on the Bravais lattice there are two possibilities: Either all reflections on every nonzero layer line, or all reflections on every third layer line, will be subject to double diffraction.

† Depending on the Bravais lattice there are three possibilities: All reflections either on every nonzero layer line, or on every second layer line, or on every third layer line, will be subject to triple diffraction.