ring on the one hand, and the amine group (N_{15}) and the two methyl groups of the triazine ring on the other hand. The interatomic distances C_3–C_{10}, C_5–C_{11} and C_5–N_{15} are 2·93, 2·93 and 2·71 Å respectively.

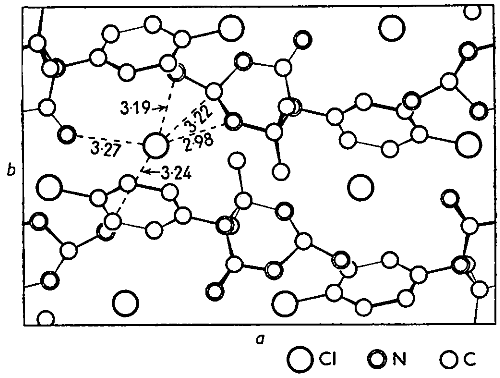

Fig. 4. Projection of the structure of the hydrochloride on (001), showing the environment of the chlorine ion.

The arrangement of the molecules in the unit cell is shown in Fig. 4. In a structure of this type there are two main requirements to be satisfied: the arrangement of the amino groups close to the Cl^- (or Br^-) ions, and the economical packing of the large organic ions. In the present structure each chlorine ion is in contact with three amino groups at 3·24, 3·19 and 3·27 Å respectively, and also with N_{14} and C_8 in the triazine ring at 2·98 and 3·22 Å respectively (Fig. 4). Thus N_{15} is in contact with one chlorine ion at 3·27 Å; N_{16} is in contact with two chlorine ions at 3·19 and 3·24 Å. These distances agree well with those of 3·10, 3·22 and 3·26 Å in *m*-tolidine (Fowweather & Hargreaves, 1950); 3·17 and 3·24 Å in geranylamine hydrochloride (Jeffrey, 1945); and 3·24 Å in glycyl-L-tyrosine hydrochloride (Smits & Wiebenga, 1953). The N_{14}–Cl distance of 2·98 Å may be compared with 3·11 Å for a similar contact in adenine hydrochloride (Broomhead, 1948). The next nearest neighbours of the chlorine ion are the two methyl groups at 3·9 Å and 4·3 Å, and the atoms of the two adjacent benzene rings in the range 4·0–4·5 Å.

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Solution of the Phase Problem for Space Group $P\bar{1}$

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A routine procedure which does not require previous knowledge of any signs has been developed for determining the signs of the structure factors for space group $P\bar{1}$. Only the magnitudes of the structure factors and the chemical composition of the crystal need to be known. The method developed here is readily extended to all the centrosymmetric space groups, and the general treatment may be found in A.C.A. Monograph No. 3.

Introduction

The probability distribution $P_1(A)$ of a structure factor for any centrosymmetric crystal is an even function of A provided that the atoms in the crystal are assumed to occupy all positions with equal probability (Karle & Hauptman, 1953, eq. 20). Thus, the structure factor is just as likely to be positive as negative, even though its magnitude may be known. However, once a set of X-ray intensities is known, the atoms in a crystal no longer occupy all positions with equal probability. If the atoms are assumed to range at random in the unit cell subject to the constraints imposed by the knowledge of a set of intensities, the resulting probability distribution of a structure factor is no longer an even function. The probability that the structure factor has a particular sign is now different from one-half. The purpose of this paper is to derive these probabilities on the basis that certain sets of intensities are specified and to derive therefrom a procedure for phase determination for space group $P\bar{1}$.

The program carried out in this paper is the culmination of ideas described in three previous articles (Karle & Hauptman, 1953; Hauptman & Karle, 1952, 1953*a*) and was formulated in the last one. The details for all centrosymmetric space groups are described in the A.C.A. Monograph No. 3 (Hauptman & Karle, 1953*b*).

Formulation

Since the joint probability distribution of the structure factors leads to a practical solution of the phase problem, it is appropriate to formulate this problem in a precise fashion. The structure factors are defined by means of

$$F_{\mathbf{h}} = \sum_{j=1}^{N/n} f_{j\mathbf{h}} \xi(x_j, y_j, z_j, \mathbf{h}) \qquad (1)$$

summed over all atoms in the asymmetric unit, where n is the symmetry number, $f_{j\mathbf{h}}$ is the atomic scattering factor, N is the number of atoms in the unit cell, and $\xi_j = \xi\ (x_j, y_j, z_j, \mathbf{h})$ is some known trigonometric function of $\mathbf{h}$ and the atomic coordinates x_j, y_j, z_j, which depends on the space group, e.g. $\xi_j = 2\cos 2\pi(hx_j+ky_j+lz_j)$ for space group $P\bar{1}$. The phase problem is the problem of determining the phases (either 0 or π) of the structure factors $F_{\mathbf{h}}$, given the magnitudes of $F_{\mathbf{h}}$ and the values of $f_{j\mathbf{h}}$ for a sufficiently large number of vectors $\mathbf{h}$.

The crystal structure alone does not, however, determine all the phases, because (1) implies that an appropriate origin has been selected. In fact the values of the atomic coordinates x_j, y_j, z_j depend upon the choice of origin. We restrict attention to space group $P\bar{1}$ and to crystals having atoms only in general positions. Since eight origins are permissible (permissible in that they are centers of symmetry), the phase of a structure factor depends not only on the structure but also on the choice of origin. It will be seen that the origin may be conveniently chosen by specifying arbitrarily the phases of a suitable set of three structure factors. All phases are then determined.

If the origin is shifted to the new center having coordinates $\varepsilon_1, \varepsilon_2, \varepsilon_3$ with respect to the first origin, where $\varepsilon_i = 0$ or $\frac{1}{2}$, $i = 1, 2, 3$, then $F_{\mathbf{h}}$ of (1) is replaced by $F_{\mathbf{h}} \cos 2\pi(h\varepsilon_1+k\varepsilon_2+l\varepsilon_3)$. Thus it is seen that the phase $\varphi_{\mathbf{h}}$ of the structure factor $F_{\mathbf{h}}$ has the same value for all eight permissible origins if, and only if, each of h, k, l is even. The sign of such a structure factor is determined by the crystal structure alone and is independent of the choice of origin. The sign of any structure factor $F_{\mathbf{h}_1}$ with h_1 odd, and k_1 and l_1 even may be specified arbitrarily. However, once this is done, then the signs of all other structure factors $F_{\mathbf{h}}$ with h odd and k and l even are determined by the crystal structure. Similarly, the sign of any structure factor $F_{\mathbf{h}_2}$ with h_2 even, k_2 odd, and l_2 even may be specified arbitrarily. However, once this is done, then the signs of all other structure factors $F_{\mathbf{h}}$ with h even, k odd, and l even are determined by the crystal structure. Furthermore, the signs of all structure factors $F_{\mathbf{h}}$ with h odd, k odd, and l even are also determined, as a consequence of specifying the signs of $F_{\mathbf{h}_1}$ and $F_{\mathbf{h}_2}$. Finally, the sign of any structure factor $F_{\mathbf{h}_3}$, with h_3 even, k_3 even, and l_3 odd may be specified arbitrarily. Then the signs of all other structure factors $F_{\mathbf{h}}$ with h even, k even, and l odd are determined. Furthermore, the chosen signs for $F_{\mathbf{h}_1}$ and $F_{\mathbf{h}_3}$ determine the signs of all structure factors $F_{\mathbf{h}}$ with h odd, k even, and l odd; and the chosen signs for $F_{\mathbf{h}_2}$ and $F_{\mathbf{h}_3}$ determine the signs of all structure factors $F_{\mathbf{h}}$ with h even, k odd, and l odd. Finally the signs of all structure factors $F_{\mathbf{h}}$ with h, k, and l all odd are also determined, as a consequence of specifying the signs of $F_{\mathbf{h}_1}$, $F_{\mathbf{h}_2}$, and $F_{\mathbf{h}_3}$.

While the previous paragraph illustrates a particular way of selecting the origin, there are many other sets of three structure factors whose phases may be arbitrarily specified. In order to treat this problem in general it is convenient to introduce the concepts of linear dependence and independence modulo 2.

First the concept of linear dependence modulo 2 is introduced. As is well known, if the integer h is even, h is said to be congruent to zero modulo 2, and we write

$$h \equiv 0 \pmod 2\,. \qquad (2)$$

Similarly we say that the vector $\mathbf{h} = (h_1, h_2, \ldots, h_p)$, where $h_1, h_2, \ldots, h_p$ are integers, is even if each of $h_1, h_2, \ldots, h_p$ is even, and we write

$$\mathbf{h} \equiv 0 \pmod 2\,. \qquad (3)$$

Two vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ are congruent modulo 2 if the difference $\mathbf{h}_1-\mathbf{h}_2$ is even; and the notation

$$\mathbf{h}_1 \equiv \mathbf{h}_2 \pmod 2 \qquad (4)$$

is used. A set of n vectors $\mathbf{h}_i$, $i = 1, 2, \ldots, n$ is said to be linearly dependent modulo 2 if there exists a set of n integers $a_i = 0$ or 1, $i = 1, 2, \ldots, n$, not all of which are zero, such that

$$\sum_{i=1}^{n} a_i \mathbf{h}_i \equiv 0 \pmod 2. \qquad (5)$$

Otherwise the set $\mathbf{h}_i$ is said to be linearly independent modulo 2. Finally the vector $\mathbf{h}$ is linearly dependent modulo 2 on, or linearly independent modulo 2 of, the set $\mathbf{h}_i$, $i = 1, 2, \ldots, n$, according as there exist or there do not exist n integers $a_i = 0$ or 1 such that

$$\mathbf{h} \equiv \sum_{i=1}^{n} a_i \mathbf{h}_i \pmod 2. \qquad (6)$$

For example $(24\bar{2})$ is linearly dependent modulo 2. Again, (124) is linearly dependent modulo 2 on (346) but is linearly independent modulo 2 of the pair (234), (465). Evidently (100), (010), (001) constitute a set of three vectors which are linearly independent modulo 2. Any set of four vectors, however, each having three components, is linearly dependent modulo 2.

This discussion leads to the following definition: *Definition.*—A set of phases $\varphi_{\mathbf{h}_i}$ is said to be linearly dependent or independent modulo 2 according as the set of vectors $\mathbf{h}_i$ is linearly dependent or independent modulo 2. The phase $\varphi_{\mathbf{h}}$ is linearly dependent modulo 2 on, or linearly independent modulo 2 of, the set of phases $\varphi_{\mathbf{h}_i}$ according as the vector $\mathbf{h}$ is linearly dependent modulo 2 on, or linearly independent modulo 2 of, the set of vectors $\mathbf{h}_i$.

It is now possible to summarize in simple terms the dependence of phase on choice of origin. In a given crystal any phase which is linearly dependent modulo 2 is determined by the crystal structure (and is thus independent of the choice of the origin, which is of course always assumed to be at a center of symmetry). In a given crystal any phase (0 or π) which is linearly independent modulo 2 may be specified arbitrarily. However, once such a phase, $\varphi_{\mathbf{h}_1}$, has been specified, then any phase, which is linearly dependent modulo 2 on $\varphi_{\mathbf{h}_1}$, is determined by the crystal structure. In a given crystal, any two phases which are linearly independent modulo 2 may be specified arbitrarily. However, once such phases, $\varphi_{\mathbf{h}_1}$ and $\varphi_{\mathbf{h}_2}$, have been specified, then any phase, which is linearly dependent modulo 2 on the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$ is determined by the crystal structure. In a given crystal, any three phases which are linearly independent modulo 2 may be specified arbitrarily. However, once such phases have been specified, then any phase is determined by the crystal structure.

Joint distribution

As has been observed previously (Hauptman & Karle, 1953*a*) the concept of the joint or compound probability distribution appears to be particularly useful in problems involving probabilities of dependent events; for the probability distribution of a structure factor, when certain magnitudes or phases are specified, is readily derivable from the joint distribution. The structure factor for the centrosymmetric crystal is given by (1). Denote by $p(\xi_{j1}, \ldots, \xi_{jm})d\xi_{j1} \ldots d\xi_{jm}$ the joint probability that $\xi_{j\mu}$ lie in the interval $\xi_{j\mu}, \xi_{j\mu}+d\xi_{j\mu}$ for $\mu = 1, 2, \ldots, m$, where

$$\xi_{j\mu} = \xi(x_j, y_j, z_j, \mathbf{h}_\mu) \tag{7}$$

and m is any positive integer. Let $P_1(A_1, \ldots, A_m)dA_1 \ldots dA_m$ be the joint probability that $F_{\mathbf{h}_\mu}$ lie in the interval $A_\mu, A_\mu+dA_\mu$, $\mu = 1, 2, \ldots, m$. We prove next the fundamental result

$$P_1(A_1, \ldots, A_m) = \frac{1}{(2\pi)^m}\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \tag{8}$$

$$\times \exp\,(-i\sum_{\mu=1}^{m} A_\mu w_\mu)\prod_{j=1}^{N/n} q(f_{j1}w_1, \ldots, f_{jm}w_m)dw_1 \ldots dw_m,$$

where

$$q(f_{j1}w_1, \ldots, f_{jm}w_m) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} p(\xi_{j1}, \ldots, \xi_{jm})$$

$$\times \exp\,(i\sum_{\mu=1}^{m} f_{j\mu}\xi_{j\mu}w_\mu)d\xi_{j1} \ldots d\xi_{jm}, \tag{9}$$

and

$$f_{j\mu} = f_j(h_\mu, k_\mu, l_\mu) = f_j(\mathbf{h}_\mu) \tag{10}$$

is the atomic scattering factor of the jth atom.

The probability, $Q(A_1, \ldots, A_m)$ that $F_{\mathbf{h}_\mu}$ be less than A_μ for every $\mu = 1, 2, \ldots, m$ is

$$Q(A_1, \ldots, A_m) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \tag{11}$$

$$\times \prod_{j=1}^{N/n} (p(\xi_{j1}, \ldots, \xi_{jm})d\xi_{j1} \ldots d\xi_{jm}) \prod_{\mu=1}^{m} T(\xi_{1\mu}, \ldots, \xi_{(N/n)\mu}),$$

where

$$\begin{aligned} T(\xi_{1\mu}, \ldots, \xi_{(N/n)\mu}) &= \frac{1}{2} - \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{\exp\,[i(F_{\mathbf{h}_\mu}-A_\mu)w_\mu]dw_\mu}{iw_\mu} \\ &= 1 \text{ if } F_{\mathbf{h}_\mu} < A_\mu\,, \\ &= 0 \text{ if } F_{\mathbf{h}_\mu} > A_\mu\,. \end{aligned} \tag{12}$$

By differentiating (11) successively with respect to $A_1, \ldots, A_m$, we obtain (8) and (9) since

$$P_1(A_1, \ldots, A_m) = \frac{\partial^m Q(A_1, \ldots, A_m)}{\partial A_1 \ldots \partial A_m}\,. \tag{13}$$

Probability distributions for *F*

Equations (8) and (9) are the starting point from which the probability distributions for the structure factors may be derived on the basis that certain sets of magnitudes or phases are known. As in the derivation of (8), the atoms are assumed to range at random throughout the asymmetric unit except in so far as they are restricted by a knowledge of the magnitudes or the phases of a specified set of structure factors. The formulas to be derived are of two types, those requiring a knowledge of intensities only, and others requiring a knowledge of the phases also.

The method used for evaluating (8) and (9) is the same in all cases and is illustrated for the simplest case, namely when $m = 2$. Using the Maclaurin expansion of the exponential, (9) now reduces to

$$q(f_{\,1}w_1, f_{j2}w_2) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p(\xi_{j1}, \xi_{j2})d\xi_{j1}d\xi_{j2}$$

$$\times\{1+i(f_{j1}\xi_{j1}w_1+f_{j2}\xi_{j2}w_2) - \frac{1}{2!}(f_{j1}\xi_{j1}w_1+f_{j2}\xi_{j2}w_2)^2$$

$$-\frac{i}{3!}(f_{j1}\xi_{j1}w_1+f_{j2}\xi_{j2}w_2)^3 + \ldots.\}\,. \tag{14}$$

The notation

$$m_{\lambda\varrho} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p(\xi_{j1}, \xi_{j2})\,\xi_{j1}^{\lambda}\xi_{j2}^{\varrho}d\xi_{j1}d\xi_{j2} \tag{15}$$

is introduced. Interpreting (15) as an expected value, or average, of $\xi^{\lambda}_{j1}\xi^{\varrho}_{j2}$ we infer that

$$m_{\lambda\varrho} = \int_0^1\int_0^1\int_0^1 \xi^{\lambda}_{j1}(x, y, z, \mathbf{h}_1)\,\xi^{\varrho}_{j2}(x, y, z, \mathbf{h}_2)\,dx\,dy\,dz\,. \quad (16)$$

The importance of (16) is due to the fact that in evaluating q from (14) it is not necessary to have an explicit expression for $p(\xi_{j1}, \xi_{j2})$. It is sufficient to evaluate the moments $m_{\lambda\varrho}$ in (16), a relatively simple matter once the functions ξ_{j1} and ξ_{j2} have been given.

We consider in detail only the space group $P\bar{1}$, so that

$$\xi_{j\mu} = 2\cos 2\pi(h_\mu x + k_\mu y + l_\mu z)\,, \quad (17)$$

but it is obvious that the same methods apply to any centrosymmetric space group. Since $m_{01} = m_{10} = m_{03} = m_{30} = 0$, $m_{11} = 0$ if $\mathbf{h}_1 \neq \mathbf{h}_2$, $m_{02} = m_{20} = 2$, and not both of m_{12}, m_{21} are different from zero so that we may assume $m_{21} = 0$, equation (14) reduces to

$$q(f_{j1}w_1, f_{j2}w_2) = 1 - f_{j1}^2 w_1^2 - f_{j2}^2 w_2^2 - (i/2) f_{j1} f_{j2}^2 w_1 w_2^2 m_{12} + \dots\,. \quad (18)$$

Thus

$$\log \prod_{j=1}^{N/2} q(f_{j1}, f_{j2}) = -w_1^2 \sum_{j=1}^{N/2} f_{j1}^2 - w_2^2 \sum_{j=1}^{N/2} f_{j2}^2 - (i/2) w_1 w_2^2 m_{12} \sum_{j=1}^{N/2} f_{j1} f_{j2}^2 + \dots\,, \quad (19)$$

and

$$\prod_{=1}^{N/2} q(f_{j1}w_1, f_{j2}w_2) = \exp\left(-w_1^2 \sum_{j=1}^{N/2} f_{j1}^2 - w_2^2 \sum_{j=1}^{N/2} f_{j2}^2\right) \times \left\{1 - (i/2) w_1 w_2^2 m_{12} \sum_{j=1}^{N/2} f_{j1} f_{j2}^2 + \dots\right\}. \quad (20)$$

Substituting from (20) into (8) we obtain

$$P_1(A_1, A_2) = \frac{\exp\left(-\dfrac{A_1^2}{2\sum\limits_{j=1}^{N} f_{j1}^2} - \dfrac{A_2^2}{2\sum\limits_{j=1}^{N} f_{j2}^2}\right)}{2\pi\left(\sum\limits_{j=1}^{N} f_{j1}^2 \sum\limits_{j=1}^{N} f_{j2}^2\right)^{\frac{1}{2}}} \times \left\{1 + \frac{m_{12} A_1 \sum\limits_{j=1}^{N} f_{j1} f_{j2}^2}{4 \sum\limits_{j=1}^{N} f_{j1}^2 \sum\limits_{j=1}^{N} f_{j2}^2}\left(\frac{A_2^2}{\sum\limits_{j=1}^{N} f_{j2}^2} - 1\right)\right\}, \quad (21)$$

where j now ranges over all N atoms in the unit cell. For $F_{\mathbf{h}_2} = A_2$, (21) yields the probability distribution for $F_{\mathbf{h}_1}$. However, unless $\mathbf{h}_1 = 2\mathbf{h}_2$, we have $m_{12} = 0$ and, to the approximation involved, (21) is an even function of A_1 and therefore yields no information concerning the sign of $F_{\mathbf{h}_1}$. Therefore let $\mathbf{h}_1 = 2\mathbf{h}_2$. Then $m_{12} = 2$ and (21) becomes

$$P_1(A_1, A_2) = \frac{\exp\left(-\dfrac{A_1^2}{2\sum\limits_{j=1}^{N} f_{j1}^2} - \dfrac{A_2^2}{2\sum\limits_{j=1}^{N} f_{j2}^2}\right)}{2\pi\left(\sum\limits_{j=1}^{N} f_{j1}^2 \sum\limits_{j=1}^{N} f_{j2}^2\right)^{\frac{1}{2}}} \times \left\{1 + \frac{A_1 \sum\limits_{j=1}^{N} f_{j1} f_{j2}^2}{2 \sum\limits_{j=1}^{N} f_{j1}^2 \sum\limits_{j=1}^{N} f_{j2}^2}\left(\frac{A_2^2}{\sum\limits_{j=1}^{N} f_{j2}^2} - 1\right)\right\}, \quad (22)$$

which (except for a normalizing factor) is the probability distribution for $F_{\mathbf{h}_1}$ after it is known that the intensity $|F_{\mathbf{h}_2}|$ is equal to A_2^2, provided that $\mathbf{h}_1 = 2\mathbf{h}_2$. It is to be emphasized that since (22) is not an even function of A_1 information concerning the sign of $F_{\mathbf{h}_1}$ is now available. In fact the probability that $F_{\mathbf{h}_1}$ be positive, once the values of $|F_{\mathbf{h}_1}|$ and $|F_{\mathbf{h}_2}|$ are known, is readily derivable from (22) and will be obtained later.

Next we define the *normalized structure factor* by means of

$$E_{\mathbf{h}} = F_{\mathbf{h}} \Big/ \left(\sum_{j=1}^{N} f_j^2\right)^{\frac{1}{2}}, \quad (23)$$

so that $E_{\mathbf{h}}$ and $F_{\mathbf{h}}$ have the same sign. Since the average value of $F_{\mathbf{h}}^2$ is given by

$$\langle F_{\mathbf{h}}^2 \rangle = \sum_{j=1}^{N} f_j^2 \quad (24)$$

($p = 2$ in equation (23) of Karle & Hauptman, 1953), (23) implies

$$\langle E_{\mathbf{h}}^2 \rangle = 1\,. \quad (25)$$

The probability distributions are considerably simplified when referred to the normalized structure factors rather than the structure factors themselves, and they will be used exclusively in this form from now on. Equation (22) then becomes

$$P(E_1, E_2) = \frac{\exp\left(-\frac{1}{2}E_1^2 - \frac{1}{2}E_2^2\right)}{2\pi} \times \left\{1 + \frac{\left(\sum\limits_{1}^{N} f_{j1} f_{j2}^2\right)}{2\left(\sum\limits_{1}^{N} f_{j1}^2\right)^{1/2}\left(\sum\limits_{1}^{N} f_{j2}^2\right)} E_1(E_2^2 - 1)\right\}, \quad (26)$$

where $P(E_1, E_2)dE_1dE_2$ is the probability that both $E_{\mathbf{h}_1}$ lie between E_1 and $E_1 + dE_1$ and $E_{\mathbf{h}_2}$ lie between E_2 and $E_2 + dE_2$. Except for a normalizing factor (Uspensky, 1937, p. 31), (26) is the probability distribution for $E_{\mathbf{h}_1}$ after it is known that $E_{\mathbf{h}_2}^2$ is equal to E_2^2 (always under the condition $\mathbf{h}_1 = 2\mathbf{h}_2$). It is to be emphasized that, since (26) is *not* an even function of E_1, information concerning the sign of $E_{\mathbf{h}_1}$ is now available. In fact the probability that $E_{\mathbf{h}_1}$ be positive, once the values of $|E_{\mathbf{h}_1}|$ and $|E_{\mathbf{h}_2}|$ are known, is readily derivable from (26) and will be obtained later.

Equation (26) is the first of a long series of similar expressions obtained from (8) by letting $m = 2, 3, 4, \ldots$, assuming suitable linear relationships among the vectors $\mathbf{h}_1, \mathbf{h}_2, \ldots, \mathbf{h}_m$, and taking as many terms in the Maclaurin expansion of the exponential in (9) as are needed to obtain significant results. Since the procedure is the same as in the derivation of (26) we write here only one more typical formula without proof:

$$\begin{aligned}P(E_1, E_2, E_3) &\\ = \exp\left(-\tfrac{1}{2}E_1^2-\tfrac{1}{2}E_2^2-\tfrac{1}{2}E_3^2\right)&\Big\{1+p_1(E_1^2, E_2^2, E_3^2)\\ +\frac{E_1}{4}\cdot\frac{\Sigma f_{j1}f_{j2}^2f_{j3}^2}{(\Sigma f_{j1}^2)^{1/2}(\Sigma f_{j2}^2)(\Sigma f_{j3}^2)}&(E_2^2-1)(E_3^2-1)\Big\},\\ \mathbf{h}_1 = \pm 2\mathbf{h}_2 \pm 2\mathbf{h}_3, &\qquad (27)\end{aligned}$$

where j ranges from 1 to N and p_1 is a symmetric polynomial in E_1^2, E_2^2, E_3^2 the exact form of which is unimportant since it does not appear in the final formulas for phase determination.

Probabilities for the sign of F

From the joint probability distributions for certain sets of normalized structure factors, the probability that the sign of a structure factor be plus, on the basis that certain magnitudes or phases are known, may be inferred. Denote by $P_+(F)$ the probability that the sign of F be plus. Then, using $P_+(F)+P_-(F) = 1$ or $P_+(F) = (P_+/P_-)/(1+(P_+/P_-))$, we find from (27)

$$\begin{aligned}P_+(F_\mathbf{h}) &\\ = \tfrac{1}{2}+\tfrac{1}{8}\cdot\frac{\Sigma f_{j\mathbf{h}}f_{j\mathbf{h}_\mu}^2f_{j\mathbf{h}_\nu}^2}{(\Sigma f_{j\mathbf{h}}^2)^{1/2}(\Sigma f_{j\mathbf{h}_\mu}^2)(\Sigma f_{j\mathbf{h}_\nu}^2)}&|E_\mathbf{h}|(E_{\mathbf{h}_\mu}^2-1)(E_{\mathbf{h}_\nu}^2-1),\\ &\qquad (28)\\ \mathbf{h} = \pm 2\mathbf{h}_\mu \pm 2\mathbf{h}_\nu,&\end{aligned}$$

where $P_+(F_\mathbf{h})$ is the probability that $F_\mathbf{h}$ be positive once the magnitudes of $E_\mathbf{h}$, $E_{\mathbf{h}_\mu}$, and $E_{\mathbf{h}_\nu}$ are known. A special significance is to be attached to (28) since it is the probability that a structure factor be positive on the basis that the magnitudes only (and not the signs) of a certain set of structure factors are known. Hence (28) forms the starting point of the procedure for phase determination to be described.

Equation (28) is an expression which in general differs only slightly from $\frac{1}{2}$. In order to become an effective tool for phase determination this formula must be modified somewhat so as to take into account a large number of observed magnitudes. This is readily done by making use of joint probability distributions of large numbers of structure factors. We conclude from (28) that the sign of $F_\mathbf{h}$, where $\mathbf{h}$ is even, is the same as the sign of

$$\sum_{\mathbf{h}_\mu\pm\mathbf{h}_\nu=\frac{1}{2}\mathbf{h}}\frac{\Sigma f_{j\mathbf{h}}f_{j\mathbf{h}_\mu}^2f_{j\mathbf{h}_\nu}^2}{(\Sigma f_{j\mathbf{h}}^2)^{1/2}(\Sigma f_{j\mathbf{h}_\mu}^2)(\Sigma f_{j\mathbf{h}_\nu}^2)}(E_{\mathbf{h}_\mu}^2-1)(E_{\mathbf{h}_\nu}^2-1). \qquad (29)$$

A great simplification of the formulas used in the procedure for sign determination may be realized if we use the relationship

$$f_{j\mathbf{h}} = Z_j f_\mathbf{h}, \qquad (30)$$

where Z_j is the atomic number of the jth atom and $f_\mathbf{h}$ is a function of $\mathbf{h}$ which is assumed to be the same for all atoms present. Then (29), for example, reduces to

$$\frac{\sum_j Z_j^5}{(\sum_j Z_j^2)^{5/2}}\cdot\sum_{\mathbf{h}_\mu\pm\mathbf{h}_\nu=\frac{1}{2}\mathbf{h}}(E_{\mathbf{h}_\mu}^2-1)(E_{\mathbf{h}_\nu}^2-1). \qquad (31)$$

Procedure for phase determination

It is assumed that the magnitudes $|F|$ of the structure factors have been adjusted to an absolute scale and for vibrational motion, e.g. by means of well known averaging procedures (Wilson, 1949). Then the 'normalized' structure-factor magnitudes $|E|$ may be readily computed from (23). The sign of any E is seen from (23) to be the same as that of its corresponding F. The E's are arranged in decreasing order and their signs (within each step) will be generally determined in this order.

Step 1.—We determine the signs of all structure factors whose phases are linearly dependent modulo 2. The sign of $E_\mathbf{h}$, where $\mathbf{h}$ is even, is the sign of

$$\Sigma = \Sigma_1+\Sigma_2+\Sigma_3+\Sigma_4, \qquad (32)$$

where[*][†][‡]

$$\Sigma_1 = \frac{\Sigma Z_j^3}{4(\Sigma Z_j^2)^{3/2}}\sum_{\mathbf{h}=2\mathbf{h}_\mu}(E_\mu^2-1), \qquad (33)$$

$$\Sigma_2 = \frac{\Sigma Z_j^3}{2(\Sigma Z_j^2)^{3/2}}\sum_{\mathbf{h}=\mathbf{h}_\mu\pm\mathbf{h}_\nu}E_\mu E_\nu, \qquad (34)$$

$$\Sigma_3 = \frac{\Sigma Z_j^4}{4(\Sigma Z_j^2)^2}\sum_{\mathbf{h}=\mathbf{h}_\mu\pm 2\mathbf{h}_\nu}E_\mu(E_\nu^2-1), \qquad (35)$$

$$\Sigma_4 = \frac{\Sigma Z_j^5}{8(\Sigma Z_j^2)^{5/2}}\sum_{\mathbf{h}=2\mathbf{h}_\mu\pm 2\mathbf{h}_\nu}(E_\mu^2-1)(E_\nu^2-1). \qquad (36)$$

Since, initially, only the magnitudes of the E's are known, only Σ_1 (which contains only one summand) and Σ_4 can contribute to Σ in (32). However, as soon as a few signs become available, Σ_3 begins to play a role and, as more and more signs become known, Σ_2 plays more and more important a role.

Step 2.—We specify arbitrarily the sign of the largest normalized structure factor $E_{\mathbf{h}_1}$, whose phase $\varphi_{\mathbf{h}_1}$ is linearly independent modulo 2, and then deter-

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[*] For convenience, the subscript $\mathbf{h}$ is suppressed when there is no danger of ambiguity, e.g. $E_{\mathbf{h}_\mu}$ is replaced by E_μ, etc.

[†] Equation (33) may be compared with the Harker–Kasper (1948) inequality (8).

[‡] Equation (34) should be compared to equation (1·3) of Sayre (1952), equation (8) of Zachariasen (1952), or equation (18) of Cochran (1952), and to the inequality (34) of Karle & Hauptman (1950).

mine the signs of all structure factors $F_{\mathbf{h}}$, where $\varphi_{\mathbf{h}}$ is linearly dependent modulo 2 on $\varphi_{\mathbf{h}_1}$. This is accomplished by using the results of Step 1. Let $\mathbf{h}_{\nu_1} \equiv \mathbf{h}_1$ (mod 2). The sign of $E_{\mathbf{h}}$, where both $\mathbf{h} \pm \mathbf{h}_{\nu_1}$ are even is the sign of

$$\Sigma' = \Sigma_2 + \Sigma_3' + \Sigma_5 + \Sigma_6 + \Sigma_7 , \tag{37}$$

where Σ_2 is given by (34) and

$$\Sigma_3' = \frac{\Sigma Z_j^4}{4(\Sigma Z_j^2)^2} \sum_{\mathbf{h} \pm \mathbf{h}_{\nu_1} = 2\mathbf{h}_\nu} E_{\nu_1}(E_\nu^2 - 1) , \tag{38}$$

$$\Sigma_5 = \frac{\Sigma Z_j^4}{2(\Sigma Z_j^2)^2} \sum_{\mathbf{h} \pm \mathbf{h}_{\nu_1} = \mathbf{h}_\mu \pm \mathbf{h}_\nu} E_{\nu_1} E_\mu E_\nu , \tag{39}$$

$$\Sigma_6 = \frac{\Sigma Z_j^5}{4(\Sigma Z_j^2)^{5/2}} \sum_{\mathbf{h} \pm \mathbf{h}_{\nu_1} = \mathbf{h}_\mu \pm 2\mathbf{h}_\nu} E_{\nu_1} E_\mu (E_\nu^2 - 1) , \tag{40}$$

$$\Sigma_7 = \frac{\Sigma Z_j^6}{8(\Sigma Z_j^2)^3} \sum_{\mathbf{h} \pm \mathbf{h}_{\nu_1} = 2\mathbf{h}_\mu \pm 2\mathbf{h}_\nu} E_{\nu_1} (E_\mu^2 - 1)(E_\nu^2 - 1) . \tag{41}$$

At first only Σ_3', Σ_5, Σ_6 and Σ_7 are important contributors to Σ' in (37), and in computing Σ_5 and Σ_6 use is made of the known signs obtained from Step 1. However, as soon as a few signs are found Σ_5 becomes more important and as more and more signs become known Σ_2 again plays the dominant role.

Step 3.—We specify arbitrarily the sign of the largest normalized structure factor $E_{\mathbf{h}_2}$, whose phase $\varphi_{\mathbf{h}_2}$ is linearly independent modulo 2 of $\varphi_{\mathbf{h}_1}$, and then determine the signs of all structure factors $F_{\mathbf{h}}$ whose phases $\varphi_{\mathbf{h}}$ are linearly dependent modulo 2 on $F_{\mathbf{h}_2}$. This is accomplished as in Step 2, but $\mathbf{h}_2$ replaces $\mathbf{h}_1$.

Step 4.—We specify arbitrarily the sign of the largest normalized structure factor $E_{\mathbf{h}_3}$, whose phase $\varphi_{\mathbf{h}_3}$ is linearly independent modulo 2 of the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$, and then determine the signs of all structure factors $F_{\mathbf{h}}$ whose phases are linearly dependent modulo 2 on $\varphi_{\mathbf{h}_3}$. This is accomplished as in Step 2, but $\mathbf{h}_3$ replaces $\mathbf{h}_1$.

Step 5.—We determine the signs of all structure factors $F_{\mathbf{h}}$ whose phases are linearly dependent modulo 2 on the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_2}$. This is accomplished by using the results of Steps 1, 2, 3. Let $\mathbf{h}_{\nu_1} \equiv \mathbf{h}_1$, $\mathbf{h}_{\nu_2} \equiv \mathbf{h}_2$ (mod 2). The sign of $F_{\mathbf{h}}$, where $\mathbf{h} \pm \mathbf{h}_{\nu_1} \pm \mathbf{h}_{\nu_2}$ are all even, is the sign of

$$\Sigma'' = \Sigma_2 + \Sigma_5' , \tag{42}$$

where

$$\Sigma_5' = \frac{\Sigma Z_j^4}{2(\Sigma Z_j^2)^2} \sum_{\mathbf{h} \pm \mathbf{h}_{\nu_1} \pm \mathbf{h}_{\nu_2} = \mathbf{h}_\nu} E_{\nu_1} E_{\nu_2} E_\nu . \tag{43}$$

At first the results of Steps 2 and 3 are mainly used, but as more signs are obtained, the results of Step 1 are used more and more.

Step 6.—We determine the signs of all structure factors $F_{\mathbf{h}}$ whose phases are linearly dependent modulo 2 on the pair $\varphi_{\mathbf{h}_1}$, $\varphi_{\mathbf{h}_3}$. This is done as in Step 5 using the results of Steps 1, 2, 4.

Step 7.—We determine the signs of all structure factors $F_{\mathbf{h}}$ whose phases are linearly dependent modulo 2 on the pair $\varphi_{\mathbf{h}_2}$, $\varphi_{\mathbf{h}_3}$. This is done as in Step 5 using the results of Steps 1, 3, 4.

Step 8.—The signs of all remaining structure factors $F_{\mathbf{h}}$ are determined. This is accomplished by using the results of Steps 1–7. The sign of $F_{\mathbf{h}}$ is the sign of Σ_2.

Concluding remarks

The solution of the phase problem described here provides a routine and practical method for phase determination for space group $P\bar{1}$. In the Monograph the solution for all centrosymmetric space groups is described. The procedure is readily adapted for IBM techniques. Only a knowledge of a sufficient number of X-ray intensities and of the chemical composition of the crystal is required.

The Monograph treats crystals having atoms in special as well as in general positions. Confirmation of the theory is obtained in several ways. The probability theory leads in a non-trivial way to the same dependence between the sign of a structure factor and the choice of origin as is obtained from an independent analysis. In a numerical example, 38 out of 40 signs were obtained correctly by the use of only a few of the simpler relationships obtained from the probability theory. Some of the formulas were qualitatively confirmed by means of a geometric interpretation.

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