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A Study on the Statistical Method for Determination of Signs of Structure Factors

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A systematic investigation has been carried out on the theory of joint probability distribution of signs of structure factors, which is applicable to centrosymmetric space groups. Joint probability of a set of centrosymmetric structure factors is also calculated in a more general way than the methods given by Bertaut in 1955 and Klug in 1958. Using the results thus obtained, various expected values for signs and their products necessary for the evaluation of corresponding probabilities are calculated. The results are discussed.

1. Introduction

The statistical methods in crystallography introduced by Wilson and continued by a number of authors have been extended to the determination of phases of structure factors. Besides the development, along the line of Wilson's theory, followed by Hauptman & Karle (1953), Cochran & Woolfson (1955), Bertaut (1955*a*, *b*), Klug (1958), and others, algebraic methods have also been worked out by Cochran (1954), Hauptman & Karle (1957), Bertaut (1959), and others. The new joint probability methods by Hauptman & Karle (1958) as well as the 'chaîne statistique' by Bertaut (1960) have also been devised. Finally Vaughan (1959) has made critical comments on these statistical methods.

In the present paper we put forward a statistical theory applicable to any centrosymmetric crystal, from the point of view mainly similar to that of Bertaut (1955*a*, *b*) and Klug (1958), but trying to generalize their methods in some respects.

In § 2 a concept of joint probability of signs is introduced which is useful in the treatment of the cases of centrosymmetric space groups and its nature is analysed.

In § 3 our method of calculating joint probability of structure factors is shown. It is mainly based on the methods of Bertaut (1955*a*, *b*) and Klug (1958). However, our results have a form more general and capable of easy application to any special centrosymmetric space group.

In § 4 various probabilities of signs and sign products as well as the corresponding expected values (mathematical expectations) are given for the case of $P\bar{1}$, using the theory of § 2 and the results obtained in § 3. The results are then discussed.

2. Joint probability distribution of signs of structure factors

In the statistical theories for the determination of signs of structure factors hitherto given by many authors, the heart of the problem is in finding the joint probability of structure factors with their magnitudes and signs. Here the magnitudes are determinable in principle from measurements. Let us introduce a concept of the joint probability distributions of signs under the condition that the corresponding magnitudes of structure factors have already been fixed in accordance with observation.

2·1. *General expression*

Denote by $\boldsymbol{E}_i$ the normalized structure factors, s_i their signs ($+1$ or -1) and E_i their magnitudes; *i.e.* $\boldsymbol{E}_i=E_is_i$, and $E_i=|\boldsymbol{E}_i|$. Introduce joint probability distribution function $P(s_1, s_2, \ldots, s_m)$ for a set of m signs $s_1, \ldots, s_m$. Then it is easily shown that, in view of $s_i=\pm 1$ and $s_i^2=+1$,

$$P(s_1, \ldots, s_m)=(1/2^m)\{1+\sum_{i=1}^{m}\langle s_i\rangle s_i+\sum_{i>j=1}^{m}\langle s_is_j\rangle s_is_j + \sum_{i>j>l=1}^{m}\langle s_is_js_l\rangle s_is_js_l+\ldots+\langle s_1\ldots s_m\rangle s_1\ldots s_m\}, \quad (1)$$

in which

$$\langle s_i\rangle = \sum_{s_1=\pm1}\ldots\sum_{s_m=\pm1} s_iP(s_1, \ldots, s_m),$$
$$\langle s_is_j\rangle = \sum_{s_1=\pm1}\ldots\sum_{s_m=\pm1} s_is_jP(s_1, \ldots, s_m),$$
$$\langle s_is_js_l\rangle = \sum_{s_1=\pm1}\ldots\sum_{s_m=\pm1} s_is_js_lP(s_1, \ldots, s_m),\ etc. \quad (2)$$

The summation is to be carried out over all the possible values, $+1$ and -1 for each sign $s_i (i=1, \ldots, m)$, and the symbol $\langle\ \rangle$ expresses the expected values (mathematical expectations) of s_i, s_is_j, $s_is_js_l$, *etc.*

It is to be noted that the expansion of the form of (1) will be generally applicable to any statistical system, such as a spin system, of m variables $s_1, \ldots, s_m$, each of which can take its value of $+1$ or -1.

2·2. *Some probabilities obtainable by reduction from joint probability of signs*

Denote by $P(s_1)$ the probability for the sign of $\boldsymbol{E}_1$ to be s_1 irrespectively of the other signs, $s_2, \ldots, s_m$. $P(s_1)$ can be derived from (1) by reduction concerning the other variables $s_2, \ldots, s_m$,

$$P(s_1) = \sum_{s_2=\pm1} \cdots \sum_{s_m=\pm1} P(s_1, \ldots, s_m) = \tfrac{1}{2}\{1+\langle s_1\rangle s_1\}\,. \quad (3)$$

In the same way, denoting by $P(s_1, s_2)$ the probability for the signs of $\boldsymbol{E}_1$ and $\boldsymbol{E}_2$ to be s_1 and s_2 respectively is given by

$$\begin{aligned} P(s_1, s_2) &= \sum_{s_3=\pm1} \cdots \sum_{s_m=\pm1} P(s_1, \ldots, s_m) \\ &= (1/2^2)\{1+\langle s_1\rangle s_1+\langle s_2\rangle s_2+\langle s_1s_2\rangle s_1s_2\}\,. \quad (4)\end{aligned}$$

Similarly,

$$\begin{aligned} P(s_1, s_2, s_3) &= \sum_{s_4=\pm1} \cdots \sum_{s_m=\pm1} P(s_1, \ldots, s_m) \\ &= (1/2^3)\{1+\langle s_1\rangle s_1+\langle s_2\rangle s_2+\langle s_3\rangle s_3+\langle s_1s_2\rangle s_1s_2 \\ &\quad +\langle s_2s_3\rangle s_2s_3+\langle s_3s_1\rangle s_3s_1+\langle s_1s_2s_3\rangle s_1s_2s_3\}\,, \quad (5)\end{aligned}$$

and so on.

2·3. *Expected values*

When the probability for s_1 to be $+1$ is denoted by $P^+(s_1)$, it is written from (3) as

$$P^+(s_1) = \tfrac{1}{2}\{1+\langle s_1\rangle\}\,, \quad (6)$$

and the probability for s_1 to be -1

$$P^-(s_1) = \tfrac{1}{2}\{1-\langle s_1\rangle\}\,. \quad (7)$$

Hence the expected value $\langle s_1\rangle$ can be interpreted as a measure of deviation of these probabilities $P^{\pm}(s_1)$ from a mean value $\frac{1}{2}$.

When a sign product s_1s_2 is considered, the probability for s_1s_2 to be $+1$ is derived from (4) to be

$$\begin{aligned} P^+(s_1s_2) &= P^{+,+}(s_1, s_2)+P^{-,-}(s_1, s_2) \\ &= (1/2^2)\{1+\langle s_1\rangle+\langle s_2\rangle+\langle s_1s_2\rangle\} \\ &\quad +(1/2^2)\{1-\langle s_1\rangle-\langle s_2\rangle+\langle s_1s_2\rangle\} = \tfrac{1}{2}\{1+\langle s_1s_2\rangle\}, \quad (8)\end{aligned}$$

and the probability for s_1s_2 to be -1 is

$$\begin{aligned} P^-(s_1s_2) &= P^{+,-}(s_1, s_2)+P^{-,+}(s_1, s_2) \\ &= (1/2^2)\{1+\langle s_1\rangle-\langle s_2\rangle-\langle s_1s_2\rangle\} \\ &\quad +(1/2^2)\{1-\langle s_1\rangle+\langle s_2\rangle-\langle s_1s_2\rangle\} = \tfrac{1}{2}\{1-\langle s_1s_2\rangle\}\,. \quad (9)\end{aligned}$$

In this case it is also shown that the expected value $\langle s_1s_2\rangle$ corresponds to the deviation similar to that in (6) and (7).

Concerning a triple product $s_1s_2s_3$, it is given that

$$P^+(s_1s_2s_3) = \tfrac{1}{2}\{1+\langle s_1s_2s_3\rangle\}\,, \quad (10)$$

$$P^-(s_1s_2s_3) = \tfrac{1}{2}\{1-\langle s_1s_2s_3\rangle\}\,. \quad (11)$$

Generally the expected value $\langle s_i\ldots s_k\rangle$ is the deviation of the probability for a sign product $s_i\ldots s_k$ to be $+1$ or -1 from $\frac{1}{2}$.

It is to be noted that the quantities required for determination of signs of structure factors in statistical theories are such expected values.

2·4. *Conditional probability*

Let the conditional probability for s_1 relative to a fixed value of s_2 be denoted by $P(s_1|s_2)$ or $P_{s_2}(s_1)$. The relation between this quantity and $P(s_1, s_2)$ is given by

$$P(s_1, s_2) = P(s_2)P(s_1|s_2)\,, \quad (12)$$

where $P(s_2)$ and $P(s_1, s_2)$ are expressed by (3) and (4). Therefore,

$$\begin{aligned} P(s_1|s_2) &\equiv P_{s_2}(s_1) \\ &= \frac{P(s_1, s_2)}{P(s_2)} = \frac{(1/2^2)\{1+\langle s_1\rangle s_1+\langle s_2\rangle s_2+\langle s_1s_2\rangle s_1s_2\}}{\frac{1}{2}\{1+\langle s_2\rangle s_2\}} \\ &= \tfrac{1}{2}\left\{1+\frac{\langle s_1\rangle+\langle s_1s_2\rangle s_2}{1+\langle s_2\rangle s_2}\,s_1\right\} \equiv \tfrac{1}{2}\{1+\langle s_1\rangle_{s_2}s_1\}\,, \quad (13)\end{aligned}$$

in which

$$\langle s_1\rangle_{s_2} = \frac{\langle s_1\rangle+\langle s_1s_2\rangle s_2}{1+\langle s_2\rangle s_2} \quad (14)$$

is the expected value for s_1 relative to the hypothesis that the value of s_2 is fixed.

In the same way as in (12), (13) and (14), the expected value for s_1 relative to the hypothesis that a fixed value is given to the sign product s_1s_2 is written

$$\langle s_1\rangle_{s_1s_2} = \frac{\langle s_1\rangle+\langle s_2\rangle s_1s_2}{1+\langle s_1s_2\rangle s_1s_2}\,. \quad (15)$$

The expected value for s_1 under the condition that s_2 and s_3 have fixed values respectively is given by

$$\langle s_1\rangle_{s_2,s_3} = \frac{\langle s_1\rangle+\langle s_1s_2\rangle s_2+\langle s_1s_3\rangle s_3+\langle s_1s_2s_3\rangle s_2s_3}{1+\langle s_2\rangle s_2+\langle s_3\rangle s_3+\langle s_2s_3\rangle s_2s_3}\,. \quad (16)$$

On the contrary, the expected value for s_1 relative to the hypothesis for the product s_2s_3 to have a fixed value is

$$\langle s_1\rangle_{s_2s_3} = \frac{\langle s_1\rangle+\langle s_1s_2s_3\rangle s_2s_3}{1+\langle s_2s_3\rangle s_2s_3}\,. \quad (17)$$

Other similar examples are

$$\langle s_1s_2\rangle_{s_2s_3} = \frac{\langle s_1s_2\rangle+\langle s_1s_3\rangle s_2s_3}{1+\langle s_2s_3\rangle s_2s_3}\,, \quad (18)$$

$$\langle s_1\rangle_{s_1 s\ \ s_2 s_3} = \frac{\langle s_1\rangle + \langle s_2\rangle s_1 s_2 + \langle s_3\rangle s_1 s_2 s_2 s_3 + \langle s_1 s_2 s_3\rangle s_2 s_3}{1+\langle s_1 s_2\rangle s_1 s_2 + \langle s_2 s_3\rangle s_2 s_3 + \langle s_1 s_3\rangle s_1 s_2 s_2 s_3}\,, \qquad (19)$$

$$\langle s_1\rangle_{s_1 s_2 s_3} = \frac{\langle s_1\rangle + \langle s_2 s_3\rangle s_1 s_2 s_3}{1+\langle s_1 s_2 s_3\rangle s_1 s_2 s_3}\,. \qquad (20)$$

Derivations of other expected values under any given condition like one of the relations from (14) to (20) can easily be made. Thus, basing oneself upon these relations up to (20), it can be understood that when three structure factors of the indices h, h', $h+h'$ are considered as possessing the relation $s_h s_{h'} s_{h+h'}=1$, the expected value for an s_h relative to the hypothesis $s_h s_{h'} s_{h+h'}=1$ is given by

$$\langle s_h\rangle_{s_h s_{h'} s_{h+h'}=1} = \frac{\langle s_h\rangle + \langle s_{h'} s_{h+h'}\rangle}{1+\langle s_h s_{h'} s_{h+h'}\rangle}\,, \qquad (21)$$

corresponding to (20). Therefore, using (21), the conditional probability for $s_h=1$ becomes

$$P^{+}_{s_h s_{h'} s_{h+h'}=1}(s_h) = \tfrac{1}{2}\{1+\langle s_h\rangle_{s_h s_{h'} s_{h+h'}=1}\}$$
$$= \tfrac{1}{2}\left\{1+\frac{\langle s_h\rangle + \langle s_{h'} s_{h+h'}\rangle}{1+\langle s_h s_{h'} s_{h+h'}\rangle}\right\}. \qquad (22)$$

2·5. *The relation between $P(s_1, s_2, \ldots, s_m)$ and $P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$*

Let the joint probability distribution for a set of m structure factors be denoted by $P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$. This is related to $P(s_1, \ldots, s_m)$ by

$$P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m) = P(E_1, \ldots, E_m) P(s_1, \ldots, s_m \mid E_1, \ldots, E_m)\,, \qquad (23)$$

in which $P(E_1, \ldots, E_m)$ is the probability for the set of $\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m$ to have the respective given magnitudes $E_1, \ldots, E_m$ independently of the values of signs $s_1, \ldots, s_m$. It is given by

$$P(E_1, \ldots, E_m) = \sum_{s_1=\pm 1} \cdots \sum_{s_m=\pm 1} P(E_1 s_1, \ldots, E_m s_m). \qquad (24)$$

$P(s_1, \ldots, s_m | E_1, \ldots, E_m)$ in (23) is nothing other than a conditional probability for a set of sign variables $s_1, \ldots, s_m$ related to the hypothesis of fixed magnitudes of $E_1, \ldots, E_m$. Therefore, it is obvious that this conditional probability $P(s_1, \ldots, s_m \mid E_1, \ldots, E_m)$ equals to $P(s_1, \ldots, s_m)$ originally given as (1).

Thus the relation (23) gives

$$P(s_1, \ldots, s_m) \equiv P(s_1, \ldots, s_m \mid E_1, \ldots, E_m)$$
$$= \frac{P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)}{P(E_1, \ldots, E_m)} = \frac{P(E_1 s_1, \ldots, E_m s_m)}{\sum_{s_1=\pm 1} \cdots \sum_{s_m=\pm 1} P(E_1 s_1, \ldots, E_m s_m)}. \qquad (25)$$

The right hand side of (25) can be expanded in a form like (1). In such an expansion the coefficients, which are expected values, will be explicitly given, if we can obtain the joint probability of structure factors $P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$.

3. A general expression for the joint probability distribution of structure factors $P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$

Consideration given in § 2 on the basis of the joint probability of signs $P(s_1, \ldots, s_m)$ in the expansion form (1) has been found to be useful for studying the relationships among a number of probability equations concerning a set of signs $s_1, \ldots, s_m$. However, by this procedure, any information about expected values themselves can never be derived. In order to obtain these values explicitly, we have to make use of the relation (25), which contains the joint probability of structure factors $P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$. Starting, in this paragraph, from *a priori* probability of 'uniform distribution' of the atoms in a unit cell, we show that the joint probability $P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$ will be obtained in a general form applicable to any centrosymmetric space group. This is a kind of generalization of Klug's theory put forward in 1958.

3·1. *Moment of ξ*

Introduce trigonometric structure factors $\xi(\mathbf{h})$:

$$\xi(\mathbf{h}) = \tau \sum_{p=0}^{s-1} \exp[2\pi i \mathbf{h}\mathbf{r}\boldsymbol{S}_p]$$
$$= \tau \sum_{p=0}^{s-1} \exp[2\pi i \boldsymbol{R}_p \mathbf{h}\mathbf{r}] \exp[2\pi i \mathbf{h}\mathbf{t}_p]\,, \qquad (26)$$

$$\boldsymbol{S}_p = (\boldsymbol{R}_p \mid \mathbf{t}_p), \quad p=0, 1, \ldots, s-1\,,$$

in which s is the order of factor group and $\boldsymbol{S}_p$ the pth operation, of which the rotational part is $\boldsymbol{R}_p$ and the translational part $\mathbf{t}_p$. τ is the order of translation group ($\tau=2$ for A, B, C, I; $\tau=3$ for R; $\tau=4$ for F).

Under the *a priori* probability stated above, a mixed moment can be defined by

$$m_{\alpha\cdots\omega}(\mathbf{h}_1, \ldots, \mathbf{h}_m) = \overline{\xi^{\alpha}(\mathbf{h}_1)\ldots\xi^{\omega}(\mathbf{h}_m)}$$
$$= \tau^{\alpha+\cdots+\omega} \int d\mathbf{r} \left\{\sum_{p=0}^{s-1} \exp[2\pi i \mathbf{h}_1 \mathbf{r} \boldsymbol{S}_p]\right\}^{\alpha} \cdots \left\{\sum_{p=0}^{s-1} \exp[2\pi i \mathbf{h}_m \mathbf{r} \boldsymbol{S}_p]\right\}^{\omega}. \qquad (27)$$

After some calculations (see Appendix I) we get the following expression as a result:

$$m_{\alpha\cdots\omega}(\mathbf{h}_1, \ldots, \mathbf{h}_m) = \tau^{\alpha+\cdots+\omega} \sum_{\sum_p \alpha_p=\alpha} \cdots \sum_{\sum_p \omega_p=\omega} \frac{\alpha!\ldots\omega!}{\prod_p(\alpha_p!\ldots\omega_p!)}$$
$$\times \exp\left[2\pi i \left\{\sum_{p=0}^{s-1}(\alpha_p \mathbf{h}_1 + \ldots + \omega_p \mathbf{h}_m)\mathbf{t}_p\right\}\right]$$
$$\times \delta\left\{\sum_{p=0}^{s-1} \boldsymbol{R}_p(\alpha_p \mathbf{h}_1 + \ldots + \omega_p \mathbf{h}_m)\right\}, \qquad (28)$$

where $\alpha_p, \ldots, \omega_p$ are the integers in the ranges $0 \le \alpha_p \le \alpha, \ldots, 0 \le \omega_p \le \omega$, respectively; the summation is to be carried out over all possible combinations of $\alpha_p, \ldots, \omega_p$ satisfying the conditions

$$\sum_{p=0}^{s-1}\alpha_p=\alpha,\ \ldots,\ \sum_{p=0}^{s-1}\omega_p=\omega\ .$$

The symbol δ, the Kronecker symbol, means

$$\delta\left\{\sum_{p=0}^{s-1}\mathbf{R}_p(\alpha_p\mathbf{h}_1+\ldots+\omega_p\mathbf{h}_m)\right\}=1,\quad\text{if}\quad \sum_{p=0}^{s-1}\mathbf{R}_p(\alpha_p\mathbf{h}_1+\ldots+\omega_p\mathbf{h}_m)=0\ ,$$
$$\delta\left\{\sum_{p=0}^{s-1}\mathbf{R}_p(\alpha_p\mathbf{h}_1+\ldots+\omega_p\mathbf{h}_m)\right\}=0,\quad\text{if}\quad \sum_{p=0}^{s-1}\mathbf{R}_p(\alpha_p\mathbf{h}_1+\ldots+\omega_p\mathbf{h}_m)\neq 0\ . \tag{29}$$

The relation (28) has been tested by us to hold for a number of cases hitherto calculated by other authors. For the case of $P\bar{1}$, (28) becomes

$$m_{\alpha\ldots\omega}(\mathbf{h}_1,\ldots,\mathbf{h}_m)=\sum_{\alpha_0+\alpha_1=\alpha}\ldots\sum_{\omega_0+\omega_1=\omega}\times\frac{\alpha!\ldots\omega!}{\alpha_0!\ldots\omega_0!\,\alpha_1!\ldots\omega_1!}\delta\{(\alpha_0-\alpha_1)\mathbf{h}_1+\ldots+(\omega_0-\omega_1)\mathbf{h}_m\}\ . \tag{30}$$

A formula corresponding to this relation has been given by Bertaut (1955*a*).

3·2. *Moment-cumulant transformation*

Following Klug (1958) let us prepare the cumulants from the moments in order to calculate the joint probability distribution of structure factors. The moment-cumulant transformation is generally expressed by

$$\sum_{n=1}^{\infty}k_n\frac{u^n}{n!}=\log\left\{\sum_{n=0}^{\infty}m_n\frac{u^n}{n!}\right\},\quad m_0=1\ , \tag{31}$$

where u is a carrying variable, m_n the moments and k_n the cumulants. As is known, it is derived from (31) that

$$\begin{aligned}&k_1=m_1,\ k_2=m_2,\ k_3=m_3,\ k_4=m_4-3m_2^2\ ,\\ &k_5=m_5-10m_2m_3\ ,\\ &k_6=m_6-10m_3^2-15m_2m_4+30m_2^3\ ,\\ &k_7=m_7-21m_2m_5-35m_3m_4+210m_2^2m_3\ ,\ \ etc.\end{aligned} \tag{32}$$

Extension of the one-dimensional case (31) to the multidimensional one gives the following relations instead of (32).

$$k_{\alpha\ldots\omega}=m_{\alpha\ldots\omega},\ \text{for}\ \ \alpha+\ldots+\omega=1,2,3\ , \tag{33}$$

$$k_{\alpha\ldots\omega}=m_{\alpha\ldots\omega}-\tfrac{1}{2}\sum_{\alpha'+\cdots+\omega'=2}\ \sum_{\alpha''+\cdots+\omega''=3}m_{\alpha'\ldots\omega'}m_{\alpha''\ldots\omega''}\times\frac{\alpha!\ldots\omega!}{(\alpha'!\ldots\omega'!)(\alpha''!\ldots\omega''!)}\delta\{\alpha-(\alpha'+\alpha'')\}\ldots\delta\{\omega-(\omega'+\omega'')\}\ , \tag{34}$$
for $\alpha+\ldots+\omega=4$,

$$k_{\alpha\ldots\omega}=m_{\alpha\ldots\omega}-\sum_{\alpha'+\cdots+\omega'=2}\ \sum_{\alpha''+\cdots+\omega''=2}m_{\alpha'\ldots\omega'}m_{\alpha''\ldots\omega''}\times\frac{\alpha!\ldots\omega!}{(\alpha'!\ldots\omega'!)(\alpha''!\ldots\omega''!)}\delta\{\alpha-(\alpha'+\alpha'')\}\ldots\delta\{\omega-(\omega'+\omega'')\}\ , \tag{35}$$
for $\alpha+\ldots+\omega=5$, *etc.*

3·3. *Moment-generating function*

Moment-generating function $M(u_1,\ldots,u_m)$ is given by the following expression (Klug, 1958)

$$M(u_1,\ldots,u_m)=\exp\left[\tfrac{1}{2}(u_1^2+\ldots+u_m^2)\right]\exp\left[\sum_{n=3}^{\infty}\frac{z_n}{S}L_n\right]\ , \tag{36}$$

in which

$$L_n=\sum_{\alpha+\cdots+\omega=n}\frac{k_{\alpha\ldots\omega}}{\alpha!\ldots\omega!}\left(\frac{u_1}{\sqrt{(\tau\varepsilon_1)}}\right)^{\alpha}\ldots\left(\frac{u_m}{\sqrt{(\tau\varepsilon_m)}}\right)^{\omega}, \tag{37}$$

$$z_n=\sum_{j=1}^{N}\varphi_j^n\quad\text{and}\quad\varphi_j=\frac{f_j}{\left(\sum_{j=1}^{N}f_j^2\right)^{\frac{1}{2}}}\ . \tag{38}$$

Further $k_{\alpha\ldots\omega}$ is a cumulant, $S=s\tau$ the symmetry number (s the order of factor group, τ the order of translation group), and $\varepsilon_1,\ldots,\varepsilon_m$ the statistical weights of special type reflections (Bertaut, 1959, 1960). f_j is the atomic structure factor, N the number of atoms contained in unit cell and φ_j the normalized scattering factor. $z_n=1/(N^{n/2-1})$ holds in the case of equal atoms (for the case of non-equal atoms, we shall in what follows ignore the dependence of φ_j and f_j on $\mathbf{h}$). Expanding (36) in series up to the term of the order of $N^{-5/2}$, we get

$$\begin{aligned}M(u_1,\ldots,u_m)=\exp&\left[\tfrac{1}{2}(u_1^2+\ldots+u_m^2)\right]\\ &\times[1+(z_3/S)L_3+\{(z_4/S)L_4+(z_3^2/2S^2)L_3^2\}\\ &+\{(z_5/S)L_5+(z_3z_4/S^2)L_3L_4+(z_3^3/6S^3)L_3^3\}\\ &+\{(z_6/S)L_6+(z_3z_5/S^2)L_3L_5+(z_4^2/2S^2)L_4^2\\ &+(z_3^2z_4/2S^3)L_3^2L_4+(z_3^4/24S^4)L_3^4\}\\ &+\{(z_7/S)L_7+(z_3z_6/S^2)L_3L_6+(z_4z_5/S^2)L_4L_5\\ &+(z_3^2z_5/2S^3)L_3^2L_5+(z_3z_4^2/2S^3)L_3L_4^2\\ &+(z_3^3z_4/6S^4)L_3^3L_4+(z_3^5/120S^5)L_3^5\}+\ldots]\ .\end{aligned} \tag{39}$$

3·4. *Joint probability distribution of structure factors: a general expression*

We can obtain the joint probability distribution for a set of structure factors $P(\mathbf{E}_1,\ldots,\mathbf{E}_m)$, which is the inversion transformation of $M(u_1,\ldots,u_m)$ as is shown by Klug (1958). Taking into consideration further the relations (28), (33), (34), (35) and (37), we get

$$
\begin{aligned}
P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m) = & 1/((2\pi)^{m/2}) \exp[-\tfrac{1}{2}(\boldsymbol{E}_1^2 + \ldots + \boldsymbol{E}_m^2)] \\
& \times [1 + (z_3/S)\Sigma_3 + (z_4/S)\{\Sigma_4 - \tfrac{1}{2}\Sigma_{22}\} + (z_3^2/2S^2)\Sigma_{33} \\
& + (z_5/S)\{\Sigma_5 - \Sigma_{32}\} + (z_3 z_4/S^2)\{\Sigma_{43} - \tfrac{1}{2}\Sigma_{322}\} \\
& + (z_3^3/6S^3)\Sigma_{333} + (z_6/S)\{\Sigma_6 - \Sigma_{42} - \tfrac{1}{2}\Sigma_{33} + \tfrac{1}{3}\Sigma_{222}\} \\
& + (z_3 z_5/S^2)\{\Sigma_{53} - \Sigma_{332}\} + (z_4^2/2S^2)\{\Sigma_{44} - \Sigma_{422} + \tfrac{1}{4}\Sigma_{2222}\} \\
& + (z_3^2 z_4/2S^3)\{\Sigma_{433} - \tfrac{1}{2}\Sigma_{3322}\} + (z_3^4/24S^4)\Sigma_{3333} \\
& + (z_7/S)\{\Sigma_7 - \Sigma_{52} - \Sigma_{43} + \Sigma_{322}\} \\
& + (z_3 z_6/S^2)\{\Sigma_{63} - \tfrac{1}{2}\Sigma_{333} - \Sigma_{432} + \tfrac{1}{3}\Sigma_{3222}\} \\
& + (z_4 z_5/S^2)\{\Sigma_{54} - \tfrac{1}{2}\Sigma_{522} - \Sigma_{432} + \tfrac{1}{2}\Sigma_{3222}\} \\
& + (z_3^2 z_5/2S^3)\{\Sigma_{533} - \Sigma_{3332}\} + (z_3 z_4^2/2S^3)\{\Sigma_{443} - \Sigma_{4322} \\
& + \tfrac{1}{4}\Sigma_{32222}\} + (z_3^3 z_4/6S^4)\{\Sigma_{4333} - \tfrac{1}{2}\Sigma_{33322}\} \\
& + (z_3^5/120S^5)\Sigma_{33333} + \ldots], \qquad (40)
\end{aligned}
$$

in which z_n is the same as in (38), S the symmetry number $s\tau$ and

$$
\begin{aligned}
\boldsymbol{\Sigma}_{a\ldots f} \equiv & \sum_{\Sigma(\alpha'_p + \cdots + \omega'_p) = a} \cdots \sum_{\Sigma(\alpha_p'''' + \cdots + \omega_p'''') = f} \\
& \times \frac{(\sqrt{(\tau/\varepsilon_1)})^{\Sigma(\alpha'_p + \cdots + \alpha_p'''')} \ldots (\sqrt{(\tau/\varepsilon_m)})^{\Sigma(\omega'_p + \cdots + \omega_p'''')}}{\prod_{p=0}^{s-1} (\alpha'_p! \ldots \omega'_p!) \ldots (\alpha_p''''! \ldots \omega_p''''!)} \\
& \times \exp\left[2\pi i \left[\sum_{p=0}^{s-1} \{(\alpha'_p + \ldots + \alpha_p'''')\mathbf{h}_1 + \ldots + (\omega'_p + \ldots + \omega_p'''')\mathbf{h}_m\}\mathbf{t}_p\right]\right] \\
& \times H_{\Sigma(\alpha'_p + \cdots + \alpha_p'''')}(\boldsymbol{E}_1) \ldots H_{\Sigma(\omega'_p + \cdots + \omega_p'''')}(\boldsymbol{E}_m) \\
& \times \delta\left\{\sum_{p=0}^{s-1} \boldsymbol{R}_p(\alpha'_p \mathbf{h}_1 + \ldots + \omega'_p \mathbf{h}_m)\right\} \ldots \\
& \delta\left\{\sum_{p=0}^{s-1} \boldsymbol{R}_p(\alpha_p'''' \mathbf{h}_1 + \ldots + \omega_p'''' \mathbf{h}_m)\right\}. \qquad (41)
\end{aligned}
$$

In (41) $H_n(\boldsymbol{E})$ is the Hermite polynomial of degree n. Further s, $\boldsymbol{R}_p$, $\mathbf{t}_p$, τ, $\varepsilon_1, \ldots, \varepsilon_m$ and $\delta\{\ldots\}$ have the same meaning as in (28), (37), *etc.* The summation is to be carried out over all possible combinations of the values of non-negative integers $\alpha'_p, \ldots, \omega'_p, \ldots, \alpha_p'''', \ldots, \omega_p''''$ which satisfy the conditions

$$\sum_{p=0}^{s-1} (\alpha'_p + \ldots + \omega'_p) = a, \quad etc.$$

(40) with (41) is a general expression of the joint probability distribution expanded in series up to the term of $O(N^{-5/2})$. This is applicable to any case of centrosymmetric groups. In Appendices II, III and IV, there will be shown some simple examples of special cases of $\Sigma_{a\ldots f}$ and $P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$.

4. Probabilities and expected values for the case of $P\bar{1}$

It is possible to write directly the explicit form of $P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$ for the case of $P\bar{1}$ by substituting in (40) the expression for $\Sigma_{a\ldots f}(\mathbf{h}_1, \ldots, \mathbf{h}_m)$, the derivation of which is omitted here to save space but can be performed by the method given in Appendix II. As the purpose of the present paper is not to give such an explicit form of $P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$ but to find the joint probability of signs $P(s_1, \ldots, s_m)$, we shall give the following cases which are derived from the results of our general and systematic calculations concerning signs.

4·1. *Expected value* $\langle s_{\mathbf{h}_1}\rangle$, *where* $\mathbf{h}_1 = 2\mathbf{h}$

The expected value of sign $s_{2\mathbf{h}}$ has been obtained from the general expression of $P(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$ as follows:

$$
\begin{aligned}
\langle s_{2\mathbf{h}}\rangle \equiv \boldsymbol{A}(2\mathbf{h}) = & A_0 + A_1 + A_2 + A'_2 \\
& + A_3 + A'_3 + A''_3 + A_4 + A'_4 + A_5 + O(N^{-5/2}), \qquad (42)
\end{aligned}
$$

$$A_0 = z_3\{\tfrac{1}{2}H_1(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})\}, \qquad (43)$$

$$
\begin{aligned}
A_1 = & -z_5\{\tfrac{1}{3}H_1(E_{2\mathbf{h}})H_4(E_{\mathbf{h}}) + \tfrac{1}{4}H_3(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})\} \\
& - z_3 z_4\{\tfrac{1}{16}H_1(E_{2\mathbf{h}})H_6(E_{\mathbf{h}}) + \tfrac{1}{16}H_5(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})\} \\
& + z_3^3\{\tfrac{1}{48}H_3(E_{2\mathbf{h}})H_6(E_{\mathbf{h}})\}, \qquad (44)
\end{aligned}
$$

$$
\begin{aligned}
A_2 = & z_5\{\tfrac{1}{12}H_3(E_{2\mathbf{h}})H_2(E_{3\mathbf{h}})\} \\
& + z_3 z_4\{\tfrac{1}{2}H_2(E_{\mathbf{h}})H_3(E_{2\mathbf{h}})H_2(E_{3\mathbf{h}}) \\
& + \tfrac{1}{6}H_4(E_{\mathbf{h}})H_1(E_{2\mathbf{h}})H_2(E_{3\mathbf{h}}) \\
& + \tfrac{1}{4}H_2(E_{\mathbf{h}})H_3(E_{2\mathbf{h}})H_2(E_{4\mathbf{h}}) \\
& + \tfrac{1}{4}H_3(E_{2\mathbf{h}})H_2(E_{3\mathbf{h}})H_2(E_{4\mathbf{h}}) \\
& + \tfrac{1}{12}\mathrm{H}_3(E_{2\mathbf{h}})H_2(E_{3\mathbf{h}})H_2(E_{6\mathbf{h}})\} \\
& + z_3^3\{\tfrac{1}{4}H_4(E_{\mathbf{h}})H_3(E_{2\mathbf{h}})H_2(E_{3\mathbf{h}}) \\
& + \tfrac{1}{16}H_2(E_{\mathbf{h}})H_5(E_{2\mathbf{h}})H_2(E_{4\mathbf{h}}) \\
& + \tfrac{1}{2}H_2(E_{\mathbf{h}})H_3(E_{2\mathbf{h}})H_2(E_{3\mathbf{h}})H_2(E_{4\mathbf{h}}) \\
& + \tfrac{1}{4}H_3(E_{2\mathbf{h}})H_2(E_{3\mathbf{h}})H_2(E_{4\mathbf{h}})H_2(E_{6\mathbf{h}})\}, \qquad (45)
\end{aligned}
$$

$$
\begin{aligned}
A'_2 = & z_5\{\tfrac{1}{24}H_4(E_{\mathbf{h}/2})H_1(E_{2\mathbf{h}})\} \\
& + z_3 z_4\{\tfrac{1}{4}H_4(E_{\mathbf{h}/2})H_2(E_{\mathbf{h}})H_1(E_{2\mathbf{h}}) \\
& + \tfrac{1}{6}H_4(E_{\mathbf{h}/2})H_2(E_{3\mathbf{h}/2})H_1(E_{2\mathbf{h}}) \\
& + \tfrac{1}{12}H_2(E_{\mathbf{h}/3})H_4(E_{2\mathbf{h}/3})H_1(E_{2\mathbf{h}})\} \\
& + z_3^3\{\tfrac{1}{16}H_4(E_{\mathbf{h}/2})H_4(E_{\mathbf{h}})H_1(E_{2\mathbf{h}}) \\
& + \tfrac{1}{2}H_4(E_{\mathbf{h}/2})H_2(E_{\mathbf{h}})H_2(E_{3\mathbf{h}/2})H_1(E_{2\mathbf{h}}) \\
& + \tfrac{1}{4}H_2(E_{\mathbf{h}/3})H_4(E_{2\mathbf{h}/3})H_2(E_{4\mathbf{h}/3})H_1(E_{2\mathbf{h}})\}, \qquad (46)
\end{aligned}
$$

$$
\begin{aligned}
A_3 = & z_5\{\tfrac{1}{4}H_1(E_{2\mathbf{h}}) \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})\} \\
& + z_3 z_4\{H_1(E_{2\mathbf{h}})H_2(E_{\mathbf{h}}) \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}}) \\
& + \tfrac{1}{2}H_1(E_{2\mathbf{h}})H_2(E_{\mathbf{h}}) \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{2\mathbf{h}+\mathbf{k}})\} \\
& + z_3^3\{\tfrac{1}{4}H_1(E_{2\mathbf{h}})H_4(E_{\mathbf{h}}) \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}}) \\
& + \tfrac{1}{4}H_3(E_{2\mathbf{h}})H_2(E_{\mathbf{h}}) \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{2\mathbf{h}+\mathbf{k}})\}, \qquad (47)
\end{aligned}
$$

$$
\begin{aligned}
A'_3 = & z_3 z_4\{\tfrac{1}{4}H_1(E_{2\mathbf{h}}) \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{2\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})\} \\
& + z_3^3\{H_1(E_{2\mathbf{h}})H_2(E_{\mathbf{h}}) \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})H_2(E_{2\mathbf{h}+\mathbf{k}})\}, \qquad (48)
\end{aligned}
$$

$$A_3'' = z_3^3\{\tfrac{1}{4}H_1(E_{2\mathbf{h}})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{2\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})H_2(E_{2\mathbf{h}+2\mathbf{k}})$$
$$+\tfrac{1}{2}H_1(E_{2\mathbf{h}})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})H_2(E_{2\mathbf{h}+\mathbf{k}})H_2(E_{2\mathbf{h}+2\mathbf{k}})\}\,, \qquad (49)$$

$$A_4 = z_3z_4\{\tfrac{1}{16}H_1(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})H_4(E_{\mathbf{h}})$$
$$+\tfrac{1}{16}H_1(E_{2\mathbf{h}})H_4(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})\}$$
$$-z_3^3\{\tfrac{1}{16}H_1(E_{2\mathbf{h}})H_2(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})H_4(E_{\mathbf{h}})\}\,, \qquad (50)$$

$$A_4' = -z_3^3\{\tfrac{1}{4}H_1(E_{2\mathbf{h}})H_2(E_{2\mathbf{h}})H_2^2(E_{\mathbf{h}})H_2(E_{3\mathbf{h}})$$
$$+\tfrac{1}{16}H_1(E_{2\mathbf{h}})H_2^2(E_{\mathbf{h}})H_4(E_{\mathbf{h}/2})$$
$$+\tfrac{1}{16}H_1(E_{2\mathbf{h}})H_4(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})H_2(E_{4\mathbf{h}})\}\,, \qquad (51)$$

$$A_5 = -z_3^3\{\tfrac{1}{4}H_1(E_{2\mathbf{h}})H_2^2(E_{\mathbf{h}})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})$$
$$+\tfrac{1}{4}H_1(E_{2\mathbf{h}})H_2(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{2\mathbf{h}+\mathbf{k}})\}\,. \qquad (52)$$

These terms $A_0, \ldots, A_5$ are divided into the following classes according to characteristics given below.*

- A_0 contains spectra $E_{\mathbf{h}}$ and $E_{2\mathbf{h}}$ only to the order $N^{-1/2}$.
- A_1 contains spectra $E_{\mathbf{h}}$ and $E_{2\mathbf{h}}$ only to the order $N^{-3/2}$.
- A_2 contains the terms of a few spectra $E_{3\mathbf{h}}$, $E_{4\mathbf{h}}$, $E_{6\mathbf{h}}$ as well as $E_{\mathbf{h}}$ and $E_{2\mathbf{h}}$, the order being $O(N^{-3/2})$.
- A_2' contains the terms of spectra $E_{\mathbf{h}/2}$, $E_{3\mathbf{h}/2}$, $E_{\mathbf{h}/3}$, $E_{2\mathbf{h}/3}$, $E_{4\mathbf{h}/3}$ in addition to $E_{\mathbf{h}}$ and $E_{2\mathbf{h}}$, $O(N^{-3/2})$.
- A_3 contains the terms depending on certain sum (average) effects of spectra in a sufficiently large range of the reciprocal lattice which are expressed by the forms $\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})$, *etc.* This term is similar to the formulae of Cochran (1954) and Klug (1958, equation (5·1)).
- A_3' contains the terms similar to the case of A_3, possessing, however, the forms of the type of $\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{2\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})$, *etc.*
- A_3'' contains the terms similar to the cases of A_3 and A_3', possessing, however, a different type of sum effects such as
$$\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{2\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})H_2(E_{2\mathbf{h}+2\mathbf{k}}),\ etc.$$
- A_4 contains the terms of spectra $E_{\mathbf{h}}$ and $E_{2\mathbf{h}}$ arising from the expansion of the denominator in (25) in evaluation of expected values.
- A_4' contains the terms arising from the same circumstance as in A_4, however, other spectra besides $E_{\mathbf{h}}$ and $E_{2\mathbf{h}}$ entering.
- A_5 contains the sum effects of many spectra arising from the expansion of the denominator in (25). This term is similar to Klug's fourth-order formula (equation (5·18)).

* Except in terms A_4, A_4' and A_5, the same spectra cannot appear more than once in one of the Hermite polynomial products. It is to be added that the summation with regard to $\mathbf{k}$ has also been carried out with this precaution. Moreover, term E_0 is not included.

4·2. *Probability* $P^+(s_{2\mathbf{h}})$

The probability $P^+(s_{2\mathbf{h}})$ is then obtained from (6) with (42)

$$P^+(s_{2\mathbf{h}}) = \tfrac{1}{2}\{1+\langle s_{2\mathbf{h}}\rangle\}\,. \qquad (53)$$

If the relating structure factors are assumed to be limited only to $E_{\mathbf{h}}$ and $E_{2\mathbf{h}}$, then

$$\langle s_{2\mathbf{h}}\rangle = A_0 + A_1 + A_4\,. \qquad (54)$$

This result is equivalent to that of Klug (1958). If the terms relating to z_3z_4 and z_3^3 in (42) are all neglected, we have

$$\langle s_{2\mathbf{h}}\rangle = z_3\{\tfrac{1}{2}H_1(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})\} - z_5\{\tfrac{1}{3}H_1(E_{2\mathbf{h}})H_4(E_{\mathbf{h}})$$
$$+\tfrac{1}{4}H_3(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})\} + z_5\{\tfrac{1}{12}H_3(E_{2\mathbf{h}})H_2(E_{3\mathbf{h}})$$
$$+\tfrac{1}{24}H_4(E_{\mathbf{h}/2})H_1(E_{2\mathbf{h}})\}$$
$$+z_5\{\tfrac{1}{4}H_1(E_{2\mathbf{h}})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})\}\,. \qquad (55)$$

This is equivalent to that of Bertaut (1955*a*). Only the first and fourth terms are found in the monograph by Hauptman & Karle (1953).

It is to be noted that the terms A_3, A_3', A_3'' and A_5 contain those used by Vaughan in his regression formulae. As Vaughan commented, when the number of spectra is taken too large, the sum terms will generally have such a strong effect that the expansion in orders of $N^{-1/2}$ might lose its effectiveness. However, as shown in Appendix V, even in such a case, we may rearrange the order of the terms so as to maintain its usefulness, the dominant terms in (43) ~ (52) bceoming A_0, A_3 and A_5.

In such a case

$$\langle s_{2\mathbf{h}}\rangle = A_0 + A_3 + A_5 = \tfrac{1}{2}z_3H_1(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})$$
$$-\tfrac{1}{4}\{(2z_3^3-z_5)+4z_3(z_3^2-z_4)H_2(E_{\mathbf{h}})\}$$
$$\times H_1(E_{2\mathbf{h}})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})$$
$$-\tfrac{1}{2}z_3(z_3^2-z_4)H_1(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{2\mathbf{h}+\mathbf{k}})\,. \qquad (56)$$

Further the case of equal atoms is now considered. Then we have

$$z_3 = N^{-1/2},\ z_5 = z_3z_4 = z_3^3 = N^{-3/2}. \qquad (57)$$

Hence,

$$\langle s_{2\mathbf{h}}\rangle = A_0 + A_3 + A_5 = (1/2N^{1/2})H_1(E_{2\mathbf{h}})H_2(E_{\mathbf{h}})$$
$$-(1/4N^{3/2})H_1(E_{2\mathbf{h}})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}+\mathbf{k}})\,. \qquad (58)$$

Substitution of (58) into (53) gives

$$P^+(s_{2\mathbf{h}}) = \tfrac{1}{2}\{1+\langle s_{2\mathbf{h}}\rangle\} = \tfrac{1}{2} + (1/8N^{1/2})E_{2\mathbf{h}}\{2(E_{\mathbf{h}}^2-1)$$
$$-(1/N)\sum_{\mathbf{k}}(E_{\mathbf{k}}^2-1)(E_{\mathbf{h}+\mathbf{k}}^2-1)\}\,. \qquad (59)$$

This is the probability formula corresponding to Cochran's relation (1954):

$$\boldsymbol{E}_{2\mathbf{h}} = N^{\frac{1}{2}}\{2(\boldsymbol{E}_{\mathbf{h}}^2-1) - N\overline{(\boldsymbol{E}_{\mathbf{k}}^2-1)(\boldsymbol{E}_{\mathbf{h}+\mathbf{k}}^2-1)}^{\mathbf{k}}\}\,, \qquad (60)$$

which Hauptman & Karle have also derived with their new joint probability method (1958), Vaughan (1959) with his regression formula and some authors rederived by the algebraic approach (Hauptman & Karle, 1957; Bertaut, 1959).

4·3. *Expected value* $\langle s_{\mathbf{h}_1} s_{\mathbf{h}_2}\rangle$

The expected value of a product of two signs $s_{\mathbf{h}_1}$ and $s_{\mathbf{h}_2}$ is obtained in the form

$$\langle s_{\mathbf{h}_1} s_{\mathbf{h}_2}\rangle = \langle s_{\mathbf{h}_1}\rangle\langle s_{\mathbf{h}_2}\rangle + \langle s_{\mathbf{h}_1} s_{\mathbf{h}_2}\rangle^*, \qquad (61)$$

where the first term in the right hand side of (61) is given by the product of two expected values of (42):

$$\begin{aligned}\langle s_{\mathbf{h}_1}\rangle\langle s_{\mathbf{h}_2}\rangle &= \boldsymbol{A}(\mathbf{h}_1)\boldsymbol{A}(\mathbf{h}_2)\\ &= z_3^2\{\tfrac{1}{4}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_2(E_{\mathbf{h}_1/2})H_2(E_{\mathbf{h}_2/2})\} + O(N^{-2})\,. \end{aligned}\qquad (62)$$

The second term $\langle s_{\mathbf{h}_1} s_{\mathbf{h}_2}\rangle^*$ is a sort of residual term

$$\langle s_{\mathbf{h}_1} s_{\mathbf{h}_2}\rangle^* \equiv \boldsymbol{B}(\mathbf{h}_1, \mathbf{h}_2) = B_1 + B_2 + B_2' + O(N^{-2})\,, \qquad (63)$$

in which

$$\begin{aligned}B_1 = z_4\{&\tfrac{1}{2}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_2(E_{\frac{1}{2}(\mathbf{h}_1+\mathbf{h}_2)})\\ &+\tfrac{1}{2}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_2(E_{\frac{1}{2}(\mathbf{h}_1-\mathbf{h}_2)})\}\,,\end{aligned}\qquad (64)$$

$$\begin{aligned}B_2 = z_3^2\{&H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_2(E_{\frac{1}{2}(\mathbf{h}_1+\mathbf{h}_2)})H_2(E_{\frac{1}{2}(\mathbf{h}_1-\mathbf{h}_2)})\\ &+\tfrac{1}{2}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_2(E_{\mathbf{h}_1+\mathbf{h}_2})H_2(E_{\frac{1}{2}(\mathbf{h}_1+\mathbf{h}_2)})\\ &+\tfrac{1}{2}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_2(E_{\mathbf{h}_1-\mathbf{h}_2})H_2(E_{\frac{1}{2}(\mathbf{h}_1-\mathbf{h}_2)})\}\,,\end{aligned}\qquad (65)$$

$$\begin{aligned}B_2' = z_4\{&\tfrac{1}{6}H_1(E_{\mathbf{h}_1})H_3(E_{\mathbf{h}_2})\delta_{\mathbf{h}_1,3\mathbf{h}_2} + \text{int.}\}\\ +z_3^2\{&[\tfrac{1}{2}H_1(E_{\mathbf{h}_1})H_3(E_{\mathbf{h}_2})H_2(E_{2\mathbf{h}_2})\delta_{\mathbf{h}_1,3\mathbf{h}_2} + \text{int.}]\\ &+[\tfrac{1}{4}H_1(E_{\mathbf{h}_1})H_3(E_{\mathbf{h}_2})H_2(E_{\mathbf{h}_2/2})\delta_{\mathbf{h}_1,2\mathbf{h}_2} + \text{int.}]\}\,,\end{aligned}\qquad (66)$$

where δ is again the Kronecker symbol, int. the expressions for $\mathbf{h}_1$ and $\mathbf{h}_2$ in the corresponding relation to be interchanged. It is to be noted that the form of the relations (61) and (67) given below may be said to have a natural appearance showing well the cooperative character of the correlation of signs. It is further added that B_1 is the term given by Bertaut (1958).

4·4. *Expected value* $\langle s_{\mathbf{h}_1} s_{\mathbf{h}_2} s_{\mathbf{h}_3}\rangle$ *for* $\mathbf{h}_1 \pm \mathbf{h}_2 \pm \mathbf{h}_3 = 0$

Our calculation on the expected value for product of three signs $s_{\mathbf{h}_1}, s_{\mathbf{h}_2}$ and $s_{\mathbf{h}_3}$ where $\mathbf{h}_1 \pm \mathbf{h}_2 \pm \mathbf{h}_3 = 0$ gives

$$\begin{aligned}\langle s_{\mathbf{h}_1} s_{\mathbf{h}_2} s_{\mathbf{h}_3}\rangle &= \langle s_{\mathbf{h}_1}\rangle\langle s_{\mathbf{h}_2}\rangle\langle s_{\mathbf{h}_3}\rangle + \langle s_{\mathbf{h}_1}\rangle\langle s_{\mathbf{h}_2} s_{\mathbf{h}_3}\rangle^*\\ &+\langle s_{\mathbf{h}_2}\rangle\langle s_{\mathbf{h}_3} s_{\mathbf{h}_1}\rangle^* + \langle s_{\mathbf{h}_3}\rangle\langle s_{\mathbf{h}_1} s_{\mathbf{h}_2}\rangle^* + \langle s_{\mathbf{h}_1} s_{\mathbf{h}_2} s_{\mathbf{h}_3}\rangle^*,\end{aligned}\qquad (67)$$

where each term in (67) possesses the same meaning as in (61); namely,

$$\begin{aligned}\langle s_{\mathbf{h}_1}\rangle\langle s_{\mathbf{h}_2}\rangle\langle s_{\mathbf{h}_3}\rangle &= \boldsymbol{A}(\mathbf{h}_1)\boldsymbol{A}(\mathbf{h}_2)\boldsymbol{A}(\mathbf{h}_3)\\ &= z_3^3\{\tfrac{1}{8}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_2(E_{\mathbf{h}_1/2})\\ &\quad\times H_2(E_{\mathbf{h}_2/2})H_2(E_{\mathbf{h}_3/2})\} + O(N^{-5/2})\,,\end{aligned}\qquad (68)$$

$$\begin{aligned}&\langle s_{\mathbf{h}_1}\rangle\langle s_{\mathbf{h}_2} s_{\mathbf{h}_3}\rangle^* + \langle s_{\mathbf{h}_2}\rangle\langle s_{\mathbf{h}_3} s_{\mathbf{h}_1}\rangle^* + \langle s_{\mathbf{h}_3}\rangle\langle s_{\mathbf{h}_1} s_{\mathbf{h}_2}\rangle^*\\ &= \boldsymbol{A}(\mathbf{h}_1)\boldsymbol{B}(\mathbf{h}_2,\mathbf{h}_3) + \boldsymbol{A}(\mathbf{h}_2)\boldsymbol{B}(\mathbf{h}_3,\mathbf{h}_1) + \boldsymbol{A}(\mathbf{h}_3)\boldsymbol{B}(\mathbf{h}_1,\mathbf{h}_2)\\ &= z_3z_4\{[\tfrac{1}{4}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})\\ &\quad\times H_2(E_{\mathbf{h}_1/2})H_2(E_{(\pm\mathbf{h}_2\mp\mathbf{h}_3)/2}) + \text{cyc.}]\\ &\quad+[\tfrac{1}{12}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_3(E_{\mathbf{h}_3})H_2(E_{\mathbf{h}_1/2})\delta_{\mathbf{h}_2,3\mathbf{h}_3} + \text{perm.}]\}\\ &\quad+z_3^3\{[\tfrac{1}{4}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})\\ &\quad\times H_2(E_{\mathbf{h}_1/2})H_2(E_{\pm\mathbf{h}_2\mp\mathbf{h}_3})H_2(E_{(\pm\mathbf{h}_2\mp\mathbf{h}_3)/2}) + \text{cyc.}]\\ &\quad+[\tfrac{1}{8}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_3(E_{\mathbf{h}_3})H_2(E_{\mathbf{h}_1/2})\\ &\quad\times H_2(E_{\mathbf{h}_3/2})\delta_{\mathbf{h}_2,2\mathbf{h}_3} + \text{perm.}]\} + O(N^{-5/2})\,,\end{aligned}\qquad (69)$$

$$\begin{aligned}\langle s_{\mathbf{h}_1} s_{\mathbf{h}_2} s_{\mathbf{h}_3}\rangle^* &\equiv \boldsymbol{C}(\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3)\\ &= C_0 + C_1 + C_1' + C_2 + C_2' + C_3 + C_4 + C_5 + O(N^{-5/2}),\end{aligned}\qquad (70)$$

$$C_0 = z_3 H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})\,, \qquad (71)$$

$$\begin{aligned}C_1 = &-z_5\{\tfrac{1}{2}H_3(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3}) + \text{cyc.}\}\\ &-z_3z_4\{\tfrac{1}{8}H_5(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3}) + \text{cyc.}\}\\ &+z_3^3\{\tfrac{1}{6}H_3(E_{\mathbf{h}_1})H_3(E_{\mathbf{h}_2})H_3(E_{\mathbf{h}_3})\}\,,\end{aligned}\qquad (72)$$

$$\begin{aligned}C_1' = z_3z_4\{&[\tfrac{1}{4}H_3(E_{\mathbf{h}_1})H_3(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})\delta_{\mathbf{h}_2,2\mathbf{h}_1} + \text{perm.}]\\ &+[\tfrac{1}{12}H_5(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})\delta_{\mathbf{h}_2,2\mathbf{h}_1}\delta_{\mathbf{h}_3,3\mathbf{h}_1} + \text{perm.}]\}\\ +z_3^3\{&\tfrac{1}{8}H_5(E_{\mathbf{h}_1})H_3(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})\delta_{\mathbf{h}_2,2\mathbf{h}_1}\delta_{\mathbf{h}_3,3\mathbf{h}_1} + \text{perm.}\}\,,\end{aligned}\qquad (73)$$

$$\begin{aligned}C_2 = z_3z_4\{&[\tfrac{1}{2}H_3(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})\\ &\times H_2(E_{(3\mathbf{h}_1\pm\mathbf{h}_2\mp\mathbf{h}_3)/2}) + \text{perm.}]\\ &+[\tfrac{1}{2}H_3(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_2(E_{2\mathbf{h}_1}) + \text{cyc.}]\\ &+[\tfrac{1}{4}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_4(E_{\mathbf{h}_1/2}) + \text{cyc.}]\}\\ +z_3^3\{&[\tfrac{1}{2}H_1(E_{\mathbf{h}_1})H_3(E_{\mathbf{h}_2})H_3(E_{\mathbf{h}_3})H_2(E_{\pm\mathbf{h}_2\mp\mathbf{h}_3}) + \text{cyc.}]\\ &+[\tfrac{1}{2}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_4(E_{\mathbf{h}_1/2})\\ &\times H_2(E_{(\pm\mathbf{h}_2\mp\mathbf{h}_3)/2}) + \text{cyc.}]\\ &+[\tfrac{1}{2}H_3(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_2(E_{2\mathbf{h}_1})\\ &\times H_2(E_{(3\mathbf{h}_1\pm\mathbf{h}_2\mp\mathbf{h}_3)/2}) + \text{perm.}]\\ &+[\tfrac{1}{8}H_3(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_4(E_{\mathbf{h}_1/2}) + \text{cyc.}]\\ &+[\tfrac{1}{8}H_5(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_2(E_{2\mathbf{h}_1}) + \text{cyc.}]\}\,,\end{aligned}\qquad (74)$$

$$\begin{aligned}C_2' = z_3^3\{&[\tfrac{1}{4}H_3(E_{\mathbf{h}_1})H_3(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_2(E_{4\mathbf{h}_1})\\ &\times\delta_{\mathbf{h}_2,2\mathbf{h}_1}\delta_{\mathbf{h}_3,3\mathbf{h}_1} + \text{perm.}]\\ &+[\tfrac{1}{4}H_3(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_4(E_{2\mathbf{h}_1})\\ &\times\delta_{\mathbf{h}_2,3\mathbf{h}_1}\delta_{\mathbf{h}_3,4\mathbf{h}_1} + \text{perm.}]\}\,,\end{aligned}\qquad (75)$$

$$\begin{aligned}C_3 = z_3^3\{&\tfrac{1}{2}H_3(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})\\ &\times\sum_{\mathbf{k}}H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}_1+\mathbf{k}}) + \text{cyc.}\}\,,\end{aligned}\qquad (76)$$

$$\begin{aligned}C_4 = z_3z_4\{&\tfrac{1}{8}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_4(E_{\mathbf{h}_1}) + \text{cyc.}\}\\ -z_3^3\{&[\tfrac{1}{2}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_2(E_{\mathbf{h}_1})\\ &\times H_2(E_{\mathbf{h}_2})H_2(E_{\mathbf{h}_3})]\\ &+[\tfrac{1}{2}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_2(E_{\mathbf{h}_2})H_2(E_{\mathbf{h}_3})\\ &\times H_2(E_{\pm\mathbf{h}_2\mp\mathbf{h}_3}) + \text{cyc.}]\\ &+[\tfrac{1}{8}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_2(E_{\mathbf{h}_1})H_4(E_{\mathbf{h}_1/2}) + \text{cyc.}]\\ &+[\tfrac{1}{8}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3})H_2(E_{2\mathbf{h}_1})H_4(E_{\mathbf{h}_1}) + \text{cyc.}]\}\,,\end{aligned}\qquad (77)$$

$$C_5 = -z_3^3\{\tfrac{1}{2}H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3}) \times H_2(E_{\mathbf{h}_1})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}_1+\mathbf{k}}) + \text{cyc.}\}. \quad (78)$$

The terms from C_0 to C_5 in (70) are divided into classes like $A_0, \ldots, A_5$ in (42).* Upon the similar consideration to that in the case of (56), we obtain

$$\langle s_{\mathbf{h}_1}s_{\mathbf{h}_2}s_{\mathbf{h}_3}\rangle = C_0 + C_3 + C_5 = z_3H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3}) - z_3^3\{H_1(E_{\mathbf{h}_1})H_1(E_{\mathbf{h}_2})H_1(E_{\mathbf{h}_3}) \times \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h}_1+\mathbf{k}}) + \text{cyc.}\}. \quad (79)$$

Therefore, using (10) and putting $z_3 = N^{-1/2}$,

$$P^+(s_{\mathbf{h}_1}s_{\mathbf{h}_2}s_{\mathbf{h}_3}) = \tfrac{1}{2}\{1 + \langle s_{\mathbf{h}_1}s_{\mathbf{h}_2}s_{\mathbf{h}_3}\rangle\} = \tfrac{1}{2} + (1/2N^{1/2})E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3} \times \{1 - (1/N)[\sum_{\mathbf{k}} (E_{\mathbf{k}}^2 - 1)(E_{\mathbf{h}_1+\mathbf{k}}^2 - 1) + \text{cyc.}]\}. \quad (80)$$

This result does not agree with any one of the results: the equality obtained by Hauptman & Karle (1958), the similar one by Vaughan (1958) and Bertaut's statistical formula (1960).

Note. The expected values of triple products of signs for the case of $\mathbf{h}_1 \pm \mathbf{h}_2 \pm \mathbf{h}_3 \neq 0$ and further the expected values of higher multiple products of signs have also been calculated. However, to save space we do not show these lengthy and complicated results here. Although they are not given, it is to be noted that all such results have been derived as natural by-products of our systematic procedure based on the theory of § 2 and § 3.

5. Conclusion

We have presented a systematic theory for deriving certain probability formulae useful for sign determinations of centrosymmetric structure factors; that is, starting from the joint probability distribution for a set of signs, *via* reduced probabilities, we derive the corresponding expected values, the following conditional expected values, and finally the various conditional probabilities for signs or sign products. Although not discussed precisely hitherto by any author, such an investigation seems to be of value in the practical procedure for determining signs of centrosymmetric structure factors.

By making use of general space-group-symmetry operators, our calculation of the joint probability distribution of structure factors has been carried out in a more general manner than that of other authors. As the results of such procedure, we finally obtained the general expression (40), with (41), for the joint probability distribution of structure factors; this is capable of easy application, not only for the case of a few chosen structure factors, but also for the case of a greater number of structure factors and even for the cases of higher symmetry space groups.

The application of the present theory to the case of $P\bar{1}$ has shown that it covers not only the results given by Hauptman & Karle, Bertaut, and Klug, but also gives in a natural manner a probability formula corresponding to the well-known Cochran relation and further the terms related in a sense to Vaughan's regression formula. It may be said that by this example of the case of $P\bar{1}$ the implications of the present theory have been demonstrated, consolidating the well-known statistical theories developed by Hauptman & Karle, Bertaut, and Klug in a more unified form, and clarifying the situations of the important relations already obtained in their theories.

* The symbol cyc. means the expression for $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ in the corresponding equations to be interchanged cyclically, the symbol perm. the expression for $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ to undergo permutation operation. In each case, the same operation is acted upon the relation $\mathbf{h}_1 \pm \mathbf{h}_2 \pm \mathbf{h}_3 = 0$ at the same time. In addition, it is to be noted that $\pm$ of the indices in these equations should agree with $\pm$ in $\mathbf{h}_1 \pm \mathbf{h}_2 \pm \mathbf{h}_3 = 0$. The condition for the summation over $\mathbf{k}$ is the same as in (42).

APPENDIX I

Defining the trigonometric structure factor $\xi(\mathbf{h})$ as (26), moment $m_{\alpha\ldots\omega}$ is given by

$$\begin{aligned} m_{\alpha\ldots\omega}(\mathbf{h}_1, \ldots, \mathbf{h}_m) &= \overline{\xi^\alpha(\mathbf{h}_1)\ldots\xi^\omega(\mathbf{h}_m)} \\ &= \tau^{\alpha+\cdots+\omega}\int d\mathbf{r}\left\{\sum_{p=0}^{s-1}\exp[2\pi i\mathbf{h}_1\mathbf{r}\boldsymbol{S}_p]\right\}^\alpha \ldots \times \left\{\sum_{p=0}^{s-1}\exp[2\pi i\mathbf{h}_m\mathbf{r}\boldsymbol{S}_p]\right\}^\omega \\ &= \tau^{\alpha+\cdots+\omega}\int d\mathbf{r}\left\{\sum_{p=0}^{s-1}\exp[2\pi i\boldsymbol{R}_p\mathbf{h}_1\mathbf{r}]\exp[2\pi i\mathbf{h}_1\mathbf{t}_p]\right\}^\alpha \ldots \\ &\quad \times \ldots \left\{\sum_{p=0}^{s-1}\exp[2\pi i\boldsymbol{R}_p\mathbf{h}_m\mathbf{r}]\exp[2\pi i\mathbf{h}_m\mathbf{t}_p]\right\}^\omega. \quad \text{(I–1)} \end{aligned}$$

A factor such as

$$\left\{\sum_{p=0}^{s-1}\exp[2\pi i\boldsymbol{R}_p\mathbf{h}_1\mathbf{r}]\exp[2\pi i\mathbf{h}_1\mathbf{t}_p]\right\}^\alpha$$

in (I–1) can be rewritten easily as

$$\sum_{\sum_{p=0}^{s-1}\alpha_p=\alpha} \frac{\alpha!}{\prod_{p=0}^{s-1}\alpha_p!}\exp\{2\pi i[\sum_p \boldsymbol{R}_p\alpha_p\mathbf{h}_1\mathbf{r}]\} \times \exp\{2\pi i[\sum_p \alpha_p\mathbf{h}_1\mathbf{t}_p]\}, \quad \text{(I–2)}$$

where $\alpha_p (p = 0, 1, \ldots, s-1)$ are the integers in the ranges $0 \le \alpha_p \le \alpha$, $(p = 0, 1, \ldots, s-1)$, respectively, and the summation is to be carried out over all possible combinations of values of $\alpha_0, \alpha_1, \ldots, \alpha_{s-1}$, satisfying the condition

$$\sum_{p=0}^{s-1}\alpha_p = \alpha.$$

Hence (I–1) can be transformed to

$$\tau^{\alpha+\cdots+\omega}\int d\mathbf{r}\left\{\sum_{\Sigma\alpha_p=\alpha}\frac{\alpha!}{\prod_p \alpha_p!}\right.$$
$$\left.\times\exp\{2\pi i[\sum_p \boldsymbol{R}_p\alpha_p\mathbf{h}_1\mathbf{r}]\}\exp\{2\pi i[\sum_p \alpha_p\mathbf{h}_1\mathbf{t}_p]\}\right\}$$
$$\times\ldots\left\{\sum_{\Sigma\omega_p=\omega}\frac{\omega!}{\prod_p \omega_p!}\right.$$
$$\left.\times\exp\{2\pi i[\sum_p \boldsymbol{R}_p\omega_p\mathbf{h}_m\mathbf{r}]\}\exp\{2\pi i[\sum_p \omega_p\mathbf{h}_m\mathbf{t}_p]\}\right\}$$
$$=\tau^{\alpha+\cdots+\omega}\sum_{\Sigma\alpha_p=\alpha}\cdots\sum_{\Sigma\omega_p=\omega}\frac{\alpha!\ldots\omega!}{\prod_p(\alpha_p!\ldots\omega_p!)}$$
$$\times\exp\{2\pi i[\sum_p(\alpha_p\mathbf{h}_1+\ldots+\omega_p\mathbf{h}_m)\mathbf{t}_p]\}$$
$$\times\int\exp\{2\pi i[\sum_p \boldsymbol{R}_p(\alpha_p\mathbf{h}_1+\ldots+\omega_p\mathbf{h}_m)\mathbf{r}]\}d\mathbf{r}\,. \tag{I-3}$$

As is known, the integration of the right hand side of (I–3) is as follows.

$$\int\exp\{2\pi i[\sum_p \boldsymbol{R}_p(\alpha_p\mathbf{h}_1+\ldots+\omega_p\mathbf{h}_m)\mathbf{r}]\}d\mathbf{r}$$
$$=\delta\left\{\sum_{p=0}^{s-1}\boldsymbol{R}_p(\alpha_p\mathbf{h}_1+\ldots+\omega_p\mathbf{h}_m)\right\}\,. \tag{I-4}$$

Thus we arrive at the final expression (28) for the moment.

APPENDIX II

Example of calculation of $\Sigma_{ab\ldots f}$

II·1. Let us consider the case of the calculation of $\Sigma a_{ab\ldots f}$ for two structure factors $\boldsymbol{E}_1\equiv\boldsymbol{E}_{2\mathbf{h}}$, $\boldsymbol{E}_2\equiv\boldsymbol{E}_{\mathbf{h}}$ in $P\bar{1}$; *i.e.* $\boldsymbol{R}_0=\mathbf{1}$, $\boldsymbol{R}_1=-\mathbf{1}$, $\mathbf{t}_0=\mathbf{t}_1=0$. From (41), it follows that

$$\Sigma_a(2\mathbf{h},\mathbf{h})$$
$$=\sum_{\alpha_0+\alpha_1+\beta_0+\beta_1=a}\frac{1}{\alpha_0!\beta_0!\alpha_1!\beta_1!}H_{\alpha_0+\alpha_1}(\boldsymbol{E}_1)H_{\beta_0+\beta_1}(\boldsymbol{E}_2)$$
$$\times\delta\{[2(\alpha_0-\alpha_1)+(\beta_0-\beta_1)]\mathbf{h}\}\,. \tag{II-1}$$

The condition that $\delta\{\ldots\}$ in (II–1) does not vanish is

$$2(\alpha_0-\alpha_1)+(\beta_0-\beta_1)=0\,. \tag{II-2}$$

The summation in (II–1) must be made under the following condition:

$$\alpha_0+\alpha_1+\beta_0+\beta_1=a\,. \tag{II-3}$$

Thus it is easily shown that

$$\begin{aligned}&\Sigma_3=H_1(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\,,\\&\Sigma_4=\tfrac{1}{4}\{H_4(\boldsymbol{E}_1)+H_4(\boldsymbol{E}_2)\}+H_2(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\,,\\&\Sigma_5=\tfrac{1}{3}H_1(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)+\tfrac{1}{2}H_3(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\,.\end{aligned} \tag{II-4}$$

In the same way, it follows from (41) that

$$\Sigma_{ab}(2\mathbf{h},\mathbf{h})$$
$$=\sum_{\alpha_0+\alpha_1+\beta_0+\beta_1=a}\ \sum_{\alpha'_0+\alpha'_1+\beta'_0+\beta'_1=b}\frac{1}{\alpha_0!\beta_0!\alpha_1!\beta_1!\alpha'_0!\beta'_0!\alpha'_1!\beta'_1!}$$
$$\times H_{\alpha_0+\alpha_1+\alpha'_0+\alpha'_1}(\boldsymbol{E}_1)H_{\beta_0+\beta_1+\beta'_0+\beta'_1}(\boldsymbol{E}_2)$$
$$\times\delta\{[2(\alpha_0-\alpha_1)+(\beta_0-\beta_1)]\mathbf{h}\}$$
$$\times\delta\{[2(\alpha'_0-\alpha'_1)+(\beta'_0-\beta'_1)]\mathbf{h}\}\,. \tag{II-5}$$

The non-vanishing conditions for $\delta\{\ldots\}$ in (II–5) are

$$2(\alpha_0-\alpha_1)+(\beta_0-\beta_1)=0$$

and

$$2(\alpha'_0-\alpha'_1)+(\beta'_0-\beta'_1)=0\,. \tag{II-6}$$

The rules in the summations are

$$\alpha_0+\alpha_1+\beta_0+\beta_1=a$$

and

$$\alpha'_0+\alpha'_1+\beta'_0+\beta'_1=b\,. \tag{II-7}$$

Thus, it is found that

$$\begin{aligned}&\Sigma_{22}=H_4(\boldsymbol{E}_1)+H_4(\boldsymbol{E}_2)+2H_2(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\,,\\&\Sigma_{33}=H_2(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)\,,\\&\Sigma_{32}=H_3(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)+H_1(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)\,,\\&\Sigma_{43}=\tfrac{1}{4}\{H_5(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)+H_1(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\}+H_3(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)\,.\end{aligned} \tag{II-8}$$

In the same way,

$$\begin{aligned}&\Sigma_{322}=H_5(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)+2H_3(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)+H_1(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\,,\\&\Sigma_{333}=H_3(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\,.\end{aligned} \tag{II-9}$$

Further terms up to Σ_{33333} have been calculated without giving the results here.

II·2. As another example, corresponding to the cases treated by other authors, the calculation of $\Sigma_{ab\ldots f}$ will be shown for three structure factors with $\boldsymbol{E}_1\equiv\boldsymbol{E}_{\mathbf{h}_1}$, $\boldsymbol{E}_2\equiv\boldsymbol{E}_{\mathbf{h}_2}$, $\boldsymbol{E}_3\equiv\boldsymbol{E}_{\mathbf{h}_3}$ and $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$ for $P\bar{1}$. From (41), it follows that

$$\Sigma_a(\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3)=\sum_{\alpha_0+\beta_0+\gamma_0+\alpha_1+\beta_1+\gamma_1=a}\frac{1}{\alpha_0!\beta_0!\gamma_0!\alpha_1!\beta_1!\gamma_1!}$$
$$\times H_{\alpha_0+\alpha_1}(\boldsymbol{E}_1)H_{\beta_0+\beta_1}(\boldsymbol{E}_2)H_{\gamma_0+\gamma_1}(\boldsymbol{E}_3)$$
$$\times\delta\{(\alpha_0-\alpha_1)\mathbf{h}_1+(\beta_0-\beta_1)\mathbf{h}_2+(\gamma_0-\gamma_1)\mathbf{h}_3\}\,. \tag{II-10}$$

The non-vanishing condition for $\delta\{\ldots\}$ is

$$\alpha_0-\alpha_1=\beta_0-\beta_1=\gamma_0-\gamma_1\,. \tag{II-11}$$

The rule in the summation is

$$\alpha_0+\beta_0+\gamma_0+\alpha_1+\beta_1+\gamma_1=a\,. \tag{II-12}$$

Thus, we obtain the following results:

$$\begin{aligned}&\Sigma_3=2H_1(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)\,,\\&\Sigma_4=\tfrac{1}{4}\{H_4(\boldsymbol{E}_1)+\text{cyc.}\}+\{H_2(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)+\text{cyc.}\}\,,\\&\Sigma_5=\{H_3(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}\}\,.\end{aligned} \tag{II-13}$$

In the same way,

$$\begin{aligned}
\Sigma_{22} &= \{H_4(\boldsymbol{E}_1)+\text{cyc.}\}+2\{H_2(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)+\text{cyc.}\}\,,\\
\Sigma_{32} &= 2\{H_3(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}\}\,,\\
\Sigma_{33} &= 4H_2(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)H_2(\boldsymbol{E}_3)\,,\\
\Sigma_{43} &= \tfrac{1}{2}\{H_5(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}\}\\
&\quad +2\{H_3(\boldsymbol{E}_1)H_3(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}\}\,,\\
\Sigma_{322} &= 2\{H_5(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}\}\\
&\quad +4\{H_3(\boldsymbol{E}_1)H_3(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}\}\,,\\
\Sigma_{333} &= 8H_3(\boldsymbol{E}_1)H_3(\boldsymbol{E}_2)H_3(\boldsymbol{E}_3)\,. \qquad \text{(II–14)}
\end{aligned}$$

In this case also, we have calculated down to the last term in (40).

II·3. $\Sigma_{ab\ldots f}$ in $P2_1/c$

As an example for higher symmetry consider the calculation of $\Sigma_{ab\ldots f}$ for two structure factors $\boldsymbol{E}_1 \equiv \boldsymbol{E}_{\mathbf{h}_1}$, $\boldsymbol{E}_2 \equiv \boldsymbol{E}_{\mathbf{h}_2}$ ($\mathbf{h}_1=(2h, 0, 2l)$, $\mathbf{h}_2=(h, k, l)$) in $P2_1/c$. In this case, it is given that

$$\boldsymbol{R}_0=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\equiv\mathbf{1},\quad \boldsymbol{R}_1=\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{bmatrix}=-\mathbf{1},$$

$$\boldsymbol{R}_2=\begin{bmatrix}-1&0&0\\0&1&0\\0&0&-1\end{bmatrix}\equiv\boldsymbol{R},\quad \boldsymbol{R}_3=\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}=-\boldsymbol{R},$$

$$\mathbf{t}_0=\mathbf{t}_1=0,\quad \mathbf{t}_2=\mathbf{t}_3=\begin{bmatrix}0\\\frac{1}{2}\\\frac{1}{2}\end{bmatrix}\equiv\mathbf{t}\,. \qquad \text{(II–15)}$$

From (41) and (II–15), it follows that

$$\begin{aligned}
\Sigma_a(\mathbf{h}_1, \mathbf{h}_2) = &\sum_{\substack{\alpha_0+\alpha_1+\alpha_2+\alpha_3\\+\beta_0+\beta_1+\beta_2+\beta_3=a}} \frac{(1/\sqrt{\varepsilon_1})^{\alpha_0+\alpha_1+\alpha_2+\alpha_3}}{\alpha_0!\beta_0!\alpha_1!\beta_1!\alpha_2!\beta_2!\alpha_3!\beta_3!}\\
&\times H_{\alpha_0+\alpha_1+\alpha_2+\alpha_3}(\boldsymbol{E}_1)H_{\beta_0+\beta_1+\beta_2+\beta_3}(\boldsymbol{E}_2)\\
&\times \exp\{2\pi i[(\alpha_2+\alpha_3)\mathbf{t}\mathbf{h}_1+(\beta_2+\beta_3)\mathbf{t}\mathbf{h}_2]\}\\
&\times \delta\{[(\alpha_0-\alpha_1)\mathbf{1}+(\alpha_2-\alpha_3)\boldsymbol{R}]\mathbf{h}_1\\
&+[(\beta_0-\beta_1)\mathbf{1}+(\beta_2-\beta_3)\boldsymbol{R}]\mathbf{h}_2\}\,, \qquad \text{(II–16)}
\end{aligned}$$

in which $\varepsilon_1=2$ is the statistical weight for the special reflection $\boldsymbol{E}_1$. The non-vanishing condition for $\delta\{\ldots\}$ is

$$[(\alpha_0-\alpha_1)\mathbf{1}+(\alpha_2-\alpha_3)\boldsymbol{R}]\mathbf{h}_1 +[(\beta_0-\beta_1)\mathbf{1}+(\beta_2-\beta_3)\boldsymbol{R}]\mathbf{h}_2=0\,, \qquad \text{(II–17)}$$

and the rule for summation is

$$\alpha_0+\alpha_1+\alpha_2+\alpha_3+\beta_0+\beta_1+\beta_2+\beta_3=a\,. \qquad \text{(II–18)}$$

From these, it is easily given that

$$\begin{aligned}
\Sigma_3 &= (4/\sqrt{2})H_1(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)(-1)^{k+l},\\
\Sigma_4 &= H_4(\boldsymbol{E}_1)+\tfrac{3}{2}H_4(\boldsymbol{E}_2)+4H_2(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\,,\\
\Sigma_5 &= \{(4/\sqrt{2})H_1(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)\\
&\quad +(4/\sqrt{2})H_3(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\}(-1)^{k+l}. \qquad \text{(II–19)}
\end{aligned}$$

In the same way, Σ_{22}, Σ_{32}, Σ_{33}, $\ldots$, Σ_{333} are easily derived and these are utilized in Appendix III·3.

II·4. *Calculation of* $\Sigma_{ab\ldots f}$ *related to any number* m *of structure factors* $\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m$ *in the case of* $P\bar{1}$

The calculation in this case has been carried out by us to $O(N^{-3/2})$, that is to the term Σ_{333} in the relation (40). Bertaut (1955*a*) has carried out a calculation, in which has been derived only the terms Σ_3, $\Sigma_4-\frac{1}{2}\Sigma_{22}$ and $\Sigma_5-\Sigma_{32}$. He has dropped some terms such as Σ_{33}, Σ_{43}, Σ_{322}, Σ_{333}. These terms are also necessary for the calculation of joint probability approximate to $O(N^{-3/2})$. Unfortunately our calculation shows that these terms have turned out lengthy and complicated. Hence we shall not write the results here explicitly. However, it may be said that our theory in § 3 has made the calculation easier than the other methods. Furthermore, it is to be noted that, although not given, these calculated results have been applied in the evaluation of the expected values described in § 4.

APPENDIX III

Joint probability distribution $\mathrm{P}(\boldsymbol{E}_1, \ldots, \boldsymbol{E}_m)$

III·1. The joint probability distribution $P(\boldsymbol{E}_1, \boldsymbol{E}_2)$ for two structure factors $\boldsymbol{E}_1 \equiv \boldsymbol{E}_{2\mathbf{h}}$, $\boldsymbol{E}_2 \equiv \boldsymbol{E}_{\mathbf{h}}$ in $P\bar{1}$ is as follows:

$$\begin{aligned}
P(\boldsymbol{E}_1, \boldsymbol{E}_2) &= (1/2\pi)\exp\{-\tfrac{1}{2}(\boldsymbol{E}_1^2+\boldsymbol{E}_2^2)\}\\
&\times[1+(z_3/2)H_1(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)-(z_4/8)\{H_4(\boldsymbol{E}_1)+H_4(\boldsymbol{E}_2)\}\\
&+(z_3^2/8)H_2(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)-z_5\{\tfrac{1}{4}H_3(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\\
&+\tfrac{1}{3}H_1(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)\}-(z_3z_4/16)\{H_5(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\\
&+H_1(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\}+(z_3^3/48)H_3(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\\
&+(z_6/2)\{\tfrac{1}{9}[H_6(\boldsymbol{E}_1)+H_6(\boldsymbol{E}_2)]-\tfrac{11}{24}H_2(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)\}\\
&-(z_3z_5/4)\{\tfrac{1}{2}H_4(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)+\tfrac{2}{3}H_2(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\}\\
&+(z_4^2/128)\{H_8(\boldsymbol{E}_1)+H_8(\boldsymbol{E}_2)+2H_4(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)\}\\
&-(z_3^2z_4/64)\{H_6(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)+H_2(\boldsymbol{E}_1)H_8(\boldsymbol{E}_2)\}\\
&+(z_3^4/384)H_4(\boldsymbol{E}_1)H_8(\boldsymbol{E}_2)+(z_7/6)\{H_5(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\\
&+H_3(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)+\tfrac{11}{8}H_1(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\}\\
&+(z_3z_6/4)\{\tfrac{1}{9}[H_7(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)+H_1(\boldsymbol{E}_1)H_8(\boldsymbol{E}_2)]\\
&-\tfrac{11}{24}H_3(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\}+(z_4z_5/16)\{\tfrac{1}{2}H_7(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\\
&+\tfrac{2}{3}H_5(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)+\tfrac{1}{2}H_3(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)+\tfrac{2}{3}H_1(\boldsymbol{E}_1)H_8(\boldsymbol{E}_2)\}\\
&-(z_3^2z_5/16)\{\tfrac{1}{2}H_5(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)+\tfrac{2}{3}H_3(\boldsymbol{E}_1)H_8(\boldsymbol{E}_2)\}\\
&+(z_3z_4^2/256)\{H_9(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)+2H_5(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\\
&+H_1(\boldsymbol{E}_1)H_{10}(\boldsymbol{E}_2)\}-(z_3^3z_4/384)\{H_7(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\\
&+H_3(\boldsymbol{E}_1)H_{10}(\boldsymbol{E}_2)\}+(z_3^5/3840)H_5(\boldsymbol{E}_1)H_{10}(\boldsymbol{E}_2)+\ldots]\,. \qquad \text{(III–1)}
\end{aligned}$$

III·2. The joint probability distribution $P(\boldsymbol{E}_1, \boldsymbol{E}_2, \boldsymbol{E}_3)$ for three structure factors $\boldsymbol{E}_1 \equiv \boldsymbol{E}_{\mathbf{h}_1}$, $\boldsymbol{E}_2 \equiv \boldsymbol{E}_{\mathbf{h}_2}$, $\boldsymbol{E}_3 \equiv \boldsymbol{E}_{\mathbf{h}_3}$ ($\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$) in $P\bar{1}$ is as follows:

$$\begin{aligned}
P(\boldsymbol{E}_1, \boldsymbol{E}_2, \boldsymbol{E}_3) &= (1/(2\pi)^{3/2})\exp\{-\tfrac{1}{2}(\boldsymbol{E}_1^2+\boldsymbol{E}_2^2+\boldsymbol{E}_3^2)\}\\
&\times[1+z_3H_1(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)-(z_4/8)\{H_4(\boldsymbol{E}_1)+\text{cyc.}\}\\
&+(z_3^2/2)H_2(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)H_2(\boldsymbol{E}_3)\\
&-(z_5/2)\{H_3(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}\}\\
&-(z_3z_4/8)\{H_5(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}\}\\
&+(z_3^3/6)H_3(\boldsymbol{E}_1)H_3(\boldsymbol{E}_2)H_3(\boldsymbol{E}_3)+z_6\{\tfrac{1}{18}[H_6(\boldsymbol{E}_1)+\text{cyc.}]
\end{aligned}$$

$$
\begin{aligned}
&-\tfrac{7}{8}H_2(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)H_2(\boldsymbol{E}_3)\}\\
&-(z_3z_5/2)\{H_4(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)H_2(\boldsymbol{E}_3)+\text{cyc.}\}\\
&+z_4^2\{\tfrac{1}{128}[H_8(\boldsymbol{E}_1)+\text{cyc.}]+\tfrac{1}{64}[H_4(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)+\text{cyc.}]\}\\
&-(z_3^2z_4/16)\{H_6(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)H_2(\boldsymbol{E}_3)+\text{cyc.}\}\\
&+(z_3^4/24)H_4(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)H_4(\boldsymbol{E}_3)\\
&+z_7\{\tfrac{1}{3}[H_5(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}]\\
&+\tfrac{1}{4}[H_3(\boldsymbol{E}_1)H_3(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}]\}\\
&+z_3z_6\{\tfrac{1}{18}[H_7(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}]\\
&-\tfrac{7}{8}H_3(\boldsymbol{E}_1)H_3(\boldsymbol{E}_2)H_3(\boldsymbol{E}_3)\}\\
&+(z_4z_5/16)\{[H_7(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}]\\
&+[(H_5(\boldsymbol{E}_1)H_3(\boldsymbol{E}_2)+H_3(\boldsymbol{E}_1)H_5(\boldsymbol{E}_2))H_1(\boldsymbol{E}_3)+\text{cyc.}]\}\\
&-(z_3^2z_5/4)\{H_5(\boldsymbol{E}_1)H_3(\boldsymbol{E}_2)H_3(\boldsymbol{E}_3)+\text{cyc.}\}\\
&+z_3z_4^2\{\tfrac{1}{128}[H_9(\boldsymbol{E}_1)H_1(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}]\\
&+\tfrac{1}{64}[H_5(\boldsymbol{E}_1)H_5(\boldsymbol{E}_2)H_1(\boldsymbol{E}_3)+\text{cyc.}]\}\\
&-(z_3^3z_4/48)\{H_7(\boldsymbol{E}_1)H_3(\boldsymbol{E}_2)H_3(\boldsymbol{E}_3)+\text{cyc.}\}\\
&+(z_3^5/120)H_5(\boldsymbol{E}_1)H_5(\boldsymbol{E}_2)H_5(\boldsymbol{E}_3)+\ldots]\,. \qquad \text{(III–2)}
\end{aligned}
$$

III·3. The joint probability distribution $P(\boldsymbol{E}_1, \boldsymbol{E}_2)$ for two structure factors $\boldsymbol{E}_1\equiv\boldsymbol{E}_{\mathbf{h}_1}$, $\boldsymbol{E}_2\equiv\boldsymbol{E}_{\mathbf{h}_2}$ ($\mathbf{h}_1=(2h, 0, 2l)$, $\mathbf{h}_2=(h, k, l)$) in $P2_1/c$ is as follows:

$$
\begin{aligned}
P(\boldsymbol{E}_1, \boldsymbol{E}_2)&=(1/2\pi)\exp\{-\tfrac{1}{2}(\boldsymbol{E}_1^2+\boldsymbol{E}_2^2)\}\\
&\times[1+(z_3/\sqrt{2})H_1(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)(-1)^{k+l}\\
&-z_4\{\tfrac{1}{4}H_4(\boldsymbol{E}_1)+\tfrac{1}{8}H_4(\boldsymbol{E}_2)\}+(z_3^2/4)H_2(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)\\
&-z_5\{(1/\sqrt{2})H_1(\boldsymbol{E}_1)H_4(\boldsymbol{E}_2)\\
&+(1/\sqrt{2})H_3(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\}(-1)^{k+l}\\
&-z_3z_4\{(1/8\sqrt{2})H_1(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)\\
&+(1/4\sqrt{2})H_5(\boldsymbol{E}_1)H_2(\boldsymbol{E}_2)\}(-1)^{k+l}\\
&+(z_3^3/12\sqrt{2})H_3(\boldsymbol{E}_1)H_6(\boldsymbol{E}_2)(-1)^{k+l}+\ldots]\,. \qquad \text{(III–3)}
\end{aligned}
$$

APPENDIX IV

In order to illustrate the usefulness of the general expressions (40) and (41), another example will be shown here of the joint probability distribution for two structure factors $\boldsymbol{E}_{\mathbf{h}'}$ and $\boldsymbol{E}_{\mathbf{h}}$ where $\mathbf{h}'$ and $\mathbf{h}$ not necessarily independent. This example of the joint probability distribution with the use of general space group operators shows a more general form than that of Appendix III, so that it is applicable to any centrosymmetric space group. For the sake of simplicity, we shall calculate the joint probability distribution $P(\boldsymbol{E}_{\mathbf{h}'}, \boldsymbol{E}_{\mathbf{h}})$ under the approximation of $O(N^{-1/2})$ which is based on two terms up to Σ_3 in (40).

In the present case, (40) and (41) give us

$$
\begin{aligned}
&P(\boldsymbol{E}_{\mathbf{h}'}, \boldsymbol{E}_{\mathbf{h}})\\
&\quad=(1/2\pi)\exp\{-\tfrac{1}{2}(\boldsymbol{E}_{\mathbf{h}'}^2+\boldsymbol{E}_{\mathbf{h}}^2)\}[1+(z_3/S)\Sigma_3]\,, \qquad \text{(IV–1)}
\end{aligned}
$$

where

$$
\begin{aligned}
\Sigma_3=&\sum_{\Sigma(\alpha_p+\beta_p)=3}\frac{(\sqrt{(\tau/\varepsilon_{\mathbf{h}'})})^{\Sigma\alpha_p}(\sqrt{(\tau/\varepsilon_{\mathbf{h}})})^{\Sigma\beta_p}}{\prod_p \alpha_p!\,\beta_p!}\\
&\times\exp\{2\pi i[(\Sigma\alpha_p\mathbf{t}_p)\mathbf{h}'+(\Sigma\beta_p\mathbf{t}_p)\mathbf{h}]\}\\
&\times H_{\Sigma\alpha_p}(\boldsymbol{E}_{\mathbf{h}'})H_{\Sigma\beta_p}(\boldsymbol{E}_{\mathbf{h}})\,\delta\left\{\left[\sum_{p=0}^{s-1}\alpha_p\boldsymbol{R}_p\right]\mathbf{h}'+\left[\sum_{p=0}^{s-1}\beta_p\boldsymbol{R}_p\right]\mathbf{h}\right\}. \qquad \text{(IV–2)}
\end{aligned}
$$

The non-vanishing condition for δ is

$$\left[\sum_{p=0}^{s-1}\alpha_p\boldsymbol{R}_p\right]\mathbf{h}'+\left[\sum_{p=0}^{s-1}\beta_p\boldsymbol{R}_p\right]\mathbf{h}=0\,. \qquad \text{(IV–3)}$$

The summation is carried out under the condition

$$\sum_{p=0}^{s-1}\alpha_p+\sum_{p=0}^{s-1}\beta_p=3\,. \qquad \text{(IV–4)}$$

Now let $\mathbf{h}'$ and $\mathbf{h}$ be two indices which satisfy a relation:

$$\text{Case I} \qquad \mathbf{h}'=2\mathbf{h}\,, \qquad \text{(IV–5)}$$

then equation (IV–3) becomes

$$\left[\sum_{p=0}^{s-1}2\alpha_p\boldsymbol{R}_p+\sum_{p=0}^{s-1}\beta_p\boldsymbol{R}_p\right]\mathbf{h}=0\,. \qquad \text{(IV–6)}$$

As the second case, let $\mathbf{h}'$ and $\mathbf{h}$ be two indices which satisfy another relation different from (IV–5); namely,

$$\text{Case II} \qquad \mathbf{h}'=(\mathbf{1}-\boldsymbol{R}_r)\mathbf{h},\ \ \boldsymbol{R}_r\neq\mathbf{1},\ -\mathbf{1}\,. \qquad \text{(IV–7)}$$

Then equation (IV–3) becomes

$$\left[\sum_{p=0}^{s-1}\alpha_p\boldsymbol{R}_p(\mathbf{1}-\boldsymbol{R}_r)+\sum_{p=0}^{s-1}\beta_p\boldsymbol{R}_p\right]\mathbf{h}=0\,. \qquad \text{(IV–8)}$$

Any other relation between two indices $\mathbf{h}'$ and $\mathbf{h}$ which give the non-zero contribution based on Σ_3 for the joint probability distribution $P(\boldsymbol{E}_{\mathbf{h}'}, \boldsymbol{E}_{\mathbf{h}})$ does not exist except those of case I and case II.

In case I, under the condition in the summation (IV–4), the possible partitions for α_p and β_p which satisfy the relation (IV–6) are given by

$$
\begin{aligned}
&\alpha_p=1,\ \bar{\beta}_p=2 \ \text{ and otherwise}\\
&\qquad\alpha=\beta=0;\ p=0, 1, \ldots, s-1\,, \qquad \text{(IV–9)}
\end{aligned}
$$

where symbol $\bar{\beta}_p$ represents the corresponding coefficient for the operation $-\boldsymbol{R}_p=\boldsymbol{I}\boldsymbol{R}_p$ (the translational part being $-\mathbf{t}_p$, and $\boldsymbol{I}$ being the operation of inversion). Hence, in this case, Σ_3 in (IV–2) becomes

$$s\frac{(\tau/\varepsilon_{2\mathbf{h}})^{\frac{1}{2}}(\tau/\varepsilon_{\mathbf{h}})}{2!}H_1(\boldsymbol{E}_{2\mathbf{h}})H_2(\boldsymbol{E}_{\mathbf{h}})\,. \qquad \text{(IV–10)}$$

With (IV–1), this gives us the joint probability distribution:

$$
\begin{aligned}
P(\boldsymbol{E}_{2\mathbf{h}}, \boldsymbol{E}_{\mathbf{h}})&=(1/2\pi)\exp\{-\tfrac{1}{2}(\boldsymbol{E}_{2\mathbf{h}}^2+\boldsymbol{E}_{\mathbf{h}}^2)\}\\
&\times[1+(z_3/2)(\tau/\varepsilon_{2\mathbf{h}}\varepsilon_{\mathbf{h}}^2)^{\frac{1}{2}}\boldsymbol{E}_{2\mathbf{h}}(\boldsymbol{E}_{\mathbf{h}}^2-1)]\,. \qquad \text{(IV–11)}
\end{aligned}
$$

In the case II, under the condition (IV–4), the possible partitions for α_p and β_p which satisfy the relation (IV–8) are given by

$$
\begin{aligned}
&\alpha_p=1,\ \bar{\beta}_p=1,\ \beta_q=1 \ \text{ and otherwise}\\
&\qquad\alpha=\beta=0;\ p=0, 1, \ldots, s-1\,, \qquad \text{(IV–12)}
\end{aligned}
$$

where β_q represents the coefficient for the rotational operation $\boldsymbol{R}_q=\boldsymbol{R}_p\boldsymbol{R}_r$ and the corresponding translational part is given by $\mathbf{t}_q=\mathbf{t}_p\boldsymbol{R}_r+\mathbf{t}_r$. Thus, in this case, Σ_3 in (IV–2) becomes

$$s(\tau/\varepsilon_{(1-\boldsymbol{R}_r)\mathbf{h}})^{\frac{1}{2}}(\tau/\varepsilon_{\mathbf{h}}) \exp\{2\pi i[\mathbf{t}_p(1-\boldsymbol{R}_r)\mathbf{h}-\mathbf{t}_p\mathbf{h}+\mathbf{t}_q\mathbf{h}]\} \times H_1(\boldsymbol{E}_{(1-\boldsymbol{R}_r)\mathbf{h}})H_2(\boldsymbol{E}_{\mathbf{h}}) = S(\tau/\varepsilon_{(1-\boldsymbol{R}_r)\mathbf{h}}\varepsilon_{\mathbf{h}}^2)^{\frac{1}{2}} \exp(2\pi i\mathbf{t}_r\mathbf{h})H_1(\boldsymbol{E}_{(1-\boldsymbol{R}_r)\mathbf{h}})H_2(\boldsymbol{E}_{\mathbf{h}}) . \quad \text{(IV–13)}$$

Therefore we obtain from (IV–1) with (IV–13)

$$P(\boldsymbol{E}_{(1-\boldsymbol{R}_r)\mathbf{h}}, \boldsymbol{E}_{\mathbf{h}}) = (1/2\pi) \exp[-\tfrac{1}{2}(\boldsymbol{E}^2_{(1-\boldsymbol{R}_r)\mathbf{h}}+\boldsymbol{E}^2_{\mathbf{h}})] \times [1+z_3(\tau/\varepsilon_{(1-\boldsymbol{R}_r)\mathbf{h}}\varepsilon^2_{\mathbf{h}})^{\frac{1}{2}}\boldsymbol{E}_{(1-\boldsymbol{R}_r)\mathbf{h}} \exp(2\pi i\mathbf{h}\mathbf{t}_r)(\boldsymbol{E}^2_{\mathbf{h}}-1)] . \quad \text{(IV–14)}$$

The result (IV–11) is not particularly new, since the same result has already been found in the case of $P\bar{1}$. The joint probability distribution (IV–14) obtained from case II consolidates the results derived for particular space groups case by case by Hauptman, Karle and others, and may be compared with MacGillavry's inequality relation (1950).

We shall show here the explicit formulae of (IV–14) for the cases of some particular space groups. (It is assumed that $\boldsymbol{E}_{\mathbf{h}}$ is a reflexion of general type.)

(1) $P2_1/c$

Using (II–15), it is easily shown that

$$(1-\boldsymbol{R}_2)\mathbf{h} = \begin{bmatrix} 2h \\ 0 \\ 2l \end{bmatrix}, \quad (1-\boldsymbol{R}_3)\mathbf{h} = \begin{bmatrix} 0 \\ 2k \\ 0 \end{bmatrix}, \quad \mathbf{h} = \begin{bmatrix} h \\ k \\ l \end{bmatrix},$$

$$\exp[2\pi i\mathbf{h}\mathbf{t}_2] = \exp[2\pi i\mathbf{h}\mathbf{t}_3] = (-1)^{k+l}. \quad \text{(IV–15)}$$

Hence, substituting (IV–15) in (IV–14), we find the following relations for the probabilities of signs.

$$P^+(s_{2h,0,2l}) = \tfrac{1}{2} + (z_3/2\sqrt{2})E_{2h,0,2l}(-1)^{k+l}(E^2_{hkl}-1) ,$$
$$P^+(s_{0,2k,0}) = \tfrac{1}{2} + (z_3/2\sqrt{2})E_{0,2k,0}(-1)^{k+l}(E^2_{hkl}-1) . \quad \text{(IV–16)}$$

(2) $P4/m$

In this case,

$$\boldsymbol{R}_0 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = 1, \quad \boldsymbol{R}_1 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

$$\boldsymbol{R}_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad \boldsymbol{R}_3 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{R}_4 = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad \boldsymbol{R}_5 = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

$$\boldsymbol{R}_6 = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{R}_7 = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\mathbf{t}_p = 0 \quad (p=0, \ldots, 7) . \quad \text{(IV–17)}$$

Hence

$$(1-\boldsymbol{R}_2)\mathbf{h} = \begin{bmatrix} 0 \\ 0 \\ 2l \end{bmatrix}, \quad (1-\boldsymbol{R}_3)\mathbf{h} = \begin{bmatrix} 2h \\ 2k \\ 0 \end{bmatrix}, \quad \text{(IV–18)}$$

$$(1-\boldsymbol{R}_4)\mathbf{h} = \begin{bmatrix} h+k \\ k-h \\ 2l \end{bmatrix}, \quad (1-\boldsymbol{R}_5)\mathbf{h} = \begin{bmatrix} h-k \\ h+k \\ 2l \end{bmatrix}, \quad \text{(IV–19)}$$

$$(1-\boldsymbol{R}_6)\mathbf{h} = \begin{bmatrix} h+k \\ k-h \\ 0 \end{bmatrix}, \quad (1-\boldsymbol{R}_7)\mathbf{h} = \begin{bmatrix} h-k \\ h+k \\ 0 \end{bmatrix}. \quad \text{(IV–20)}$$

Now two relations in (IV–19) give the same probability formula, since they relate to each other by a symmetry operation; and similarly in (IV–20). As the summary of results, from these equations with (IV–14), we obtain:

$$P^+(s_{2h,2k,0}) = \tfrac{1}{2} + (z_3/2\sqrt{2})E_{2h,2k,0}(E^2_{hkl}-1) ,$$
$$P^+(s_{0,0,2l}) = \tfrac{1}{2} + (z_3/4)E_{0,0,2l}(E^2_{hkl}-1) ,$$
$$P^+(s_{h+k,k-h,0}) = \tfrac{1}{2} + (z_3/2\sqrt{2})E_{h+k,k-h,0}(E^2_{hkl}-1) ,$$
$$P^+(s_{h+k,k-h,2l}) = \tfrac{1}{2} + (z_3/2)E_{h+k,k-h,2l}(E^2_{hkl}-1) . \quad \text{(IV–21)}$$

(3) $R\bar{3}$

In this case,

$$\boldsymbol{R}_0 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = 1, \quad \boldsymbol{R}_1 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

$$\boldsymbol{R}_2 = \begin{bmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{bmatrix}, \quad \boldsymbol{R}_3 = \begin{bmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{bmatrix},$$

$$\boldsymbol{R}_4 = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}, \quad \boldsymbol{R}_5 = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix},$$

$$\mathbf{t}_p = 0 \quad (p=0, \ldots, 5) . \quad \text{(IV–22)}$$

Hence,

$$(1-\boldsymbol{R}_2)\mathbf{h} = \begin{bmatrix} h+k \\ k+l \\ l+h \end{bmatrix}, \quad (1-\boldsymbol{R}_3)\mathbf{h} = \begin{bmatrix} h+l \\ k+h \\ l+k \end{bmatrix}, \quad \text{(IV–23)}$$

$$(1-\boldsymbol{R}_4)\mathbf{h} = \begin{bmatrix} h-k \\ k-l \\ l-h \end{bmatrix}, \quad (1-\boldsymbol{R}_5)\mathbf{h} = \begin{bmatrix} h-l \\ k-h \\ l-k \end{bmatrix}. \quad \text{(IV–24)}$$

The two equations in (IV–23) and (IV–24) do not lead to independent probability formulae, for the same reason as in example (2). As the results of these two sets of equations, we obtain:

$$P^+(s_{h+k,k+l,l+h}) = \tfrac{1}{2} + (z_3/2)E_{h+k,k+l,l+h}(E^2_{hkl}-1) ,$$
$$P^+(s_{h-k,k-l,l-h}) = \tfrac{1}{2} + (z_3/2)E_{h-k,k-l,l-h}(E^2_{hkl}-1) . \quad \text{(IV–25)}$$

APPENDIX V

It is of interest to look into the case in which the number $n_{\mathbf{k}}$ of the terms in the summations contained in A_3, A_3', A_3'' and A_5 of the relation (42) increases with the increase of the number N of the atoms in unit cell. In this case the sequence of expanded terms becomes not necessarily adequate, since the effects of the sum terms such as $\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h+k}})$ are not small compared with those of the single terms. In order to estimate the effects of these sum terms appropriately, let us consider their variances. When both $n_{\mathbf{k}}$ and N are large, each variance of the sum terms becomes as follows (see Klug, 1958 and Vaughan, 1959).

$$(n_{\mathbf{k}}^2/N^2):\ \text{for } \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h+k}}),\ \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{2h+k}}) \text{ in } A_3 \text{ and } A_5, \quad \text{(V–1)}$$

$$(n_{\mathbf{k}}^2/N^3):\ \text{for } \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{2k}})H_2(E_{\mathbf{h+k}}),\ \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h+k}})H_2(E_{\mathbf{2h+k}}) \text{ in } A_3', \quad \text{(V–2)}$$

$$(n_{\mathbf{k}}^2/N^4):\ \text{for } \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{2k}})H_2(E_{\mathbf{h+k}})H_2(E_{\mathbf{2h+2k}}),\ \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h+k}})H_2(E_{\mathbf{2h+k}})H_2(E_{\mathbf{2h+2k}}) \text{ in } A_3''. \quad \text{(V–3)}$$

Now, as discussed by Klug (1958) and Cochran (1958), $n_{\mathbf{k}}$ is to be taken as

$$n_{\mathbf{k}} \propto N^2. \quad \text{(V–4)}$$

Furthermore we shall assume that $z_3 \simeq N^{-1/2}$ and $z_3^3 \simeq z_3 z_4 \simeq z_5 \simeq N^{-3/2}$ hold approximately even for the case of non-equal atoms. In such a case each order of $A_0, \ldots, A_5$ in (42) becomes $O(N^{-1/2})$ for A_0, A_3 and A_5, $O(N^{-1})$ for A_3', $O(N^{-3/2})$ for $A_1, A_2, A_2', A_3'', A_4$ and A_4'. Taking these facts into account, rearrange the sequence of series in (42) as follows:

$$\begin{aligned}\langle s_{\mathbf{2h}}\rangle = {} & A_0+A_3+A_5 \ldots\ldots\ldots\ldots\ldots O(N^{-1/2})\\ & +A_3' \ldots\ldots\ldots\ldots\ldots\ldots\ldots O(N^{-1})\\ & +A_1+A_2+A_2'+A_3''+A_4+A_4' \ldots O(N^{-3/2}).\end{aligned} \quad \text{(V–5)}$$

This new series becomes an adequately convergent progression when N is large. Thus, as a first approximation, we have

$$\langle s_{\mathbf{2h}}\rangle \cong A_0+A_3+A_5 . \quad \text{(V–6)}$$

Now it is seen that A_3, A_3', A_3'' and A_5 contain a number of terms which Vaughan has used in his regression calculation. His treatment corresponds to the termination in the second line, $O(N^{-1})$, in (V–5). Writing

$$\langle s_{\mathbf{2h}}\rangle \equiv E_{\mathbf{2h}}\Sigma_{\mathbf{2h}} , \quad \text{(V–7)}$$

and using his notation:

$$\begin{aligned}1(a) &\equiv H_2(E_{\mathbf{h}}) ,\\ 2(b) &\equiv H_2(E_{\mathbf{2h}})H_2(E_{\mathbf{h}}) ,\\ 2(c) &\equiv \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h+k}}) ,\\ 3(b) &\equiv H_2(E_{\mathbf{h}})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{2h+k}}) ,\\ 3(d) &\equiv H_2(E_{\mathbf{h}})\sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h+k}}) ,\\ 3(e) &\equiv \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{2k}})H_2(E_{\mathbf{h+k}}) ,\\ 3(g) &\equiv \sum_{\mathbf{k}} H_2(E_{\mathbf{k}})H_2(E_{\mathbf{h+k}})H_2(E_{\mathbf{2h+k}}) ,\end{aligned} \quad \text{(V–8)}$$

our result can be expressed by

$$\begin{aligned}\Sigma_{\mathbf{2h}} = {} & \tfrac{1}{2}z_3[1(a)]+(\tfrac{1}{4}z_5-\tfrac{1}{2}z_3^3)[2(c)]+(\tfrac{1}{2}z_3z_4-\tfrac{1}{2}z_3^3)[3(b)]\\ & +(z_3z_4-z_3^3)[3(d)]+\tfrac{1}{4}z_3z_4[3(e)]+z_3^3[1(a)][3(g)].\end{aligned} \quad \text{(V–9)}$$

On the other hand, Vaughan gave the following example of his regression formula

$$\begin{aligned}\Sigma_{\mathbf{2h}} = {} & c_1[1(a)]+c_2[2(b)]+c_3[2(c)]+c_4[3(b)]\\ & +c_5[3(e)]+c_6[3(g)] ,\end{aligned} \quad \text{(V–10)}$$

where the coefficients $c_1, \ldots, c_6$ are the numerical constants. In our treatment, the term corresponding to Vaughan's $2(b)$ has been excluded since it is $O(N^{-3/2})$, although it might be contained in A_1 and A_4 in (42). Moreover, for the case of equal atoms, the terms $3(b)$ and $3(d)$ in our expression disappear. Similarly to ours, the coefficient c_4 of $3(b)$ in Vaughan's formula is considerably small and the term $3(d)$ is absent. It is of interest to notice that both expressions are formally in harmony with each other, except the slight difference between the terms relating to $3(g)$.

The convergence of our expression (V–5) becomes more and more rapid as N increases. However, in the case of Vaughan's example where $N=8$, the convergence will not be good enough for practical calculations.

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