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Structure Factor Algebra in the Probabilistic Procedure for Phase Determination. I

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It is possible to take the statistical weight of reflexions into account in the $\sum_1$, Sayre and tangent formulae. A suitable new use of the normalized structure factors is proposed in these procedures for phase determination; new generalized formulae are derived in a form suitable for automatic computer calculation.

Introduction

Hauptman & Karle (1953) defined the normalized structure factor $E_{\mathbf{h}}$ as

$$E_{\mathbf{h}}^2 = F_{\mathbf{h}}^2/\varepsilon \sum_{1}^{N} {}_j f_j^2(\mathbf{h}) \qquad (1)$$

where

$$\varepsilon = \frac{m_{20}+m_{02}}{m}\;;\; m_{20} = \iiint \psi^2(\mathbf{h})d\mathbf{r}\,;\; m_{02} = \iiint \eta^2(\mathbf{h})d\mathbf{r}\,.$$

m is the symmetry number of the space group, ψ and η are the trigonometric functions for the real and imaginary parts of the structure factor.

The quasi-normalized structure factor $\mathscr{E}_{\mathbf{h}}$ is also frequently used in structure determination: it is

$$\mathscr{E}_{\mathbf{h}} = \sigma_2^{-1/2} \sum_{1}^{N} {}_j Z_j \exp 2\pi i \mathbf{k}\mathbf{r}_j \qquad (2)$$

where $\sigma_2 = \sum_{1}^{N} {}_j Z_j^2$: no space-group weight of reflexions is considered. The $E_{\mathbf{h}}$ was defined to ensure always that mean-square $\langle E_{\mathbf{h}}^2\rangle = 1$, the quasi-normalized $\mathscr{E}_{\mathbf{h}}$ to guarantee simplicity in the derivation of algebraic relationships.

Karle & Karle (1966) advised, on an experimental basis, the use in symbolic-addition procedures of the $E_{\mathbf{h}}'$ factors where

$$|E_{\mathbf{h}}'|^2 = \frac{|F_{\mathbf{h}}|^2}{\varepsilon' \sum_{1}^{N} {}_j f_j^2(\mathbf{h})}\,. \qquad (3)$$

ε' is a number which corrects for space-group extinctions: the relation proposed between $\mathscr{E}_{\mathbf{h}}$ and $E_{\mathbf{h}}'$ is

$$|\mathscr{E}_{\mathbf{h}}|^2(1-q) = |E_{\mathbf{h}}'|^2,$$

where q is the fraction of reflexions in the $\mathbf{h}$ set which are space-group extinctions.

This work justifies in Sayre, tangent and $\sum_1$ formulas a new use of the normalized structure factors on the basis of their algebra; a combination of the linearization theory (Bertaut & Waser, 1957; Bertaut, 1959*a*,*b*) and of the probability distribution functions have been used to derive the method in a form suitable for automatic computing. A method, similar in some aspects, has been used in the centrosymmetric case by Naya, Nitta & Oda (1964).

Algebraic considerations

For equal atoms, if m is the space-group order, according to (2), (Bertaut & Waser, 1957)

$$\mathscr{E}_{\mathbf{h}} = N^{-1/2} \sum_{1}^{N/m} {}_j\, p_{\mathbf{h}} \sum_{1}^{m/p_{\mathbf{h}}} {}_s \exp 2\pi i \mathbf{h} \mathbf{C}_s \mathbf{x}_j = N^{-1/2} \sum_{1}^{N/m} {}_j\, \xi_j(\mathbf{h}) \qquad (4)$$

where $\mathbf{C}_s\mathbf{x} = \mathbf{R}_s\mathbf{x} + \mathbf{T}_s$: $\mathbf{C}_s$ is the s-symmetry operation ($\mathbf{R}_s$ rotation component, $\mathbf{T}_s$ translation component), $p_{\mathbf{h}}$ is the statistical weight.

Following Woolfson (1954), we impose for general reflexions the condition that $\mathbf{k}$ varies while $\mathscr{E}_{\mathbf{k}}$ and $\mathscr{E}_{\mathbf{h}-\mathbf{k}}$ are constant: we obtain, by the application of the central-limit theorem (Cramér, 1951).

$$\langle \mathscr{E}_{\mathbf{h}} \rangle = N^{-1/2} \sum_{1}^{N/m} {}_j \langle \xi_j(\mathbf{h}) \rangle = N^{-1/2} \mathscr{E}_{\mathbf{k}} \mathscr{E}_{\mathbf{h}-\mathbf{k}}\,, \qquad (5)$$

$$V_{\mathbf{h}} = N^{-1} \sum_{1}^{N/m} {}_j \langle |\xi_j(h)|^2 \rangle - |\langle \xi_j(h) \rangle|^2 = N^{-1} \sum_{1}^{N/m} {}_j \left\{ m - \frac{|\mathscr{E}_{\mathbf{k}} \mathscr{E}_{\mathbf{h}-\mathbf{k}}|^2 m^2}{N^2} \right\}. \qquad (6)$$

If the number N/m of the independent atoms in the cell is large enough

$$V_{\mathbf{h}} = 1\,. \qquad (7)$$

By following the Cochran (1955) treatment and expressing in E terms, we obtain the well known results:

$$\langle \varphi_{\mathbf{h}} \rangle = \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}\,, \qquad (8)$$

$$P(\varphi_{\mathbf{h}}) = \exp\{G_{\mathbf{h},\mathbf{k}} \cos(\varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}})\}/2\pi I_0(G_{\mathbf{h},\mathbf{k}}), \qquad (9)$$

where

$$G_{\mathbf{h},\mathbf{k}} = 2\,\frac{|E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}|}{\sqrt{N}}\,,$$

and I_0 is a modified Bessel function of the second kind (Watson, 1922).

Starting from equations (5), (7), (8) and (9) Karle & Karle (1966) established, by probability considerations, the tangent formula

$$\tan \varphi_{\mathbf{h}} = \tan \frac{\sum_{\mathbf{k}} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \sin (\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})}{\sum_{\mathbf{k}} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \cos (\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})} \tag{10}$$

with variance

$$V_{\mathbf{h}} = \frac{\pi^2}{3} + [I_0(\alpha)]^{-1} \sum_{1}^{\infty} {}_n \frac{I_{2n}(\alpha)}{n^2} - 4[I_0(\alpha)]^{-1} \sum_{0}^{\infty} {}_n \frac{I_{2n+1}(\alpha)}{(2n+1)^2}, \tag{11}$$

where

$$\alpha = \left\{ \left[\sum_{\mathbf{k}} G_{\mathbf{h},\mathbf{k}} \cos (\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}) \right]^2 + \left[\sum_{\mathbf{k}} G_{\mathbf{h},\mathbf{k}} \sin (\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}}) \right]^2 \right\}^{1/2}. \tag{12}$$

The central-limit theorem, employed to obtain equations (5), (7), (8), (9) disregards the actual algebraic form of the ξ function, and therefore these equations are not strictly applicable in the case of special reflexions.

In order to generalize the previous formulae probability theory will be used here.

Probability considerations

Following Hauptman & Karle (1953) and employing the Klug (1958) notation, for a general centrosymmetrical group of order m, the joint probability distribution results:

$$\begin{aligned} P(E_1,E_2,E_3) = {} & \frac{1}{(2\pi)^{3/2}} \exp \left[-\tfrac{1}{2}(E_1^2+E_2^2+E_3^2) \right] \\ & \times \left\{ 1 + \frac{1}{t^{1/2}} \left[\frac{\lambda_{111}}{1!1!1!} E_1E_2E_3 \right] \right. \\ & + \frac{1}{t} \left[\frac{\lambda_{400}}{4!0!0!} H_4(E_1) + \frac{\lambda_{040}}{0!4!0!} H_4(E_2) + \dots \right] \\ & + \frac{1}{2t} \left[\frac{\lambda^2{}_{111}}{1!1!1!} H_2(E_1)H_2(E_2)H_2(E_3) \right] \\ & \left. + \frac{1}{t^{3/2}} \left[\frac{\lambda_{113}}{1!1!3!} H_1(E_1)H_1(E_2)H_3(E_3) + \dots \right] \right\}, \end{aligned} \tag{13}$$

where

$$E_1 = E_{\mathbf{h}},\ E_2 = E_{\mathbf{k}},\ E_3 = E_{\mathbf{h}+\mathbf{k}},$$

and

$$\lambda_{rsw} = \frac{K_{rsw}}{K_{200}^{r/2}K_{020}^{q/2}K_{002}^{w/2}} = \frac{K_{rsw}}{(m)^{(r+s+w)/2}}.$$

K_{rsw} is a multivariate cumulant of order $r+s+w$, and $H(z)$ is a Hermite polynomial defined by the equation:

$$H_\nu(x) = (-1)^\nu \exp [\tfrac{1}{2}x^2] \frac{d^\nu}{dx^\nu} \exp [-\tfrac{1}{2}x^2].$$

The first moment of the conditional probability distribution $P(E_1|E_2,E_3)$ is, retaining terms to order $1/t^{1/2}$,

$$\langle E_1 | E_2,E_3 \rangle = \frac{\lambda_{111}}{t^{1/2}} E_2E_3. \tag{14}$$

As

$$K_{111} = m_{111} = \left\langle \frac{\xi(\mathbf{h})}{\sqrt{p_{\mathbf{h}}}} \frac{\xi(\mathbf{k})}{\sqrt{p_{\mathbf{k}}}} \frac{\xi(\mathbf{h}+\mathbf{k})}{\sqrt{p_{\mathbf{h}+\mathbf{k}}}} \right\rangle,$$

where $p_{\mathbf{h}}$, $p_{\mathbf{k}}$, $p_{\mathbf{h}+\mathbf{k}}$ are the statistical weights of $E_{\mathbf{h}}$, $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}}$, we find

$$\langle E_{\mathbf{h}} | E_{\mathbf{k}}, E_{\mathbf{h}+\mathbf{k}} \rangle = \left\langle \frac{\xi(\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}+\mathbf{k})}{m^{3/2}\sqrt{p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{h}+\mathbf{k}}}} \right\rangle \times \frac{1}{t^{1/2}} E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}} = W_{\mathbf{h},\mathbf{k}}(N^{-1/2}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}), \tag{15}$$

where

$$W_{\mathbf{h},\mathbf{k}} = \frac{1}{m\sqrt{p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{h}+\mathbf{k}}}} \left\langle \sum_{1}^{m} {}_{s,r}\, \xi[\mathbf{h}(\mathbf{C}_s-\mathbf{I})+\mathbf{k}(\mathbf{C}_r-\mathbf{I})] \right\rangle. \tag{16}$$

$W_{\mathbf{h},\mathbf{k}}$ takes the statistical weights of the normalized structure factors $E_{\mathbf{h}}$, $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}}$ into account. Formula (16) has been worked out in the Appendix and is very suitable for automatic computing.

As is well known, the second moment of the $E_{\mathbf{h}}$ conditional distribution is, from equation (13), retaining terms to order $1/t^{1/2}$, equal to unity, whatever the statistical weights may be.

If we expand the $E_{\mathbf{h}}$ conditional probability in the form of the Gram–Charlier series (Cramér, 1951) we obtain

$$P(E_{\mathbf{h}} | E_{\mathbf{k}}, E_{\mathbf{h}+\mathbf{k}}) = \frac{1}{\sqrt{2\pi}} \times \exp \left[-\tfrac{1}{2} \left(E_{\mathbf{h}} - \frac{W_{\mathbf{h},\mathbf{k}}}{N^{1/2}} E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}} \right)^2 \right] + \dots .$$

As

$$P_+ = \left(\frac{P_-}{P_+} + 1 \right)^{-1},$$

we easily obtain

$$P_+(E_{\mathbf{h}}) = \tfrac{1}{2} + \tfrac{1}{2} \tanh \left[\frac{W_{\mathbf{h},\mathbf{k}}}{N^{1/2}} |E_{\mathbf{h}}| E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}} \right],$$

or in general

$$P_+(E_{\mathbf{h}}) = \tfrac{1}{2} + \tfrac{1}{2} \tanh \left[\frac{|E_{\mathbf{h}}|}{N^{1/2}} \sum_{1}^{r} {}_j\, W_{\mathbf{h},\mathbf{k}_j} E_{\mathbf{k}_j} E_{\mathbf{h}+\mathbf{k}_j} \right]. \tag{17}$$

Σ_1 formula

From Klug (1958) we derive, for a centrosymmetric space group of order m, the probability distribution

$$P(E_1,E_2)=\frac{1}{2\pi}\exp[-\tfrac{1}{2}(E_1^2+E_2^2)]$$
$$\times\Big\{1+\frac{1}{t^{1/2}}\frac{\lambda_{12}}{1!2!}H_1(E_1)H_2(E_2)$$
$$+\frac{1}{t}\Big[\frac{\lambda_{40}}{4!0!}H_4(E_1)+\frac{\lambda_{04}}{0!4!}H_4(E_2)$$
$$+\tfrac{1}{2}\left(\frac{\lambda_{12}}{1!2!}\right)^2H_2(E_1)H_4(E_2)\Big]+\ldots\Big\},\quad(18)$$

where

$$E_1=E_{2\mathbf{h}},\quad E_2=E_{\mathbf{h}}$$

and

$$\lambda_{ij}=\frac{K_{ij}}{(K_{20})^{i/2}(K_{02})^{j/2}}=\frac{K_{ij}}{m^{(i+j)/2}}.$$

The first conditional moment $\langle E_{2\mathbf{h}}|E_{\mathbf{h}}\rangle$ gives, retaining terms to order $1/t^{1/2}$,

$$\langle E_{2\mathbf{h}}|E_{\mathbf{h}}\rangle=\frac{1}{t^{1/2}}\frac{\lambda_{12}}{1!2!}(E_{\mathbf{h}}^2-1)\ .$$

As (see Appendix)

$$K_{12}=m_{12}=\frac{\langle\xi^2(\mathbf{h})\xi(2\mathbf{h})\rangle}{(p_{\mathbf{h}})^{3/2}}$$
$$=\left\langle\frac{\sum_{1}^{m}{}_q\,\xi[\mathbf{h}(\mathbf{I}-\mathbf{R}_q)]\xi[\mathbf{h}(\mathbf{I}-\mathbf{R}_2)]}{p_{\mathbf{h}}^{\ 3/2}}\right\rangle=\frac{m}{\sqrt{p_{\mathbf{h}}}},$$

we obtain

$$\langle E_{2\mathbf{h}}|E_{\mathbf{h}}\rangle=\frac{1}{2N^{1/2}\sqrt{p_{\mathbf{h}}}}(E_{\mathbf{h}}^2-1)\ .$$

As the variance is equal to unity, by expanding the $E_{2\mathbf{h}}$ conditional distribution in Gram–Charlier series, we can write

$$P(E_{2\mathbf{h}}|E_{\mathbf{h}})=\frac{1}{\sqrt{2\pi}}\exp\left[-\tfrac{1}{2}\left(E_{2\mathbf{h}}-\frac{(E_{\mathbf{h}}^2-1)}{2N^{1/2}\sqrt{p_{\mathbf{h}}}}\right)^2\right].$$

This equation can be compared with previous results [*i.e.* Cochran & Woolfson (1955), equation (3.8)].

The probability $P_+(E_{2\mathbf{h}})$ is finally obtained as

$$P_+(E_{2\mathbf{h}})=\tfrac{1}{2}+\tfrac{1}{2}\tanh\left[\frac{1}{2N^{1/2}\sqrt{p_{\mathbf{h}}}}|E_{2\mathbf{h}}|(E_{\mathbf{h}}^2-1)\right].\ (19)$$

To obtain other $\sum_1$ formulas, we modify the probability distribution (18) by putting $E_2=E_{\mathbf{h}}(\mathbf{I}-\mathbf{R}_s)$, where $\mathbf{R}_s$ is a matrix rotation of the space groups. In this case we obtain

$$\lambda_{12}=\frac{\langle\xi^2(\mathbf{h})\xi[\mathbf{h}(\mathbf{I}-\mathbf{R}_s)]\rangle}{m^{3/2}p_{\mathbf{h}}\sqrt{p_{\mathbf{h}}(\mathbf{I}-\mathbf{R}_s)}}$$
$$=\frac{\langle\sum_{1}^{m}{}_q\,\xi_q[\mathbf{h}(\mathbf{I}-\mathbf{R}_q)]\xi[\mathbf{h}(\mathbf{I}-\mathbf{R}_s)]\rangle}{m^{3/2}p_{\mathbf{h}}\sqrt{p_{\mathbf{h}}(\mathbf{I}-\mathbf{R}_s)}}=\frac{\sqrt{p_{\mathbf{h}}(\mathbf{I}-\mathbf{R}_s)}}{m^{1/2}p_{\mathbf{h}}}$$

and

$$\langle E_{\mathbf{h}}(\mathbf{I}-\mathbf{R}_s)\,|\,E_{\mathbf{h}}\rangle=\frac{1}{2N^{1/2}}\frac{\sqrt{p_{\mathbf{h}}(\mathbf{I}-\mathbf{R}_s)}}{p_{\mathbf{h}}}(|E_{\mathbf{h}}|^2-1)$$
$$\times\exp 2\pi i\mathbf{h}T_s\,.$$

Likewise equation (19) is modified to

$$P_+[E_{\mathbf{h}}(\mathbf{I}-\mathbf{R}_s)]=\tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{W}{2N^{1/2}}|E_{\mathbf{h}}(\mathbf{I}-\mathbf{R}_s)|\,(|E_{\mathbf{h}}|^2-1)$$
$$\times\exp 2\pi i\mathbf{h}\mathbf{T}_s$$

where W is equal to $\sqrt{p_{\mathbf{h}}(\mathbf{I}-\mathbf{R}_s)}/p_{\mathbf{h}}$.

Non-centrosymmetric crystal

As is well known, the characteristic function C of the multivariate distribution $P(A_1,A_2,A_3,B_1,B_2,B_3)$ may be expanded in terms of cumulants:

$$C(u_1,u_2,u_3,v_1,v_2,v_3)=\exp\left[t\sum_{2}^{\infty}{}_{r+s+\ldots+w}\frac{\lambda'_{rs\ldots w}}{r!s!\ldots w!}\right.$$
$$\left.\times\left(\frac{iu_1}{t^{1/2}}\right)^r\left(\frac{iu_2}{t^{1/2}}\right)^s\cdots\left(\frac{iv_3}{t^{1/2}}\right)^w\right]$$

where

$$\lambda'_{rs\ldots w}=\frac{K_{rs\ldots w}}{m^{(r+s+\ldots+w)/2}}.$$

$K_{rs\ldots w}$ is a cumulant (with indices $r,s,\ldots,w$) of the distribution:

$$A_1=|E_{\mathbf{h}}|\cos\varphi_{\mathbf{h}},$$
$$A_2=|E_{\mathbf{k}}|\cos\varphi_{\mathbf{k}},$$
$$A_3=|E_{\mathbf{h}-\mathbf{k}}|\cos\varphi_{\mathbf{h}-\mathbf{k}},\ \ldots\,.$$

By taking the Fourier transform we can derive (retaining terms to order $1/t^{1/2}$) the formula

$$P(A_1,A_2,A_3,B_1,B_2,B_3)=\frac{1}{(2\pi)^3}\cdot\frac{1}{\sqrt{\lambda}}$$
$$\times\exp\left\{-\tfrac{1}{2}\left[\frac{A_1^2}{\lambda'_{200000}}+\frac{A_2^2}{\lambda'_{020000}}+\ldots+\frac{B_2^2}{\lambda'_{000020}}\right.\right.$$
$$\left.\left.+\frac{B_3^2}{\lambda'_{000002}}\right]\right\}\cdot\left\{1+\frac{1}{t^{1/2}}\left[\frac{\lambda'_{111000}A_1A_2A_3}{\lambda'_{200000}\cdot\lambda'_{020000}\cdot\lambda'_{002000}}\right.\right.$$
$$+\frac{\lambda'_{001110}A_3B_1B_2}{\lambda'_{002000}\cdot\lambda'_{000200}\cdot\lambda'_{000020}}+\frac{\lambda'_{010101}A_2B_1B_3}{\lambda'_{020000}\cdot\lambda'_{000200}\cdot\lambda'_{000002}}$$
$$\left.+\frac{\lambda'_{100011}A_1B_2B_3}{\lambda'_{200000}\cdot\lambda'_{000020}\cdot\lambda'_{000002}}+\ldots\right\},\quad(20)$$

where

$$\lambda=\lambda'_{200000}\cdot\lambda'_{020000}\ldots\lambda'_{000002},$$

and

$$\lambda'_{200000}=\frac{K_{200000}}{m}=\frac{\langle\psi^2(\mathbf{h})\rangle}{mp_{\mathbf{h}}},\ \ldots\quad.$$

It is easily shown that the distribution (20) coincides, in the case of general reflexions, with the known formula (Karle & Hauptman, 1956),

$$P(|E_1|,|E_2|,|E_3|,\varphi_1,\varphi_2,\varphi_3)=\frac{1}{\pi^3}|E_1|\,|E_2|\,|E_3|$$
$$\times\exp(-|E_1|^2-|E_2|^2-|E_3|^2)$$
$$\times\left\{1+\frac{2}{\sqrt{N}}|E_1|\,|E_2|\,|E_3|\cos(\varphi_1-\varphi_2-\varphi_3)\right\}.$$

The conditional mean values

$$\langle A_2A_3-B_2B_3\rangle=\langle|E_{\mathbf{k}}E_{\mathbf{h-k}}|\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})\rangle,$$

and

$$\langle A_2B_3+A_3B_2\rangle=\langle|E_{\mathbf{k}}E_{\mathbf{h-k}}|\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})\rangle,$$

when A_1 and B_1 are fixed and the fact that

$$K_{111000}=m_{111000}=\frac{\langle\psi(\mathbf{h})\psi(\mathbf{k})\psi(\mathbf{h-k})\rangle}{\sqrt{p_{\mathbf{h}}p_{\mathbf{k}}p_{\mathbf{h-k}}}}\ ,\ etc.,$$

gives the result

$$\langle|E_{\mathbf{k}}E_{\mathbf{h-k}}|\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})\rangle$$
$$=\frac{1}{t^{1/2}}\left\{\frac{\lambda'_{111000}-\lambda'_{100011}}{\lambda'_{200000}}A_1\right\}=\frac{1}{N^{1/2}}\frac{\sqrt{p_{\mathbf{h}}}}{\langle\psi^2(\mathbf{h})\rangle}$$
$$\times\left\{\frac{\langle\psi(\mathbf{h})\,[\psi(\mathbf{k})\psi(\mathbf{h-k})-\eta(\mathbf{k})\eta(\mathbf{h-k})]\rangle}{\sqrt{p_{\mathbf{k}}p_{\mathbf{h-k}}}}\right\}$$
$$\times|E_{\mathbf{h}}|\cos\varphi_{\mathbf{h}}\,. \tag{21}$$

In the same way we find

$$\langle|E_{\mathbf{k}}E_{\mathbf{h-k}}|\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})\rangle$$
$$=\frac{1}{t^{1/2}}\left\{\frac{\lambda'_{001110}+\lambda'_{010101}}{\lambda'_{000200}}B_1\right\}=\frac{1}{N^{1/2}}\frac{\sqrt{p_{\mathbf{h}}}}{\langle\eta^2(\mathbf{h})\rangle}$$
$$\times\left\{\frac{\langle\eta(\mathbf{h})\,[\eta(\mathbf{k})\psi(\mathbf{h-k})+\psi(\mathbf{k})\eta(\mathbf{h-k})]\rangle}{\sqrt{p_{\mathbf{k}}p_{\mathbf{h-k}}}}\right\}$$
$$\times|E_{\mathbf{h}}|\sin\varphi_{\mathbf{h}}\,. \tag{22}$$

From the distribution (20) we derive the conditional mean values $\langle A_{\mathbf{h}}\rangle$ and $\langle B_{\mathbf{h}}\rangle$ when $A_{\mathbf{k}}$, $A_{\mathbf{h-k}}$, $B_{\mathbf{k}}$, $B_{\mathbf{h-k}}$ are fixed. After some calculations

$$\langle|E_{\mathbf{h}}|\cos\varphi_{\mathbf{h}}\rangle=\frac{1}{t^{1/2}}\left\{\lambda'_{111000}\frac{A_2A_3}{\lambda'_{020000}\cdot\lambda'_{002000}}\right.$$
$$\left.+\frac{\lambda'_{100011}}{\lambda'_{000020}\cdot\lambda'_{000002}}B_2B_3\right\}$$
$$=\frac{\sqrt{p_{\mathbf{k}}p_{\mathbf{h-k}}}}{\sqrt{p_{\mathbf{h}}}}\frac{m}{N^{1/2}}|E_{\mathbf{k}}E_{\mathbf{h-k}}|\left\{\frac{\langle\psi(\mathbf{h})\psi(\mathbf{k})\psi(\mathbf{h-k})\rangle}{\langle\psi^2(\mathbf{k})\rangle\langle\psi^2(\mathbf{h-k})\rangle}\right.$$
$$\times\cos\varphi_{\mathbf{k}}\cos\varphi_{\mathbf{h-k}}$$
$$\left.+\frac{\langle\psi(\mathbf{h})\eta(\mathbf{k})\eta(\mathbf{h-k})\rangle}{\langle\eta^2(\mathbf{k})\rangle\langle\eta^2(\mathbf{h-k})\rangle}\sin\varphi_{\mathbf{k}}\sin\varphi_{\mathbf{h-k}}\right\}; \tag{23}$$

$$\langle|E_{\mathbf{h}}|\sin\varphi_{\mathbf{h}}\rangle=\frac{\sqrt{p_{\mathbf{k}}p_{\mathbf{h-k}}}}{\sqrt{p_{\mathbf{h}}}}\frac{m}{N^{1/2}}|E_{\mathbf{k}}E_{\mathbf{h-k}}|$$
$$\times\left\{\frac{\langle\eta(\mathbf{h})\eta(\mathbf{k})\psi(\mathbf{h-k})\rangle}{\langle\eta^2(\mathbf{k})\rangle\langle\psi^2(\mathbf{h-k})\rangle}\sin\varphi_{\mathbf{k}}\cos\varphi_{\mathbf{h-k}}\right.$$
$$\left.+\frac{\langle\eta(\mathbf{h})\psi(\mathbf{k})\eta(\mathbf{h-k})\rangle}{\langle\psi^2(\mathbf{k})\rangle\langle\eta^2(\mathbf{h-k})\rangle}\cos\varphi_{\mathbf{k}}\sin\varphi_{\mathbf{h-k}}\right\}. \tag{24}$$

If $E_{\mathbf{h}}$, $E_{\mathbf{k}}$, $E_{\mathbf{h-k}}$ are general reflexions we obtain

$$\langle|E_{\mathbf{h}}|\cos\varphi_{\mathbf{h}}\rangle=\frac{1}{\sqrt{N}}|E_{\mathbf{k}}E_{\mathbf{h-k}}|\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})\,,$$

$$\langle|E_{\mathbf{h}}|\sin\varphi_{\mathbf{h}}\rangle=\frac{1}{\sqrt{N}}|E_{\mathbf{k}}E_{\mathbf{h-k}}|\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}});$$

so that in all space groups the relation (8) is justified.

If $E_{\mathbf{k}}$ is a centrosymmetric reflexion [$\eta(\mathbf{k})=0$], we find

$$\langle|E_{\mathbf{h}}|\cos\varphi_{\mathbf{h}}\rangle=\frac{\sqrt{p_{\mathbf{k}}p_{\mathbf{h-k}}}}{\sqrt{p_{\mathbf{h}}}}\frac{m}{N^{1/2}}|E_{\mathbf{k}}E_{\mathbf{h-k}}|$$
$$\times\left\{\frac{\langle\psi(\mathbf{h})\psi(\mathbf{k})\psi(\mathbf{h-k})\rangle}{\langle\psi^2(\mathbf{k})\rangle\langle\psi^2(\mathbf{h-k})\rangle}\cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})\right\}, \tag{25}$$

$$\langle|E_{\mathbf{h}}|\sin\varphi_{\mathbf{h}}\rangle=\frac{\sqrt{p_{\mathbf{k}}p_{\mathbf{h-k}}}}{\sqrt{p_{\mathbf{h}}}}\frac{m}{N^{1/2}}|E_{\mathbf{k}}E_{\mathbf{h-k}}|$$
$$\times\left\{\frac{\langle\eta(\mathbf{h})\psi(\mathbf{k})\eta(\mathbf{h-k})\rangle}{\langle\psi^2(\mathbf{k})\rangle\langle\psi^2(\mathbf{h-k})\rangle}\sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h-k}})\right\}. \tag{26}$$

As in this case

$$\frac{\langle\psi(\mathbf{h})\psi(\mathbf{k})\psi(\mathbf{h-k})\rangle}{\langle\psi^2(\mathbf{k})\rangle\langle\psi^2(\mathbf{h-k})\rangle}=\frac{\langle\eta(\mathbf{h})\psi(\mathbf{k})\eta(\mathbf{h-k})\rangle}{\langle\psi^2(\mathbf{k})\rangle\langle\psi^2(\mathbf{h-k})\rangle} \tag{27}$$

the relation (8) is still valid.

Analogously, if one $E_{\mathbf{h-k}}$ reflexion is centrosymmetrical, equation (25) still holds, and relations similar to (26) and (27) can be worked out. Following Cochran (1955), one can easily deduce that in the distribution (9) a suitable weight must be applied: in the example of Table 1,

$$G_{\mathbf{h},\mathbf{k}}=m\frac{\sqrt{p_{\mathbf{k}}p_{\mathbf{h-k}}}}{\sqrt{p_{\mathbf{h}}}}\frac{\langle\psi(\mathbf{h})\psi(\mathbf{k})\psi(\mathbf{h-k})\rangle}{\langle\psi^2(\mathbf{k})\rangle\langle\psi^2(\mathbf{h-k})\rangle}$$
$$\times2\frac{|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h-k}}|}{\sqrt{N}}=W_{\mathbf{h},\mathbf{k}}2\frac{|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h-k}}|}{\sqrt{N}}\,. \tag{28}$$

A more general expression for these weights, valid in all space groups will be identified in the following paper (Giacovazzo, 1974).

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APPENDIX

From the theory of linearization (Bertaut, 1959*a*,*b*) we obtain for a general space group of order m,

Table 1. $-\mathbf{h}_i+\mathbf{k}_j+\mathbf{h}_k=0$

	$h_1k_1l_1$ $h_2k_2l_2$ $h_3k_3l_3$	$h_1k_1l_1$ h_2k_20 $h_3k_3l_3$	$h_1k_1l_1$ h_200 $h_3k_3l_3$	$h_1k_1l_1$ h_2k_20 h_30l_3	$h_1k_1l_1$ h_200 $0k_3l_3$	h_1k_10 h_2k_20 h_3k_30	h_1k_10 h_20l_2 $0k_3l_3$	h_1k_10 h_2k_20 h_300	h_1k_10 h_200 $0k_30$	h_100 h_200 h_300	h_100 $h_2k_2l_2$ $h_3k_3l_3$
$\langle\psi(\mathbf{h})\psi(\mathbf{k})\psi(\mathbf{h}-\mathbf{k})\rangle$	1	2	4	4	8	4	8	8	16	16	4
$\langle\eta(\mathbf{h})\eta(\mathbf{k})\psi(\mathbf{h}-\mathbf{k})\rangle$	1	0	0	0	0	0	0	0	0	0	0
$\langle\eta(\mathbf{h})\psi(\mathbf{k})\eta(\mathbf{h}-\mathbf{k})\rangle$	1	2	4	0	0	0	0	0	0	0	0
$\langle\psi(\mathbf{h})\eta(\mathbf{k})\eta(\mathbf{h}-\mathbf{k})\rangle$	−1	0	0	0	0	0	0	0	0	0	−4
$W_{\mathbf{h},\mathbf{k}}$	1	1	$\sqrt{2}$	1	$\sqrt{2}$	1	2	$\sqrt{2}$	2	$\sqrt{2}$	$2\sqrt{2}$

Table 2. $\mathbf{h}_i+\mathbf{h}_j+\mathbf{h}_k=0$

Parity classes	$h_1k_1l_1$ $h_2k_2l_2$ $h_3k_3l_3$	$h_1k_1l_1$ h_2k_20 $h_3k_3l_3$	$h_1k_1l_1$ h_200 $h_3k_3l_3$	$h_1k_1l_1$ h_2k_20 h_30l_3	$h_1k_1l_1$ h_200 $0k_3l_3$	h_1k_10 h_2k_20 h_3k_30	h_1k_10 h_20l_2 $0k_3l_3$	h_1k_10 h_2k_20 h_300	h_1k_10 h_200 $0k_30$	h_100 h_200 h_300
$\langle\xi(\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}+\mathbf{k})\rangle$	8	16	32	32	64	32	64	64	128	128
$\dfrac{\langle\xi(\mathbf{h})\xi(\mathbf{k})\xi(\mathbf{h}+\mathbf{k})\rangle}{\sqrt{p_\mathbf{h}}\sqrt{p_\mathbf{k}}\sqrt{p_{\mathbf{h}+\mathbf{k}}}}$	8	$8\sqrt{2}$	16	16	$16\sqrt{2}$	$8\sqrt{2}$	$16\sqrt{2}$	16	$16\sqrt{2}$	16
$W_{\mathbf{h},\mathbf{k}}$	1	$\sqrt{2}$	2	2	$2\sqrt{2}$	$\sqrt{2}$	$2\sqrt{2}$	2	$2\sqrt{2}$	2

$$\xi(\mathbf{H}_3)\xi(\mathbf{H}_1)=\sum_1^m{}_s\,\xi(\mathbf{H}_3+\mathbf{H}_1\mathbf{C}_s)$$
$$=\sum_1^m{}_s\,a_s(\mathbf{H}_1)\xi(\mathbf{H}_3+\mathbf{H}_1\mathbf{R}_s),\quad\text{(A1)}$$

where $a_s(\mathbf{H})=\exp 2\pi i\mathbf{H}\mathbf{T}_s$.

If we multiply equation (A1) for $\xi(\mathbf{H}_2)$, by setting $\mathbf{H}_3=\bar{\mathbf{H}}_1+\bar{\mathbf{H}}_2$, we find

$$\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)=\sum_1^m{}_s\sum_1^m{}_r\,\xi[\mathbf{H}_1(\mathbf{C}_s-\mathbf{I})+\mathbf{H}_2(\mathbf{C}_r-\mathbf{I})]$$
$$=\sum_1^m{}_{s,r}\,a_s(\mathbf{H}_1)a_r(\mathbf{H}_2)$$
$$\times\,\xi[\mathbf{H}_1(\mathbf{R}_s-\mathbf{I})+\mathbf{H}_2(\mathbf{R}_r-\mathbf{I})]\,.\quad\text{(A2)}$$

The mean value $\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\rangle$ is different from the zero for all $\mathbf{C}_r$, $\mathbf{C}_s$ operations for which

$$\mathbf{H}_1(\mathbf{R}_s-\mathbf{I})+\mathbf{H}_2(\mathbf{R}_r-\mathbf{I})=0\,.\quad\text{(A3)}$$

For example, if $\mathbf{C}_s$ is a operation for which $\mathbf{H}_1(\mathbf{R}_s-\mathbf{I})=0$, the condition (A3) is verified for all r operations $\mathbf{C}_r$ such that

$$\mathbf{H}_2(\mathbf{R}_r-\mathbf{I})=0\,.$$

Therefore, if $E_{\mathbf{H}_3}$ is non-special reflexion, we obtain

$$\langle\xi(\mathbf{H}_1)\xi(\mathbf{H}_2)\xi(\mathbf{H}_3)\rangle=p_{\mathbf{H}_1}p_{\mathbf{H}_2}\xi(0)=p_{\mathbf{H}_1}p_{\mathbf{H}_2}m\,.$$

Numerical values for different parity classes are shown in Table 2 for the space group *Pmmm*.

In a similar way it results

$$\xi^2(\mathbf{h})\xi(2\mathbf{h})=\sum_1^m{}_{s,r}\,\xi[\mathbf{h}(\mathbf{I}-\mathbf{C}_s+2\mathbf{C}_r)]\,.$$

If the $\mathbf{h}$ reflexion is general, $\langle\xi^2(\mathbf{h})\xi(2\mathbf{h})\rangle$ is different from zero for $\mathbf{C}_s=-\mathbf{I}$ and $\mathbf{C}_r=\mathbf{I}$: then

$$\langle\xi^2(\mathbf{h})\xi(2\mathbf{h})\rangle=m\,.$$

If $E_\mathbf{h}$ has statistical weight $p_\mathbf{h}$,

$$\langle\xi^2(\mathbf{h})\xi(2\mathbf{h})\rangle=p_\mathbf{h}\sum_1^{m/p_\mathbf{h}}{}_{s,r}\,\xi[\mathbf{h}(\mathbf{I}-\mathbf{C}_s+2\mathbf{C}_r)]=mp_\mathbf{h}\,.$$

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