latitude in successive rings from the N pole to the S pole, is thus the most concise description. There not being strict proofs of the absoluteness of the maxima encountered, there remains, in many cases, the doubt as to whether some solutions of low symmetry may not be better. Clearly the most symmetrical figures are the most easily calculated and are unduly preferred.

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The Use of Structural Information in the Phase Probability of a Triple Product

BY J. J. L. HEINERMAN

Laboratorium voor Structuurchemie, Rijksuniversiteit, Padualaan 8, *Utrecht, The Netherlands*

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A derivation is given of the probability distribution of the phase of a triple product $\varphi=\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3}$ with $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=\mathbf{0}$, employing *a priori* structural information. This derivation is valid if normalized group scattering factors are small and certain conditions for $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ are fulfilled. To derive this distribution it is necessary to regard the atomic position vectors as primitive random variables, not all independent in view of the structural information. It is also shown that if no structural information is available the expression for the probability distribution of the phase of a triple product, where the atomic position vectors are regarded as the primitive random variables, is identical to the one where $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ are regarded as the primitive random variables. In the first case certain conditions for $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ must be fulfilled; in the second the atomic position vectors are subject to certain conditions.

Introduction

Recently Main (1975) has generalized Cochran's (1955) formula for the phase probability of a triple product. In Main's formula *a priori* knowledge about the structure can be used. The kinds of information which he has considered are (*a*) randomly positioned atoms, (*b*) randomly positioned and randomly oriented atomic groups, (*c*) randomly positioned but correctly oriented atomic groups, (*d*) correctly positioned atoms.

A rigorous mathematical derivation of Main's formula, which also shows its limitations, will be given for space group $P1$.

The primitive random variables

In this section we define the normalized structure factor for equal-atom structures by

$$E_{\mathbf{h}}=\frac{1}{N^{1/2}}\sum_{j=1}^{N}\exp(2\pi i\mathbf{h}\,.\,\mathbf{r}_j), \qquad (1)$$

where N is the number of atoms in the unit cell and $\mathbf{r}_j$ is the position vector of atom j. In deriving joint probability distributions of structure factors defined by (1), two methods can be followed. The first is to regard the structure as fixed, although unknown, and one or more reciprocal lattice vectors as the primitive random variables. The second is to regard the atomic position vectors as the primitive random variables and the reciprocal lattice vectors as fixed.

Let $\varphi_{\mathbf{h}}$ denote the phase of $E_{\mathbf{h}}$ and let $P(\Phi|R_1,R_2,R_3)$ denote the conditional probability distribution of $\varphi=\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3}$ with $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=\mathbf{0}$, given $|E_{\mathbf{h}_1}|$, $|E_{\mathbf{h}_2}|$ and $|E_{\mathbf{h}_3}|$ (equal to R_1, R_2 and R_3 respectively). Then $P(\Phi|R_1,R_2,R_3)\mathrm{d}\Phi$ is the probability that φ lies between Φ and $\Phi+\mathrm{d}\Phi$, given $|E_{\mathbf{h}_1}|$, $|E_{\mathbf{h}_2}|$ and $|E_{\mathbf{h}_3}|$. If the reciprocal lattice vectors $\mathbf{h}_1$, $\mathbf{h}_2$ and $\mathbf{h}_3$ are the primitive random variables, $P(\Phi|R_1,R_2,R_3)\mathrm{d}\Phi$ is equal to the fraction of the triple products $E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}$ of a fixed structure and with fixed values for $|E_{\mathbf{h}_1}|$, $|E_{\mathbf{h}_2}|$ and $|E_{\mathbf{h}_3}|$, for which $\Phi<\varphi<\Phi+\mathrm{d}\Phi$. If the atomic position vectors $\mathbf{r}_j$ are the primitive random variables, $P(\Phi|R_1,R_2,R_3)\mathrm{d}\Phi$ is equal to the fraction of the triple products $E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}$, with $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ fixed, of all structures with N atoms in the unit cell and with fixed values for $|E_{\mathbf{h}_1}|$, $|E_{\mathbf{h}_2}|$ and $|E_{\mathbf{h}_3}|$, for which $\Phi<\varphi<\Phi+\mathrm{d}\Phi$.

It has been found that with $\mathbf{h}_1$, $\mathbf{h}_2$ and $\mathbf{h}_3$ as the primitive random variables the only information

about the structure which enters $P(\Phi|R_1,R_2,R_3)$ is the number of atoms in the unit cell (Hauptman, 1975). If $\mathbf{h}_1$ is fixed and $\mathbf{h}_2$ and $\mathbf{h}_3$ are the primitive random variables ($\mathbf{h}_3=-\mathbf{h}_1-\mathbf{h}_2$), the number of atoms in the unit cell and $|E_{\mathbf{h}_1}|$, which depends on the structure, appear in $P(\varphi|\mathbf{h}_1,R_2,R_3)$ (Hauptman, 1975). However, *a priori* structural information, *e.g.* knowledge that there is a special group of atoms, does not alter these distributions. In the approach where the $\mathbf{r}_j$'s are regarded as the primitive random variables such *a priori* information can be used. For example, suppose that the structure contains a benzene ring. Then only the position vector and orientation of the benzene ring, instead of the position vectors of the atoms of the benzene ring, form part of the primitive random variables. If nothing else is known, *i.e.* the position vectors of the other atoms in the unit cell are also primitive random variables, then $P(\Phi|R_1,R_2,R_3)\mathrm{d}\Phi$ is equal to the fraction of the triple products $E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}$, with $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$ fixed, of all structures containing a benzene ring, with N atoms in the unit cell and with fixed values for $|E_{\mathbf{h}_1}|$, $|E_{\mathbf{h}_2}|$ and $|E_{\mathbf{h}_3}|$, for which $\Phi<\varphi<\Phi+\mathrm{d}\Phi$.

The phase of a triple product is independent of the position of the origin of the unit cell. This implies that in the derivation of the phase probability of a triple product we may add the origin of the unit cell to the set of primitive random variables, or alternatively, we may add the position vector of the group of correctly placed atoms to the set of primitive random variables. This last approach simplifies the calculations and will be adopted.

The structure factor

Define the structure factor $F_{\mathbf{h}}$ by

$$F_{\mathbf{h}}=\sum_{j=1}^{p} g_j(\mathbf{h})\exp(2\pi i\mathbf{h}\,.\,\mathbf{r}_j), \tag{2}$$

where for $1\leq j\leq p_1$ the $\mathbf{r}_j$'s are the atomic position vectors and the $g_j(\mathbf{h})$ are the scattering factors $f_j(\mathbf{h})$, and for $p_1+1\leq j\leq p$ the $\mathbf{r}_j$'s are the group position vectors and the $g_j(\mathbf{h})$ are the group scattering factors. Next define the normalized structure factor $E_{\mathbf{h}}$ by

$$E_{\mathbf{h}}=\frac{F_{\mathbf{h}}}{\langle|F_{\mathbf{h}}|^2\rangle_{\text{p.r.v.}}^{1/2}}, \tag{3}$$

where $\langle|F_{\mathbf{h}}|^2\rangle_{\text{p.r.v.}}$ denotes the average of $|F_{\mathbf{h}}|^2$, the variables being the primitive random variables (p.r.v.):

(*a*) $1\leq j\leq p_1$, the atomic position vectors

(*b*) $p_1+1\leq j\leq p_2$, the position vectors and orientational parameters of the groups

(*c*) $p_2+1\leq j\leq p$, the position vectors of the groups with known orientation (this includes the position vector of the group with known orientation and known position; see the preceding section). (4)

It can be shown that the average of $|F_{\mathbf{h}}|^2$ is

$$\langle|F_{\mathbf{h}}|^2\rangle_{\text{p.r.v.}}=\sum_{j=1}^{p_1} g_j(\mathbf{h})^2+\sum_{j=p_1+1}^{p_2}\langle|g_j(\mathbf{h})|^2\rangle_{\text{orient}}+\sum_{j=p_2+1}^{p}|g_j(\mathbf{h})|^2. \tag{5}$$

The expressions for the individual terms (Main, 1975) are calculated by

(*a*) $1\leq j\leq p_1$, $g_j(\mathbf{h})=f_j(\mathbf{h})$ (6)

(*b*) $p_1+1\leq j\leq p_2$, $\langle|g_j(\mathbf{h})|^2\rangle_{\text{orient}}$

$$=\sum_{i_1}\sum_{i_2} f_{i_1}(\mathbf{h})f_{i_2}(\mathbf{h})\frac{\sin 2\pi q r_{i_1i_2}}{2\pi q r_{i_1i_2}}\ \text{(Debye, 1915)} \tag{7}$$

(*c*) $p_2+1\leq j\leq p$, $|g_j(\mathbf{h})|^2$

$$=\sum_{i_1}\sum_{i_2} f_{i_1}(\mathbf{h})f_{i_2}(\mathbf{h})\cos 2\pi\mathbf{h}\,.\,\mathbf{r}_{i_1i_2}, \tag{8}$$

where the Σ's denote summations over the atoms of the jth group, q is the magnitude of $\mathbf{h}$ and $r_{i_1i_2}$ is the magnitude of $\mathbf{r}_{i_1i_2}=\mathbf{r}_{i_1}-\mathbf{r}_{i_2}$.

In the calculations which are given in the next sections, we use normalized structure factors. It must be stressed that normalized structure factors are only used to simplify the calculations and the resulting formulae for the probability distributions. For the same reason we introduce the normalized scattering factor $t_j(\mathbf{h})$, defined by

$$t_j(\mathbf{h})=\frac{g_j(\mathbf{h})}{\langle|F_{\mathbf{h}}|^2\rangle_{\text{p.r.v.}}^{1/2}}. \tag{9}$$

Denote the absolute value and phase of $t_j(\mathbf{h})$ by $u_j(\mathbf{h})$ and $\beta_j(\mathbf{h})$ respectively,

$$t_j(\mathbf{h})=u_j(\mathbf{h})\exp[i\beta_j(\mathbf{h})]. \tag{10}$$

From (5), (9) and (10) the following relation between the $u_j(\mathbf{h})$ is obtained,

$$\sum_{j=1}^{p_1}u_j(\mathbf{h})^2+\sum_{j=p_1+1}^{p_2}\langle u_j(\mathbf{h})^2\rangle_{\text{orient}}+\sum_{j=p_2+1}^{p}u_j(\mathbf{h})^2=1. \tag{11}$$

From (2) and (9) the normalized structure factor, as defined in (3), can be written as

$$E_{\mathbf{h}}=\sum_{j=1}^{p} t_j(\mathbf{h})\exp(2\pi i\mathbf{h}\,.\,\mathbf{r}_j), \tag{12a}$$

or, from (10),

$$E_{\mathbf{h}}=\sum_{j=1}^{p} u_j(\mathbf{h})\exp\{i[2\pi\mathbf{h}\,.\,\mathbf{r}_j+\beta_j(\mathbf{h})]\}. \tag{12b}$$

The conditional probability distribution of $\varphi=\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3}$

Denote by $P(R_1,R_2,R_3;\Phi_1,\Phi_2,\Phi_3)$ the joint probability distribution of the magnitudes $|E_{\mathbf{h}_1}|$, $|E_{\mathbf{h}_2}|$, $|E_{\mathbf{h}_3}|$ and the phases $\varphi_{\mathbf{h}_1},\varphi_{\mathbf{h}_2},\varphi_{\mathbf{h}_3}$, where $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=\mathbf{0}$ and the primitive random variables are given in (4). Then, from Appendix II, $P(R_1,R_2,R_3;\Phi_1,\Phi_2,\Phi_3)$ is given by

$$P(R_1,R_2,R_3;\Phi_1,\Phi_2,\Phi_3)=\frac{R_1R_2R_3}{(2\pi)^6}\int_0^\infty\int_0^{2\pi}\int_0^\infty\int_0^{2\pi}\int_0^\infty\int_0^{2\pi}\exp\left[-i\sum_{\nu=1}^{3}R_\nu\varrho_\nu\cos(\theta_\nu-\Phi_\nu)\right]\times\left[\prod_{j=1}^{p}q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)\right]\varrho_1\varrho_2\varrho_3\mathrm{d}\varrho_1\mathrm{d}\theta_1\mathrm{d}\varrho_2\mathrm{d}\theta_2\mathrm{d}\varrho_3\mathrm{d}\theta_3, \quad (13)$$

where

$$q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)=\left\langle\exp\left\{i\sum_{\nu=1}^{3}u_j(\mathbf{h}_\nu)\varrho_\nu\cos\left[2\pi\mathbf{h}_\nu\,.\,\mathbf{r}_j+\beta_j(\mathbf{h}_\nu)-\theta_\nu\right]\right\}\right\rangle_{\text{p.r.v.}\,j}. \quad (14)$$

The random variables for group or atom j (p.r.v.j) are given in (4). Appendix III contains the calculation of the average in (14) for all j, and the calculation of the product of the q_j's. The result is

$$\prod_{j=1}^{p}q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)\simeq\exp\left[-\tfrac{1}{4}(\varrho_1^2+\varrho_2^2+\varrho_3^2)-\tfrac{1}{4}iQ_{123}\varrho_1\varrho_2\varrho_3\cos(\theta_1+\theta_2+\theta_3-q_{123})\right], \quad (15)$$

where

$$Q_{123}\exp(iq_{123})=\sum_{j=1}^{p_1}t_j(\mathbf{h}_1)t_j(\mathbf{h}_2)t_j(\mathbf{h}_3)+\sum_{j=p_1+1}^{p_2}\langle t_j(\mathbf{h}_1)t_j(\mathbf{h}_2)t_j(\mathbf{h}_3)\rangle_{\text{orient}}+\sum_{j=p_2+1}^{p}t_j(\mathbf{h}_1)t_j(\mathbf{h}_2)t_j(\mathbf{h}_3). \quad (16)$$

In the derivation of (15) it is assumed that the $u_j(\mathbf{h})$ are small and that

$$\left.\begin{aligned}&\mathbf{h}_i\neq\mathbf{0}\quad i=1,2,3,\\&\mathbf{h}\neq\mathbf{h}_{i_2}\quad\text{and}\quad 2\mathbf{h}_{i_1}\neq\mathbf{h}_{i_2}\quad i_1,i_2=1,2,3\quad i_1\neq i_2.\end{aligned}\right\} \quad (17)$$

The expressions for the individual terms in (16) are

$$(a)\quad 1\leq j\leq p_1,\ t_j(\mathbf{h}_1)t_j(\mathbf{h}_2)t_j(\mathbf{h}_3)=\frac{f_j(\mathbf{h}_1)f_j(\mathbf{h}_2)f_j(\mathbf{h}_3)}{\langle|F_{\mathbf{h}_1}|^2\rangle_{\text{p.r.v.}}^{1/2}\langle|F_{\mathbf{h}_2}|^2\rangle_{\text{p.r.v.}}^{1/2}\langle|F_{\mathbf{h}_3}|^2\rangle_{\text{p.r.v.}}^{1/2}} \quad (18)$$

$$(b)\quad p_1+1\leq j\leq p_2,\ \langle t_j(\mathbf{h}_1)t_j(\mathbf{h}_2)t_j(\mathbf{h}_3)\rangle_{\text{orient}}=\frac{\sum_{i_1}\sum_{i_2}\sum_{i_3}f_{i_1}(\mathbf{h}_1)f_{i_2}(\mathbf{h}_2)f_{i_3}(\mathbf{h}_3)B(z,t)}{\langle|F_{\mathbf{h}_1}|^2\rangle_{\text{p.r.v.}}^{1/2}\langle|F_{\mathbf{h}_2}|^2\rangle_{\text{p.r.v.}}^{1/2}\langle|F_{\mathbf{h}_3}|^2\rangle_{\text{p.r.v.}}^{1/2}}, \quad (19)$$

where $B(z,t)$, the orientational average of $\exp[2\pi i(\mathbf{h}_1\,.\,\mathbf{r}_{i_1i_3}+\mathbf{h}_2\,.\,\mathbf{r}_{i_2i_3})]$, has been calculated by Hauptman (1965). His result is given in Appendix VI.

$$(c)\quad p_2+1\leq j\leq p,\ t_j(\mathbf{h}_1)t_j(\mathbf{h}_2)t_j(\mathbf{h}_3)=\frac{\sum_{i_1}\sum_{i_2}\sum_{i_3}f_{i_1}(\mathbf{h}_1)f_{i_2}(\mathbf{h}_2)f_{i_3}(\mathbf{h}_3)\exp[2\pi i(\mathbf{h}_1\,.\,\mathbf{r}_{i_1i_3}+\mathbf{h}_2\,.\,\mathbf{r}_{i_2i_3})]}{\langle|F_{\mathbf{h}_1}|^2\rangle_{\text{p.r.v.}}^{1/2}\langle|F_{\mathbf{h}_2}|^2\rangle_{\text{p.r.v.}}^{1/2}\langle|F_{\mathbf{h}_3}|^2\rangle_{\text{p.r.v.}}^{1/2}}. \quad (20)$$

Appendix IV contains the calculation of the integral in (13). The result is

$$P(R_1,R_2,R_3;\Phi_1,\Phi_2,\Phi_3)\simeq\frac{R_1R_2R_3}{\pi^3}\exp\left[-R_1^2-R_2^2-R_3^2+2Q_{123}R_1R_2R_3\cos(\Phi_1+\Phi_2+\Phi_3-q_{123})\right]. \quad (21)$$

The conditional probability distribution $P(\Phi|R_1,R_2,R_3)$ for the phase $\varphi=\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3}$, given $|E_{\mathbf{h}_1}|$, $|E_{\mathbf{h}_2}|$ and $|E_{\mathbf{h}_3}|$, follows directly from (21),

$$P(\Phi|R_1,R_2,R_3)\simeq\frac{1}{L}\exp\left[2Q_{123}R_1R_2R_3\cos(\Phi-q_{123})\right], \quad (22)$$

where L, the normalizing constant, is calculated from (I.8),

$$L=2\pi I_0(2Q_{123}R_1R_2R_3). \quad (23)$$

(22) was first given by Main (1975) as a generalization of Cochran's (1955) formula. Our derivation for space group $P1$ shows that for this space group the generalization is correct, but an important observation is still to be made. Our derivation is only valid if the $u_j(\mathbf{h})$ are small. This implies that, if the orientation of a large part of the contents of the unit cell is known, (22) is not correct: higher-order terms should be included. A formula which is correct for all values of the $u_j(\mathbf{h})$ should give a delta function centred on $\Phi=\varphi$ for the case that the whole structure is known. For this case (22) gives

$$P(\Phi|R_1=R_2=R_3=Q_{123}=1)\simeq\frac{\exp[2\cos(\Phi-\varphi)]}{2\pi I_0(2)}. \quad (24)$$

This distribution has its maximum at $\Phi=\varphi$ and half its maximum values at $\Phi=\varphi\pm49°$. This clearly shows the limitations of (22), and suggests that (22) gives an underestimate of the probability that the phase of a triple product is equal to q_{123}, especially when the orientation of a large part of the contents of the unit

cell is known. Main (1975) stated that the atoms with known positions should give no contributions to the $\langle|F_{\mathbf{h}}|^2\rangle$ in Q_{123}. Then (22) indeed becomes a delta function for the case that the whole structure is known. In this way a better value for the phase probability of a triple product may be obtained. Our calculations are not valid for this case and therefore cannot give a justification or rejection of this procedure. In this connexion we note that Kroon & Krabbendam (1970) derived for space group $P\bar{1}$ the sign probability of a triple product, orientational information taken into account. They used Wilson statistics, regarding the peak positions in the double Patterson synthesis as independent random variables, except for the peak on the origin and the peaks known from the orientational information. After applying the central limit theorem they obtained an expression [their formula (6)] which leads to a delta function in the case that the whole structure is known.

No specific structural information

If no specific structural information is known, then from (5), (6), (16) and (18) it follows that

$$Q_{123}=\frac{\sum_{j=1}^{N} f_j(\mathbf{h}_1)f_j(\mathbf{h}_2)f_j(\mathbf{h}_3)}{\left[\sum_{j=1}^{N} f_j(\mathbf{h}_1)^2\right]^{1/2}\left[\sum_{j=1}^{N} f_j(\mathbf{h}_2)^2\right]^{1/2}\left[\sum_{j=1}^{N} f_j(\mathbf{h}_3)^2\right]^{1/2}} \tag{25}$$

and

$$q_{123}=0, \tag{26}$$

where N is the number of atoms in the unit cell. Next, assuming that all atoms have the same unitary scattering factor $\hat{f}(\mathbf{h})$ [Lipson & Cochran (1968), pp. 74–75], we write

$$f_j(\mathbf{h})=Z_j\hat{f}(\mathbf{h}), \tag{27}$$

where Z_j is the atomic number of atom j. From (22), (23), (25) and (26) we find

$$P(\Phi|R_1,R_2,R_3)\simeq\frac{\exp\left(2\frac{\sigma_3}{\sigma_2^{3/2}}R_1R_2R_3\cos\Phi\right)}{2\pi I_0\left(2\frac{\sigma_3}{\sigma_2^{3/2}}R_1R_2R_3\right)}, \tag{28}$$

where

$$\sigma_n=\sum_{j=1}^{N} Z_j^n. \tag{29}$$

In the case that the structure consists of non-vibrating point atoms, $t_j(\mathbf{h})=Z_j/\sigma_2^{1/2}$, we also obtain (28). In Appendix V it is shown that the formula for the phase probability of a triple product for structures consisting of non-vibrating point atoms, derived on the basis that the reciprocal lattice vectors $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ are the primitive random variables, is the same as in the case that all the atomic position vectors are the primitive random variables. So in both cases (28) is obtained. [For equal atoms, $\sigma_3/\sigma_2^{3/2}=1/N^{1/2}$, (28) reduces to formula (3.4) of Hauptman (1975), which has been derived on the basis that $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ are the primitive random variables.] However, the conditions are different (apart from the condition that the $Z_j/\sigma_2^{1/2}$ are small, which must hold in both cases): (*a*) in the case that the atomic position vectors are the primitive random variables the conditions are given in (17); (*b*) in the case that $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ are the primitive random variables the condition is that there are no integers m_j, not all zero, such that

$$\sum_{j=1}^{N} m_j\mathbf{r}_j=\mathbf{r}, \tag{30}$$

where the components of $\mathbf{r}$ are integers (Appendix V). More elaborate calculations than those given in Appendix V show that the condition for the $\mathbf{r}_j$'s is too stringent. They suggest that it is sufficient if there are no integers m_j, not all zero and for which $\sum_{j=1}^{N} m_j=0$ and $\sum_{j=1}^{N}|m_j|\leq m$, m small but larger than 3, such that (30) holds. The condition $\sum_{j=1}^{N} m_j=0$ is a consequence of the fact that $\varphi=\varphi_{\mathbf{h}_1}+\varphi_{\mathbf{h}_2}+\varphi_{\mathbf{h}_3}$ is independent of the choice of the origin, and $\sum_{j=1}^{N}|m_j|\leq m$ expresses the fact that atomic position vectors which are interrelated by (30) such that $\sum_{j=1}^{N}|m_j|$ is not small, only affect higher-order terms.

Conclusions

A formula for the probability distribution of the phase of a triple product, in which *a priori* structural information is used, has been derived [formula (22)]. It was argued that this formula gives an underestimate of the probability that the phase of a triple product is equal to q_{123} [q_{123} in (16)], especially if the orientation of a large part of the contents of the unit cell is known. In deriving this distribution it was a requirement that the atomic position vectors be regarded as the primitive random variables. In view of the *a priori* structural information these primitive random variables are not all independent.

We have also shown that if no structural information is available this formula reduces to (28), which is identical to the one obtained with $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ (subject to $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=\mathbf{0}$) as the primitive random variables. However, it is stressed that the conditions are different [*cf.* (17) with (30)].

It is anticipated that the procedure adopted in this paper can be used to include *a priori* structural information in the probability distributions of the phases of other structure (sem)invariants.

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APPENDIX I

Some formulae

Bessel functions

From [Watson (1966), p. 22, formulae (3) and (4)]

$$\exp(iz\cos\varphi)=J_0(z)+2\sum_{n=1}^{\infty}i^nJ_n(z)\cos n\varphi, \quad (I\cdot1)$$

where $J_n(z)$ is the Bessel function of the first kind of order n, and [Watson (1966), p. 15, formula (2)]

$$J_{-n}(z)=(-1)^nJ_n(z), \quad (I\cdot2)$$

we find

$$\exp(iz\cos\varphi)=\sum_{n=-\infty}^{\infty}i^nJ_n(z)\cos n\varphi. \quad (I\cdot3)$$

The expression for $J_n(z)$ in the form of an ascending series of powers of z is [Watson (1966), p. 15, formula (1)]

$$J_n(z)=\sum_{m=0}^{\infty}\frac{(-1)^m(\frac{1}{2}z)^{n+2m}}{m!(n+m)!}, \quad n\geq0. \quad (I\cdot4)$$

The integral for $J_0(z)$ [Watson (1966), p. 20, formula (5)] written as

$$J_0(z)=\frac{1}{2\pi}\int_0^{2\pi}\exp(-iz\cos\varphi)\mathrm{d}\varphi \quad (I\cdot5)$$

and [Watson (1966), p. 393, formula (1)]

$$\int_0^{\infty}J_0(at)\exp(-p^2t^2)t\mathrm{d}t=\frac{1}{2p^2}\exp\left(-\frac{a^2}{4p^2}\right) \quad (I\cdot6)$$

lead to

$$\frac{1}{2\pi}\int_0^{\infty}\int_0^{2\pi}\exp(-p^2t^2-iat\cos\varphi)t\mathrm{d}t\mathrm{d}\varphi=\frac{1}{2p^2}\exp\left(-\frac{a^2}{4p^2}\right). \quad (I\cdot7)$$

From (I·5) and the definition of $I_0(z)$, the modified Bessel function of the first kind of order zero [Watson (1966), p. 77], it is found that

$$I_0(z)=\frac{1}{2\pi}\int_0^{2\pi}\exp(z\cos\varphi)\mathrm{d}\varphi. \quad (I\cdot8)$$

A trigonometric formula

From elementary trigonometry (Hauptman, 1971)

$$\sum_i A_i\cos(\varphi+\alpha_i)=X\cos(\varphi+\xi), \quad (I\cdot9)$$

where

$$X=\left[\sum_i\sum_j A_iA_j\cos(\alpha_i-\alpha_j)\right]^{1/2} \quad (I\cdot10)$$

$$\cos\xi=X^{-1}\sum_i A_i\cos\alpha_1 \quad (I\cdot11)$$

and

$$\sin\xi=X^{-1}\sum_i A_i\sin\alpha_i. \quad (I\cdot12)$$

APPENDIX II

The derivation of (13)

Denote by $P(X_1,X_2,X_3;Y_1,Y_2,Y_3)$ the joint probability distribution of the real and imaginary parts, $A_{\mathbf{h}_1},A_{\mathbf{h}_2},A_{\mathbf{h}_3},B_{\mathbf{h}_1},B_{\mathbf{h}_2},B_{\mathbf{h}_3}$, of $E_{\mathbf{h}_1}$, $E_{\mathbf{h}_2}$ and $E_{\mathbf{h}_3}$. Then

$$P(X_1,X_2,X_3;Y_1,Y_2,Y_3)=\frac{1}{(2\pi)^6}\times\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\exp\left[-i\sum_{\nu=1}^{3}(X_\nu x_\nu+Y_\nu y_\nu)\right]\times Q(x_1,x_2,x_3;y_1,y_2,y_3)\mathrm{d}x_1\mathrm{d}x_2\mathrm{d}x_3\mathrm{d}y_1\mathrm{d}y_2\mathrm{d}y_3, \quad (II\cdot1)$$

where the characteristic function

$$\begin{aligned}Q(x_1,x_2,x_3;y_1,y_2,y_3)&=\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\exp\left[i\sum_{\nu=1}^{3}(X_\nu x_\nu+Y_\nu y_\nu)\right]\\&\times P(X_1,X_2,X_3;Y_1,Y_2,Y_3)\mathrm{d}X_1\mathrm{d}X_2\mathrm{d}X_3\mathrm{d}Y_1\mathrm{d}Y_2\mathrm{d}Y_3\\&=\left\langle\exp\left[i\sum_{\nu=1}^{3}(A_{\mathbf{h}_\nu}x_\nu+B_{\mathbf{h}_\nu}y_\nu)\right]\right\rangle_{\text{p.r.v.}}\\&=\left\langle\prod_{j=1}^{p}\exp\left(i\sum_{\nu=1}^{3}\{u_j(\mathbf{h}_\nu)x_\nu\cos[2\pi\mathbf{h}_\nu\,.\,\mathbf{r}_j+\beta_j(\mathbf{h}_\nu)]\right.\right.\\&\left.\left.+u_j(\mathbf{h}_\nu)y_\nu\sin[2\pi\mathbf{h}_\nu\,.\,\mathbf{r}_j+\beta_j(\mathbf{h}_\nu)]\}\right)\right\rangle_{\text{p.r.v.}}. \quad (II\cdot2)\end{aligned}$$

Next, using the transformations

$$X_\nu=R_\nu\cos\Phi_\nu, \quad Y_\nu=R_\nu\sin\Phi_\nu, \quad (II\cdot3)$$

and

$$x_\nu=\varrho_\nu\cos\theta_\nu, \quad y_\nu=\varrho_\nu\sin\theta_\nu, \quad (II\cdot4)$$

we obtain, analogous to the derivation of formula (3.1.7) of Karle & Hauptman (1958),

$$P(R_1,R_2,R_3;\Phi_1,\Phi_2,\Phi_3)=\frac{R_1R_2R_3}{(2\pi)^6}\times\int_0^{\infty}\int_0^{2\pi}\int_0^{\infty}\int_0^{2\pi}\int_0^{\infty}\int_0^{2\pi}\exp\left[-i\sum_{\nu=1}^{3}R_\nu\varrho_\nu\cos(\theta_\nu-\Phi_\nu)\right]\times Q(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)\varrho_1\varrho_2\varrho_3\mathrm{d}\varrho_1\mathrm{d}\theta_1\mathrm{d}\varrho_2\mathrm{d}\theta_2\mathrm{d}\varrho_3\mathrm{d}\theta_3, \quad (II\cdot5)$$

where

$$Q(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)=\left\langle\prod_{j=1}^{p}\exp\left\{i\sum_{\nu=1}^{3}u_j(\mathbf{h}_\nu)\varrho_\nu\times\cos[2\pi\mathbf{h}_\nu\,.\,\mathbf{r}_j+\beta_j(\mathbf{h}_\nu)-\theta_\nu]\right\}\right\rangle_{\text{p.r.v.}}. \quad (II\cdot6)$$

The primitive random variables are given in (4). Denoting the random variables for group or atom j by p.r.v. j, we obtain from (II.6)

$$Q(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)=\prod_{j=1}^{p}\left\langle\exp\left\{i\sum_{\nu=1}^{3}u_j(\mathbf{h}_\nu)\varrho_\nu\times\cos[2\pi\mathbf{h}_\nu\,.\,\mathbf{r}_j+\beta_j(\mathbf{h}_\nu)-\theta_\nu]\right\}\right\rangle_{\text{p.r.v.}\,j}. \quad (II\cdot7)$$

APPENDIX III

The calculation of $\prod_{j=1}^{p} q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)$

First we consider $p_1+1\leq j\leq p_2$. From the result for this case, those for $1\leq j\leq p_1$ and $p_2+1\leq j\leq p$ are easily obtained.

$$q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)=\left\langle \exp\left\{ i\sum_{\nu=1}^{3} u_j(\mathbf{h}_\nu)\varrho_\nu \times\cos\left[2\pi\mathbf{h}_\nu\,.\,\mathbf{r}_j+\beta_j(\mathbf{h}_\nu)-\theta_\nu\right]\right\}\right\rangle_{\mathbf{r}_j,\,\mathrm{orient}}. \quad (\mathrm{III}\cdot 1)$$

Expand the exponential in Bessel functions, using (I·3),

$$q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)=\sum_{n_1=-\infty}^{\infty}\sum_{n_2=-\infty}^{\infty}\sum_{n_3=-\infty}^{\infty} i^{n_1+n_2+n_3} \times\langle J_{n_1}[u_j(\mathbf{h}_1)\varrho_1]J_{n_2}[u_j(\mathbf{h}_2)\varrho_2]J_{n_3}[u_j(\mathbf{h}_3)\varrho_3] \times\langle\cos n_1[2\pi\mathbf{h}_1\,.\,\mathbf{r}_j+\beta_j(\mathbf{h}_1)-\theta_1] \times\cos n_2[2\pi\mathbf{h}_2\,.\,\mathbf{r}_j+\beta_j(\mathbf{h}_2)-\theta_2] \times\cos n_3[2\pi\mathbf{h}_3\,.\,\mathbf{r}_j+\beta_j(\mathbf{h}_3)-\theta_3]\rangle_{\mathbf{r}_j}\rangle_{\mathrm{orient}}. \quad (\mathrm{III}\cdot 2)$$

The product of three cosines in (III·2) can be written as

$$\tfrac{1}{4}\sum_{\varepsilon_1}\sum_{\varepsilon_2}\cos\{n_1[\beta_j(\mathbf{h}_1)-\theta_1]+\varepsilon_1 n_2[\beta_j(\mathbf{h}_2)-\theta_2] +\varepsilon_2 n_3[\beta_j(\mathbf{h}_3)-\theta_3]+2\pi(n_1\mathbf{h}_1+\varepsilon_1 n_2\mathbf{h}_2+\varepsilon_2 n_3\mathbf{h}_3)\,.\,\mathbf{r}_j\}, \quad (\mathrm{III}\cdot 3)$$

where ε_1 and ε_2 take the values -1 and 1. Averaging (III·3) over $\mathbf{r}_j$, we obtain

$$\tfrac{1}{4}\sum_{\varepsilon_1}\sum_{\varepsilon_2}\cos\{n_1[\beta_j(\mathbf{h}_1)-\theta_1]+\varepsilon_1 n_2[\beta_j(\mathbf{h}_2)-\theta_2] +\varepsilon_2 n_3[\beta_j(\mathbf{h}_3)-\theta_3]\}\delta(n_1\mathbf{h}_1+\varepsilon_1 n_2\mathbf{h}_2+\varepsilon_2 n_3\mathbf{h}_3), \quad (\mathrm{III}\cdot 4)$$

where $\delta(\mathbf{n})=1$ if $\mathbf{n}=\mathbf{0}$ and $\delta(\mathbf{n})=0$ if $\mathbf{n}\neq\mathbf{0}$. From (I·2) and (I·4) it follows that $J_n(z)=0(z^{|n|})$. We shall only consider terms with $u_j(\mathbf{h}_1)^{|n_1|}u_j(\mathbf{h}_2)^{|n_2|}u_j(\mathbf{h}_3)^{|n_3|}$ for which $|n_1|+|n_2|+|n_3|\leq 3$. If $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ are such that for $|n_1|+|n_2|+|n_3|\leq 3$, $n_1\mathbf{h}_1+\varepsilon_1 n_2\mathbf{h}_2+\varepsilon_2 n_3\mathbf{h}_3\neq\mathbf{0}$ except for $n_1=\varepsilon_1 n_2=\varepsilon_2 n_3=0,-1,1$ then, using (I·2), we find for $q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)$

$$q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3) \simeq\langle J_0[u_j(\mathbf{h}_1)\varrho_1]J_0[u_j(\mathbf{h}_2)\varrho_2]J_0[u_j(\mathbf{h}_3)\varrho_3]\rangle_{\mathrm{orient}} -2i\langle J_1[u_j(\mathbf{h}_1)\varrho_1]J_1[u_j(\mathbf{h}_2)\varrho_2]J_1[u_j(\mathbf{h}_3)\varrho_3] \times\cos\left[\beta_j(\mathbf{h}_1)+\beta_j(\mathbf{h}_2)+\beta_j(\mathbf{h}_3)-\theta_1-\theta_2-\theta_3\right]\rangle_{\mathrm{orient}}. \quad (\mathrm{III}\cdot 5)$$

Next we employ the expansion (I·4),

$$q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3) \simeq 1-\tfrac{1}{4}[\langle u_j(\mathbf{h}_1)^2\rangle_{\mathrm{orient}}\varrho_1^2+\langle u_j(\mathbf{h}_2)^2\rangle_{\mathrm{orient}}\varrho_2^2 +\langle u_j(\mathbf{h}_3)^2\rangle_{\mathrm{orient}}\varrho_3^2]-\tfrac{1}{4}i\langle u_j(\mathbf{h}_1)u_j(\mathbf{h}_2)u_j(\mathbf{h}_3)\varrho_1\varrho_2\varrho_3 \times\cos\left[\beta_j(\mathbf{h}_1)+\beta_j(\mathbf{h}_2)+\beta_j(\mathbf{h}_3)-\theta_1-\theta_2-\theta_3\right]\rangle_{\mathrm{orient}}. \quad (\mathrm{III}\cdot 6)$$

The condition for $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$, as mentioned above, can be given in a simpler form, *viz* $m_1\mathbf{h}_1+m_2\mathbf{h}_2+m_3\mathbf{h}_3\neq\mathbf{0}$ for $|m_1|+|m_2|+|m_3|\leq 3$ except $m_1=m_2=m_3=0,-1,1$, or: $\mathbf{h}_i\neq\mathbf{0}$ $i=1,2,3$, $\mathbf{h}_{i_1}\neq\mathbf{h}_{i_2}$ and $2\mathbf{h}_{i_1}\neq\mathbf{h}_{i_2}$ $i_1,i_2=1,2,3$ $i_1\neq i_2$.

For $1\leq j\leq p_1$ there is no orientational average and $\beta_j(\mathbf{h})=0$,

$$q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3) \simeq 1-\tfrac{1}{4}[u_j(\mathbf{h}_1)^2\varrho_1^2+u_j(\mathbf{h}_2)^2\varrho_2^2+u_j(\mathbf{h}_3)^2\varrho_3^2] -\tfrac{1}{4}iu_j(\mathbf{h}_1)u_j(\mathbf{h}_2)u_j(\mathbf{h}_3)\varrho_1\varrho_2\varrho_3\cos(\theta_1+\theta_2+\theta_3). \quad (\mathrm{III}\cdot 7)$$

For $p_2+1\leq j\leq p$ there is no orientational average,

$$q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3) \simeq 1-\tfrac{1}{4}[u_j(\mathbf{h}_1)^2\varrho_1^2+u_j(\mathbf{h}_2)^2\varrho_2^2+u_j(\mathbf{h}_3)^2\varrho_3^2] -\tfrac{1}{4}iu_j(\mathbf{h}_1)u_j(\mathbf{h}_2)u_j(\mathbf{h}_3)\varrho_1\varrho_2\varrho_3 \times\cos\left[\beta_j(\mathbf{h}_1)+\beta_j(\mathbf{h}_2)+\beta_j(\mathbf{h}_3)-\theta_1-\theta_2-\theta_3\right]. \quad (\mathrm{III}\cdot 8)$$

(III·7) and (III·8) are subject to the same conditions for $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ as (III·6).

From (III·6)–(III·8), (10) and (11) we calculate, following Hauptman (1971),

$$\prod_{j=1}^{p} q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3) =\exp\left[\sum_{j=1}^{p}\log q_j(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3)\right] \simeq\exp\left[-\tfrac{1}{4}(\varrho_1^2+\varrho_2^2+\varrho_3^2) -\tfrac{1}{4}iQ_{123}\varrho_1\varrho_2\varrho_3\cos(\theta_1+\theta_2+\theta_3-q_{123})\right], \quad (\mathrm{III}\cdot 9)$$

where $Q_{123}\exp(iq_{123})$ is given by (16).

APPENDIX IV

The integrations in (13)

First combine the terms which depend on ϱ_1 and θ_1,

$$\tfrac{1}{4}\varrho_1^2+iR_1\varrho_1\cos(\theta_1-\Phi_1) +\tfrac{1}{4}iQ_{123}\varrho_1\varrho_2\varrho_3\cos(\theta_1+\theta_2+\theta_3-q_{123}) =\tfrac{1}{4}\varrho_1^2+iX_1\varrho_1\cos(\theta_1+\xi_1), \quad (\mathrm{IV}\cdot 1)$$

where, from (I·9)–(I·12), X_1 and ξ_1 do not depend on θ_1, and

$$X_1^2\simeq R_1^2+\tfrac{1}{2}Q_{123}R_1\varrho_2\varrho_3\cos(\Phi_1+\theta_2+\theta_3-q_{123}). \quad (\mathrm{IV}\cdot 2)$$

Next, using (I·7), we obtain

$$P(R_1,R_2,R_3;\Phi_1,\Phi_2,\Phi_3)\simeq\frac{R_1R_2R_3}{(2\pi)^4\pi} \times\exp(-R_1^2)\int_0^{\infty}\int_0^{2\pi}\int_0^{\infty}\int_0^{2\pi}\exp\{-i[R_2\varrho_2\cos(\theta_2-\Phi_2) +R_3\varrho_3\cos(\theta_3-\Phi_3)]-\tfrac{1}{4}(\varrho_2^2+\varrho_3^2)-\tfrac{1}{2}Q_{123}R_1\varrho_2\varrho_3 \times\cos(\Phi_1+\theta_2+\theta_3-q_{123})\}\varrho_2\varrho_3\mathrm{d}\varrho_2\mathrm{d}\theta_2\mathrm{d}\varrho_3\mathrm{d}\theta_3. \quad (\mathrm{IV}\cdot 3)$$

For ϱ_2,θ_2 and ϱ_3,θ_3 we follow the same procedure. Combine the terms which depend on ϱ_2 and θ_2,

$$\tfrac{1}{4}\varrho_2^2 + iR_2\varrho_2\cos(\theta_2-\Phi_2) + \tfrac{1}{2}Q_{123}R_1\varrho_2\varrho_3\cos(\Phi_1+\theta_2+\theta_3-q_{123}) = \tfrac{1}{4}\varrho_2^2 + iX_2\varrho_2\cos(\theta_2+\xi_2), \quad (IV\cdot 4)$$

where

$$X_2^2 \simeq R_2^2 - iQ_{123}R_1R_2\varrho_3\cos(\Phi_1+\Phi_2+\theta_3-q_{123}). \quad (IV\cdot 5)$$

After integrating with respect to ϱ_2 and θ_2, we obtain

$$P(R_1,R_2,R_3;\Phi_1,\Phi_2,\Phi_3) \simeq \frac{R_1R_2R_3}{(2\pi)^2\pi^2}\exp(-R_1-R_2) \times \int_0^{\infty}\int_0^{2\pi}\exp[-iR_3\varrho_3\cos(\theta_3-\Phi_3) - \tfrac{1}{4}\varrho_3^2 + iQ_{123}R_1R_2\varrho_3\cos(\Phi_1+\Phi_2+\theta_3-q_{123})]\varrho_3 d\varrho_3 d\theta_3. \quad (IV\cdot 6)$$

Combine the terms which depend on ϱ_3 and θ_3,

$$\tfrac{1}{4}\varrho_3^2 + iR_3\varrho_3\cos(\theta_3-\Phi_3) - iQ_{123}R_1R_2\varrho_3\cos(\Phi_1+\Phi_2+\theta_3-q_{123}) = \tfrac{1}{4}\varrho_3^2 + iX_3\varrho_3\cos(\theta_3+\xi_3), \quad (IV\cdot 7)$$

where

$$X_3^2 \simeq R_3^2 - 2Q_{123}R_1R_2R_3\cos(\Phi_1+\Phi_2+\Phi_3-q_{123}). \quad (IV\cdot 8)$$

Finally, the integrations with respect to ϱ_3 and θ_3 are carried out. The result is given by (21).

APPENDIX V

$\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ or all the atomic position vectors as the primitive random variables

The calculations in Appendix II up to and including (II·6) are also valid in the case that $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ are the primitive random variables. For structures consisting of non-vibrating point atoms, $u_j(\mathbf{h})=Z_j/\sigma_2^{1/2}$ and $\beta_j(\mathbf{h})=0$, we find from (II.6)

$$Q(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3) = \left\langle \prod_{j=1}^{N}\exp\left[i\frac{Z_j}{\sigma_2^{1/2}}\sum_{\nu=1}^{3}\varrho_\nu\cos(2\pi\mathbf{h}_\nu.\mathbf{r}_j-\theta_\nu)\right]\right\rangle_{\text{p.r.v.}}, \quad (V\cdot 1)$$

where the primitive random variables are the atomic position vectors or the reciprocal lattice vectors. If the atomic position vectors are the primitive random variables, then from (V.1) [or (II.7)]

$$Q(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3) = \prod_{j=1}^{N}\left\langle \exp\left[i\frac{Z_j}{\sigma_2^{1/2}}\sum_{\nu=1}^{3}\varrho_\nu\cos(2\pi\mathbf{h}_\nu.\mathbf{r}_j-\theta_\nu)\right]\right\rangle_{\mathbf{r}_j}. \quad (V\cdot 2)$$

If the reciprocal lattice vectors are the primitive random variables and if there are no integers m_j, two of them not zero, such that $\sum_{j=1}^{N} m_j\mathbf{r}_j=\mathbf{r}$, where the components of $\mathbf{r}$ are integers, then from (V·1)

$$Q(\varrho_1,\varrho_2,\varrho_3;\theta_1,\theta_2,\theta_3) = \prod_{j=1}^{N}\left\langle \exp\left[i\frac{Z_j}{\sigma_2^{1/2}}\sum_{\nu=1}^{3}\varrho_\nu\times\cos(2\pi\mathbf{h}_\nu.\mathbf{r}_j-\theta_\nu)\right]\right\rangle_{\substack{\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3\\ \mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=\mathbf{0}}}. \quad (V\cdot 3)$$

As can be seen from the calculations in Appendix III, (V.2) and (V.3) lead to the same result if in the case that the $\mathbf{r}_j$'s are the primitive random variables certain conditions for $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ are fulfilled and if in the case that $\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3$ are the primitive random variables there are no atoms with three rational coordinates. Having found that the resulting formulae for the Q's are the same, it follows that both approaches lead to the same expression for $P(\Phi|R_1,R_2,R_3)$.

APPENDIX VI

The $B(z,t)$ formula

The average of $\exp[2\pi i(\mathbf{h}_1.\mathbf{r}_{i_1i_3}+\mathbf{h}_2.\mathbf{r}_{i_2i_3})]$ over all orientations of the triangle formed by the atoms i_1, i_2 and i_3 has been calculated by Hauptman (1965). His result, denoted by $B(z,t)$, is

$$B(z,t) = \left(\frac{\pi}{2z}\right)^{1/2}\sum_{n=0}^{\infty}\frac{t^{2n}}{(n!)^2}J_{(4n+1)/2}(z), \quad (VI\cdot 1)$$

where

$$z = 2\pi(q^2r^2+2qrq^1r^1\cos\varphi_q\cos\varphi_r+q^{1^2}r^{1^2})^{1/2}, \quad (VI\cdot 2)$$

$$t = \frac{1}{z}2\pi^2qrq^1r^1\sin\varphi_q\sin\varphi_r, \quad (VI\cdot 3)$$

and $J_{(4n+1)/2}(z)$ is the Bessel function of the first kind [Watson (1966), ch. III], q, q^1, r and r^1 are the magnitudes of $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{r}_{i_1i_3}$ and $\mathbf{r}_{i_2i_3}$ respectively, φ_q is the angle between $\mathbf{h}_1$ and $\mathbf{h}_2$ and φ_r is the angle between $\mathbf{r}_{i_1i_3}$ and $\mathbf{r}_{i_2i_3}$. A table of values of the function $B(z,t)$ has been published by Hauptman (1964).

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