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Quintets in $P\bar{1}$: Probabilistic Theory of the Five-Phase Structure Invariant in the Space Group $P\bar{1}$*

BY SUZANNE FORTIER AND HERBERT HAUPTMAN

Medical Foundation of Buffalo Inc., 73 *High Street*, *Buffalo*, *New York* 14203, *USA*

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It is assumed that a crystal structure in $P\bar{1}$ is fixed and that the 15 non-negative numbers R_1, R_2, R_3, R_4, R_5; $R_{12}, R_{13}, R_{14}, R_{15}, R_{23}, R_{24}, R_{25}, R_{34}, R_{35}, R_{45}$ are also specified. The random vector $(\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n})$ is assumed to be uniformly distributed over the subset of the fivefold Cartesian product $W\times W\times W\times W\times W$ of reciprocal space W defined by

$$|E_{\mathbf{h}}|=R_1, |E_{\mathbf{k}}|=R_2, |E_{\mathbf{l}}|=R_3, |E_{\mathbf{m}}|=R_4, |E_{\mathbf{n}}|=R_5; \tag{1}$$

$$\begin{aligned}&|E_{\mathbf{h}+\mathbf{k}}|=R_{12}, |E_{\mathbf{h}+\mathbf{l}}|=R_{13}, |E_{\mathbf{h}+\mathbf{m}}|=R_{14}, |E_{\mathbf{h}+\mathbf{n}}|=R_{15},\\ &|E_{\mathbf{k}+\mathbf{l}}|=R_{23}, |E_{\mathbf{k}+\mathbf{m}}|=R_{24}, |_{\mathbf{k}+\mathbf{n}}|=R_{25}, |E_{\mathbf{l}+\mathbf{m}}|=R_{34},\\ &|E_{\mathbf{l}+\mathbf{n}}|=R_{35}, |E_{\mathbf{m}+\mathbf{n}}|=R_{45};\end{aligned} \tag{2}$$

and

$$\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}+\mathbf{n}=0. \tag{3}$$

Then the structure invariant

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}, \tag{4}$$

as a function of the primitive random variables $\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n}$, is itself a random variable, and its conditional probability distribution, given (1) and (2), is derived. The distribution yields reliable estimates for large numbers of quintets φ in terms of the 15 magnitudes (1) and (2).

1. Introduction and probabilistic background

The probabilistic theory of quartets and quintets has recently been initiated (*e.g.* Hauptman, 1975, 1976; Green & Hauptman, 1976; Hauptman & Green, 1976; Fortier & Hauptman, 1977; Hauptman & Fortier, 1977; Giacovazzo, 1977). It is assumed that the reader is thoroughly familiar with this earlier work, in particular with the recently formulated neighborhood concept and probabilistic background, so that the present paper is greatly abbreviated.

Suppose that a crystal structure consisting of N atoms (not necessarily identical) per unit cell in $P\bar{1}$ is fixed and that the 15 non-negative numbers R_1, R_2, R_3, R_4, R_5; $R_{12}, R_{13}, R_{14}, R_{15}, R_{23}, R_{24}, R_{25}, R_{34}, R_{35}, R_{45}$ are also specified. Define the fivefold Cartesian product $W\times W\times W\times W\times W$ of reciprocal space W to be the collection of all ordered quintuples $(\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n})$ where $\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n}$ are reciprocal vectors. Suppose next that the ordered quintuple of reciprocal vectors $(\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n})$ is a random variable which is uniformly distributed over the subset of $W\times W\times W\times W\times W$ defined by

$$|E_{\mathbf{h}}|=R_1, |E_{\mathbf{k}}|=R_2, |E_{\mathbf{l}}|=R_3, |E_{\mathbf{m}}|=R_4, |E_{\mathbf{n}}|=R_5; \tag{1.1}$$

$$\begin{aligned}&|E_{\mathbf{h}+\mathbf{k}}|=R_{12}, |E_{\mathbf{h}+\mathbf{l}}|=R_{13}, |E_{\mathbf{h}+\mathbf{m}}|=R_{14}, |E_{\mathbf{h}+\mathbf{n}}|=R_{15},\\ &|E_{\mathbf{k}+\mathbf{l}}|=R_{23}, |E_{\mathbf{k}+\mathbf{m}}|=R_{24}, |E_{\mathbf{k}+\mathbf{n}}|=R_{25}, |E_{\mathbf{l}+\mathbf{m}}|=R_{34},\\ &|E_{\mathbf{l}+\mathbf{n}}|=R_{35}, |E_{\mathbf{m}+\mathbf{n}}|=R_{45};\end{aligned} \tag{1.2}$$

and

$$\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}+\mathbf{n}=0. \tag{1.3}$$

It follows that the random variables $\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n}$, the components of the ordered quintuple $(\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n})$, are not independently distributed in reciprocal space. In order to ensure that the domain of the random variable $(\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n})$ be non-vacuous, it is necessary to interpret the exact equality $|E_{\mathbf{h}}|=R_1$ of (1.1) for examples, as an inequality, $R_1\le|E_{\mathbf{h}}|\le R_1+\mathrm{d}R_1$, where $\mathrm{d}R_1$ is a small positive quantity, *etc.* Then the structure invariant

$$\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}, \tag{1.4}$$

as a function of the primitive random variables $\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n}$, is itself a random variable, and its conditional probability distribution, given the 15 magnitudes (1.1) and (1.2), the major result of this paper, is derived.

Finally, the following usual definition is made

$$\sigma_n=\sum_{j=1}^{N} f_j^n, \tag{1.5}$$

where f_j is the zero-angle atomic scattering factor for the atom labeled j. In the X-ray diffraction case the f_j are equal to the atomic numbers Z_j and are therefore all positive; in the neutron diffraction case some of the f_j may be negative.

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2. The conditional probability distribution of the quintet φ, given the 15 magnitudes in its second neighborhood

Under the hypotheses of §1, denote by $P^+_{\bar{1}|15}(P^-_{\bar{1}|15})$ the conditional probability, given the 15 magnitudes (1.1) and (1.2), that

$$\cos\varphi = +1\,(-1), \tag{2.1}$$

where φ is the quintet (1.4). In order to find $P^{\pm}_{\bar{1}|15}$ it is necessary first to derive the joint probability distribution of the 15 structure factors whose magnitudes, (1.1) and (1.2), constitute the second neighborhood of φ (Appendix I) and then the conditional joint probability distribution, given the 15 magnitudes (1.1) and (1.2), of the five phases $\varphi_{\mathbf{h}}, \varphi_{\mathbf{k}}, \varphi_{\mathbf{l}}, \varphi_{\mathbf{m}}, \varphi_{\mathbf{n}}$ (Appendix II). Only the final formula, the major result of this paper, obtained directly from Appendix III, is given here:

$$P^{\pm}_{\bar{1}|15} = \frac{1}{K} Z^{\pm} \tag{2.2}$$

where

$$K = Z^+ + Z^- \tag{2.3}$$

and

$$Z^{\pm} = \exp(\pm T) \sum_{\eta_{12},\ldots,\eta_{45}=\pm 1}^{1024} \exp(U \pm V), \tag{2.4}$$

$$T = \frac{1}{\sigma_2^{9/2}} (15\sigma_3^3 - 10\sigma_2\sigma_3\sigma_4 + \sigma_2^2\sigma_5) R_1R_2R_3R_4R_5\,, \tag{2.5}$$

$$\begin{aligned} U = \frac{\sigma_3}{\sigma_2^{3/2}} (&\eta_{12}R_1R_2R_{12} + \eta_{13}R_1R_3R_{13} + \eta_{14}R_1R_4R_{14} \\ &+ \eta_{15}R_1R_5R_{15} + \eta_{23}R_2R_3R_{23} + \eta_{24}R_2R_4R_{24} \\ &+ \eta_{25}R_2R_5R_{25} + \eta_{34}R_3R_4R_{34} + \eta_{35}R_3R_5R_{35} \\ &+ \eta_{45}R_4R_5R_{45})\,, \end{aligned} \tag{2.6}$$

$$\begin{aligned} V = \frac{\sigma_3}{\sigma_2^{3/2}} [&(\eta_{23}\eta_{45}R_{23}R_{45} + \eta_{24}\eta_{35}R_{24}R_{35} \\ &+ \eta_{25}\eta_{34}R_{25}R_{34})R_1 + \eta_{13}\eta_{45}R_{13}R_{45} \\ &+ \eta_{14}\eta_{35}R_{14}R_{35} + \eta_{15}\eta_{34}R_{15}R_{34})R_2 \\ &+ (\eta_{12}\eta_{45}R_{12}R_{45} + \eta_{14}\eta_{25}R_{14}R_{25} \\ &+ \eta_{15}\eta_{24}R_{15}R_{24})R_3 + (\eta_{12}\eta_{35}R_{12}R_{35} \\ &+ \eta_{13}\eta_{25}R_{13}R_{25} + \eta_{15}\eta_{23}R_{15}R_{23})R_4 \\ &+ (\eta_{12}\eta_{34}R_{12}R_{34} + \eta_{13}\eta_{24}R_{13}R_{24} \\ &+ \eta_{14}\eta_{23}R_{14}R_{23})R_5] \\ - \left(\frac{3\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3}\right) &(\eta_{45}R_{45}R_1R_2R_3 + \eta_{35}R_{35}R_1R_2R_4 \\ &+ \eta_{34}R_{34}R_1R_2R_5 + \eta_{25}R_{25}R_1R_3R_4 \\ &+ \eta_{24}R_{24}R_1R_3R_5 + \eta_{23}R_{23}R_1R_4R_5 \\ &+ \eta_{15}R_{15}R_2R_3R_4 + \eta_{14}R_{14}R_2R_3R_5 \\ &+ \eta_{13}R_{13}R_2R_4R_5 + \eta_{12}R_{12}R_3R_4R_5)\,, \end{aligned} \tag{2.7}$$

and the summation (2.4) is taken over the 1024 sets of values

$$\eta_{12} = \pm 1, \ldots, \eta_{45} = \pm 1\,. \tag{2.8}$$

It is readily verified that the expected value and variance of $\cos\varphi$ are given by

$$\varepsilon(\cos\varphi) = \frac{Z^+ - Z^-}{Z^+ + Z^-} \tag{2.9}$$

and

$$\operatorname{var}(\cos\varphi) = \frac{4Z^+Z^-}{(Z^+ + Z^-)^2} \tag{2.10}$$

respectively.

2.1. *The special case that*

$$R_{23} \simeq R_{24} \simeq R_{25} \simeq R_{34} \simeq R_{35} \simeq R_{45} \simeq 0\,. \tag{2.11}$$

In this case (2.4) reduces to

$$\begin{aligned} Z^{\pm}_{\bar{1}|15} \simeq \exp&\left(\pm \frac{15\sigma_3^3 - 10\sigma_2\sigma_3\sigma_4 + \sigma_2^2\sigma_5}{\sigma_2^{9/2}} R_1R_2R_3R_4R_5\right) \\ &\times \cosh\left[R_{12}\left(\frac{\sigma_3}{\sigma_2^{3/2}} R_1R_2 \mp \frac{3\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3} R_3R_4R_5\right)\right] \\ &\times \cosh\left[R_{13}\left(\frac{\sigma_3}{\sigma_2^{3/2}} R_1R_3 \mp \frac{3\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3} R_2R_4R_5\right)\right] \\ &\times \cosh\left[R_{14}\left(\frac{\sigma_3}{\sigma_2^{3/2}} R_1R_4 \mp \frac{3\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3} R_2R_3R_5\right)\right] \\ &\times \cosh\left[R_{15}\left(\frac{\sigma_3}{\sigma_2^{3/2}} R_1R_5 \mp \frac{3\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3} R_2R_3R_4\right)\right], \end{aligned} \tag{2.12}$$

so that, in this special case,

$$P^+_{\bar{1}|15} < \tfrac{1}{2} \tag{2.13}$$

provided that R_{12}, R_{13}, R_{14} and R_{15} are sufficiently large, in agreement with the prediction of the second row of Table 2 of Hauptman (1977). Clearly there are four other similar cases obtained by symmetry.

2.2. *The special case that*

$$R_{14} \simeq R_{15} \simeq R_{24} \simeq R_{25} \simeq R_{34} \simeq R_{35} \simeq R_{45} \simeq 0\,. \tag{2.14}$$

In this case (2.4) reduces to

$$\begin{aligned} Z^{\pm} \simeq \exp&\left(\pm \frac{15\sigma_3^3 - 10\sigma_2\sigma_3\sigma_4 + \sigma_2^2\sigma_5}{\sigma_2^{9/2}} R_1R_2R_3R_4R_5\right) \\ &\times \cosh\left[R_{12}\left(\frac{\sigma_3}{\sigma_2^{3/2}} R_1R_2 \mp \frac{3\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3} R_3R_4R_5\right)\right] \\ &\times \cosh\left[R_{13}\left(\frac{\sigma_3}{\sigma_2^{3/2}} R_1R_3 \mp \frac{3\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3} R_2R_4R_5\right)\right] \\ &\times \cosh\left[R_{23}\left(\frac{\sigma_3}{\sigma_2^{3/2}} R_2R_3 \mp \frac{3\sigma_3^2 - \sigma_2\sigma_4}{\sigma_2^3} R_1R_4R_5\right)\right], \end{aligned} \tag{2.15}$$

so that, in this special case too,

$$P^{+}_{1|15} < \tfrac{1}{2} \tag{2.16}$$

provided that R_{12}, R_{13} and R_{23} are sufficiently large, again in agreement with the prediction of Table 2 (row 7) of Hauptman (1977). Now there are nine other similar cases obtained by symmetry.

3. The discriminant

In recent work on quintets in $P1$ (Hauptman & Fortier, 1977) it appeared that the value of the quintet was strongly correlated with the value of a certain fourth-degree polynomial in the ten magnitudes (1.2), the so-called discriminant Δ of the quintet φ:

$$\Delta = \frac{2\sigma_3^3}{\sigma_2^{9/2}} \sum_{15} R_{12}^2 R_{34}^2 - \frac{2\sigma_3}{\sigma_2^{9/2}} (3\sigma_3^2 - \sigma_2\sigma_4) \sum_{10} R_{12}^2 + \frac{2}{\sigma_2^{9/2}} (15\sigma_3^3 - 10\sigma_2\sigma_3\sigma_4 + \sigma_2^2\sigma_5) \tag{3.1}$$

where

$$\begin{aligned}\sum_{15} R_{12}^2 R_{34}^2 = {} & R_{12}^2 R_{34}^2 + R_{12}^2 R_{35}^2 + R_{12}^2 R_{45}^2 + R_{13}^2 R_{24}^2 \\ & + R_{13}^2 R_{25}^2 + R_{13}^2 R_{45}^2 + R_{14}^2 R_{23}^2 + R_{14}^2 R_{25}^2 \\ & + R_{14}^2 R_{35}^2 + R_{15}^2 R_{23}^2 + R_{15}^2 R_{24}^2 + R_{15}^2 R_{34}^2 \\ & + R_{23}^2 R_{45}^2 + R_{24}^2 R_{35}^2 + R_{25}^2 R_{34}^2 ,\end{aligned} \tag{3.2}$$

and

$$\begin{aligned}\sum_{10} R_{12}^2 = {} & R_{12}^2 + R_{13}^2 + R_{14}^2 + R_{15}^2 + R_{23}^2 \\ & + R_{24}^2 + R_{25}^2 + R_{34}^2 + R_{35}^2 + R_{45}^2 .\end{aligned} \tag{3.3}$$

In view of the similarities of the quintet distributions in $P1$ and $P\bar{1}$, it is now suggested, and the initial applications confirm (Fortier, Fronckowiak & Hauptman, 1977; Fronckowiak, Fortier, De Titta & Hauptman, 1977), that the quintet in $P\bar{1}$ and the discriminant Δ are strongly correlated, the largest values of Δ (or $R_1R_2R_3R_4R_5\Delta$) corresponding to $\varphi = 0$ and the smallest values of Δ (or $R_1R_2R_3R_4R_5\Delta$) corresponding to $\varphi = \pi$.

It is readily confirmed, by inspection of the distribution (2.2)–(2.4), that if the 15 magnitudes of the second neighborhood, (1.1) and (1.2), are mostly large, then $\varphi \simeq 0$. If, on the other hand, the conditions described in §2.1 or §2.2 are satisfied, then it follows from (2.13) and (2.16) that $\varphi \simeq \pi$. Inspection of the discriminant shows that, in the first case, $\Delta \gg 0$ but, in the second case, $\Delta \ll 0$, in agreement with the conjecture that $\varphi \simeq 0$ or $\varphi \simeq \pi$ in the respective cases.

4. Concluding remarks

As described in the preceding paragraphs, the initial applications of quintets in $P\bar{1}$ have been made. In one case, with $N = 90$ identical nonhydrogen atoms in the unit cell, 10 000 quintets were generated from a basis set of 246 reflections. When ranked on the variance (2.10), the first error occurred at the 1004th quintet; when ranked on the discriminant the first error occurred at the 405th quintet. Two additional applications, one with $N = 40$, the other with $N = 104$, were made with similar results. Although the most reliable estimates were always $\varphi = 0$, in all cases a handful of reliable estimates with $\varphi = \pi$ were also available. In these applications the quintets alone, whether estimated from the distribution (2.2) or the discriminant Δ, determined unique values, with perfect accuracy, of the phases in the basis sets, thus leading unambiguously to the crystal structure. A noteworthy feature of these applications was the fact that only a small fraction, some 10–20%, of available quintets were actually generated and used in the phase-determination process. Thus it seems clear that both the distribution (2.2) and the discriminant Δ are capable of yielding reliable estimates for large numbers of quintets which in turn lead to unique values for a sufficient number of individual phases to determine crystal structures of at least moderate complexity. Finally, although the discriminant Δ appears to be somewhat less reliable than the true distribution (2.2), its ease of calculation makes it a viable alternative.

On the basis of the initial applications described here, it appears that quintets will prove to be at least as useful in the applications as the quartets have been. However, quartet formulas derived from the third and higher neighborhoods are now known to be superior to those associated with the second neighborhood (see, for example, Gilmore, 1976; Kruger, Green, Langs & Weeks, 1976) so that comparisons based on further studies are needed in order to assess the relative importance of quintets and quartets.

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APPENDIX I

The joint probability distribution of 15 structure factors

Suppose that a crystal structure, consisting of N atoms (not necessarily identical) per unit cell in $P\bar{1}$, is fixed. Suppose that the ordered quintuple of reciprocal vectors $(\mathbf{h}, \mathbf{k}, \mathbf{l}, \mathbf{m}, \mathbf{n})$ is a random variable (vector) which is uniformly distributed over the subset of the fivefold Cartesian product $W \times W \times W \times W \times W$ of reciprocal space W defined by

$$\mathbf{h} + \mathbf{k} + \mathbf{l} + \mathbf{m} + \mathbf{n} = 0 . \tag{I.1}$$

Then the fifteen normalized structure factors

$$\begin{aligned} & E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{l}}, E_{\mathbf{m}}, E_{\mathbf{n}} ; \\ & E_{\mathbf{h}+\mathbf{k}}, E_{\mathbf{h}+\mathbf{l}}, E_{\mathbf{h}+\mathbf{m}}, E_{\mathbf{h}+\mathbf{n}}, E_{\mathbf{k}+\mathbf{l}}, \\ & E_{\mathbf{k}+\mathbf{m}}, E_{\mathbf{k}+\mathbf{n}}, E_{\mathbf{l}+\mathbf{m}}, E_{\mathbf{l}+\mathbf{n}}, E_{\mathbf{m}+\mathbf{n}}, \end{aligned} \tag{I.2}$$

as functions of the primitive random variables **h**,**k**,**l**,**m**,**n**, are themselves random variables. Denote by

$$P_{15}=P(S_1,S_2,S_3,S_4,S_5;\ S_{12},S_{13},S_{14},S_{15},\ S_{23},S_{24},S_{25},S_{34},S_{35},S_{45}) \quad (I.3)$$

the joint probability distribution of the 15 structure factors (I.2) and note that, since the space group is $P\bar{1}$, each S in (I.3) is real and has the range $(-\infty,+\infty)$. Following the methods referred to earlier (in particular, Green & Hauptman, 1976; Fortier & Hauptman, 1977), one finds P_{15} correct up to and including terms of order $1/N^{3/2}$.*

It turns out that many of the terms in (I.4) contribute only to terms of order higher than $1/N^{3/2}$ in the conditional distribution $P^{\pm}_{\bar{1}|15}$ [equation (2.2)]. If one retains only those terms of (I.4) which contribute to terms of order at most $1/N^{3/2}$ in $P^{\pm}_{\bar{1}|15}$, then (I.4) reduces to

$$\begin{aligned}P_{15}=\frac{1}{(2\pi)^{15/2}}\exp\Big[&-\tfrac{1}{2}(S_1^2+S_2^2+S_3^2+S_4^2+S_5^2\\&+S_{12}^2+S_{13}^2+S_{14}^2+S_{15}^2+S_{23}^2+S_{24}^2+S_{25}^2\\&+S_{34}^2+S_{35}^2+S_{45}^2)\\&+\frac{\sigma_3}{\sigma_2^{3/2}}(S_1S_2S_{12}+S_1S_3S_{13}+S_1S_4S_{14}+S_1S_5S_{15}\\&+S_2S_3S_{23}+S_2S_4S_{24}+S_2S_5S_{25}+S_3S_4S_{34}\\&+S_3S_5S_{35}+S_4S_5S_{45})\\&+\frac{\sigma_3}{\sigma_2^{3/2}}(S_1S_{23}S_{45}+S_1S_{24}S_{35}+S_1S_{25}S_{34}\\&+S_2S_{13}S_{45}+S_2S_{14}S_{35}+S_2S_{15}S_{34}+S_3S_{12}S_{45}\\&+S_3S_{14}S_{25}+S_3S_{15}S_{24}+S_4S_{12}S_{35}+S_4S_{13}S_{25}\\&+S_4S_{15}S_{23}+S_5S_{12}S_{34}+S_5S_{13}S_{24}+S_5S_{14}S_{23})\\&-\left(\frac{3\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}\right)(S_1S_2S_3S_{45}+S_1S_2S_4S_{35}\\&+S_1S_2S_5S_{34}+S_1S_3S_4S_{25}+S_1S_3S_5S_{24}\\&+S_1S_4S_5S_{23}+S_2S_3S_4S_{15}+S_2S_3S_5S_{14}\\&+S_2S_4S_5S_{13}+S_3S_4S_5S_{12})\\&+\left(\frac{15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5}{\sigma_2^{9/2}}\right)S_1S_2S_3S_4S_5\Big]\\&\times\left[1+O\left(\frac{1}{N}\right)\right],\end{aligned} \quad (I.5)$$

where $O(1/N)$ consists of terms of order $1/N$ or higher which make a contribution only to terms of order $1/N^2$ or higher in the final conditional distribution $P^{\pm}_{\bar{1}|15}$.

* P_{15} [equation (I.4)] has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32702 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

APPENDIX II

The joint conditional probability distribution of the five phases $\varphi_{\mathbf{h}},\varphi_{\mathbf{k}},\varphi_{\mathbf{l}},\varphi_{\mathbf{m}},\varphi_{\mathbf{n}}$, given 15 magnitudes

Refer to § 1 for the probabilistic background. Then the five phases $\varphi_{\mathbf{h}},\varphi_{\mathbf{k}},\varphi_{\mathbf{l}},\varphi_{\mathbf{m}},\varphi_{\mathbf{n}}$, as functions of the primitive random variables **h**,**k**,**l**,**m**,**n**, are themselves random variables. Denote by

$$P_{5|15}=(\Phi_1,\Phi_2,\Phi_3,\Phi_4,\Phi_5|R_1,R_2,R_3,R_4,R_5;\ R_{12},R_{13},R_{14},R_{15},R_{23},R_{24},R_{25},R_{34},R_{35},R_{45}) \quad (II.1)$$

the joint conditional probability distribution of the five phases $\varphi_{\mathbf{h}},\varphi_{\mathbf{k}},\varphi_{\mathbf{l}},\varphi_{\mathbf{m}},\varphi_{\mathbf{n}}$, given (1.1)–(1.3). Then $P_{5|15}$ is found from P_{15} [equation (I.5)] by fixing the magnitudes of S_1, S_2, S_3, S_4, S_5; S_{12}, S_{13}, S_{14}, S_{15}, S_{23}, S_{24}, S_{25}, S_{34}, S_{35}, S_{45} in accordance with the scheme

$$|S_1|=R_1,\ |S_2|=R_2,\ |S_3|=R_3,\ |S_4|=R_4,\ |S_5|=R_5; \quad (II.2)$$

$$|S_{12}|=R_{12},\ |S_{13}|=R_{13},\ |S_{14}|=R_{14},\ |S_{15}|=R_{15},\ |S_{23}|=R_{23},\ |S_{24}|=R_{24},\ |S_{25}|=R_{25},\ |S_{34}|=R_{34},\ |S_{35}|=R_{35},\ |S_{45}|=R_{45}, \quad (II.3)$$

i.e.

$$S_1=R_1\cos\Phi_1,\ S_2=R_2\cos\Phi_2,\ S_3=R_3\cos\Phi_3,\ S_4=R_4\cos\Phi_4,\ S_5=R_5\cos\Phi_5; \quad (II.4)$$

$$\begin{aligned}&S_{12}=R_{12}\cos\Phi_{12},\ S_{13}=R_{13}\cos\Phi_{13},\ S_{14}=R_{14}\cos\Phi_{14},\\&S_{15}=R_{15}\cos\Phi_{15},\ S_{23}=R_{23}\cos\Phi_{23},\ S_{24}=R_{24}\cos\Phi_{24},\\&S_{25}=R_{25}\cos\Phi_{25},\ S_{34}=R_{34}\cos\Phi_{34},\ S_{35}=R_{35}\cos\Phi_{35},\\&S_{45}=R_{45}\cos\Phi_{45},\end{aligned} \quad (II.5)$$

where Φ_{12} is the variable associated with the phase φ_{h+k}, *etc.*, summing with respect to the ten S's, $S_{12},S_{13},\ldots,S_{45}$, over their two possible signs ($+$ and $-$) or, equivalently, summing with respect to the ten Φ's, $\Phi_{12},\Phi_{13},\ldots,\Phi_{45}$, over their two possible values (0 and π), and multiplying the result by a suitable normalizing factor:

$$P_{5|15}=\frac{1}{K_5}Z_{5|15}, \quad (II.6)$$

$$\begin{aligned}Z_{5|15}=\sum_{\varepsilon_{12},\ldots,\varepsilon_{45}=\pm1}^{1024}\exp\Big\{&\frac{3}{\sigma_2^{3/2}}\\&\times[\varepsilon_{12}R_1R_2R_{12}\cos(\Phi_1+\Phi_2)\\&+\varepsilon_{13}R_1R_3R_{13}\cos(\Phi_1+\Phi_3)+\varepsilon_{14}R_1R_4R_{14}\\&\times\cos(\Phi_1+\Phi_4)+\varepsilon_{15}R_1R_5R_{15}\cos(\Phi_1+\Phi_5)\\&+\varepsilon_{23}R_2R_3R_{23}\cos(\Phi_2+\Phi_3)+\varepsilon_{24}R_2R_4R_{24}\\&\times\cos(\Phi_2+\Phi_4)+\varepsilon_{25}R_2R_5R_{25}\cos(\Phi_2+\Phi_5)\\&+\varepsilon_{34}R_3R_4R_{34}\cos(\Phi_3+\Phi_4)+\varepsilon_{35}R_3R_5R_{35}\\&\times\cos(\Phi_3+\Phi_5)+\varepsilon_{45}R_4R_5R_{45}\cos(\Phi_4+\Phi_5)]\\&+\frac{\sigma_3}{\sigma_2^{3/2}}[(\varepsilon_{23}\varepsilon_{45}R_{23}R_{45}+\varepsilon_{24}\varepsilon_{35}R_{24}R_{35}\\&+\varepsilon_{25}\varepsilon_{34}R_{25}R_{34})R_1\cos\Phi_1\\&+(\varepsilon_{13}\varepsilon_{45}R_{13}R_{45}+\varepsilon_{14}\varepsilon_{35}R_{14}R_{35}\end{aligned}$$

$$
\begin{aligned}
&+\varepsilon_{15}\varepsilon_{34}R_{15}R_{34})R_2\cos\Phi_2\\
&+(\varepsilon_{12}\varepsilon_{45}R_{12}R_{45}+\varepsilon_{14}\varepsilon_{25}R_{14}R_{25}\\
&+\varepsilon_{15}\varepsilon_{24}R_{15}R_{24})R_3\cos\Phi_3\\
&+(\varepsilon_{12}\varepsilon_{35}R_{12}R_{35}+\varepsilon_{13}\varepsilon_{25}R_{13}R_{25}\\
&+\varepsilon_{15}\varepsilon_{23}R_{15}R_{23})R_4\cos\Phi_4\\
&+(\varepsilon_{12}\varepsilon_{34}R_{12}R_{34}+\varepsilon_{13}\varepsilon_{24}R_{13}R_{24}\\
&+\varepsilon_{14}\varepsilon_{23}R_{14}R_{23})R_5\cos\Phi_5]\\
&-\frac{3\sigma_3^2-\sigma_2\sigma_4}{\sigma_2^3}[\varepsilon_{45}R_{45}R_1R_2R_3\cos(\Phi_1+\Phi_2+\Phi_3)\\
&+\varepsilon_{35}R_{35}R_1R_2R_4\cos(\Phi_1+\Phi_2+\Phi_4)\\
&+\varepsilon_{34}R_{34}R_1R_2R_5\cos(\Phi_1+\Phi_2+\Phi_5)\\
&+\varepsilon_{25}R_{25}R_1R_3R_4\cos(\Phi_1+\Phi_3+\Phi_4)\\
&+\varepsilon_{24}R_{24}R_1R_3R_5\cos(\Phi_1+\Phi_3+\Phi_5)\\
&+\varepsilon_{23}R_{23}R_1R_4R_5\cos(\Phi_1+\Phi_4+\Phi_5)\\
&+\varepsilon_{15}R_{15}R_2R_3R_4\cos(\Phi_2+\Phi_3+\Phi_4)\\
&+\varepsilon_{14}R_{14}R_2R_3R_5\cos(\Phi_2+\Phi_3+\Phi_5)\\
&+\varepsilon_{13}R_{13}R_2R_4R_5\cos(\Phi_2+\Phi_4+\Phi_5)\\
&+\varepsilon_{12}R_{12}R_3R_4R_5\cos(\Phi_3+\Phi_4+\Phi_5)]\Big\}\\
&\times\exp\left[\frac{15\sigma_3^3-10\sigma_2\sigma_3\sigma_4+\sigma_2^2\sigma_5}{\sigma_2^{9/2}}R_1R_2R_3R_4R_5\right.\\
&\qquad\left.\times\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5)\right]. \qquad \text{(II.7)}
\end{aligned}
$$

Under the transformation

$$
\left.\begin{aligned}\eta_{ij}&=\varepsilon_{ij} && \text{if } \Phi_i=\Phi_j\\ \eta_{ij}&=-\varepsilon_{ij} && \text{if } \Phi_i\neq\Phi_j\end{aligned}\right\}\ i,j=1,2,3,4,5 \qquad \text{(II.8)}
$$

where the Φ's are equal to 0 or π, (II.7) becomes

$$
Z_{5|15}=\exp[T\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5)]
$$

$$
\times\sum_{\eta_{12},\ldots,\eta_{45}=\pm1}^{1024}\exp[U+V\cos(\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5)] \qquad \text{(II.9)}
$$

in which T,U,V are given by (2.5)–(2.7) and the dependence on the sum $\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5$ is explicit. The notation

$$
\sum_{\eta_{12},\ldots,\eta_{45}=\pm1}^{1024}
$$

in (II.9) means that the sum is carried out over all 1024 sets $(\eta_{12},\ldots,\eta_{45})$ as the ten η's range independently over the two values ±1. The normalizing parameter K_5 is not needed for the present purpose. Since (II.9) is a function of the sum $\Phi_1+\Phi_2+\Phi_3+\Phi_4+\Phi_5$, it leads directly to the conditional probability distribution of the structure invariant (1.4), given the 15 magnitudes in the second neighborhood, as shown in Appendix III.

APPENDIX III

The conditional probability distribution of the structure invariant $\varphi=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}+\varphi_{\mathbf{m}}+\varphi_{\mathbf{n}}$, given the 15 magnitudes in its second neighborhood

From the probabilistic background described in §1, the structure invariant (1.4), as a function of the primitive random variables **h**,**k**,**l**,**m**,**n**, is itself a random variable. Denote by

$$
\begin{aligned}
&P_{1|15}=P(\Phi|R_1,R_2,R_3,R_4,R_5;\\
&R_{12},R_{13},R_{14},R_{15},R_{23},R_{24},R_{25},R_{34},R_{35},R_{45}) \qquad \text{(III.1)}
\end{aligned}
$$

the conditional probability distribution of the structure invariant, φ, given the 15 magnitudes (1.1) and (1.2). Then (II.6) and (II.9) imply

$$
P_{1|15}=\frac{1}{K}Z_{1|15} \qquad \text{(III.2)}
$$

where

$$
Z_{1|15}=\exp(T\cos\Phi)\sum_{\eta_{12},\ldots,\eta_{45}=\pm1}^{1024}(U+V\cos\Phi), \qquad \text{(III.3)}
$$

where T,U,V are given by (2.5)–(2.7) and the normalizing parameter K is obtained by summing the right-hand side of (III.2) over the two possible values, 0 and π, for Φ and setting the result equal to unity. In this way the major result of this paper, (2.2)–(2.4), is derived.

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