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Pairs in $P2_1$ Probability Distributions Which Lead to Estimates of the Two-Phase Structure Seminvariants in the Vicinity of $\pi/2$

by

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Abstract

The second sequence of nested neighborhoods of the two phase structure seminvariant

$$\phi_{12} = \phi_{h_1 k_1} - \phi_{h_2 k_2}$$

in the space group $P2_1$ is defined, and conditional probability distributions associated with the first four neighborhoods derived. In the favorable case that the variance of a distribution happens to be small, the distribution yields a particularly reliable value for $\phi_{12}$. The most reliable estimates are obtained when $\phi_{12} = \pm \pi/2$, thus facilitating enantiomorph specification in this space group.
Appendix I. Derivation of (5.1)

In order to derive the conditional probability distribution (5.1) it is necessary first to obtain the joint probability distribution \( P = P(R_1, R_2, \theta_1, \theta_2, \phi_1, \phi_2, S_1, S_2) \) of the three complex-valued normalized structure factors \( E_{h_1k_1l_1}, E_{h_2k_2l_2}, E_{h_0k_0l_0} \) and the two real-valued structure factors \( E_{h_1+k_2,0,0}, E_{h_1-k_2,0,0} \) on the basis that the ordered pair \( (h_1k_1l_1, h_2k_2l_2) \) is the primitive random variable defined by (1.2) and (1.3):

\[
P = \frac{R_1 R_2 R_0}{(2\pi)^6} \int_{0, \theta_{12}, \theta_{12}=-\infty}^{\infty} \int_{\phi_1, \phi_2, \phi_0=0}^{2\pi} \int_{\theta_1, \theta_2, \theta_0=0}^{2\pi} \exp \left\{ -i \left[ R_1 \cos(\theta_1 - \theta_1') \cos(\phi_1 - \phi_1') + R_2 \cos(\theta_2 - \theta_2') + R_0 \cos(\theta_0 - \theta_0') \right] \right. \\
\left. + \omega_{12} \omega_{12} + \omega_{12} \omega_{12} \right\} \times \\
\frac{N}{4} \sum_{i=1}^{N/2} \rho_{1i} \rho_{2i} \rho_{0i} \rho_{1i} \rho_{2i} \rho_{0i} \rho_{1i} \rho_{2i} \rho_{0i} \\
\sum_{i=1}^{N/2} \rho_{1i} \rho_{2i} \rho_{0i} \rho_{1i} \rho_{2i} \rho_{0i} \rho_{1i} \rho_{2i} \rho_{0i} \\
\left( \text{I.1} \right)
\]
where

\[ e_j = \exp \left( \frac{\text{imaginary part}}{\sigma_1^{1/2}} \right) \left[ i \sigma_1 \cos \left( 2\pi (h_1 \cdot \gamma_j - k_1 \cdot \gamma_j) - \phi_1 \right) + \sigma_2 \cos \left( 2\pi (h_2 \cdot \gamma_j + k_2 \cdot \gamma_j) - \phi_2 \right) + 2^{1/2} \sigma_0 \cos(4\pi \gamma_j \cdot \gamma_0) \right] \]

\[ + 2 \sigma_{12} \cos \left( 2\pi (h_1 \cdot h_2) - k_1 \cdot \gamma_j - 2 \sigma_{12} \cos 2\pi (h_1 \cdot h_2) \right) \]

\[ = \exp \left( \frac{\text{imaginary part}}{\sigma_1^{1/2}} \right) \left[ i \sigma_1 \cos \left( 2\pi (h_1 \cdot \gamma_j - k_1 \cdot \gamma_j) - \phi_1 \right) + \sigma_2 \cos \left( 2\pi (h_2 \cdot \gamma_j + k_2 \cdot \gamma_j) - \phi_2 \right) + 2^{1/2} \sigma_0 \cos(4\pi \gamma_j \cdot \gamma_0) \right] \]

\[ + 2 \sigma_{12} \cos \left( 2\pi (h_1 \cdot h_2) - k_1 \cdot \gamma_j - 2 \sigma_{12} \cos 2\pi (h_1 \cdot h_2) \right) \]

\[ h_1, h_2, k \]  (I.2)

and the average is taken over all two-dimensional vectors \( h_1 \) and \( h_2 \), (3.8), the components of whose sum are even, and over all integers \( k \) such that \( k \equiv k' \pmod{2} \), where the fixed integer \( k' = 0 \) or \( 1 \).

Note that the two-dimensional vector \( \gamma_j \), (3.9), and \( \gamma_j \) together define the position of the atom labeled \( j \). Following the recent methods (Fortier and Hauptman, 1977, Appendix) the expression for

\[ \frac{N}{2} \sum_{j=1}^{N/2} e_j \]

is readily obtained:

\[ \frac{N}{2} \sum_{j=1}^{N/2} e_j = \exp \left\{ - \frac{1}{4} \left( \sigma_1^2 + \sigma_2^2 + \sigma_0^2 + 2 \sigma_{12}^2 \right) \right\} \]

\[ - \frac{17}{4} \frac{1}{2} \frac{1}{2} \left[ (-1)^{k'} \frac{\phi_0 \cdot \phi_1 \cdot \phi_2 \cdot \phi_3}{1/2} \cos (\phi_0 - 2\phi_1) + (-1)^{k'} \frac{\phi_0 \cdot \phi_1 \cdot \phi_2 \cdot \phi_3}{2^{1/2}} \cos (\phi_0 - 2\phi_2) \right] \]

\[ + 2(-1)^{k'} \frac{\phi_0 \cdot \phi_1 \cdot \phi_2 \cdot \phi_3}{2^{1/2}} \cos (\phi_0 - 2\phi_2) \]
\[
\begin{aligned}
+ \frac{\sigma_4}{8\sigma_2^2} \left[ z^{3/2} \rho_2 \sigma_1 \sigma_2 \cos(\theta_1 - \theta_2) + 2^{3/2} (-1)^{k'} \rho_0 \rho_2 \sigma_1 \sigma_2 \cos(\theta_0 - \theta_1 - \theta_2) \right] \\
+ 2(-1)^{k'} \sigma_2^2 \sigma_2^2 + 2(-1)^{k'} \sigma_2^2 \sigma_2^2 + \frac{\sigma_2^2}{2} \frac{\sigma_2^2}{2} \cos(2\theta_1 - 2\theta_2) \right] \right] X \left\{ 1 + O\left(\frac{1}{R}\right) \right\} \\
\right)
\end{aligned}
\]

where \( O(\frac{1}{R}) \) represents terms of order \( 1/R \) or higher in which the terms of order \( 1/R \) are independent of the \( F \)'s. Substituting from (1.3) into (1.1) and carrying out the indicated eight-fold integration in accordance with recently secured techniques (Fortier and Hauptman, Appendix, 1977), one obtains the desired joint probability distribution of the five structure factors:

\[
F_{h_1 k_1}, F_{h_2 k_2}, F_{02k0}, F_{h_1+h_2, 0, k_1+k_2}, F_{h_1-h_2, 0, k_1-k_2}:
\]

\[
P \propto \frac{E \cdot R \cdot R_0}{\pi^2} \exp \left\{ -\frac{1}{2} (4R_0^2 + 2R_1^2 + 2R_2^2 + 2+2) \right\} \times \exp \left\{ \frac{2\sigma_3}{\sigma_2^2} \left[ z^{1/2} (-1)^{k'} R_0 R_1^2 \cos(\theta_0 - \theta_1) + 2^{1/2} (-1)^{k'} R_0 R_2^2 \cos(\theta_0 - \theta_2) + \right. \right. \\
\left. \left. + (-1)^{k'} R_1 R_2 \sigma_2 \cos(\theta_1 - \theta_2) + R_1 R_2 \sigma_2 \cos(\theta_1 - \theta_2) \right] \right\}
\]
\[- \left( \frac{4\sigma_2^2 - c_0^2 c_4}{c_2^3} \right) R_1^2 R_2^2 \cos^2 \left( \frac{\Phi_{12} - \Phi_{22}}{2} \right) - 2^{3/2} \left( \frac{2c_3 - c_2 c_4}{c_2^2} \right) \times \]

\[ \left[ R_0 R_1 R_2 S_{12} \cos \left( \Phi_0 - \Phi_{11} - \Phi_{22} \right) + (-1)^k R_0 R_1 R_2 S_{12} \cos \left( \Phi_0 - \Phi_{11} - \Phi_{22} \right) \right] \]

\[- \left( \frac{2c_3^2 - c_2^2 c_4}{c_2^3} \right) \left( -1 \right)^k \left[ R_1^2 S_{12} \tilde{S}_{12} + R_2^2 S_{12} \tilde{S}_{12} \right] \]

\[+ \left( \frac{2c_3^2 - c_2^2 c_4}{c_2^3} \right) \left( -1 \right)^k S_{12} \tilde{S}_{12} \times \left[ 1 + \left( \frac{1}{N} \right) \right] \]

\[(I.4)\]

where \(O\left(\frac{1}{N}\right)\) represents terms of order \(\frac{1}{N}\) or higher in which the terms of order \(\frac{1}{N}\) are independent of the \(\phi\)'s and \(k' = 0\) or 1 according as \(k\) is even or odd, respectively. Hence, by fixing \(R_1 R_2 R_0^2 R_{12} = |S_{12}|, R_{12} = |S_{12}|\), integrating (I.4) with respect to \(\frac{\Phi_{12}}{2}, \frac{\Phi_{22}}{2}\), summing over the two possible values, 0, \(\pi\) of each of \(\frac{\Phi_{12}}{2}, \frac{\Phi_{22}}{2}\) defined by

\[S_{12} = R_{12} \cos \frac{\Phi_{12}}{2} \]

\[(I.5)\]

\[S_{12}^* = R_{12} \cos \frac{\Phi_{12}}{2} \]

\[(I.6)\]

and multiplying by a suitable normalization factor, (I.4) implies (5.1) correct up to and including terms of order \(1/N\).