treatment may lower the GoF significantly. Corrections for thermal diffuse scattering (Helmholdt & Vos, 1975) may also be important. To what extent these changes in data reduction will affect the charge-density parameters is uncertain but it may well be that the resolution of the bonding-density features could be further improved.

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References


Pairs in P2₁: Probability Distributions which Lead to Estimates of the Two-Phase Structure Seminvariants in the Vicinity of 0 or π

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The first sequence of nested neighborhoods of the two-phase structure seminvariant \( \varphi_{12} = \varphi_{h_1 k_1 l_1} - \varphi_{h_2 k_2 l_2} \) in the space group P2₁ 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 \( \varphi_{12} \). The most reliable estimates are obtained when \( \varphi_{12} \approx 0 \) or \( \pi \).

1. Introduction

In the space group P2₁, the linear combination of two phases

\[ \varphi_{12} = \varphi_{hkl} - \varphi_{h'k'l'} \]  

(1.1)
is a structure seminvariant if and only if

\[ (h_1 - h_2, 0, l_1 - l_2) \equiv 0 \pmod{\omega} \]  

(1.2)

where \( \omega \), the seminvariant modulus in P2₁, is defined by

\[ \omega = (2,0,2). \]  

(1.3)

In short, \( \varphi_{12} \) is a structure seminvariant if and only if
In other words, if the magnitudes \((2.4)\) are large,
\[
\varphi_{12} \simeq 0 \text{ or } \pi \tag{2.6}
\]
according as \(q\) is even or odd, respectively. Accordingly, the first neighborhood of \(\varphi_{12}\) is defined to consist of the three magnitudes \((2.4)\) which are shown in the first shell of Fig. 1. Since \(q\) is an arbitrary non-zero integer, there are many first neighborhoods.

2.2. The second neighborhoods

The second neighborhood of the two-phase seminvariant \(\varphi_{12}\) is defined to be the second neighborhood of the four-phase structure invariant \((2.1)\) (Hauptman, 1975a,b). Thus, the second neighborhood consists of the three magnitudes \((2.4)\) and the three additional magnitudes
\[
|E_{h,k,q,l,t,u}|, \quad |E_{h,k,q,l,t,u}|, \quad |E_{h,k,q,l,t,u}| \tag{2.7}
\]
shown in the second shell of Fig. 1.

In view of the quartet theory, if the six magnitudes \((2.4)\) and \((2.7)\) are all large, the quartet \((2.1)\) is probably close to zero, and
\[
\varphi_{12} \simeq \pi q. \tag{2.8}
\]

However, if the three magnitudes \((2.4)\) are large and the three magnitudes \((2.7)\) are small, then the quartet \((2.1)\)
is probably close to \( \pi \), and
\[
\varphi_{12} \approx \pi(q + 1).
\]  
(2.9)

Since \( q \) is an arbitrary non-zero integer, there are many second neighborhoods.

2.3. The third neighborhoods

The third neighborhood of \( \varphi_{12} \) is again obtained by arguments similar to those used previously for the four-phase structure invariant (Hauptman, 1977a). If \( h_3 k l_3 \) is a reciprocal lattice vector which satisfies
\[
(h_2 k l_2) - (h_3 k l_3) \equiv 0 \pmod{\omega},
\]  
(2.10)

then
\[
\varphi_{23} = \varphi_{hkl_2} - \varphi_{hkl_3}
\]  
(2.11)
is a two-phase structure seminvariant. The second neighborhood of \( \varphi_{23} \) consists of the six magnitudes
\[
\begin{align*}
|E_{hkl_1}|, & |E_{hkl_2}|, |E_{hkl_3}|, |E_{h(k-h),r},l(l_i-z)|, \\
|E_{h(k-h),r},l(l_i-z)|, & |E_{h(k-h),r},l(l_i-z)|,
\end{align*}
\]  
(2.12)
where \( r \) is an arbitrary non-zero integer. Since \( \varphi_{12} \) and \( \varphi_{23} \) are both two-phase seminvariants, \( \varphi_{31} = \varphi_{hkl_1} - \varphi_{hkl_3} \) is also a structure seminvariant and has a second neighborhood consisting of the six magnitudes
\[
\begin{align*}
|E_{hkl_1}|, & |E_{hkl_2}|, |E_{h(k-h),r},l(l_i-z)|, \\
|E_{h(k-h),r},l(l_i-z)|, & |E_{h(k-h),r},l(l_i-z)|,
\end{align*}
\]  
(2.13)
where \( s \) is an arbitrary non-zero integer. However, from (1.1), (2.11), and (2.13), the following identity holds:
\[
\varphi_{12} + \varphi_{23} + \varphi_{31} = 0.
\]  
(2.15)

Therefore, in the favourable case that the six-magnitude estimates yield values for \( \varphi_{12}, \varphi_{23}, \) and \( \varphi_{31} \) in accord with (2.15), \( \varphi_{12} \) will be well estimated in terms of the 15 magnitudes (2.4), (2.7), (2.12), and (2.14) of which only the following 15 are distinct:
\[
\begin{align*}
|E_{hkl_1}|, & |E_{hkl_2}|, |E_{h(k-h),r},l(l_i-z)|, \\
|E_{h(k-h),r},l(l_i-z)|, & |E_{h(k-h),r},l(l_i-z)|,
\end{align*}
\]  
(2.16)
Thus, the third (15-magnitude) neighborhood of \( \varphi_{12} \) is obtained by adjoining to the second (six-magnitude) neighborhood, (2.4) and (2.7), the nine additional magnitudes shown in the third shell of Fig. 1,
\[
\begin{align*}
|E_{h(k-h),r},l(l_i-z)|, & |E_{h(k-h),r},l(l_i-z)|, \\
|E_{h(k-h),r},l(l_i-z)|, & |E_{h(k-h),r},l(l_i-z)|,
\end{align*}
\]  
(2.17)
where \( r \) and \( s \) are arbitrary non-zero integers; hence there are many third neighborhoods.

One naturally anticipates that the conditional variance of the two-phase structure seminvariant \( \varphi_{12} \), given the 15 magnitudes in its third neighborhood, will be small if the six-magnitude second neighborhoods of \( \varphi_{12}, \varphi_{23}, \varphi_{31} \) yield estimates for the latter in accord with the identity (2.15). Thus, those neighborhoods are most useful for which
\[
|E_{h(k-h),r},l(l_i-z)|, |E_{h(k-h),r},l(l_i-z)|, |E_{h(k-h),r},l(l_i-z)|
\]  
(2.18)

are large.

2.4. The fourth neighborhoods

Again, as in § 2.3, the fourth neighborhood of \( \varphi_{12} \) is obtained by the same method as that used for quartets (Hauptman, 1977a). If \( (h_4 k l_4) \) is a reciprocal lattice vector satisfying
\[
(h_i k l_i) - (h_4 k l_4) \equiv 0 \pmod{\omega},
\]  
(2.19)
then
\[
\varphi_{14} = \varphi_{hkl_1} - \varphi_{hkl_4}
\]  
(2.20)
is a structure seminvariant. The second neighborhood of \( \varphi_{14} \) consists of the six magnitudes
\[
\begin{align*}
|E_{hkl_1}|, & |E_{hkl_2}|, |E_{h(k-h),r},l(l_i-z)|, \\
|E_{h(k-h),r},l(l_i-z)|, & |E_{h(k-h),r},l(l_i-z)|,
\end{align*}
\]  
(2.21)
where \( t \) is an arbitrary non-zero integer.

From (1.2), (1.3), (2.10) and (2.19), it is seen that \( h_3 \) and \( h_4 \) have the same parity, as do \( l_3 \) and \( l_4 \), so that
\[
\varphi_{34} = \varphi_{hkl_1} - \varphi_{hkl_4}
\]  
(2.22)
is also a structure seminvariant. The second neighborhood of \( \varphi_{34} \) consists of the six magnitudes
\[
\begin{align*}
|E_{hkl_1}|, & |E_{hkl_2}|, |E_{h(k-h),r},l(l_i-z)|, \\
|E_{h(k-h),r},l(l_i-z)|, & |E_{h(k-h),r},l(l_i-z)|,
\end{align*}
\]  
(2.23)
where \( v \) is an arbitrary non-zero integer, and the three seminvariants \( \varphi_{31}, \varphi_{14}, \varphi_{34} \) satisfy the identity
\[
\varphi_{31} + \varphi_{14} + \varphi_{34} = 0.
\]  
(2.24)
In view of (1.2), (1.3) and (2.19) \( h_2 \) and \( h_4 \) have the same parity, as do \( l_2 \) and \( l_4 \), so that
\[
\varphi_{42} = \varphi_{hkl_1} - \varphi_{hkl_4}
\]  
(2.25)
is also a structure seminvariant. The second neighborhood of \( \varphi_{42} \) consists of the six magnitudes
\[
\begin{align*}
|E_{hkl_1}|, & |E_{hkl_2}|, |E_{h(k-h),r},l(l_i-z)|, \\
|E_{h(k-h),r},l(l_i-z)|, & |E_{h(k-h),r},l(l_i-z)|,
\end{align*}
\]  
(2.26)
where \( u \) is an arbitrary non-zero integer. Since \( \varphi_{42} = -\varphi_{42} \), in particular \( \varphi_{43} = -\varphi_{44} \), the identity
\[
\varphi_{23} + \varphi_{34} + \varphi_{42} = 0
\]  
(2.27)holds. The 28-magnitude fourth neighborhood of \( \varphi_{12} \) is obtained by adjoining the 13 distinct magnitudes in
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We expect that, in the favorable case that the six-magnitude estimates of the structure seminvariants \( \phi_{12}, \phi_{13}, \phi_{14}, \phi_{23}, \phi_{24}, \phi_{34} \) conform to the identities (2.15), (2.25) and (2.28), then the variance of the conditional probability distribution of \( \phi_{12} \), given the 28 magnitudes in its fourth neighborhood, will be reduced and the corresponding estimate for \( \phi_{12} \) better than those of the lower-order distributions.

3. Probabilistic background and notation

It is assumed that a crystal structure in \( P2_1 \) consisting of \( N \) atoms, not necessarily identical, in the unit cell is fixed, and that the three non-negative numbers \( R_1, R_2, R_12/10 \) are also specified. Suppose that the ordered pair \( [(h_1 k_1 l_1), (h_2 k_2 l_2)] \) of reciprocal vectors is a random variable which is uniformly distributed over that subset of the two-fold Cartesian product \( \mathbb{W} \times \mathbb{W} \) of reciprocal space \( \mathbb{W} \) defined by (1.2), (1.3) and

\[
|E_{h_1 k_1 l_1}| = R_1, \quad |E_{h_2 k_2 l_2}| = R_2, \quad |E_{(h_1-h_0,a,0,l_1-l_0)}| = R_{12/10},
\]

(3.1)

The structure seminvariant, \( \phi_{12} \), is then a random variable whose conditional probability distribution, \( P_{12} \), given the three magnitudes (3.1) in its first neighborhood, depends on the parameters \( R_1, R_2, R_{12/10} \).

Suppose that the non-negative numbers \( R_{12/11}, R_{12/13}, R_{12} \) are also specified, and it is assumed that the primitive random variable \( [(h_1 k_1 l_1), (h_2 k_2 l_2)] \) is uniformly distributed over the subset of \( \mathbb{W} \times \mathbb{W} \) defined by (1.2), (1.3), (2.10) and (3.1) and

\[
|E_{(h_1+h_0,a,q,k_1,l_1+l_0)}| = R_{12/11}, \\
|E_{(h_1+h_0,a,q,-k_1,l_1+l_0)}| = R_{12/13}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{12/10},
\]

(3.2)

then one is led to the conditional probability distribution, \( P_{12} \), of the structure seminvariant \( \phi_{12} \), given the six magnitudes (3.1) and (3.2) in its second neighborhood.

One continues in this way to specify the nine additional non-negative numbers \( R_3, R_{23/20}, R_{23/21}, R_{23/22}, R_{23/23}, R_{23/24}, R_{23/25}, R_{23/26}, R_{23/27} \) and then to assume that the ordered triple \( [(h_1 k_1 l_1), (h_2 k_2 l_2), (h_3 k_3 l_3)] \) is a random variable which is uniformly distributed over the subset of the threefold Cartesian product \( \mathbb{W} \times \mathbb{W} \times \mathbb{W} \) defined by (1.2), (1.3), (2.10), (3.1), (3.2) and by

\[
|E_{h_1 k_1 l_1}| = R_3, \quad |E_{(h_1-h_0,a,r,l_1-l_0)}| = R_{23/20}, \\
|E_{(h_1+h_0,a,q+k_1,l_1+l_0)}| = R_{23/21}, \\
|E_{(h_1+h_0,a,q-k_1,l_1+l_0)}| = R_{23/22}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{23/23}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{23/24}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{23/25}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{23/26}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{23/27},
\]

(3.3)

Now one arrives at the conditional probability distribution, \( P_{123} \), of \( \phi_{123} \) given the 15 magnitudes (3.1)–(3.3) in its third neighborhood. In a similar way one is led to the conditional distribution of \( \phi_{123} \), \( P_{123} \), given the 15 magnitudes (3.1)–(3.3) and the 13 additional magnitudes:

\[
|E_{h_1 k_1 l_1}| = R_4, \quad |E_{(h_1-h_0,a,r,l_1-l_0)}| = R_{43/20}, \\
|E_{(h_1+h_0,a,q+k_1,l_1+l_0)}| = R_{43/21}, \\
|E_{(h_1+h_0,a,q-k_1,l_1+l_0)}| = R_{43/22}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{43/23}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{43/24}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{43/25}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{43/26}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{43/27}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{43/28}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{43/29}, \\
|E_{h_1-h_0,0,l_1-l_0}| = R_{43/30},
\]

(3.4)

In \( P2_1 \) the normalized structure factor \( E_{hkl} \) is defined by

\[
E_{hkl} = |E_{hkl}| \exp(i\varphi_{hkl}) = \frac{2}{(8\pi)^{1/2}} \sum_{j=1}^{N/2} f_j \cos 2\pi \left( \mathbf{h} \cdot \mathbf{r}_j + \frac{k}{4} \right) \exp \left[ 2\pi i \left( k\mathbf{y}_j - \frac{k}{4} \right) \right],
\]

(3.5)

where \( \varepsilon = 2 \) if \( h = l = 0 \) and 1 otherwise; finally, \( (x_j, y_j, z_j) \) is the position vector of the \( j \)th atom. The \( h \) and \( r_j \) are two-dimensional vectors defined by

\[
\mathbf{h} = (h, h), \\
\mathbf{r}_j = (x_j, z_j),
\]

(3.6)

and \( f_j \) is the zero-angle atomic scattering factor of the atom labeled \( j \); the term \( \sigma_n \) is defined by

\[
\sigma_n = \sum_{j=1}^{N} f_j^2
\]

(3.8)

In the case of X-ray diffraction, the \( f_j \) are equal to the atomic numbers \( Z_j \). In the neutron diffraction case some of the \( f_j \) may be negative.

In the sequel conditional probability distributions of \( \phi_{12} \), given the magnitudes in each of its first four neighborhoods, are described. Only the briefest sketch of the derivations is given in Appendix I for the typical case of the second neighborhood; the heavy dependence on earlier work permits substantial abbreviation.

4. The conditional probability distribution of the two-phase structure seminvariant \( \phi_{12} = \phi_{h_1 k_1 l_1} - \phi_{h_2 k_2 l_2} \) given the three magnitudes in its first neighborhood

Suppose that the non-negative numbers \( R_1, R_2, R_{12/10} \) defined in (3.1) are specified. Then, complete to terms
of order $1/N$, $P_{113} = P_{113}(\Phi)$, the conditional probability distribution of $\Phi_{12}$, given the three magnitudes (3.1) of the first neighborhood, is found to be

$$P_{113} \approx \frac{1}{K_{113}} \exp \left\{ \frac{\sigma_4}{\sigma_2^2} \left[ 12(-1)^q R_1 R_2 (R_{12/10}^2 - 1) \cos \Phi + R_1^2 R_2^2 \cos 2\Phi \right] \right\},$$

(4.1)

which is correct through terms of order $1/N$. Although an analytical representation for the normalization factor $K_{113}$ may be found, it is not needed for the present purpose and, in any event, is more easily computed numerically in any given case.

5. The conditional probability distribution of $\Phi_{12}$, given the six magnitudes in its second neighborhood

Assume that the six non-negative numbers $R_1$, $R_2$, $R_{12/10}$, $R_{12/11}$, $R_{12/11}$, $R_{12/11}$ defined in (3.1), (3.2) are specified. Then, complete to terms of order $1/N$, the conditional probability distribution, $P_{116} = P_{116}(\Phi)$, of $\Phi_{12}$, given the six magnitudes of the second neighborhood, is found to be

$$P_{116} = \frac{1}{K_{116}} \exp \left\{ -\frac{2(-1)^q R_1 R_2}{\sigma_2^2} \left[ (3\sigma_2^2 - \sigma_2 \sigma_4) R_{12/10}^2 \right. \right.$$

$$\left. + (\sigma_2^2 - \sigma_2 \sigma_4) (R_{12/11}^2 + R_{12/11}^2) - 3(\sigma_2^2 - \sigma_2 \sigma_4) \right] \cos \Phi$$

$$- \left( \frac{\sigma_3^2 - \sigma_2 \sigma_4}{\sigma_2^2} \right) R_1^2 R_2^2 \cos 2\Phi \right\}$$

$$\times \exp\left\{ \frac{\sigma_3 R_{12/10}}{\sigma_2^{3/2}} \left[ (-1)^q (R_{12/10}^2 - 1) + 2R_1 R_2 \cos \Phi \right] \right\}$$

$$\times \cosh\left\{ \frac{\sigma_3 R_{12/11}}{\sigma_2^{3/2}} \left[ (-1)^q (R_{12/11}^2 - 1) + 2R_1 R_2 \cos \Phi \right] \right\}$$

$$\times I_0 \left\{ \frac{2\sigma_4}{\sigma_2^{3/2}} R_{12/10} R_{12/11}^2 R_{12/11}^{\sigma_2^{3/2}} + 2(-1)^q R_1 R_2 \cos \Phi \right\}^{1/2}\right\}$$

$$\times I_0 \left\{ \frac{2\sigma_4}{\sigma_2^{3/2}} R_{12/11} R_{12/11}^2 R_{12/11}^{\sigma_2^{3/2}} + 2(-1)^q R_1 R_2 \cos \Phi \right\}^{1/2}\right\}.$$  

(5.1)

The numbers $R_1$, $R_2$, $R_{12/10}$, $R_{12/11}$, $R_{12/11}$, $R_{12/11}$ are parameters of the distribution. The normalization factor $K_{116}$ is best evaluated numerically, if desired, since its analytical representation is a complicated expression involving a multiple infinite series of products of Bessel functions. Details of the derivation of (5.1) are given in Appendix I.*

6. The conditional probability distribution of $\Phi_{12}$, given the 15 magnitudes in its third neighborhood

Assume that the 15 non-negative numbers $R_1$, $R_2$, $R_{12/10}$, $R_{12/11}$, $R_{12/11}$ defined by (3.1)-(3.3) are specified. Then, $P_{115} = P_{115}(\Phi)$, the conditional probability distribution of $\Phi_{12}$, given the 15 magnitudes (3.1)-(3.3) of the third neighborhood, is found to be

$$P_{115} \approx \frac{1}{K_{115}} \exp \left\{ -\frac{2}{25} \sum_{0}^{25} Q_1(\Phi_{23}) \right\}$$

(6.1)

where

$$Q_1(\Phi_{23}) = \exp \left\{ -2 \left( \frac{3\sigma_2^2 - \sigma_2 \sigma_4}{\sigma_2^2} \right) \right\}$$

$$\times \left[ (-1)^q R_2 R_3 R_{23/20} \cos \Phi_{23} + \Phi \right]$$

$$+ (-1)^q R_3 R_1 R_{23/30} \cos (\Phi_{23} + \Phi)$$

$$+ (-1)^q R_1 R_1 \cos (\Phi_{23} + \Phi)$$

$$- \left( \frac{\sigma_3^2 - \sigma_2 \sigma_4}{\sigma_2^2} \right) R_2^2 R_3^2 \cos 2\Phi_{23}$$

$$+ R_2 R_3 \cos (2\Phi_{23} + 2\Phi)$$

$$\times \cosh\left\{ \frac{\sigma_3 R_{23/20}}{\sigma_2^{3/2}} \left[ (-1)^q (R_{23/20}^2 - 1) + 2R_2 R_3 \cos \Phi_{23} \right] \right\}$$

$$\times \cosh\left\{ \frac{\sigma_3 R_{23/30}}{\sigma_2^{3/2}} \left[ (-1)^q (R_{23/30}^2 - 1) + 2R_2 R_3 \cos \Phi_{23} \right] \right\}$$

$$\times I_0 \left\{ \frac{2\sigma_4}{\sigma_2^{3/2}} R_{23/20} R_{23/21} R_{23/21}^{\sigma_2^{3/2}} + 2(-1)^q R_2 R_3 \right.$$

$$\times \cos (\Phi_{23}) \right\}^{1/2}\right\}$$

$$\times I_0 \left\{ \frac{2\sigma_4}{\sigma_2^{3/2}} R_{23/30} R_{23/31} R_{23/31}^{\sigma_2^{3/2}} + 2(-1)^q R_2 R_3 \right.$$

$$\times \cos (\Phi_{23}) \right\}^{1/2}\right\}$$

$$\times I_0 \left\{ \frac{2\sigma_4}{\sigma_2^{3/2}} R_{23/30} R_{23/31} R_{23/31}^{\sigma_2^{3/2}} + 2(-1)^q R_2 R_3 \right.$$

$$\times \cos (\Phi_{23}) \right\}^{1/2}\right\}.$$  

(6.2)

A simple expression for (6.1) appears not to exist. Hence, one must either resort to an approximate analytical expression for the integral or evaluate the expression via numerical techniques. With either technique the integration leads to a function of order $1/N^2$, which contains the information associated with
the 'trio relation', (2.15). Therefore, the conditional distribution, \( P_{1;15} \), of \( \phi_{12} \) given the 15 magnitudes (3.1)-(3.3) consists of all terms of order \( 1/N \) plus those terms of order \( 1/N^2 \) which reflect the information in (2.15).

7. The conditional probability distribution of \( \phi_{12} \) given the 28 magnitudes in its fourth neighborhood

Denote by \( P_{1;28} = P_{1;28}(\Phi) \) the conditional probability distribution of \( \phi_{12} \), given the 28 magnitudes in the fourth neighborhood defined by (3.1)-(3.4). Then

\[
P_{1;28} = \frac{1}{K_{1;28}} \int P_1(\Phi_{23}) \int Q_2(\Phi_{23}, \Phi_{14}) d\Phi_{14} d\Phi_{23}
\]

where

\[
Q_2(\Phi_{23}, \Phi_{14}) = \exp \left\{ -\frac{2}{\sigma_j^2} (3\sigma_j^2 - \sigma_j^2 - \sigma_j^2) \right\}
\]

\[
 \times \left\{ (-1)^q R_4 R_2 R_4 R_{14/40} \cos \Phi_{14} + (-1)^q R_4 R_2 R_{42/50} \cos(\Phi - \Phi_{14}) + (-1)^q R_4 R_4 R_{43/60} \cos(\Phi + \Phi_{23} - \Phi_{14}) \right\}
\]

\[
 \times \frac{6}{\sigma_j^2} (3\sigma_j^2 - \sigma_j^2 - \sigma_j^2) \int (-1)^q R_4 R_4 \cos \Phi_{14}
\]

\[
\times \left\{ (-1)^q R_4 R_4 \cos(\Phi - \Phi_{14}) + (-1)^q R_4 R_4 \cos(\Phi + \Phi_{23} - \Phi_{14}) \right\}
\]

\[
\times \int \frac{2}{\sigma_j^2} R_{45/50} R_{42/51} \left[ R_2^2 + 2(1)^q R_4 R_2 \times \cos(\Phi - \Phi_{14}) \right]^{1/2}
\]

\[
\times \int \frac{2}{\sigma_j^2} R_{45/50} R_{43/61} \left[ R_3^2 + 2(1)^q R_4 R_3 \times \cos(\Phi - \Phi_{14}) \right]^{1/2}
\]

\[
\times \int \frac{2}{\sigma_j^2} R_{45/60} R_{43/61} \left[ R_3^2 + 2(1)^q R_4 R_3 \times \cos(\Phi + \Phi_{23} - \Phi_{14}) \right]^{1/2}
\]

\[
(7.1)
\]

The double integral in (7.1) is also evaluated by standard numerical integration techniques, and leads to terms of order \( 1/N^2 \) which contain the information associated with the identities (2.15), (2.25), and (2.28).

8. The applications

The figures which accompany this section show \( P_{1;13}, P_{1;16} \) and \( P_{1;15} \) as functions of \( \Phi \) in the interval \(-180^\circ \leq \Phi \leq +180^\circ \). They illustrate the properties of these probability distributions for a structure containing \( N = 100 \) identical atoms in the unit cell. The values given for the various magnitudes are mostly selected to exemplify ideal behavior of these distributions (i.e. to minimize their variance), and thus to illustrate the most reliable estimates of \( \phi_{12} \) which are possible in a structure of this size. They confirm the plausible reasoning of §2.

Fig. 2. The distribution \( P_{1;3} \) for the values of the parameters shown. (a) \( q \) is even (—); (b) \( q \) is odd (—).
8.1. The first neighborhood

Fig. 2 shows that reliable estimates of $\phi_{12}$ occur if the three magnitudes (3.1) are large. If $q$ is even, the most probable value of $\phi_{12}$ is zero. If $q$ is odd the most probable value of $\phi_{12}$ is $180^\circ$.

8.2. The second neighborhood

Figs. 3 and 4 illustrate two kinds of distributions based on the six magnitudes of the second neighborhood. If the three magnitudes (3.1) are large and the three additional magnitudes (3.2) are also large, $\phi_{12}$ is likely to be near 0 if $q$ is even or likely to be near $\pm 180^\circ$ if $q$ is odd. This is shown in Fig. 3. If the three magnitudes (3.1) are large and the three magnitudes (3.2) are small, then the most probable value of $\phi_{12}$ is 0 if $q$ is odd and $180^\circ$ if $q$ is even. This result is shown in Fig. 4.

8.3. The third neighborhood

Fig. 5 shows the conditional probability distribution of $\phi_{12}$ given that all 28 magnitudes of the third neighborhood are large. If $q$ and $r + s$ are both even, then the most probable value of $\phi_{12}$ is 0. If, on the other hand, $q$ and $r + s$ are both odd, then the most probable value of $\phi_{12}$ is $180^\circ$. In either of these two cases, the estimate for $\phi_{12}$ is extremely reliable. If, however, $q + r + s$ is odd, then the most probable value of $\phi_{12}$ is $\pm \alpha$ where $0 < \alpha < 180^\circ$. Thus, if $q$ is even and $r + s$ is odd, then $\phi_{12} \approx \pm 60^\circ$; if $q$ is odd and $r + s$ is even, then $\phi_{12} \approx \pm 120^\circ$. In the latter cases the reliability of the estimate will in general be too low to be useful for very complex structures, as shown, for example, by the relatively large variance of Fig. 5(c). Fig. 6 shows the result obtained when the three 'cross-terms'
(\(R_{12}, R_{12/11}, R_{12/11}, \text{etc.}\)) of the second neighborhoods of each of \(\phi_{12}\) and \(\phi_{31}\) are small. Reliable estimates of \(\phi_{12}\) are obtained if \(q\) and \(r + s\) are both odd or if \(q\) and \(r + s\) are both even. In the former case \(\phi_{12} \approx 0^\circ\), and in the latter \(\phi_{12} \approx 180^\circ\). Other parity combinations of \(q\) and \(r + s\) lead to estimates of \(\phi_{12}\) having values between 0 and 180°, but with generally reduced reliability (e.g. Fig. 6c).

From the favorable cases considered in Figs. 2–6 it is seen that as the size of the neighborhood increases, one may obtain a more reliable estimate of \(\phi_{12}\); the larger the neighborhood, the greater is the potential for obtaining a distribution with a very small variance.

In the applications one naturally selects those seminvariants and those of \(q, r, s, \ldots\) which lead to distributions having the smallest possible variance, i.e. the favorable cases.

9. Concluding remarks

The first sequence of nested neighborhoods of the two-phase structure seminvariant \(\phi_{12}\) in \(P_2\), has been found. The conditional probability distributions of \(\phi_{12}\), given, in the first instance, the three magnitudes of the first neighborhood; in the second instance, the six magnitudes of the second neighborhood; thirdly, the 15 magnitudes of the third neighborhood; and finally, the 28 magnitudes of the fourth neighborhood, have been derived. The distributions yield estimates for \(\phi_{12}\) which may lie anywhere in the interval \((-\pi, \pi)\) but which are most reliable in the case that \(\phi_{12} \approx 0\) or \(\pi\). As anticipated, when more magnitudes are used more reliable estimates are obtainable, but in practice the gain in using distributions of order higher than \(P_{1/2}\) may only be marginal, as Figs. 3–6 suggest.

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