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On Integrating the Techniques of Direct Methods with Anomalous Dispersion: the One-Phase Structure Seminvariants in the Monoclinic and Orthorhombic Systems. I. Theoretical Background

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Abstract

Conditional probability distributions are derived for the one-phase structure seminvariant in the presence of anomalous scattering for the monoclinic and orthorhombic systems. The results are presented in a compact tabular form. The applications of these results are discussed in the following paper [Velmurugan, Hauptman & Potter (1989). *Acta Cryst.* **A45**, 163–165].

1. Introduction

Hauptman (1982*a*) generalized the traditional direct methods formalism to the case that the atomic scattering factors are arbitrary complex-valued functions of $(\sin\theta)/\lambda$, thus including the special case that one or more anomalous scatterers are present. Using the neighborhood concept, he briefly summarized for the space group $P1$ the probabilistic theory of the two- and three-phase structure invariants. The results led to unique estimates of the two- and three-phase structure invariants and, at least with respect to the three-phase structure invariant, the estimates were in the range $-\pi$ to π. The results clearly imply that the fusion of the traditional techniques of direct methods with anomalous dispersion will facilitate the solution of those crystal structures which contain one or more anomalous scatterers. The method is here extended to the probabilistic theory of the one-phase structure seminvariant for the monoclinic and orthorhombic systems. Although the distributions derived here are, strictly speaking, bimodal, *i.e.* have two maxima, only those distributions are useful for which the variances are small, which is to say that one maximum is dominant. Hence, as in the case of the two- and three-phase structure invariants, these distributions yield unique estimates for the one-phase structure seminvariants in the favorable cases that the variances are small. Applications are described in the following paper (Velmurugan, Hauptman & Potter, 1989).

In the presence of anomalous scatterers the normalized structure factor

$$E_{\mathbf{H}} = |E_{\mathbf{H}}| \exp(i\varphi_{\mathbf{H}}) \tag{1.1}$$

is defined by

$$E_{\mathbf{H}} = \alpha_{\mathbf{H}}^{-1/2} \sum_{j=1}^{N} f_{j\mathbf{H}} \exp(2\pi i \mathbf{H}\,.\,\mathbf{r}_j) \tag{1.2}$$

$$= \alpha_{\mathbf{H}}^{-1/2} \sum_{j=1}^{N} |f_{j\mathbf{H}}| \exp[i(\delta_{j\mathbf{H}} + 2\pi\mathbf{H}\,.\,\mathbf{r}_j)] \tag{1.3}$$

where

$$f_{j\mathbf{H}} = |f_{j\mathbf{H}}| \exp(i\delta_{j\mathbf{H}}) \tag{1.4}$$

is the (in general complex) atomic scattering factor (a function of $|\mathbf{H}|$ as well as of j) of the atom labeled j, $\mathbf{r}_j$ is its position vector, N is the number of atoms in the unit cell, and

$$\alpha_{\mathbf{H}} = \sum_{j=1}^{N} |f_{j\mathbf{H}}|^2. \tag{1.5}$$

For a normal scatterer, $\delta_{j\mathbf{H}} = 0$; for an atom which scatters anomalously, $\delta_{j\mathbf{H}} \neq 0$. Owing to the presence of the anomalous scatterers, the atomic scattering factors $f_{j\mathbf{H}}$, as functions of $(\sin\theta)/\lambda$, do not have the same shape for different atoms, even approximately. Hence the dependence of the $f_{j\mathbf{H}}$ on $|\mathbf{H}|$ cannot be ignored, in contrast to the usual practice when anomalous scatterers are not present. For this reason the subscript $\mathbf{H}$ is not suppressed in the symbols $f_{j\mathbf{H}}$ and $\alpha_{\mathbf{H}}$ [see (1.5)].

Monoclinic system

*Space group P*2, *b as unique axis.* In the space group $P2$, the single phases which are structure seminvariants are of the form $S = \varphi_{2h,0,2l}$. One embeds the one-phase structure seminvariant S in the three-phase structure invariant T, an extension of the seminvariant S:

$$T = \varphi_{2h,0,2l} + \varphi_{\bar{h}k\bar{l}} + \varphi_{\bar{h}\bar{k}\bar{l}} \tag{1.6}$$

where k is an arbitrary integer. The first neighborhood of T consists of the three magnitudes $|E_{2h,0,2l}|$, $|E_{\bar{h}k\bar{l}}|$, and $|E_{\bar{h}\bar{k}\bar{l}}|$. The first neighborhood of S is then defined

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to consist of the same three magnitudes $|E_{2h,0,2l}|$, $|E_{\bar{h}k\bar{l}}|$ and $|E_{\bar{h}\bar{k}\bar{l}}|$. It should be noted that in (1.6) k is arbitrary; hence there are many extensions of S and therefore many first neighborhoods of S.

In the present paper the joint probability distribution of the three structure factors whose magnitudes constitute a neighborhood of S is first derived, for the space group $P2$, when anomalous scatterers are present (see Appendix). This distribution leads directly to the major result of this paper, equation (3.2), the conditional probability distribution of the one-phase structure seminvariant $\varphi_{2h,0,2l}$, assuming as known the three magnitudes in any of its first neighborhoods. Owing to their extreme length, details of the derivations are omitted altogether. For the space group $P2_1$, only the final results are given.

In the orthorhombic system three kinds of one-phase structure seminvariants, namely $\varphi_{0,2k,2l}$, $\varphi_{2h,0,2l}$ and $\varphi_{2h,2k,0}$ exist. Clearly, final results for only one kind need to be derived; the others are obtained by cyclic permutation of the indices.

2. The joint probability distribution of the three structure factors $E_{2h,0,2l}$, $E_{\bar{h}k\bar{l}}$ and $E_{\bar{h}\bar{k}\bar{l}}$

The first neighborhood of the one-phase structure seminvariant $\varphi_{2h,0,2l}$ has been defined to consist of the three magnitudes:

$$|E_{2h,0,2l}|, \quad |E_{\bar{h}k\bar{l}}|, \quad \text{and } |E_{\bar{h}\bar{k}\bar{l}}|. \qquad (2.1)$$

The atomic position vectors $\mathbf{r}_j$'s and the integer k are fixed; the ordered pair of integers (h, l) is assumed to be the primitive random variable. The phases of the associated structure factors are denoted by

$$\varphi_{2h,0,2l}, \quad \varphi_{\bar{h}k\bar{l}}, \quad \varphi_{\bar{h}\bar{k}\bar{l}}. \qquad (2.2)$$

For space group $P2$, we introduce the abbreviations

$$f_{j\,2h,0,2l} = f_j; \quad \delta_j = \delta_{j\,2h,0,2l}$$
$$f_{j\bar{h}k\bar{l}} (= f_{j\mathbf{K}}) = f_{j\bar{h}\bar{k}\bar{l}} (= f_{j\bar{\mathbf{K}}})$$
$$\delta_{j\mathbf{K}} = \delta_{j\bar{\mathbf{K}}} \qquad (2.3)$$

$$\alpha = \sum_{j=1}^{N} |f_j|^2, \quad \alpha_{\mathbf{K}} = \sum_{j=1}^{N} |f_{j\mathbf{K}}|^2. \qquad (2.4)$$

Our major goal is to determine the conditional probability distribution of the one-phase structure seminvariant $\varphi_{2h,0,2l}$, given the three magnitudes (2.1) in its first neighborhood, which, in the favorable case that the variance of the distribution happens to be small, yields a reliable estimate of the seminvariant (the neighborhood principle).

2.1. *Notation and definitions*

Define C, S, C_2 and S_2 by means of

$$C = \alpha^{-1} \sum_{j=1}^{N} |f_j|^2 \cos 2\delta_j \qquad (2.5)$$

$$S = \alpha^{-1} \sum_{j=1}^{N} |f_j|^2 \sin 2\delta_j \qquad (2.6)$$

$$C_2 = \alpha_{\mathbf{K}}^{-1} \sum_{j=1}^{N} |f_{j\mathbf{K}}|^2 \cos 2\delta_{j\mathbf{K}} \qquad (2.7)$$

$$S_2 = \alpha_{\mathbf{K}}^{-1} \sum_{j=1}^{N} |f_{j\mathbf{K}}|^2 \sin 2\delta_{j\mathbf{K}} \qquad (2.8)$$

where f_j, δ_j, f_{jK}, δ_{jK}, α and $\alpha_{\mathbf{K}}$ are defined in (2.3) and (2.4).

Define X and ε by means of

$$X \cos \varepsilon = C, \quad X \sin \varepsilon = -S \qquad (2.9)$$

$$X = (C^2 + S^2)^{1/2}, \quad \tan \varepsilon = -S/C. \qquad (2.10)$$

In a similar way X_2 and ε_2 are defined by

$$X_2 \cos \varepsilon_2 = C_2, \quad X_2 \sin \varepsilon_2 = -S_2 \qquad (2.11)$$

$$\tan \varepsilon_2 = -S_2/C_2, \quad X_2 = (C_2^2 + S_2^2)^{1/2}. \qquad (2.12)$$

Next, make the definitions

$$C_1 = \alpha^{-1/2} \alpha_{\mathbf{K}}^{-1} \sum_{j=1}^{N} |f_j f_{j\mathbf{K}}^2| \cos \delta_j \qquad (2.13)$$

$$S_1 = \alpha^{-1/2} \alpha_{\mathbf{K}}^{-1} \sum_{j=1}^{N} |f_j f_{j\mathbf{K}}^2| \sin \delta_j \qquad (2.14)$$

$$C_{12} = \alpha^{-1/2} \alpha_{\mathbf{K}}^{-1} \sum_{j=1}^{N} |f_j f_{j\mathbf{K}}^2| \cos (\delta_j + 2\delta_{j\mathbf{K}}) \qquad (2.15)$$

$$S_{12} = \alpha^{-1/2} \alpha_{\mathbf{K}}^{-1} \sum_{j=1}^{N} |f_j f_{j\mathbf{K}}^2| \sin (\delta_j + 2\delta_{j\mathbf{K}}) \qquad (2.16)$$

$$C_{\bar{1}2} = \alpha^{-1/2} \alpha_{\mathbf{K}}^{-1} \sum_{j=1}^{N} |f_j f_{j\mathbf{K}}^2| \cos (-\delta_j + 2\delta_{j\mathbf{K}}) \qquad (2.17)$$

$$S_{\bar{1}2} = \alpha^{-1/2} \alpha_{\mathbf{K}}^{-1} \sum_{j=1}^{N} |f_j f_{j\mathbf{K}}^2| \sin (-\delta_j + 2\delta_{j\mathbf{K}}). \qquad (2.18)$$

Then X_1, ε_1, X_{12}, ε_{12}, $X_{\bar{1}2}$ and $\varepsilon_{\bar{1}2}$ are defined by the following equations:

$$X_1 \cos \varepsilon_1 = C_1, \quad X_1 \sin \varepsilon_1 = -S_1 \qquad (2.19)$$

$$\tan \varepsilon_1 = -S_1/C_1, \quad X_1 = (C_1^2 + S_1^2)^{1/2} \qquad (2.20)$$

$$X_{12} \cos \varepsilon_{12} = C_{12}, \quad X_{12} \sin \varepsilon_{12} = -S_{12} \qquad (2.21)$$

$$\tan \varepsilon_{12} = -S_{12}/C_{12}, \quad X_{12} = (C_{12}^2 + S_{12}^2)^{1/2} \qquad (2.22)$$

$$X_{\bar{1}2} \cos \varepsilon_{\bar{1}2} = C_{\bar{1}2}, \quad X_{\bar{1}2} \sin \varepsilon_{\bar{1}2} = -S_{\bar{1}2} \qquad (2.23)$$

$$\tan \varepsilon_{\bar{1}2} = -S_{\bar{1}2}/C_{\bar{1}2}, \quad X_{\bar{1}2} = (C_{\bar{1}2}^2 + S_{\bar{1}2}^2)^{1/2}. \qquad (2.24)$$

Following the procedure described in the Appendix we finally arrive at the joint probability distribution [see equation (*A*.4)] of the three structure factors $E_{2h,0,2l}$, $E_{\bar{h}k\bar{l}}$, $E_{\bar{h}\bar{k}\bar{l}}$ as

$$P \simeq (RR_{\mathbf{K}}\bar{R}_{\mathbf{K}}/\pi^3)\exp[-(R^2+R_{\mathbf{K}}^2+\bar{R}_{\mathbf{K}}^2)]$$
$$\times\exp[XR^2\cos(2\Phi+\varepsilon)$$
$$+2X_1R(R_{\mathbf{K}}^2+\bar{R}_{\mathbf{K}}^2-2)\cos(\Phi+\varepsilon_1)]$$
$$\times\exp[2X_2R_{\mathbf{K}}\bar{R}_{\mathbf{K}}\cos(\Phi_{\mathbf{K}}+\bar{\Phi}_{\mathbf{K}}+\varepsilon_2)$$
$$+2X_{12}RR_{\mathbf{K}}\bar{R}_{\mathbf{K}}\cos(\Phi_{\mathbf{K}}+\bar{\Phi}_{\mathbf{K}}+\Phi+\varepsilon_{12})$$
$$+2X_{\bar{1}2}RR_{\mathbf{K}}\bar{R}_{\mathbf{K}}\cos(\Phi_{\mathbf{K}}+\bar{\Phi}_{\mathbf{K}}-\Phi+\varepsilon_{\bar{1}2})]. \quad (2.25)$$

3. Conditional probability distribution of the one-phase structure seminvariant $\varphi_{2h,0,2l}$ (=S) given the three magnitudes $|E_{2h,0,2l}|$, $|E_{\bar{h}k\bar{l}}|$ and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood: space group $P2$

Refer to § 2 for the probabilistic background. The conditional probability distribution of S assuming as known the three magnitudes (2.1) in its first neighborhood is denoted by

$$P(\Phi|R, R_{\mathbf{K}}, \bar{R}_{\mathbf{K}}). \quad (3.1)$$

Then $P(\Phi|R, R_{\mathbf{K}}, \bar{R}_{\mathbf{K}})$ is obtained from (A.4) of the Appendix by fixing R, $R_{\mathbf{K}}$ and $\bar{R}_{\mathbf{K}}$ in accordance with (2.1) and integrating P [equation (A.4)] with respect to $\Phi_{\mathbf{K}}$ and $\bar{\Phi}_{\mathbf{K}}$ between the limits 0 and 2π, and multiplying by a suitable normalizing parameter.

The final formula, the major result of this paper, is simply

$$P(\Phi|R, R_{\mathbf{K}}, \bar{R}_{\mathbf{K}}) = (1/M)\exp[a\cos\Phi+b\cos 2\Phi$$
$$+c'\sin\Phi+d\sin 2\Phi]$$
$$\times I_0[e+A\cos\Phi+B\cos 2\Phi$$
$$+C'\sin\Phi+D\sin 2\Phi]^{1/2} \quad (3.2)$$

where M is a suitable normalizing constant, I_0 is the modified Bessel function and

$$a = 2R(R_{\mathbf{K}}^2+\bar{R}_{\mathbf{K}}^2-2)C_1$$
$$b = R^2C$$
$$c' = 2R(R_{\mathbf{K}}^2+\bar{R}_{\mathbf{K}}^2-2)S_1$$
$$d = R^2S$$
$$e = 4R_{\mathbf{K}}^2\bar{R}_{\mathbf{K}}^2[(C_2^2+S_2^2)$$
$$+R^2(C_{12}^2+C_{\bar{1}2}^2+S_{12}^2+S_{\bar{1}2}^2)] \quad (3.3)$$
$$A = 8RR_{\mathbf{K}}^2\bar{R}_{\mathbf{K}}^2[C_2(C_{12}+C_{12})+S_2(S_{12}+S_{\bar{1}2})]$$
$$B = 8R^2R_{\mathbf{K}}^2\bar{R}_{\mathbf{K}}^2[C_{12}C_{\bar{1}2}+S_{12}S_{\bar{1}2}]$$
$$C' = 8RR_{\mathbf{K}}^2\bar{R}_{\mathbf{K}}^2[C_2(S_{12}-S_{\bar{1}2})-S_2(C_{12}-C_{\bar{1}2})]$$
$$D = 8R^2R_{\mathbf{K}}^2\bar{R}_{\mathbf{K}}^2(S_{12}C_{\bar{1}2}-C_{12}S_{\bar{1}2}).$$

4. Conditional probability distribution, $P(\Phi|R, R_{\mathbf{K}}, \bar{R}_{\mathbf{K}})$, of $\varphi_{2h,0,2l}$, given the three magnitudes $|E_{2h,0,2l}|$, $|E_{\bar{h}k\bar{l}}|$, $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood, for space group $P2_1$

Following the same steps as for space group $P2$, we obtain the desired conditional probability distribution,

$$P(\Phi|R, R_{\mathbf{K}}, \bar{R}_{\mathbf{K}}) = (1/M')\exp[a'\cos\Phi+b\cos 2\Phi$$
$$+c_1'\sin\Phi+d\sin 2\Phi]$$
$$\times I_0[e+A'\cos\Phi+B\cos\Phi$$
$$+C_1'\sin\Phi+D\sin 2\Phi]^{1/2} \quad (4.1)$$

where M' is the suitable normalizing constant and

$$a' = (-1)^k a$$
$$c_1' = (-1)^k c'$$
$$A' = (-1)^k A \quad (4.2)$$
$$C_1' = (-1)^k C'.$$

The symbols have the same meaning as in (3.3).

5. Orthorhombic system: space group $P222$

In the orthorhombic space groups we have three kinds of one-phase structure seminvariants, $\varphi_{0,2k,2l}$, $\varphi_{2h,0,2l}$ and $\varphi_{2h,2k,0}$, each having three magnitudes in its first neighborhood.

In analogy with the monoclinic system we will first summarize the results for the one-phase structure seminvariant $\varphi_{2h,0,2l}$.

5.1. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{K}}, \bar{R}_{\mathbf{K}})$ of the one-phase structure seminvariant $\varphi_{2h,0,2l}$, given the three magnitudes $|E_{2h,0,2l}|$, $|E_{\bar{h}k\bar{l}}|$ and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

The first neighborhood of the one-phase structure seminvariant $\varphi_{2h,0,2l}$ consists of the three magnitudes

$$|E_{2h,0,2l}| = R, |E_{\bar{h}k\bar{l}}| = R_{\mathbf{K}} \text{ and } |E_{\bar{h}\bar{k}\bar{l}}| = \bar{R}_{\mathbf{K}}. \quad (5.1)$$

The expression for q_j [equation (A.3) of the Appendix] has to be modified to incorporate the space-group symmetry information for the space group $P222$. Proceeding along similar lines as in § 2 one arrives at the conditional probability distribution of the one-phase structure seminvariant $\varphi_{2h,0,2l}$ for space group $P222$. This turns out to be the same as that for the space group $P2$ [see (3.2)].

However, we have two more one-phase structure seminvariants, namely, $\varphi_{2h,2k,0}$ and $\varphi_{0,2k,2l}$.

By suitably modifying the expression for q_j [see equation (A.3)] and proceeding along similar lines as in § 2 one arrives at the following final results for the conditional probability distribution of the one-phase structure seminvariants $\varphi_{2h,2k,0}$ and $\varphi_{0,2k,2l}$.

5.2. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{L}}, \bar{R}_{\mathbf{L}})$ of the one-phase structure seminvariant $\varphi_{2h,2k,0}$ given the three magnitudes $|E_{2h,2k,0}|$, $|E_{\bar{h}\bar{k}l}|$, $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

Equation (3.2) is still valid with the following modified notations:

(i) $f_j = f_{j\,2h,2k,0}$.
(ii) $R = |E_{2h,2k,0}|$, $R_{\mathbf{L}} = |E_{\bar{h}\bar{k}l}|$, $\bar{R}_{\mathbf{L}} = |E_{\bar{h}\bar{k}\bar{l}}|$.
(iii) In (3.3), replace the subscript **K** by **L**.
(iv) On the right-hand side of (2.7), (2.8) and (2.13)–(2.18) replace the subscript **K** by **L**.

5.3. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{H}}, \bar{R}_{\mathbf{H}})$ of the one-phase structure seminvariant $\varphi_{0,2k,2l}$ given the three magnitudes $|E_{0,2k,2l}|$, $|E_{h\bar{k}\bar{l}}|$, $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

Equation (3.2) is still valid with the following modified notations:

(i) $f_j = f_{j\,0,2k,2l}$.
(ii) $R = |E_{0,2k,2l}|$, $R_{\mathbf{H}} = |E_{h\bar{k}\bar{l}}|$ and $\bar{R}_{\mathbf{H}} = |E_{\bar{h}\bar{k}\bar{l}}|$.
(iii) In (3.3), replace the subscript **K** by **H**.
(iv) On the right-hand side of (2.7), (2.8), and (2.13)–(2.18) replace the subscript **K** by **H**.

6. Space group $P222_1$

6.1. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{K}}, \bar{R}_{\mathbf{K}})$ of the one-phase structure seminvariant $\varphi_{2h,0,2l}$, given the three magnitudes $|E_{2h,0,2l}|$, $|E_{\bar{h}k\bar{l}}|$, and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

The steps to be followed are identical to those described in § 5.1 except that the expression for q_j [see equation (A.3)] must now be modified. The conditional probability distribution is the same as in (4.1) except that, in (4.2), the term $(-1)^k$ is to be replaced by $(-1)^l$.

6.2. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{L}}, \bar{R}_{\mathbf{L}})$ of the one-phase structure seminvariant $\varphi_{2h,2k,0}$, given the three magnitudes $|E_{2h,2k,0}|$, $|E_{\bar{h}\bar{k}l}|$, and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

The expression for q_j is to be modified. To arrive at the conditional probability distribution, follow steps (i)–(iv) of § 5.2. In step (iii) include the term $(-1)^l$ as a multiplier on the right-hand side of (3.3) for the definition of a, c', A and C'.

6.3. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{H}}, \bar{R}_{\mathbf{H}})$ of the one-phase structure seminvariant $\varphi_{0,2k,2l}$ given the three magnitudes $|E_{0,2k,2l}|$, $|E_{h\bar{k}\bar{l}}|$, and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

The conditional probability distribution is the same as in § 5.3.

7. Space group $P2_12_12$

7.1. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{K}}, \bar{R}_{\mathbf{K}})$ of the one-phase structure seminvariant $\varphi_{2h,0,2l}$, given the three magnitudes $|E_{2h,0,2l}|$, $|E_{\bar{h}k\bar{l}}|$, and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

For the conditional probability distribution, refer to § 4. In equation (4.2) replace $(-1)^k$ by $(-1)^{h+k}$.

7.2. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{L}}, \bar{R}_{\mathbf{L}})$ of the one-phase structure seminvariant $\varphi_{2h,2k,0}$, given the three magnitudes $|E_{2h,2k,0}|$, $|E_{\bar{h}\bar{k}l}|$, and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

The conditional probability distribution is the same as in § 5.2.

7.3. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{H}}, \bar{R}_{\mathbf{H}})$ of the one-phase structure seminvariant $\varphi_{0,2k,2l}$, given the three magnitudes $|E_{0,2k,2l}|$, $|E_{h\bar{k}\bar{l}}|$, and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

Steps (i)–(iv) of § 5.3 have first to be followed. In step (iii), the term $(-1)^{h+k}$ has to be included as a multiplier on the right-hand side of (3.3) for the definition of a, c', A and C'.

8. Space group $P2_12_12_1$

8.1. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{K}}, \bar{R}_{\mathbf{K}})$ of the one-phase structure seminvariant $\varphi_{2h,0,2l}$, given the three magnitudes $|E_{2h,0,2l}|$, $|E_{\bar{h}k\bar{l}}|$, and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

Refer to § 4. In equation (4.2), replace $(-1)^k$ by $(-1)^{k+l}$.

8.2. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{L}}, \bar{R}_{\mathbf{L}})$ of the one-phase structure seminvariant $\varphi_{2h,2k,0}$, given the three magnitudes $|E_{2h,2k,0}|$, $|E_{\bar{h}\bar{k}l}|$, and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

Steps (i)–(iv) of § 5.2 have first to be followed. In step (iii), the term $(-1)^{l+h}$ has to be included as a multiplier on the right-hand side of (3.3) for the definition of a, c', A and C'.

8.3. *The conditional probability distribution $P(\Phi|R, R_{\mathbf{H}}, \bar{R}_{\mathbf{H}})$ of the one-phase structure seminvariant $\varphi_{0,2k,2l}$, given the three magnitudes $|E_{0,2k,2l}|$, $|E_{h\bar{k}\bar{l}}|$, and $|E_{\bar{h}\bar{k}\bar{l}}|$ in its first neighborhood*

The conditional probability distribution is the same as in § 7.3.

9. Concluding remarks

In general, the conditional probability distribution function for the one-phase structure seminvariant in the monoclinic and orthorhombic systems can be written in a compact form as follows:

$$P(\Phi|R, R_1, R_2) = (1/M) \exp[a\cos\Phi + b\cos 2\Phi + c'\sin\Phi + d\sin 2\Phi] \times I_0(e + A\cos\Phi + B\cos 2\Phi + C'\sin\Phi + D\sin 2\Phi)^{1/2} \quad (9.1)$$

where

$$a = P[2R(R_1^2 + R_2^2 - 2)C_1]$$
$$b = R^2 C$$
$$c' = P[2R(R_1^2 + R_2^2 - 2)S_1]$$
$$d = R^2 S$$
$$e = 4R_1^2 R_2^2[(C_2^2 + S_2^2) + R^2(C_{12}^2 + C_{\bar{1}2}^2 + S_{12}^2 + S_{\bar{1}2}^2)] \quad (9.2)$$
$$A = P\{8RR_1^2R_2^2[C_2(C_{12} + C_{\bar{1}2}) + S_2(S_{12} + S_{\bar{1}2})]\}$$
$$B = 8R^2R_1^2R_2^2(C_{12}C_{\bar{1}2} + S_{12}S_{\bar{1}2})$$
$$C' = P\{8RR_1^2R_2^2[C_2(S_{12} - S_{\bar{1}2}) - S_2(C_{12} - C_{\bar{1}2})]\}$$
$$D = 8R^2R_1^2R_2^2(S_{12}C_{\bar{1}2} - C_{12}S_{\bar{1}2});$$

$$C = (1/\alpha)\sum_{j=1}^{N}|f_j|^2\cos 2\delta_j$$
$$S = (1/\alpha)\sum_{j=1}^{N}|f_j|^2\sin 2\delta_j$$
$$C_2 = (1/\alpha_1)\sum_{j=1}^{N}|f_{j1}|^2\cos 2\delta_{j1}$$
$$S_2 = (1/\alpha_1)\sum_{j=1}^{N}|f_{j1}|^2\sin 2\delta_{j1}$$
$$C_1 = \alpha^{-1/2}\alpha_1^{-1}\sum_{j=1}^{N}|f_jf_{j1}^2|\cos\delta_j$$
$$S_1 = \alpha^{-1/2}\alpha_1^{-1}\sum_{j=1}^{N}|f_jf_{j1}^2|\sin\delta_j \quad (9.3)$$
$$C_{12} = \alpha^{-1/2}\alpha_1^{-1}\sum_{j=1}^{N}|f_jf_{j1}^2|\cos(\delta_j + 2\delta_{j1})$$
$$S_{12} = \alpha^{-1/2}\alpha_1^{-1}\sum_{j=1}^{N}|f_jf_{j1}^2|\sin(\delta_j + 2\delta_{j1})$$
$$C_{\bar{1}2} = \alpha^{-1/2}\alpha_1^{-1}\sum_{j=1}^{N}|f_jf_{j1}^2|\cos(-\delta_j + 2\delta_{j1})$$
$$S_{\bar{1}2} = \alpha^{-1/2}\alpha_1^{-1}\sum_{j=1}^{N}|f_jf_{j1}^2|\sin(-\delta_j + 2\delta_{j1}).$$

The factor P is listed in Table 1 for the various space groups.

It is seen from (9.1) that the conditional probability distribution function is a product of two functions, namely the exponential function and the modified Bessel function, the arguments of which are trigonometric functions of the phase. The probability distributions are in general not unimodal. However, in those favorable cases when one of the two maxima is substantially larger than the other the distribution yields a unique estimate of the structure seminvariant. Of the many distributions for each one-phase structure seminvariant, the best estimate is clearly the one having minimum variance. For each structure seminvariant the mode yields the estimate.

Table 1. *Parameters occurring in equations* (9.1)-(9.3) *for the conditional probability distribution of the one-phase structure seminvariant in the monoclinic and orthorhombic systems*

	$\Phi_{2h,0,2l}$	$\Phi_{2h,2k,0}$	$\Phi_{0,2k,2l}$
	$R = \lvert E_{2h,0,2l}\rvert$	$R = \lvert E_{2h,2k,0}\rvert$	$R = \lvert E_{0,2k,2l}\rvert$
	$R_1 = \lvert E_{\bar{h}k\bar{l}}\rvert$	$R_2 = \lvert E_{\bar{h}\bar{k}l}\rvert$	$R_1 = \lvert E_{h\bar{k}\bar{l}}\rvert$
	$R_2 = \lvert E_{\bar{h}\bar{k}\bar{l}}\rvert$	$R_2 = \lvert E_{\bar{h}k\bar{l}}\rvert$	$R_2 = \lvert E_{\bar{h}k\bar{l}}\rvert$
	$f_j = f_{j2h,0,2l} = \lvert f_j\rvert e^{i\delta_j}$	$f_j = f_{j2h,2k,0}$	$f_j = f_{j0,2k,2l}$
	$f_{j1} = f_{j\bar{h}k\bar{l}} = f_{j\mathbf{K}} = \lvert f_{j1}\rvert e^{i\delta_{j1}}$	$f_{j1} = f_{j\bar{h}\bar{k}l} = f_{j\mathbf{L}}$	$f_{j1} = f_{jh\bar{k}\bar{l}} = f_{j\mathbf{H}}$
	$\alpha = \sum_{j=1}^{N}\lvert f_j\rvert^2$	$\alpha = \sum_{j=1}^{N}\lvert f_j\rvert^2$	$\alpha = \sum_{j=1}^{N}\lvert f_j\rvert^2$
	$\alpha_1 = \sum_{j=1}^{N}\lvert f_{j1}\rvert^2$	$\alpha_1 = \sum_{j=1}^{N}\lvert f_{j1}\rvert^2$	$\alpha_1 = \sum_{j=1}^{N}\lvert f_{j1}\rvert^2$
Space group	P	P	P
$P2$	1		
$P2_1$	$(-1)^k$		
$P222$	1	1	1
$P222_1$	$(-1)^l$	$(-1)^l$	1
$P2_12_12$	$(-1)^{h+k}$	1	$(-1)^{h+k}$
$P2_12_12_1$	$(-1)^{k+1}$	$(-1)^{l+h}$	$(-1)^{h+k}$

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APPENDIX

The joint probability distribution of the three structure factors $E_{2h,0,2l}$, $E_{\bar{h}k\bar{l}}$ and $E_{\bar{h}\bar{k}\bar{l}}$ for the space group $P2$ when anomalous scatterers are present

In order to derive the conditional probability distribution (A.4) it is necessary first to obtain the joint probability distribution

$$P = P(R, R_{\mathbf{K}}, \bar{R}_{\mathbf{K}}; \Phi, \Phi_{\mathbf{K}}, \bar{\Phi}_{\mathbf{K}}) \quad (A.1)$$

of the three magnitudes $|E_{2h,0,2l}|$, $|E_{\bar{h}k\bar{l}}|$, $|E_{\bar{h}\bar{k}\bar{l}}|$ and the phases $\varphi_{2h,0,2l}$, $\varphi_{\bar{h}k\bar{l}}$ and $\varphi_{\bar{h}\bar{k}\bar{l}}$ [refer to (2.1) and (2.2) respectively] of the three structure factors whose magnitudes constitute the first neighborhood of the one-phase structure seminvariant $\varphi_{2h,0,2l}$. The atomic position vectors $\mathbf{r}_j$ and the integers k are fixed; the ordered pair of integers (h, l) is assumed to be the primitive random variable. Then, following the early work of Karle & Hauptman (1958), P is given by the sixfold integral

$$P=[RR_{\mathbf{K}}\bar{R}_{\mathbf{K}}/(2\pi)^6]\int\limits_{0}^{\infty}\limits_{\rho_1,\rho_2,\rho_3}\int\limits_{0}^{2\pi}\limits_{\theta_1,\theta_2,\theta_3}\rho_1\rho_2\rho_3 \times\exp\{-i[R\rho_1\cos(\theta_1-\Phi) + R_{\mathbf{K}}\rho_2\cos(\theta_2-\Phi_{\mathbf{K}})+\bar{R}_{\mathbf{K}}\rho_3\cos(\theta_3-\bar{\Phi}_{\mathbf{K}})]\} \times\prod_{j=1}^{N/2} q_j\,d\rho_1\,d\rho_2\,d\rho_3\,d\theta_1\,d\theta_2\,d\theta_3 \quad (A.2)$$

where

$$q_j=\langle\exp[\![(i|f_j|/\alpha^{1/2}) \times\{\rho_1\cos[\delta_j+4\pi(hx_j+lz_j)-\theta_1] + \rho_1\cos[\delta_j+4\pi(-hx_j-lz_j)-\theta_1]\}+(i|f_{j\mathbf{K}}|/\alpha_{\mathbf{K}}^{1/2}) \times\{\rho_2\cos[\delta_{j\mathbf{K}}+2\pi(-hx_j+ky_j-lz_j)-\theta_2] + \rho_2\cos[\delta_{j\mathbf{K}}+2\pi(hx_j+ky_j+lz_j)-\theta_2] + \rho_3\cos[\delta_{j\mathbf{K}}+2\pi(-hx_j-ky_j-lz_j)-\theta_3] + \rho_3\cos[\delta_{j\mathbf{K}}+2\pi(hx_j-ky_j+lz_j)-\theta_3]\}]\!]\rangle_{h,l}. \quad (A.3)$$

The mathematical formalism devised and streamlined in recent years to evaluate q_j, $\prod_{j=1}^{N/2} q_j$ and the sixfold integral (*A*.2) has been described elsewhere (*e.g.* Hauptman, 1975, 1982*a*, *b*). This work, suitably modified to incorporate the space-group symmetries and to accommodate the anomalous scatterers, finally yields, after lengthy analysis, the remarkably simple formula

$$P\simeq(RR_{\mathbf{K}}\bar{R}_{\mathbf{K}}/\pi^3)\exp[-(R^2+R_{\mathbf{K}}^2+\bar{R}_{\mathbf{K}}^2)] \times\exp[XR^2\cos(2\Phi+\varepsilon) +2X_1R(R_{\mathbf{K}}^2+\bar{R}_{\mathbf{K}}^2-2)\cos(\Phi+\varepsilon_1)] \times\exp[2X_2R_{\mathbf{K}}\bar{R}_{\mathbf{K}}\cos(\Phi_{\mathbf{K}}+\bar{\Phi}_{\mathbf{K}}+\varepsilon_2) +2X_{12}RR_{\mathbf{K}}\bar{R}_{\mathbf{K}}\cos(\Phi_{\mathbf{K}}+\bar{\Phi}_{\mathbf{K}}+\Phi+\varepsilon_{12}) +2X_{\bar{1}2}RR_{\mathbf{K}}\bar{R}_{\mathbf{K}}\cos(\Phi_{\mathbf{K}}+\bar{\Phi}_{\mathbf{K}}-\Phi+\varepsilon_{\bar{1}2})] \quad (A.4)$$

where the parameters X, X_2, X_1, X_{12}, $X_{\bar{1}2}$, ε, ε_1, ε_2, ε_{12} and $\varepsilon_{\bar{1}2}$ are defined in equations (2.9)-(2.24).

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On Integrating the Techniques of Direct Methods with Anomalous Dispersion: the One-Phase Structure Seminvariants in the Monoclinic and Orthorhombic Systems. II. Applications

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Abstract

Applications are considered of the conditional probability distributions of the one-phase structure seminvariants in the monoclinic and orthorhombic systems when anomalous scatterers are present. Test results with error-free data show accurate estimates of seminvariants, the accuracy varying with the complexity of the structure and with the number and strength of the anomalous scatterers.

Introduction

As an extension of the theory of the fusion of traditional direct methods with anomalous dispersion (Hauptman, 1982), the probabilistic theory of the one-phase structure seminvariant for the monoclinic and orthorhombic systems has been described (Velmurugan & Hauptman, 1989). The major result is that the conditional probability distribution of the one-phase structure seminvariant, given the three magnitudes R, R_1 and R_2 in its first neighborhood, has the form

$$P(\Phi|R,R_1,R_2)=(1/M)\exp[a\cos\Phi+b\cos2\Phi +c'\sin\Phi+d\sin2\Phi] \times I_0(e+A\cos\Phi+B\cos2\Phi +C'\sin\Phi+D\sin2\Phi)^{1/2} \quad (1)$$

[see equations (9.1)-(9.3) and Table 1 of Velmurugan & Hauptman (1989)] where Φ is the one-phase structure seminvariant, I_0 is the modified Bessel function,

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