sixfold integral

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

where

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

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

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

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

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

[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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Table 1. *The average magnitudes of the error among the first* 50 *seminvariants for six structures each containing* 186 *atoms in the asymmetric unit*

Number and type of anomalous scatterers in the asymmetric unit	$\langle\|E\|\rangle$	Average magnitude of error (°) $\langle\|\Phi_{true}-\Phi_{est}\|\rangle$
1 S	1·339	72·2
5 S	1·312	61·5
1 I	1·717	6·2
5 I	1·795	2·6
1 U	1·077	2·8
5 U	0·859	1·7

Table 2. *The average magnitudes of the error among the first* 50 *seminvariants for six structures each containing* 300 *atoms in the asymmetric unit*

Number and type of anomalous scatterers in the asymmetric unit	$\langle\|E\|\rangle$	Average magnitude of error (°) $\langle\|\Phi_{true}-\Phi_{est}\|\rangle$
1 S	1·182	43·4
5 S	1·238	54·2
1 I	1·513	9·6
5 I	0·822	8·8
1 U	1·127	8·3
5 U	0·596	1·6

Table 3. *The average magnitudes of the error among the first* 50 *seminvariants for six structures each containing* 404 *atoms in the asymmetric unit*

Number and type of anomalous scatterers in the asymmetric unit	$\langle\|E\|\rangle$	Average magnitude of error (°) $\langle\|\Phi_{true}-\Phi_{est}\|\rangle$
1 S	1·134	64·8
5 S	0·990	72·6
1 I	1·351	20·7
5 I	1·315	13·8
1 U	1·139	8·8
5 U	0·712	1·9

and the parameters M, a, b, ... are expressible in terms of R, R_1, R_2 and the complex-valued atomic scattering factors, presumed to be known.

Applications

The present paper deals mainly with the application of (1) in some test structures. The formula is tested in structures belonging to $P2_1$ and $P2_12_12_1$. Since the results in $P2_1$ are quite similar to those in $P2_12_12_1$, a discussion is given only for those structures in $P2_12_12_1$.

Structures (1)-(3) are made from isoleucinomycin (Pletnev, Galitskii, Smith, Weeks & Duax, 1980) by replacing the H atoms by C atoms. These three structures correspond to the above structure in which five of the light atoms were replaced by five S, five I, and five U atoms, respectively. The number of atoms in the asymmetric unit is 186. The number of molecules in the unit cell is four.

Structures (4)-(9) correspond to structures constructed from insulin. Structures (4)-(6) contain 300 atoms in the asymmetric unit which were obtained by removing some main and side chains from insulin. They contain five S, five I, and five U atoms as anomalous scatterers, respectively. The number of molecules in the unit cell is four. Structures (7)-(9) contain 404 atoms in the asymmetric unit which were obtained by removing some side chains from insulin. They contain five S, five I, and five U atoms as anomalous scatterers, respectively. The number of molecules in the unit cell is four.

The formula (1) was tested in structures (1)-(9). Since there are many first neighborhoods for each seminvariant, only the distribution having the minimum variance was employed. The various structure seminvariants were then arranged in increasing order of their variances. For all the structures, the mode was used to estimate the seminvariant. For each seminvariant, the magnitude of its normalized structure factor and the phase-angle error ($=\Phi_{true}-\Phi_{est}$) in degrees was also computed. Tables 1-3 list the average of the absolute value of the normalized structure factors and also the average magnitude of the phase-angle error in degrees for the first 50 structure seminvariants arranged in increasing order of the variance.

Figs. 1(a)-(i) represent scatter diagrams of the true *vs* estimated one-phase structure seminvariant Φ, for the first 50 seminvariants for structures (1)-(9) respectively, as well as the line $\Phi_{true}=\Phi_{est}$. The number of atoms and the number and type of anomalous scatterers in the asymmetric unit are also marked in each figure.

Discussion

From a study of Tables 1-3, the following conclusions may be made.

(i) In the case of strong anomalous scatterers, increasing the number of anomalous scatterers improves the result.

(ii) Generally speaking, the result is improved if the strength of the anomalous signal is increased.

(iii) In the case of a moderate anomalous scatterer, say S, increasing the number of anomalous scatterers from one to five does not improve the estimate.

From a study of Figs. 1(a)-(i) the following conclusions may be drawn.

(i) For structures having as many as 400 atoms per asymmetric unit, the presence of five or more I or U atoms permits reliable estimates to be made of some 50 phases which are structure seminvariants.

(ii) For structures having more than 186 atoms per asymmetric unit, the presence of five or fewer S atoms does not permit sufficiently reliable estimates of the one-phase structure seminvariants to be made to be useful in the applications.

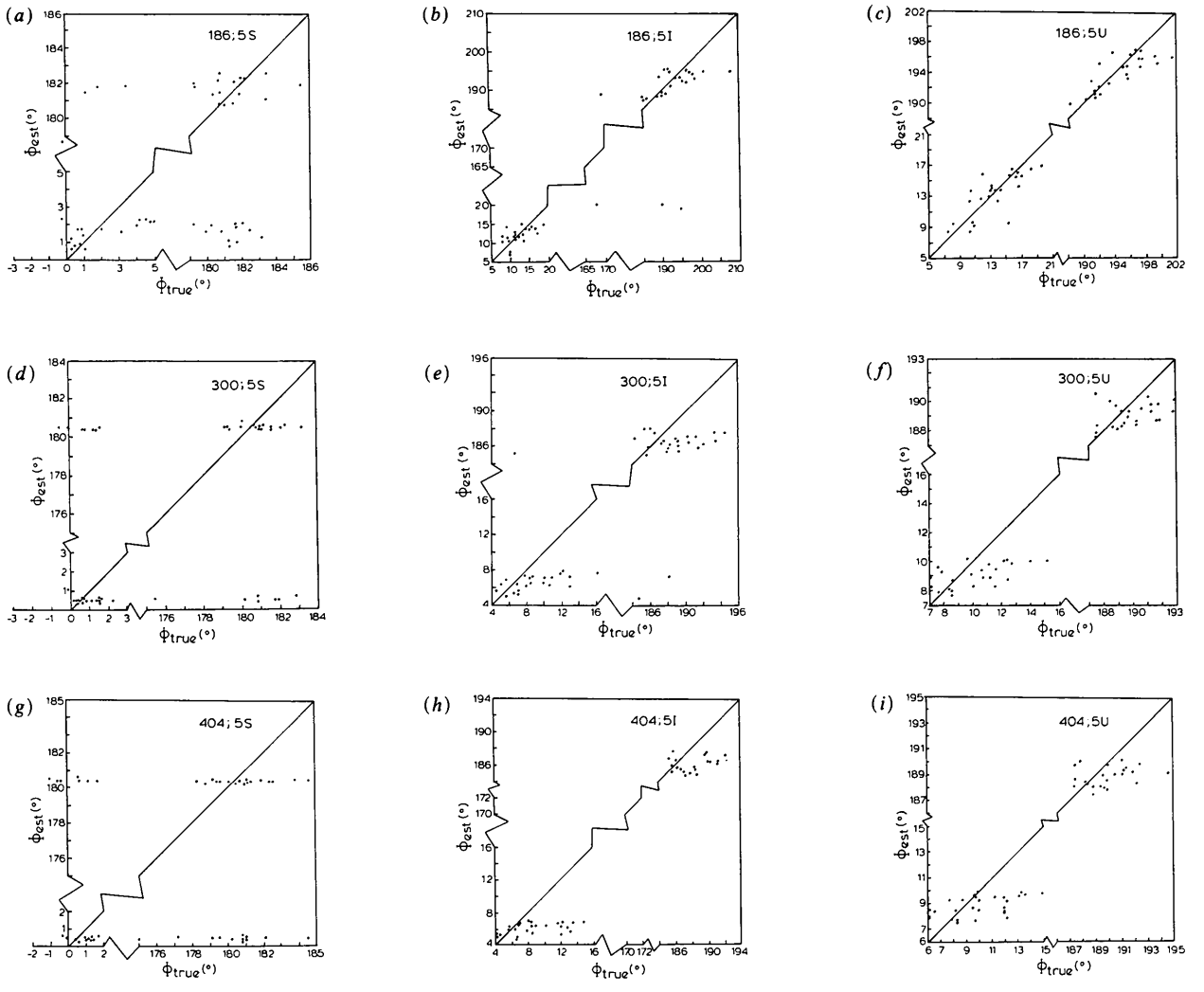

Fig. 1. (*a*)-(*i*) Scatter diagram of Φ_{true} *versus* Φ_{est}, using the first 50 seminvariants, for structures (1) to (9), as well as the line $\Phi_{true} = \Phi_{est}$.

Concluding remarks

Estimates for the one-phase structure seminvariants, taking into account the effect of anomalous scattering, for the monoclinic and orthorhombic systems have been tested with error-free data on some known structures of varying complexities. The results suggest that the ability to estimate reliably substantial numbers of the one-phase structure seminvariants when the anomalous signal is sufficiently strong may find application in the determination of structures containing as many as 400 non-hydrogen atoms in the asymmetric units. These results will clearly serve only to supplement existing techniques. The effect of experimental error will be discussed at a later time.

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