1977), unit-cell parameters and atomic coordinates were refined. The T–O, O–O and T–T distances were set to 1.628, 2.6585 and 3.1053 Å, respectively. Table 3 lists the refinement results including T-atom coordinates, unit cells and R factors. The highest space group for each net is used in the refinement and R varies from 0.01 to 0.004. Unit-cell changes are usually within 15% owing to geometrical distortion. These refined results can be used for powder-pattern calculation and comparison with unknown phases.

Concluding remarks

Four nets in this family occur in known mineral structures. Although the other nets are possible candidates for zeolite phases with as yet unsolved structures, no likely matches turned up in a comparison of theoretical and observed cell dimensions and space groups. Examination of twinned crystals of the four zeolite families should give clues to the possibility of finding new minerals with bru-based nets. Presumably, the connectivity across the twin contact might match one of these in the theoretical nets. Because all the theoretical nets contain odd-number rings, alternation of elements in the T sites, as in aluminophosphates, is not possible.

This study extends the enumeration of nets based on the bru polyhedral subunit and provides a topological description of each net. Further studies on selected polyhedral units will yield many more theoretical 3D nets of both mathematical and practical value.

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References

Akporiaye, D. E. & Price, G. D. (1989). *Zeolites*, **9**, 23–32.
Alberti, A. (1979). *Am. Mineral.* **64**, 1188–1198.
Andries, K. & Smith, J. V. (1992). Ninth International Zeolite Conference, Extended Abstracts and Program, RP190, RP195, RP209.
Andries, K. & Smith, J. V. (1993). *Proc. R. Soc. London*. In the press.
Baerlocher, C., Hepp, A. & Meier, W. M. (1977). *DLS-76, a Program for the Simulation of Crystal Structures by Geometrical Refinement*. ETH, Zürich.
Deem, M. W. & Newsam, J. M. (1989). *Nature (London)*, **342**, 260–262.
Kirchner, R. M. & McGuire, N. K. (1992). Ninth International Zeolite Conference, Extended Abstracts and Program, RP214.
Meier, W. M. (1968). *Molecular Sieves*, pp. 10–27. London: Society of the Chemical Industry.
O'Keeffe, M. (1991). *Z. Kristallogr.* **196**, 21–37.
Pluth, J. J. & Smith, J. V. (1990). *Am. Mineral.* **75**, 501–507.
Pluth, J. J. & Smith, J. V. (1992). Ninth International Zeolite Conference, Extended Abstracts and Program, RP189, RP208.
Smith, J. V. (1978). *Am. Mineral.* **63**, 960–969.
Smith, J. V. (1988). *Chem. Rev.* **88**, 149–182.
Smith, J. V. (1989). *Zeolites: Facts, Figures, Future*, edited by P. A. Jacobs & R. A. Van Santen pp. 29–47. Amsterdam: Elsevier.
Smith, J. V. & Han, S. (1992). Ninth International Zeolite Conference, Extended Abstracts and Program, RP191.
Smith, J. V. & Pluth, J. J. (1992). Ninth International Zeolite Conference, Extended Abstracts and Program, RP207.
Wood, I. G. & Price, G. D. (1992). *Zeolites*, **12**, 320–327.

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On Integrating the Techniques of Direct Methods with Anomalous Dispersion. III. Estimation of Two-Wavelength Two-Phase Structure Invariants

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Abstract

For diffraction data at two wavelengths from a crystal with anomalous scatterers, there are six types of two-phase structure invariants for Friedel pairs. Two of the six are single-wavelength invariants; the other four are mixed-wavelength invariants. It is shown that the latter can be estimated by a straightforward extension of results from the probabilistic direct-methods theory for the single-wavelength anomalous scattering case described in paper I [Hauptman (1982). *Acta Cryst.* A**38**, 632–641]. Statistical tests of the mixed-wavelength estimates are reported for small-molecule and macromolecular examples.

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Introduction

In recent years, the effectiveness of the multiple-wavelength anomalous diffraction (MAD) method for determining protein-crystal structures has been demonstrated by a number of impressive successes (*e.g.* Fanchon & Hendrickson, 1990; Hendrickson, Pahler, Smith, Satow, Merritt & Phizackerley, 1989). A general algebraic treatment of the MAD method was given by Karle (1980) and implemented, in a somewhat different form, by Hendrickson (1985).

Probabilistic theory for the two-phase structure invariants (TPSI) for Friedel pairs from a structure with anomalous scatterers has been published for the one-wavelength case (Hauptman, 1982) but not yet for two- or multiple-wavelength cases. The one-wavelength theory yields estimates of the TPSI as

$$\varphi_{\mathbf{H}} + \varphi_{-\mathbf{H}} \simeq -\xi \qquad (1.0)$$

and the quantity ξ is given by

$$\tan \xi = -S_{\mathbf{H}}/C_{\mathbf{H}}, \qquad (1.1)$$

where

$$S_{\mathbf{H}} = \alpha_{\mathbf{H}}^{-1} \sum_{j=1}^{N} |f_{j\mathbf{H}}|^2 \sin 2\delta_{j\mathbf{H}}, \qquad (1.2)$$

$$C_{\mathbf{H}} = \alpha_{\mathbf{H}}^{-1} \sum_{j=1}^{N} |f_{j\mathbf{H}}|^2 \cos 2\delta_{j\mathbf{H}}, \qquad (1.3)$$

$$\alpha_{\mathbf{H}} = \sum_{j=1}^{N} |f_{j\mathbf{H}}|^2, \qquad (1.4)$$

N is the number of atoms in the unit cell and the atomic scattering factors $f_{j\mathbf{H}} = f^0_{j\mathbf{H}} + f'_j + if''_j$ are expressed in polar form as $f_{j\mathbf{H}} = |f_{j\mathbf{H}}| \exp(i\delta_{j\mathbf{H}})$ with

$$|f_{j\mathbf{H}}| = [(f^0_{j\mathbf{H}} + f'_j)^2 + f''^2_j]^{1/2} \qquad (1.5)$$

and

$$\delta_{j\mathbf{H}} = \tan^{-1}[f''_j/(f^0_{j\mathbf{H}} + f'_j)]. \qquad (1.6)$$

Since the imaginary dispersion coefficients f'' correspond to a phase advance, they are intrinsically positive and it follows that the probabilistic TPSI estimates $-\xi$ are also positive. The estimates thus resolve the twofold ambiguity in the Harker (1956) single isomorphous replacement (SIR) phase construction applied to the single-wavelength anomalous dispersion (SAD) case. Furthermore, to calculate the estimate for a given $\mathbf{H}$, only the chemical composition of the structure [and the $f'(\lambda)$ and $f''(\lambda)$ values] need to be known. The unexpectedness of these results has been remarked on by Fortier, Fraser & Moore (1986) but empirical statistical evidence of their validity has been compiled by Guo & Hauptman (1989), Guo (1990) and Guo, Blessing & Hauptman (1991; paper II). The probabilistic theory predicts and the statistical data confirm that the phase-invariant estimates $\varphi_{\mathbf{H}} + \varphi_{-\mathbf{H}} \simeq -\xi > 0$ are reliable for Friedel pairs with large $|E|$ values, say $|E| > 1$ to 1.5, and more reliable for larger $|E|$ values.

Extension to the two-wavelength case

For anomalous-dispersion data measured at two wavelengths, the normalized structure factors for a Friedel pair of reflection $\mathbf{H}$ and anti-reflection $-\mathbf{H}$ are

$$E_{\mathbf{H}} = |E_{\mathbf{H}}| \exp i\varphi_{\mathbf{H}} \quad \text{and} \quad E_{-\mathbf{H}} = |E_{-\mathbf{H}}| \exp i\varphi_{-\mathbf{H}} \qquad (2.1)$$

at wavelength 1 and

$$G_{\mathbf{H}} = |G_{\mathbf{H}}| \exp i\psi_{\mathbf{H}} \quad \text{and} \quad G_{-\mathbf{H}} = |G_{-\mathbf{H}}| \exp i\psi_{-\mathbf{H}} \qquad (2.2)$$

at wavelength 2. To these, there correspond six TPSI:

$$\omega_1 = \varphi_{\mathbf{H}} + \varphi_{-\mathbf{H}}, \qquad (3.1)$$

$$\omega_2 = \psi_{\mathbf{H}} + \psi_{-\mathbf{H}}, \qquad (3.2)$$

$$\omega_3 = \varphi_{\mathbf{H}} - \psi_{\mathbf{H}}, \qquad (3.3)$$

$$\omega_4 = \varphi_{-\mathbf{H}} + \psi_{\mathbf{H}}, \qquad (3.4)$$

$$\omega_5 = \varphi_{\mathbf{H}} + \psi_{-\mathbf{H}}, \qquad (3.5)$$

$$\omega_6 = \varphi_{-\mathbf{H}} - \psi_{-\mathbf{H}}. \qquad (3.6)$$

Probabilistic estimates of the two single-wavelength TPSI, $\omega_1 \simeq -\xi_1$ at wavelength 1 and $\omega_2 \simeq -\xi_2$ at wavelength 2, are readily calculated using (1.0)–(1.6). It is then straightforward to estimate the four mixed-wavelength TPSI, ω_3 to ω_6, provided that the anomalous scattering is small compared to the normal scattering. In that case, the anomalous-dispersion effects can be taken to be wavelength-dependent perturbative adjustments Δ to the wavelength-independent phases φ^0 of the normal scattering and, to a first approximation, Δ can be taken to be the same for $\varphi_{\mathbf{H}}$ and $\varphi_{-\mathbf{H}}$. The Friedel-pair phases at wavelength 1 can then be approximated as

$$\varphi_{\mathbf{H}} = \varphi^0_{\mathbf{H}} + \Delta_1 \quad \text{and} \quad \varphi_{-\mathbf{H}} = \varphi^0_{-\mathbf{H}} + \Delta_1$$

and, since $\varphi^0_{-\mathbf{H}} = -\varphi^0_{\mathbf{H}}$, the corresponding TPSI is

$$\omega_1 = \varphi_{\mathbf{H}} + \varphi_{-\mathbf{H}} = 2\Delta_1 \simeq -\xi_1. \qquad (4.1)$$

Similarly, at wavelength 2,

$$\omega_2 = \psi_{\mathbf{H}} + \psi_{-\mathbf{H}} = 2\Delta_2 \simeq -\xi_2. \qquad (4.2)$$

For the mixed-wavelength TPSI, the perturbation approximations give

$$\omega_3 = \varphi_{\mathbf{H}} - \psi_{\mathbf{H}} = \varphi^0_{\mathbf{H}} - \psi^0_{\mathbf{H}} + \Delta_1 - \Delta_2,$$

$$\omega_4 = \varphi_{-\mathbf{H}} + \psi_{\mathbf{H}} = \varphi^0_{-\mathbf{H}} + \psi^0_{\mathbf{H}} + \Delta_1 + \Delta_2,$$

$$\omega_5 = \varphi_{\mathbf{H}} + \psi_{-\mathbf{H}} = \varphi^0_{\mathbf{H}} + \psi^0_{-\mathbf{H}} + \Delta_1 + \Delta_2,$$

$$\omega_6 = \varphi_{-\mathbf{H}} - \psi_{-\mathbf{H}} = \varphi^0_{-\mathbf{H}} - \psi^0_{-\mathbf{H}} + \Delta_1 - \Delta_2;$$

and, since $\varphi^0_{\mathbf{H}} = \psi^0_{\mathbf{H}} = -\varphi^0_{-\mathbf{H}} = -\psi^0_{-\mathbf{H}}$, it follows that

$$\omega_3 = \omega_6 = \Delta_1 - \Delta_2 = (\omega_1 - \omega_2)/2 \simeq -(\xi_1 - \xi_2)/2 \tag{4.3}$$

and

$$\omega_4 = \omega_5 = \Delta_1 + \Delta_2 = (\omega_1 + \omega_2)/2 \simeq -(\xi_1 + \xi_2)/2. \tag{4.4}$$

If the single-wavelength estimates give $\omega_1 > \omega_2$, then the mixed-wavelength estimates ω_3 to ω_6 will also be positive.

We refer to the estimates for the mixed-wavelength TPSI as semi-empirical because we first noticed them as statistical patterns in the empirical test calculations described below. After noticing the patterns, we realized the simple rationale treating the anomalous dispersion as a perturbation. Rigorous derivation of the mixed-wavelength TPSI estimates from the joint and conditional probability distributions for the four magnitudes $|E_{\mathbf{H}}|$, $|E_{-\mathbf{H}}|$, $|G_{\mathbf{H}}|$ and $|G_{-\mathbf{H}}|$ and four phases $\varphi_{\mathbf{H}}$, $\varphi_{-\mathbf{H}}$, $\psi_{\mathbf{H}}$ and $\psi_{-\mathbf{H}}$ at two wavelengths (Guo & Hauptman, 1986) seems to be unnecessary and the statistical results show that the simple perturbation treatment provides practically useful TPSI estimates.

The results (4.1)–(4.4) all follow from (1.0) and like (1.0) must be understood to have probabilistic and statistical validity. There will, of course, be Friedel pairs whose TPSI differ from the estimates in magnitude or sign, or in both, but the estimates are more likely to be accurate for larger corresponding $|E|$ and $|G|$ magnitudes.

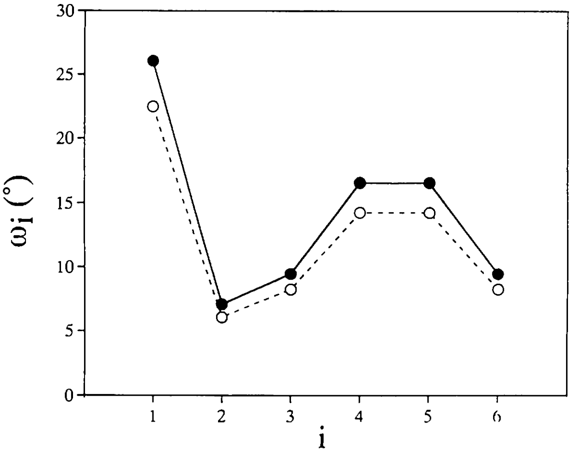

Fig. 1. True and estimated TPSI for the $|E| = 1.57$, $\mathbf{H} = 4,0,22$ reflection of cocaine methiodide at Cu $K\alpha$ and Mo $K\alpha$ wavelengths. The six true TPSI defined by (3.1)–(3.6) are denoted by filled circles and the corresponding TPSI estimates from (4.1)–(4.4) are denoted by open circles.

Test calculations

Statistical comparisons of true and estimated TPSI have been carried out for the known crystal structures of the small molecule cocaine methiodide (*N*-methylcocaine iodide), $C_{18}H_{24}NO_4I$ (Shen, Ruble & Hite, 1975) and the single-site $PtCl_4^{2-}$ derivative of the protein cytochrome c_{550}, $FeS_6O_{203}N_{170}C_{637}$ (Timkovich & Dickerson, 1973, 1976), both of which

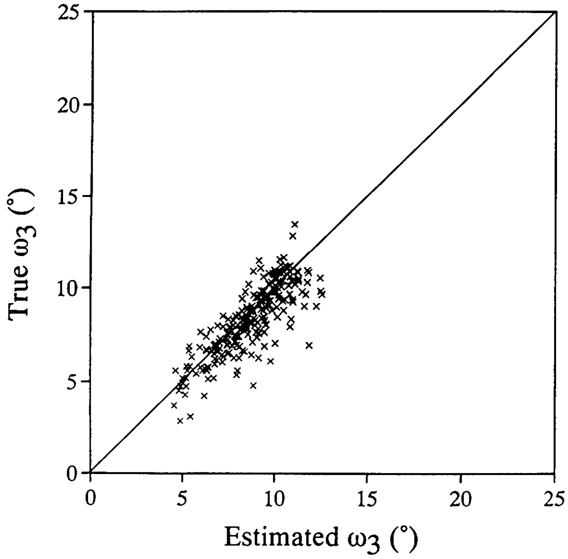

Fig. 2. Correlation plot for the true and estimated mixed-wavelength TPSI of type ω_3 [(3.3) and (4.3)] for the 227 Friedel pairs with $|E| \geq 1.5$ for cocaine methiodide at Cu $K\alpha$ and Mo $K\alpha$ wavelengths. An analogous plot for the TPSI of type ω_6 is virtually indistinguishable from Fig. 2.

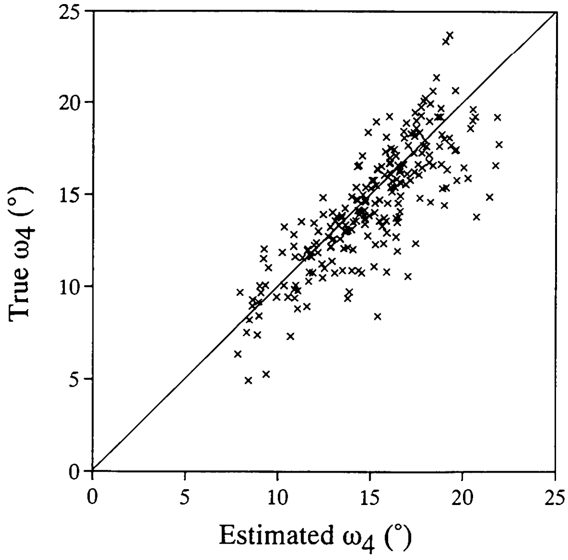

Fig. 3. As Fig. 2 but for the TPSI of type ω_4 [(3.4) and (4.4)]. An analogous plot for the TPSI of type ω_5 is virtually indistinguishable from Fig. 3.

crystallize in $P2_12_12_1$ with $Z=4$. Statistical evidence for the validity of the single-wavelength TPSI estimates (1.0)–(1.6) for the same two examples was presented in an earlier report (Guo, Blessing & Hauptman, 1991).

The reported atomic coordinates for cocaine methiodide were used to calculated normalized structure factors for all Friedel pairs corresponding to the measured reflections, and the phases for Friedel pairs with $|E| \geq 1.0$ at Cr *Kα*, Cu *Kα* and Mo *Kα* wavelengths were used to form the sets of six TPSI defined by (3.1)–(3.6) for comparison to the estimates given by (1.0)–(1.6) and (4.1)–(4.4). A typical result for the six TPSI for the Cu *Kα* and Mo *Kα* wavelengths for an $|E| \simeq 1.5$ reflection is shown in Fig. 1, which illustrates the common pattern $\omega_3 \simeq \omega_6 \simeq (\omega_1 - \omega_2)/2$ and $\omega_4 \simeq \omega_5 \simeq (\omega_1 + \omega_2)/2$. The excellent correlation between the true and estimated Cu *Kα* and Mo *Kα* mixed-wavelength TPSI for the 227 Friedel pairs with $|E| \geq 1.5$ is shown in Figs. 2 and 3. As the structure is rather small and contains a strongly anomalously scattering I atom, the TPSI estimates were almost as good for the shorter-wavelength Cu *Kα* and Mo *Kα* pairs as for the longer-wavelength Cr *Kα* and Cu *Kα* pairs and the true TPSI were positive for all 227 Friedel pairs with $|E| > 1.5$.

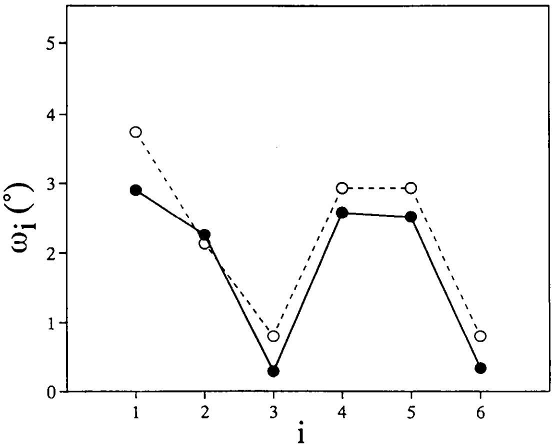

Fig. 4. True and estimated TPSI for the $|E| = 2.91$, $\mathbf{H} = 2,17,4$ reflection of cytochrome $c_{550}.PtCl_4^{2-}$ at Cr *Kα* and Cu *Kα* wavelengths. The six true TPSI defined by (3.1)–(3.6) are denoted by filled circles and the corresponding TPSI estimates from (4.1)–(4.4) are denoted by open circles.

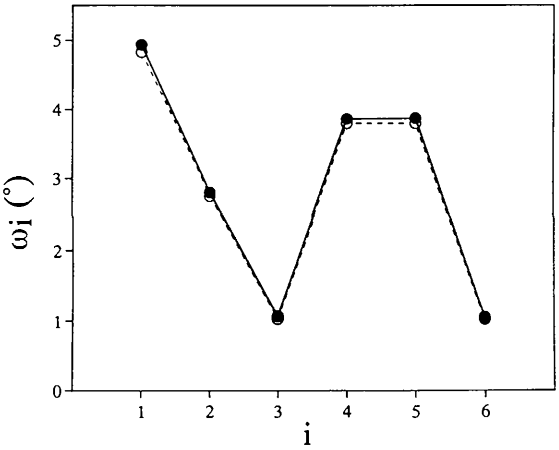

Fig. 5. As Fig. 4 but for the *averages* of the true and estimated TPSI for the 676 Friedel pairs with $|E| \geq 1.5$.

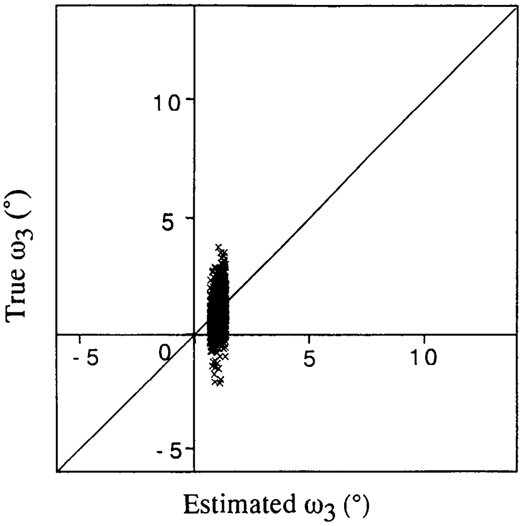

Fig. 6. Correlation plot for the true and estimated mixed-wavelength TPSI of type ω_3 [(3.3) and (4.3)] for the 676 Friedel pairs with $|E| \geq 1.5$ for cytochrome $c_{550}.PtCl_4^{2-}$ at Cr *Kα* and Cu *Kα* wavelengths. An analogous plot for the TPSI of type ω_6 is virtually indistinguishable from Fig. 6.

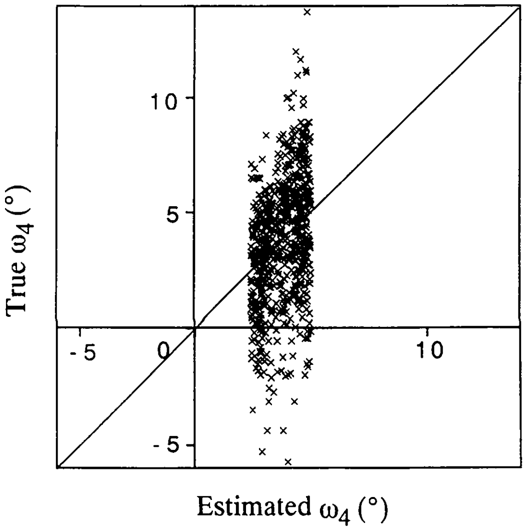

Fig. 7. As Fig. 6 but for the TPSI of type ω_4 [(3.4) and (4.4)]. An analogous plot for the TPSI of type ω_5 is virtually indistinguishable from Fig. 7.

For the cytochrome $c_{550}.PtCl_4^{2-}$ structure, the reported atomic coordinates were used to calculate normalized structure factors and form the sets of six TPSI for the 676 Friedel pairs with $|E| \geq 1.5$ in the resolution range $8 \geq d \geq 2$ Å at Cr $K\alpha$ and Cu $K\alpha$ wavelengths. A typical result for the six true and estimated TPSI for a strong $|E| \simeq 3$ reflection is illustrated in Fig. 4 and the essentially perfect behavior *on the average* over the 676 Friedel pairs is shown in Fig. 5. Over the 676 Friedel pairs, the percentage incidences of true TPSI with negative sign were 8.3, 8.1, 11.2, 8.0, 8.0 and 10.9% for the TPSI types ω_1 to ω_6, respectively. The scatter in the correlation between the true and estimated mixed-wavelength TPSI is illustrated in Figs. 6 and 7, which show that the range of true TPSI values is considerably wider than the range of the estimated values.

The incidence of true TPSI with negative sign and the scatter between the true and estimated TPSI magnitudes are, unsurprisingly, worse for the protein than for the small molecule. Still, the incidence of negative TPSI is only ~10% for the protein Friedel pairs with $|E| \geq 1.5$ and the errors in the estimated TPSI magnitudes are no worse for the mixed-wavelength estimates (4.3) and (4.4) than for the single-wavelength estimates (4.1) and (4.2). This indicates that the simple extension of the probabilistic TPSI-estimation theory from the one-wavelength case to the two-wavelength case, as expressed in the results (4.1)–(4.4), should be practically useful for structure determinations with two-wavelength anomalous-dispersion data.

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References

FANCHON, E. & HENDRICKSON, W. A. (1990). *Acta Cryst.* A**46**, 809–820.
FORTIER, S., FRASER, M. E. & MOORE, N. J. (1986). *Acta Cryst.* A**42**, 149–156.
GUO, D. Y. (1990). *Acta Cryst.* A**46**, 942–944.
GUO, D. Y., BLESSING, R. H. & HAUPTMAN, H. A. (1991). *Acta Cryst.* A**47**, 340–345.
GUO, D. Y. & HAUPTMAN, H. A. (1986). Am. Crystallogr. Assoc. Meeting, Hamilton, Ontario, Abstract L4. *ACA Abstr. Ser.* 2, **14**, 46.
GUO, D. Y. & HAUPTMAN, H. A. (1989). *Chin. Sci. Bull.* **34**, 137–141.
HARKER, D. (1956). *Acta Cryst.* **9**, 1–9.
HAUPTMAN, H. A. (1982). *Acta Cryst.* A**38**, 632–641.
HENDRICKSON, W. A. (1985). *Trans. Am. Crystallogr. Assoc.* **21**, 11–21.
HENDRICKSON, W. A., PAHLER, A., SMITH, J. L., SATOW, Y., MERRITT, E. A. & PHIZACKERLEY, R. P. (1989). *Proc. Natl Acad. Sci. USA*, **86**, 2190–2194.
KARLE, J. (1980). *Int. J. Quantum Chem. Symp.* **7**, 356–367.
SHEN, M., RUBLE, J. R. & HITE, G. (1975). *Acta Cryst.* B**31**, 2706–2709.
TIMKOVICH, R. & DICKERSON, R. E. (1973). *J. Mol. Biol.* **79**, 39–56.
TIMKOVICH, R. & DICKERSON, R. E. (1976). *J. Biol. Chem.* **251**, 4033–4046.

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Triplet and Quartet Relationships and the 'Positivity' Postulate

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Abstract

Positivity and atomicity are traditionally considered as basic conditions for direct methods. While the role of atomicity is well understood, the theoretical and practical consequences for a direct-methods procedure generated by the violation of the positivity criterion are not quite clear. Triplet and quartet relationships are analyzed in connection with the positivity postulate.

Symbols and notation

f_j Scattering factor of the jth atom. It is assumed to be a real positive function of $\sin\theta/\lambda$ for X-ray scattering, coinciding with the scattering length b_j (a positive or negative real constant) for neutron scattering
$F_{\mathbf{h}}$ Structure factor with vectorial index $\mathbf{h} \equiv (h,k,l)$

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