CLEMENTI, E. & ROETTI, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177-478.
COPPENS, P., CSONKA, L. N. & WILLOUGHBY, T. V. (1971). *Acta Cryst.* **A27**, 248-250.
COPPENS, P., GURU ROW, T. N., LEUNG, P. C. W., STEVENS, E. D., BECKER, P. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63-72.
COPPENS, P., HOLLADAY, A. & STEVENS, E. D. (1982). *J. Am. Chem. Soc.* **104**, 3546-3547.
FIGGIS, B. N., MASON, R., SMITH, A. R. P., VARGHESE, J. N. & WILLIAMS, G. A. (1983). *J. Chem. Soc. Dalton Trans.* **4**, 703-712.
FIGGIS, B. N., REYNOLDS, P. A. & MASON, R. (1983). *J. Am. Chem. Soc.* **105**, 440-443.
FIGGIS, B. N., WILLIAMS, G. A., FORSYTH, J. B. & MASON, R. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1837-1845.
FREEMAN, A. J. & FRANKEL, R. B. (1967). In *Hyperfine Interactions.* New York: Academic Press.
GILLON, B. (1983). Thesis, Univ. of Paris.
GILLON, B., BECKER, P. & ELLINGER, Y. (1983). *Mol. Phys.* **48**, 763-774.
HANSEN, N. K. & COPPENS, P. (1978). *Acta Cryst.* **A34**, 909-921.
HOLLADAY, A., LEUNG, P. C. W. & COPPENS, P. (1983). *Acta Cryst.* **A39**, 377-387.
HUBBARD, J., RIMMER, D. E. & HOPGOOD, F. R. A. (1966). *Proc. Phys. Soc. London*, **28**, 13-36.
LIN, W. C. (1979). In *The Porphyrins*, edited by D. DOLPHIN, Vol. IV pp. 255-377. New York: Academic Press.
MASON, R. (1982). In *Electron Distributions and the Chemical Bond*, edited by P. COPPENS & M. B. HALL, pp. 351. New York: Plenum Press.
RAKHECHA, V. C. & SATYA MURTHY, N. S. (1978). *J. Phys. Chem.* **11**, 4389-4404.
STEWART, R. F. (1969). *J. Chem. Phys.* **50**, 2485-2495.
STEWART, R. F. (1970). *J. Chem. Phys.* **52**, 431-438.
STEWART, R. F. (1976). *Acta Cryst.* **A32**, 565-574.
SUGANO, S., TANAKA, K. & KAMIMURA, H. (1970). *Multiplets of Transition Metal Ions in Crystals.* New York: Academic Press.
TOFIELD, B. C. (1975). *Struct. Bonding (Berlin)*, **21**, 2-87.
WATSON, R. E. & FREEMAN, A. J. (1960). *Phys. Rev.* **120**, 1125-1134, 1134-1141.

Acta Cryst. (1985). A**41**, 182-189

Many Algebraic Formulas for the Evaluation of Triplet Phase Invariants from Isomorphous Replacement and Anomalous Dispersion Data

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Abstract

An algebraic analysis is presented for the calculation of triplet phase invariants from isomorphous replacement and anomalous dispersion data. The analysis applies when there is one type or one predominant type of anomalously scattering atoms. The use of the formulas largely parallels a recent approach that is based on a General Rule for evaluating triplet phase invariants. It involves the mixing of terms from isomorphous replacement with various types of terms arising in anomalous dispersion or the mixing of various terms arising in anomalous dispersion alone. The mixing of terms gives rise to a myriad of formulas that can generate values anywhere in the range from $-\pi$ to π. In the tests performed, it was found that the algebraic formulas offered an improvement in accuracy over that obtained from the General Rule. The accuracy is potentially high but depends ultimately on the reliability of the experimental data.

Introduction

Several analyses based on the mathematical and physical properties of diffraction data from isomorphous replacement and anomalous dispersion experiments have led to a large number of formulas for evaluating triplet phase invariants. The formulas are generated by several rules (Karle, 1983, 1984*b*, *c*), which have been generalized and extended by the development of a General Rule (Karle, 1984*d*). In the application of the General Rule, it is possible to combine various sets of isomorphous replacement data or isomorphous replacement data with anomalous dispersion data or various sets of anomalous dispersion data in many different ways. The variety of combinations increases considerably when anomalous dispersion data are collected at more than one wavelength.

A number of tests of the General Rule were performed on exact data computed from the coordinates for cytochrome c550.$PtCl_4^{2-}$ from *Paracoccus denitrificans* (Timkovich & Dickerson, 1976). Values for a variety of different types of triplet phase invariants were computed from combinations of isomorphous replacement and anomalous dispersion data at 2·5 Å resolution by use of the General Rule. The average magnitude of error for thousands of invariants ranged from 30 to 45°. These are significant errors to combine with the experimental error of an actual application and it would evidently be much more desirable if the error inherent in the theory could be reduced.

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It is the objective of this investigation to present an algebraic analysis of the structure factor equations appropriate to the isomorphous replacement and anomalous dispersion techniques, which leads to formulas for evaluating triplet phase invariants that are more accurate than those associated with the General Rule (Karle, 1984*d*). Formulas are obtained that express the tangents of the triplet phase invariants in terms of the measured intensity data. In forming the tangent formulas, quantities that depend upon knowledge of the heavy-atom structure are cancelled out, so that it is not necessary to know this structure. In addition, one type of formula gives the values of the structure factor magnitudes for the heavy-atom structure in terms of the measured intensities.

The algebraic analysis is carried out in general terms, thus permitting the end result to represent a large number of formulas composed from almost the same large variety of terms to which the General Rule applies. The very large number of formulas that obtain permit a very large number of triplet phase invariants to be evaluated.

The algebraic analysis to be presented here is closely related to an exact algebraic analysis that has already been published (Karle, 1980). The latter can take into account any number or types of anomalous scatterers and can use data from isomorphous replacement experiments coupled with data from single- or multiple-wavelength anomalous dispersion experiments or from anomalous dispersion experiments alone. This exact algebraic theory has been extended to include the evaluation of triplet phase invariants (Karle, 1984*e*) with the only source of error, besides the experimental error, the uncertainty concerning the deviation from zero of the values for triplet phase invariants associated with the heavy-atom structures. Owing to the simplicity that is ordinarily found for the heavy-atom structures that derive from heavy-atom substitution in macromolecules, it is generally easy to satisfy the condition that the triplet phase invariants have a value close to zero for large numbers of invariants.

The question arises concerning the relationship between the theory to be presented here and the latter analysis and the roles that both theories might ultimately play. The variables appearing in the present theory are somewhat different than those employed in the exact algebraic theory, although they are closely related. The myriad of formulas that occur in the present treatment appear to afford additional options for handling the data to those obtained from the exact algebraic treatment. When dealing with experimental data, the additional options may be useful.

Considerations of optimal usage of experimental information extends beyond the two theories and should encompass the well-established procedures for handling isomorphous replacement and anomalous dispersion data and the newer possibilities from probability theory (Hauptman, 1982; Pontenagel, Krabbendam, Peerdeman & Kroon, 1983; Giacovazzo, 1983). It would appear that many future studies will be required to effect suitable evaluations.

The formulas to be presented here are most accurate when there is a single type of anomalous scatterer but are still rather accurate when there is one predominant type of anomalous scatterer. Inspection of the nature of the real and imaginary corrections to the atomic scattering factors shows that these circumstances can prevail in a broad range of applications.

Theory

The theoretical development begins with the relation

$$_m\mathcal{F}_{1,\mathbf{h}} = {_m\mathcal{F}_{2,\mathbf{h}}} + {_m\mathcal{F}_{3,\mathbf{h}}}, \tag{1}$$

where the symbolism associated with the letter $\mathcal{F}$ represents the eight cases listed in Table 1. For each individual case, m, it is easily shown from the definitions of the structure factors that the listed quantities obey (1). The first case, labeled with i, represents isomorphous replacement, the next three (1-3) represent single-wavelength anomalous dispersion and the last four (4-7) represent multiwavelength anomalous dispersion. Contained within this symbolism is a large number of additional possibilities that would arise if there were data from several different isomorphous replacement experiments and from anomalous dispersion experiments performed at a number of wavelengths. The case of $m = i$, for example, could be extended to $i_1, i_2, \ldots$ if there were several isomorphous derivatives. Evidently the other cases are a function of wavelength.

The quantity $F_{\mathbf{h}PH}$ is the structure factor associated with the substituted substance, for example, a macromolecule with heavy-atom substituents, $F_{\mathbf{h}P}$ is the corresponding structure factor for the unsubstituted substance and $F_{\mathbf{h}H}$ is the corresponding structure factor for the substituents. The quantity $F_{\lambda_p\mathbf{h}}$ is the structure factor associated with a measured intensity at wavelength λ_p and includes the contribution from anomalous dispersion, $F^n_{\mathbf{h}}$ is the corresponding structure factor when the contribution from anomalous dispersion is omitted and $F^a_{\lambda_p\mathbf{h}}$ is the corresponding structure factor that represents only the contribution from anomalous dispersion at wavelength λ_p. The quantities are related by

$$F_{\mathbf{h}PH} = F_{\mathbf{h}P} + F_{\mathbf{h}H} \tag{2}$$

and

$$F_{\lambda_p\mathbf{h}} = F^n_{\mathbf{h}} + F^a_{\lambda_p\mathbf{h}}. \tag{3}$$

It follows from (2) and (3) that for all the cases in Table 1 (1) is satisfied. The atomic scattering factor for the jth atom that scatters anomalously is given by

$$f_{j,\mathbf{h}} = f^n_{j,\mathbf{h}} + f'_j + if''_j, \tag{4}$$

Table 1. *Quantities involved in the evaluation of triplet phase invariants*

The symbols ${}_m\mathscr{F}_{1,\mathbf{h}}$, ${}_m\mathscr{F}_{2,\mathbf{h}}$ and ${}_m\mathscr{F}_{3,\mathbf{h}}$ are defined by the corresponding entries in columns 2, 3, 4, respectively, for $m = i, 1, 2, \ldots, 7$. The symbol i refers to isomorphous replacement whereas the numerical values for m refer to different cases for anomalous dispersion. The various symbolic entries are defined in the text. Case i may refer to a number of isomorphous derivatives, i_1, $i_2, \ldots$ and cases $m = 1$-7 may refer to data collected at a variety of wavelengths. The asterisk implies the complex conjugate.

Case m	${}_m\mathscr{F}_{1,\mathbf{h}}$	${}_m\mathscr{F}_{2,\mathbf{h}}$	${}_m\mathscr{F}_{3,\mathbf{h}}$	$\delta_{m\lambda j}$	$f_{m\lambda j}$
i	$F_{\mathbf{h}PH}$	$F_{\mathbf{h}P}$	$F_{\mathbf{h}H}$	0	$f^n_{j,\mathbf{h}}$
1	$F_{\lambda_p\mathbf{h}}$	$F^*_{\lambda_p\bar{\mathbf{h}}}$	$F^a_{\lambda_p\mathbf{h}} - F^{a*}_{\lambda_p\bar{\mathbf{h}}}$	$\begin{cases} \pi/2 \text{ if } f''_{\lambda_p j} + \\ -\pi/2 \text{ if } f''_{\lambda_p j} - \end{cases}$	$f^a_{\lambda_p j}$
2	$F_{\lambda_p\mathbf{h}} + F^*_{\lambda_p\bar{\mathbf{h}}}$	$2F^n_{\mathbf{h}}$	$F^a_{\lambda_p\mathbf{h}} + F^{a*}_{\lambda_p\bar{\mathbf{h}}}$	$\begin{cases} 0 \text{ if } f'_{\lambda_p j} + \\ \pi \text{ if } f'_{\lambda_p j} - \end{cases}$	$f^a_{\lambda_p j}$
3	$F_{\lambda_p\mathbf{h}}$	$F^n_{\mathbf{h}}$	$F^a_{\lambda_p\mathbf{h}}$	$\delta_{\lambda_p j}$	$f^a_{\lambda_p j}$
4	$F_{\lambda_1\mathbf{h}}$	$F_{\lambda_2\mathbf{h}}$	$F^a_{\lambda_1\mathbf{h}} - F^a_{\lambda_2\mathbf{h}}$	$\delta^{-,-}_{\lambda_1\lambda_2 j}$	$f^{a-,-}_{\lambda_1\lambda_2 j}$
5	$F_{\lambda_1\mathbf{h}} + F_{\lambda_2\mathbf{h}}$	$2F^n_{\mathbf{h}}$	$F^a_{\lambda_1\mathbf{h}} + F^a_{\lambda_2\mathbf{h}}$	$\delta^{+,+}_{\lambda_1\lambda_2 j}$	$f^{a+,+}_{\lambda_1\lambda_2 j}$
6	$F_{\lambda_1\bar{\mathbf{h}}}$	$F^*_{\lambda_2\bar{\mathbf{h}}}$	$F^a_{\lambda_1\mathbf{h}} - F^{a*}_{\lambda_2\bar{\mathbf{h}}}$	$\delta^{+,-}_{\lambda_1\lambda_2 j}$	$f^{a+,-}_{\lambda_1\lambda_2 j}$
7	$F_{\lambda_1\mathbf{h}} + F^*_{\lambda_2\bar{\mathbf{h}}}$	$2F^n_{\mathbf{h}}$	$F^a_{\lambda_1\mathbf{h}} + F^{a*}_{\lambda_2\bar{\mathbf{h}}}$	$\delta^{-,+}_{\lambda_1\lambda_2 j}$	$f^{a-,+}_{\lambda_1\lambda_2 j}$

where $f^n_{j,\mathbf{h}}$ is the normal atomic scattering factor and f'_j and f''_j are the real and imaginary parts of the anomalous correction, respectively.

The general definition for ${}_m\mathscr{F}_{3,h}$, based on the results of previous mathematical analyses (Karle, 1983, 1984*b*, *c*), is

$$ {}_m\mathscr{F}_{3,\mathbf{h}} = \sum_{j=2}^{q+1} (f_{m\lambda j}/f^n_{j,\mathbf{h}}) \exp(i\delta_{m\lambda j}) F^n_{j,\mathbf{h}}, \tag{5} $$

where $f_{m\lambda j}$ and $\delta_{m\lambda j}$ are given in Table 1 for the various cases, $f^n_{j,\mathbf{h}}$ is the normal atomic scattering factor for the jth type of anomalous scatterer in a substance containing q types of anomalous scatterers (the subscript 1 is reserved for atoms that essentially do not scatter anomalously) and the $F^n_{j,\mathbf{h}}$ are the normal structure factors for each type of anomalously scattering atom. Additional definitions required for the use of Table 1 are

$$ f^a_{\lambda_p j} = (f'^2_{\lambda_p j} + f''^2_{\lambda_p j})^{1/2} \tag{6} $$

$$ \delta_{\lambda_p j} = \tan^{-1} (f''_{\lambda_p j}/f'_{\lambda_p j}) \tag{7} $$

$$ f^{a-,-}_{\lambda_1\lambda_2 j} = [(f''_{\lambda_1 j} - f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} - f'_{\lambda_2 j})^2]^{1/2} \tag{8} $$

$$ \delta^{-,-}_{\lambda_1\lambda_2 j} = \tan^{-1} [(f''_{\lambda_1 j} - f''_{\lambda_2 j})/(f'_{\lambda_1 j} - f'_{\lambda_2 j})] \tag{9} $$

$$ f^{a+,+}_{\lambda_1\lambda_2 j} = [(f''_{\lambda_1 j} + f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} + f'_{\lambda_2 j})^2]^{1/2} \tag{10} $$

$$ \delta^{+,+}_{\lambda_1\lambda_2 j} = \tan^{-1} [(f''_{\lambda_1 j} + f''_{\lambda_2 j})/(f'_{\lambda_1 j} + f'_{\lambda_2 j})] \tag{11} $$

$$ f^{a+,-}_{\lambda_1\lambda_2 j} = [(f''_{\lambda_1 j} + f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} - f'_{\lambda_2 j})^2]^{1/2} \tag{12} $$

$$ \delta^{+,-}_{\lambda_1\lambda_2 j} = \tan^{-1} [(f''_{\lambda_1 j} + f''_{\lambda_2 j})/(f'_{\lambda_1 j} f'_{\lambda_2 j})] \tag{13} $$

$$ f^{a-,+}_{\lambda_1\lambda_2 j} = [(f''_{\lambda_1 j} - f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} + f'_{\lambda_2 j})^2]^{1/2} \tag{14} $$

$$ \delta^{-,+}_{\lambda_1\lambda_2 j} = \tan^{-1} [(f''_{\lambda_1 j} - f''_{\lambda_2 j})/(f'_{\lambda_1 j} + f'_{\lambda_2 j})]. \tag{15} $$

From (1), it follows that

$$ \begin{aligned} |{}_m\mathscr{F}_{1,\mathbf{h}}|^2 &= |{}_m\mathscr{F}_{2,\mathbf{h}}|^2 + |{}_m\mathscr{F}_{3,\mathbf{h}}|^2 \\ &\quad + 2|{}_m\mathscr{F}_{2,\mathbf{h}}|\,|{}_m\mathscr{F}_{3,\mathbf{h}}| \cos({}_m\psi_{2,\mathbf{h}} - {}_m\psi_{3,\mathbf{h}}), \end{aligned} \tag{16} $$

Table 2. *Expressions for* ${}_m\mathscr{F}_{3,\mathbf{h}}$ *and* $|{}_m\mathscr{F}_{3,\mathbf{h}}|$ *when there is only one type of anomalous scatterer*

The entries maintain approximate validity when there is one predominant type of anomalous scatterer.

Case, m	${}_m\mathscr{F}_{3,\mathbf{h}}$	$\lvert{}_m\mathscr{F}_{3,\mathbf{h}}\rvert$
i	$F^n_{2,\mathbf{h}}$	$\lvert F^n_{2,\mathbf{h}}\rvert$
1	$2i(f''_{\lambda 2}/f^n_{2,\mathbf{h}})F^n_{2,\mathbf{h}}$	$2(f''_{\lambda 2}/f^n_{2,\mathbf{h}})\lvert F^n_{2,\mathbf{h}}\rvert$
2	$2(f'_{\lambda 2}/f^n_{2,\mathbf{h}})F^n_{2,\mathbf{h}}$	$2(f'_{\lambda 2}/f^n_{2,\mathbf{h}})\lvert F^n_{2,\mathbf{h}}\rvert$
3	$(f^a_{\lambda 2}/f^n_{2,\mathbf{h}}) \exp(i\delta_{\lambda 2})F^n_{2,\mathbf{h}}$	$(f^a_{\lambda 2}/f^n_{2,\mathbf{h}})\lvert F^n_{2,\mathbf{h}}\rvert$
4	$(f^{a-,-}_{\lambda_1\lambda_2 2}/f^n_{2,\mathbf{h}}) \exp(i\delta^{-,-}_{\lambda_1\lambda_2 2})F^n_{2,\mathbf{h}}$	$(f^{a-,-}_{\lambda_1\lambda_2 2}/f^n_{2,\mathbf{h}})\lvert F^n_{2,\mathbf{h}}\rvert$
5	$(f^{a+,+}_{\lambda_1\lambda_2 2}/f^n_{2,\mathbf{h}}) \exp(i\delta^{+,+}_{\lambda_1\lambda_2 2})F^n_{2,\mathbf{h}}$	$(f^{a+,+}_{\lambda_1\lambda_2 2}/f^n_{2,\mathbf{h}})\lvert F^n_{2,\mathbf{h}}\rvert$
6	$(f^{a+,-}_{\lambda_1\lambda_2 2}/f^n_{2,\mathbf{h}}) \exp(i\delta^{+,-}_{\lambda_1\lambda_2 2})F^n_{2,\mathbf{h}}$	$(f^{a+,-}_{\lambda_1\lambda_2 2}/f^n_{2,\mathbf{h}})\lvert F^n_{2,\mathbf{h}}\rvert$
7	$(f^{a-,+}_{\lambda_1\lambda_2 2}/f^n_{2,\mathbf{h}}) \exp(i\delta^{-,+}_{\lambda_1\lambda_2 2})F^n_{2,\mathbf{h}}$	$(f^{a-,+}_{\lambda_1\lambda_2 2}/f^n_{2,\mathbf{h}})\lvert F^n_{2,\mathbf{h}}\rvert$

where ψ is the phase angle associated with the magnitude, $|\mathscr{F}|$. With the assumption that

$$ |{}_m\mathscr{F}_{2,\mathbf{h}}| \gg |{}_m\mathscr{F}_{3,\mathbf{h}}|, \tag{17} $$

(16) becomes to good approximation, with neglect of $|{}_m\mathscr{F}_{3,\mathbf{h}}|^2$ and expansion of the square root to the linear term in the cosine,

$$ |{}_m\mathscr{F}_{1,\mathbf{h}}| - |{}_m\mathscr{F}_{2,\mathbf{h}}| \simeq |{}_m\mathscr{F}_{3,\mathbf{h}}| \cos({}_m\psi_{2,\mathbf{h}} - {}_m\psi_{3,\mathbf{h}}). \tag{18} $$

Examination of Tables 1 and 2 shows that condition (17) can be well satisfied by large numbers of intensity data from macromolecules.

We proceed with the case of one type of predominant anomalous scatterer. Thus, from (5) for $j = 2$,

$$ {}_m\psi_{3,\mathbf{h}} = \varphi^n_{2,\mathbf{h}} + \delta_{m\lambda 2}, \tag{19} $$

where $\varphi^n_{2,\mathbf{h}}$ is the phase angle associated with the structure factor for the normal part of the scattering from the anomalously scattering atoms and $\delta_{m\lambda 2}$ is listed in Table 1 for the various m.

We now rewrite (18) with the use of (19),

$$|{}_m\mathscr{F}_{1,\mathbf{h}}|-|{}_m\mathscr{F}_{2,\mathbf{h}}|\simeq|{}_\mathrm{m}\mathscr{F}_{3,\mathbf{h}}|[\cos({}_m\psi_{2,\mathbf{h}}-\varphi^n_{2,\mathbf{h}})\cos\delta_{m\lambda 2}$$
$$+\sin({}_m\psi_{2,\mathbf{h}}-\varphi^n_{2,\mathbf{h}})\sin\delta_{m\lambda 2}]. \quad (20)$$

A comparable equation can be written for $\bar{\mathbf{h}}$,

$$|{}_m\mathscr{F}_{1,\bar{\mathbf{h}}}|-|{}_m\mathscr{F}_{2,\bar{\mathbf{h}}}|\simeq|{}_m\mathscr{F}_{3,\bar{\mathbf{h}}}|[\cos(-{}_m\psi_{2,\bar{\mathbf{h}}}+\varphi^n_{2,\bar{\mathbf{h}}}\cos\delta_{m\lambda 2}$$
$$-\sin(-{}_m\psi_{2,\bar{\mathbf{h}}}+\varphi^n_{2,\bar{\mathbf{h}}})\sin\delta_{m\lambda 2}]. \quad (21)$$

The angles ${}_m\psi_{2,\mathbf{h}}$ and $-{}_m\psi_{2,\bar{\mathbf{h}}}$ are now replaced in (20) and (21) with the average angle defined by

$$0{\cdot}5({}_m\psi_{2,\mathbf{h}}-{}_m\psi_{2,\bar{\mathbf{h}}})={}_m\bar{\psi}_{2,\mathbf{h}} \quad (22)$$

and noting that

$$-\varphi^n_{j,\bar{\mathbf{h}}}=\varphi^n_{j,\mathbf{h}} \quad (23)$$

it is possible to solve (20) and (21) as simultaneous equations to obtain

$$\cos({}_m\bar{\psi}_{2,\mathbf{h}}-\varphi^n_{2,\mathbf{h}})\simeq\frac{|{}_m\mathscr{F}_{1,\mathbf{h}}|-|{}_m\mathscr{F}_{2,\mathbf{h}}|+|{}_m\mathscr{F}_{1,\bar{\mathbf{h}}}|-|{}_m\mathscr{F}_{2,\bar{\mathbf{h}}}|}{(|{}_m\mathscr{F}_{3,\mathbf{h}}|+|{}_m\mathscr{F}_{3,\bar{\mathbf{h}}}|)\cos\delta_{m\lambda 2}} \quad (24)$$

$$\sin({}_m\bar{\psi}_{2,\mathbf{h}}-\varphi^n_{2,\mathbf{h}})\simeq\frac{|{}_m\mathscr{F}_{1,\mathbf{h}}|-|{}_m\mathscr{F}_{2,\mathbf{h}}|-|{}_m\mathscr{F}_{1,\bar{\mathbf{h}}}|+|{}_m\mathscr{F}_{2,\bar{\mathbf{h}}}|}{(|{}_m\mathscr{F}_{3,\mathbf{h}}|+|{}_m\mathscr{F}_{3,\bar{\mathbf{h}}}|)\sin\delta_{m\lambda 2}}. \quad (25)$$

It is apparent that the values of ${}_m\bar{\psi}_{2,\mathbf{h}}-\varphi^n_{2,\mathbf{h}}$ and of $|{}_m\mathscr{F}_{3,\mathbf{h}}|+|{}_m\mathscr{F}_{3,\bar{\mathbf{h}}}|$ can be obtained from (24) and (25) since the numerators are composed of measured quantities. When there is one type of predominant anomalous scatterer, $|{}_m\mathscr{F}_{3,\mathbf{h}}|=|{}_m\mathscr{F}_{3,\bar{\mathbf{h}}}|$ and Table 2 shows that such quantities can be expressed in terms of $|F^n_{2,\mathbf{h}}|$ and tabulated values of the real and imaginary corrections to the normal atomic scattering factors. Note also that $\delta_{m\lambda 2}$ is known in terms of the latter tabulated quantities.

The results of applying (24) and (25) are used to form the sines and cosines of numerous phase invariants. This leads to the evaluation of triplet phase invariants of the form ${}_m\bar{\psi}_{2,\mathbf{h}}+{}_m\bar{\psi}_{2,\mathbf{k}}+{}_m\bar{\psi}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}$ from the measured intensities of scattering. We set

$$\Omega_\mathbf{h}={}_m\bar{\psi}_{2,\mathbf{h}}-\varphi^n_{2,\mathbf{h}} \quad (26)$$

and similarly for $\mathbf{k}$ and $\bar{\mathbf{h}}+\bar{\mathbf{k}}$. The subscript 2 in ${}_m\bar{\psi}_{2,\mathbf{h}}$ is associated with ${}_m\mathscr{F}_{2,\mathbf{h}}$ whereas the 2 in $\varphi^n_{2,\mathbf{h}}$ refers to the predominant type of anomalously scattering atoms. To form the triplet phase invariants, we observe that

$$\begin{aligned}\cos(\Omega_\mathbf{h}+\Omega_\mathbf{k}+\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}})&=\cos\Omega_\mathbf{h}\cos\Omega_\mathbf{k}\cos\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}\\&-\cos\Omega_\mathbf{h}\sin\Omega_\mathbf{k}\sin\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}\\&-\sin\Omega_\mathbf{h}\cos\Omega_\mathbf{k}\sin\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}\\&-\sin\Omega_\mathbf{h}\sin\Omega_\mathbf{k}\cos\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}} \quad (27)\end{aligned}$$

and

$$\begin{aligned}\sin(\Omega_\mathbf{h}+\Omega_\mathbf{k}+\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}})&=\sin\Omega_\mathbf{h}\cos\Omega_\mathbf{k}\cos\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}\\&-\sin\Omega_\mathbf{h}\sin\Omega_\mathbf{k}\sin\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}\\&+\cos\Omega_h\sin\Omega_\mathbf{k}\cos\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}\\&+\cos\Omega_\mathbf{h}\cos\Omega_\mathbf{k}\sin\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}. \quad (28)\end{aligned}$$

The information required for the right sides of (27) and (28) is obtainable from (24) and (25).

It is seen from (26) that the triplet $\Omega_\mathbf{h}+\Omega_\mathbf{k}+\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}$ of (27) and (28) is actually the difference between two triplet phase invariants, one for the entire structure and one for the heavy-atom structure,

$$\Omega_\mathbf{h}+\Omega_\mathbf{k}+\Omega_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}={}_m\bar{\psi}_{2,\mathbf{h}}+{}_m\bar{\psi}_{2,\mathbf{k}}+{}_m\bar{\psi}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}$$
$$-(\varphi^n_{2,\mathbf{h}}+\varphi^n_{2,\mathbf{k}}+\varphi^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}). \quad (29)$$

For the simple structures formed from heavy-atom substituents, the triplet phase invariants associated with the larger magnitudes of products of normal structure factors, $|F^n_{2,\mathbf{h}}F^n_{2,\mathbf{k}}F^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$, for the heavy-atom structure can be expected to be close to zero to very good approximation. Thus, the sum composed of the terms $\varphi^n_{2,\mathbf{h}}+\varphi^n_{2,\mathbf{k}}\pm\varphi^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}$ could be eliminated from (29), leaving ${}_m\bar{\psi}_{2,\mathbf{h}}+{}_m\bar{\psi}_{2,\mathbf{k}}+\bar{\psi}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}$. Larger magnitudes for the products of normal structure factors for the heavy-atom structure are ensured by basing the selection of $\mathbf{h}$, $\mathbf{k}$ and $\bar{\mathbf{h}}+\bar{\mathbf{k}}$ on the larger differences, $||{}_m\mathscr{F}_{1,\mathbf{h}}|-|{}_m\mathscr{F}_{2,\mathbf{h}}||$. It is seen from Table 2 that values for the $|F^n_{2,\mathbf{h}}|$ can be obtained from the $|{}_m\mathscr{F}_{3,\mathbf{h}}|$, which in turn can be evaluated by use of (24) and (25). Given sufficient accuracy, such calculations can be used to evaluate $|F^n_{2,\mathbf{h}}F^n_{2,\mathbf{k}}F^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$, obviating the necessity to use the largest magnitude differences $||{}_m\mathscr{F}_{1,\mathbf{h}}|-|{}_m\mathscr{F}_{2,\mathbf{h}}||$. The distribution of values for the cosines of triplet phase invariants for some simple structures has been investigated (Karle, 1984*d*).

On the basis of the above discussion, it follows that by taking the ratio of (28) to (27) an evaluation of ${}_m\bar{\psi}_{2,\mathbf{h}}+{}_m\bar{\psi}_{2,\mathbf{k}}+{}_m\bar{\psi}_{2,(\bar{h}+\bar{k})}$ may be obtained, namely,

$${}_m\bar{\psi}_{2,\mathbf{h}}+{}_m\bar{\psi}_{2,\mathbf{k}}+{}_m\bar{\psi}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}=\tan^{-1}\left[\frac{\text{right side of (28)}}{\text{right side of (27)}}\right]. \quad (30)$$

The signs of the numerator and the denominator uniquely determine the sum of the phases, Ψ, in (30) in the interval $-\pi<\Psi\le\pi$. The quantities $|{}_m\mathscr{F}_{3,\mathbf{h}}|+|{}_m\mathscr{F}_{3,\bar{\mathbf{h}}}|$ concerned with the heavy-atom structure are eliminated in taking the ratio (30). An alternative procedure to the one presented by (30) to evaluate the triplet phase invariants would be to use (24) and (25) to obtain the values for individual phase differences and add up appropriate values to obtain values for the right side of (29). As before, in those instances when the triplet phase invariants for the structure of the anomalously scattering atoms are estimated to be close to zero, the desired result is obtained.

Formulas for ${}_m\bar{\psi}_{1,\mathbf{h}}-\varphi^n_{2,\mathbf{h}}$

It is possible to obtain formulas for ${}_m\bar{\psi}_{1,\mathbf{h}}-\varphi^n_{2,\mathbf{h}}$ that are comparable to (24) and (25). This is accomplished by rewriting (1) as

$$ {}_m\mathscr{F}_{2,\mathbf{h}} = {}_m\mathscr{F}_{1,\mathbf{h}} - {}_m\mathscr{F}_{3,\mathbf{h}}. \tag{31}$$

From (31), it follows that

$$ |{}_m\mathscr{F}_{2,\mathbf{h}}|^2 = |{}_m\mathscr{F}_{1,\mathbf{h}}|^2 + |{}_m\mathscr{F}_{3,\mathbf{h}}|^2 - 2|{}_m\mathscr{F}_{1,\mathbf{h}}|\,|{}_m\mathscr{F}_{3,\mathbf{h}}| \cos({}_m\psi_{1,\mathbf{h}} - {}_m\psi_{3,\mathbf{h}}). \tag{32}$$

With the assumption that

$$ |{}_m\mathscr{F}_{1,\mathbf{h}}| \gg |{}_m\mathscr{F}_{3,\mathbf{h}}|, \tag{33}$$

(32) becomes to good approximation, with neglect of $|{}_m\mathscr{F}_{3,\mathbf{h}}|^2$ and expansion of the square root to the linear term in the cosine,

$$ |{}_m\mathscr{F}_{1,\mathbf{h}}| \simeq |{}_m\mathscr{F}_{2,\mathbf{h}}| + |{}_m\mathscr{F}_{3,\mathbf{h}}| \cos({}_m\psi_{1,\mathbf{h}} - {}_m\psi_{3,\mathbf{h}}). \tag{34}$$

Clearly, (34) is the same as (18) except that ${}_m\psi_{1,\mathbf{h}}$ replaces ${}_m\psi_{2,\mathbf{h}}$. This means that, to this approximation, we can use the same mathematics to make evaluations for triplet phase invariants that involve various ${}_m\bar{\psi}_{1,\mathbf{h}}$ as is used for the ${}_m\bar{\psi}_{2,\mathbf{h}}$. At this approximation, they are interchangeable.

Combining of cases, m, having values on cardinal points

There are several cases, m, for which either $\cos\delta$ or $\sin\delta$ is equal to zero. Under such circumstances, it is not possible to use both (24) and (25) to obtain values for the triplet phase invariants in the manner so far described. Cases i, 1 and 2 (Table 1) are examples, the first and third being associated with $\sin\delta=0$ and the second with $\cos\delta=0$. It is suggested that these cases may be usefully combined. In the following, cases i and 1 will be so treated. The combination of cases 1 and 2 may be treated similarly.

Case i receives a contribution from (24) and case 1 from (25). In order to use these equations in the previously described manner, it is necessary to express $|{}_m\mathscr{F}_{3,\mathbf{h}}|$, $m=i$ and 1, in terms of $|F^n_{2,\mathbf{h}}|$. This can be obtained from Table 2 and the particular expressions for i and 1, respectively, when one predominant type of anomalous scatterer is present, are

$$ \cos({}_i\bar{\psi}_{2,\mathbf{h}} - \varphi^n_{2,\mathbf{h}}) \simeq \frac{|{}_i\mathscr{F}_{1,\mathbf{h}}| - |{}_i\mathscr{F}_{2,\mathbf{h}}| + |{}_i\mathscr{F}_{1,\bar{\mathbf{h}}}| - |{}_i\mathscr{F}_{2,\bar{\mathbf{h}}}|}{2\cos\delta_{i\lambda 2}|F^n_{2,\mathbf{h}}|} \tag{35}$$

and

$$ \sin({}_1\bar{\psi}_{2,\mathbf{h}} - \varphi^n_{2,\mathbf{h}}) \simeq \frac{|{}_1\mathscr{F}_{1,\mathbf{h}}| - |{}_1\mathscr{F}_{2,\mathbf{h}}| - |{}_1\mathscr{F}_{1,\bar{\mathbf{h}}}| + |{}_1\mathscr{F}_{2,\bar{\mathbf{h}}}|}{4\sin\delta_{1\lambda 2}(f''_{\lambda 2}/f^n_{2,\mathbf{h}})|F^n_{2,\mathbf{h}}|}, \tag{36}$$

where, by (22),

$$ {}_i\bar{\psi}_{2,\mathbf{h}} = {}_i\psi_{2,\mathbf{h}} \tag{37}$$

and

$$ {}_1\bar{\psi}_{2,\mathbf{h}} = 0{\cdot}5({}_1\psi_{2,\mathbf{h}} - {}_1\psi_{2,\bar{\mathbf{h}}}). \tag{38}$$

According to the previous section, the replacement of ${}_i\bar{\psi}_{2,\mathbf{h}}$ and ${}_1\bar{\psi}_{2,\mathbf{h}}$ by ${}_i\bar{\psi}_{1,\mathbf{h}}$ and ${}_1\bar{\psi}_{1,\mathbf{h}}$, respectively, may be made in (35)-(38). In order to test the accuracy of triplet phase invariants obtained from combining (35) and (36), comparisons of calculated values are made with known values of

$$ \tfrac{1}{8}({}_i\bar{\psi}_{2,\mathbf{h}} + {}_1\bar{\psi}_{2,\mathbf{h}})({}_i\bar{\psi}_{2,\mathbf{k}} + {}_1\bar{\psi}_{2,\mathbf{k}})({}_i\bar{\psi}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})} + {}_1\bar{\psi}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}). \tag{39}$$

The symbol U is employed to refer to the combination of cases, $m=i$ and $m=1$.

Correction for systematic error

In cases, $m=2$, 3, 5 *and* 7, the quantity $|F^n_{\mathbf{h}}|$ is required. It may be computed from the measured intensities by means of (Karle, 1984*a*)

$$ |F^n_{\mathbf{h}}| = 0{\cdot}5\,W_{\lambda_p\mathbf{h}}(|F_{\lambda_p\mathbf{h}}| + |F_{\lambda_p\bar{\mathbf{h}}}|), \tag{40}$$

where λ_p represents any particular wavelength, and

$$ W_{\lambda_p\mathbf{h}} = \left\{ \frac{\sum_{j=1}^{N_{\text{non}}} f^2_{j\mathbf{h}} + \sum_{j=1}^{N_{\text{ano}}} f^{n2}_{j\mathbf{h}}}{\sum_{j=1}^{N_{\text{non}}} f^2_{j\mathbf{h}} + \sum_{j=1}^{N_{\text{ano}}} [(f^n_{j\mathbf{h}} + f'_j)^2 + f''^2_j]} \right\}^{1/2}. \tag{41}$$

It has been found that use of (40) can introduce a systematic error into the values obtained for the triplet phase invariants. This is especially true for the triplet phase invariants symbolized by 333, 555 and 777, types in which functions (24) and (25), having the same value of m, contribute to the evaluation of the invariants. Correction of the systematic error can be effected by making use of the General Rule (Karle, 1984*d*). The correction is quite simple, involving a uniform adjustment of the values of the computed triplet phase invariants so that the average of their values agrees with those predicted by the General Rule. To adjust the averages, it is necessary to treat those triplet phase invariants associated with positive products of magnitude differences (Karle, 1984*d*) separately from those associated with negative products. The value to which the average for the estimations associated with positive products must be adjusted differs by π from that for the estimations associated with the negative products.

Test calculations

Test calculations were performed on exact data computed from the coordinates for cytochrome c550.PtCl$_4^{2-}$ from *Paracoccus denitrificans* (Timkovich

Table 3. *Calculations based on cytochrome c550.PtCl$_4^{2-}$ at 2·5 Å resolution illustrating the closeness of values between several angles*

Average differences are shown between the average angles ${}_m\bar{\psi}_{1,\mathbf{h}}$ and the angles associated with the structure factor in the absence of anomalous dispersion, $\varphi^n_{\mathbf{h}}$, and the average angles ${}_m\bar{\psi}_{2,\mathbf{h}}$. Average differences are also shown between ${}_m\psi_{1,\mathbf{h}}$ and $-{}_m\psi_{1,\bar{\mathbf{h}}}$. The sequence of the 2900 contributors to the averages was determined by ordering the $\|{}_m\mathscr{F}_{1,\mathbf{h}}|-|{}_m\mathscr{F}_{2,\mathbf{h}}\|$ with the largest first. Averages denoted by the letter *a* concern the first 100 in the sequence, by *b* the last 100 in the sequence and by *c* all 2900.

Case, m	Sequence of $\|{}_m\mathscr{F}_{1,\mathbf{h}}-{}_m\mathscr{F}_{2,\mathbf{h}}\|$	$\langle\lvert{}_m\bar{\psi}_{1,\mathbf{h}}-\varphi^n_{\mathbf{h}}\rvert\rangle$ (rad)	$\langle\lvert{}_m\bar{\psi}_{1,\mathbf{h}}-{}_m\bar{\psi}_{2,\mathbf{h}}\rvert\rangle$ (rad)	$\langle\lvert{}_m\psi_{1,\mathbf{h}}+{}_m\psi_{1,\bar{\mathbf{h}}}\rvert\rangle$ (rad)
1	*a*	0·047	0·026	0·067
	b	0·011	0·020	0·079
	c	0·024	0·022	0·070
2	*a*	0·021	0·021	0·000
	b	0·025	0·024	0·000
	c	0·024	0·024	0·000
3	*a*	0·044	0·044	0·113
	b	0·021	0·021	0·060
	c	0·024	0·024	0·070
4	*a*	0·034	0·018	0·099
	b	0·025	0·017	0·050
	c	0·023	0·015	0·070
5	*a*	0·031	0·031	0·096
	b	0·010	0·010	0·067
	c	0·017	0·017	0·075
6	*a*	0·049	0·032	0·079
	b	0·008	0·006	0·076
	c	0·024	0·015	0·070
7	*a*	0·036	0·036	0·008
	b	0·006	0·006	0·015
	c	0·017	0·017	0·015

Table 4. *Average magnitude of error for a variety of triplet phase invariants from isomorphous replacement and anomalous dispersion data based on cytachrome* c550.PtCl$_4^{2-}$ *at* 2·5 Å *resolution computed by use of* (24), (25), (35), (36) *and ultimately* (30)

The invariants are composed of average angles as given in (22) or as averages of average angles as appear in (39). The symbols of the calculations are composed from the cases *m* that contribute to the calculation. (U represents a combination of $m=i$ and 1). The selection was based on the largest $\|{}_m\mathscr{F}_{1,\mathbf{h}}|-|{}_m\mathscr{F}_{2,\mathbf{h}}\|$, as described in the text. In the case of U, selection was based on $m=i$ rather than $m=1$. Errors were based on known values for the triplet phase invariants composed of the average phases. When two wavelengths were required, Cu *Kα* and Mo *Kα* were used. Otherwise only Cu *Kα* was used. The values of $|F^n_{\mathbf{h}}|$ employed in types 3 and 5 were computed from (40) with use of Mo *Kα* data. For the calculations marked by an asterisk in the last column, the data involved Pt, Fe, Cl and S as anomalous scatterers but the data were treated as if Pt were the only anomalous scatterer. In the remaining calculations, the data inolved Pt as the only anomalous scatterer. Further calculations relevant to these results appear in Tables 5 and 6.

Row	Number of invariants	Symbol of calculation	Average error (rad)
1	991	*UUU*	0·12
2	787	*UUU*	0·32*
3	1168	*UU*3	0·19
4	1190	*UU*4	0·10
5	1193	*UU*5	0·21
6	1227	*UU*6	0·09
7	1039	*U*33	0·33
8	1225	*U*44	0·10
9	960	*U*55	0·31
10	1078	*U*66	0·07
11	2260	*U*46	0·08
12	929	*U*46	0·44*
13	1973	*U*35	0·31
14	1258	*U*35	0·41*
15	1904	345	0·34
16	794	345	0·36*
17	1535	356	0·31
18	1210	356	0·39*
19	1469	333	0·46
20	1107	333	0·54*
21	2167	444	0·10
22	1373	555	0·43
23	1169	555	0·52*
24	1416	666	0·05

& Dickerson, 1976). The structure factors were computed in two ways. One calculation introduced anomalous effects from the Pt atom alone and the second included anomalous effects from the Pt, Fe, S and Cl atoms. The first calculation evidently models the case when, strictly speaking, there would be only one type of anomalous scatterer. Its purpose is to provide a basis of comparison for determining the effect on the error of including all four types of anomalous scatterers in the data while treating the data as if the Pt atoms were the one predominant type of anomalous scatterer.

The calculations presented in Table 3 involve only the data that contain anomalous effects from Pt, Fe, S and Cl atoms. Column 3 indicates that there is a very small difference between the average angles ${}_m\bar{\Psi}_{1,\mathbf{h}}$ and $\varphi^n_{\mathbf{h}}$, the angle associated with the structure factor $F^n_{\mathbf{h}}$, which is the structure factor that would be obtained if all atoms scattered non-anomalously. Column 4 indicates that there is a very small difference between the average angles ${}_m\bar{\psi}_{1,\mathbf{h}}$ and ${}_m\bar{\psi}_{2,\mathbf{h}}$. Column 5 shows that the differences between ${}_m\psi_{1,\mathbf{h}}$ and $-{}_m\psi_{1,\bar{\mathbf{h}}}$ are also rather modest. The calculations did not include data for which $|F_{\lambda\mathbf{h}}|$ and $|F_{\lambda\bar{\mathbf{h}}}|<100$, thus eliminating the smallest magnitudes. This was also done in the calculations included in Tables 4–6.

Test calculations that involved use of (24), (25), (35), (36) and, ultimately, (30) are illustrated in Tables 4, 5 and 6. The invariants are composed of average angles as given in (22) or (39) and no distinction is made between ${}_m\psi_{2,\mathbf{h}}$ and ${}_m\bar{\psi}_{1,\mathbf{h}}$. The symbols of the calculations are composed from the cases m that contribute to the calculations (U represents a combination of $m=i$ and 1).

The selection of the reflections for the test calculations was based on the appropriate largest magnitude differences $\|{}_m\mathscr{F}_{1,\mathbf{h}}|-|{}_m\mathscr{F}_{2,\mathbf{h}}\|$ in a manner entirely analogous to that for the application of the General Rule (Karle, 1984*d*). The reflections were chosen from a list of the 400 top magnitude differences for each case when there were either two or three different values of m in the symbolic representation of a calculation. When there was only one value of m in the symbol, the choice of reflections was based on the 800 top magnitude differences appropriate to the calculation. The average error listed is the average of the magnitudes of the differences between the known

Table 5. *Calculations in which the* $|F_{\mathbf{h}}^{n}|$ *have exact values instead of values computed from* (40) *with the use of* Mo $K\alpha$ *data*

Comparison with Table 4 shows that there is considerable reduction of the average magnitude of error.

Row in Table 4	Number of invariants	Symbol of calculation	Average error (rad)
3	1305	*UU*3	0·10
5	1224	*UU*5	0·11
9	1135	*U*55	0·10
15	2088	345	0·07
17	1792	356	0·06
19	1753	333	0·10
22	1508	555	0·10

values for the triplet phase invariants formed from the $\bar{\psi}$ and those computed by the methods described in this paper.

In Table 4, the asterisk denotes those calculations in which the data contain anomalous scattering contributions from the Pt, Fe, S and Cl atoms. The ones without the asterisk concern calculations in which the data contain anomalous scattering contributions only from the Pt atoms. The smallest errors are incurred when the data are based on a single type of anomalous scatterer and the calculation does not involve the evaluation of the $|F_{\mathbf{h}}^{n}|$ by use of (40). The largest errors are incurred for calculations involving $m=3$ or 5, which require the use of (40), and for those that used data that contain anomalous scattering contributions from the Fe, S and Cl atoms as well as from the Pt atom. Table 5 shows the reduction in average magnitude of error that would accrue if it were possible to obtain the $|F_{\mathbf{h}}^{n}|$ more accurately than from use of (40) with Mo $K\alpha$ radiation. In two tests, use of Ag $K\alpha$ gave only very modest improvements, 1 and 5°. Table 6 shows some rather significant improvements in the average magnitude of error from use of the correction for systematic error. The average errors listed in the final column of Table 6 may be compared with those of the corresponding rows of Table 4, *i.e.* 19, 20, 22 and 23, respectively. It is seen that improvements ranging from 0·12 to 0·28 rad are obtained.

Concluding remarks

It is apparent from Table 4 that many more data could have been included in the calculations than were actually used and from the existence of numerous additional types of calculations that the evaluation of a very large number of invariants is potentially possible. In context, these calculations bear close similarities to those described in terms of a General Rule (Karle, 1984*d*) that is based on some mathematical and physical properties of isomorphous replacement and anomalous dispersion data. The General Rule applies when there is one predominant type of anomalous scatterer. The same is also true for the algebraic analysis presented here. Comparisons between the results of the calculations presented here and those based on the General Rule show an improvement of accuracy with use of the algebra. In the paper concerning the General Rule, test calculations were made only on data containing contributions from the anomalous scattering of Pt, Fe, S and Cl atoms. When the General Rule is applied to data containing contributions from the anomalous scattering of Pt alone, a decrease in error has been observed, but it still remains higher than that obtained from the corresponding algebraic equations in this paper.

In the tests presented in Tables 4, 5 and 6, it is seen that the average of the magnitudes of error range from only a very few degrees to about 25° (after application of the corrections in Table 6). This is the error introduced by use of the mathematics. Additional errors that derive from experimental uncertainties will determine the extent to which these calculations can be applicable to practical procedures for phase determination. This is a matter for much future study.

An exact algebraic analysis of multiwavelength anomalous dispersion experiments has been published (Karle, 1980). In order to obtain information concerning individual phase values in the latter analysis it would be necessary to know the structure of at least one type of anomalously scattering atoms. The exact algebraic analysis is applicable to any number

Table 6. *Application of correction for systematic error in the calculation of* $|F_{\mathbf{h}}^{n}|$ *from* (40) *with the use of* Mo $K\alpha$ *data*

Comparison with Table 4 shows a reduction of the average magnitude of error.

Symbol of calculation	Anomalously scattering atoms	Number of invariants (+product)	Average error (rad)	After Correction for systematic error	Number of invariants (−product)	Average error (rad)	After correction for systematic error	Total invariants	Overall corrected error (rad)
333	Pt	423	0·44	0·31	1046	0·47	0·12	1469	0·18
333	Pt, Fe S, Cl	402	0·48	0·39	705	0·58	0·30	1107	0·34
555	Pt	560	0·42	0·29	813	0·43	0·32	1373	0·31
555	Pt, Fe S, Cl	493	0·48	0·45	676	0·55	0·35	1169	0·39

and type of anomalously scattering atoms and can readily incorporate information from isomorphous replacement. If a heavy-atom structure is not known, it is still possible to evaluate triplet phase invariants (Karle, 1984*e*) from the exact algebraic analysis.

The algebraic analysis presented here involves somewhat different quantities. In its range of applicability, individual phase information would also be derivable from the present analysis if the heavy-atom structure were known since, then, $\varphi^n_{2,\mathbf{h}}$ in (24) and (25) would be known. The two kinds of algebraic analyses are expected to yield closely equivalent results in their areas of common applicability.

In order to apply the results of this paper, which concern one predominant type of anomalous scatterer, it is only necessary to know the chemical identity of this type of anomalous scatterer.

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References

GIACOVAZZO, C. (1983). *Acta Cryst.* **A39**, 585-592.
HAUPTMAN, H. (1982). *Acta Cryst.* **A38**, 289-294, 632-641.
KARLE, J. (1980). *Int. J. Quantum Chem.* **7**, 357-367.
KARLE, J. (1983). *Acta Cryst.* **A39**, 800-805.
KARLE, J. (1984*a*). *Acta Cryst.* **A40**, 1-4.
KARLE, J. (1984*b*). *Acta Cryst.* **A40**, 4-11.
KARLE, J. (1984*c*). *Acta Cryst.* **A40**, 366-373.
KARLE, J. (1984*d*). *Acta Cryst.* **A40**, 374-379.
KARLE, J. (1984*e*). *Acta Cryst.* **A40**, 526-531.
PONTENAGEL, W. M. G. F., KRABBENDAM, H., PEERDEMAN, A. F. & KROON, J. (1983). Eighth Eur. Crystallogr. Meet., 8-12 August, Abstract 4.01-P, p. 257.
TIMKOVITCH, R. & DICKERSON, R. E. (1976). *J. Biol. Chem.* **251**, 4033-4046.

Acta Cryst. (1985). **A41**, 189-195

Intensities, Structure Factors and their Variances

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Abstract

Hypothetical variances are checked and improved and observations are tested for normal and independent distribution by means of χ^2 distributions. For the conversion of σ_I^2 into σ_F^2 and of I into F the quantity $X(I)=\operatorname{sign}(I)|I|^{1/2}$ instead of $F=pI^{1/2}$ ($p=$ Lorentz correction *etc.*) is considered. With the probability density function $f(I)$ for I the variance of F is

$$\sigma_F^2=p^2\left\{\int\limits_{-\infty}^{+\infty} X^2(I)f(I)\,\mathrm{d}I-\left[\int\limits_{-\infty}^{+\infty} X(I)f(I)\,\mathrm{d}I\right]^2\right\}.$$

This formula is also valid if the observed intensity is zero or negative. Unexpectedly, the approximate $\sigma'_F=p\sigma_I/(2I^{1/2})$ are in most cases smaller than the correct ones. The simple formula $F=pI^{1/2}$ yields F that in the mean are too low. The correction formula valid for all ratios I/σ_I is $F_{\rm corr}=p(2I^{1/2}-A)$, where I is the observed intensity and A the second integral in the above formula for σ_F^2. Since the expressions σ_F^2 and $F_{\rm corr}$ are known, there is no other reason to discard weak intensities than the fact that this saves computing time. Examples are given and the normal probability plot is applied.

Introduction

Hypothetical variances σ_I^2 of integrated intensities I of the rotating-crystal method can be obtained by means of Poisson's formula:

$$I=IT-\alpha(BL+BH) \quad (1)$$

$$\sigma_I^2=IT+\alpha^2(BL+BH). \quad (2)$$

IT is the sum of all X-ray quanta recorded by the counter during the rotation of the crystal through the reflecting orientation. BL and BH are the low- and high-angle background counts and α is the ratio of the times that were spent for the measurements of IT and of $(BL+BH)$. It is not essential that I and σ_I^2 are obtained by as simple formulae as (1) and (2); the arguments given in the following apply also if more sophisticated measuring procedures and formulae for the determination of I and σ_I^2 are used as, for example, proposed by Shoemaker (1968), Blessing, Coppens & Becker (1974) or Lehmann (1975).

The necessity and procedures to correct pure Poisson variances have been discussed by many authors, *e.g.* Jeffery (1964), Jeffery & Rose (1964),

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