Acta Cryst. (1984). A40, 374–379

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

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(*Received* 6 *December* 1983; *accepted* 24 *February* 1984)

Abstract

On the basis of a common characteristic observed in previously derived formulas for the evaluation of triplet phase invariants from either isomorphous replacement data or anomalous dispersion data, it has been found possible to combine mathematical expressions, certain differences of magnitudes, arising in the analysis of the two techniques to form a myriad of new mixed formulas. The common characteristic is that the various types of differences of magnitudes that are involved in the formulas are all definable in terms of the heavy-atom structure. The formulas involve the mixing of terms arising from several isomorphous derivatives or from a combination of such terms with various types of terms arising in anomalous dispersion or the mixing of various terms arising in anomalous dispersion alone. The evaluation of the triplet phase invariants is facilitated by the use of a simple rule, called the General Rule, that is generally applicable to the case of one predominant type of anomalous scatterer. In the case of more than one predominant type of anomalous scatterer, a slightly more complicated calculation is required and is described. Test calculations show that a very large number of invariants may be evaluated by these means with reliabilities that are potentially high, but depend, of course, on the reliability of the experimental data. A benefit from having the large variety of formulas is that triplet phase invariants can be evaluated at many points throughout the range $-\pi$ to π and their reliability is enhanced because much information is obtained from only the largest differences of magnitudes.

Introduction

Formulas for the evaluation of triplet phase invariants from isomorphous-replacement data have been derived from special mathematical and physical characteristics of the isomorphous replacement technique (Karle, 1983). Similarly, by making use of mathematical and physical characteristics of the anomalous dispersion technique, formulas have been obtained for the evaluation of triplet phase invariants from anomalous dispersion data at one wavelength (Karle, 1983*b*) and at two wavelengths (Karle, 1984*c*).

The formal characteristics of the analysis for both techniques, isomorphous replacement and anomalous dispersion, are quite similar, thus facilitating the development of a very large number of formulas that not only are formed from a combination of the two techniques but also may be comprised solely of hybrid combinations of terms from more than one isomorphous derivative or from the large variety of terms that occurred in the earlier work on anomalous dispersion.

The characteristics of interest concern observations related to the differences of magnitudes of selected types of structure factors and also the expected values of triplet phase invariants associated with the structure of the heavy atoms acting as heavy-atom replacements in isomorphous replacement or as anomalous scatterers. The conceptual basis for these observations and their nature will be described in general terms in the next section.

The result to be obtained in this paper is a table from which a large variety of terms can be selected to form triple products of magnitude differences and sums of phases that are the essence of a large number of different formulas for evaluating triplet phase invariants. The virtue of having a large number of different formulas is that a large number of the most reliable evaluations can be performed and they are distributed among many points that range from $-\pi$ to π.

Conceptual basis

The concepts that form the basis for generating the large variety of formulas are illustrated in Fig. 1. This figure has already provided the basis for the development of formulas for evaluating triplet phase invariants from isomorphous-replacement data (Karle, 1983) and from anomalous dispersion data in the case of single-wavelength data (Karle, 1984*b*) and multiple-wavelength data (Karle, 1984*c*). The symbolism associated with the letter $\mathcal{F}$ represents the eight cases listed in Table 1. The first case, labelled 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

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Table 1. *Quantities involved in the evaluation of triplet phase invariants by use of the General Rule*

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. Note that case i may refer to a number of isomorphous derivatives, $i_1, i_2, \ldots$, and that cases $m = 1$–7 may refer to data collected at a variety of wavelengths.

Case, m	${}_m\mathscr{F}_{1,\mathbf{h}}$	${}_m\mathscr{F}_{2,\mathbf{h}}$	${}_m\mathscr{F}_{3,\mathbf{h}}$	δ_{mj}	f_{mj}
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	$F_{\lambda_p\mathbf{h}}$	$F^n_{\mathbf{h}}$	$F^a_{\lambda_p\mathbf{h}}$	$\delta^{\pm}_{\lambda_p j}$	$f^{a\pm}_{\lambda_p j}$
4	$F_{\lambda_1\mathbf{h}}$	$F_{\lambda_2\mathbf{h}}$	$F^a_{\lambda_1\mathbf{h}} - F^a_{\lambda_2\mathbf{h}}$	$\delta^{\pm,\mp}_{\lambda_1\lambda_2 j}$	$f^{a\pm,\mp}_{\lambda_1\lambda_2 j}$
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	$F_{\lambda_1\mathbf{h}} + F^*_{\lambda_2\bar{\mathbf{h}}}$	$2F^n_{\mathbf{h}}$	$F^a_{\lambda_1\mathbf{h}} + F^{a*}_{\lambda_2\bar{\mathbf{h}}}$	$\delta^{-,+}_{\lambda_1\lambda_2 j}$	$f^{a-,+}_{\lambda_1\lambda_2 j}$

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 material, for example, a macromolecule with heavy-atom substituents, $F_{\mathbf{h}P}$ is the corresponding structure factor for the unsubstituted material 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

$$F_{\mathbf{h}PH} = F_{\mathbf{h}P} + F_{\mathbf{h}H} \tag{1}$$

and

$$F_{\lambda_p\mathbf{h}} = F^n_{\mathbf{h}} + F^a_{\lambda_p\mathbf{h}}. \tag{2}$$

It follows from (1) and (2) that, for all the cases in Table 1,

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

The atomic scattering factor for the qth atom that scatters anomalously is given by

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

where $f^n_{q,\mathbf{h}}$ is the normal atomic scattering factor and f'_q and f''_q are the real and imaginary parts of the anomalous correction, respectively. The entries for δ_{mj} in Table 1, items 4–7, will be defined below. They play a key role in the evaluation of the triplet phase invariants. The f_{mj} will also be defined below. They play a significant role when there is more than one predominant type of anomalous scatterer.

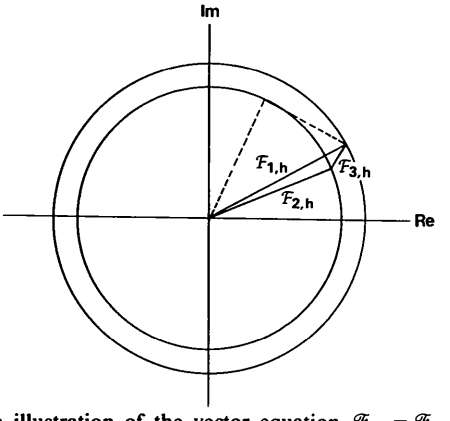

Fig. 1. An illustration of the vector equation $\mathscr{F}_{1,\mathbf{h}} = \mathscr{F}_{2,\mathbf{h}} + \mathscr{F}_{3,\mathbf{h}}$. The largest magnitude differences, $\|\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}\|$, are associated with the largest possible values of $|\mathscr{F}_{3,\mathbf{h}}|$. This case is represented by the triangle formed from the solid lines. The placement of the dotted line representing an alternative position for $\mathscr{F}_{2,\mathbf{h}}$ would not be possible if the magnitude of the dotted line connecting it to $\mathscr{F}_{1,\mathbf{h}}$ would exceed the maximum possible value. This implies that, for the largest magnitude differences, the phase angles for $\mathscr{F}_{1,\mathbf{h}}$ and $\mathscr{F}_{2,\mathbf{h}}$ do not differ by much.

As indicated above, the insights afforded by Fig. 1 have already provided the basis for the evaluation of triplet phase invariants in isomorphous-replacement and anomalous-dispersion experiments. The insights are also applicable to the derivation of the combination formulas to be described. For convenience, therefore, the characteristics of Fig. 1 are repeated here.

The solid lines forming the closed triangle in Fig. 1 represent the vector equation (3), with the presubscript m omitted. Given, for example, the vector $\mathscr{F}_{1,\mathbf{h}}$ as in Fig. 1, the dotted line of radius $|\mathscr{F}_{2,\mathbf{h}}|$ could be a possible location for $\mathscr{F}_{2,\mathbf{h}}$, but not necessarily. It would not be possible if the dotted line connecting this vector with $\mathscr{F}_{1,\mathbf{h}}$ would have to have a magnitude that exceeds the maximum possible value for $|\mathscr{F}_{3,\mathbf{h}}|$. The implication of this observation is that if the largest differences $\|\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}\|$ were selected from a data set, they would be associated with the largest possible values of $|\mathscr{F}_{3,\mathbf{h}}|$ and $\mathscr{F}_{1,\mathbf{h}}$ and $\mathscr{F}_{2,\mathbf{h}}$ would have phases that do not differ greatly. We formalize these observations and their implications as follows:

1. The largest magnitude differences, $\|\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}\|$, are associated with the largest values of the magnitudes $|\mathscr{F}_{3,\mathbf{h}}|$.

2. Triplet phase invariants associated with the largest $|\mathscr{F}_{3,\mathbf{h}}\mathscr{F}_{3,\mathbf{k}}\mathscr{F}_{3,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ can be expected to have values close to zero, especially for simple 'heavy-atom' structures. [The triplet phase invariants refer to the non-anomalous portion of the scattering, $(\varphi^n_{j,\mathbf{h}} +$

$\varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}$); additional phase functions arise from the anomalous portion of the scattering and can be readily evaluated from appropriate tables.]

3. For the larger values of $\|\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}\|$, the phase of $\mathscr{F}_{1,\mathbf{h}}$ will differ little in value from the phase of $\mathscr{F}_{2,\mathbf{h}}$.

Theory

The development of the combination formulas depends upon the analysis of the triplet product that follows from (3),

$$({}_u\mathscr{F}_{1,\mathbf{h}} - {}_u\mathscr{F}_{2,\mathbf{h}})({}_v\mathscr{F}_{1,\mathbf{k}} - {}_v\mathscr{F}_{2,\mathbf{k}})({}_w\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})} - {}_w\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}) = ({}_u\mathscr{F}_{3,\mathbf{h}})({}_v\mathscr{F}_{3,\mathbf{k}})({}_w\mathscr{F}_{3,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}), \quad (5)$$

where the u, v and w can independently assume any of the eight values of m and their corresponding definitions, as given in Table 1. The left side of (5) may be rewritten

$$\begin{aligned}
&|{}_u\mathscr{F}_{1,\mathbf{h}}\ {}_v\mathscr{F}_{1,\mathbf{k}}\ {}_w\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad\times\exp[i({}_u\varphi_{1,\mathbf{h}} + {}_v\varphi_{1,\mathbf{k}} + {}_w\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad-|{}_u\mathscr{F}_{1,\mathbf{h}}\ {}_v\mathscr{F}_{1,\mathbf{k}}\ {}_w\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad\times\exp[i({}_u\varphi_{1,\mathbf{h}} + {}_v\varphi_{1,\mathbf{k}} + {}_w\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad-|{}_u\mathscr{F}_{1,\mathbf{h}}\ {}_v\mathscr{F}_{2,\mathbf{k}}\ {}_w\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad\times\exp[i({}_u\varphi_{1,\mathbf{h}} + {}_v\varphi_{2,\mathbf{k}} + {}_w\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad+|{}_u\mathscr{F}_{1,\mathbf{h}}\ {}_v\mathscr{F}_{2,\mathbf{k}}\ {}_w\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad\times\exp[i({}_u\varphi_{1,\mathbf{h}} + {}_v\varphi_{2,\mathbf{k}} + {}_w\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad-|{}_u\mathscr{F}_{2,\mathbf{h}}\ {}_v\mathscr{F}_{1,\mathbf{k}}\ {}_w\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad\times\exp[i({}_u\varphi_{2,\mathbf{h}} + {}_v\varphi_{1,\mathbf{k}} + {}_w\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad+|{}_u\mathscr{F}_{2,\mathbf{h}}\ {}_v\mathscr{F}_{1,\mathbf{k}}\ {}_w\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad\times\exp[i({}_u\varphi_{2,\mathbf{h}} + {}_v\varphi_{1,\mathbf{k}} + {}_w\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad+|{}_u\mathscr{F}_{2,\mathbf{h}}\ {}_v\mathscr{F}_{2,\mathbf{k}}\ {}_w\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad\times\exp[i({}_u\varphi_{2,\mathbf{h}} + {}_v\varphi_{2,\mathbf{k}} + {}_w\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad-|{}_u\mathscr{F}_{2,\mathbf{h}}\ {}_v\mathscr{F}_{2,\mathbf{k}}\ {}_w\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad\times\exp[i({}_u\varphi_{2,\mathbf{h}} + {}_v\varphi_{2,\mathbf{k}} + {}_w\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})]. \quad (6)
\end{aligned}$$

On the basis of observation 3 above, when the appropriate magnitude differences are large, the triplet phase invariants in (6) may be replaced by some average value, $\langle {}_t\Phi_{\mathbf{hk}}\rangle$, and then (6) may be rewritten

$$(|{}_u\mathscr{F}_{1,\mathbf{h}}| - |{}_u\mathscr{F}_{2,\mathbf{h}}|)(|{}_v\mathscr{F}_{1,\mathbf{k}}| - |{}_v\mathscr{F}_{2,\mathbf{k}}|) \times(|{}_w\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| - |{}_w\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|)\exp(i\langle {}_t\Phi_{\mathbf{hk}}\rangle), \quad (7)$$

where the components of $\mathbf{t}$ are u, v and w, *i.e.* $\mathbf{t} \equiv (u, v, w)$. By comparing (7) with the right side of (5) and making use of observations 1 and 2, the opportunity for evaluating $\langle {}_t\Phi_{\mathbf{hk}}\rangle$ will ensue for the numerical combinations of eight cases listed in Table 1. It is because ${}_m\mathscr{F}_{3,\mathbf{h}}$ is definable in terms of the 'heavy-atom' structure for all cases m given in Table 1 that it is possible to make combination formulas in which u, v and w can independently assume any value of m. If desired, the evaluation may be applied to those triplet phase invariants in (6) that are associated only with the largest products of $\mathscr{F}$ magnitudes. Previous calculations (Karle, 1983) have indicated that an increase in accuracy may be achieved in this way, although it may not be of any great practical significance to do so.

When there is a single predominant type of anomalous scatterer, it is a simple matter to evaluate the large variety of triplet phase invariants by use of Table 1. Otherwise, somewhat more complicated and somewhat approximate calculations are required unless the structure of the anomalous scatterers is known. The information in Table 1, however, is still pertinent to the more complex calculations.

Definitions of appropriate mathematical quantities

Since the left side of (5), as approximated by (7), is to be compared with the right side of (5) as a means for evaluating the average triplet phase invariants $\langle {}_t\Phi_{\mathbf{hk}}\rangle$, definitions for the ${}_m\mathscr{F}_{3,\mathbf{h}}$ will now be given. The definitions are based on the results of previous mathematical analyses (Karle, 1983, 1984*b*, *c*).

We have the general definition

$${}_m\mathscr{F}_{3,\mathbf{h}} = \sum_{j=2}^{q+1} (f_{mj}/f^n_{j,\mathbf{h}})\exp(i\delta_{mj})F^n_{j,\mathbf{h}}, \quad (8)$$

where f_{mj} and δ_{mj} 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 structure factors for each type of anomalously scattering atom. Additional definitions required for the use of Table 1 are

$$f^a_{\lambda_{pj}} = (f'^2_{\lambda_{pj}} + f''^2_{\lambda_{pj}})^{1/2} \quad (9)$$

$$\delta_{\lambda_{pj}} = \tan^{-1}(f''_{\lambda_{pj}}/f'_{\lambda_{pj}}) \quad (10)$$

$$f^{a-,-}_{\lambda_1\lambda_2 j} = [(f''_{\lambda_1 j} - f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} - f'_{\lambda_2 j})^2]^{1/2} \quad (11)$$

$$\delta^{-,-}_{\lambda_1\lambda_2 j} = \tan^{-1}[(f''_{\lambda_1 j} - f''_{\lambda_2 j})/(f'_{\lambda_1 j} - f'_{\lambda_2 j})] \quad (12)$$

$$f^{a+,+}_{\lambda_1\lambda_2 j} = [(f''_{\lambda_1 j} + f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} + f'_{\lambda_2 j})^2]^{1/2} \quad (13)$$

$$\delta^{+,+}_{\lambda_1\lambda_2 j} = \tan^{-1}[(f''_{\lambda_1 j} + f''_{\lambda_2 j})/(f'_{\lambda_1 j} + f'_{\lambda_2 j})] \quad (14)$$

$$f^{a+,-}_{\lambda_1\lambda_2 j} = [f''_{\lambda_1 j} + f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} - f'_{\lambda_2 j})^2]^{1/2} \quad (15)$$

$$\delta^{+,-}_{\lambda_1\lambda_2 j} = \tan^{-1}[(f''_{\lambda_1 j} + f''_{\lambda_2 j})/(f'_{\lambda_1 j} - f'_{\lambda_2 j})] \quad (16)$$

$$f^{a-,+}_{\lambda_1\lambda_2 j} = [(f''_{\lambda_1 j} - f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} + f'_{\lambda_2 j})^2]^{1/2} \quad (17)$$

$$\delta^{-,+}_{\lambda_1\lambda_2 j} = \tan^{-1}[(f''_{\lambda_1 j} - f''_{\lambda_2 j})/(f'_{\lambda_1 j} + f'_{\lambda_2 j})]. \quad (18)$$

One predominant type of anomalous scatterer

If there is one predominant type of anomalous scatterer, the right side of (5) may be written, by use

of (8),

$$(f_{u2}f_{v2}f_{w2}/f^n_{2,\mathbf{h}}f^n_{2,\mathbf{k}}f^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}) \times \exp[i(\delta_{u2}+\delta_{v2}+\delta_{w2})]|F^n_{2,\mathbf{h}}F^n_{2,\mathbf{k}}F^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp[i(\varphi^n_{2,\mathbf{h}}+\varphi^n_{2,\mathbf{k}}+\varphi^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})], \quad (19)$$

where the subscript 2 refers to the predominant type of anomalous scatterer. According to observation 2, for large values of $|F^n_{2,\mathbf{h}}F^n_{2,\mathbf{k}}F^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ obtained by use of observation 1, the triplet phase invariants $(\varphi^n_{2,\mathbf{h}}+\varphi^n_{2,\mathbf{k}}+\varphi^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})$ will have values close to zero and the initial factor in (19) has a positive value. A comparison of (19) with (7) leads to the following General Rule for the case of one predominant type of anomalous scatterer:

General Rule: *If the sign of the product of the largest magnitude differences,* $(|_u\mathscr{F}_{1,\mathbf{h}}|-|_u\mathscr{F}_{2,\mathbf{h}}|)(|_v\mathscr{F}_{1,\mathbf{k}}|-|_v\mathscr{F}_{2,\mathbf{k}}|)(|_w\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|-|_w\mathscr{F}_{2(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|)$, *is plus, the value of the associated average triplet phase invariant,* $\langle_t\Phi_{\mathbf{hk}}\rangle$, *is close to* $(\delta_{u2}+\delta_{v2}+\delta_{w2})$ *and, when it is minus, the value of the average triplet phase invariant is close to* $(\delta_{u2}+\delta_{v2}+\delta_{w2})+\pi$.

The General Rule includes the one rule, R_{iso}, for isomorphous replacement (Karle, 1983) and the seven rules, $R_{\text{ano},n}$ $(n=1,\ldots,7)$, for anomalous dispersion (Karle, 1984*b*, *c*). These arise when $u=v=w$. It also contains numerous other possibilities because each of u, v and w can independently assume any value of m given in Table 1 and individual values of m can represent several possibilities.

The General Rule, in effect, assigns the estimate to all eight triplet phase invariants in (6). As a modification to the General Rule, the estimates may be assigned only to those triplet phase invariants that are associated with the larger products of structure-factor magnitudes among the eight possibilities given in (6), instead of to all eight of them. Improved accuracy may be obtained this way.

It is a very simple matter to use the General Rule, Table 1 and definitions (9)–(18) to evaluate a myriad of triplet phase invariants. Once u, v and w are identified, the fifth column of Table 1 identifies the corresponding angles and $(\delta_{u2}+\delta_{v2}+\delta_{w2})$ can then be computed from the appropriate definitions. In addition, Table 1 can be used to select the proper structure-factor expressions and form the triple products of the largest differences. Depending upon whether the triple products of magnitude differences are positive or negative, the values of the average triplet phase invariants are estimated to be $(\delta_{u2}+\delta_{v2}+\delta_{w2})$ or $(\delta_{u2}+\delta_{v2}+\delta_{w2})+\pi$, respectively.

More than one predominant type of anomalous scatterer

In general, the right side of (5) can be expressed as the product of three sums, as given on the right side of (8). The three sums could be readily evaluated if the heavy-atom structure were known and compared with (7). If only the chemical composition of the heavy-atom structure were known, a suitable approximation would be the neglect of cross terms in the product of the three sums to give

$$\sum_{j=2}^{q+1}(f_{uj}f_{vj}f_{wj}/f^n_{j,\mathbf{h}}f^n_{j,\mathbf{k}}f^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})} \times \exp[i(\delta_{uj}+\delta_{vj}+\delta_{wj})]|F^n_{j,\mathbf{h}}F^n_{j,\mathbf{k}}F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp[i(\varphi^n_{j,\mathbf{h}}+\varphi^n_{j,\mathbf{k}}+\varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})]. \quad (20)$$

With knowledge of the chemical composition of the heavy atoms, the values of the $|F_{j,\mathbf{h}}F_{j,\mathbf{k}}F_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ could be evaluated approximately on the assumption that the quantity $[|F^n_{j,\mathbf{h}}|/f^n_{j,\mathbf{h}}n_j^{1/2}]$, where n_j is the number of atoms of type j, is the same for all j in some average sense. By making use of this assumption and the fact that the triplet phase invariants have values close to zero when the products $|F^n_{j,\mathbf{h}}F^n_{j,\mathbf{k}}F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ are large, (20) becomes

$$c\sum_{j=2}^{q+1} n_j^{3/2}f_{uj}f_{vj}f_{wj}\exp[i(\delta_{uj}+\delta_{vj}+\delta_{wj})], \quad (21)$$

where c is a proportionality constant of no significance to the application. If, then, the right side of (5) is known accurately because the heavy-atom structure is known, or it is known approximately in terms of (21) when the chemical composition of the heavy atoms is known, the right side of (5) is a complex number that can be expressed in terms of a magnitude and a phase. It is this latter phase, or this latter phase plus π, that forms the estimate of $\langle_t\Phi_{\mathbf{hk}}\rangle$ depending upon whether the product of magnitude differences in (7) is positive or negative, respectively. This result for more than one predominant type of anomalous scatterer will reduce to the result for the estimate of average triplet phase invariants given above for the case of one predominant type of anomalous scatterer.

Test calculations

Test calculations were performed on exact data computed from the coordinates for cytochrome c550 . $PtCl_4^{2-}$ from *Paracoccus denitrificans* (Timkovich & Dickerson, 1976). 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 facilitated by Table 1. The Pt atoms were regarded as the predominant type of anomalous scatterer. The results are shown in Table 2. For formulas requiring single-wavelength data, Cu $K\alpha$ radiation was used. When two wavelengths were required, Cu $K\alpha$ and Mo $K\alpha$ radiation were used. The values of $|F^n_{\mathbf{h}}|$ employed in terms corresponding to cases $m=3$ and 5 of Table 1 were computed with use of Mo $K\alpha$ radiation from (Karle, 1984*a*)

$$|F^n_{\mathbf{h}}| \simeq 0{\cdot}5\,W_{\lambda_p\mathbf{h}}(|F_{\lambda_p\mathbf{h}}|+|F_{\lambda_p\bar{\mathbf{h}}}|), \quad (22)$$

Table 2. *Estimates of values of a variety of triplet phase invariants from isomorphous replacement and anomalous dispersion data for cytochrome* c550 . $PtCl_4^{2-}$ *at* 2·5 Å *resolution by use of the General Rule and Table* 1

For formulas requiring single-wavelength data, Cu $K\alpha$ was used. When two wavelengths were required, Cu $K\alpha$ and Mo $K\alpha$ were used. The values of $|F_{\mathbf{h}}^n|$ employed in terms of types 3 and 5 were computed from (22) with use of Mo $K\alpha$ data. The symbols in column 2 refer to the types of magnitude differences, as defined in Table 1, comprising the triple products of magnitude differences. Errors and average values are based on the correct values of the average triplet phase invariants.

Row	Number of invariants	Symbol of calculation	Estimate	Actual average value	Average error (rad)
1	981	*ii*1	1·57	1·46	0·56
2	970	*ii*1	−1·57	−1·50	0·56
3	748	*i*11	3·14	3·18	0·79
4	775	*i*11	0·00	0·06	0·62
5	1956	*ii*6	1·76	1·77	0·54
6	2155	*ii*6	−1·38	−1·24	0·52
7	1853	*i*66	−2·77	−2·48	0·71
8	1725	*i*66	0·37	0·53	0·58
9	1018	116	−1·38	−1·31	0·73
10	972	116	1·76	1·91	0·76
11	1177	166	−1·20	−0·96	0·70
12	1197	166	1·94	2·27	0·79
13	466	*i*16	−2·95	−2·80	0·67
14	519	*i*16	0·19	0·17	0·56
15	2189	*i*16	−2·95	−2·72	0·77
16	2237	*i*16	0·19	0·32	0·62
17	524	*i*13	−2·49	−2·61	0·68
18	655	*i*13	0·65	0·28	0·58
19	524	*i*15	−2·91	−2·68	0·73
20	619	*i*15	0·15	0·46	0·59
21	350	135	−0·64	−0·46	0·56
22	335	135	2·51	2·68	0·53

where λ_p represents any particular wavelength, and

$$W_{\lambda_p \mathbf{h}} = \left\{ \frac{\sum_{j=1}^{N_{\text{non}}} f_{j\mathbf{h}}^2 + \sum_{j=1}^{N_{\text{ano}}} f_{j\mathbf{h}}^{n2}}{\sum_{j=1}^{N_{\text{non}}} f_{j\mathbf{h}}^2 + \sum_{j=1}^{N_{\text{ano}}} [(f_{j\mathbf{h}}^n + f_j')^2 + f_j''^2]} \right\}^{1/2} . \quad (23)$$

The symbols in column 2 of Table 2 correspond to the cases, m, in Table 1. The symbol *ii*1, for example, implies that (5) is composed of two terms based on isomorphous replacement data and one term of case $m = 1$ for anomalous dispersion data and that the triplet phase invariants are being evaluated for this specific combination of terms according to the General Rule.

All reported average errors in Table 2 are based on the known average values of sets of eight invariants as occur in (6). In forming the magnitude differences for application of the General Rule when $m = 5$, $|F_{\lambda_1 \mathbf{h}} + F_{\lambda_2 \mathbf{h}}|$ was replaced with $|F_{\lambda_1 \mathbf{h}}| + |F_{\lambda_2 \mathbf{h}}|$. In the application of cases $m = 2$ and 7, a comparable approximation would be required.

The invariants used for the calculations in Table 2 were composed from the largest 800 magnitude differences for each case represented by the symbol for the calculation in column 2, except for rows 13, 14 and 17–22. In the latter case, the largest 400 magnitude differences were used. Comparison of rows 13–16 shows that use of 800 magnitudes increases by about a factor of four the number of triplet phase invariants obtained with a very modest increase in error. Table 2 shows that the evaluation of many thousands of triplet phase invariants can be obtained for the exact data with use of the combination formulas implied by the General Rule, and that the various formulas distribute the evaluations to many points in the range $-\pi$ to π.

Concluding remarks

A probabilistic approach to the development of formulas for evaluating triplet phase invariants composed of a mixture of phases for anomalous dispersion data at two different wavelengths or for isomorphous substitution data has been presented recently by Pontenagel, Krabbendam, Peerdeman & Kroon (1983). The combining of data for the two techniques and at different wavelengths bears some connection with the present investigation. Instead of an inherently probabilistic approach, however, the analysis here has been based on certain mathematical and physical characteristics of the techniques of isomorphous replacement and anomalous dispersion, although there are evident probabilistic implications in this approach that can be developed in the future.

A main aspect of this investigation is the development of a simple General Rule for evaluating a large variety of triplet phase invariants, applicable when there is one predominant type of anomalous scatterer. The numerous combinations of formulas using both isomorphous replacement and anomalous dispersion data permit, in fact, the evaluation of a large number of triplet phase invariants as well as a large variety of them. The General Rule includes the rule R_{iso} for isomorphous replacement (Karle, 1983) and the seven rules $R_{\text{ano},n}$ ($n = 1, \ldots, 7$) for anomalous dispersion (Karle, 1984*b*, *c*) and, in effect, numerous others. With a modest increase in the complexity of the calculations, it is also possible to employ the numerous combinations of formulas in the case that there is more than one predominant type of anomalous scatterer. In the special case given by *iii*, which symbolically represents the circumstances of isomorphous replacement, *i.e.* when R_{iso} applies, the number of different predominant types of heavy-atom constituents does not affect the manner of making evaluations or the nature of the evaluations.

If there is more than one isomorphous derivative or if the anomalous dispersion experiments are performed at several wavelengths, there is the opportunity to generate large numbers of additional combinations of terms from Table 1. For example, mixed formulas could be generated for isomorphous replacement by combining terms that arise from the various derivatives.

The calculations presented in Table 2 have been made with exact data. The feasibility of applying the

General Rule to experimental data will evidently depend upon the accuracy of the experimental data. This is a matter for future development and detailed study.

In order to apply the results of this paper to the case of one predominant type of anomalous scatterer, it is only necessary to know the chemical identity of the anomalous scatterer. In the case of more than one type of predominant anomalous scatterer, it is also necessary to have an estimate of the amount of each anomalous scatterer.

I wish to thank Mr Stephen Brenner for writing the appropriate programs and making the computations reported here.

This research was supported in part by USPHS grant GM30902.

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Modified Two-Beam Description of X-ray Fields and Intensities near a Three-Beam Diffraction Point. General Formulation and First-Order Solution

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(*Received* 30 *August* 1983; *accepted* 24 *January* 1984)

Abstract

The dynamical three-beam problem in Renninger geometry is cast in a pseudo-two-beam formulation for the primary **0H** reflection, with the inverse of the excitation error ξ_L with respect to the third reciprocal-lattice point **L** acting as a perturbation parameter for modifying the true two-beam solutions. This approach introduces a quasi-universal angular scale x for measuring the onset of all three-beam effects, and it leads to a first-order solution that preserves all features of a two-beam case, but around a shifted Lorentz point, and with modified structure factors. The modified structure factors, odd in x, cause pronounced asymmetries in the diffracted intensities on both sides of the three-beam point, for $|x| \gtrsim 1$. In this range of x, the first-order solution provides a simple *analytic* expression for the integrated diffracted intensity *vs* angle, for a sequence of neighboring three-beam or higher-order points. This is exemplified for the Ge 222 primary reflection. The physics of the onset of the three-beam interaction, and the limitations of the first-order solution are also discussed.

1. Introduction

Multiple diffraction of X-rays in crystals has been fully described mathematically ever since Ewald's (1916) dynamical theory. Its prototype, the two-beam case, has been exhaustively treated analytically (Laue, 1960; James, 1963; Batterman & Cole, 1964), and exploited quantitatively in applications ranging from anomalous transmission (Borrmann, 1950) to interferometry (Bonse & Hart, 1965).

Except in special cases, three-beam or higher interactions have not been describable by equally simple analysis or by general conceptual insights into the nature of the normal modes of propagation. While full computer-implemented solutions of any specific problem exist (*e.g.* Uebach, 1973; Colella, 1974; Kohn, 1979), their conclusions are usually not generalizable, unless statistical sampling of the effects of altering various parameters is undertaken (Hümmer & Billy, 1982).

Recent exploration of the fine structure of multiple interactions ranges from structure-factor phase determination (Post, 1979; Chang, 1982) and surface physics (Cowan, Golovchenko & Robbins, 1980) to nonlinear couplings to other waves (LeRoux, Colella & Bray, 1975; Juretschke & Wasserstein-Robbins, 1982). Hildebrandt (1982) has reviewed other applications. Further work should be stimulated by a description of multiple diffraction that allows a simple mathematical formulation of its basic dynamical features, and relies as much as possible on familiar concepts.

0108-7673/84/040379-11$01.50 © 1984 International Union of Crystallography