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On Integrating the Techniques of Direct Methods with Anomalous Dispersion. I. The Theoretical Basis*

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Abstract

The recently secured mathematical formalism of direct methods is here generalized to the case that the atomic scattering factors are arbitrary complex numbers, thus including the special case that one or more anomalous scatterers are present. Once again the neighborhood concept plays the central role. Final results from the probabilistic theory of the two- and three-phase structure invariants are briefly summarized. In particular, the conditional probability distribution of the three-phase structure invariant, given the six magnitudes $|E|$ in its first neighborhood, is described. The distribution yields an estimate for the three-phase structure invariant which is particularly good in the favorable case that the variance of the distribution happens to be small (the neighborhood principle). Particularly noteworthy is the fact that, in sharp contrast to all earlier work, the estimate is unique in the whole range 0 to 2π. An example shows that the method is capable of yielding unique estimates for tens of thousands of three-phase structure invariants with unprecedented accuracy, even in the macromolecular case. The clear implication is that the fusion of the traditional techniques of direct methods with anomalous dispersion, which is described here, will facilitate the solution of those crystal structures which contain one or more anomalous scatterers.

1. Introduction

Most crystal structures containing as many as 80–100 independent nonhydrogen atoms are more or less routinely solvable nowadays by direct methods. On the other hand, it has been known for a long time (Peerdeman & Bijvoet, 1956; Ramachandran & Raman, 1956; Okaya & Pepinsky, 1956) that the presence of one or more anomalous scatterers facilitates the solution of the phase problem; and some recent work (Kroon, Spek & Krabbendam, 1977; Heinerman, Krabbendam, Kroon & Spek, 1978), employing Bijvoet inequalities and the double Patterson function, leads in a similar way to estimates of the sines of the three-phase structure invariants. Again, some early work of Rossmann (1961), employing the difference synthesis $(|F_{\mathbf{H}}| - |F_{\bar{\mathbf{H}}}|)^2$ in order to locate the anomalous scatterers and recently applied by Hendrickson & Teeter (1981) in their solution of the crambin structure, shows that the presence of anomalous scatterers facilitates the determination of crystal structures. This work strongly suggests that the ability to integrate the techniques of direct methods, in particular the recent advances in the mathematical formalism, with anomalous dispersion would lead to improved methods for phase determination. The present paper is devoted to this task. That the anticipated improvement is in fact realized is also shown (Tables 1 and 2 and Fig. 1). Not only do the new formulas lead to improved estimates of the structure invariants but, more important still, because the distributions derived here are unimodal in the whole interval $(0,2\pi)$, the twofold ambiguity inherent in all the earlier work is removed. It is believed that this resolution of the twofold ambiguity results from the ability now to make use of the individual magnitudes in the first neighborhood of the structure invariant and the avoidance of explicit dependence on the Bijvoet differences; the explicit use of the Bijvoet differences, as is done in all previous work, leads apparently to a loss of information resulting in a twofold ambiguity in estimates of the structure invariants. It may be of some interest to observe that in the earlier work with anomalous dispersion only the sine of the invariant may be estimated; in the absence of anomalous scatterers only the cosine of the invariant may be estimated; as a result of the work described here both the sine and the cosine, that is to say the invariant itself, may be estimated. Since, in the presence of anomalous scatterers, the observed intensities are known to determine a unique enantiomorph, and therefore unique values for all the structure seminvariants, formulas of the kind described here should not be unexpected; nevertheless not even their existence appears to have been anticipated.

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In the present paper the final results from the probabilistic theory of the three-phase structure invariant are concisely described. The joint probability distribution of the six structure factors $E_{\mathbf{H}}$, $E_{\mathbf{K}}$, $E_{\mathbf{L}}$, $E_{\bar{\mathbf{H}}}$, $E_{\bar{\mathbf{K}}}$, $E_{\bar{\mathbf{L}}}$, where $\mathbf{H}+\mathbf{K}+\mathbf{L}=0$, which plays the central role in the probabilistic theory of the three-phase structure invariant, is briefly described in Appendix I. This distribution leads directly to the major result of this paper, equation (3.65), the conditional probability distribution of the three-phase structure invariant, assuming as known the six magnitudes in its first neighborhood. Owing to their extreme length, details of the derivations are omitted altogether. A brief account of the two-phase invariant is also given. Particularly noteworthy is the use of the neighborhood principle first formulated in 1975 (Hauptman, 1975*a*).

In the presence of anomalous scatterers the normalized structure factor

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

is defined by

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

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

where

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

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

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

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

The reciprocal-lattice vector $\mathbf{H}$ is assumed to be fixed, and the primitive random variables are taken to be the atomic position vectors $\mathbf{r}_j$ which are assumed to be uniformly and independently distributed. Then $E_{\mathbf{H}}$, as a function, (1.3), of the primitive random variables $\mathbf{r}_j$, is itself a random variable and, as it turns out,

$$\langle |E_{\mathbf{H}}|^2 \rangle_{\mathbf{r}_j} = 1. \tag{1.6}$$

2. The probabilistic theory of the two-phase structure invariant $\varphi_{\mathbf{H}} + \varphi_{\bar{\mathbf{H}}}$

Replacing $\mathbf{H}$ by $\bar{\mathbf{H}}$ in (1.1) and (1.3), and employing

$$f_{j\mathbf{H}} = f_{j\bar{\mathbf{H}}}, \tag{2.1}$$

one obtains

$$E_{\bar{\mathbf{H}}} = |E_{\bar{\mathbf{H}}}| \exp(i\varphi_{\bar{\mathbf{H}}}) \tag{2.2}$$

and

$$E_{\bar{\mathbf{H}}} = \frac{1}{\alpha_{\mathbf{H}}^{1/2}} \sum_{j=1}^{N} |f_{j\mathbf{H}}| \exp|i(\delta_{j\mathbf{H}} - 2\pi\mathbf{H}.\mathbf{r}_j)|. \tag{2.3}$$

Thus the two-phase structure invariant,

$$\psi = \varphi_{\mathbf{H}} + \varphi_{\bar{\mathbf{H}}}, \tag{2.4}$$

as a function of the primitive random variables $\mathbf{r}_j$, is itself a random variable. A subsidiary goal in the present paper is to describe the conditional probability distribution of ψ, assuming as known the two magnitudes $|E_{\mathbf{H}}|$, $|E_{\bar{\mathbf{H}}}|$ which, owing to the breakdown of Friedel's law, are in general distinct. This distribution leads to an estimate of the two-phase structure invariant which is particularly good in the favorable case that the variance of the distribution happens to be small (the neighborhood principle). Thus the first neighborhood of the two-phase structure invariant ψ is defined to consist of the two magnitudes

$$|E_{\mathbf{H}}|, |E_{\bar{\mathbf{H}}}|. \tag{2.5}$$

Define $C_{\mathbf{H}}$ and $S_{\mathbf{H}}$ by means of

$$C_{\mathbf{H}} = \frac{1}{\alpha_{\mathbf{H}}} \sum_{j=1}^{N} |f_{j\mathbf{H}}|^2 \cos 2\delta_{j\mathbf{H}}, \tag{2.6}$$

$$S_{\mathbf{H}} = \frac{1}{\alpha_{\mathbf{H}}} \sum_{j=1}^{N} |f_{j\mathbf{H}}|^2 \sin 2\theta_{j\mathbf{H}}, \tag{2.7}$$

where $f_{j\mathbf{H}}$, $\delta_{j\mathbf{H}}$, and $\alpha_{\mathbf{H}}$ are defined in (1.4) and (1.5). Define X and ξ by means of

$$X\cos\xi = C_{\mathbf{H}}, \quad X\sin\xi = -S_{\mathbf{H}}, \tag{2.8}$$

$$X = (C_{\mathbf{H}}^2 + S_{\mathbf{H}}^2)^{1/2}, \quad \tan\xi = -S_{\mathbf{H}}/C_{\mathbf{H}}. \tag{2.9}$$

Then the joint probability distribution of the magnitudes $|E_{\mathbf{H}}|$, $|E_{\bar{\mathbf{H}}}|$ and the phases $\varphi_{\mathbf{H}}$, $\varphi_{\bar{\mathbf{H}}}$ of the Friedel pair $E_{\mathbf{H}}$, $E_{\bar{\mathbf{H}}}$ is given by

$$P(R,\bar{R};\Phi,\bar{\Phi}) = \frac{R\bar{R}}{\pi^2(1-X^2)} \exp\left\{-\frac{R^2+\bar{R}^2}{1-X^2} + \frac{2R\bar{R}X}{1-X^2}\cos(\Phi+\bar{\Phi}+\xi)\right\}, \tag{2.10}$$

and of the magnitudes $|E_{\mathbf{H}}|$, $|E_{\bar{\mathbf{H}}}|$ alone by

$$P(R,\bar{R}) = \frac{4}{1-X^2} R\bar{R} \exp\left\{-\frac{R^2+\bar{R}^2}{1-X^2}\right\} I_0\left\{\frac{2R\bar{R}X}{1-X^2}\right\}, \tag{2.11}$$

where I_0 is the modified Bessel function.

Suppose now that R and $\bar{R}$, instead of being variables as in (2.10) and (2.11), are fixed non-negative numbers. Then the conditional probability distribution of the two-phase structure invariant $\varphi_{\mathbf{H}} + \varphi_{\bar{\mathbf{H}}}$, given that

$$|E_{\mathbf{H}}| = R, \quad |E_{\bar{\mathbf{H}}}| = \bar{R}, \tag{2.12}$$

is

$$P(\Psi|R,\bar{R}) = \left[2\pi I_0\left(\frac{2R\bar{R}X}{1-X^2}\right)\right]^{-1} \times \exp\left\{\frac{2R\bar{R}X}{1-X^2}\cos(\Psi+\xi)\right\}. \tag{2.13}$$

From (2.11) it follows that the correlation coefficient of the Friedel pair $|E_{\mathbf{H}}|^2$, $|E_{\bar{\mathbf{H}}}|^2$ is

$$r = X^2, \tag{2.14}$$

where X is defined by (2.9). Since (2.13) has a unique maximum at $\Psi = -\xi$, it follows that

$$\varphi_{\mathbf{H}} + \varphi_{\bar{\mathbf{H}}} \simeq -\xi \tag{2.15}$$

provided that the variance of the distribution (2.13) is small, *i.e.* provided that

$$A = \frac{2R\bar{R}X}{1-X^2} \text{ is large.} \tag{2.16}$$

It should be noted that, while A depends on R, $\bar{R}$ and $|\mathbf{H}|$, for a fixed chemical composition ξ depends only on $|\mathbf{H}|$ (or $\sin\theta/\lambda$) and is independent of R and $\bar{R}$.

In view of (2.9),

$$r = X^2 = C_{\mathbf{H}}^2 + S_{\mathbf{H}}^2, \tag{2.17}$$

where $C_{\mathbf{H}}$ and $S_{\mathbf{H}}$, as given by (2.6) and (2.7), are seen to be functions of $|\mathbf{H}|$. Hence r is also a function of $|\mathbf{H}|$. It follows that if, instead of fixing $\mathbf{H}$ and averaging over $\mathbf{r}_j$, the crystal structure is supposed to be fixed and the correlation coefficient r of the Friedel pair ($|E_{\mathbf{H}}|^2$, $|E_{\bar{\mathbf{H}}}|^2$) is calculated for those reciprocal-lattice vectors $\mathbf{H}$ for which $|\mathbf{H}|$ (or $\sin\theta/\lambda$) is fixed, *i.e.* over a spherical shell in reciprocal space, then (2.17) still holds even though the corresponding average value of $|E_{\mathbf{H}}|^2$ (or of $|E_{\bar{\mathbf{H}}}|^2$) may no longer be unity.

3. The probabilistic theory of the three-phase structure invariant

3.1. *Probabilistic background*

It will be assumed throughout that $\mathbf{H}$, $\mathbf{K}$, and $\mathbf{L}$ are fixed reciprocal-lattice vectors satisfying

$$\mathbf{H} + \mathbf{K} + \mathbf{L} = 0. \tag{3.1}$$

Owing to the breakdown of Friedel's law there are now eight distinct three-phase structure invariants:

$$\psi_0 = \varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{\mathbf{L}}, \tag{3.2}$$

$$\psi_1 = -\varphi_{\bar{\mathbf{H}}} + \varphi_{\mathbf{K}} + \varphi_{\mathbf{L}}, \tag{3.3}$$

$$\psi_2 = \varphi_{\mathbf{H}} - \varphi_{\bar{\mathbf{K}}} + \varphi_{\mathbf{L}}, \tag{3.4}$$

$$\psi_3 = \varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} - \varphi_{\bar{\mathbf{L}}}, \tag{3.5}$$

$$\psi_{\bar{0}} = \varphi_{\bar{\mathbf{H}}} + \varphi_{\bar{\mathbf{K}}} + \varphi_{\bar{\mathbf{L}}}, \tag{3.6}$$

$$\psi_{\bar{1}} = -\varphi_{\mathbf{H}} + \varphi_{\bar{\mathbf{K}}} + \varphi_{\bar{\mathbf{L}}}, \tag{3.7}$$

$$\psi_{\bar{2}} = \varphi_{\bar{\mathbf{H}}} - \varphi_{\mathbf{K}} + \varphi_{\bar{\mathbf{L}}}, \tag{3.8}$$

$$\psi_{\bar{3}} = \varphi_{\bar{\mathbf{H}}} + \varphi_{\bar{\mathbf{K}}} - \varphi_{\mathbf{L}}. \tag{3.9}$$

The first neighborhood of each of the three-phase structure invariants (3.2)–(3.9) is defined to consist of the six magnitudes:

$$|E_{\mathbf{H}}|, |E_{\mathbf{K}}|, |E_{\mathbf{L}}|, |E_{\bar{\mathbf{H}}}|, |E_{\bar{\mathbf{K}}}|, |E_{\bar{\mathbf{L}}}| \tag{3.10}$$

which, again owing to the breakdown of Friedel's law, are not in general equal in pairs.

Fix the reciprocal-lattice vectors $\mathbf{H}$, $\mathbf{K}$, and $\mathbf{L}$, subject to (3.1). Suppose that the six non-negative numbers R_1, R_2, R_3, $R_{\bar{1}}$, $R_{\bar{2}}$, and $R_{\bar{3}}$ are also specified. Define the N-fold Cartesian product W to consist of all ordered N-tuples $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, where $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ are atomic position vectors. Suppose that the primitive random variable is the N-tuple $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ which is assumed to be uniformly distributed over the subset of W defined by

$$|E_{\mathbf{H}}| = R_1, \quad |E_{\mathbf{K}}| = R_2, \quad |E_{\mathbf{L}}| = R_3, \tag{3.11}$$

$$|E_{\bar{\mathbf{H}}}| = R_{\bar{1}}, \quad |E_{\bar{\mathbf{K}}}| = R_{\bar{2}}, \quad |E_{\bar{\mathbf{L}}}| = R_{\bar{3}}, \tag{3.12}$$

where the normalized structure factors E are defined by (1.2). Then the eight structure invariants

$$\psi_j, \psi_{\bar{j}}, j = 0, 1, 2, 3, \tag{3.13}$$

(3.2)–(3.9), as functions of the primitive random variables $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, are themselves random variables.

Our major goal is to determine the conditional probability distribution of each of the three-phase structure invariants (3.2)–(3.9), given the six magnitudes (3.11) and (3.12) in its first neighborhood, which, in the favorable case that the variance of the distribution happens to be small, yields a reliable estimate of the invariant (the neighborhood principle).

3.2. *Notation and definitions*

C_H and S_H have already been defined [(2.6) and (2.7)]. In a similar way C_K, S_K, C_L, and S_L are defined.

Then X_1, ξ_1, X_2, ξ_2, X_3, ξ_3 are uniquely defined by equations (3.14)–(3.19):

$$X_1 \cos \xi_1 = C_H, \quad X_1 \sin \xi_1 = -S_H, \tag{3.14}$$

$$\tan \xi_1 = -\frac{S_H}{C_H}, \quad X_1 = (C_H^2 + S_H^2)^{1/2}. \tag{3.15}$$

$$X_2 \cos \xi_2 = C_K, \quad X_2 \sin \xi_2 = -S_K, \tag{3.16}$$

$$\tan \xi_2 = -\frac{S_K}{C_K}, \quad X_2 = (C_K^2 + S_K^2)^{1/2}. \tag{3.17}$$

$$X_3 \cos \xi_3 = C_L, \quad X_3 \sin \xi_3 = -S_L, \tag{3.18}$$

$$\tan \xi_3 = -\frac{S_L}{C_L}, \quad X_3 = (C_L^2 + S_L^2)^{1/2}. \tag{3.19}$$

Next, make the definitions:

$$C_{HKL} = \frac{1}{(\alpha_H \alpha_K \alpha_L)^{1/2}} \sum_{j=1}^{N} |f_{jH} f_{jK} f_{jL}| \cos(\delta_{jH} + \delta_{jK} + \delta_{jL}), \tag{3.20}$$

$$S_{HKL} = \frac{1}{(\alpha_H \alpha_K \alpha_L)^{1/2}} \sum_{j=1}^{N} |f_{jH} f_{jK} f_{jL}| \sin(\delta_{jH} + \delta_{jK} + \delta_{jL}). \tag{3.21}$$

$$C_{\bar{H}KL} = \frac{1}{(\alpha_H \alpha_K \alpha_L)^{1/2}} \sum_{j=1}^{N} |f_{jH} f_{jK} f_{jL}| \cos(-\delta_{jH} + \delta_{jK} + \delta_{jL}), \tag{3.22}$$

$$S_{\bar{H}KL} = \frac{1}{(\alpha_H \alpha_K \alpha_L)^{1/2}} \sum_{j=1}^{N} |f_{jH} f_{jK} f_{jL}| \sin(-\delta_{jH} + \delta_{jK} + \delta_{jL}). \tag{3.23}$$

$$C_{H\bar{K}L} = \frac{1}{(\alpha_H \alpha_K \alpha_L)^{1/2}} \sum_{j=1}^{N} |f_{jH} f_{jK} f_{jL}| \cos(\delta_{jH} - \delta_{jK} + \delta_{jL}), \tag{3.24}$$

$$S_{H\bar{K}L} = \frac{1}{(\alpha_H \alpha_K \alpha_L)^{1/2}} \sum_{j=1}^{N} |f_{jH} f_{jK} f_{jL}| \sin(\delta_{jH} - \delta_{jK} + \delta_{jL}). \tag{3.25}$$

$$C_{HK\bar{L}} = \frac{1}{(\alpha_H \alpha_K \alpha_L)^{1/2}} \sum_{j=1}^{N} |f_{jH} f_{jK} f_{jL}| \cos(\delta_{jH} + \delta_{jK} - \delta_{jL}), \tag{3.26}$$

$$S_{HK\bar{L}} = \frac{1}{(\alpha_H \alpha_K \alpha_L)^{1/2}} \sum_{j=1}^{N} |f_{jH} f_{jK} f_{jL}| \sin(\delta_{jH} + \delta_{jK} - \delta_{jL}). \tag{3.27}$$

$$\begin{aligned}\gamma_0 = {} & C_{HKL}[1 - (C_H C_K C_L - C_H S_K S_L - S_H C_K S_L - S_H S_K C_L)] + S_{HKL}[S_H S_K S_L - S_H C_K C_L - C_H S_K C_L - C_H C_K S_L] \\ & + C_{\bar{H}KL}[-C_H + (C_K C_L - S_K S_L)] + S_{\bar{H}KL}[S_H + (C_K S_L + S_K C_L)] \\ & + C_{H\bar{K}L}[-C_K + (C_H C_L - S_H S_L)] + S_{H\bar{K}L}[S_K + (C_H S_L + S_H C_L)] \\ & + C_{HK\bar{L}}[-C_L + (C_H C_K - S_H S_K)] + S_{HK\bar{L}}[S_L + (C_H S_K + S_H C_K)].\end{aligned} \tag{3.28}$$

$$\begin{aligned}\sigma_0 = {} & C_{HKL}[S_H S_K S_L - S_H C_K C_L - C_H S_K C_L - C_H C_K S_L] + S_{HKL}[1 + (C_H C_K C_L - C_H S_K S_L - S_H C_K S_L - S_H S_K C_L)] \\ & + C_{\bar{H}KL}[-S_H + (C_K S_L + S_K C_L)] + S_{\bar{H}KL}[-C_H - (C_K C_L - S_K S_L)] \\ & + C_{H\bar{K}L}[-S_K + (C_H S_L + S_H C_L)] + S_{H\bar{K}L}[-C_K - (C_H C_L - S_H S_L)] \\ & + C_{HK\bar{L}}[-S_L + (C_H S_K + S_H C_K)] + S_{HK\bar{L}}[-C_L - (C_H C_K - S_H S_K)].\end{aligned} \tag{3.29}$$

$$\begin{aligned}\gamma_1 = {} & C_{HKL}[-C_H + (C_K C_L - S_K S_L)] + S_{HKL}[-S_H + (C_K S_L + S_K C_L)] \\ & + C_{\bar{H}KL}[1 - (C_H C_K C_L - C_H S_K S_L + S_H C_K S_L + S_H S_K C_L)] \\ & + S_{\bar{H}KL}[-(S_H S_K S_L - S_H C_K C_L + C_H S_K C_L + C_H C_K S_L)] + C_{H\bar{K}L}[-C_L + (C_H C_K + S_H S_K)] + S_{H\bar{K}L}[-S_L - (C_H S_K - S_H C_K)] + C_{HK\bar{L}}[-C_K + (C_H C_L + S_H S_L)] + S_{HK\bar{L}}[-S_K - (C_H S_L - S_H C_L)].\end{aligned} \tag{3.30}$$

$$\begin{aligned}\sigma_1 = {} & C_{HKL}[S_H + (C_K S_L + S_K C_L)] + S_{HKL}[-C_H - (C_K C_L - S_K S_L)] \\ & + C_{\bar{H}KL}[-(S_H S_K S_L - S_H C_K C_L + C_H S_K C_L + C_H C_K S_L)] + S_{\bar{H}KL}[1 + (C_H C_K C_L - C_H S_K S_L + S_H C_K S_L + S_H S_K C_L)] \\ & + C_{H\bar{K}L}[-S_L + (C_H S_K - S_H C_K)] + S_{H\bar{K}L}[C_L + (C_H C_K + S_H S_K)] \\ & + C_{HK\bar{L}}[-S_K + (C_H S_L - S_H C_L)] + S_{HK\bar{L}}[C_K + (C_H C_L + S_H S_L)].\end{aligned} \tag{3.31}$$

$$\begin{aligned}\gamma_2 = {} & C_{HKL}[-C_K + (C_H C_L - S_H S_L)] \\ & + S_{HKL}[-S_K + (C_H S_L + S_H C_L)] \\ & + C_{\bar{H}KL}[-C_L + (C_K C_H + S_K S_H)] \\ & + S_{\bar{H}KL}[-S_L - (C_K S_H - S_K C_H)] \\ & + C_{H\bar{K}L}[1 - (C_H C_K C_L + C_H S_K S_L \\ & - S_H C_K S_L + S_H S_K C_L)] \\ & + S_{H\bar{K}L}[-(S_H S_K S_L + S_H C_K C_L - C_H S_K C_L \\ & + C_H C_K S_L)] + C_{HK\bar{L}}[-C_H + (C_K C_L \\ & + S_K S_L)] + S_{HK\bar{L}}[-S_H - (C_K S_L - S_K C_L)].\end{aligned} \tag{3.32}$$

$$\begin{aligned}\sigma_2 = {} & C_{HKL}[S_K + (C_H S_L + S_H C_L)] \\ & + S_{HKL}[-C_K - (C_H C_L - S_H S_L)] \\ & + C_{\bar{H}KL}[-S_L + (C_K S_H - S_K C_H)] \\ & + S_{\bar{H}KL}[C_L + (C_K C_H + S_K S_H)] \\ & + C_{H\bar{K}L}[-(S_H S_K S_L + S_H C_K C_L - C_H S_K C_L \\ & + C_H C_K S_L)] + S_{H\bar{K}L}[1 + (C_H C_K C_L \\ & + C_H S_K S_L - S_H C_K S_L + S_H S_K C_L)] \\ & + C_{HK\bar{L}}[-S_H + (C_K S_L - S_K C_L)] \\ & + S_{HK\bar{L}}[C_H + (C_K C_L + S_K S_L)].\end{aligned} \tag{3.33}$$

$$\begin{aligned}\gamma_3 = {} & C_{HKL}[-C_L + (C_H C_K - S_H S_K)] \\ & + S_{HKL}[-S_L + (C_H S_K + S_H C_K)] \\ & + C_{\bar{H}KL}[-C_K + (C_L C_H + S_L S_H)] \\ & + S_{\bar{H}KL}[-S_K - (C_L S_H - S_L C_H)] \\ & + C_{H\bar{K}L}[-C_H + (C_L C_K + S_L S_K)] \\ & + S_{H\bar{K}L}[-S_H - (C_L S_K - S_L C_K)] \\ & + C_{HK\bar{L}}[1 - (C_H C_K C_L - C_H S_K S_L \\ & + S_H C_K S_L - S_H S_K C_L)] \\ & + S_{HK\bar{L}}[-(S_H S_K S_L + S_H C_K C_L + C_H S_K C_L \\ & - C_H C_K S_L)].\end{aligned} \tag{3.34}$$

$$\begin{aligned}\sigma_3 = {} & C_{HKL}[S_L + (C_H S_K + S_H C_K)] \\ & + S_{HKL}[-C_L - (C_H C_K - S_H S_K)] \\ & + C_{\bar{H}KL}[-S_K + (C_L S_H - S_L C_H)] \\ & + S_{\bar{H}KL}[C_K + (C_L C_H + S_L S_H)] \\ & + C_{H\bar{K}L}[-S_H + (C_L S_K - S_L C_K)] \\ & + S_{H\bar{K}L}[C_H + (C_K C_L + S_K S_L)] \\ & + C_{HK\bar{L}}[-(S_H S_K S_L + S_H C_K C_L + C_H S_K C_L \\ & - C_H C_K S_L)] + S_{HK\bar{L}}[1 + (C_H C_K C_L \\ & + C_H S_K S_L + S_H C_K S_L - S_H S_K C_L)].\end{aligned} \tag{3.35}$$

Then Z_j and ζ_j, $j = 0, 1, 2, 3$, are uniquely defined by equations (3.36) and (3.37):

$$Z_j \cos \zeta_j = \gamma_j, \quad Z_j \sin \zeta_j = \sigma_j, \quad j = 0, 1, 2, 3. \tag{3.36}$$

$$\tan \zeta_j = \frac{\sigma_j}{\gamma_j}, \quad Z_j = (\gamma_j^2 + \sigma_j^2)^{1/2}, \quad j = 0, 1, 2, 3. \tag{3.37}$$

In the definitions which follow R_1, R_2, R_3, $R_{\bar{1}}$, $R_{\bar{2}}$, $R_{\bar{3}}$ are the fixed values of the six magnitudes $|E_H|$, $|E_K|$, $|E_L|$, $|E_{\bar{H}}|$, $|E_{\bar{K}}|$, $|E_{\bar{L}}|$, respectively [(3.11) and (3.12)], and τ_1, τ_2, τ_3 are defined by

$$\tau_j = \frac{I_1\left(\dfrac{2R_j R_{\bar{j}} X_j}{1 - X_j^2}\right)}{I_0\left(\dfrac{2R_j R_{\bar{j}} X_j}{1 - X_j^2}\right)}, \quad j = 1, 2, 3. \tag{3.38}$$

where I_0 and I_1 are the modified Bessel functions and X_1, X_2, and X_3 have been defined in (3.15), (3.17), and (3.19).

$$\begin{aligned}C_0 = {} & Z_0[R_1 R_2 R_3 \cos \zeta_0 + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_2 \tau_3 \\ & \times \cos(\xi_1 + \xi_2 + \xi_3 + \zeta_0)] \\ & + Z_1[R_{\bar{1}} R_2 R_3 \tau_1 \cos(\xi_1 - \zeta_1) \\ & + R_1 R_{\bar{2}} R_{\bar{3}} \tau_2 \tau_3 \cos(\xi_2 + \xi_3 + \zeta_1)] \\ & + Z_2[R_1 R_{\bar{2}} R_3 \tau_2 \cos(\xi_2 - \zeta_2) \\ & + R_{\bar{1}} R_2 R_{\bar{3}} \tau_1 \tau_3 \cos(\xi_1 + \xi_3 + \zeta_2)] \\ & + Z_3[R_1 R_2 R_{\bar{3}} \tau_3 \cos(\xi_3 - \zeta_3) \\ & + R_{\bar{1}} R_{\bar{2}} R_3 \tau_1 \tau_2 \cos(\xi_1 + \xi_2 + \zeta_3)].\end{aligned} \tag{3.39}$$

$$\begin{aligned}S_0 = {} & Z_0[R_1 R_2 R_3 \sin \zeta_0 - R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_2 \tau_3 \\ & \times \sin(\xi_1 + \xi_2 + \xi_3 + \zeta_0)] \\ & - Z_1[R_{\bar{1}} R_2 R_3 \tau_1 \sin(\xi_1 - \zeta_1) \\ & + R_1 R_{\bar{2}} R_{\bar{3}} \tau_2 \tau_3 \sin(\xi_2 + \xi_3 + \zeta_1)] \\ & - Z_2[R_1 R_{\bar{2}} R_3 \tau_2 \sin(\xi_2 - \zeta_2) \\ & + R_{\bar{1}} R_2 R_{\bar{3}} \tau_1 \tau_3 \sin(\xi_1 + \xi_3 + \zeta_2)] \\ & - Z_3[R_1 R_2 R_{\bar{3}} \tau_3 \sin(\xi_3 - \zeta_3) \\ & + R_{\bar{1}} R_{\bar{2}} R_3 \tau_1 \tau_2 \sin(\xi_1 + \xi_2 + \zeta_3)].\end{aligned} \tag{3.40}$$

$$\begin{aligned}C_1 = {} & Z_0[R_1 R_2 R_3 \tau_1 \cos(\xi_1 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_2 \tau_3 \\ & \times \cos(\xi_2 + \xi_3 + \zeta_0)] + Z_1[R_{\bar{1}} R_2 R_3 \cos \zeta_1 \\ & + R_1 R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_2 \tau_3 \cos(-\xi_1 + \xi_2 + \xi_3 + \zeta_1)] \\ & + Z_2[R_1 R_{\bar{2}} R_3 \tau_1 \tau_2 \cos(\xi_1 - \xi_2 + \zeta_2) \\ & + R_{\bar{1}} R_2 R_{\bar{3}} \tau_3 \cos(\xi_3 + \zeta_2)] \\ & + Z_3[R_1 R_2 R_{\bar{3}} \tau_1 \tau_3 \cos(\xi_1 - \xi_3 + \zeta_3) \\ & + R_{\bar{1}} R_{\bar{2}} R_3 \tau_2 \cos(\xi_2 + \zeta_3)].\end{aligned} \tag{3.41}$$

$$S_1 = Z_0[R_1 R_2 R_3 \tau_1 \sin(\xi_1 + \zeta_0) - R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_2 \tau_3 \times \sin(\xi_2 + \xi_3 + \zeta_0)] + Z_1[R_{\bar{1}} R_2 R_3 \sin\zeta_1 - R_1 R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_2 \tau_3 \sin(-\xi_1 + \xi_2 + \xi_3 + \zeta_1)] + Z_2[R_1 R_{\bar{2}} R_3 \tau_1 \tau_2 \sin(\xi_1 - \xi_2 + \zeta_2) - R_{\bar{1}} R_2 R_{\bar{3}} \tau_3 \sin(\xi_3 + \zeta_2)] + Z_3[R_1 R_2 R_{\bar{3}} \tau_1 \tau_3 \sin(\xi_1 - \xi_3 + \zeta_3) - R_{\bar{1}} R_{\bar{2}} R_3 \tau_2 \sin(\xi_2 + \zeta_3)]. \quad (3.42)$$

$$C_2 = Z_0[R_1 R_2 R_3 \tau_2 \cos(\xi_2 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_3 \cos(\xi_1 + \xi_3 + \zeta_0)] + Z_1[R_{\bar{1}} R_2 R_3 \tau_1 \tau_2 \cos(-\xi_1 + \xi_2 + \zeta_1) + R_1 R_{\bar{2}} R_{\bar{3}} \tau_3 \cos(\xi_3 + \zeta_1)] + Z_2[R_1 R_{\bar{2}} R_3 \cos\zeta_2 + R_{\bar{1}} R_2 R_{\bar{3}} \tau_1 \tau_2 \tau_3 \cos(\xi_1 - \xi_2 + \xi_3 + \zeta_2)] + Z_3[R_1 R_2 R_{\bar{3}} \tau_2 \tau_3 \cos(\xi_2 - \xi_3 + \zeta_3) + R_{\bar{1}} R_{\bar{2}} R_3 \tau_1 \cos(\xi_1 + \zeta_3)]. \quad (3.43)$$

$$S_2 = Z_0[R_1 R_2 R_3 \tau_2 \sin(\xi_2 + \zeta_0) - R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_3 \sin(\xi_1 + \xi_3 + \zeta_0)] + Z_1[R_{\bar{1}} R_2 R_3 \tau_1 \tau_2 \sin(-\xi_1 + \xi_2 + \zeta_1) - R_1 R_{\bar{2}} R_{\bar{3}} \tau_3 \sin(\xi_3 + \zeta_1)] + Z_2[R_1 R_{\bar{2}} R_3 \sin\zeta_2 - R_{\bar{1}} R_2 R_{\bar{3}} \tau_1 \tau_2 \tau_3 \sin(\xi_1 - \xi_2 + \xi_3 + \zeta_2)] + Z_3[R_1 R_2 R_{\bar{3}} \tau_2 \tau_3 \sin(\xi_2 - \xi_3 + \zeta_3) - R_{\bar{1}} R_{\bar{2}} R_3 \tau_1 \sin(\xi_1 + \zeta_3)]. \quad (3.44)$$

$$C_3 = Z_0[R_1 R_2 R_3 \tau_3 \cos(\xi_3 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_2 \cos(\xi_1 + \xi_2 + \zeta_0)] + Z_1[R_{\bar{1}} R_2 R_3 \tau_1 \tau_3 \cos(-\xi_1 + \xi_3 + \zeta_1) + R_1 R_{\bar{2}} R_{\bar{3}} \tau_2 \cos(\xi_2 + \zeta_1)] + Z_2[R_1 R_{\bar{2}} R_3 \tau_2 \tau_3 \cos(-\xi_2 + \xi_3 + \zeta_2) + R_{\bar{1}} R_2 R_{\bar{3}} \tau_1 \cos(\xi_1 + \zeta_2)] + Z_3[R_1 R_2 R_{\bar{3}} \cos\zeta_3 + R_{\bar{1}} R_{\bar{2}} R_3 \tau_1 \tau_2 \tau_3 \cos(\xi_1 + \xi_2 - \xi_3 + \zeta_3)]. \quad (3.45)$$

$$S_3 = Z_0[R_1 R_2 R_3 \tau_3 \sin(\xi_3 + \zeta_0) - R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_2 \sin(\xi_1 + \xi_2 + \zeta_0)] + Z_1[R_{\bar{1}} R_2 R_3 \tau_1 \tau_3 \sin(-\xi_1 + \xi_3 + \zeta_1) - R_1 R_{\bar{2}} R_{\bar{3}} \tau_2 \sin(\xi_2 + \zeta_1)] + Z_2[R_1 R_{\bar{2}} R_3 \tau_2 \tau_3 \sin(-\xi_2 + \xi_3 + \zeta_2) - R_{\bar{1}} R_2 R_{\bar{3}} \tau_1 \sin(\xi_1 + \zeta_2)] + Z_3[R_1 R_2 R_{\bar{3}} \sin\zeta_3 - R_{\bar{1}} R_{\bar{2}} R_3 \tau_1 \tau_2 \tau_3 \sin(\xi_1 + \xi_2 - \xi_3 + \zeta_3)]. \quad (3.46)$$

$$C_{\bar{0}} = Z_0[R_1 R_2 R_3 \tau_1 \tau_2 \tau_3 \cos(\xi_1 + \xi_2 + \xi_3 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \cos\zeta_0] + Z_1[R_{\bar{1}} R_2 R_3 \tau_2 \tau_3 \cos(\xi_2 + \xi_3 + \zeta_1) + R_1 R_{\bar{2}} R_{\bar{3}} \tau_1 \cos(\xi_1 - \zeta_1)] + Z_2[R_1 R_{\bar{2}} R_3 \tau_1 \tau_3 \cos(\xi_1 + \xi_3 + \zeta_2) + R_{\bar{1}} R_2 R_{\bar{3}} \tau_2 \cos(\xi_2 - \zeta_2)] + Z_3[R_1 R_2 R_{\bar{3}} \tau_1 \tau_2 \cos(\xi_1 + \xi_2 + \zeta_3) + R_{\bar{1}} R_{\bar{2}} R_3 \tau_3 \cos(\xi_3 - \zeta_3)]. \quad (3.47)$$

$$S_{\bar{0}} = Z_0[-R_1 R_2 R_3 \tau_1 \tau_2 \tau_3 \sin(\xi_1 + \xi_2 + \xi_3 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \sin\zeta_0] - Z_1[R_{\bar{1}} R_2 R_3 \tau_2 \tau_3 \sin(\xi_2 + \xi_3 + \zeta_1) + R_1 R_{\bar{2}} R_{\bar{3}} \tau_1 \sin(\xi_1 - \zeta_1)] - Z_2[R_1 R_{\bar{2}} R_3 \tau_1 \tau_3 \sin(\xi_1 + \xi_3 + \zeta_2) + R_{\bar{1}} R_2 R_{\bar{3}} \tau_2 \sin(\xi_2 - \zeta_2)] - Z_3[R_1 R_2 R_{\bar{3}} \tau_1 \tau_2 \sin(\xi_1 + \xi_2 + \zeta_3) + R_{\bar{1}} R_{\bar{2}} R_3 \tau_3 \sin(\xi_3 - \zeta_3)]. \quad (3.48)$$

$$C_{\bar{1}} = Z_0[R_1 R_2 R_3 \tau_2 \tau_3 \cos(\xi_2 + \xi_3 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_1 \cos(\xi_1 + \zeta_0)] + Z_1[R_{\bar{1}} R_2 R_3 \tau_1 \tau_2 \tau_3 \cos(-\xi_1 + \xi_2 + \xi_3 + \zeta_1) + R_1 R_{\bar{2}} R_{\bar{3}} \cos\zeta_1] + Z_2[R_1 R_{\bar{2}} R_3 \tau_3 \cos(\xi_3 + \zeta_2) + R_{\bar{1}} R_2 R_{\bar{3}} \tau_1 \tau_2 \cos(\xi_1 - \xi_2 + \zeta_2)] + Z_3[R_1 R_2 R_{\bar{3}} \tau_2 \cos(\xi_2 + \zeta_3) + R_{\bar{1}} R_{\bar{2}} R_3 \tau_1 \tau_3 \cos(\xi_1 - \xi_3 + \zeta_3)]. \quad (3.49)$$

$$S_{\bar{1}} = Z_0[-R_1 R_2 R_3 \tau_2 \tau_3 \sin(\xi_2 + \xi_3 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_1 \sin(\xi_1 + \zeta_0)] + Z_1[-R_{\bar{1}} R_2 R_3 \tau_1 \tau_2 \tau_3 \sin(-\xi_1 + \xi_2 + \xi_3 + \zeta_1) + R_1 R_{\bar{2}} R_{\bar{3}} \sin\zeta_1] + Z_2[-R_1 R_{\bar{2}} R_3 \tau_3 \sin(\xi_3 + \zeta_2) + R_{\bar{1}} R_2 R_{\bar{3}} \tau_1 \tau_2 \sin(\xi_1 - \xi_2 + \zeta_2)] + Z_3[-R_1 R_2 R_{\bar{3}} \tau_2 \sin(\xi_2 + \zeta_3) + R_{\bar{1}} R_{\bar{2}} R_3 \tau_1 \tau_3 \sin(\xi_1 - \xi_3 + \zeta_3)]. \quad (3.50)$$

$$C_{\bar{2}} = Z_0[R_1 R_2 R_3 \tau_1 \tau_3 \cos(\xi_1 + \xi_3 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_2 \cos(\xi_2 + \zeta_0)] + Z_1[R_{\bar{1}} R_2 R_3 \tau_3 \cos(\xi_3 + \zeta_1) + R_1 R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_2 \cos(-\xi_1 + \xi_2 + \zeta_1)] + Z_2[R_1 R_{\bar{2}} R_3 \tau_1 \tau_2 \tau_3 \cos(\xi_1 - \xi_2 + \xi_3 + \zeta_2) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \cos\zeta_2] + Z_3[R_1 R_2 R_{\bar{3}} \tau_1 \cos(\xi_1 + \zeta_3) + R_{\bar{1}} R_{\bar{2}} R_3 \tau_2 \tau_3 \cos(\xi_2 - \xi_3 + \zeta_3)]. \quad (3.51)$$

$$S_{\bar{2}} = Z_0[-R_1 R_2 R_3 \tau_1 \tau_3 \sin(\xi_1 + \xi_3 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_2 \sin(\xi_2 + \zeta_0)] + Z_1[-R_{\bar{1}} R_2 R_3 \tau_3 \sin(\xi_3 + \zeta_1) + R_1 R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_2 \sin(-\xi_1 + \xi_2 + \zeta_1)] + Z_2[-R_1 R_{\bar{2}} R_3 \tau_1 \tau_2 \tau_3 \sin(\xi_1 - \xi_2 + \xi_3 + \zeta_2) + R_{\bar{1}} R_2 R_{\bar{3}} \sin \zeta_2] + Z_3[-R_1 R_2 R_{\bar{3}} \tau_1 \sin(\xi_1 + \zeta_3) + R_{\bar{1}} R_{\bar{2}} R_3 \tau_2 \tau_3 \sin(\xi_2 - \xi_3 + \zeta_3)]. \quad (3.52)$$

$$C_{\bar{3}} = Z_0[R_1 R_2 R_3 \tau_1 \tau_2 \cos(\xi_1 + \xi_2 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_3 \cos(\xi_3 + \zeta_0)] + Z_1[R_{\bar{1}} R_2 R_3 \tau_2 \cos(\xi_2 + \zeta_1) + R_1 R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_3 \cos(-\xi_1 + \xi_3 + \zeta_1)] + Z_2[R_1 R_{\bar{2}} R_3 \tau_1 \cos(\xi_1 + \zeta_2) + R_{\bar{1}} R_2 R_{\bar{3}} \tau_2 \tau_3 \cos(-\xi_2 + \xi_3 + \zeta_2)] + Z_3[R_1 R_2 R_{\bar{3}} \tau_1 \tau_2 \tau_3 \cos(\xi_1 + \xi_2 - \xi_3 + \zeta_3) + R_{\bar{1}} R_{\bar{2}} R_3 \cos \zeta_3]. \quad (3.53)$$

$$S_{\bar{3}} = Z_0[-R_1 R_2 R_3 \tau_1 \tau_2 \sin(\xi_1 + \xi_2 + \zeta_0) + R_{\bar{1}} R_{\bar{2}} R_{\bar{3}} \tau_3 \sin(\xi_3 + \zeta_0)] + Z_1[-R_{\bar{1}} R_2 R_3 \tau_2 \sin(\xi_2 + \zeta_1) + R_1 R_{\bar{2}} R_{\bar{3}} \tau_1 \tau_3 \sin(-\xi_1 + \xi_3 + \zeta_1)] + Z_2[-R_1 R_{\bar{2}} R_3 \tau_1 \sin(\xi_1 + \zeta_2) + R_{\bar{1}} R_2 R_{\bar{3}} \tau_2 \tau_3 \sin(-\xi_2 + \xi_3 + \zeta_2)] + Z_3[-R_1 R_2 R_{\bar{3}} \tau_1 \tau_2 \tau_3 \sin(\xi_1 + \xi_2 - \xi_3 + \zeta_3) + R_{\bar{1}} R_{\bar{2}} R_3 \sin \zeta_3]. \quad (3.54)$$

Next, B_j, $\omega_j B_{\bar{j}}$ and $\omega_{\bar{j}}$, $j = 0, 1, 2, 3$, are uniquely defined by equations (3.55)–(3.58):

$$B_j \cos \omega_j = C_j, \quad B_j \sin \omega_j = S_j, \quad j = 0, 1, 2, 3, \quad (3.55)$$

$$\tan \omega_j = \frac{S_j}{C_j}, \quad B_j = (C_j^2 + S_j^2)^{1/2}, \quad j = 0, 1, 2, 3, \quad (3.56)$$

$$B_{\bar{j}} \cos \omega_{\bar{j}} = C_{\bar{j}}, \quad B_{\bar{j}} \sin \omega_{\bar{j}} = S_{\bar{j}}, \quad j = 0, 1, 2, 3, \quad (3.57)$$

$$\tan \omega_{\bar{j}} = \frac{S_{\bar{j}}}{C_{\bar{j}}}, \quad B_{\bar{j}} = (C_{\bar{j}}^2 + S_{\bar{j}}^2)^{1/2}, \quad j = 0, 1, 2, 3, \quad (3.58)$$

where C_j, S_j, $C_{\bar{j}}$, $S_{\bar{j}}$ are given by equations (3.39)–(3.54). Finally, A_j, $A_{\bar{j}}$, K_j, and $K_{\bar{j}}$ are defined by

$$A_j = \frac{2B_j}{(1 - X_1^2)(1 - X_2^2)(1 - X_3^2)}, \quad j = 0, 1, 2, 3, \quad (3.59)$$

$$A_{\bar{j}} = \frac{2B_{\bar{j}}}{(1 - X_1^2)(1 - X_2^2)(1 - X_3^2)}, \quad j = 0, 1, 2, 3, \quad (3.60)$$

$$K_j = 2\pi I_0(A_j), \quad j = 0, 1, 2, 3, \quad (3.61)$$

$$K_{\bar{j}} = 2\pi I_0(A_{\bar{j}}), \quad j = 0, 1, 2, 3, \quad (3.62)$$

where X_1, X_2, and X_3 have been defined in (3.15), (3.17), and (3.19), respectively.

3.3. *The conditional probability distribution of each of the three-phase structure invariants $\psi_j, j = 0, 1, 2, 3, \bar{0}, \bar{1}, \bar{2}, \bar{3}$ (3.2)–(3.9), given the six magnitudes $|E_{\mathbf{H}}|$, $|E_{\mathbf{K}}|$, $|E_{\mathbf{L}}|$, $|E_{\bar{\mathbf{H}}}|$, $|E_{\bar{\mathbf{K}}}|$, $|E_{\bar{\mathbf{L}}}|$ in its first neighborhood*

Refer to § 3.1 for the probabilistic background. Then the eight three-phase structure invariants

$$\psi_j, \quad j = 0, 1, 2, 3, \bar{0}, \bar{1}, \bar{2}, \bar{3}, \quad (3.63)$$

(3.2)–(3.9), as functions of the primitive random variable $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, are themselves random variables. Denote by

$$P_j(\Omega_j | R_1, R_2, R_3, R_{\bar{1}}, R_{\bar{2}}, R_{\bar{3}}) = P_j(\Omega_j), \quad j = 0, 1, 2, 3, \bar{0}, \bar{1}, \bar{2}, \bar{3}, \quad (3.64)$$

the conditional probability distribution of each ψ_j, assuming as known the six magnitudes (3.11) and (3.12) in its first neighborhood. Then $P_0(\Omega_0)$, for example, is obtained from (I.4) of Appendix I by fixing R_1, R_2, R_3, $R_{\bar{1}}$, $R_{\bar{2}}$, $R_{\bar{3}}$ in accordance with (3.11) and (3.12), integrating P [equation (I.4)] with respect to $\Phi_{\bar{1}}$, $\Phi_{\bar{2}}$, $\Phi_{\bar{3}}$ between the limits 0 and 2π, and multiplying by a suitable normalizing parameter. Again, $P_1(\Omega_1)$ is obtained from (I.4) in a similar way except that the integrations are taken with respect to Φ_1, $\Phi_{\bar{2}}$, $\Phi_{\bar{3}}$, *etc.* The final formulas, the major results of this paper, are simply

$$P_j(\Omega_j) = \frac{1}{K_j} \exp\{A_j \cos(\Omega_j - \omega_j)\}, \quad j = 0, 1, 2, 3, \bar{0}, \bar{1}, \bar{2}, \bar{3}, \quad (3.65)$$

where the parameters A_j, K_j, ω_j are defined by (3.20)–(3.37), (3.38)–(3.54), and (3.55)–(3.62). Since the K_j's and A_j's are positive, the maximum of (3.65) occurs at $\Omega_j = \omega_j$. Hence, when the variance of the distribution (3.65) is small, *i.e.* when A_j is large, one obtains the reliable estimate

$$\psi_j = \omega_j, \quad j = 0, 1, 2, 3, \bar{0}, \bar{1}, \bar{2}, \bar{3}, \quad (3.66)$$

for the structure invariant ψ_j, (3.2)–(3.9). It should be emphasized that the estimate (3.66) is unique in the whole interval $(0,2\pi)$ [or, equivalently, $(-\pi,+\pi)$] and is explicitly expressed *via* (3.20)–(3.65), together with the weight A_j, in terms of the complex scattering factors $f_{j\mathbf{H}}$, $f_{j\mathbf{K}}$, $f_{j\mathbf{L}}$, presumed to be known, and the observed

Table 1. *Twenty-one estimates* ω_j (°) *of the structure invariants* ψ_j (°) *sampled from the top* 2000 *for the* $PtCl_4^{2-}$ *derivative of Cytochrome* c_{550}

Serial no.	$\lvert E_{\mathbf{H}}\rvert$	$\lvert E_{\bar{\mathbf{H}}}\rvert$	$\lvert E_{\mathbf{K}}\rvert$	$\lvert E_{\bar{\mathbf{K}}}\rvert$	$\lvert E_{\mathbf{L}}\rvert$	$\lvert E_{\bar{\mathbf{L}}}\rvert$	A_j	Estimated value ω_j of ψ_j	True value of ψ_j	Magnitude of the error $\lvert\omega_j-\psi_j\rvert$
1	2·17	2·04	0·89	1·03	0·85	0·67	6·92	−58	−88	30
100	1·91	2·06	1·61	1·49	0·85	0·67	5·62	148	130	18
200	1·91	2·06	1·96	2·06	1·41	1·57	4·83	−79	−121	42
300	2·36	2·48	1·56	1·69	0·82	0·68	4·52	52	2	50
400	2·17	2·04	1·34	1·48	1·28	1·15	4·31	79	96	17
500	1·85	1·94	0·85	0·67	0·78	0·92	4·21	56	42	14
600	2·17	2·04	0·92	1·04	0·86	0·70	4·10	146	148	2
700	1·39	1·28	0·85	0·67	0·87	0·75	4·02	−72	−68	4
800	1·41	1·57	1·61	1·49	0·71	0·85	3·93	70	50	20
900	1·88	1·98	1·28	1·15	0·85	0·67	3·87	104	96	8
1000	1·29	1·43	0·79	0·71	0·85	0·67	3·80	−88	−138	50
1100	1·34	1·48	1·34	1·22	1·25	1·16	3·76	−72	−126	54
1200	1·56	1·69	1·41	1·57	0·98	0·90	3·72	73	78	5
1300	1·98	2·07	2·08	1·94	1·08	1·21	3·68	−161	−124	37
1400	1·56	1·67	1·41	1·57	1·24	1·33	3·63	−72	−3	69
1500	2·38	2·50	1·91	2·06	0·74	0·64	3·59	84	77	7
1600	1·91	2·06	1·34	1·22	0·72	0·83	3·55	−64	−94	30
1700	1·91	2·06	2·02	2·12	2·15	2·24	3·51	−64	−72	8
1800	2·38	2·50	1·61	1·49	0·78	0·90	3·46	78	82	4
1900	2·38	2·50	1·63	1·70	1·81	1·93	3·43	63	123	60
2000	0·85	0·67	0·97	0·83	1·02	1·09	3·42	−96	−126	30

magnitudes $|E_{\mathbf{H}}|$, $|E_{\mathbf{K}}|$, $|E_{\mathbf{L}}|$, $|E_{\bar{\mathbf{H}}}|$, $|E_{\bar{\mathbf{K}}}|$, $|E_{\bar{\mathbf{L}}}|$, (3.11) and (3.12). No prior knowledge of the positions of the anomalous scatterers is needed, nor is it required that the anomalous scatterers be identical.

4. The applications

Using the presumed known coordinates of the $PtCl_4^{2-}$ derivative of the protein Cytochrome c_{550} from *Paracoccus denitrificans* (Timkovich & Dickerson, 1976), molecular weight $M_r \simeq 14\,500$, space group $P2_12_12_1$, some 8300 normalized structure factors E [(1.3) and (2.3)] were calculated (to a resolution of 2·5 Å). In addition to the anomalous scatterers Pt and Cl, this structure contains one Fe and six S atoms which also scatter anomalously at the wavelength used (Cu $K\alpha$). Using the 4000 phases φ_{hkl} corresponding to the 4000 largest $|E_{hkl}|$'s with $hkl \neq \bar{0}$, the three-phase structure invariants $\psi_j, j = 0, 1, 2, 3, \bar{0}, \bar{1}, \bar{2}, \bar{3}$, [(3.2)–(3.9)] were generated and the parameters ω_j and A_j [(3.55)–(3.60)], needed to define the distributions (3.65), were calculated. All calculations were done on the VAX 11/780 computer; double precision (approximately 15 significant digits) was used in order to eliminate round-off errors. The values of the A_j's were arranged in descending order and the first 2000, sampled at intervals of 100, were used in the construction of Table 1; the top 60 000 were used for Table 2.

Table 1 lists 21 values of A_j, sampled as shown from the top 2000, the corresponding estimates ω_j (in degrees) of the invariants ψ_j, the true values of the ψ_j, and the magnitude of the error, $|\omega_j - \psi_j|$. Also listed are the six magnitudes $|E|$ in the first neighborhood of the corresponding invariant.

Table 2. *Average magnitude of the error* (°) *in the top* 60 000 *estimated values of the three-phase structure invariants, cumulated in the nine groups shown, for the* $PtCl_4^{2-}$ *derivative of Cytochrome* c_{550}

Group no.	Number in group	Average value of A	Average magnitude of error
1	100	6·01	27·9
2	500	4·90	29·3
3	1000	4·44	28·8
4	2000	4·02	28·0
5	5000	3·49	31·4
6	10000	3·09	33·8
7	20000	2·71	36·1
8	40000	2·35	38·6
9	60000	2·15	39·8

Table 2 gives the average magnitude of the error,

$$\langle|\omega_j - \psi_j|\rangle, \tag{4.1}$$

in the nine cumulative groups shown, for the 60 000 most reliable estimates ω_j of the invariants ψ_j.

Tables 1 and 2 show firstly that, owing to the unexpectedly large number of large values of A_j, our formulas yield reliable (and unique) estimates of tens of thousands of the three-phase structure invariants. Secondly, the invariants which are most reliably estimated lie anywhere in the range from −180 to +180°, and appear to be uniformly distributed in this range (Columns 9 and 10 of Table 1). Finally, in sharp contrast to the case that no anomalous scatterers are present, the most reliable estimates are not necessarily

of invariants corresponding to the most intense reflections but of those corresponding instead to reflections of only moderate intensity (Columns 2–7 of Table 1).

Fig. 1 shows a scatter diagram of ω_j *versus* ψ_j for the $PtCl_4^{2-}$ derivative of Cytochrome c_{550}, using 201 invariants sampled at intervals of length ten from the top 2000, as well as the line $\omega_j = \psi_j$. Since the line falls evenly among the points, it appears that the ω_j are unbiased estimates of the invariants ψ_j.

5. Concluding remarks

In this paper the goal of integrating the techniques of direct methods with anomalous dispersion is realized. Specifically, the conditional probability distribution of the three-phase structure invariant, assuming as known the six magnitudes in its first neighborhood, is obtained. In the favorable case that the variance of the distribution happens to be small, the distribution yields a reliable estimate of the invariant (the neighborhood principle). It is particularly noteworthy that, in strong contrast to all previous work, the estimate is unique in the whole interval $(0,2\pi)$ [or, equivalently, $(-\pi,\pi)$] and that any estimate in this range is possible (even, for example, in the vicinity of $\pm\pi/2$ or π). The first applications of this work using error-free diffraction data have been made, and these show that in a typical case some tens of thousands of three-phase structure invariants may be estimated with unprecedented accuracy, even for a macromolecular crystal structure. Some preliminary calculations on a number of structures, not detailed here, show that the accuracy of the estimates depends in some complicated way on the complexity of the crystal structure, the number of anomalous scatterers, the strength of the anomalous signal, and the range of sin θ/λ. With smaller structures the accuracy may be greatly increased, average errors of only three or four degrees for thousands of invariants being not uncommon.

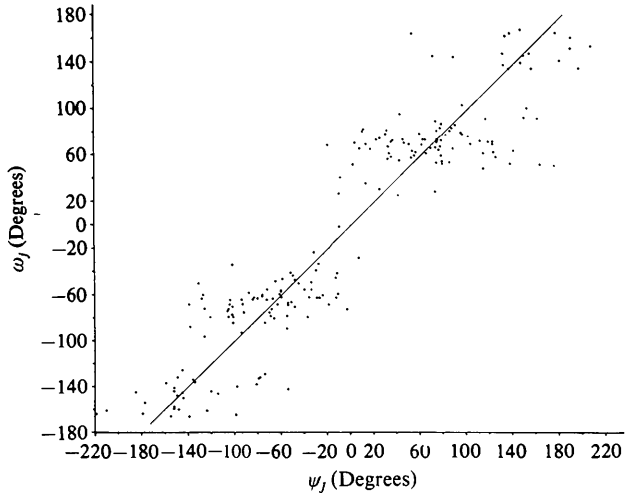

Fig. 1. A scatter diagram of ω_j *versus* ψ_j, using 201 invariants sampled at intervals of length ten from the top 2000, for the $PtCl_4^{2-}$ derivative of Cytochrome c_{550}, as well as the line $\omega_j = \psi_j$.

Inspection of the formulas, in particular (3.39)–(3.58), shows that the estimates, ω_j, are relatively insensitive to errors in the observed $|E|$'s provided that these errors are positively correlated for the Friedel pairs $|E_{\mathbf{H}}|$, $|E_{\bar{\mathbf{H}}}|$. However, a detailed study of the effect of experimental errors is outside the scope of the present paper and will be presented at a future date.

It should be stated in conclusion that the availability of reliable estimates for large numbers of the three-phase structure invariants implies that the traditional machinery of direct methods, in particular the tangent formula, suitably modified to accommodate the non-zero estimates of the invariants, may be carried over without essential change to estimate the values of the individual phases and thus to facilitate structure determination *via* anomalous dispersion. In view of the calculations summarized in Tables 1 and 2 and Fig. 1, it seems likely that, in time, even macromolecules will prove to be solvable in this way. It is clear too, that, owing to the ability to estimate both the sine and cosine invariants, that is to say both the signs and magnitudes of the invariants, the unique enantiomorph determined by the observed intensities is automatically obtained.

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APPENDIX I

The joint probability distribution of the six structure factors $E_{\mathbf{H}}, E_{\mathbf{K}}, E_{\mathbf{L}}, E_{\bar{\mathbf{H}}}, E_{\bar{\mathbf{K}}}, E_{\bar{\mathbf{L}}}$, where $\mathbf{H} + \mathbf{K} + \mathbf{L} = 0$

As usual, fix the reciprocal-lattice vectors **H**, **K**, **L** subject to (3.1). Suppose that the ordered N-tuple $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ of atomic position vectors is the primitive random variable which is assumed to be uniformly distributed over the N-fold Cartesian product W. Then the six normalized structure factors $E_{\mathbf{H}}, E_{\mathbf{K}}, E_{\mathbf{L}}, E_{\bar{\mathbf{H}}}, E_{\bar{\mathbf{K}}}, E_{\bar{\mathbf{L}}}$, as functions of the primitive random variable $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, are themselves random variables.

Denote by

$$P = P(R_1, R_2, R_3, R_{\bar{1}}, R_{\bar{2}}, R_{\bar{3}}; \Phi_1, \Phi_2, \Phi_3, \Phi_{\bar{1}}, \Phi_{\bar{2}}, \Phi_{\bar{3}}) \tag{I.1}$$

the joint probability distribution of the magnitudes $|E_{\mathbf{H}}|$, $|E_{\mathbf{K}}|$, $|E_{\mathbf{L}}|$, $|E_{\bar{\mathbf{H}}}|$, $|E_{\bar{\mathbf{K}}}|$, $|E_{\bar{\mathbf{L}}}|$ and the phases $\varphi_{\mathbf{H}}$,

φ_K, φ_L, $\varphi_{\bar{H}}$, $\varphi_{\bar{K}}$, $\varphi_{\bar{L}}$ of the six structure factors E_H, E_K, E_L, $E_{\bar{H}}$, $E_{\bar{K}}$, $E_{\bar{L}}$ whose magnitudes, (3.10), constitute the first neighborhood of each of the structure invariants (3.2)–(3.9). Then, following the early work of Karle & Hauptman (1958), P is given by the twelvefold integral

$$\begin{aligned}P = &\frac{R_1 R_2 R_3 R_{\bar{1}} R_{\bar{2}} R_{\bar{3}}}{(2\pi)^{1/2}} \\ &\times \int_{\rho_1,\rho_2,\rho_3,\rho_{\bar{1}},\rho_{\bar{2}},\rho_{\bar{3}}=0}^{\infty} \int_{\theta_1,\theta_2,\theta_3,\theta_{\bar{1}},\theta_{\bar{2}},\theta_{\bar{3}}=0}^{2\pi} \rho_1\rho_2\rho_3\rho_{\bar{1}}\rho_{\bar{2}}\rho_{\bar{3}} \\ &\times \exp\{-i[R_1\rho_1\cos(\theta_1-\Phi_1) \\ &+ R_2\rho_2\cos(\theta_2-\Phi_2) + R_3\rho_3\cos(\theta_3-\Phi_3) \\ &+ R_{\bar{1}}\rho_{\bar{1}}\cos(\theta_{\bar{1}}-\Phi_{\bar{1}}) + R_{\bar{2}}\rho_{\bar{2}}\cos(\theta_{\bar{2}}-\Phi_{\bar{2}}) \\ &+ R_{\bar{3}}\rho_{\bar{3}}\cos(\theta_{\bar{3}}-\Phi_{\bar{3}})]\} \\ &\times \prod_{j=1}^{N} q_j \,\mathrm{d}\rho_1\,\mathrm{d}\rho_2\,\mathrm{d}\rho_3\,\mathrm{d}\rho_{\bar{1}}\,\mathrm{d}\rho_{\bar{2}}\,\mathrm{d}\rho_{\bar{3}} \\ &\times \mathrm{d}\theta_1\,\mathrm{d}\theta_2\,\mathrm{d}\theta_3\,\mathrm{d}\theta_{\bar{1}}\,\mathrm{d}\theta_{\bar{2}}\,\mathrm{d}\theta_{\bar{3}}, \qquad \text{(I.2)}\end{aligned}$$

where

$$\begin{aligned}q_j = \Big\langle \exp\Big\{ &\frac{i|f_{j\mathbf{H}}|}{\alpha_H^{1/2}}[\rho_1\cos(\delta_{j\mathbf{H}} + 2\pi\mathbf{H}.\mathbf{r}_j - \theta_1) \\ &+ \rho_{\bar{1}}\cos(\delta_{j\mathbf{H}} - 2\pi\mathbf{H}.\mathbf{r}_j - \theta_{\bar{1}})] + \frac{i|f_{j\mathbf{K}}|}{\alpha_K^{1/2}} \\ &\times [\rho_2\cos(\delta_{j\mathbf{K}} + 2\pi\mathbf{K}.\mathbf{r}_j - \theta_2) \\ &+ \rho_{\bar{2}}\cos(\delta_{j\mathbf{K}} - 2\pi\mathbf{K}.\mathbf{r}_j - \theta_{\bar{2}})] + \frac{i|f_{j\mathbf{L}}|}{\alpha_L^{1/2}} \\ &\times [\rho_3\cos(\delta_{j\mathbf{L}} + 2\pi\mathbf{L}.\mathbf{r}_j - \theta_3) \\ &+ \rho_{\bar{3}}\cos(\delta_{j\mathbf{L}} - 2\pi\mathbf{L}.\mathbf{r}_j - \theta_{\bar{3}})]\Big\}\Big\rangle_{\mathbf{r}_j}. \qquad \text{(I.3)}\end{aligned}$$

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

$$\begin{aligned}P \simeq &\frac{R_1 R_2 R_3 R_{\bar{1}} R_{\bar{2}} R_{\bar{3}}}{\pi^6(1-X_1^2)(1-X_2^2)(1-X_3^2)} \\ &\times \exp\left\{-\frac{R_1^2+R_{\bar{1}}^2}{1-X_1^2} - \frac{R_2^2+R_{\bar{2}}^2}{1-X_2^2} - \frac{R_3^2+R_{\bar{3}}^2}{1-X_3^2}\right\} \\ &\times \exp\left\{\frac{2R_1R_{\bar{1}}X_1}{1-X_1^2}\cos(\Phi_1+\Phi_{\bar{1}}+\xi_1)\right. \\ &+ \frac{2R_2R_{\bar{2}}X_2}{1-X_2^2}\cos(\Phi_2+\Phi_{\bar{2}}+\xi_2) \\ &\left.+ \frac{2R_3R_{\bar{3}}X_3}{1-X_3^2}\cos(\Phi_3+\Phi_{\bar{3}}+\xi_3)\right\} \\ &\times \exp\left\{\frac{2}{(1-X_1^2)(1-X_2^2)(1-X_3^2)}\right. \\ &\times [Z_0(R_1R_2R_3\cos(\Phi_1+\Phi_2+\Phi_3-\zeta_0) \\ &+ R_{\bar{1}}R_{\bar{2}}R_{\bar{3}}\cos(\Phi_{\bar{1}}+\Phi_{\bar{2}}+\Phi_{\bar{3}}-\zeta_0)) \\ &+ Z_1(R_{\bar{1}}R_2R_3\cos(-\Phi_{\bar{1}}+\Phi_2+\Phi_3-\zeta_1) \\ &+ R_1R_{\bar{2}}R_{\bar{3}}\cos(-\Phi_1+\Phi_{\bar{2}}+\Phi_{\bar{3}}-\zeta_1)) \\ &+ Z_2(R_1R_{\bar{2}}R_3\cos(\Phi_1-\Phi_{\bar{2}}+\Phi_3-\zeta_2) \\ &+ R_{\bar{1}}R_2R_{\bar{3}}\cos(\Phi_{\bar{1}}-\Phi_2+\Phi_{\bar{3}}-\zeta_2)) \\ &+ Z_3(R_1R_2R_{\bar{3}}\cos(\Phi_1+\Phi_2-\Phi_{\bar{3}}-\zeta_3) \\ &\left.\left.+ R_{\bar{1}}R_{\bar{2}}R_3\cos(\Phi_{\bar{1}}+\Phi_{\bar{2}}-\Phi_3-\zeta_3))]\right\}, \qquad \text{(I.4)}\end{aligned}$$

where the parameters X_j, ξ_j ($j = 1, 2, 3$) are defined by (3.14)–(3.19) and the parameters Z_j, ζ_j ($j = 0, 1, 2, 3$) by (3.36) and (3.37).

The distribution (I.4), which should be compared with (2.10), plays the central role in the probabilistic theory of the three-phase structure invariants. In particular, the conditional distributions (3.65), the major result of the present paper, are derived directly from (I.4), as described earlier.

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