diffracted to the secondary r.l.p. (the 'transit' reflection). Extensive use of this technique leads to essentially unambiguous indexing.

4.3. *Determination of triplet phases*

The objectives of our initial phase investigations (Nicolosi, 1982; Ladell, 1982; Post, 1982; Gong & Post, 1983) were limited to the separation of the 'observed' triplet phases into two groups. The phases of all triplets in either group were identical. Their nature ('positive' or 'negative') was not specified at the separation stage. Gradually, as more phases were determined, it became clear that, for r.l.p.s entering the Ewald sphere, positive phases were invariably associated with the 'attenuation followed by enhancement sequence'. These experimental findings are inconsistent with the theoretical predictions of Hummer & Billy (1982). The criteria outlined above were used to assign phases to the triplets listed in Table 1 and displayed in Fig. 4.

Peaks 1, 5, 8, 9 and 14 display relatively weak phase indications. Careful examination, however, reveals accumulations of intensity on one side of each of these maxima, near the background line. These characterize 'enhancement' for all maxima. In the cases cited, where the 'attenuation' is not displayed as clearly as might be desired, the phase assignments are based primarily on these intensity enhancements.

In previous investigations of the phases of germanium triplets by one of the authors (B. Post), only eight of the 17 phases were determined. The others were rendered indeterminate by the relatively high backgrounds and the effects of overlapping peaks in the n-beam patterns. Those patterns were recorded using polychromatic incident beams from 'fine-focus' sources, in conjunction with large source-to-detector distances. The latter reduced the incident-beam divergence to about 2' and made possible the elimination of most $K\alpha_2$ from the diffracted beams.

The biaxial diffractometer provides an incident beam whose $K\alpha_2$ content we could not detect, and an incident-beam divergence of about 30 to 40"; these made possible the improved pattern shown in Fig. 4.

Efforts are under way to reduce the beam divergence to 10 and 15". Under these conditions the angular range of primary radiation 'seen' by the detector should be of the order of the half-widths of most interactions. The sensitivity of apparatus to very weak interactions should then be greatly increased. It should also be noted that step sizes of 0·005° were used to record data shown in Fig. 4. These will be reduced, as needed, to 0·001° with corresponding improvements in resolution.

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Enantiomorph-Dependent Probability Distributions of Origin-Invariant Phases

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Abstract

By integrating joint probability distributions of two related invariant phases with respect to one of the variables over the range 0 to π, enantiomorph-dependent phase indications may be obtained. In the present paper the full potential of such a strategy is described. For probability distributions correct up to and including terms of order N^{-1}, all cases of interest appear to consist of combinations of two invariants with one or two structure factors in common. For each case the joint probability distribution of the phases of such a pair of invariants, given a number of suitable structure-factor amplitudes, is derived.

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Subsequently, all these distribution functions are integrated from 0 to π with respect to one or other variable, thus exploring the full range of enantiomorph-dependent distributions. The resulting expressions are grouped together according to whether the chosen enantiomorph definer is a triplet, quartet, quintet or higher-order invariant, thereby facilitating their future implementation in direct-methods procedures.

1. Introduction

Although in many crystal structure determinations direct methods have proven to be a successful technique for handling the phase problem, the crystallographer is often confronted with an enantiomorph ambiguity when direct methods are applied to noncentrosymmetric structures. This ambiguity arises because the intensities of diffracted X-rays are insensitive to an inversion of the crystal structure if the relatively small effects of anomalous dispersion are ignored. In direct methods probability distributions of phases are obtained directly from these intensities and therefore these results should necessarily be ambiguous (*i.e.* any outcome will fit both enantiomorphs equally well), unless subsidiary enantiomorph-dependent information is employed. Up to now only limited attention has been paid to the resolution of this problem. Van der Putten, Schenk & Hauptman (1980) have described and tested a procedure to identify those three-phase structure seminvariants and variants in $P2_1$, of which the most probable phases are either $+\pi/2$ or $-\pi/2$. Unique phase indications, however, are not obtained by their approach. Hauptman (1977) was the first to attain this goal. After deriving the joint probability distribution of two related quartet phases, given a number of structure-factor amplitudes, he arrived at a unique phase indication for one of the quartets by assuming the other quartet phase to be known. Hauptman & Green (1978) used an analogous approach to estimate two-phase structure seminvariants in $P2_1$. However, these approaches depend on the value of the phase of the enantiomorph definer, which has to be established first. Recently, Pontenagel (1984) obtained a unimodal enantiomorph-dependent probability distribution of triple-product phases without assigning a specific value to the enantiomorph definer except that its phase is restricted to be in the range of 0 to π (or π to 2π). Such a restriction was made by integrating the joint probability distribution of two related triple-product phases with respect to one of the variables over the range 0 to π. An important feature of the resulting enantiomorph-dependent distribution, which was successfully applied to the determination of a $P1$ structure, is the position of the mode. Contrary to the enantiomorph-insensitive distribution (Cochran, 1955), of which the mode is always on zero, it was found that the enantiomorph-dependent distribution of a triple-product phase may have its mode anywhere between $-\frac{1}{2}\pi$ and $+\frac{1}{2}\pi$.

From this it is anticipated that application of the same procedure to quartet phases may lead to a distribution function with a single mode anywhere between 0 and 2π as a consequence of the fact that (up to and including terms of order N^{-1}) the quartet distribution in exponential form appears to have its mode on either 0 or π. [It should be noted that the inclusion of higher-order terms leads to bimodal distributions with modes on φ and $2\pi-\varphi$, possibly deviating from 0 or π (Hauptman, 1975*b*; Heinerman, 1976, 1977; Giacovazzo, 1976, 1977).]

Using the mathematical procedure outlined in the previous paper (Pontenagel, 1984), new enantiomorph-dependent distribution functions will be derived and it will be shown that it is possible to obtain unique phase indications anywhere between zero and 2π without employing *a priori* structural information or anomalous diffraction data.

2. Approach

Two origin-invariant products of structure factors

$$I_{\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3,\ldots} \equiv E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}\ldots E_{-\mathbf{h}_1-\mathbf{h}_2-\mathbf{h}_3-\ldots}$$

and

$$I_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\ldots} \equiv E_{\mathbf{k}_1}E_{\mathbf{k}_2}E_{\mathbf{k}_3}\ldots E_{-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3-\ldots}$$

will be called single related if they have only one structure factor in common, *i.e.* $E_{-\mathbf{h}_1-\mathbf{h}_2-\mathbf{h}_3-\ldots}=E_{-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3-\ldots}$. If Friedel's law is supposed to be valid, which will be assumed throughout this paper, $I_1(=I_{\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3,\ldots})$ and $I_2(=I_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\ldots})$ are also called single related if I_1 and the complex conjugate of I_2 have only one structure factor in common.

Generally, we define two products I_1 and I_2 to be n-fold related if I_1 and I_2 or I_1 and I_2^* have precisely n structure factors in common. Adding or subtracting the phases of I_1 and I_2 eliminates the common structure-factor phase(s) and gives the phase of a third origin-invariant product of structure factors (I_3). For example, if

$$I_1=E_{\mathbf{h}}E_{\mathbf{k}}E_{-\mathbf{h}-\mathbf{k}} \text{ and } I_2=E_{\mathbf{h}+\mathbf{k}}E_{\mathbf{l}}E_{-\mathbf{h}-\mathbf{k}-\mathbf{l}}$$

then

$$I_3=E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{-\mathbf{h}-\mathbf{k}-\mathbf{l}},$$

where the phase

$$\varphi_3(=\varphi_{\mathbf{h},\mathbf{k},\mathbf{l}}=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$$

of I_3 equals the sum of the phases

$$\varphi_1(=\varphi_{\mathbf{h},\mathbf{k}}=\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}})$$

and

$$\varphi_2(=\varphi_{\mathbf{h}+\mathbf{k},\mathbf{l}}=\varphi_{\mathbf{h}+\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}).$$

In this example I_1 and I_2 are single related, while I_1 and I_3 and also I_2 and I_3 are double related.

The joint probability distribution of the phases $\varphi_{\mathbf{h},\mathbf{k}}$ and $\varphi_{\mathbf{h}+\mathbf{k},\mathbf{l}}$ of two single-related triple products has been calculated previously (Pontenagel, 1984). The resulting conditional joint probability distribution

$$P(T_1, T_2|R_1, R_2, R_3, R_4, R_{12}, R_{13}, R_{23}),$$

given the magnitudes of $E_{\mathbf{h}}$, $E_{\mathbf{k}}$, $E_{\mathbf{l}}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$, $E_{\mathbf{h}+\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{l}}$ and $E_{\mathbf{k}+\mathbf{l}}$, contains a $\cos(T_1+T_2)$ term, which ultimately leads to the deviation from 0 of the mode of the enantiomorph-dependent distribution of $\varphi_{\mathbf{h},\mathbf{k}}$. It is of interest to note that the $\cos(T_1+T_2)$ term, where T_1+T_2 corresponds to the quartet phase $\varphi_{\mathbf{h},\mathbf{k},\mathbf{l}}$, is due to the incorporation of the magnitudes of $E_{\mathbf{h}+\mathbf{l}}$ and $E_{\mathbf{k}+\mathbf{l}}$, which, together with the magnitude of $E_{\mathbf{h}+\mathbf{k}}$, constitute the cross terms of $\varphi_{\mathbf{h},\mathbf{k},\mathbf{l}}$.

In our present approach the following strategy is adopted to determine which structure factors have to be considered in the derivation of the joint probability distribution of two related origin-invariant phases:

(a) define the two origin invariants I_1 and I_2, which are n-fold related;

(b) determine I_3 by adding or subtracting φ_1 of I_1 and φ_2 of I_2 such that the phases of the n common structure factors cancel;

(c) include, apart from the structure factors in I_1 and I_2, also the cross terms of I_1, I_2 and I_3.

In our calculations we will only consider terms up to and including those of order N^{-1}, which implies that only cross terms of quartets are of interest. For example, for the single-related triple product $I_{\mathbf{h},\mathbf{k}}$ and the quartet $I_{\mathbf{h}+\mathbf{k},\mathbf{l},\mathbf{m}}$ we only need to consider the cross terms of $I_{\mathbf{h}+\mathbf{k},\mathbf{l},\mathbf{m}}$ and not those of the quintet $I_{\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m}}$. Moreover, the restriction limits our calculations to those combinations of related invariants for which at least one invariant is a triplet or a quartet (see Table 1).

For each combination three different joint probability distributions $P(\xi_1, \xi_2|R\text{'s})$ of two related invariant phases, given the relevant structure-factor amplitudes, can be calculated. (ξ_1 and ξ_2 correspond to the phases of I_1 and I_2 or to I_1 and I_3 or to I_2 and I_3, respectively.) For case 1 (see Table 1) we will give two of the three distributions to show that they are easily obtained from each other by simple substitutions (§ 3a); for all other cases only the distributions of the phases of I_1 and I_2 will be given (§§ 3b–3g). From the 21 available $P(\xi_1, \xi_2|R\text{'s})$ functions 42 enantiomorph-dependent probability distributions can be calculated by integrating over the range 0 to π (or π to 2π), with respect to either ξ_1 or ξ_2. Only a limited number of them appears to depend on the phase of an origin invariant when only terms up to and including order N^{-1} are considered. In § 4 all these distributions are grouped together according to whether the chosen enantiomorph definer is a triplet, quartet, quintet or higher-order invariant.

Table 1. *Relevant combinations of related invariants when only terms up to and including order $1/N$ are considered in the probability distributions*

Case	I_1	I_2	I_3	
1	$I_{\mathbf{h},\mathbf{k}}$	$I_{\mathbf{h}+\mathbf{k},\mathbf{l}}$	$I_{\mathbf{h},\mathbf{k},\mathbf{l}}$	(triplet, triplet, quartet)
2	$I_{\mathbf{h},\mathbf{k}}$	$I_{\mathbf{h}+\mathbf{k},\mathbf{l},\mathbf{m}}$	$I_{\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m}}$	(triplet, quartet, quintet)
3	$I_{\mathbf{h},\mathbf{k}}$	$I_{\mathbf{h}+\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n},\ldots}$	$I_{\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n},\ldots}$	[triplet, M-tet, ($M+1$)-tet; $M \geq 5$]
4	$I_{\mathbf{h},\mathbf{k},\mathbf{l}}$	$I_{\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m},\mathbf{n}}$	$I_{\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n}}$	(quartet, quartet, sextet)
5	$I_{\mathbf{h},\mathbf{k},\mathbf{l}}$	$I_{\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m},\mathbf{n},\mathbf{r},\ldots}$	$I_{\mathbf{h},\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n},\mathbf{r},\ldots}$	[quartet, M-tet, ($M+2$)-tet; $M \geq 5$]
6	$I_{\mathbf{h},\mathbf{k},\mathbf{l}}$	$I_{-\mathbf{l},\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m}}$	$I_{\mathbf{h},\mathbf{k},\mathbf{m}}$	(quartet, quartet, quartet)
7	$I_{\mathbf{h},\mathbf{k},\mathbf{l}}$	$I_{-\mathbf{l},\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m},\mathbf{n},\ldots}$	$I_{\mathbf{h},\mathbf{k},\mathbf{m},\mathbf{n},\ldots}$	(quartet, M-tet, M-tet; $M \geq 5$)

3. Joint probability distributions of the phases of two related invariants

All distributions given in this section are correct up to and including terms of order N^{-1}. They were obtained by calculations *via* the joint probability distributions of the relevant individual structure factors, which, for cases 1, 2 and 6, could be obtained from the literature (Hauptman, 1975a; Fortier & Hauptman, 1977; Heinerman, 1976; Giacovazzo, 1976; Hauptman, 1977), while for cases 3, 4, 5 and 7 the distributions had to be derived *via* the characteristic functions. None of these calculations will be given in this paper. However, details of a simplified procedure, which appeared to give the same results, are given in Appendix I.

In the following, the symbol C will be used to indicate an appropriate normalizing constant.

3(a) *Triplet, triplet, quartet* (*case* 1)

The joint probability distribution

$$P(T_1, T_2|R_1, R_2, R_{12}, R_3, R_4, R_{13}, R_{23})$$

of $\varphi_{\mathbf{h},\mathbf{k}}$ and $\varphi_{\mathbf{h}+\mathbf{k},\mathbf{l}}$, given the magnitudes of $E_{\mathbf{h}}$, $E_{\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{k}}$, $E_{\mathbf{l}}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$, $E_{\mathbf{h}+\mathbf{l}}$ and $E_{\mathbf{k}+\mathbf{l}}$, was calculated by Pontenagel (1984):

$$\begin{aligned} P(T_1, T_2|R\text{'s}) = C \exp[&2N^{-1/2}R_1R_2R_{12}\cos T_1 \\ &+2N^{-1/2}R_3R_4R_{12}\cos T_2 \\ &+2N^{-1}(R_{13}^2+R_{23}^2-2) \\ &\times R_1R_2R_3R_4\cos(T_1+T_2)]. \end{aligned} \quad (1a)$$

Since $\varphi_{\mathbf{h},\mathbf{k}}+\varphi_{\mathbf{h}+\mathbf{k},\mathbf{l}}-\varphi_{\mathbf{h},\mathbf{k},\mathbf{l}} \equiv 0$ (the three invariants form an identity), the joint probability distribution of a triple-product phase and a double-related quartet phase is easily obtained from (1a) by substituting $T_1 = Q - T_2$:

$$\begin{aligned} P(T_2, Q|R\text{'s}) = C \exp[&2N^{-1/2}R_3R_4R_{12}\cos T_2 \\ &+2N^{-1/2}R_1R_2R_{12}\cos(Q-T_2) \\ &+2N^{-1}(R_{13}^2+R_{23}^2-2) \\ &\times R_1R_2R_3R_4\cos Q]. \end{aligned} \quad (1b)$$

In the same way the substitution $T_2 = Q - T_1$ can be used to obtain a third distribution function. In this case the result is analogous to (1*b*), but in general three different formulae are obtained by the respective substitutions.

3(*b*) *Triplet, quartet, quintet* (*case* 2)

The joint probability distribution

$$P(T, Q|R_1, R_2, R_{12}, R_3, R_4, R_5, R_{34}, R_{35}, R_{45})$$

of $\varphi_{\mathbf{h},\mathbf{k}}$ and $\varphi_{\mathbf{h}+\mathbf{k},\mathbf{l},\mathbf{m}}$, given the magnitudes of $E_\mathbf{h}$, $E_\mathbf{k}$, $E_{\mathbf{h}+\mathbf{k}}$, $E_\mathbf{l}$, $E_\mathbf{m}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}$, $E_{\mathbf{l}+\mathbf{m}}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{m}}$ and $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$, appears to be

$$\begin{aligned}P(T, Q|R\text{'s}) = C \exp [&2N^{-1/2}R_1R_2R_{12} \cos T\\ &+2N^{-1}(R_{34}^2+R_{35}^2+R_{45}^2-2)\\ &\times R_{12}R_3R_4R_5 \cos Q]. \qquad (2)\end{aligned}$$

The result was obtained from the previously published P_{15} distribution [Fortier & Hauptman, (1977); after disregarding all terms of order $N^{-3/2}$ and fixing the magnitudes, (2) is obtained by integrating with respect to the phases subject to the conditions $\varphi_1+\varphi_2-\varphi_{12}=T$ and $\varphi_{12}+\varphi_3+\varphi_4-\varphi_5=Q$].

3(*c*) *Triplet, M-tet,* $(M+1)$*-tet*; $M\geq 5$ (*case* 3)

The joint probability distribution

$$P(T, M|R_1, R_2, R_{12}, R_3, R_4, R_5, \ldots)$$

of $\varphi_{\mathbf{h},\mathbf{k}}$ and $\varphi_{\mathbf{h}+\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n},\ldots}$, given the magnitudes of $E_\mathbf{h}$ and $E_\mathbf{k}$ and all the magnitudes of the structure factors in $I_{\mathbf{h}+\mathbf{k},\mathbf{l},\mathbf{m},\mathbf{n},\ldots}$, was found to be

$$P(T, M|R\text{'s}) = C \exp [2N^{-1/2}R_1R_2R_{12} \cos T], \qquad (3)$$

which, however, does not depend on the phase of the M-tet.

3(*d*) *Quartet, quartet, sextet* (*case* 4)

The joint probability distribution

$$P(Q_1, Q_2|R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_{12}, R_{13}, R_{23}, R_{45}, R_{46}, R_{56})$$

of $\varphi_{\mathbf{h},\mathbf{k},\mathbf{l}}$ and $\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m},\mathbf{n}}$, given the magnitudes of $E_\mathbf{h}$, $E_\mathbf{k}$, $E_\mathbf{l}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$, $E_\mathbf{m}$, $E_\mathbf{n}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}+\mathbf{n}}$, $E_{\mathbf{h}+\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{l}}$, $E_{\mathbf{k}+\mathbf{l}}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{n}}$ and $E_{\mathbf{m}+\mathbf{n}}$, appears to be

$$\begin{aligned}P(Q_1, Q_2|R\text{'s}) = C \exp [&2N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)\\ &\times R_1R_2R_3R_4 \cos Q_1\\ &+2N^{-1}(R_{45}^2+R_{46}^2+R_{56}^2-2)\\ &\times R_4R_5R_6R_7 \cos Q_2]. \qquad (4)\end{aligned}$$

3(*e*) *Quartet, M-tet,* $(M+2)$*-tet*; $M\geq 5$ (*case* 5)

The joint probability distribution

$$P(Q, M|R_1, R_2, R_3, R_4, R_5, R_6, R_7, \ldots, R_{12}, R_{13}, R_{23})$$

of $\varphi_{\mathbf{h},\mathbf{k},\mathbf{l}}$ and $\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m},\mathbf{n},\mathbf{r},\ldots}$, given $|E_\mathbf{h}|$, $|E_\mathbf{k}|$, $|E_\mathbf{l}|$, all the magnitudes of the structure factors in $I_{\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m},\mathbf{n},\mathbf{r},\ldots}$ and $|E_{\mathbf{h}+\mathbf{k}}|$, $|E_{\mathbf{h}+\mathbf{l}}|$ and $|E_{\mathbf{k}+\mathbf{l}}|$, was calculated to be

$$\begin{aligned}P(Q, M|R\text{'s}) = C \exp [&2N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)\\ &\times R_1R_2R_3R_4 \cos Q]. \qquad (5)\end{aligned}$$

As for case 3, this distribution does not depend on the phase of the M-tet.

3(*f*) *Quartet, quartet, quartet* (*case* 6)

For the joint probability distribution

$$P(Q_1, Q_2|R_1, R_2, R_3, R_4, R_5, R_6, R_{12}, R_{13}, R_{23}, R_{35}, R_{45}, R_{15}, R_{25})$$

of $\varphi_{\mathbf{h},\mathbf{k},\mathbf{l}}$ and $\varphi_{-\mathbf{l},\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m}}$, given the magnitudes of $E_\mathbf{h}$, $E_\mathbf{k}$, $E_\mathbf{l}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$, $E_\mathbf{m}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{m}}$, $E_{\mathbf{h}+\mathbf{k}}$, $E_{\mathbf{h}+\mathbf{l}}$, $E_{\mathbf{k}+\mathbf{l}}$, $E_{\mathbf{l}-\mathbf{m}}$, $E_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}$, $E_{\mathbf{h}+\mathbf{m}}$ and $E_{\mathbf{k}+\mathbf{m}}$, the following expression was obtained from Hauptman (1977) after rewriting his formula (2.13) in exponential form.

$$\begin{aligned}P(Q_1, Q_2|R\text{'s}) = C \exp [&2N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)\\ &\times R_1R_2R_3R_4 \cos Q_1\\ &+2N^{-1}(R_{12}^2+R_{35}^2+R_{45}^2-2)\\ &\times R_3R_4R_5R_6 \cos Q_2\\ &+2N^{-1}(R_{12}^2+R_{15}^2+R_{25}^2-2)\\ &\times R_1R_2R_5R_6 \cos (Q_1+Q_2)]. \qquad (6)\end{aligned}$$

3(*g*) *Quartet, M-tet, M-tet*; $M\geq 5$ (*case* 7)

The joint probability distribution

$$P(Q, M|R_1, R_2, R_3, R_4, R_5, R_6, \ldots, R_{12}, R_{13}, R_{23})$$

of $\varphi_{\mathbf{h},\mathbf{k},\mathbf{l}}$ and $\varphi_{-\mathbf{l},\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m},\mathbf{n},\ldots}$, given $|E_\mathbf{h}|$, $|E_\mathbf{k}|$, $|E_\mathbf{l}|$ and all the magnitudes of the structure factors in $I_{-\mathbf{l},\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m},\mathbf{n},\ldots}$ and $|E_{\mathbf{h}+\mathbf{k}}|$, $|E_{\mathbf{h}+\mathbf{l}}|$ and $|E_{\mathbf{k}+\mathbf{l}}|$, appears to be

$$\begin{aligned}P(Q, M|R\text{'s}) = C \exp [&2N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)\\ &\times R_1R_2R_3R_4 \cos Q]. \qquad (7)\end{aligned}$$

Again, as for cases 3 and 5, this distribution does not depend on the phase of the M-tet.

4. The enantiomorph-dependent distribution functions

From a joint probability distribution $P(\xi_1, \xi_2|R\text{'s})$ of two related invariant phases φ_1 and φ_2, given a number of structure-factor amplitudes, an enantiomorph-dependent distribution can be obtained by integrating with respect to ξ_2 over the range 0 to π. This distribution will be denoted by $P(\xi_1|R\text{'s};\ 0\leq\xi_2<\pi)$. In Appendix II a general expression is derived for the resulting formula. As an enantiomorph can be chosen only once, it is essential to state explicitly which invariant phase is restricted. This implies that the reciprocal vectors corresponding to the restricted invariant are no longer arbitrary and therefore the derived enantiomorph-dependent distributions can only be applied to a subset of the available invariants. For example, if in case 1 $\varphi_{\mathbf{h},\mathbf{k}}$ is restricted, the reciprocal vectors $\mathbf{h}$ and $\mathbf{k}$ are specified and consequently only $\mathbf{l}$ can be chosen arbitrary throughout reciprocal space. Therefore, the number of invariant phases to which the enantiomorph-dependent distribution $P(T_2|R\text{'s}; 0\leq T_1<\pi)$ of $\varphi_{\mathbf{h}+\mathbf{k},\mathbf{l}}$ can be applied is of order Y, where Y is the number of structure factors from which the invariants are constructed. As the enantiomorph-dependent distributions of $\varphi_{\mathbf{h},\mathbf{l}}$ and $\varphi_{\mathbf{k},\mathbf{l}}$ are affected by the same $\varphi_{\mathbf{h},\mathbf{k}}$ the total number of triple products with an enantiomorph-dependent phase indication will be of order $3Y$. This number of invariants to which a distribution can be applied will be given for all formulae.

4(*a*) *Triplets*

If an enantiomorph is chosen by restricting a triple-product phase to the range 0 to π we obtain from (1*a*) (for $3Y$ triple products):

$$\begin{aligned}P(T_1|R\text{'s}; 0\leq T_2<\pi)\\ &=C\exp[2N^{-1/2}R_1R_2R_{12}\cos T_1\\ &\quad-4\pi^{-1}N^{-1}(R_{13}^2+R_{23}^2-2)R_1R_2R_3R_4\sin T_1];\end{aligned} \tag{8a}$$

and from (1*b*) (for $3Y$ quartets):

$$\begin{aligned}P(Q|R\text{'s}; 0\leq T_2<\pi)\\ &=C\exp[4\pi^{-1}N^{-1/2}R_1R_2R_{12}\sin Q\\ &\quad+2N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)R_1R_2R_3R_4\cos Q\\ &\quad-8\pi^{-2}N^{-1}R_1^2R_2^2R_{12}^2\sin^2 Q]\end{aligned} \tag{8b}$$

and from (2), after substituting $Q=F-T$:

$$\begin{aligned}P(F|R\text{'s}; 0\leq T<\pi)\\ &=C\exp[4\pi^{-1}N^{-1}(R_{34}^2+R_{35}^2+R_{45}^2-2)\\ &\quad\times R_{12}R_3R_4R_5\sin F],\end{aligned} \tag{8c}$$

which is applicable to $3Y^2$ quintet phases ($\mathbf{l}$ and $\mathbf{m}$ arbitrary).

4(*b*) *Quartets*

After restricting a quartet phase to the range 0 to π we obtain from (1*b*) (for six triplet phases):

$$\begin{aligned}P(T_2|R\text{'s}; 0\leq Q<\pi)\\ &=C\exp[2N^{-1/2}R_3R_4R_{12}\cos T_2\\ &\quad+4\pi^{-1}N^{-1/2}R_1R_2R_{12}\sin T_2\\ &\quad-8\pi^{-2}N^{-1}R_1^2R_2^2R_{12}^2\sin^2 T_2];\end{aligned} \tag{9a}$$

from (6) (for $6Y$ quartet phases):

$$\begin{aligned}P(Q_1|R\text{'s}; 0\leq Q_2<\pi)\\ &=C\exp[2N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)\\ &\quad\times R_1R_2R_3R_4\cos Q_1\\ &\quad-4\pi^{-1}N^{-1}(R_{12}^2+R_{15}^2+R_{25}^2-2)\\ &\quad\times R_1R_2R_5R_6\sin Q_1];\end{aligned} \tag{9b}$$

from (2), after substituting $T=F-Q$:

$$\begin{aligned}P(F|R\text{'s}; 0\leq Q<\pi)\\ &=C\exp[4\pi^{-1}N^{-1/2}R_1R_2R_{12}\sin F\\ &\quad-8\pi^{-2}N^{-1}R_1^2R_2^2R_{12}^2\sin^2 F],\end{aligned} \tag{9c}$$

which is applicable to $4Y$ quintet phases; and from (4), after substituting $Q_1=S-Q_2$:

$$\begin{aligned}P(S|R\text{'s}; 0\leq Q_2<\pi)\\ &=C\exp[4\pi^{-1}N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)\\ &\quad\times R_1R_2R_3R_4\sin S],\end{aligned} \tag{9d}$$

which is applicable to $4Y^2$ sextet phases.

4(*c*) *Quintets*

By integrating a quintet phase from 0 to π we obtain from (2), after substituting $Q=F-T$:

$$\begin{aligned}P(T|R\text{'s}; 0\leq F<\pi)\\ &=C\exp[2N^{-1/2}R_1R_2R_{12}\cos T\\ &\quad+4\pi^{-1}N^{-1}(R_{34}^2+R_{35}^2+R_{45}^2-2)\\ &\quad\times R_{12}R_3R_4R_5\sin T],\end{aligned} \tag{10a}$$

which is applicable to ten triple-product phases; and also from (2), after substituting $T=F-Q$:

$$\begin{aligned}P(Q|R\text{'s}; 0\leq F<\pi)\\ &=C\exp[4\pi^{-1}N^{-1/2}R_1R_2R_{12}\sin Q\\ &\quad+2N^{-1}(R_{34}^2+R_{35}^2+R_{45}^2-2)\\ &\quad\times R_{12}R_3R_4R_5\cos Q\\ &\quad-8\pi^{-2}N^{-1}R_1^2R_2^2R_{12}^2\sin^2 Q],\end{aligned} \tag{10b}$$

which is applicable to ten quartet phases.

From (7), for $M=5$ we obtain, after substituting $Q=F_2-F_1$:

$$\begin{aligned}P(F_1|R\text{'s}; 0\leq F_2<\pi)\\ &=C\exp[4\pi^{-1}N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)\\ &\quad\times R_1R_2R_3R_4\sin F_1],\end{aligned} \tag{10c}$$

which is applicable to $10Y$ quintet phases. From (3), for $M=5$ we obtain, after substituting $T=S-F$:

$$\begin{aligned}P(S|R\text{'s}; 0\leq F<\pi)\\ &=C\exp[4\pi^{-1}N^{-1/2}R_1R_2R_{12}\sin S\\ &\quad-8\pi^{-2}N^{-1}R_1^2R_2^2R_{12}^2\sin^2 S],\end{aligned} \tag{10d}$$

Table 2. *Summary of enantiomorph-dependent distributions*

Enantiomorph definer	Related invariant (ξ)	$P(\xi\|R\text{'s};\ 0\le Z\text{-tet phase} < \pi)$	Maximum number of related invariants	Equation
Triplet ($Z=3$)	$T(=Z)$	$N^{-1/2}\cos - N^{-1}\sin$	$3Y$	(8*a*)
	$Q(=Z+1)$	$N^{-1/2}\sin + N^{-1}\cos - N^{-1}\sin^2$	$3Y$	(8*b*)
	$F(=Z+2)$	$N^{-1}\sin$	$3Y^2$	(8*c*)
Quartet ($Z=4$)	$T(=Z-1)$	$N^{-1/2}\cos + N^{-1/2}\sin - N^{-1}\sin^2$	6	(9*a*)
	$Q(=Z)$	$N^{-1}\cos - N^{-1}\sin$	$6Y$	(9*b*)
	$F(=Z+1)$	$N^{-1/2}\sin - N^{-1}\sin^2$	$4Y$	(9*c*)
	$S(=Z+2)$	$N^{-1}\sin$	$4Y^2$	(9*d*)
Quintet ($Z=5$)	$T(=Z-2)$	$N^{-1/2}\cos + N^{-1}\sin$	10	(10*a*)
	$Q(=Z-1)$	$N^{-1/2}\sin + N^{-1}\cos - N^{-1}\sin^2$	10	(10*b*)
	$F(=Z)$	$N^{-1}\sin$	$10Y$	(10*c*)
	$S(=Z+1)$	$N^{-1/2}\sin - N^{-1}\sin^2$	$5Y$	(10*d*)
	$H(=Z+2)$	$N^{-1}\sin$	$5Y^2$	(10*e*)
Sextet ($Z=6$)	$Q(=Z-2)$	$N^{-1}\cos + N^{-1}\sin$	20	—
	$F(=Z-1)$	$N^{-1/2}\sin - N^{-1}\sin^2$	15	—
	$S(=Z)$	$N^{-1}\sin$	$15Y$	—
	$H(=Z+1)$	$N^{-1/2}\sin - N^{-1}\sin^2$	$6Y$	—
	$O(=Z+2)$	$N^{-1}\sin$	$6Y^2$	—

which is applicable to $5Y$ sextet phases; and from (5) for $M=5$ we obtain after substituting $Q=H-F$:

$$P(H|R\text{'s};\ 0\le F<\pi)$$
$$=C\exp[4\pi^{-1}N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)$$
$$\times R_1R_2R_3R_4\sin H], \qquad (10e)$$

which is applicable to $5Y^2$ heptet phases.

4(*d*) *Sextet and higher-order invariants*

When a sextet phase is restricted (4) will lead to an enantiomorph-dependent probability distribution for 20 different quartets. Furthermore, (3) with $M=5$ and (7), (3) and (5) with $M=6$ lead to distributions for quintets, sextets, heptets and octets, respectively. Analogous results will be obtained when higher-order invariants are used to resolve the enantiomorph ambiguity. In general, when a Z-tet phase is restricted ($Z>6$), (3), (5) and (7) will lead to enantiomorph-dependent probability distributions for $(Z-2)$-, $(Z-1)$-, Z-, $(Z+1)$- and $(Z+2)$-tet phases. All formulae can easily be obtained from (1) to (7) and Appendix II, and will not be given here.

5. Discussion

From the results in § 4, summarized in Table 2, it follows that the choice of an enantiomorph by restricting a Z-tet phase ($Z\ge3$) to the range 0 to π (π to 2π) leads to enantiomorph-dependent probability distributions for $(Z-2)$-, $(Z-1)$-, Z-, $(Z+1)$- and $(Z+2)$-tet phases.* The formulae are applicable to about Y^0, Y^0, Y^1, Y^1 and Y^2 related invariant phases, respectively, where Y is the number of structure factors from which the invariants are constructed.

All enantiomorph-dependent distributions can be written as

$$P(\xi_1|R\text{'s};\ 0\le\xi_2<\pi)$$
$$=C\exp[a\cos\xi_1+b\sin\xi_1+c\sin^2\xi_1], \qquad (11)$$

where ξ_1 and ξ_2 correspond to the phases of two related invariants, C is a suitable normalizing constant and a, b and c are known parameters depending on the R's and on N. Both a and b can be of order $N^{-1/2}$ or N^{-1}, while $c=-\frac{1}{2}b^2$ if b is of order $N^{-1/2}$ or $c=0$ if b is of order N^{-1}. In the latter case (11) can be written as a Von Mises distribution:

$$P(\xi_1|R\text{'s};\ 0\le\xi_2<\pi)=C\exp[Q\cos(\xi_1-q)], \qquad (12)$$

where $Q\cos q=a$ and $Q\sin q=b$.

From § 4 it follows that such a unimodal symmetric distribution is obtained for all $(Z-2)$-, Z- and $(Z+2)$-tet phases. The mode of (12) can be anywhere between 0 and 2π, depending on the values of a and b. If $a\ge0$ and $b\ge0$ (not $a=b=0$) then $0\le q\le\frac{1}{2}\pi$; if $a\le0$ and $b\ge0$ then $\frac{1}{2}\pi\le q\le\pi$ *etc.* In (8*a*) a is always positive, while the sign of b depends on R_{13} and R_{23}. Consequently, the mode of (8*a*) can only be found between $-\frac{1}{2}\pi$ and $+\frac{1}{2}\pi$ as has already been mentioned (Pontenagel, 1984). Equation (8*c*) is an example of a distribution with a mode either on $-\frac{1}{2}\pi$ or on $+\frac{1}{2}\pi$, while (9*b*) *can have its mode anywhere between* 0 *and* 2π. The latter result is obtained by restricting a quartet phase $\varphi_{-\mathbf{l},\mathbf{h}+\mathbf{k}+\mathbf{l},\mathbf{m}}$ to the range 0 to π, while now both a and b can be positive or negative, depending on the cross-term amplitudes of the double-related quartets $I_{\mathbf{h},\mathbf{k},\mathbf{l}}$ and $I_{\mathbf{h},\mathbf{k},\mathbf{m}}$.

For $(Z-1)$- and $(Z+1)$-tet phases, the enantiomorph-dependent sine term in (11) is of order $N^{-1/2}$ and the parameter c equals $-\frac{1}{2}b^2$. Consequently, (11) cannot be written as a Von Mises distribution if an

* However, note that origin-invariant phases of order less than three are identical to 0 if the relatively small effects of anomalous dispersion are neglected.

accuracy up to and including terms of order N^{-1} is required, which makes it somewhat more intricate to obtain the mode.

A second point of interest is the relationship between (8*a*) and (8*b*). By comparing these two distributions it appears that the conditions for which they are valid are identical (the same amplitudes are given and in both cases a triple product is used as an enantiomorph definer). Therefore, it is anticipated that the amount of information to be gained from the two distributions must be the same, although the actual form in which it is presented differs considerably: (8*a*) describes individual triple-product phases, while (8*b*) concerns sums of two single-related triple-product phases. It will depend on the chosen strategy to process the estimated invariants which of the distributions is to be preferred.

In the third place, we want to draw attention to the difficulties encountered in the definitions of neighbourhoods and/or phasing shells of invariants, after an enantiomorph has been chosen. In the previous paper (Pontenagel, 1984) this subject was discussed but the conclusion that our enantiomorph-dependent approach must lead to a reconsideration of the neighbourhood/phasing shell concept is generally applicable. As an example, it can be seen in (8*c*) that the first neighbourhood of the quintet $I_{\mathbf{h,k,l,m}}$ is only partly present in the main term of the probability distribution of $\varphi_{\mathbf{h,k,l,m}}$ ($R_{\mathbf{l}}$ and R_2 do not appear in the N^{-1} order term). From this it is concluded that, once $\varphi_{\mathbf{h,k}}$ is restricted to the range 0 to π, all double-related quintet phases $\varphi_{\mathbf{h,k,l,m}}$ will be distributed according to (8*c*), irrespective of the actual values of $|E_{\mathbf{h}}|$ and $|E_{\mathbf{k}}|$. Similar conclusions can be drawn on all enantiomorph-sensitive distributions.

6. Conclusions

From § 4 it follows that the choice of an enantiomorph by restricting a Z-tet phase to the range 0 to π leads to a number of enantiomorph-dependent phase relations. Although this number is approximately independent of the chosen enantiomorph definer, the number of reliable phase indications may differ considerably when different invariants are restricted. This indicates that new procedures have to be developed to determine the 'best' enantiomorph definer for a particular problem. In favourable cases one could obtain many reliable phase indications *anywhere between* 0 *and* 2π, thus breaking the systematics of the all-zero or π estimates inherent to the use of enantiomorph-independent distributions. As the introduction of false symmetry is avoided as much as possible by using such a novel strategy, a subsequent determination of structure-factor phases is not expected to run off the track as easily as may happen when more conventional direct methods are applied.

APPENDIX I

A simplified procedure to calculate the conditional joint probability distribution of the phases of two related invariants

A distribution $P(\xi_1, \xi_2|R\text{'s})$ of the phases of two invariants I_1 and I_2, given the amplitudes of a number of structure factors, can easily be determined if the following considerations are assumed to be valid:

(1) If the origin of the crystal structure has not yet been specified, only origin-invariant phase combinations appear in the distribution functions.

(2) If the enantiomorph ambiguity has not yet been resolved, all distributions $P(\xi_1, \xi_2|R\text{'s})$ should be even functions with respect to ξ_1 and ξ_2, *i.e.* $P(\xi_1, \xi_2|R\text{'s})$ should be invariant with respect to a simultaneous change of sign of the two variables. Therefore, we assume that only cosines of origin-invariant phase combinations can be present.

(3) Assuming that all triple-product terms are of order $N^{-1/2}$, while quartet phases will only appear in the N^{-1} order terms, only triplet and quartet phase combinations are of interest for $P(\xi_1, \xi_2|R\text{'s})$ to be correct up to and including terms of order N^{-1}.

(4) Up to and including terms of order N^{-1}, the conditional probability distribution of a triple-produce phase $\varphi_{\mathbf{h,k}}$ is given by the Cochran distribution

$$P(\xi_{\mathbf{h,k}}|R\text{'s}) = C \exp[2N^{-1/2}R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{h+k}}\cos\xi_{\mathbf{h,k}}], \quad (\mathrm{I.1})$$

no matter which or how many extra amplitudes are given. This statement is based on the knowledge that the second neighbourhood and/or the second phasing shell of $\varphi_{\mathbf{h,k}}$ only affects the $N^{-3/2}$ order terms of the probability distribution of $\varphi_{\mathbf{h,k}}$.

(5) Likewise, the conditional probability distribution of $\varphi_{\mathbf{h,k,l}}$, correct up to and including terms of order N^{-1}, is given by

$$\begin{aligned} P(\xi_{\mathbf{h,k,l}}|R\text{'s}) &= C \exp[2N^{-1}(R^2_{\mathbf{h+k}} + R^2_{\mathbf{h+l}} + R^2_{\mathbf{k+l}} - 2) \\ &\quad \times R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{l}}R_{\mathbf{h+k+l}}\cos\xi_{\mathbf{h,k,l}}] \quad (\mathrm{I.2}) \end{aligned}$$

irrespective of the extra amplitudes that are supposed to be given apart from the first and second neighbourhoods of $\varphi_{\mathbf{h,k,l}}$.

Considerations 1 to 5 are sufficient to obtain the conditional joint probability distribution of two arbitrary invariant phases φ_1 and φ_2 given an arbitrary set of structure-factor amplitudes. The desired distributions can always be written as

$$\begin{aligned} P(\xi_1, \xi_2|R\text{'s}) = C \exp[&A_1\cos\xi_1 + A_2\cos\xi_2 \\ &+ A_3\cos(\xi_1+\xi_2) + A_4\cos(\xi_1-\xi_2)] \end{aligned} \quad (\mathrm{I.3})$$

if only terms up to and including order N^{-1} are considered. After specifying the nature of ξ_1 and ξ_2, the order of the parameters $A_i (i=1,2,3,4)$ can be determined. For example, if φ_1 and φ_2 are two single-related quartet phases $\varphi_{\mathbf{h,k,l}}$ and $\varphi_{\mathbf{h+k+l,m,n}}$ the parameters A_1 and A_2 will both be of order N^{-1}, while A_3 and A_4 can be put equal to zero as $(\varphi_1+\varphi_2)$ and $(\varphi_1-\varphi_2)$ lead to a sextet and an octet phase combination, respectively. The exact form of A_1 and A_2 depends on the given set of structure-factor amplitudes and can be determined by comparing the two marginal distributions $P(\xi_1|R\text{'s})$ and $P(\xi_2|R\text{'s})$ obtained from (I.3) with the quartet distribution (I.2). For example, if the given set of amplitudes is supposed to consist of $|E_{\mathbf{h}}|$, $|E_{\mathbf{k}}|$, $|E_{\mathbf{l}}|$, $|E_{\mathbf{h+k+l}}|$, $|E_{\mathbf{m}}|$, $|E_{\mathbf{n}}|$, $|E_{\mathbf{h+k+l+m+n}}|$, $|E_{\mathbf{h+k}}|$, $|E_{\mathbf{h+l}}|$, $|E_{\mathbf{k+l}}|$, $|E_{\mathbf{h+k+l+m}}|$, $|E_{\mathbf{h+k+l+n}}|$ and $|E_{\mathbf{m+n}}|$ (case 4 of the main text) we obtain from (I.2):

$$\begin{aligned} P(\xi_1|R_1, R_2, R_3, R_4, R_5, R_6,& \\ R_7, R_{12}, R_{13}, R_{23}, R_{45}, R_{46}, R_{56})& \\ = C \exp[2N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)& \\ \times R_1R_2R_3R_4 \cos\xi_1]& \qquad (\text{I.4}) \end{aligned}$$

and

$$\begin{aligned} P(\xi_2|R\text{'s}) = C \exp[2N^{-1}(R_{45}^2+R_{46}^2+R_{56}^2-2)& \\ \times R_4R_5R_6R_7 \cos\xi_2].& \qquad (\text{I.5}) \end{aligned}$$

The two marginal distributions can also be obtained from $P(\xi_1, \xi_2|R\text{'s})$ by integrating with respect to ξ_1 or ξ_2 from 0 to 2π, after expanding $P(\xi_1, \xi_2|R\text{'s})$ in a power series.

The results are (in exponential form)

$$P(\xi_1|R\text{'s}) = C \exp[A_1 \cos\xi_1] \qquad (\text{I.6})$$

and

$$P(\xi_2|R\text{'s}) = C \exp[A_2 \cos\xi_2]. \qquad (\text{I.7})$$

Therefore, we conclude that

$$\begin{aligned} P(\xi_1, \xi_2|R\text{'s}) = C \exp[2N^{-1}(R_{12}^2+R_{13}^2+R_{23}^2-2)& \\ \times R_1R_2R_3R_4 \cos\xi_1& \\ +2N^{-1}(R_{45}^2+R_{46}^2+R_{56}^2-2)& \\ \times R_4R_5R_6R_7 \cos\xi_2].& \qquad (\text{I.8}) \end{aligned}$$

In the same way, all distributions 1–7 of the main text can be obtained.

APPENDIX II
Derivation of the enantiomorph-dependent distribution functions

All distributions of two invariant phases of the main text can be written as

$$\begin{aligned} P(\xi_1, \xi_2|R\text{'s}) = C \exp[x\cos\xi_1 + y\cos\xi_2& \\ + z\cos(\xi_1+\xi_2)],& \qquad (\text{II.1}) \end{aligned}$$

where x, y and z are at least of order $N^{-1/2}$.

By expanding the terms containing ξ_2 in a power series we obtain up to and including terms of order N^{-1}:

$$\begin{aligned} P(\xi_1, \xi_2|R\text{'s}) = C \exp[x\cos\xi_1]& \\ \times[1 + y\cos\xi_2 + z\cos(\xi_1+\xi_2)& \\ +\tfrac{1}{2}y^2\cos^2\xi_2 + \tfrac{1}{2}z^2\cos^2(\xi_1+\xi_2)& \\ + yz\cos\xi_2\cos(\xi_1+\xi_2)].& \qquad (\text{II.2}) \end{aligned}$$

The enantiomorph-dependent distribution $P(\xi_1|R\text{'s}; 0\le\xi_2<\pi)$ is obtained by integrating (II.2) with respect to ξ_2 from 0 to π:

$$\begin{aligned} P(\xi_1|R\text{'s}; 0\le\xi_2<\pi)& \\ = C \exp[x\cos\xi_1]& \\ \times\pi[1-2\pi^{-1}z\sin\xi_1 + \tfrac{1}{2}yz\cos\xi_1],& \qquad (\text{II.3}) \end{aligned}$$

where terms of order N^{-1}, not depending on ξ_1, have been omitted.

The power series can be written in exponential form [using $1+u \simeq \exp(u-\frac{1}{2}u^2)$]:

$$\begin{aligned} P(\xi_1|R\text{'s}; 0\le\xi_2<\pi)& \\ = C \exp[(x+\tfrac{1}{2}yz)\cos\xi_1 - 2\pi^{-1}z\sin\xi_1& \\ -2\pi^{-2}z^2\sin^2\xi_1].& \qquad (\text{II.4}) \end{aligned}$$

For the other enantiomorph, which implies $\pi\le\xi_2<2\pi$, only the sign of the $2\pi^{-1}z\sin\xi_1$ term has to be changed.

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