

Concerning Phase Relationships Which are Not Structure Invariants or Seminvariants

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Abstract

Often some primitive random variables (e.g. the atomic coordinates) are non-uniformly distributed over the unit cell. Prior information about such distributions is often available but not always used in current direct-methods procedures. Examples are described according to which primitive random variables are restricted to some domains (attended domains) or, in an equivalent way, are prevented from frequenting some domains (forbidden domains). Emphasis has been put on the fact that non-uniform distributions generate phase relationships which are not structure invariants or seminvariants, but it is also anticipated that formulas for estimating phase invariants and seminvariants are deeply affected by such prior information.

Symbols and abbreviations

r_j : atomic positional vector of the j th atom.
 f_j : scattering factor of the j th atom.
 N : number of atoms in the unit cell.
 $\varphi_{\mathbf{h}}$: structure factor with vectorial index \mathbf{h} .
 $\phi_{\mathbf{h}}$: phase of $F_{\mathbf{h}}$.
 $E_{\mathbf{h}}$: normalized structure factor.
 $R_{\mathbf{h}}$: modulus of the normalized structure factor.
 M : order of the point group.
 $C_s = (\mathbf{R}_s, \mathbf{T}_s)$: symmetry operators. \mathbf{R}_s is the rotational part, \mathbf{T}_s the translational part.
 $\sigma_i = \sum_{j=1}^N f_j^i$.
 s.i.: structure invariant.
 s.s.: structure seminvariant.

1. The background

A crucial result for the solution of the phase problem in crystallography was the discovery (Hauptman & Karle, 1953) of the properties of the structure invariants (s.i.'s) and structure seminvariant (s.s.'s). A s.i. is a product of structure factors $F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h}_n}$ such that

$$\sum_{i=1}^n \mathbf{h}_i = 0. \quad (1)$$

Then the value of the phase sum

$$\Phi_n = \sum_{i=1}^n \varphi_{\mathbf{h}_i} \quad (2)$$

does not depend on the chosen origin of the unit cell and is said to be a s.i. itself.

The idea of s.s. arises from the space-group symmetry. The product $F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h}_n}$ is a s.s. if the value of (2) does not vary when the origin is restricted to the *permitted* origins. For each space group a vector \mathbf{h}_s may be seminvariantly associated with each vector \mathbf{h}_i and a seminvariant modulus ω_s may be found: thus $F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h}_n}$ is a s.s. if

$$\sum_{i=1}^n \mathbf{h}_s \equiv 0 \pmod{\omega_s} \quad (3)$$

is satisfied.

The invariance and seminvariance concepts were crucial for the development of the joint probability distribution methods (Hauptman & Karle, 1953; Klug, 1958). The importance of the methods lies in the introduction of the idea that certain combinations of phases (s.i.'s or s.s.'s) may be calculated when the related structure factors have their observed values.

More recently the representations method (Giacovazzo, 1977a, 1980) [see also Hauptman (1975, 1978) for related concepts] brought back the seminvariance to the invariance concept. It was shown that:

(a) two types of s.s.'s exist, first rank and second rank;

(b) n -phase s.s.'s of first rank may be estimated *via* suitable $(n+2)$ -phase s.i.'s; n -phase s.s.'s of second rank may be estimated *via* suitable $(n+4)$ -phase s.i.'s; and

(c) any n -phase s.i. (2) may be estimated *via* the joint probability distribution of a subset of structure factors chosen in a sequence of sets of reflexions, each contained in the succeeding one, arranged in order of their expected effectiveness (in the statistical sense) for the estimation of the s.i. Accordingly, the second representation of the s.i. (2) uses the magnitudes involved in the estimation of the $(n+2)$ -phase invariant

$$\Phi_{n+2} = \left(\sum_{i=1}^n \varphi_{\mathbf{h}_i} \right) + \varphi_{\mathbf{k}} - \varphi_{\mathbf{k}},$$

the third representation of Φ_n uses the magnitudes involved in the $(n+4)$ -phase invariant,

$$\Phi_{n+4} = \left(\sum_{i=1}^n \varphi_{h_i} \right) + \varphi_{\mathbf{k}} - \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{l}},$$

and so on, where $\mathbf{k}, \mathbf{l}, \dots$ are free vectors of the reciprocal space. In this way the information contained in all the diffraction magnitudes may be used in order to estimate single s.i. or s.s.

The invariant and seminvariant concepts have completely dominated direct-methods evolution. The unique phase relationships extensively used today in direct-methods procedures are:

(a) one-phase s.s.'s of first rank, according to \sum_1 formulas (Hauptman & Karle, 1953; Cochran & Woolfson, 1955) and to their second representation (Casarano, Giacobozzo, Calabrese, Burla, Nunzi, Polidori & Viterbo, 1984);

(b) two-phase s.s.'s of first rank estimated according to their first representation (Casarano, Giacobozzo, Polidori, Spagna & Viterbo, 1982);

(c) triplet invariants estimated according to the Cochran (1955) formula for the non-centrosymmetrical case, to the Cochran & Woolfson (1955) formula for centrosymmetrical cases, to the MDKS formula (Hauptman, 1977) and to a second representation formula (Casarano, Giacobozzo, Camalli, Spagna, Burla, Nunzi & Polidori, 1984); and

(d) quartet invariants according to Schenk (1973), Hauptman (1975), Giacobozzo (1977b).

It may be asked now if the invariance and seminvariance concepts are the only ones which may be invoked in order to obtain phase relationships. Only two cases have been found in the literature in which invariance and seminvariance conditions are not used for phase estimation. The first occurs when a correctly positioned molecular fragment is available. Then (Sim, 1959) any phase $\varphi_{\mathbf{h}}$ may be estimated from the conditional probability distribution function

$$P(\varphi_{\mathbf{h}} | R_{\mathbf{h}}, R_{\rho_{\mathbf{h}}}, \varphi_{\rho_{\mathbf{h}}}) \\ \approx [2\pi I_0(\alpha)]^{-1} \exp[\alpha \cos(\varphi_{\mathbf{h}} - \varphi_{\rho_{\mathbf{h}}})]$$

where $\alpha = 2R_{\mathbf{h}}R_{\rho_{\mathbf{h}}}/(1 - \sigma'_1/\sigma_1)$, σ'_1 is calculated by summing over the known partial structure, and $\varphi_{\rho_{\mathbf{h}}}$ is the phase of the structure factor for the partial structure.

The second case has been recently described by Giacobozzo (1988) and occurs in space groups for which the origin may freely float along some directions (e.g. $P2$, Pm , $Pmm2$, ...). If some molecular fragments have been correctly oriented but have unknown positions then phase relationships may be found which are not s.i.'s or s.s.'s. For example, in $P2$ the origin may float along the binary axis $2_{[010]}$, the seminvariance condition is $(h, k, l) \equiv 0 \pmod{2}$, $0, 2$, and Φ_n , as given by (2), may be estimated

provided that

$$\sum_{i=1}^n \mathbf{h}_i = (0 \ k \ 0).$$

Likewise in Pm the corresponding algebraic condition on Φ_n is

$$\sum_{i=1}^n \mathbf{h}_i = (h \ 0 \ l).$$

Apparently cases 1 and 2 seem to have little in common. Indeed, new phase relationships arise: (a) in the first case from constraints to some primitive random variables (some atomic positions have fixed values); and (b) in the second case, from additional degrees of freedom (the origin may freely float along one or more directions).

A better interpretation is, however, possible for the case 2: free floating of the origin has its counterpart in free constraints which may be applied to atomic coordinates of a molecular fragment. Thus a first suggestion is given: phase relationships which are not s.i.'s or s.s.'s arise when suitable constraints are applied to some primitive random variables, or, in more general terms, when some primitive random variables are non-uniformly distributed over the unit cell.

We will limit ourselves in this paper to deal with constraints on random variables which concern only forbidden domains (inaccessible to some random variables) or attended domains (one or more random variables are restricted to some domains).

The idea of forbidden or attended domains is not new in crystallography. It was first discussed in a very lucid way by Bertaut (1958). Applications of forbidden domains were made: (i) to the structure-factor statistics in order to study (Wilson, 1964; Pradhan & Nigam, 1986; Wilson, 1987) how excess average intensity in some groups of reflexions, caused by symmetry elements which do not produce absences, is compensated by diminution of the mean intensity elsewhere in the reciprocal space; and (ii) to determinantal methods (von Eller, 1962; Lajz rowicz & Lajz rowicz, 1966; Knossow, de Rango, Mauguen, Sarrazin & Tsoucaris, 1977) in order to improve phase estimates.

In both (i) and (ii) the effects are connected with the finite size of atoms and with the inaccessible space surrounding them. Attention was always focused on s.i. relationships, no matter whether they explicitly appear as $|F_{\mathbf{h}}|^2$ in intensity statistics, or as single triplets, or implicitly in Karle-Hauptman determinants.

Prior information provided by attended domains has been used in different ways:

(a) for structure-factor statistics (Wilson, 1949; Howells, Phillips & Rogers, 1950; Hauptman & Karle, 1953; Hargreaves, 1955), in order to study the

influence on intensity distributions of atoms occurring on symmetry elements;

(b) for phase estimates when a partial structure is known (Karle, 1970; Main, 1976; Prick, Beurskens & Gould, 1983; Giacovazzo, 1983; Camalli, Giacovazzo & Spagna, 1985);

(c) when well oriented but wrongly positioned fragments are available (Main, 1976; Bruins Slot & Beurskens, 1985).

While in cases (a) and (b) the nature of the attended domains is quite clear (they coincide with the set of known atomic coordinates), in the case (c) the random variables (atomic positions) may assume any value in the cell. However, if we look at the primitive random variables, that is no longer true (Giacovazzo, 1988). Indeed when the orientation of a molecular fragment is fixed, then the atomic positions \mathbf{r}_j are no longer independent random variables: once \mathbf{r}_1 has been fixed, the other atomic positions in the same fragment may be written down as

$$\mathbf{r}_j = \mathbf{r}_1 + \mathbf{u}_j \quad (4)$$

where \mathbf{u}_j are vectors fixed by prior information. Thus \mathbf{r}_1 is the only independent random variable while $\mathbf{r}_j (j \neq 1)$ are variables restricted by (4). According to Giacovazzo (1988) restrictions on \mathbf{r}_1 due to space-group symmetry give rise to phase relationships which are not s.s.'s or s.i.'s.

It is now clear that restrictions to some random variables can give rise to new phase relationships other than s.s.'s or s.i.'s. The number of possible restrictions is quite large: they may be of interest both in small-molecule and in macromolecular crystallography. We will give in §§ 2 and 3 a few examples together with a brief statistical treatment: further papers will be devoted to a more exhaustive probabilistic study of the subject.

2. Phase relationships and attended domains

Crystal structures consisting of planar (or quasi-planar) molecules are often solved with difficulty by direct methods if some kind of supplementary prior information is not used. Sometimes the molecular form of the planar fragment is known *a priori* while no information is available about orientations and positions of the layers in which the molecules are stacked. Then correct orientations may be found by orientation search programs, and the structure may be solved by translational search routines or by special methods such as those described by Main (1976), Giacovazzo (1988) and (if planes in which molecules are stacked are known) Bruins Slot & Beurskens (1985).

Sometimes the molecular form of the planar fragments is unknown but layers in which fragments are stacked are *a priori* known. Possible sources of this

information may be crystallochemical reasons, or previous direct-methods trials, or diffraction data. Excellent examples of the third case are: the polytypes 'LSeF' 140 (Nguyen-Huy Dung & Laruelle, 1980), 10M (Nguyen-Huy Dung & Laruelle, 1977a), 8M (Nguyen-Huy Dung & Laruelle, 1977b), 6O (Nguyen-Huy Dung, Dagron & Laruelle, 1975a), 4M (Nguyen-Huy Dung, Dagron & Laruelle, 1975b), 2O (Nguyen-Huy Dung, 1973); the polytypes 'Fe₂Ga₂S₅' 3R (Dogguy-Smiri & Nguyen-Huy Dung, 1982) and 2H (Cascarano, Dogguy-Smiri & Nguyen-Huy Dung, 1987); the structure KCr₅Se₈ (Nguyen-Huy Dung, Vo-van Tien, Behm & Beurskens, 1987). In all the above structures reflexions hkl and $h, k, l + 2n$ have nearly identical normalized structure factors, suggesting that a large percentage of atoms should be stacked on two parallel symmetry planes.

Let us now suppose that the planes on which atoms are stacked are known but the geometry of the plane fragments is unknown. Then special phase relationships (which are not s.i.'s or s.s.'s) will arise according to the following considerations:

(a) *Assumptions*: space group $P1$; n atoms lie on the fixed plane (P) while $q = N - n$ atoms have completely unknown positions. Then

$$F_{\mathbf{h}} = \sum_n f_j \exp(2\pi i \mathbf{h} \mathbf{r}_j) + \sum_q f_j \exp(2\pi i \mathbf{h} \mathbf{r}_j).$$

Let \mathbf{r}_0 be the positional vector of an arbitrary point of (P): then $\mathbf{r}_j = \mathbf{r}_0 + \mathbf{u}_j$, where $\mathbf{u}_j \in (P)$. Without loss of generality we can choose $\mathbf{r}_0 \perp (P)$: thus, according to our assumptions, \mathbf{r}_0 is *a priori* fixed while \mathbf{u}_j is a primitive random variable conditioned to lie on (P). Then

$$F_{\mathbf{h}} = \exp(2\pi i \mathbf{h} \mathbf{r}_0) \sum_n f_j \exp(2\pi i \mathbf{h} \mathbf{u}_j) + \sum_q \exp(2\pi i \mathbf{h} \mathbf{r}_j).$$

Averaging on primitive random variables gives

$$\langle F_{\mathbf{h}} \rangle = Q_1 \exp(2\pi i \mathbf{h} \mathbf{r}_0) \quad \text{if } \mathbf{h} \in \{A\}, \quad (5)$$

where $Q_1 = \sum_{j=1}^n f_j$;

$$\langle F_{\mathbf{h}} \rangle = 0 \quad \text{if } \mathbf{h} \notin \{A\}.$$

$\{A\}$ is the set of reciprocal vectors perpendicular to (P) (for them $\mathbf{h} \mathbf{u}_j = 0$).

The phase estimate

$$\varphi_{\mathbf{h}} \approx 2\pi \mathbf{h} \mathbf{r}_0 \quad (6)$$

provided by (5), even if remarkable from a theoretical point of view (it is not a s.i. or a s.s. phase relationship), is negligible for practical applications (the set $\{A\}$ is too small).

Let us now assume that \mathbf{h}_1 and \mathbf{h}_2 are two reciprocal vectors satisfying the following conditions:

$$\mathbf{h}_1 \notin \{A\}, \quad \mathbf{h}_2 \notin \{A\}, \quad \mathbf{h}_1 + \mathbf{h}_2 \in \{A\}.$$

Then

$$\langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \rangle = Q_2 \exp [2\pi i (\mathbf{h}_1 + \mathbf{h}_2) \mathbf{r}_0]$$

where

$$Q_2 = \sum_{j=1}^n f_j(\mathbf{h}_1) f_j(\mathbf{h}_2).$$

More generally, let

$$\begin{aligned} \mathbf{h}_1 \notin \{A\}, \quad \mathbf{h}_2 \notin \{A\}, \quad \dots, \quad \mathbf{h}_m \notin \{A\}, \\ \mathbf{h}_1 + \mathbf{h}_2 + \dots + \mathbf{h}_m \in \{A\}. \end{aligned} \quad (7)$$

Then

$$\begin{aligned} \langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h}_m} \rangle \\ = Q_m \exp [2\pi i (\mathbf{h}_1 + \mathbf{h}_2 + \dots + \mathbf{h}_m) \mathbf{r}_0] \end{aligned} \quad (8)$$

where

$$Q_m = \sum_{j=1}^n f_{j_1}(\mathbf{h}_1) f_{j_2}(\mathbf{h}_2) \dots f_{j_m}(\mathbf{h}_m). \quad (9)$$

Equation (8) suggests the phase indication

$$\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \dots + \varphi_{\mathbf{h}_m} \simeq 2\pi (\mathbf{h}_1 + \mathbf{h}_2 + \dots + \mathbf{h}_m) \mathbf{r}_0. \quad (10)$$

Unlike (6), relations (8) may be important for practical applications because a very large number of m -plets may be found satisfying (7).

(b) *Assumptions*: space group $P1$; n_i atoms lie on the plane (P_i) , for $i = 1, 2, \dots, r$; (P_i) parallel to (P_j) for $i, j = 1, 2, \dots, r$; $q = (N - \sum_{i=1}^r n_i)$ atoms have completely unknown positions. Then

$$\begin{aligned} F_{\mathbf{h}} = \sum_{i=1}^r \left[\sum_{j=1}^{n_i} f_{ji} \exp 2\pi i \mathbf{h} (\mathbf{r}_{0i} + \mathbf{u}_{ji}) \right] \\ + \sum_q f_j \exp (2\pi i \mathbf{h} \mathbf{r}_j) \end{aligned}$$

where \mathbf{r}_{0i} is the distance vector of (P_i) from the origin, $\mathbf{u}_{ji} \in (P_i)$, and f_{ji} is the scattering factor of the j th atom on the plane (P_i) .

Then

$$\langle F_{\mathbf{h}} \rangle = \sum_{i=1}^r Q_1(i) \exp (2\pi i \mathbf{h} \mathbf{r}_{0i}), \quad (11)$$

where

$$Q_1(i) = \sum_{j=1}^{n_i} f_{ji}.$$

Suppose now that relationships (7) are verified. Then

$$\begin{aligned} \langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h}_m} \rangle \\ = \sum_{i=1}^r Q_m(i) \exp [2\pi i (\mathbf{h}_1 + \mathbf{h}_2 + \dots + \mathbf{h}_m) \mathbf{r}_{0i}] \end{aligned} \quad (12)$$

where

$$Q_m(i) = \sum_{j=1}^{n_i} f_{j_1}(\mathbf{h}_1) f_{j_2}(\mathbf{h}_2) \dots f_{j_m}(\mathbf{h}_m). \quad (13)$$

(c) *Assumptions*: n atoms lie on (P) ; $(P)_s$, $s = 1, \dots, M$, are planes symmetry equivalent to (P) .

Then, for $j = 1, \dots, n$,

$$\mathbf{C}_s \mathbf{r}_j = \mathbf{C}_s (\mathbf{r}_0 + \mathbf{u}_j) = \mathbf{R}_s \mathbf{u}_j + \mathbf{C}_s \mathbf{r}_0$$

so that

$$\begin{aligned} F_{\mathbf{h}} = \sum_{s=1}^M \exp (2\pi i \mathbf{h} \mathbf{C}_s \mathbf{r}_0) \sum_{j=1}^n f_j \exp 2\pi i \mathbf{h} \mathbf{R}_s \mathbf{u}_j \\ + \sum_q f_j \sum_{s=1}^m f_j \exp (2\pi i \mathbf{h} \mathbf{C}_s \mathbf{r}_j). \end{aligned}$$

Accordingly $\langle F_{\mathbf{h}} \rangle \neq 0$ only when \mathbf{h} is perpendicular to at least one of the planes $(P)_s$ ($\{A\}$ will be the set of these reciprocal vectors); then

$$\langle F_{\mathbf{h}} \rangle = \sum'_s Q_1(s) \exp (2\pi i \mathbf{h} \mathbf{C}_s \mathbf{r}_0).$$

The prime on the summation warns the reader that the summation goes only over planes $(P)_s$ for which $\mathbf{h} \perp (P)_s$.

Suppose now that

$$\begin{aligned} \mathbf{h}_1 \notin \{A\}, \quad \mathbf{h}_2 \notin \{A\}, \quad \dots, \quad \mathbf{h}_m \notin \{A\}, \\ \mathbf{h}_1 + \mathbf{h}_2 + \dots + \mathbf{h}_m \in \{A\}. \end{aligned}$$

Then

$$\begin{aligned} \langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h}_m} \rangle \\ = Q_m \sum'_s \exp [2\pi i (\mathbf{h}_1 + \mathbf{h}_2 + \dots + \mathbf{h}_m) \mathbf{C}_s \mathbf{r}_0] \end{aligned}$$

where

$$Q_m = \sum_{j=1}^n f_j(\mathbf{h}_1) f_j(\mathbf{h}_2) \dots f_j(\mathbf{h}_m).$$

(d) As a practical application let us consider the crystal structure KCr_5Se_8 (Nguyen-Huy Dung, Vovan Tien, Behm & Beurskens, 1988), space group $B2/m$ with unique axis \mathbf{c} , $Z=2$. The reflexion intensities for homologous series hkl , $l=0, 2, 4$ were very similar: the same was true for hkl , $l=1, 3, 5$. The heavy atoms were therefore expected to be located in the mirror planes (at $z=0$ and $z=\frac{1}{2}$). In the absence of any supplementary information one half of the atoms are here assumed to lie on the mirror plane at $z=0$, and the other half on the mirror plane at $z=\frac{1}{2}$ (actually, only the K atom is out of a symmetry plane). Then, according to (11),

$$\langle F_{00l} \rangle = (8f_{\text{Se}} + 5f_{\text{Cr}} + f_{\text{K}}) + (8f_{\text{Se}} + 5f_{\text{Cr}} + f_{\text{K}})(-1)^l. \quad (14)$$

While no forecast can be made about the sign of F_{00l} with odd values of l , all F_{00l} with even l values are expected to be positive. In accordance with (14), $E_{002} = 2.416$ and $E_{004} = 2.741$ are actually positive.

Let us now assume that

$$\begin{aligned} \mathbf{h}_1 \equiv h_1 k_1 l_1 \notin \{00l\}, \quad \mathbf{h}_2 \equiv h_2 k_2 l_2 \notin \{00l\}, \\ \mathbf{h}_1 + \mathbf{h}_2 \in \{00l\}. \end{aligned} \quad (15)$$

Table 1. *BOBBY*: indices, $|E|$, true phases and calculated phases for reflexions with $|E| > 1.2$ satisfying condition $h+k+l=0$

h	k	l	$ E $	φ_t (°)	φ_c (°)	h	k	l	$ E $	φ_t (°)	φ_c (°)
5	4	9	5.24	-11	0	3	2	5	2.17	-51	0
0	6	6	4.21	0	0	5	1	6	2.07	218	180
6	1	7	3.73	76	180	0	8	8	1.97	0	0
0	7	7	3.56	90	*	2	6	8	1.89	31	0
4	3	7	3.27	206	180	4	5	9	1.87	275	180
3	5	8	3.09	200	180	6	3	9	1.47	232	180
1	7	8	2.91	197	180	1	2	3	1.46	18	0
2	3	5	2.49	173	180	7	1	8	1.45	205	180
3	4	7	2.49	127	180	2	4	6	1.33	-43	0
2	5	7	2.30	154	180	2	2	4	1.30	66	0
1	6	7	2.19	36	0	6	2	8	1.23	-76	0
3	1	4	2.18	184	180	5	3	8	1.22	215	180

* This is a restricted ($\pm\pi/2$) phase reflexion: it cannot be estimated by the present theory.

Then

$$\langle F_{h_1} F_{h_2} \rangle = 8f_{Se}(h_1)f_{Se}(h_2) + 5f_{Cr}(h_1)f_{Cr}(h_2) + f_K(h_1)f_K(h_2)[1 + (-1)^{l_1+l_2}]$$

Again no forecast may be made about the sign of $F_{h_1}F_{h_2}$ if (l_1+l_2) is odd, while all $F_{h_1}F_{h_2}$ are expected to be positive if (l_1+l_2) is even.

7968 pairs of reflexions satisfying (15) have been found among the 208 reflexions with largest values of $|E|$. A large percentage of them are positive, as expected: probabilistic considerations, here not developed, will rank them in order of calculated reliability.

Sometimes crystallochemical information suggests that some heavy atoms are certainly located on proper symmetry axes. Examples are given below in (e) and (f).

(e) *Assumptions*: $P2$ is the space group, n the number of atoms lying on binary axes. Then

$$F_h = \sum_n f_j \exp(2\pi i k y_j) \cos 2\pi(hx_j + lz_j) + \sum_q f_j \exp 2\pi i(ky_j) \cos 2\pi(hx_j + lz_j)$$

For p atoms the coordinates x_j and y_j are multiples of $\frac{1}{2}$, so that

$$\langle F_h \rangle = 0 \quad \text{if } h \notin \{A\}, \quad (16)$$

$$\langle F_h \rangle = Q_1 \quad \text{if } h \in \{A\},$$

$$\langle F_{h_1} F_{h_2} \dots F_{h_m} \rangle = Q_m \quad \text{if } (h_1 + h_2 + \dots + h_m) \in \{A\}, \quad (17)$$

where $\{A\}$ is the set of $(h0l)$ reciprocal vectors with even values of h and l .

(f) As a practical application of the method let us consider the crystal structure $\text{CaNaN}(\text{CH}_2\text{CO}_2)_3$ (*BOBBY* in code), space group $P2_13$, $Z=3$ (B. L. Barnett, unpublished). Ca, Na and N atoms must lie on ternary symmetry axes. The set $\{A\}$ is now the set

of reciprocal vectors for which $h+k+l=0$: for $h \in \{A\}$

$$\langle F_h \rangle = 3f_{Ca} + 3f_{Na} + 3f_N, \quad (18)$$

from which the estimate $\varphi_h = 0$ is obtained. In Table 1 indices, R values and true phases are shown for all reflexions $h \in \{A\}$ with $R > 1.2$, arranged in decreasing order of R (probabilistic considerations will rank them in order of phase reliability). The agreement between estimated and calculated phases is rather satisfactory, so confirming how relevant the exploited prior information may be.

3. Phase relationships and forbidden domains

Inaccessible domains may be located around symmetry elements not compatible with molecule point symmetry. A larger variety of forbidden domains may be imagined for macromolecular structures, where diffracting matter occupies a reduced percentage of the unit-cell volume.

Let $P(x, y, z)$ be the probability that an atom lies at (x, y, z) : then

$$\langle F_h \rangle = \int_0^1 \int_0^1 \int_0^1 P(x, y, z) F_h dx dy dz$$

In the absence of any prior information $P(x, y, z) = 1$. If a forbidden domain δ exists and no prior information is available about the distribution of the atoms in the allowed domain $C\delta$, then

$$P(x, y, z) = (1 - D)^{-1}$$

where D is the volume (in fractional coordinates) of δ . Thus

$$\langle F_h \rangle = (1 - D)^{-1} \int_{C\delta} F_h dx dy dz = -(1 - D)^{-1} \int_{\delta} F_h dx dy dz. \quad (19)$$

The second or the third term of (19) may be used for practical applications according to circumstances.

Some examples of forbidden domains are given below, in order to show how, from their existence, special phase relationships arise.

(a) *Assumptions*: space group $P1$, forbidden domain defined by

$$0 \leq x \leq 1, \quad y_1 \leq y \leq y_2, \quad 0 \leq z \leq 1.$$

Then $\langle F_h \rangle = 0$ always, except when $h \in \{A\}$, where $\{A\}$ is the set of $(0k0)$ reciprocal vectors. In this case

$$\langle F_{0k0} \rangle = [-\sigma_1 / (1 - D)] (1/2\pi k) \times [(\sin 2\pi k y_2 - \sin 2\pi k y_1) - i(\cos 2\pi k y_2 - \cos 2\pi k y_1)]$$

from which $\langle \varphi_{0k0} \rangle$ is easily calculated.

Assume now that

$$h_1 \notin \{A\}, \quad h_2 \notin \{A\}, \quad h_1 + h_2 \in \{A\}.$$

Then

$$\begin{aligned} \langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \rangle = & [-\sigma_2 / (1 - D)] [1/2\pi(k_1 + k_2)] \\ & \times \{ \sin 2\pi(k_1 + k_2)y_2 - \sin 2\pi(k_1 + k_2)y_1 \\ & - i[\cos 2\pi(k_1 + k_2)y_2 \\ & - \cos 2\pi(k_1 + k_2)y_1] \} \end{aligned} \quad (20)$$

where

$$\sigma_2 = \sum_{j=1}^N f_j(\mathbf{h}_1) f_j(\mathbf{h}_2).$$

From (20) $\langle (\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2}) \rangle$ is easily obtained.

Generalization of (20) to $\langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h}_m} \rangle$ is straightforward.

(b) *Assumptions*: space group Pm ; no atom lies on or near symmetry planes; inaccessible domain defined by

$$-d \leq y \leq d, \quad \frac{1}{2} - d \leq y \leq \frac{1}{2} + d;$$

no prior information is available on the distribution of the atoms in the accessible domain.

Since

$$F_{\mathbf{h}} = 2 \sum_{j=1}^{N/2} f_j \exp [2\pi i(hx_j + lz_j)] \cos 2\pi ky_j,$$

$\langle F_{\mathbf{h}} \rangle = 0$ unless h and l are equal to zero. In this case, according to (19),

$$\begin{aligned} \langle F_{0k0} \rangle = & [\sigma_1 / (0.5 - 2d)] \int_d^{\frac{1}{2}-d} \cos 2\pi ky \, dy \\ = & -\sigma_1 / (0.5 - 2d) \\ & \times (\sin 2\pi kd \cos 2\pi k/2 + \sin 2\pi kd) / 2\pi k. \end{aligned} \quad (21)$$

If k is odd, then $\langle F_{0k0} \rangle = 0$; if k is even

$$F_{0k0} = [-2\sigma_1 / (0.5 - 2d)] (\sin 2\pi kd) / 2\pi k. \quad (22)$$

Equation (22) provides reliable phase information only for low-resolution reflexions. In order to give some numerical insight, let us suppose that $d = 0.125$ (corresponding to about $d = 2.7$ and $b = 21 \text{ \AA}$): then

$$\langle F_{020} \rangle = -0.64\sigma_1, \quad \langle F_{040} \rangle = 0, \quad \langle F_{060} \rangle = -0.21\sigma_1.$$

Thus only a few reliable phase estimates are supplied by (22), and this amount of information is too small to be useful in practice.

Let us now suppose that

$$\mathbf{h}_1 \notin \{A\}, \quad \mathbf{h}_2 \notin \{A\}, \quad \mathbf{h}_1 + \mathbf{h}_2 \in \{A\},$$

where $\{A\}$ is the set of reciprocal vectors $(0k0)$ with even values of k . Then

$$\begin{aligned} F_{\mathbf{h}_1} F_{\mathbf{h}_2} = & 4 \sum_{j=1}^{N/2} f_j(\mathbf{h}_1) f_j(\mathbf{h}_2) \cos 2\pi k_1 y_j \cos 2\pi k_2 y_j \\ & + \text{mixed terms} \end{aligned}$$

from which

$$\begin{aligned} \langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \rangle = & 4 \sum_{j=1}^{N/2} f_j(\mathbf{h}_1) f_j(\mathbf{h}_2) \\ & \times \langle \frac{1}{2} \cos 2\pi(k_1 + k_2)y_j + \cos 2\pi(k_1 - k_2)y_j \rangle \\ = & [-\sigma_2 / (0.5 - 2d)] \\ & \times \{ [\sin 2\pi(k_1 + k_2)d \cos 2\pi(k_1 + k_2)/2 \\ & + \sin 2\pi(k_1 + k_2)d] [2\pi(k_1 + k_2)]^{-1} \\ & + [\sin 2\pi(k_1 - k_2)d \cos 2\pi(k_1 - k_2)/2 \\ & + \sin 2\pi(k_1 - k_2)d] [2\pi(k_1 - k_2)]^{-1} \}. \end{aligned}$$

Since both $k_1 + k_2$ and $k_1 - k_2$ are even, $\langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \rangle \neq 0$: i.e.

$$\begin{aligned} \langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \rangle = & \frac{-2\sigma_2}{0.5 - 2d} \left\{ \frac{\sin 2\pi(k_1 + k_2)d}{2\pi(k_1 + k_2)} \right. \\ & \left. + \frac{\sin 2\pi(k_1 - k_2)d}{2\pi(k_1 - k_2)} \right\}. \end{aligned} \quad (23)$$

Equation (23) is more useful than (22). Indeed, by means of (23) a very large number of pairs $(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2})$ can be estimated: the largest mean values of $E_{\mathbf{h}_1}, E_{\mathbf{h}_2}$ will be obtained for pairs of reflexions for which $(k_1 + k_2)$ or $(k_1 - k_2)$ are sufficiently small, independently of whether $E_{\mathbf{h}_1}$ or $E_{\mathbf{h}_2}$ are low- or high-resolution reflexions.

If

$$\mathbf{h}_1 \notin \{A\}, \quad \mathbf{h}_2 \notin \{A\}, \quad \mathbf{h}_3 \notin \{A\}, \quad \mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 \in \{A\},$$

then (23) may be easily generalized to

$$\begin{aligned} \langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} F_{\mathbf{h}_3} \rangle = & \frac{2\sigma_3}{0.5 - 2d} \left\{ \frac{\sin 2\pi(k_1 + k_2 + k_3)d}{2\pi(k_1 + k_2 + k_3)} \right. \\ & + \frac{\sin 2\pi(k_1 + k_2 - k_3)d}{2\pi(k_1 + k_2 - k_3)} \\ & + \frac{\sin 2\pi(k_1 - k_2 + k_3)d}{2\pi(k_1 - k_2 + k_3)} \\ & \left. + \frac{\sin 2\pi(k_1 - k_2 - k_3)d}{2\pi(k_1 - k_2 - k_3)} \right\} \end{aligned} \quad (24)$$

where

$$\sigma_3 = \sum_{j=1}^N f_j(\mathbf{h}_1) f_j(\mathbf{h}_2) f_j(\mathbf{h}_3).$$

The largest mean values $\langle E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_3} \rangle$ will be obtained (in a probabilistic sense) if $k_1 + k_2 + k_3$ or $k_1 + k_2 - k_3$ or $k_1 - k_2 + k_3$ or $k_1 - k_2 - k_3$ are small enough.

Generalization of (24) for the estimation of $\langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h}_m} \rangle$ is trivial.

(c) *Assumptions*: space group $P2_1$; four inaccessible domains δ_i , $i = 1, \dots, 4$, of cylindrical shape of radius d around symmetry axes.

Since

$$F_{\mathbf{h}} = 2 \sum_{j=1}^{N/2} f_j \exp(2\pi i k y_j) \cos 2\pi(hx_j + lz_j),$$

$\langle F_{\mathbf{h}} \rangle = 0$ if $k \neq 0$. Thus, in accordance with (19),

$$\begin{aligned} \langle F_{h0l} \rangle &= -\sigma_1 T^{-1} \sum_{i=1}^4 \int_{\delta_1} \cos 2\pi(hx + lz) dx dz \\ &= -\sigma_1 T^{-1} \sum_{m_1, m_2=0, 1/2} \cos \pi(hm_1 + lm_2) \\ &\quad \times \int_{\delta_1} \cos 2\pi(hx + lz) dx dz, \end{aligned} \quad (25)$$

where $T = (ac \sin \beta - 4\pi d^2)$.

According to (25), $\langle F_{h0l} \rangle$ vanishes unless h and l are even numbers.

Since

$$\int_0^{2\pi} \int_0^d \rho \cos(2\pi \rho s \cos \varphi) d\rho d\varphi = (d/s) J_1(2\pi s d),$$

transforming (25) into cylindrical coordinates gives

$$F_{h0l} = -4\sigma_1 T^{-1} (d/s) J_1(2\pi s d), \quad (26)$$

where h and l are even numbers, $s = 2(\sin \theta)\lambda$, and J_1 is the ordinary Bessel function of order 1.

Even if the h and l indices span a reciprocal plane, (26) is of limited usefulness in practice because reliable phase indications may be obtained only for low-resolution reflexions.

Let us now suppose that

$$\mathbf{h}_1 \notin \{A\}, \quad \mathbf{h}_2 \notin \{A\}, \quad \mathbf{h}_1 + \mathbf{h}_2 \in \{A\},$$

where $\{A\}$ is the set of reciprocal vectors $\{h0l\}$ with even values of h and l . Then

$$\begin{aligned} \langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} \rangle &= \sigma_2 \langle \cos 2\pi[(h_1 + h_2)x + (l_1 + l_2)z] \\ &\quad + \cos 2\pi[(h_1 - h_2)x + (l_1 - l_2)z] \rangle \\ &= -\sigma_2 T^{-1} 4 \left\{ \int_{\delta_1} \cos 2\pi[(h_1 + h_2)x \right. \\ &\quad \left. + (l_1 + l_2)z] dx dz \right. \\ &\quad \left. + \int_{\delta_1} \cos 2\pi[(h_1 - h_2)x + (l_1 - l_2)z] dx dz \right\} \\ &= -4\sigma_2 T^{-1} \{ (d/s_1) J_1(2\pi s_3 d) \\ &\quad + (d/s_2) J_2(2\pi s_4 d) \}, \end{aligned} \quad (27)$$

where s_3 and s_4 are $2(\sin \theta)/\lambda$ values for $(\mathbf{h}_1 + \mathbf{h}_2)$ and for $(\mathbf{h}_1 + \mathbf{h}_2 \mathbf{R}_2)$ reflexions respectively (\mathbf{R}_2 denotes the rotation matrix corresponding to the binary axis). Large values of $\langle E_{\mathbf{h}_1} E_{\mathbf{h}_2} \rangle$ may be obtained for small values of s_3 and s_4 , independently of whether $F_{\mathbf{h}_1}$ and $F_{\mathbf{h}_2}$ are low- or high-resolution reflexions. Relation (27) may thus be applied more widely than (26).

It is not difficult to verify that, if

$$\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3 \notin \{A\}, \quad \mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 \in \{A\},$$

then

$$\begin{aligned} \langle F_{\mathbf{h}_1} F_{\mathbf{h}_2} F_{\mathbf{h}_3} \rangle &= -4\sigma_3 T^{-1} \{ (d/s_4) J_1(2\pi s_4 d) \\ &\quad + (d/s_5) J_1(2\pi s_5 d) + (d/s_6) J_1(2\pi s_6 d) \\ &\quad + (d/s_7) J_1(2\pi s_7 d) \}, \end{aligned} \quad (28)$$

where s_4, s_5, s_6, s_7 are the values of $2(\sin \theta)/\lambda$ for $F_{\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3}$, $F_{\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 \mathbf{R}_2}$, $F_{\mathbf{h}_1 + \mathbf{h}_2 \mathbf{R}_2 + \mathbf{h}_3}$, $F_{\mathbf{h}_1 + \mathbf{h}_2 \mathbf{R}_2 + \mathbf{h}_3 \mathbf{R}_2}$ respectively.

The importance of (26), (27) and (28) for practical applications will depend on the ratio (volume of the forbidden domain)/(volume of cell). If d more or less represents the average atomic radius, forbidden domains around inversion centres are rather negligible: accordingly, inaccessible domains around mirror planes will influence phase estimates more than domains around proper symmetry axes.

As a practical example, we quote for CEPHA [$C_{18}H_{21}NO_3$, space group $C2$, $Z = 8$; $a = 22.834$, $b = 8.158$, $c = 19.534$ Å, $\beta = 117.7^\circ$ (Arora, Bates, Grady, Germain, Declercq & Powell, 1976)] the phase values for seminvariant reflexions for which $|h + l| \leq 4$:

$$\begin{aligned} \varphi_{200} = 180; \quad \varphi_{002} = 180; \quad \varphi_{004} = 180; \\ \varphi_{400} = 0; \quad \varphi_{202} = 180; \quad \varphi_{20\bar{2}} = 180. \end{aligned}$$

Inaccessible domains around binary axes suggest the phase value 180° for all of them.

4. Concluding remarks

It has been shown that non-uniform distributions of the primitive random variables (e.g. the atomic coordinates) over the unit cell may give rise to phase relationships which are not s.i.'s or s.s.'s. In this sense a very general and frequent case occurs in macromolecule crystallography when the molecular envelope is known: the electron probability density in the solvent region is set to a constant low value (solvent flattening), while different positivity constraints are applied to the protein region.

Attended domains sometimes coincide with symmetry elements, inaccessible domains sometimes lie around symmetry elements. In these cases combinations of phases predictable by the present method occasionally reduce to s.s.'s of first rank.

A good example is given in § 2(f): in $P2_13$ s.s.'s are reflexions \mathbf{h} for which $h + k + l \equiv 0 \pmod{2}$, and first-rank seminvariants are reflexions for which (Giacovazzo, 1980) one of the following algebraic conditions is satisfied (by \mathbf{h} or its symmetry equivalents):

- (i) $(h + k + l) \equiv 0 \pmod{0}$ because of $3_{[111]}$
- (ii) $(h, k, l) \equiv 0 \pmod{2, 2, 0}$ because of $2_{[001]}$.

Since attended domains for Na, Ca, N are ternary axes, only first-rank seminvariants of type (i) may be estimated.

If attended domains coincide with or inaccessible domains lie around the allowed origins of the space

group, then the combinations of phases which are predictable by our method occasionally coincide with the s.s.'s. For example, in $P2/m$ s.s.'s are reflexions for which $(h, k, l) \equiv 0 \pmod{(2, 2, 2)}$, and may be estimated if allowed domains coincide with or inaccessible domains lie around inversion centres.

First-rank s.s.'s are today estimated *via* conditional probability distributions, given suitable sets of diffraction magnitudes on the minimal assumption that positive random variables (*i.e.* the atomic positions) are uniformly distributed over the unit cell.

In these conditions the estimate of the s.s.'s requires the use, as prior information, of a suitable set of diffraction magnitudes. For the example given in § 2(d), the estimation of φ_{006} requires statistical calculations involving the set of magnitudes $\{R_{hk3}\}$, with h and k free indices. According to the theory of representations, the estimation of the two-phase s.s. $\varphi_{352} + \varphi_{\bar{3}\bar{5}\bar{6}}$ requires statistical calculations involving the basis and the cross magnitudes of the sets of quartets

$$\varphi_{352} + \varphi_{\bar{3}\bar{5}\bar{6}} + \varphi_{hk4} + \varphi_{\bar{h}\bar{k}4},$$

$$\varphi_{352} + \varphi_{\bar{3}\bar{5}\bar{6}} + \varphi_{hk2} + \varphi_{\bar{h}\bar{k}2},$$

where again h and k are free indices.

By contrast, if prior information about attended domains is exploited, the estimation of φ_{006} and of $\varphi_{352} + \varphi_{\bar{3}\bar{5}\bar{6}}$ may be obtained *via* R_{006} and $R_{352}R_{\bar{3}\bar{5}\bar{6}}$ respectively (even if improved estimates could be attained if supplementary diffraction magnitudes are used).

Since any s.s. can be estimated *via* suitable sets of s.i.'s, a further question arises: are the s.i.'s affected by the presence of attended domains? The answer is probably positive: the effectiveness of the new formulas will depend on the types of attended or inaccessible domains, and, in general, on the distribution of primitive random variables over the unit cell. Further contributions, however, are needed for the study of such probabilistic aspects.

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