A Linear Equation for Products of Normalized Structure Factors.
I. Fourier Formalism

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Abstract

A new relationship between products of two structure factors with coefficients calculated as the Fourier transform of a modified Patterson function is presented. The relation is alternatively expressed in terms of triple phase invariants and also a new weighted form of Sayre's equation [Sayre (1952). *Acta Cryst.* **5**, 60–65] emerges as a special case. The advantages of the new equations with respect to Sayre's equation are discussed and, with simple one-dimensional models, examples of direct calculation of the cosines of triple-phase invariants are included.

Introduction

Several formulae for estimating the cosines of triple phase invariants have been derived in the past, some on the basis of probability theory and others algebraically, but none is completely reliable. In an attempt to improve such estimates, the present work introduces a new equation which, in its basic form, is homogeneous in products of two E's with phase-independent coefficients which are calculated from the Patterson function. This equation gives rise to a system of linear equations for the cosines of triple phase invariants and it is shown by solving for the cosines in some simple examples that the rank of the system is greater than the rank of the corresponding system of Sayre equations.

A new phase relationship

The normalized structure factor $E(\mathbf{h})$ for the reciprocal vector $\mathbf{h}$ is defined in the usual way:

$$E(\mathbf{h}) = \left(\sum_{\mu=1}^{N} z_\mu^2 \right)^{-1/2} \sum_{\mu=1}^{N} z_\mu \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_\mu), \qquad (1)$$

where $\mathbf{r}_\mu$ is the position vector of the μth atom, z_μ is its atomic number and N is the number of atoms in the unit cell. The product of two E's with reciprocal vectors

$\mathbf{h}_1 + \mathbf{H}$ and $\mathbf{h}_2 - \mathbf{H}$ is

$$E(\mathbf{h}_1 + \mathbf{H})\, E(\mathbf{h}_2 - \mathbf{H}) = \left(\sum_{\mu=1}^{N} z_\mu^2 \right)^{-1} \sum_{\mu,\nu=1}^{N} z_\mu z_\nu$$

$$\times \exp[2\pi i(\mathbf{h}_1 \cdot \mathbf{r}_\mu + \mathbf{h}_2 \cdot \mathbf{r}_\nu)]$$

$$\times \exp[2\pi i \mathbf{H} \cdot (\mathbf{r}_\mu - \mathbf{r}_\nu)]. \qquad (2)$$

Let us assume that there exists a set of coefficients $X(\mathbf{H})$ such that

$$\sum_{\mathbf{H}} X(\mathbf{H}) \exp[2\pi i \mathbf{H} \cdot (\mathbf{r}_\mu - \mathbf{r}_\nu)] = \lambda, \qquad (3)$$

for $\mu, \nu = 1, 2, \ldots, N$, where λ is a constant. That is, the sum in (3) is a constant for all interatomic vectors but no other special constraints are imposed. Then, multiplying both sides of (2) by $X(\mathbf{H})$ and summing over $\mathbf{H}$, it follows that

$$\sum_{\mathbf{H}} X(\mathbf{H})\, E(\mathbf{h}_1 + \mathbf{H})\, E(\mathbf{h}_2 - \mathbf{H}) = \lambda E(\mathbf{h}_1)\, E(\mathbf{h}_2). \qquad (4)$$

This is the main equation of the present work and obviously its usefulness depends upon whether it is possible in practice to obtain a proper set of coefficients $X(\mathbf{H})$. The method for calculating the $X(\mathbf{H})$ suggested by (3) is to modify the Patterson function so that its values at all interatomic vectors are equalized, the $X(\mathbf{H})$ then being obtained as the Fourier coefficients of the modified Patterson.

For equal-atom structures with no superposition of interatomic vectors, it is only necessary to modify the Patterson at the origin. Karle & Hauptman (1957) obtained for this case an equation similar to (4) but with a term $E(\mathbf{h}_1 + \mathbf{h}_2)$ added to the left-hand side. In terms of the present, more general, algebra, the equation of Karle & Hauptman corresponds to having $X(\mathbf{H}) = |E(\mathbf{H})|^2 - 1$ and the extra term compensates for the fact that the summation for $\mu = \nu$ in (3) is then zero. Alternatively, putting $X(\mathbf{H}) = |E(\mathbf{H})|^2 - 1 + 1/N$ brings the Patterson at the origin to single-peak height and satisfies both (3) and (4). This suggests a general alternative way for calculating the $X(\mathbf{H})$: by subtract-

ing from $|E(\mathbf{H})|^2$ the transform of all multiple peaks to bring them to single-peak level.

As shown above, for (4) to be true, it is necessary that the $X(\mathbf{H})$ satisfy (3); but this is not sufficient to ensure that (4) provides useful relationships between E's. For instance, if the Patterson map is modified to give a constant level everywhere, then (4) becomes trivial $[X(\mathbf{0}) = \lambda, \; X(\mathbf{H}) = 0 \text{ for } \mathbf{H} \neq \mathbf{0}]$ because all structural information is lost. It would seem desirable that the $X(\mathbf{H})$, as well as satisfying (3), carry as much as possible of the structural information in the Patterson function for points which are not interatomic vectors.

As $\mathbf{h}_1$ and $\mathbf{h}_2$ range over some set of reciprocal vectors, (4) gives rise to a set of linear equations with $\exp[i(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2})]$ as unknowns, the phases $\varphi_{\mathbf{h}}$ being defined by $E(\mathbf{h}) = |E(\mathbf{h})| \exp(i\varphi_{\mathbf{h}})$. The coefficients of these equations are functions only of the $|E|$'s and, accordingly, if a system of such equations had a unique solution, we should expect the solution to be origin and enantiomorph independent. To recast (4) in terms of unknowns which have these properties, multiply both sides by $E(\mathbf{h}_3)$, where

$$\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = 0 \qquad (5)$$

and take the real part. Then

$$\sum_{\mathbf{H}} X(\mathbf{H})|E(\mathbf{h}_1 + \mathbf{H}) \, E(\mathbf{h}_2 - \mathbf{H}) \, E(\mathbf{h}_3)|$$

$$\times \cos(\varphi_{\mathbf{h}_1 + \mathbf{H}} + \varphi_{\mathbf{h}_2 - \mathbf{H}} + \varphi_{\mathbf{h}_3})$$

$$= \lambda|E(\mathbf{h}_1) \, E(\mathbf{h}_2) \, E(\mathbf{h}_3)| \cos(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3}). \qquad (6)$$

In an attempt to understand the significance of (6) as a possible aid to phase determination, the problems of constructing a system of such equations and finding solutions for the cosines will be considered; but, first, a formal analogy with Sayre's equation is drawn.

Analogy with the Sayre–Hughes equation

Let us assume that there are some coefficients $C(\mathbf{H})$ and a constant λ such that

$$\sum_{\mathbf{H}} C(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}_\mu) = \lambda, \qquad (7)$$

for $\mu = 1, \ldots, N$. Then, replacing $\mathbf{h}$ by $\mathbf{h} - \mathbf{H}$ in (1), multiplying by $C(\mathbf{H})$ and summing over $\mathbf{H}$, we have

$$\sum_{\mathbf{H}} C(\mathbf{H}) \, E(\mathbf{h} - \mathbf{H}) = \lambda E(\mathbf{h}). \qquad (8)$$

But if we put $C(\mathbf{H}) = E(\mathbf{H})$, (7) requires that the structure has equal atoms, and (8) becomes the Sayre–Hughes equation (Sayre, 1952; Hughes, 1953), derived in a manner analogous to the derivation of (4).

On the other hand, if in (4) we put $\mathbf{h}_1 = 0$ and $\mathbf{h}_2 = \mathbf{h}$, we get

$$\sum_{\mathbf{H}} X(\mathbf{H}) \, E(\mathbf{H}) \, E(\mathbf{h} - \mathbf{H}) = \lambda E(\mathbf{0}) \, E(\mathbf{h}), \qquad (9)$$

which is a weighted form of the Sayre–Hughes equation, valid even when the atoms are not equal, provided that the proper $X(\mathbf{H})$ can be determined.

Thus there is a formal similarity between (7) and (8) on the one hand and (3) and (4) on the other; but the requirement of equal peaks in the E map, which is the basis of the Sayre–Hughes equation, is replaced in the new equations by the requirement of equal peaks in the modified Patterson map which can, in favourable circumstances, preserve much of the structural information of the original Patterson. This suggests that the new equations, as well as being less dependent on the assumption of equal atoms, may be better related to the structural information which is contained in the Patterson function and expressed in the $X(\mathbf{H})$. Also it will be seen that because each equation of the form (4), or the alternative form (6), is identified by a pair of labels $\mathbf{h}_1$ and $\mathbf{h}_2$ while each Sayre equation only has a single label, the number of the new equations of either form which are available for a given set of reciprocal vectors is potentially greater than the number of Sayre equations.

Setting up a linear system

Equation (4), which is the main equation of this paper, might in principle be used in various ways. In what follows, a system of equations obtained from the derived form (6) is solved for the cosines of triple phase invariants for some simple, one-dimensional, model structures. Notice that in (6), instead of treating the cosines as the linearly related variables, we can substitute

$$T(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3) = |E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_3}| \cos(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3}) \qquad (10)$$

and find the T's as the solution of

$$\sum_{\mathbf{H}} X(\mathbf{H}) \, T(\mathbf{h}_1 + \mathbf{H}, \mathbf{h}_2 - \mathbf{H}, \mathbf{h}_3) = \lambda T(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3). \qquad (11)$$

The results presented in the next section were obtained by this method. It was found that solving for the T's gives marginally better values for the cosines than solving directly for the latter, which seems to be due to different least-squares weighting in the two schemes. However, the notation used in (6) is retained because it is more explicit. The fact that (11) can be solved for the T's gives an indication of the degree of structural information imparted to the equations in the $X(\mathbf{H})$ coefficients.

For the following calculations on one-dimensional structures, the reciprocal vectors in (6) become scalars and the summation over H is terminated at some limit M; (6) then becomes

$$\sum_{H=-M}^{M} X(H)|E(h_1 + H) E(h_2 - H) E(h_3)|$$

$$\times \cos(\varphi_{h_1 + H} + \varphi_{h_2 - H} + \varphi_{h_3})$$

$$= \lambda|E(h_1) E(h_2) E(h_3)| \cos(\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3}). \quad (12)$$

The right-hand side of (12) can be combined with the term for $H = 0$ on the left and, since the cosines for $H = -h_1$ and $H = h_2$ are equal to unity, the corresponding terms in the summation can be taken to the right-hand side as known. Repetition of this for all combinations h_1, h_2 consistent with the limit M produces a system of non-homogeneous linear equations for the unknown cosines. If only terms for $H \geq 0$ needed to be considered, all the E's in the system would belong to the set $\{E(j): j = -M, ..., M\}$ and there would be, at least formally, more equations than unknowns. Unfortunately, the terms for $H < 0$ must be included because the $X(H)$ are assumed to be the Fourier coefficients of a modified Patterson function. This generates too many unknowns for direct solution to be possible and, in general, approximations are required. It should be noted that the generation of additional unknowns by the necessary inclusion of negative indices in the summation also applies to Sayre's equation.

There is a very particular situation in which it is possible to close the system of equations given by (12) (i.e. not to have more unknowns than equations) while keeping the equations exact; and this is when all the fractional atomic coordinates are multiples of $1/2M$ so that the E's are periodic with period $2M$. Under the same circumstances, Sayre's equation also is finite and exact; that is

$$\sum_{H=-M}^{M} |E(H) E(h - H) E(-h)| \cos(\varphi_H + \varphi_{h-H} + \varphi_{-h})$$

$$= \lambda|E(h)|^2, \quad (13)$$

for $h = 1, ..., M$. But this system of M Sayre's equations is not sufficient to solve for the cosines.

In the following examples, we first consider a structure whose fractional atomic coordinates are multiples of $1/2M$ and solve for the cosines of all the triple phase invariants with non-zero moduli. Clearly, this cannot provide a practical means of phase calculation, firstly because the E's are not periodic in general and, secondly, because there would be too many unknowns for any structure not trivially small: but the calculations are intended to give a better understanding of the new equations. We then consider a one-dimensional structure without the above-mentioned restrictions on its atomic positions. In that

case, estimation of a number of cosine invariants is rendered feasible on the basis of two different approximations for the remaining unknowns. In the first approximation, some terms are simply omitted from the equations; and in the second some cosines are replaced by their expectation values derived from the Cochran (1955) distribution.

Examples

A computer program for small one-dimensional structures calculates the $X(H)$ to be used in (12) as the Fourier coefficients of a modified Patterson function whose multiple peaks have been reduced approximately to the height, λ, of a single peak. The program then sets up the system of equations according to the various conditions indicated in the last section and computes the unknown cosines as the least-squares solution for the overdetermined system. Results are presented for two structures, each with five equal atoms. In the first example, the fractional atomic coordinates are multiples of $1/2M$ so that the equations are complete and exact; but this restriction is removed in the second example.

Example 1. Fractional atomic coordinates 0·10, 0·25, 0·40, 0·55, 0·70 and $M = 10$. This structure is centrosymmetric and its Patterson function is adequately represented with only 20 intervals because of the exact multiple superposition of interatomic intervals. The complete system of equations contains only 15 unknowns because $E(4) = E(8) = E(12) = E(16) = 0$. An exact solution was obtained as shown in Table 1. Values for $|\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3}|$ obtained from the calculated

Table 1. *Calculated and true absolute values for the 15 triple phase invariants of example* 1

This is effectively the complete set of invariants because all the rest have zero modulus.

Indices of invariant				$\|\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3}\|$	
h_1	h_2	h_3	$\|E_{h_1} E_{h_2} E_{h_3}\|$	True	Calculated
−2	1	1	0·268	180	180
−3	1	2	0·123	180	180
−6	1	5	0·451	180	180
−7	1	6	2·038	0	0
−10	1	9	0·111	180	180
−5	2	3	0·079	0	0
−7	2	5	0·500	0	0
−9	2	7	0·397	0	0
−11	2	9	0·070	180	180
−6	3	3	0·148	0	0
−9	3	6	0·164	180	180
−10	3	7	0·289	0	0
−10	5	5	0·089	0	0
−11	5	6	0·230	0	0
−13	6	7	5·914	0	0

cosines are compared with the true values obtained directly from the atomic coordinates with (1).

Example 2. Fractional atomic coordinates 0·000, 0·171, 0·324, 0·449, 0·673 and $M = 15$. These coordinates deviate from multiples of $1/2M$ by amounts of up to half an interval. The Patterson function for this more realistic model is not properly resolved. It is not possible to find $X(H)$ which satisfy (3) exactly and therefore all the equations are only approximate. An additional problem is that the complete system involves more unknowns than equations (for reasons explained in the last section) and some of the unknowns have to be given values before

solution for the rest is possible. Table 2 gives the solution for the largest 40 invariants after simply omitting all triplets which involve an index h with $|h| > 15$. Table 3 gives the corresponding solution when the cosines involving an index h with $15 < |h| \le 30$ are given their expectation values derived from the Cochran distribution (Karle & Karle, 1966; Germain, Main & Woolfson, 1970).

After eliminating the triplets which involve an index with $|h| > 15$, the total remaining number of unknown triplets is 56, and the solution for this system has a large overall error while the errors for the largest invariants are much smaller. As the number of unknowns is reduced by removing invariants with the smallest moduli, the overall error decreases while the smaller errors for the largest invariants remain fairly

Table 2. *Calculated and true absolute values for the 40 triple phase invariants corresponding to the largest 40 values for $|E_{h_1} E_{h_2} E_{h_3}|$ in example 2*

All triplets involving an index h with $|h| > 15$ have simply been omitted from the calculation.

Table 3. *Results corresponding to those of Table 2 when the triplets involving an index h with $15 < |h| \le 30$ are estimated according to the Cochran distribution*

Indices of invariant				$|\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3}|$		Indices of invariant				$|\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3}|$	
h_1	h_2	h_3	$|E_{h_1} E_{h_2} E_{h_3}|$	True	Calculated	h_1	h_2	h_3	$|E_{h_1} E_{h_2} E_{h_3}|$	True	Calculated
−4	1	3	0·330	144	180	−4	1	3	0·330	144	180
−6	1	5	0·155	169	84	−6	1	5	0·155	169	0
−7	1	6	0·980	46	41	−7	1	6	0·980	46	26
−8	1	7	0·567	16	16	−8	1	7	0·567	16	21
−9	1	8	0·671	78	94	−9	1	8	0·671	78	83
−10	1	9	0·301	146	180	−10	1	9	0·301	146	180
−12	1	11	0·422	49	180	−12	1	11	0·422	49	98
−13	1	12	0·639	120	89	−13	1	12	0·639	120	103
−14	1	13	0·569	25	72	−14	1	13	0·569	25	44
−15	1	14	0·640	69	82	−15	1	14	0·640	69	82
−6	2	4	0·169	2	0	−6	2	4	0·169	2	0
−8	2	6	0·192	115	0	−8	2	6	0·192	115	0
−9	2	7	0·164	122	180	−9	2	7	0·164	122	97
−14	2	12	0·191	49	180	−14	2	12	0·191	49	66
−6	3	3	0·802	66	0	−6	3	3	0·802	66	0
−7	3	4	0·618	104	144	−7	3	4	0·618	104	139
−9	3	6	1·435	15	0	−9	3	6	1·435	15	0
−10	3	7	0·315	177	180	−10	3	7	0·315	177	180
−11	3	8	0·376	119	180	−11	3	8	0·376	119	180
−12	3	9	1·153	8	25	−12	3	9	1·153	8	0
−13	3	10	0·256	86	180	−13	3	10	0·256	86	180
−14	3	11	0·465	153	180	−14	3	11	0·465	153	146
−15	3	12	0·890	89	69	−15	3	12	0·890	89	27
−8	4	4	0·659	23	46	−8	4	4	0·659	23	33
−9	4	5	0·175	32	0	−9	4	5	0·175	32	32
−10	4	6	0·581	12	128	−10	4	6	0·581	12	73
−11	4	7	0·501	9	96	−11	4	7	0·501	9	84
−12	4	8	1·040	74	57	−12	4	8	1·040	74	66
−13	4	9	0·898	89	83	−13	4	9	0·898	89	89
−14	4	10	0·416	33	0	−14	4	10	0·416	33	47
−15	4	11	0·458	78	87	−15	4	11	0·458	78	98
−11	5	6	0·155	77	180	−11	5	6	0·155	77	180
−12	5	7	0·233	80	157	−12	5	7	0·233	80	72
−14	5	9	0·246	91	180	−14	5	9	0·246	91	129
−12	6	6	3·525	43	21	−12	6	6	3·525	43	0
−13	6	7	1·490	31	0	−13	6	7	1·490	31	0
−14	6	8	1·819	22	0	−14	6	8	1·819	22	0
−15	6	9	1·983	31	0	−15	6	9	1·983	31	0
−14	7	7	1·314	40	28	−14	7	7	1·314	40	44
−15	7	8	0·970	93	77	−15	7	8	0·970	93	63

constant. This is shown in Figs. 1 and 2 respectively for the two different methods of approximating invariants involving $|h| > 15$. The ordinate, D, in these figures is the root-mean-square difference (r.m.s.d.) in degrees between the true values for $|\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3}|$ and the values obtained from the calculated cosines; the abscissa, R, is the number of unknowns of smallest modulus which have been removed from the system. In each figure, the upper plot is the overall r.m.s.d. and the lower plot is the r.m.s.d. for the ten invariants with the largest moduli. The results given in Tables 2 and 3 correspond to the points $R = 16$ in the figures.

Note that for both examples the number of cosines calculated is greater than the maximum number, M, of Sayre equations available for the same complete set of indices.
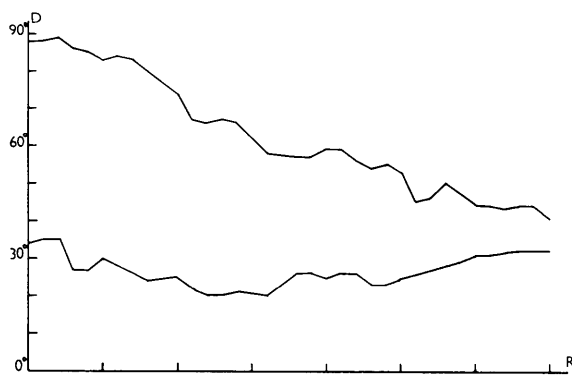

Fig. 1. Errors for example 2 when all invariants involving an index h with $|h| > 15$ are omitted from the system which then has a total of 56 unknowns. D is the root-mean-square difference in degrees between the calculated and true absolute values of triple phase invariants and R is the number of unknown invariants successively removed in order of increasing modulus. The upper plot is the r.m.s.d. for the $(56-R)$ calculated triple phase angles; the lower plot is the r.m.s.d. for the ten with largest moduli.
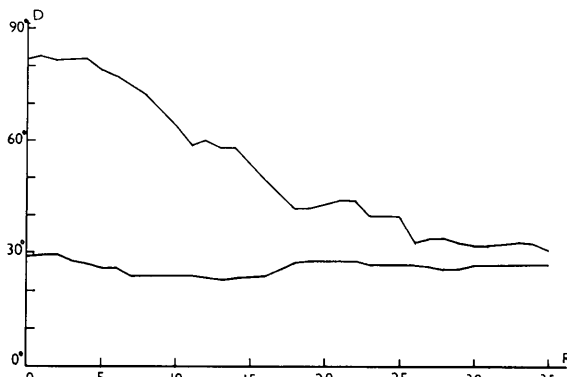

Fig. 2. Errors for example 2 when invariants involving an index h with $15 < |h| \le 30$ are estimated according to the Cochran distribution. Otherwise as for Fig. 1.

Conclusion

The new relationship between products of E's, which is derived from a Patterson function modified so that its values at interatomic vectors are made as nearly equal as possible, is expressed in somewhat different forms in (4), (6) and (9). It is clear that, at least formally, the relationship provides a greater number of equations for a given number of triple products than the equivalent system of Sayre's equations and the calculations reported in this paper verify that in idealized circumstances the new equation determines the cosines of a number of triple phase invariants which is greater than the number of Sayre's equations. The calculations also show that the new equations produce reasonable phases for the invariants with large moduli even when overall errors are large and when many of the unknowns have been eliminated on the basis of approximations of arguable validity. It should also be noted that for example 2 the values of the modified Patterson function at interatomic vectors, which are supposed to be equal in order to satisfy (3), had a relative standard deviation of about 20%. This suggests that the equations are not critically sensitive to errors in the $X(H)$ coefficients.

Clearly it is impractical to think of solving a system of equations for the large number of cosine invariants associated with a real structure having more than just a few atoms but the principle that the new relationship provides a greater overdetermination of phases than Sayre's equation would seem to be important. This idea would, of course, have its ultimate test in the solution of real structures. Work towards this is in progress.

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