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A Linear Equation for Products of Normalized Structure Factors. II. Tensor Formalism

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Abstract

New, finite and exact relationships between products of two normalized structure factors, with coefficients which are a function of the squared moduli of structure factors, are presented. The equations allow new linear relationships between the cosine and sine of triple-phase invariants to be set up. The meaning of the new equations is discussed in connexion with the direct calculation of cosines of triple-phase invariants and the results show, for simple one-dimensional model structures, that it is possible to obtain exact solutions.

Introduction

This paper is closely related to two previous ones (Navaza & Silva, 1979; Silva, Tate & Woolfson, 1981), which will be hereafter referred to as papers *A* and *B* respectively. In paper *A*, by means of vector algebra, various relationships between *E*'s were derived, some of them finite and exact. Paper *B* deals with a new equation involving products of *E*'s which leads to a linear relation between the cosines of triple-phase invariants. One of the results of the present paper is concerned with an equation similar to that derived in paper *B*, but using in its derivation an extension of the algebra of paper *A*.

The main equation derived in paper *B* is

$$\sum_l X(\mathbf{H}_l)E(\mathbf{h}_1 - \mathbf{H}_l)\,E(\mathbf{h}_2 + \mathbf{H}_l) = \lambda E(\mathbf{h}_1)E(\mathbf{h}_2), \quad (1)$$

where the X's satisfy

$$\sum_l X(\mathbf{H}_l)\exp\left[2\pi i\mathbf{H}_l.(\mathbf{r}_i - \mathbf{r}_j)\right] = \lambda, \quad \text{for } i,j = 1, \ldots, N, \quad (2)$$

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$\mathbf{r}_s$ being atomic positions. Then, for (1) to be valid the summation in (2) must be a constant λ for all interatomic vectors and therefore the X's were calculated as a Fourier transform of a modified Patterson function where all interatomic peaks were brought to a constant level λ.

On the other hand, if in (1) $\mathbf{h}_2 = -\mathbf{H}_m$ and $\mathbf{h}_1 = \mathbf{H}_m$ are chosen, it reads

$$\sum_l X(\mathbf{H}_l)\,|E(\mathbf{H}_l - \mathbf{H}_m)|^2 = \lambda\,|E(\mathbf{H}_m)|^2, \qquad (3)$$

which means that the X's could also be determined as a solution of this linear system. The $|E|^2$'s in the summation are elements of a Karle–Hauptman matrix (Karle & Hauptman, 1950) and therefore the rank of the system is equal to the number of different interatomic vectors (Goedkoop, 1950). Therefore only a finite number of X's can be calculated from (3), which strongly suggests that in spite of (1) being in principle an infinite summation, since the X's are calculated from (2) by means of a Fourier transform, it might be reduced to a finite summation. In fact the main results of the present paper are finite linear relationships between products of two E's with coefficients depending only upon moduli of E's. They are used for setting up linear systems of equations whose solutions are the cosine and sine of triple-phase invariants.

In paper *A* the problem of finding a finite 'linear' relationship between single E's was considered (but unfortunately in that case the coefficients depend upon phases and therefore the relationship is not really linear). In trying to find an equation between products of E's a formalism very similar to that followed in paper *A* will be used and so some of its ideas will be summarized. (The notation is similar to the notation of papers *A* and *B*, except that in the z_j's the normalization constant is included.)

For each $\mathbf{h}$ in reciprocal space, define a vector $\mathbf{V}(\mathbf{h})$ in a complex N-dimensional vector space $\mathcal{N}$, as follows,

$$\mathbf{V}(\mathbf{h}) = \sum_{j=1}^{N} \exp(2\pi i\,\mathbf{h}.\mathbf{r}_j)\mathbf{e}_j, \qquad (4)$$

where the inner products between base vectors $\mathbf{e}_j$ satisfy the condition $(\mathbf{e}_j \mid \mathbf{e}_l) = \delta_{lj} z_j$. It follows that the inner product of two vectors $\mathbf{V}$ is $[\mathbf{V}(\mathbf{h})|\mathbf{V}(\mathbf{k})] = E(\mathbf{k} - \mathbf{h})$. The vector $\mathbf{V}(\mathbf{0})$ can be expanded in a new base defined by the vectors $\{\mathbf{V}(\mathbf{h}_q), q = 1, \ldots, N\}$, that is

$$\mathbf{V}(\mathbf{0}) = \sum_{q=1}^{N} C_q^* \mathbf{V}(\mathbf{h}_q), \qquad (5)$$

and its inner products with a set of vectors $\{\mathbf{V}(\mathbf{k}_p), p = 1, \ldots, N\}$ lead to

$$E(\mathbf{k}_p) = \sum_{q=1}^{N} C_q E(\mathbf{k}_p - \mathbf{h}_q), \quad p = 1, \ldots, N. \qquad (6)$$

This linear system defines the coefficients C_q. Note that if $\{\mathbf{k}_q, q = 1, \ldots, N\} \equiv \{\mathbf{h}_p, p = 1, \ldots, N\}$, the E's on the right-hand side of (6) are elements of a Karle–Hauptman matrix. Finally, the inner product of (5) with an arbitrary vector $\mathbf{V}(\mathbf{m})$ gives

$$E(\mathbf{m}) = \sum_{q=1}^{N} C_q E(\mathbf{m} - \mathbf{h}_q), \qquad (6')$$

which is one of the main equations of paper *A* and it has also been found by other authors in the context of probabilistic theories as a regression equation (de Rango, Tsoucaris & Zelwer, 1974; Podjarny, Yonath & Traub, 1976). This equation means that any E can be written as a finite sum of N other E's, with a fixed set of coefficients depending upon moduli and phases of several E's.

Tensor formalism

The relationship between single E's, equation (6'), was established with a simple vector algebra in an N-dimensional vector space. The present objects of interest are products of two E's and they can be related with a similar algebra but in a tensor product space.

Choose the vectors $\{\mathbf{V}(\mathbf{h}_q), q = 1, \ldots, N\}$ as a basis of $\mathcal{N}$. The tensor product $\mathcal{N} \otimes \mathcal{N}$ is an N^2-dimensional vector space with bases $\{\mathbf{e}_i \otimes \mathbf{e}_j;\ i,j = 1, \ldots, N\}$ and $\{\mathbf{V}(\mathbf{h}_p) \otimes \mathbf{V}(\mathbf{h}_q);\ p, q = 1, \ldots, N\}$. Defining in $\mathcal{N} \otimes \mathcal{N}$, $\mathbf{W}(\mathbf{h},\mathbf{k}) \equiv \mathbf{V}(\mathbf{h}) \otimes \mathbf{V}(-\mathbf{k})$, and using (4), it is clear that

$$\mathbf{W}(\mathbf{h},\mathbf{k}) \equiv \mathbf{V}(\mathbf{h}) \otimes \mathbf{V}(-\mathbf{k}) = \sum_{i,j}^{N} \exp[2\pi i(\mathbf{h}.\mathbf{r}_i - \mathbf{k}.\mathbf{r}_j)]\,\mathbf{e}_i \otimes \mathbf{e}_j. \qquad (7)$$

Defining $\mathbf{e}_i \otimes \mathbf{e}_j = \mathbf{e}_{ij}$, it follows that their inner products are

$$(\mathbf{e}_{ij}|\mathbf{e}_{st}) = z_i z_j \delta_{is}\delta_{jt} \qquad (8)$$

and therefore

$$\begin{aligned}[\mathbf{W}(\mathbf{l},\mathbf{m})|\mathbf{W}(\mathbf{h},\mathbf{k})] &= \sum_{i,j,s,t}^{N} \exp[-2\pi i(\mathbf{l}.\mathbf{r}_i - \mathbf{m}.\mathbf{r}_j)] \\ &\quad \times \exp[2\pi i(\mathbf{h}.\mathbf{r}_s - \mathbf{k}.\mathbf{r}_t)]\,(\mathbf{e}_{ij}|\mathbf{e}_{st}) \\ &= \sum_{i,j}^{N} \exp[2\pi i(\mathbf{h}-\mathbf{l}).\mathbf{r}_i] \\ &\quad \times \exp[-2\pi i(\mathbf{k}-\mathbf{m}).\mathbf{r}_j]\, z_i z_j \\ &= E(\mathbf{h}-\mathbf{l})E(\mathbf{m}-\mathbf{k}). \end{aligned} \qquad (9)$$

This means that the inner product of two elements belonging to $\mathcal{N} \otimes \mathcal{N}$ is equal to a product of two E's.

In particular, note that

$$[\mathbf{W}(\mathbf{k},\mathbf{k})|\mathbf{W}(\mathbf{h},\mathbf{h})] = |E(\mathbf{h}-\mathbf{k})|^2 \qquad (10)$$

and

$$[\mathbf{W}(\mathbf{k},\mathbf{k})|\mathbf{W}(\mathbf{h},\mathbf{m})] = E(\mathbf{h}-\mathbf{k})\,E(\mathbf{k}-\mathbf{m}). \qquad (11)$$

In the Appendix it is proved that the vectors of the form $\mathbf{W}(\mathbf{h},\mathbf{h})$ lie in $\mathscr{S}$ which is a subspace of $\mathscr{N}\otimes\mathscr{N}$ whose dimension is at most $N(N-1)+1$. In fact it is equal to the number of different interatomic vectors. The symbol $\mathbf{S}(\mathbf{m})$ will be used for the vectors in $\mathscr{S}$, that is

$$\mathbf{S}(\mathbf{m}) \equiv \mathbf{W}(\mathbf{m},\mathbf{m}), \qquad (12)$$

and now with this change of notation (10) and (11) can be written

$$[\mathbf{S}(\mathbf{k})|\mathbf{S}(\mathbf{h})] = |E(\mathbf{h}-\mathbf{k})|^2 \qquad (13)$$

$$[\mathbf{S}(\mathbf{k})|\mathbf{W}(\mathbf{h},\mathbf{m})] = E(\mathbf{h}-\mathbf{k})E(\mathbf{k}-\mathbf{m}). \qquad (14)$$

In $\mathscr{S}$ the vector $\mathbf{S}(\mathbf{0})$ can be expanded as a linear combination of the base vectors $\mathbf{S}(\mathbf{h}_p)$,

$$\mathbf{S}(\mathbf{0}) = \sum_{p=1}^{M} \beta_p \mathbf{S}(\mathbf{h}_p), \qquad (15)$$

where M is equal to the dimension of $\mathscr{S}$. The inner products of this equation with a set of vectors $\{\mathbf{S}(\mathbf{k}_q), q = 1,\ldots,M\}$ are, according to (13),

$$|E(\mathbf{k}_q)|^2 = \sum_{p=1}^{M} \beta_p |E(\mathbf{h}_p-\mathbf{k}_q)|^2, \quad q = 1,\ldots,M. \qquad (16)$$

This linear system defines the β's and therefore they do not depend upon phases. Note again that if $\{\mathbf{k}_p, p = 1,\ldots,M\} \equiv \{\mathbf{h}_q, q = 1,\ldots,M\}$, the $|E|^2$'s on the right-hand side of (16) are elements of a Karle–Hauptman matrix.

The inner product of (15) with an arbitrary element of $\mathscr{N}\otimes\mathscr{N}$, namely $\mathbf{W}(\mathbf{h},\mathbf{k})$, is, according to (14),

$$E(-\mathbf{h})E(\mathbf{k}) = \sum_{p=1}^{M} \beta_p E(\mathbf{h}_p-\mathbf{h})E(\mathbf{k}-\mathbf{h}_p), \qquad (17)$$

which is formally similar to equation (1) (the main equation of paper *B*), but with coefficients which guarantee its finite character. Multiplying (17) by $E(\mathbf{h}-\mathbf{k})$ it becomes

$$E(-\mathbf{h})E(\mathbf{k})E(\mathbf{h}-\mathbf{k}) = \sum_{p=1}^{M} \beta_p E(\mathbf{h}_p-\mathbf{h}) \times E(\mathbf{k}-\mathbf{h}_p)E(\mathbf{h}-\mathbf{k}). \qquad (18)$$

This is a linear, finite and exact relationship among triple products with coefficients depending only upon $|E|^2$'s. On the other hand, if in (17) $\mathbf{h} = \mathbf{0}$, it can be written

$$E(\mathbf{k}) = \frac{1}{E(\mathbf{0})} \sum_{p=1}^{M} \beta_p E(\mathbf{k}-\mathbf{h}_p)E(\mathbf{h}_p) \qquad (19)$$

(Navaza, 1974), which can be regarded as a weighted form of a Sayre–Hughes equation (Sayre, 1952; Hughes, 1953), but again this is an exact equation with a finite number of terms. There is also some similarity between (19) and equation (5) of Rothbauer (1976) but only in the sense that both are valid for structures with equal and unequal atoms. It is interesting to note, particularly in connexion with the last equation, that the β's are real and they can be negative.

Another useful relationship between E's can be obtained by means of the vector

$$\mathbf{T} = \sum_{i=1}^{N} \mathbf{e}_{ii}, \qquad (20)$$

which lies in $\mathscr{S}$. As such it can be expanded in the base $\{\mathbf{S}(\mathbf{h}_p), p = 1,\ldots,M\}$, that is

$$\mathbf{T} = \sum_{p=1}^{M} \gamma_p S(\mathbf{h}_p). \qquad (21)$$

Since $[\mathbf{S}(\mathbf{h}_p)|\mathbf{T}] = \sum_{j=1}^{n} z_j^2 = 1$, it follows that the system of equations defining the coefficients γ is

$$\sum_{p=1}^{M} \gamma_p |E(\mathbf{h}_p-\mathbf{h}_p)|^2 = 1, \quad q = 1,\ldots,M. \qquad (22)$$

On the other hand, noting that

$$[\mathbf{T}|\mathbf{W}(\mathbf{h},\mathbf{k})] = \sum_{j=1}^{N} z_j^2 \exp[2\pi i(\mathbf{h}-\mathbf{k}).\mathbf{r}_j] = E_2(\mathbf{h}-\mathbf{k}), \qquad (23)$$

and taking the inner product of $\mathbf{W}(\mathbf{h},\mathbf{k})$ with both sides of (21), an equation similar to (17) is obtained, that is

$$\sum_{p=1}^{M} \gamma_p E(\mathbf{h}-\mathbf{h}_p)E(\mathbf{h}_p-\mathbf{k}) = E_2(\mathbf{h}-\mathbf{k}), \qquad (24)$$

where the resemblance to the Sayre–Hughes equation is more striking. If we multiply both sides of (24) by $E(\mathbf{k}-\mathbf{h})$ and considering structures with equal atoms, it becomes

$$\sum_{p=1}^{M} \gamma_p E(\mathbf{h}-\mathbf{h}_p)E(\mathbf{h}_p-\mathbf{k})E(\mathbf{k}-\mathbf{h}) = \frac{1}{\sqrt{N}}|E(\mathbf{h}-\mathbf{k})|^2, \qquad (25)$$

which expresses $|E|^2$ as a linear combination of triple-phase invariants.

Calculations and discussion

In an attempt to gain an understanding of the new equations, (18) and (25), direct calculations of the cosines of triple-phase invariants for one-dimensional model structures were performed. For those calculations which have much in common with those reported in paper *B*, only the main differences will be mentioned.

A system of linear equations for cosines was set up with (18). There are two important differences between these equations and the similar equations of paper *B*: firstly, the coefficients, β's, are calculated directly in reciprocal space by means of (16); and secondly, because this way of calculating the β's allows the summation in (18) to be performed on any set of indices, it is possible to build a system with, formally, more equations than unknowns. The resulting equations are always exactly satisfied regardless of the atomic positions. The number of terms in each equation can be very large since it is the number of different interatomic vectors; hence, a favourable situation is when there are a considerable number of superpositions in the Patterson function. This is really a notable fact since the failure of many direct-methods procedures is often blamed on these superpositions.

In attempting to solve the system of equations for the cosines it was found, as in paper *B*, that the system is singular and it is necessary to eliminate some unknowns (*e.g.* those with the smallest moduli) in order to solve for the others. The results for these cosines are only marginally better than those reported in paper *B* which could therefore be taken as representative examples of the results obtained with (18). The main differences are that with (18) the results are equally good for any distribution of atoms and that the relationship between the rank of the system and the quality of the solution is clearer.

It was found that for all the three-atom structures considered the complete system was singular, but after eliminating one unknown the solution for the rest was almost perfect; that is, the co-rank of the system is equal to one. When the number of atoms increases it seems that the co-rank also increases and more unknowns have to be eliminated. The system to be solved is then less exact and the quality of the solution deteriorates.

When similar procedures were applied, but with equation (25), it was found that the linear systems were not singular. Therefore, it was possible to obtain exact solutions for the cosine of the triple-phase invariants for linear structures with up to five atoms (this limit being imposed by the dimension of the systems). As is evident from (25) the use of the procedure is restricted to the case of equal atoms. But of course the main limitation is that the size of the system increases very rapidly with the number of atoms. The freedom in choosing the vectors **h** and **k** can be used to construct the system of equations with the smallest dimension. For linear structures this choice seems evident, but we have no answer for the three-dimensional case.

At any rate, it is, to our knowledge, the first time that the triple-phase invariants could be exactly determined by solving a linear system of equations involving $|E|^2$'s.

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APPENDIX

The vectors $\mathbf{S(h)} = \mathbf{W(h,h)} = \mathbf{V(h)} \otimes \mathbf{V(-h)} = \mathbf{V(h)} \otimes \mathbf{V^*(h)}$ lie in a vector subspace $\mathscr{S}$ of $\mathscr{N} \otimes \mathscr{N}$, generated by vectors $\mathbf{x} \otimes \mathbf{x}^*$, $\mathbf{x}$ in $\mathscr{N}$. Writing $X_j = \exp(2\pi i \mathbf{h}.\mathbf{r}_j)$, the vectors $\mathbf{S(h)}$ can be expressed as

$$\begin{aligned}\mathbf{S(h)} = \mathbf{V(h)} \otimes \mathbf{V^*(h)} &= \sum_{i,j}^{N} \exp[2\pi i \mathbf{h}(\mathbf{r}_i - \mathbf{r}_j)]\, \mathbf{e}_i \otimes \mathbf{e}_j \\ &= \sum_{i,j} X_i X_j^* \mathbf{e}_{ij} \\ &= \sum_i \mathbf{e}_{ii} + \sum_{\substack{ij \\ i<j}} X_i X_j^* \mathbf{e}_{ij} \\ &\quad + \sum_{\substack{ij \\ i>j}} X_i X_j^* \mathbf{e}_{ij}.\end{aligned}$$

It follows that the vectors $\mathbf{S(h)}$ lie in a vector subspace of $\mathscr{N} \otimes \mathscr{N}$ generated by the $1 + N(N-1)$ linearly independent vectors $\{(\sum_i \mathbf{e}_{ii}), \mathbf{e}_{12}, \mathbf{e}_{21}, \ldots, \mathbf{e}_{N-1,N}, \mathbf{e}_{N,N-1}\}$. Then the dimension of $\mathscr{S}$ is at most $1 + N(N-1)$. Alternatively, as $[\mathbf{S(h}_p)|\mathbf{S(h}_q)] = |E(\mathbf{h}_p - \mathbf{h}_q)|^2$, the metric tensor of $\mathscr{S}$ is a Karle–Hauptman matrix whose elements are $|E|^2$'s. The rank of this matrix and therefore the dimension of $\mathscr{S}$ equals the number of different interatomic vectors, which is at most equal to $1 + N(N-1)$.

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