

Short Communications

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Symmetry relations among structure factors.* By GEORGE M. BROWN, *Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.*

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The usefulness of a simple dyadic equation, generally overlooked, of Patterson for specifying symmetry relations among structure factors is emphasized and restated in matrix notation for convenience of application.

The task of generalizing the symmetry subroutine of a computer program for direct solution of the phase problem has emphasized to the author the unfortunate fact that in the literature of structure analysis the discussion of phase relations among symmetrically equivalent reflections is fragmented and generally unsatisfactory. The deficiency of Vol. I of *International Tables for X-ray Crystallography* (1952) in this regard is notorious; it specifies all relations for each of the triclinic, monoclinic, and orthorhombic space groups but only some of the relations for higher symmetries, without so much as noting the absence of the others. The specifications are given in a rather awkward manner according to the even or odd character of the sums of indices for various groups of reflections. The most useful and modern of the texts on crystal-structure analysis are also deficient; they either ignore the subject, dismiss it with a reference to *International Tables*, or treat it so obscurely as to make application difficult. It seems to have been generally overlooked that Patterson (1952), in a perhaps too succinct discussion incidental to a paper on another subject, derived in dyadic notation the simple equation needed to identify symmetry-related reflections and to specify the phase relations among them. The equation is restated here in matrix notation for convenience of application.

Consider the expression \mathbf{S} for any given symmetry operator of a space group such that

$$\mathbf{x}' \equiv \mathbf{S}\mathbf{x} \equiv \mathbf{A}\mathbf{x} + \mathbf{t}, \quad (1)$$

where \mathbf{x} and \mathbf{x}' are the column matrices of fractional (contravariant) coordinates x^i of a given point and x'^i of the symmetrically related point, \mathbf{A} is the matrix of the operator for the proper or improper rotation involved, and \mathbf{t} is the column matrix of translational components t^i . (In each symbol where it appears the superscript i takes the values 1, 2, and 3.) The equations

$$F(\tilde{\mathbf{A}}^{-1}\mathbf{h}) = F(\tilde{\mathbf{h}}\mathbf{A}^{-1}) = \exp\{2\pi i\tilde{\mathbf{h}}\mathbf{A}^{-1}\mathbf{t}\}F(\mathbf{h}) \quad (2)$$

and

$$F(\tilde{\mathbf{A}}\mathbf{h}) = F(\tilde{\mathbf{h}}\mathbf{A}) = \exp\{-2\pi i\tilde{\mathbf{h}}\mathbf{t}\}F(\mathbf{h}) \quad (3)$$

correspond to equations (5a) and (5b) in Patterson's paper

and are appropriate for the structure factor defined as $F(\mathbf{h}) = \sum_N f_N(\mathbf{h}) \exp\{2\pi i\tilde{\mathbf{h}}\mathbf{x}_N\}$. In these equations \mathbf{h} is the column matrix of reflection indices h, k, l and each superscript tilde ($\tilde{}$) over the symbol for a matrix denotes the transpose of that matrix. By either equation (2) or equation (3) each symmetry operation of the space group identifies a structure factor related to $F(\mathbf{h})$ and specifies the phase relation through the translational components t^i . These equations are mathematical expressions corresponding to geometrical arguments given earlier (Buerger, 1949; see also Buerger, 1960). Because every space group includes for each operation given by equation (1) the reciprocal operation

$$\mathbf{S}^{-1}\mathbf{x} = \mathbf{A}^{-1}\mathbf{x} - \mathbf{A}^{-1}\mathbf{t}, \quad (4)$$

equations (2) and (3) are equivalent and only one of them is needed. Since in the general case the operation of transposing a matrix is simpler than inverting it, equation (3) is to be preferred over equation (2); and only equation (3) will be used in the subsequent discussion here.

To each symmetry operator \mathbf{S} of the space group (including the identity operator) there corresponds one triplet of transformed coordinates x'^1, x'^2, x'^3 in the set of general positions of the space group. For a given operator \mathbf{S} the element A_{ij} of the matrix \mathbf{A} is the coefficient of x^j in the expression for x'^i ; the element t^i of \mathbf{t} is the translational part of x'^i . Thus the matrices required for use in equation (3) are available from *International Tables* (1952), and the equation is easily applied. The matrix multiplications are very simple to program for electronic computing.

For centrosymmetric space groups the entire set of equivalences may be generated with equation (3) by use of the whole set of operators \mathbf{S} of the group, or, perhaps more conveniently, by first using only those symmetry operators not related by inversion and then using the relation $F(-h, -k, -l) = F(h, k, l)$ for each $F(h, k, l)$ of the intermediate set. For noncentrosymmetric space groups all the operators \mathbf{S} are used, and the phases of the Friedel mates are obtained, to the approximation of Friedel's law, by reversing the signs of the phase angles. In the case of the conventional centered space groups the symmetry operation related to a given one by the centering operation only need not be considered along with the given one, as its use leads only to a redundant relation. Redundant relations will in general be generated for reflections whose reciprocal-lattice points lie on symmetry elements.

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Discussions in the literature by others,* some of whom were evidently unaware of Patterson's treatment, have in general contributed little toward understanding of the subject. Waser (1955) added an embellishment by pointing out that to obtain all of the *independent* relations among the structure factors one need consider only those symmetry operators S whose rotational components generate the point group isomorphous with the space group and that one can, therefore, derive all independent relations from the Hermann-Mauguin symbol of the space group. The entire set of symmetry relations for a given structure factor can be deduced by appropriate repetitive use of the independent relations.

Unfortunately, Waser's paper may mislead the uninitiated user of Patterson's equation. Waser rederives Patterson's dyadic equation by a slightly different method; consistent with the dyadic notation, the discussion under his *Example* is presented in terms of point operations. Matrices are not even mentioned. However, the discussion, especially the last sentence, may easily be taken to imply that in general the matrix to be used in equation (3) above is A^{-1} instead of the correct \tilde{A} . Waser's dyadic equation $h \cdot A = A^{-1} \cdot h$ requires transposing the corresponding matrix A , not inverting it. The reader not already familiar with dyadic notation should be able to use the discussion on dyadics of Patterson (*International Tables*, 1959, p. 57), especially his transformation tables, to verify that this last statement is true. The essential point is that the matrix A^{-1} , from the definition of A in equation (1), is in general an appropriate symmetry operator only for the fractional (contravariant) coordinates x^i . From the well-known transformation rules for base vectors, fractional coordinates, and indices (summarized, for example, in *International Tables*, 1952, p. 16), the matrix \tilde{A} is the matrix appropriate for transforming the indices (covariant coordinates) according to the same point operation that is represented by A^{-1} as a multiplier of x . In brief, \tilde{A} represents in reciprocal space the inverse of the point operation represented by A in direct space. The matrices \tilde{A} and A^{-1} are related by the equation

$$\tilde{A} = gA^{-1}g^{-1}, \quad (5)$$

where g is the matrix whose general element g_{ij} is $\mathbf{a}_i \cdot \mathbf{a}_j$, the dot product of the base vectors \mathbf{a}_i and \mathbf{a}_j of the crystal lattice, and g^{-1} , the reciprocal of g , is the matrix whose general element g^{ij} is $\mathbf{a}^i \cdot \mathbf{a}^j$, the dot product of two reciprocal base vectors. Equation (5) follows from the fact that g^{-1} transforms covariant coordinates to contravariant and g does the reverse (*International Tables*, 1959, p. 56).

Instead of restating the result of a dyadic derivation, one may of course derive equation (3) using matrix methods from the beginning. The procedure exactly parallels that of Waser except that the matrix operations $\tilde{h}x$, $\tilde{h}t$, and $\tilde{h}A$ are used in place of the dyadic operations $h \cdot r$, $h \cdot t$, and $h \cdot A$ in Waser's equations.

Since the equality of the conjugate dyadic A_C and the reciprocal dyadic A^{-1} is emphasized by Waser [see also Zachariasen, 1945, equation (2.5b)] as the condition which ensures invariance of distances under a linear transformation, it is of interest to show that equation (5) is a matrix

expression of this condition for the particular case of a symmetry transformation. The square of the distance between two points a and b defined by column matrices $^a x$ and $^b x$ is given by $(^b \tilde{x} - ^a \tilde{x})g(^b x - ^a x)$; the corresponding square for the two points related to a and b by a rotation A is $(^b \tilde{x} - ^a \tilde{x})\tilde{A}gA(^b x - ^a x)$. If the two distances are to be equal, then

$$g = \tilde{A}gA. \quad (6)$$

This condition, which corresponds to Zachariasen's equation (2.15), is easily transformed to

$$A^{-1} = g^{-1}\tilde{A}g \quad (7)$$

and to equation (5).

Equation (7) reduces to $A^{-1} = \tilde{A}$, that is to say, A is orthogonal, when \tilde{A} commutes with g (or with g^{-1}), as is the case for each of the rotational operations of space group $Pn3n$ used in the *Example* of Waser. The relation $A^{-1} = \tilde{A}$ is obviously true for all operations of the triclinic, monoclinic, and orthorhombic groups, for which the matrices are all diagonal. The crystallographic matrices A which are not orthogonal are those which contain four non-zero elements; such matrices are associated only with some symmetry operations of hexagonal space groups and of trigonal space groups referred to hexagonal axes.

For an example of a symmetry operation in which \tilde{A} does not equal A^{-1} , one may consider space group $P3_121$ and the point $\tilde{x}, y-x, \frac{1}{3}-z$, equivalent to x, y, z . The matrices A and \tilde{A} are $(\bar{1}00/\bar{1}10/00\bar{1})$ and $(\bar{1}\bar{1}0/010/00\bar{1})$, respectively, and $A^{-1} = A$. By equation (3), the phase relation is

$$F(-h-k, k, -l) = \exp\{-\frac{1}{3}\pi il\} F(h, k, l).$$

The procedure for finding symmetry relations emphasized by Bertaut & Waser (1957) and later by Bertaut (1964) was not explained in terms of the simple matrix formulation of equation (3); however, the procedure is mathematically equivalent to the direct application of this equation.

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* Some papers not specifically cited here are cited in the various references given.