The Symmetry of the Rotation Function

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The rotation function represents the sum of a point-by-point product of two different Patterson functions rotated with respect to one another. The magnitude of the rotation function can be plotted in a three-dimensional space where the three coordinates are measures of the three angular rotations. The space group of the rotation function expresses the relationship between equivalent rotations where identical magnitudes would be recorded. This symmetry depends upon the symmetry of the two original Patterson functions and the nature of the choice of the variables used to express the rotations. The rotation function need to be evaluated only over the asymmetric unit in rotation space. A simple method is described for obtaining the symmetry of the rotation functions in terms of Eulerian angles. The latter are shown to have considerable advantages over other choices of variables.

Introduction

The rotation function was derived by Rossmann & Blow (RB) in 1962. It has been used in determining the orientation of a known or unknown group with respect to another identical group either in the same or in a different crystal. The method bears much resemblance to the method used so successfully by Nordman & Nakatsu (1963), and much of the content of this paper will be equally true for their techniques. In both cases the amount of computing required is formidable. It is therefore essential to be able to calculate *a priori* the range of angles which needs to be explored before all independent rotation operations have been considered. A method for calculating the range of angles required is discussed in this paper. This method is general and easy to apply in contrast to the special and somewhat arbitrary procedure of RB.

The rotation space group

Let us rewrite the rotation function in the form

$$R = \int_U P_2(\mathbf{X}_2) P_1(\mathbf{X}_1) d\mathbf{X}_1 \tag{1}$$

where we are comparing the Patterson function P_1 at $\mathbf{X}_1$ with the Patterson function P_2 at $\mathbf{X}_2$. The position vectors $\mathbf{X}_1$ and $\mathbf{X}_2$ are referred to a common orthogonal coordinate system in real space, and satisfy the relationship.

$$\mathbf{X}_2 = [\varrho]\mathbf{X}_1 \tag{2}$$

for all points within the volume U. The matrix $[\varrho]$ describes the rotation which transforms $\mathbf{X}_1$ into $\mathbf{X}_2$. The Patterson functions P_1 and P_2 may be the same functions, or may be different when derived from two different crystalline forms of the same molecular species.

The symmetry of the two functions P_1 and P_2 within the volume U will fall into one of eleven Laue groups. In considering the symmetry of the rotation function, R, it is only necessary to consider the symmetry elements of the Laue group which describe proper rotations, that is, rotations without inversion. Thus, for each of P_2 and P_1 a 'proper rotation group' can be written down. A proper rotation group contains all the proper rotations present in the corresponding Laue group, of which it is a sub-group. For example, 222 is the proper rotation group of Laue group *mmm*.

If the symmetry operations of the proper rotation groups of P_1 and P_2 are described by the sets of matrices $[T_i]$ and $[T_j]$, respectively, then

$$R = \int_U P_2([T_j]\mathbf{X}_2) P_1([T_i]\mathbf{X}_1) d\mathbf{X}_1 \tag{3}$$

will have the same value for all $[T_i]$ and $[T_j]$. Note that $[T_i]$ and $[T_j]$ are symmetry operations applied to the orthogonal coordinates as listed by Patterson (1959, p. 63). Hence from (2)

$$[T_j]\mathbf{X}_2 = [\varrho][T_i]\mathbf{X}_1$$

or
$$\mathbf{X}_2 = [T_j]^{-1}[\varrho][T_i]\mathbf{X}_1$$
$$= [T_j]^T[\varrho][T_i]\mathbf{X}_1 \tag{4}$$

where $[T_j]^T$ is the transpose of $[T_j]$. Equation (4) implies that R will have the same value for each rotation which leaves $[T_j]^T[\varrho][T_i]$ unchanged for all values of i and j. The elements of the rotation matrix $[\varrho]$ are determined by the three angles of rotation $(\alpha_1\alpha_2\alpha_3)$. If we consider plotting the magnitude of the rotation function in a three-dimensional space defined by these three angles, then a unit-cell translation is performed whenever one of the angles is increased by 2π. If the sets of angles associated with $[\varrho']$ and $[\varrho]$ are $(\alpha_1' \alpha_2' \alpha_3')$ and $(\alpha_1 \alpha_2 \alpha_3)$, respectively, when $[\varrho']$ and $[\varrho]$ satisfy one of the sets of equations of the type

$$[\varrho'] = [T_j]^T[\varrho][T_i], \tag{5}$$

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then $(\alpha_1' \; \alpha_2' \; \alpha_3')$ and $(\alpha_1 \; \alpha_2 \; \alpha_3)$ are equivalent sets of rotation angles. They represent equivalent positions in the space defined above. The combination of all the symmetry operations of this type forms the rotation space group, an example of which is given by RB.

Let us define $_jS_i$ as the symmetry operation which results from satisfying one of the equations (5). Further let S_i be the symmetry operator when $[T_j]^T = [1]$, that is, when the Patterson function P_2 is of the Laue class $\bar{1}$ or proper rotation group 1. Similarly $_jS$ is the symmetry operator when P_1 is of the Laue class $\bar{1}$. Thus S_i represents the symmetry operation that satisfies the equation

$$[\varrho_i] = [\varrho][T_i] . \qquad (6)$$

It follows that

$$[\varrho'] = [T_j]^T[\varrho_i]$$
$$= [T_j]^T[\varrho][T_i] . \qquad (7)$$

Now the symmetry operation $_jS$ satisfies (7). Thus the total symmetry operation which satisfies (4) is a 'product' of S_i and $_jS$, where multiplication implies successive application of S_i and $_jS$.

As there are only eleven proper rotation groups there will only be eleven different results for S_i and for $_jS$. In general, therefore, to determine the rotation space group for any desired rotation function we need only look up S_i and $_jS$ for the proper rotation groups of the Patterson functions P_1 and P_2 respectively. Multiplication, in the sense defined above, of these two sets of symmetry operations leads to the complete set $_jS_i$ which describe the equivalent general positions of the rotation space group.

The relationship between
the symmetry operation $_jS_i$ and $_iS_j$

The order in which the Patterson functions are arranged in equation (1) is important. We may ask what angular relationships there are between equivalent points if the order is reversed.

Let

$$R_1 = \int_U P_2(\mathbf{X}_2)P_1(\mathbf{X}_1)d\mathbf{X}_1$$

corresponding to the relationship

$$\mathbf{X}_2 = [\varrho]\mathbf{X}_1$$

and rotation space group expressed by the symmetry operations $_jS_i$.
Let also

$$R_2 = \int_U P_2(\mathbf{X}_1)P_1(\mathbf{X}_2)d\mathbf{X}_2$$

corresponding to the relationship

$$\mathbf{X}_1 = [\varrho']\mathbf{X}_2$$

and rotation space group symmetry operations $_iS_j$. Then we may write $\mathbf{X}_2 = [\varrho']^{-1}\mathbf{X}_1$ and it follows that

$$R_2 = R_1 \text{ when} [\varrho] = [\varrho']^{-1} = [\varrho']^T . \qquad (8)$$

Thus, reversal of the Patterson functions produces a different though related rotation function with a different rotation space group. All of the foregoing results can be applied to any set of angular variables used to describe the rotations. In the particular case of Eulerian variables, as defined by RB, inspection of the matrix $[\varrho]$ shows that the relationship between the two rotation functions is

$$R_1(\theta_1\theta_2\theta_3) = R_2(-\theta_3, \; -\theta_2, \; -\theta_1) . \qquad (9)$$

For all proper rotation groups, other than the cubic groups, $_jS_i$ takes the form

$$R_1(\theta_1\theta_2\theta_3) = R_2(a_1 + b_1\theta_1, \; a_2 + b_2\theta_2, \; a_3 + b_3\theta_3) \qquad (10)$$

where the a's and b's are constants for a particular rotation group. Hence, from relationship (9), the $_iS_j$ have the form

$$R_2(\theta_1\theta_2\theta_3) = R_2(-a_3 + b_3\theta_1, \; -a_2 + b_2\theta_2, \; -a_1 + b_1\theta_3) . \qquad (11)$$

Thus, from (10) and (11) the $_iS_j$ can be derived from the $_jS_i$.

Tabulation of
all possible symmetry operators $_jS$ and S_i

The Eulerian angles $(\theta_1\theta_2\theta_3)$ are particularly useful for describing the symmetry operation S_i as they take a simple form for all but cubic groups. Apart from these cases the S_i can be described by symmetry planes and axes in the Eulerian variable space, and hence a rotation space group can be written down. The cubic groups lead to symmetry relationships of a different type and these are discussed in the next section.

Table 1 lists the eleven Laue groups, the corresponding proper rotation groups, the rotation axes with their directions relative to the Cartesian set $\mathbf{X}$, and the Cartesian unique set of axes required to define the proper rotation groups. Table 2 lists the forms of $_jS$ and S_i for each of the symmetry elements which can occur in the proper rotation groups apart from cubic groups. An example of the derivation of S_i is the case of a twofold axis along [010]. In this case

$$[T_i] = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} .$$

We are now required to find a set of Eulerian angles $\theta_1' \; \theta_2' \; \theta_3'$ which go to form the elements of the matrix $[\varrho']$ identical with the elements of the matrix product $[\varrho] \; [T_i]$ (equation 6). Upon equating all nine elements of the Eulerian rotation matrix (RB) independently, we see that these nine equations are satisfied only when

$$\theta_1' = \pi - \theta_1, \; \theta_2' = \pi + \theta_2, \; \theta_3' = \theta_3 .$$

Let us now take, as an example, the determination of the rotation space groups in Eulerian variables when P_1 has symmetry $Pmmm$ and P_2 has symmetry $P2/m$. Table 1 shows that mmm corresponds to the proper rotation group 222 which has two unique axes, parallel

Table 1. *Properties of proper rotation groups*

Laue group	Proper rotation group	[001]	Unique axes [010]	[100]	[111]
$\bar{1}$	1	1			
$2/m$ (b axis unique)	2		2		
$2/m$ (c axis unique)	2	2			
mmm	222	2	2		
$4/m$	4	4			
$4/mmm$	422	4	2		
$\bar{3}$	3	3			
$\bar{3}m$	321	3	2		
$6/m$	6	6			
$6/mmm$	622	6	2		
Cubic					
$m3$	23	2			3
$m3m$	432	4			3

to **b** and **c**, say. We also see that $2/m$, in the usual monoclinic setting, has one twofold rotation axis parallel to **b**. Inspection of Table 2 then shows:

S_i, the symmetry operators on P_1, are:

$S_1 \quad \theta_1 \, \theta_2 \, \theta_3 \rightarrow \pi + \theta_1, \ -\theta_2, \ \pi + \theta_3$
(onefold axis*)

$S_2 \quad \theta_1 \, \theta_2 \, \theta_3 \rightarrow \pi - \theta_1, \ \pi + \theta_2 \, \theta_3$
(twofold axis parallel to **b**)

$S_3 \quad \theta_1 \, \theta_2 \, \theta_3 \rightarrow \pi + \theta_1, \ \theta_2, \ \theta_3$
(twofold axis parallel to **c**)

$_jS$, the symmetry operators on P_2 are

$_1S \quad \theta_1 \, \theta_2 \, \theta_3 \rightarrow \pi + \theta_1, \ -\theta_2, \ \pi + \theta_3$
(onefold axis)

$_2S \quad \theta_1 \, \theta_2 \, \theta_3 \rightarrow \theta_1, \ \pi + \theta_2, \ \pi - \theta_3$
(twofold axis parallel to **b**)

The set of equivalent general positions obtained by combining these is

θ_1,	θ_2,	θ_3	
θ_1,	$\pi + \theta_2$,	$\pi - \theta_3$	$(_2S)$
θ_1,	$-\theta_2$,	$\pi + \theta_3$	$(S_3 \, . \, S_1)$
θ_1,	$\pi - \theta_2$,	$-\theta_3$	$(S_3 \, . \, _2S \, . \, S_1)$
$\pi + \theta_1$,	θ_2,	θ_3	(S_3)
$\pi + \theta_1$,	$\pi + \theta_2$,	$\pi - \theta_3$	$(_2S \, . \, S_3)$
$\pi + \theta_1$,	$-\theta_2$,	$\pi + \theta_3$	(S_1)
$\pi + \theta_1$,	$\pi - \theta_2$,	$-\theta_3$	$(_2S \, . \, S_1)$

where the operations to obtain these positions are given in brackets after them. Multiplication implies the application of the operators consecutively. Alternatively the space group can be found by recognizing that the

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* The necessity of considering this operation arises out of the peculiar property of Eulerian angles, namely that there are always two related sets of operations which produce the same orientation. Another peculiar property is that in the plane $\theta_2 = 0$ all magnitudes for which $\theta_1 + \theta_3$ is a constant are identical. This leads to a twofold axis in this plane.
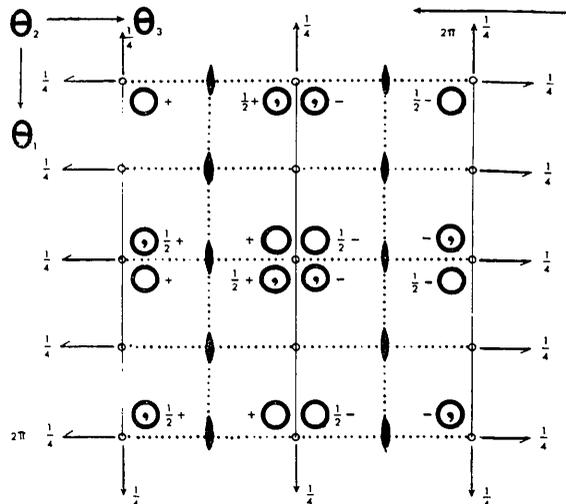

Fig. 1. Rotation space group diagram for rotation function of a *Pmmm* Patterson function (P_1) against a *P2/m* Patterson function (P_2). The Eulerian angles $\theta_1, \theta_2, \theta_3$ repeat themselves after an interval of 2π. Heights above the plane are given in fractions of a revolution.

symmetry operators S_1 and $_1S$ are n-glide planes in $\theta_1, \theta_2, \theta_3$ space perpendicular to θ_2, $_2S$ is a b-glide plane perpendicular to θ_3 and S_3 divides the total cell into two identical parts along θ_1. The latter combined with S_1 or $_1S$ leads to a c-glide plane perpendicular to θ_2. The combination of these operations gives two cells each of space group *Pbcb*, keeping the order $\theta_1\theta_2\theta_3$ (Fig. 1).

The non-linear symmetry relationships

If one attempts to develop the forms of S_i for the cubic groups in terms of $(\theta_1\theta_2\theta_3)$ or for other proper rotation groups in terms of other angles, for example, the angles $(\kappa\psi\varphi)$ defined by RB, one finds that the re-

$-\theta_1$,	$-\theta_2$,	$-\theta_3$	$(_2S \, . \, S_2 \, . \, S_1)$
$-\theta_1$,	$\pi - \theta_2$,	$\pi + \theta_3$	$(S_2 \, . \, S_1)$
$-\theta_1$,	θ_2,	$\pi - \theta_3$	$(S_2 \, . \, _2S \, . \, S_3)$
$-\theta_1$,	$\pi + \theta_2$,	θ_3	$(S_3 \, . \, S_2)$
$\pi - \theta_1$,	$-\theta_2$,	$-\theta_3$	$(S_3 \, . \, _2S \, . \, S_2 \ S_1)$
$\pi - \theta_1$,	$\pi - \theta_2$,	$\pi + \theta_3$	$(S_3 \, . \, S_2 \, . \, S_1)$
$\pi - \theta_1$,	θ_2,	$\pi - \theta_3$	$(_2S \, . \, S_2)$
$\pi - \theta_1$,	$\pi + \theta_2$,	θ_3	(S_2)

lationship between $(\alpha_1' \ \alpha_2' \ \alpha_3')$ and $(\alpha_1 \ \alpha_2 \ \alpha_3)$ cannot be written down as a linear transformation, and hence cannot be expressed as symmetry planes and axes in the appropriate variable space. An example of such non-linear symmetry operations is obtained when $[\varrho]$ is operated on by $[T_i] = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$ which represents a threefold axis along 111. The relationship between $(\theta_1' \ \theta_2' \ \theta_3')$ and $(\theta_1 \ \theta_2 \ \theta_3)$ in this case is

Table 2. *Symmetry elements S_i and $_jS$ for all possible types of space group rotations*

Axis	Direction	S_i	$_jS$
1		$(\pi+\theta_1, -\theta_2, \pi+\theta_3)$	$(\pi+\theta_1, -\theta_2, \pi+\theta_3)$
2	[010]	$(\pi-\theta_1, \pi+\theta_2, \theta_3)$	$(\theta_1, \pi+\theta_2, \pi-\theta_3)$
2	[001]	$(\pi+\theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, \pi+\theta_3)$
4	[001]	$(-\pi/2+\theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, \pi/2+\theta_3)$
3	[001]	$(-2\pi/3+\theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, 2\pi/3+\theta_3)$
6	[001]	$(-\pi/3+\theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, \pi/3+\theta_3)$
*2	[110]	$(3\pi/2-\theta_1, \pi-\theta_2, \pi+\theta_3)$	$(\pi+\theta_1, \pi-\theta_2, -3\pi/2-\theta_3)$

* This axis is not unique (that is, it can always be generated by two other unique axes), but is included for completeness.

$\cos \theta'_1 = -\cos \theta'_2$

$\sin \theta'_1 = -\cos \theta_1 \sin \theta_2/\sin \theta'_2$

$\sin \theta'_3 = (-\sin \theta_1 \cos \theta_2 \sin \theta_3 + \cos \theta_1 \cos \theta_3)/\sin \theta'_2$

$\cos \theta'_3 = (-\sin \theta_1 \cos \theta_2 \cos \theta_3 - \cos \theta_1 \sin \theta_3)/\sin \theta'_2$

$\cos \theta'_2 = \sin \theta_1 \sin \theta_2$

$\sin \theta'_2 = \pm[\sin^2 \theta_1 \cos^2 \theta_2 + \cos^2 \theta_1]^{\frac{1}{2}}$.

This is a threefold operation, in the sense that the application of this operation three times brings the original point back on itself. It is consistent with the infinite lattice in $(\theta_1 \theta_2 \theta_3)$ space and can combine with other linear or non-linear operations to form a group, although it cannot be described by one of the 230 space groups.

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The Secondary Extinction Correction Applied to a Crystal of Arbitrary Shape

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Zachariasen's formula for the secondary-extinction correction has been successfully applied to a $BeAl_2O_4$ crystal of irregular shape. An existing program for absorption correction of single-crystal diffraction data from arbitrarily shaped crystals could, after some minor modifications, be used for the necessary calculations.

The procedure used is described in some detail. It is shown that secondary-extinction errors can affect not only the vibrational parameters but also the positional parameters.

A re-examination of the Darwin formula for the secondary extinction correction (1922) was recently reported by Zachariasen (1963). It was shown that it contained an error in the X-ray diffraction case and a new formula was derived. This was tested on 'a perfect crystal sphere for which $\mu r = 0.69$'.

The expression for the corrected structure factor derived by Zachariasen is

$$F_{corr} \simeq F_0[1 + c . I_o . \beta(2\theta)] \qquad (1)$$

where

$$\beta(2\theta) = \frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2} . \frac{A^{*'}(2\theta)}{A^{*'}(0)}, \qquad (2)$$

F_0 is the observed structure factor and F_{corr} is the former corrected for secondary extinction, both on the same scale. I_o is the uncorrected observed integrated intensity on an arbitrary scale, and c is a scale factor to be adjusted. $A^* = A^{-1}$ is the absorption factor for the reflexion and $A^{*'}$ is $dA^*/d\mu$, where μ is the linear absorption coefficient.

One of the present authors (Werner, 1964a, b) has constructed a program for the absorption correction of X-ray data from single crystals of arbitrary shape. It was found possible to make a slight change in the program so that the derivative $A^{*'}$, required in Zachariasen's formula, could be computed. Hitherto this change has been made only for the particular version of the absorption program handling single-crystal diffractometer data. The expression computed is

$$A^{*'} = \frac{\sum\limits_{1}^{m^3} \frac{1}{V_0}(r_\alpha+r_\beta) . \exp[-(r_\alpha+r_\beta)\mu] . \Delta V}{\left[\sum\limits_{1}^{m^3} \frac{1}{V_0} . \exp[-(r_\alpha+r_\beta)\mu] . \Delta V\right]^2} \qquad (3)$$