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The Asymmetric Regions of Rotation Functions Between Patterson Functions of Arbitrarily High Symmetry

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Abstract

Rotation functions between Patterson functions can be calculated and analyzed more efficiently when it is possible to consider only a unique or asymmetric region of rotation space. Previous authors have succeeded in characterizing the symmetries and asymmetric units of rotation functions between Patterson functions whose symmetries are less than cubic. Here we describe a simple and general solution that applies to rotation functions between Patterson functions of any symmetry, including cubic. The method relies on partitioning rotation space into Dirichlet domains.

Introduction

The relative orientation between the molecules in a crystal and either a molecular model or a similar molecule in a different crystal form can often be determined in the absence of phase information by use of a rotation function (reviewed by Rossmann, 1972; Lattman, 1985), which is essentially an overlap integral between two Patterson functions as a function of their relative orientation. The rotational symmetries of the Patterson functions being compared lead to symmetry or redundancy in the rotation function if it is calculated over all of rotation space. In implementations of the rotation function that are computationally intensive, it is useful to be able to perform the calculation only over a region of rotation space that is unique to avoid wasteful duplication. Even in implementations such as the fast rotation function (Crowther, 1972) where the calculation can be performed quickly over all space, an understanding of the symmetry of the resulting rotation function is critical in analyzing the output. For example, one must be able to determine which of the function peaks are unique and which are related to others by symmetry.* Again, this is most easily accomplished if the rotation function can be divided into asymmetric or unique regions that contain no duplication. Several authors have treated this problem successfully for rotation functions between Patterson functions whose symmetries are less than cubic (Tollin, Main & Rossmann, 1966; Rao, Jih & Hartsuck, 1980; Moss, 1985). Tollin *et al.* (1966) pointed out the problem of nonlinearity in the cubic case when the rotations are parameterized by Euler angles and Burdina (1970) provided a partial solution for one specific cubic case by describing a region of rotation space that was larger than the desired asymmetric unit by a factor of 1.6.

Here we describe a simple and complete solution to the problem for any symmetries, based on Dirichlet domains (Coxeter, 1961), and show that the boundaries of the asymmetric units are in fact linear in terms of the rotation-matrix elements.

Derivation

A set of points, V, in space can be used to divide that space into convex regions called Dirichlet domains or Voronoi polyhedra (Coxeter, 1961). Each point in space is assigned to a domain according to which point in V it is nearest. The boundary between two adjacent domains in a plane is the perpendicular bisector of the line segment joining the respective points in V. If the space has space-group symmetry and the points in V are all related by symmetry, then the space becomes divided into crystallographically equivalent domains, each one representing an asymmetric unit of the space. An example for the two-dimensional plane group $p2gg$ is shown in Fig. 1. Dirichlet domains can also be used to partition three-dimensional rotation space with the distance between two rotations defined, according to Lattman (1972), as the magnitude of the angular rotation that separates them. The following analysis shows that this method of division is especially powerful for dividing a rotation function relating two Patterson functions into unique or asymmetric regions of space.

(*A*) *Symmetry-equivalent points in rotation space*

Let the rotation function, F, between a fixed Patterson function, $P_1(\mathbf{x})$, and a rotated Patterson function, $P_2(R\mathbf{x})$, be written as a function of the

* Rotation-function peaks related by cubic symmetry may not have identical magnitudes, since sampling occurs on an Eulerian grid that does not obey cubic symmetry.

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rotation R,

$$F(R) = \int P_1(\mathbf{x}) P_2(R\mathbf{x})\, d\mathbf{x} \qquad (1)$$

with the integration performed over a spherical region. If ${}^iS$ are the n elements of the proper rotation-symmetry group of P_1 and ${}^jT$ are the m elements of the symmetry group of P_2, then

$$P_1(\mathbf{x}) = P_1({}^iS\mathbf{x}) \qquad (2)$$

and

$$P_2(R\mathbf{x}) = P_2[R({}^jT)\mathbf{x}]. \qquad (3)$$

Equations (1), (2) and (3) give

$$F(R) = \int P_1({}^iS\mathbf{x}) P_2[R({}^jT)\mathbf{x}]\, d\mathbf{x}. \qquad (4)$$

Since both functions P_1 and P_2 can be rotated simultaneously by ${}^iS^{-1}$ without affecting the integral,

$$F(R) = \int P_1(\mathbf{x}) P_2[{}^iS^{-1}R({}^jT)\mathbf{x}]\, d\mathbf{x}. \qquad (5)$$

Comparing (1) and (5) and dropping the inverse notation,* one obtains

$$F(R) = F[{}^iSR({}^jT)]. \qquad (6)$$

Equation (6) describes the symmetry of the rotation function, F, in rotation space; equivalent equations were described by Tollin *et al.* (1966), Burdina (1970) and Moss (1985).

* $({}^iS)^{-1}$ must also be an element of S.

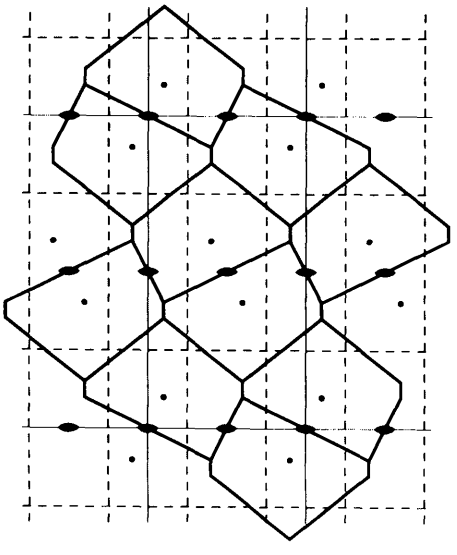

Fig. 1. Division of a plane with $p2gg$ plane-group symmetry into Dirichlet domains, each of which represents an asymmetric unit. The plane is partitioned according to the shortest distance to one of the symmetry-related points shown by solid circles. The glide planes are indicated by dashed lines.

Given an arbitrary* rotation, Q, the set of $n \times m$ rotations ${}^iSQ({}^jT)$ constitute a set of points in rotation space that are related by rotation-function symmetry. These points will be the Dirichlet points, V, which partition rotation space into $n \times m$ unique regions.

(B) *Distance in rotation space*

The difference, D, in rotation space between two rotations ${}^1R$ and ${}^2R$ may be written as

$${}^2R = D({}^1R); \qquad D = {}^2R({}^1R)^{-1} = {}^2R({}^1R)^T. \qquad (7)$$

If D is represented as a matrix, then the angular distance, κ, between ${}^1R$ and ${}^2R$ satisfies

$$1 + 2\cos\kappa = \mathrm{tr}\,(D) = \mathrm{tr}\,[{}^2R({}^1R)^T], \qquad (8)$$

where tr denotes the trace (*i.e.* the sum of the diagonal elements). Furthermore, since the trace of a product is equal to the sum of the products of all corresponding elements [$\mathrm{tr}\,(AB) = \sum_{ij} A_{ij}B_{ji}$],

$$1 + 2\cos\kappa = \sum_{kl} {}^2R_{kl}({}^1R_{kl}). \qquad (9)$$

Note that a small angular difference, κ, corresponds to a large value of the contracted product $\sum_{kl} {}^2R_{kl}({}^1R_{kl})$.

(C) *Partitioning rotation-function space*

Equation (9) allows us to calculate with ease the angular distance κ between an arbitrary rotation R and each of the symmetry-related rotations ${}^iSQ({}^jT)$, the elements of V. If the members of V are denoted by

$${}^iV^j = {}^iSQ({}^jT), \qquad (10)$$

then assigning an arbitrary rotation R to a domain simplifies to the problem of finding the member of V, ${}^iV^j$, for which the corresponding angular distance κ is a minimum or, by (8), for which

$$\sum_{kl} {}^iV^j{}_{kl}R_{kl} \text{ is a maximum.} \qquad (11)$$

A particular asymmetric region (i, j) of rotation space is therefore defined by a set of inequalities that are linear in terms of the rotation-matrix elements, R_{kl},

$$\sum_{kl} {}^iV^j{}_{kl}R_{kl} \geq \sum_{kl} {}^pV^q{}_{kl}R_{kl} \quad (p, q \neq i, j). \qquad (12)$$

(D) *Cross-rotation function with a model Patterson function*

When one of the Patterson functions (say P_2) has no rotational symmetry, we may choose the rotation Q, which generates the set V, to be the identity matrix and the members of V are simply the members of S by (10). For this case, the problem of partitioning rotation space into asymmetric units reduces to a

* Restrictions on Q when P_1 and P_2 both have rotational symmetry are discussed later.

question of identifying which symmetry operation, ${}^iS$, gives the maximum value of $\sum_{kl} ({}^iS)_{kl} R_{kl}$ for each rotation R. Consider as an example a rotation function between a model Patterson function and an observed Patterson function with cubic octahedral symmetry. If rotation space is parameterized in terms of Eulerian angles, then, for each point on a grid of angles, the rotation matrix R can be calculated and classified into one of the 24 Dirichlet domains according to which one of the 24 symmetry operators in S gives the largest contracted product [(11)] with R. The rotation function would then only be evaluated (or reported) for grid points that fell inside one prechosen domain. Fig. 2 shows the partitioning of rotation space in a section through Eulerian space for the case of octahedral symmetry.

The method applies equally well to lower symmetries. For a rotation function between a model Patterson function with $\bar{1}$ symmetry and a Patterson function in an axial or dihedral group, domain boundaries that are linear in terms of Eulerian angles are obtained when Q is chosen with $\beta = 0$. If the symmetric Patterson function has a symmetry axis of order n parallel to the z axis and Q is the identity rotation then one of the Dirichlet domains is described by

$$-\pi/n \leq (\alpha + \gamma) \leq \pi/n. \qquad (13)$$

Note that $\alpha + \gamma$ is equivalent to the pseudo-Eulerian angle θ_+ introduced by Lattman (1972). For a dihedral group, the domain is further restricted to $0 \leq \beta \leq \pi/2$.

(E) *Rotation function between two symmetric Patterson functions*

If the Patterson functions P_1 and P_2 both have rotational symmetry then the rotation Q may not be chosen arbitrarily, since all ${}^iV^j = {}^iSQ({}^jT)$ must be unique. In particular, if P_1 and P_2 have any symmetry operations (other than the identity transformation) in common, then Q cannot be the identity matrix. For practical purposes, Q may be chosen to be a small rotation about an oblique axis.* Given the choice of Q, the members of V can be calculated according to (10) and points R in rotation space can be classified by (11) as before. The only real difference from the previous case is that now the matrix elements of ${}^iV^j$ are not generally zero or unity but this presents no difficulty. Fig. 3 shows one possible partitioning of rotation space in a section though Eulerian space for a cross-rotation function between Patterson functions with cubic tetrahedral ($n = 12$) and C_3 ($m = 3$) symmetries. Different choices for the 'generating matrix' Q lead to different but equally valid partitionings of rotation space. Q is a member of V and, in fact, any member of V may be considered to be the matrix Q.

For cross-rotation functions between Patterson functions with cyclic or dihedral symmetry, certain special choices for Q may produce domain boundaries that are linear in terms of Eulerian angles, but these domains are generally more complicated than those described by Rao *et al.* (1980) and Moss (1985). For cubic symmetry, the domain boundaries cannot be made linear in Eulerian space but they are still linear in terms of the rotation-matrix elements.

(F) *Self-rotation function*

Moss (1985) was the first to point out the additional symmetry that arises when the two Patterson

* The formal restriction on Q is that it cannot relate any element of P_1 to any element of P_2 by a similarity transformation, ${}^iS \neq Q^{-1}({}^jT)Q$.

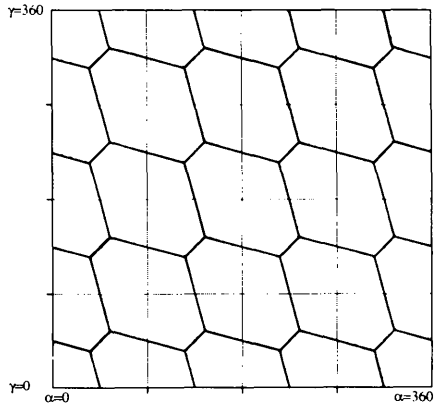

Fig. 2. Partitioning of rotation space as seen in a section of constant β (=60°) for a rotation function between symmetries O (432) and C_1. Rotation space is divided into 24 asymmetric regions or Dirichlet domains, 16 of which are visible in this section of Eulerian-angle space.

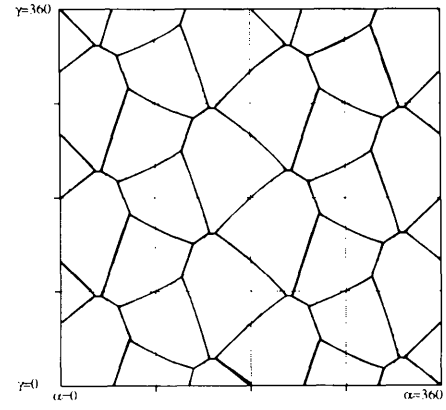

Fig. 3. Partitioning of rotation space in a section of constant β (=90°) for a rotation function between Patterson functions with tetrahedral cubic ($n = 12$) and C_3 ($m = 3$) symmetries. Of the 36 asymmetric regions, 24 are visible in this section. The generating matrix Q (see text) corresponds to the Eulerian angles (30, 30, 30°).

functions being compared are identical. If $P_1 = P_2$,

$$F(R) = F(R^{-1}). \quad (14)$$

This introduces a twofold increase in symmetry and a related set of Dirichlet points must be included,

$$[{}^iSQ({}^jS)]^{-1} = ({}^iV^j)^{-1} = ({}^iV^j)^T. \quad (15)$$

These $({}^iV^j)^T$ and the original ${}^iV^j$ lead to $2n^2$ asymmetric domains.

Concluding remarks

A rotation function between two Patterson functions with arbitrarily high symmetry can be divided easily into unique or asymmetric regions by an approach based on Dirichlet domains. If the rotational-symmetry groups of the two Patterson functions are of order n and m then rotation space is partitioned into $n \times m$ equivalent domains; for a self-rotation function, the number of equivalent domains is $2n^2$. The generality of the method makes it applicable to cubic space groups, for which the problem of the rotation-function asymmetric unit was previously unsolved. Because the analysis is cast in terms of rotation matrices, it is independent of the particular choice of Eulerian-angle conventions. For example, two programs using different angle conventions can be made to refer to the same asymmetric region of rotation space. The method also applies to point-group symmetries that are not crystallographic (*e.g.* icosahedral) and generalizes to rotations in higher-dimensional space.

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Combined X-ray Single-Crystal and Neutron Powder Refinement of Modulated Structures and Application to the Incommensurately Modulated Structure of $Bi_2Sr_2CaCu_2O_{8+y}$

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Abstract

A method is described for the refinement of modulated structures from a combined set of single-crystal and powder diffraction data or from powder data only. The method is especially useful when information on light atoms is to be obtained and no single crystals of suitable size for neutron diffraction are available. The program in which the method is encoded allows for differences in composition between the single-crystal and powder samples. Application to the incommensurately modulated superconductor $Bi_2Sr_2CaCu_2O_{8+y}$ (2212) using powder neutron and single-crystal X-ray data confirms that the oxygen modulation in the Bi-O layer is sawtooth-like, as observed in the preceding study based solely on X-ray data [Petricek, Gao, Lee & Coppens (1990). *Phys. Rev. B*, **42**, 387-392], but with improved accuracy in the resulting parameters. The extra oxygen content is explicitly related to the modulation model and corresponds to 0.14 (4) per formula unit. With the refined site occupancies for the heavy atoms and the results of an anomalous-scattering study on the bismuth distribution [Coppens, Lee, Gao & Sheu (1991). *J. Phys. Chem. Solids*, **52**, 1267-1272], a copper valency of 2.31 is obtained for the single-crystal sample. The powder value of 2.40 is somewhat less reliable as no anomalous-scattering data are available for the powder sample.

Introduction

The widespread occurrence of incommensurate modulations in the high-T_c superconducting phases

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