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Representation of the Fast-Rotation Function in a Polar Coordinate System

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Crowther's fast-rotation function [Crowther (1972), *The Molecular Replacement Method,* edited by M. G. Rossmann, pp. 173–183. New York: Gordon & Breach] expression has been modified in a manner in which it is convenient to explore spherical polar coordinates rather than Eulerian angles.

The 'rotation function' (Rossmann & Blow, 1962) has been widely used in the initial stages of the solution of protein structures. The computation of this function (Tollin & Rossmann, 1966) is, however, exceedingly time consuming. Crowther (1972) has shown that the same function can be computed very much faster in Eulerian space when each Patterson function is expanded as a product sum of spherical harmonics and spherical Bessel functions. It is, however, often convenient to plot the rotation function in terms of spherical coordinates where specific sections represent searches for specific rotation axes (*e.g.* diads, triads *etc.*). Shown here is how Crowther's fast-rotation function can be easily recast in terms of spherical coordinates, necessitating only minor changes in the corresponding computer program. This is done by applying Eulerian rotations to *both* Patterson functions such that the third rotation is relative to a polar axis.

Rossmann & Blow (1962) defined the rotation function as the integral of the product of the Patterson function $P_1(\mathbf{x})$ and the rotated Patterson function $\mathscr{R}P_2(\mathbf{x})$ such that

$$R(\Omega) = \int_U \{P_1(\mathbf{x})\} \{\mathscr{R}P_2(\mathbf{x})\} \mathrm{d}V,$$

where Ω is the angle of rotation, the integral is evaluated within a volume U, and $\mathrm{d}V$ is an elementary unit of volume. If the rotation $\mathscr{R}$ is expressed in terms of Eulerian angles α, β, γ as defined by Rossmann & Blow (1962), and if the first Patterson function is also rotated by $\alpha, \beta, 0$ then

$$R(\alpha, \beta, \gamma) = \int_U \{\mathscr{R}(\alpha, \beta, \gamma = 0)P_1(\mathbf{x})\} \{\mathscr{R}(\alpha, \beta, \gamma)P_2(\mathbf{x})\} \mathrm{d}V$$

$$= \int_U \{P_1(\mathbf{x})\} \{\mathscr{R}^{-1}(\alpha, \beta, \gamma = 0)\mathscr{R}(\alpha, \beta, \gamma)P_2(\mathbf{x})\} \mathrm{d}V.$$

But

$$\mathscr{R}^{-1}(\alpha, \beta, \gamma = 0)\mathscr{R}(\alpha, \beta, \gamma) = \mathscr{R}'(\gamma, \beta, \alpha) \equiv \mathscr{R}_p(\varphi, \psi, \kappa)$$

(see Table 1 for derivation of equivalency), where $\mathscr{R}_p(\varphi,\psi,\kappa)$ is a rotation in polar coordinates by an angle $\kappa=\gamma$ about an axis whose inclination ψ from the positive X_3 axis is equal to β and whose projection onto the (X_1,X_2) plane makes an angle $\varphi=\alpha+\pi$ with X_2 (Fig. 1). With Crowther's definition of Eulerian angles, $\alpha=\pi/2+\varphi$.

If U represents a sphere, then, following Crowther (1972), we can express the value of each Patterson function at the polar coordinates (r,θ,φ) by

$$P_1(r,\theta,\varphi) = \sum_{lmn} a^*_{lmn}\hat{j}_l(k_{ln}r)\hat{Y}^{m*}_l(\theta,\varphi),$$

and

$$P_2(r,\theta,\varphi) = \sum_{l'm'n'} b_{l'm'n'}\hat{j}_{l'}(k_{l'n'}r)\hat{Y}^{m'}_{l'}(\theta,\varphi).$$

Here $\hat{Y}^m_l(\theta,\varphi)$ is the normalized spherical harmonic of order l, $\hat{j}_l(k_{ln}r)$ is the normalized spherical Bessel function of order l, and a_{lmn}, b_{lmn} are complex coefficients.

The rotated spherical harmonic can then be expressed as

$$\mathscr{R}(\alpha,\beta,\gamma)Y^m_l(\theta,\varphi) = \sum_{q=-l}^{l} D^l_{qm}(\alpha,\beta,\gamma)\hat{Y}^q_l(\theta,\varphi),$$

where $D^l_{qm}(\alpha,\beta,\gamma)=e^{iq\gamma}d^l_{qm}(\beta)e^{im\alpha}$, and $d^l_{qm}(\beta)$ are the matrix elements of the three-dimensional rotation group. It then follows that

$$R(\kappa,\psi,\pi+\varphi)=R(\alpha,\beta,\gamma)$$

$$= \int_U \{\sum_{lmn} a^*_{lmn}\hat{j}_l(k_{ln}r)\mathscr{R}(\alpha,\beta,\gamma=0)\hat{Y}^{m*}_l(\theta,\varphi)\}$$

$$\times \{\sum_{l'm'n'} b_{l'm'n'}\hat{j}_{l'}(k_{l'n'}r)\mathscr{R}(\alpha,\beta,\gamma)\hat{Y}^{m'}_{l'}(\theta,\varphi)\}dV$$

$$= \int_U \{\sum_{lmn} a^*_{lmn}\hat{j}_l(k_{ln}r)[\sum_q D^{l*}_{qm}(\alpha,\beta,\gamma=0)\hat{Y}^{q*}_l(\theta,\varphi)]$$

$$\times \{\sum_{l'm'n'} b_{l'm'n'}\hat{j}_{l'}(k_{l'n'}r)[\sum_{q'} D^{l'}_{q'm'}(\alpha,\beta,\gamma)\hat{Y}^{q'}_{l'}(\theta,\varphi)]\}dV.$$
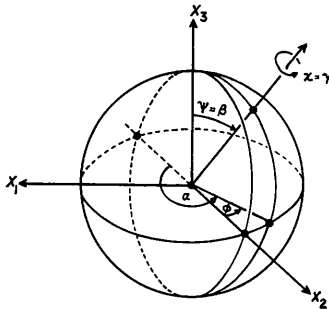

Fig. 1. The variables ψ and $\alpha=\pi+\varphi$, where ψ and φ are polar coordinates which specify a direction about which the axes may be rotated through an angle κ.

Table 1. *Derivation of* $\mathscr{R}^{-1}(\alpha,\beta,\gamma=0)\mathscr{R}(\alpha,\beta,\gamma)=\mathscr{R}'(\alpha,\beta,\gamma)\equiv\mathscr{R}_p(\varphi,\psi,\kappa)$

$\mathscr{R}'(\alpha,\beta,\gamma=0)\equiv\mathscr{R}(\alpha,\beta,\gamma)$

$=\mathscr{R}'(\gamma,\beta,\alpha)\equiv\mathscr{R}_p(\varphi,\psi,\kappa),$

With the orthogonality conditions discussed by Crowther (1972) this reduces to

$$R(\kappa, \psi, \pi + \varphi)$$
$$= \sum_{lmm'} (\sum_n a^*_{lmn} b_{lm'n}) \sum_q d^l_{qm}(\beta) d^l_{qm'}(\beta) e^{i\gamma q} e^{i(m'-m)\alpha}.$$

Now substituting the equivalent polar angles for the Eulerian angles

$$R(\kappa, \psi, \varphi) = \sum_{lmm'} (\sum_n a^*_{lmn} b_{lm'n})$$
$$\times \sum_q d^l_{qm}(\psi) d^l_{qm'}(\psi) e^{i\kappa q} e^{i(m'-m)\varphi}(-1)^{(m'-m)}. \quad (1)$$

This result should be compared with that of Crowther's which corresponds to the special case where the Patterson function $P_1(x)$ remains stationary. In that case

$$R(\alpha, \beta, \gamma) = \sum_{lmm'} (\sum_n a^*_{lmn} b_{lm'n}) d^l_{m'm}(\beta) e^{im'\gamma} e^{im\alpha}. \quad (2)$$

The small modification which will be necessary to alter the Crowther fast-rotation function program to use

spherical coordinates can be seen by comparing expressions (1) and (2).

The procedure has been satisfactorily tested by comparing the results of a 'slow' rotation function with a modified 'fast' rotation function program.

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The Role of Coulombic Interactions in Explaining the Anomalous Structure of Pentaphenylantimony

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The observation of anomalous square-pyramidal geometry for pentaphenylantimony, $(C_6H_5)_5Sb$, has long been rationalized as a packing effect. The analogous P and As molecules are trigonal-bipyramidal in the solid state as expected. In this work calculations have been made of the energies resulting from intra- and intermolecular nonbonded interactions in both observed and hypothetical crystal structures of square-pyramidal and trigonal-bipyramidal pentaphenylantimony, pentaphenylarsenic, and pentaphenylphosphorus in order to determine if the solid state does indeed stabilize a non-equilibrium molecular geometry of $(C_6H_5)_5Sb$, and if so, how much energy is involved. The energies have been taken as pairwise sums over nonbonded atoms; the atom–atom potential functions used include repulsive, van der Waals, and Coulombic terms. Results of these calculations have been compared with work in which the potential functions did not include such $1/r$ terms. Both observed and hypothetical structures of all three molecules lie in true minima of the energy surface with respect to variations in cell constants and molecular position and orientation whether or not electrostatic terms are included. However, only the potential functions with Coulombic terms predict the crystallization of pentaphenylantimony as a square pyramid. The lattice-energy stabilization is then calculated to be about 15 kJ mol^{-1}.

Introduction

Considerable attention has been focused on pentaphenylantimony, $(C_6H_5)_5Sb$, since its observed geometries, square-pyramidal in one crystal form and trigonal-bipyramidal in another (a cyclohexane solvate) are thought to be strongly influenced by crystal packing forces. A comparison of the five known X-ray structures of penta-aryl Group V molecules (Brock & Webster, 1976) shows that $(C_6H_5)_5Sb$ is alone in exhibiting a square-pyramidal form. It is, in fact, unique among all five-coordinate molecules having identical ligands and a spherical shell of d-electrons in displaying a non-trigonal-bipyramidal geometry.

Since the results of solid-state structure determinations are often used to interpret molecular behavior in the gaseous and liquid states, it is important to understand the extent to which crystal packing forces may influence molecular geometry. In this and previous work (Brock & Ibers, 1976) an attempt has been made