SHORT COMMUNICATIONS

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Chirality in rotational superposition.

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Abstract

It is shown that in the rotational superposition method proposed by Diamond (1988), which always produces orthogonal transformations with positive determinants, a simple test exists for the existence of an enantiomorphic relationship between the vector sets, and, if required, an enantiomorphous orthogonal superposition may be provided at no extra cost.

In a recently published paper [(Diamond, 1988), here referred to as (I)] an analysis of the rotational superposition problem was presented using the quaternion variables, in terms of which the quadratic residual after rotational fitting was shown to be a quadratic form of order four. It was also shown that the orthogonal transformations so generated necessarily have positive determinants even if the vector sets to be superposed have opposite chirality: a situation which may be troublesome to other methods.

In the notation of that paper it was shown that if a vector set **x** is to be superimposed on **X** using an orthogonal transformation, **R**, with positive determinant, so as best to satisfy

$$\mathbf{X} = \mathbf{R}\mathbf{x}, \tag{1}$$

then **R** may be constructed from a four-dimensional vector, $\boldsymbol{\rho}$ (a unit quaternion), which is the eigenvector of largest eigenvalue of a matrix **P** which, in turn, is constructed from the three-row rectangular matrices **X** and **x**.

If the eigenvalues of **P** are p_1 through p_4, arranged in descending order, with associated eigenvectors $\boldsymbol{\rho}_1$ through $\boldsymbol{\rho}_4$, then, from equation (23) of (I),

$$E_{\min} = E_0 - 2p_1 \tag{2}$$

where

$$\begin{aligned} E &= \sum W(\mathbf{X} - \mathbf{R}\mathbf{x}).(\mathbf{X} - \mathbf{R}\mathbf{x}) \\ E_0 &= \sum W(\mathbf{X} - \mathbf{x}).(\mathbf{X} - \mathbf{x}) \end{aligned} \tag{3}$$

with weights W, in which **x** and **X** are, for the moment, treated as individual corresponding column vectors.

If we use a prime to denote the fitting, by proper rotation, of $\mathbf{R}'\mathbf{x}$ onto $-\mathbf{X}$, the enantiomer of **X**, then likewise

$$\begin{aligned} E' &= \sum W(\mathbf{X} + \mathbf{R}'\mathbf{x}).(\mathbf{X} + \mathbf{R}'\mathbf{x}) \\ E'_0 &= \sum W(\mathbf{X} + \mathbf{x}).(\mathbf{X} + \mathbf{x}) \end{aligned} \tag{4}$$

$$E'_{\min} = E'_0 - 2p'_1. \tag{5}$$

However, negating **X** or **x**, but not both, negates **P** and therefore all of its eigenvalues, so that

$$p'_1 = -p_4. \tag{6}$$

Equations (3) and (4) give

$$\begin{aligned} E_0 &= \mathrm{tr}[(\mathbf{X} - \mathbf{x})\mathbf{W}(\mathbf{X}^T - \mathbf{x}^T)] \\ &= \mathrm{tr}(\mathbf{X}\mathbf{W}\mathbf{X}^T) - 2\mathrm{tr}(\mathbf{x}\mathbf{W}\mathbf{X}^T) + \mathrm{tr}(\mathbf{x}\mathbf{W}\mathbf{x}^T) \\ E'_0 &= \mathrm{tr}[(\mathbf{X} + \mathbf{x})\mathbf{W}(\mathbf{X}^T + \mathbf{x}^T)] \\ &= \mathrm{tr}(\mathbf{X}\mathbf{W}\mathbf{X}^T) + 2\mathrm{tr}(\mathbf{x}\mathbf{W}\mathbf{X}^T) + \mathrm{tr}(\mathbf{x}\mathbf{W}\mathbf{x}^T) \end{aligned} \tag{7}$$

in which **x** and **X** are again rectangular and **W** is diagonal. Therefore

$$E'_{\min} - E_{\min} = 4\mathrm{tr}(\mathbf{x}\mathbf{W}\mathbf{X}^T) + 2p_1 + 2p_4. \tag{8}$$

But

$$\begin{aligned} p_1 + p_2 + p_3 + p_4 &= \mathrm{tr}\mathbf{P} = \mathrm{tr}\mathbf{Q} \\ &= \mathrm{tr}\mathbf{M} + \mathrm{tr}\mathbf{M}^T - 2\mathrm{tr}\mathbf{I}.\mathrm{tr}\mathbf{M} \\ &= -4\mathrm{tr}(\mathbf{x}\mathbf{W}\mathbf{X}^T) \end{aligned} \tag{9}$$

from equations (17) and (22) of (I). Therefore

$$E'_{\min} - E_{\min} = p_1 - p_2 - p_3 + p_4. \tag{10}$$

Thus, if the right-hand side of (10) is negative it is certain that **x** can be superimposed on $-\mathbf{X}$ more closely than on **X**, which fact may thus be established before transforming any coordinates. Furthermore, the associated rotation matrix, $\mathbf{R}'$, may be constructed from $\boldsymbol{\rho}_4$ in the same way that **R** is constructed from $\boldsymbol{\rho}_1$ using equation (7) of (I). Routines used to find p_1 normally provide all eigenvalues anyway.

Reference

DIAMOND, R. (1988). *Acta Cryst.* A**44**, 211–216.

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