Acta Cryst. (1984). A**40**, 165–166

Quaternion transformation of molecular orientation.

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(*Received* 20 *September* 1983; *accepted* 24 *October* 1983)

Abstract

For comparing two molecules, since the most general positional relationship is the combination of a translation and a rotation, where the translational component can be removed by referring both molecules to their centres of gravity, a rotation taking one to the other must be found. Rather than using a 3×3 rotation matrix, it is better to represent the rotation by a unit quaternion, since the equations to be solved to find, by least squares, the best quaternion, are linear.

The comparison of two molecules, or parts of molecules or groups of atoms, has frequently been discussed, since the rotation matrix describing a rotation through an angle θ about an axis with direction cosines l, m, n, although it requires only three parameters, is excessively cumbrous. Given the two set of corresponding coordinates the derivation of the best matrix is also tedious. The rotation matrix (for a pure rotation without dilatation) is

$$[R]=\begin{bmatrix} ll(1-\cos\theta)+\cos\theta, & ml(1-\cos\theta)+n\sin\theta, & nl(1-\cos\theta)-m\sin\theta \\ lm(1-\cos\theta)-n\sin\theta, & mm(1-\cos\theta)+\cos\theta, & nm(1-\cos\theta)+l\sin\theta \\ ln(1-\cos\theta)+m\sin\theta, & mn(1-\cos\theta)-l\sin\theta, & nn(1-\cos\theta)+\cos\theta \end{bmatrix} \quad (1)$$

Quaternions have long been employed for describing rotations. Bernal (1923), for example, used them for deriving the 230 space groups, but the method has remained somewhat unfamiliar. There are advantages in quaternions for describing the rotations of many-jointed robot arms and they are thus suitable for dealing with related molecular systems like protein chains.

The problem of finding the 3×3 matrix $[R]$ describing a pure rotation has been approached in a number of ways. For example:

(*a*) by Dollase (1974), who used a concatenation of infinitesimal rotations;

(*b*) by Kabsch (1978), who has implemented a rigorous procedure, at the cost of considerable complexity;

(*c*) by Mackay (1977), who used the generalized inverse to obtain a general affine transformation $[A]$ with nine fitted parameters which could be reduced, if necessary, to two rotations, S and R, and a dilation, L, by solving $A=SLS^TR$.

In order to compare two molecules geometrically, it is necessary to superimpose them as nearly as possible, so that the r.m.s. distance between corresponding atoms should be a minimum. It has been shown that reduction of the two coordinate systems to origins at the centres of gravity of the two molecules is the appropriate preliminary. The problem lies in then choosing the best rotation with the appropriate values of θ and l, m, n, the direction cosines (of which only two are independent).

Rooney (1977) has compared the various systems of describing rotations and has conveniently collected the relevant formulae.

A quaternion Q consists of four numbers, a scalar p_s and a vector $\mathbf{p}$ which can be resolved along the orthogonal unit vectors $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$. A unit quaternion with a unit norm $(p_s^2+|\mathbf{p}|^2)=1$ relates two unit vectors $\mathbf{r}'$ and $\mathbf{r}$, rotating $\mathbf{r}$ to $\mathbf{r}'$ by a rotation θ about an axis with direction cosines l, m, n. Q is not uniquely defined by one pair of related vectors since the axis of rotation relating them could lie anywhere in the plane of symmetry, so that several pairs $\mathbf{r}'$ and $\mathbf{r}$ are necessary for finding Q. $\mathbf{r}'$ and $\mathbf{r}$ are related by $\mathbf{r}'=Q^{-1}\mathbf{r}Q$, where

$$Q=\cos\theta/2+l\sin\theta/2\mathbf{i}+m\sin\theta/2\mathbf{j}+n\sin\theta/2\mathbf{k}$$

and

$$Q^{-1}=\cos\theta/2-l\sin\theta/2\mathbf{i}-m\sin\theta/2\mathbf{j}-n\sin\theta/2\mathbf{k}.$$

$Q^{-1}Q=1$ and $Q=\cos\theta/2+\sin\theta/2\mathbf{n}$, where $\mathbf{n}$ is the unit vector along the rotation axis.

Two quaternions give a (non-commutative) product which is a quaternion. Hamilton's conditions, $i^2=j^2=k^2=-1$, $ij=-ji$, $ij=k$, *etc.*, being applied to simplify the product. The quaternion product of two vectors $\mathbf{R}_1$ and $\mathbf{R}_2$ is $\mathbf{R}_1\mathbf{R}_2=-\mathbf{R}_1\,.\,\mathbf{R}_2+\mathbf{R}_1\times\mathbf{R}_2$, where the terms are the normal scalar and vector products. The product of two quaternions P and Q is

$$PQ=(p_sq_s-\mathbf{p}\,.\,\mathbf{q})+(p_s\mathbf{q}+q_s\mathbf{q}+\mathbf{p}\times\mathbf{q}).$$

The product of a quaternion with a vector is

$$Q\mathbf{r}=(-\mathbf{q}\,.\,\mathbf{r})+(q_s\mathbf{r}+\mathbf{q}\times\mathbf{r})$$

and

$$\mathbf{r}P=(-\mathbf{r}\,.\,\mathbf{p})+(p_s\mathbf{r}+\mathbf{r}\times\mathbf{p})$$

so that

$$\begin{aligned} Q\mathbf{r}P=&[-q_s(\mathbf{p}\,.\,\mathbf{r})-p_s(\mathbf{q}\,.\,\mathbf{r})-\mathbf{q}\,.\,\mathbf{r}\times\mathbf{p}]\\ &+[q_sp_s\mathbf{r}+q_s(\mathbf{r}\times\mathbf{p})-(\mathbf{r}\,.\,\mathbf{p})\mathbf{q}\\ &+p_s(\mathbf{q}\times\mathbf{r})+(\mathbf{q}\,.\,\mathbf{p})\mathbf{r}-(\mathbf{q}\,.\,\mathbf{r})\mathbf{p}], \end{aligned}$$

i.e. [a scalar part]+[a vector part], thus, if $Q=\cos\theta/2+\sin\theta/2\mathbf{n}$ and $Q^{-1}=\cos\theta/2-\sin\theta/2\mathbf{n}$,

$$\begin{aligned} \mathbf{r}'=Q^{-1}\mathbf{r}Q=&(\cos^2\theta/2-\sin^2\theta/2)\mathbf{r}\\ &-\sin\theta(\mathbf{n}\times\mathbf{r})+2\sin^2\theta/2(\mathbf{n}\,.\,\mathbf{r})\mathbf{n}, \end{aligned}$$

the scalar part is zero. This expression is needed for calculating $\mathbf{r}'$ from $\mathbf{r}$ for each atom when θ and l, m, n have been found, although the rotation matrix $[R]$ [from (1) above] could be used instead.

0108-7673/84/020165-02$01.50

To find θ and l, m, n we begin with $Q\mathbf{r}'=\mathbf{r}Q$ (since $Q^{-1}Q=1$) so that

$$\mathbf{q}\,.\,\mathbf{r}'+\mathbf{q}\times\mathbf{r}'+q_s\mathbf{r}'=q_s\mathbf{r}+\mathbf{q}\,.\,\mathbf{r}-\mathbf{q}\times\mathbf{r}$$

$$\therefore\quad \mathbf{q}\,.\,(\mathbf{r}'-\mathbf{r})+q_s(\mathbf{r}'-\mathbf{r})+\mathbf{q}\times(\mathbf{r}'+\mathbf{r})=0.$$

Equating parts: $\mathbf{q}\,.\,(\mathbf{r}'-\mathbf{r})=0$, $q_s=\cos\theta/2$ and $|\mathbf{q}|=\sin\theta/2$, so that

$$(\mathbf{r}-\mathbf{r}')=\tan\theta/2\mathbf{n}\times(\mathbf{r}+\mathbf{r}').$$

Converting to orthonormal coordinates:

$$(x-x')\mathbf{i}+(y-y')\mathbf{j}+(z-z')\mathbf{k}$$
$$=\tan\theta/2\begin{vmatrix}\mathbf{i} & \mathbf{j} & \mathbf{k}\\ l & m & n\\ (x+x') & (y+y') & (z+z')\end{vmatrix}.$$

So that, finally, we have three linear equations for each pair of related atoms and thus $3N$ in all (if there are N pairs). Writing t for $\tan\theta/2$:

$$\begin{aligned} mt(z+z')-nt(y+y')&=(x'-x)\\ -lt(z+z')\qquad\qquad +nt(x+x')&=(y'-y)\\ lt(y+y')-mt(x+x')\qquad\qquad &=(z'-z).\end{aligned}$$

These $3N$ equations are then solved by the least-squares procedure $AX=H$ giving $X=[A^TA]^{-1}A^TH$ for the three unknowns, lt, mt and nt. $\tan^2\theta/2$ is obtained by squaring and adding these solutions. Division then gives l, m, n, the direction cosines. A value of θ between 0 and 180° is obtained, the procedure failing if $\theta=180°$, when $\tan\theta/2$ is infinite. When this case is detected a special procedure must be implemented as $Q=(1, 0, 0, 0)$, which is the same as the identity. Since the case of 180° rotation is frequent, this is the main disadvantage of the method. It may also be necessary to change the sign of θ since the positive square root is returned.

A straightforward program (in Basic) has been written to follow the procedure described. The two molecules are referred to their centres of gravity and the vectors to each atom from the centre of gravity are normalized to unity, the lengths being retained as weights for the least-squares procedure. Clearly, other weighting schemes could be applied also. The $3N$ linear equations are then set up and solved by least squares, the inversion of the 3×3 matrix being written explicitly. θ and l, m, n having been obtained, the second molecule can be rotated to the orientation of the first for comparison, the differences in the positions of corresponding atoms being printed out.

The program can be run on a microcomputer, such as a Sinclair Spectrum, and is useful for investigating quantitatively the symmetry of configurations as well as for comparing molecules. The program is normally run interactively, changes being made in the program to suit particular cases rather than writing sections for all possible contingencies. Copies are available on request as it comprises only about 150 lines.*

Quaternion algebra is thus recommended as an effective method of handling the rotation of molecules.

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* A listing of the program has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38938 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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