

Par ailleurs Ascher (1965) a énuméré les 31 classes 'pyroconductives' décrivant le symétrie ponctuelle des cristaux porteurs de courants électriques spontanés \mathbf{j} . On remarque que ces 31 classes sont comprises dans les 58 classes magnétoélectriques (au contraire les 31 classes pyroélectriques et les 31 classes pyromagnétiques ne sont pas toutes magnétoélectriques): les tenseurs magnétoélectriques Q_{ij} correspondants sont non symétriques. Dans les autres classes magnétoélectriques, les tenseurs magnétoélectriques sont symétriques.

Cette propriété s'interprète aisément. Dans une classe pyroconductive, un vecteur de Poynting $\mathbf{E} \times \mathbf{B}$ construit à partir d'un champ électrique \mathbf{E} et d'un champ magnétique \mathbf{B} est invariant. En effet $\mathbf{E} \times \mathbf{B}$ et \mathbf{j} se transforment de la même manière dans les opérations $\bar{1}$ (centrosymétrie) et $1'$ (renversement du temps).

Considérons alors une classe magnétoélectrique. Si le tenseur Q_{ij} correspondant est symétrique, on ne peut former aucun invariant magnétoélectrique antisymétrique du type $E_i B_j - E_j B_i$ ($i, j = x, y, z$), donc on ne peut construire aucun vecteur $\mathbf{E} \times \mathbf{B}$ ou \mathbf{j} invariant: la classe considérée n'est pas pyroconductive.

Considérons maintenant une classe magnétoélectrique dans laquelle le tenseur Q_{ij} n'est pas symétrique. On peut alors isoler la partie antisymétrique de Q_{ij} et former des invariants antisymétriques du type $E_i B_j - E_j B_i$. Par suite, la classe considérée est pyroconductive.

Ainsi dans la classe $4/m'$, le tenseur \mathbf{Q} a la forme:

$$\begin{pmatrix} Q_{11} & Q_{12} & 0 \\ -Q_{12} & Q_{11} & 0 \\ 0 & 0 & Q_{33} \end{pmatrix},$$

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Rapid comparison of protein structures. By A. D. McLACHLAN, MRC Laboratory of Molecular Biology, Hills Road, Cambridge CB2 2QH, England

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Abstract

An unusually fast method of superposing two sets of atomic coordinates for related molecular structures by least squares is described. It exploits the special nature of the problem and uses the method of conjugate gradients. The calculation takes about 0.003 s and is fast enough to be used in on-line graphics systems.

The object of this paper is to describe a very fast and simple iterative method for calculating the rigid-body rotations which are needed to match protein structures to one another. The analysis of structures often requires two sets of coordinates for a group of atoms to be compared by finding the rigid-body rotation and translation which matches them as closely as possible. This least-squares fitting approach has

d'où l'unique invariant antisymétrique $E_x B_y - E_y B_x = (\mathbf{E} \times \mathbf{B})_z$. Cette classe autorise donc l'existence de courants spontanés parallèles à l'axe z .

De même dans la classe $2'/m$, \mathbf{Q} a la forme:

$$\begin{pmatrix} 0 & 0 & Q_{13} \\ 0 & 0 & Q_{23} \\ Q_{31} & Q_{32} & 0 \end{pmatrix}$$

(en choisissant l'axe binaire parallèle à Oz), d'où les invariants antisymétriques $E_x B_z - E_z B_x = (\mathbf{E} \times \mathbf{B})_y$ et $E_y B_z - E_z B_y = (\mathbf{E} \times \mathbf{B})_x$. Cette classe autorise donc l'existence de courants spontanés parallèles au plan xy .

En conclusion, les classes magnétoélectriques dans lesquelles le tenseur \mathbf{Q} n'est pas symétrique sont pyroconductives: la forme de \mathbf{Q} indique la direction des courants spontanés autorisés.

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been used to compare closely-related proteins (Freer, Kraut, Robertus, Wright & Xuong, 1970; Huber, Epp, Steigemann & Formanek, 1971; Lesk & Chothia, 1980) or different functional forms of the same molecule (Baldwin & Chothia, 1979); to assess the validity of energy minimization methods (Cohen & Sternberg, 1980); and to superpose repeated structural elements within the same protein (McLachlan, 1972a). In simple one-to-one comparisons the time spent in the superposition calculation is unimportant, but more general methods involve multiple comparisons, with a systematic search for fragments of structure anywhere in one protein, A , which are similar to any part of a second protein, B (Rao & Rossmann, 1973; Rossmann & Argos, 1976, 1977; Remington & Matthews, 1978; McLachlan, 1979). Studies of this kind have been used to assess the significance of structural relationships between proteins which may have descended from a common evolutionary ancestor (Remington & Matthews, 1980; Schulz, 1980).

In a typical search it may be necessary to do as many as one million structural superpositions, and so a fast simple method of calculation is essential. The Eulerian angle procedures used to find the rigid-body rotations in earlier work (Rao & Rossmann, 1973; Remington & Matthews, 1978) were cumbersome and they have been superseded by matrix methods which calculated the rotation matrix \mathbf{R} from a special three by three matrix \mathbf{U} [defined below, equation (3)] which contains all the information necessary to solve the least-squares problem. In Remington & Matthews's zone comparison search the matrix \mathbf{U} can be updated very simply by adding a new atom to the end of the existing zone for each fragment, A or B , and removing one from the beginning of the zone (McLachlan, 1979). This corresponds to moving one step down a diagonal of the comparison matrix. The rate-limiting step in the calculation is now the solution of the rotation problem. Several approaches have been tried. One is through least-squares matrix methods and the generalized inverse matrix of the atomic coordinates (Diamond, 1966, 1976; Mackay, 1977; Penrose, 1955). Another deals directly with the \mathbf{U} matrix (McLachlan, 1972*b*). Thus Kabsch (1976, 1978) described a fast procedure which uses the square root of the matrix $\mathbf{U}'\mathbf{U}$ (\mathbf{U}' is the transpose of \mathbf{U}), and McLachlan (1979) later described a fast method which uses the eigenvalues and eigenvectors of a six by six partitioned matrix constructed from \mathbf{U} and \mathbf{U}' . This last method even allows the root-mean-square distance between two sets of coordinates to be obtained by a minimum of calculation without the need to calculate the rotation \mathbf{R} .

The new method described below seems to be the fastest yet devised for zone comparison calculations where the rotation matrix \mathbf{R} is required. It is a simple iterative procedure based on the well-known conjugate gradient minimization method (Hestenes & Stiefel, 1952; Fletcher & Powell, 1963; Fletcher & Reeves, 1964; Walsh, 1975). It uses a succession of finite rotations about conjugate axes. For each chosen axis the rotation angle required to reach the local minimum around that axis can be calculated exactly in one simple step. The method is therefore particularly simple and only needs an elementary computer program. The mathematical basis has much in common with previous methods (McLachlan, 1972*b*, 1979).

Let $\mathbf{a}_n, \mathbf{b}_n$, ($n = 1, \dots, N$) be the position vectors of two sets of atoms from molecular fragments A and B , and w_n be a weight for each atom. We wish to find an orthogonal proper rotation matrix \mathbf{R} with determinant +1, and a translation vector \mathbf{t} which converts the coordinates \mathbf{a}_{in} ($i = 1, 2, 3$) to

$$\mathbf{r}_{in} = \sum_j R_{ij} \mathbf{a}_{jn} + \mathbf{t}_i \quad (1)$$

and minimizes the residual

$$E = \frac{1}{2} \sum_n w_n (\mathbf{r}_n - \mathbf{b}_n)^2. \quad (2)$$

The best translation \mathbf{t} is that which superimposes the centroids of both sets of atoms. The common centroid is chosen as the origin of coordinates. The rotation is derived by considering two special matrices \mathbf{U} and $\mathbf{V} = \mathbf{R}\mathbf{U}$:

$$U_{ij} = \sum_n w_n a_{in} b_{jn}, \quad V_{ij} = \sum_n w_n r_{in} b_{jn}. \quad (3)$$

Since $\mathbf{r}_n^2 = a_n^2$ the residual can be written

$$E = \frac{1}{2} \sum_n w_n (\mathbf{a}_n^2 + \mathbf{b}_n^2) - v, \quad (4)$$

where v is the diagonal sum

$$v = V_{11} + V_{22} + V_{33} = \sum_n w_n \mathbf{r}_n \cdot \mathbf{b}_n. \quad (5)$$

Suppose that we apply a rotation \mathbf{R} followed by a further finite rotation \mathbf{Q} through a variable angle θ about a chosen direction \mathbf{l} . The position vector \mathbf{r} of any atom before the rotation can be resolved into a parallel component $(\mathbf{r} \cdot \mathbf{l}) \mathbf{l}$ and a perpendicular one $-\mathbf{l} \times (\mathbf{l} \times \mathbf{r})$. The rotated position then becomes

$$\mathbf{r}' = \mathbf{r} \cos \theta + (\mathbf{l} \times \mathbf{r}) \sin \theta + (\mathbf{r} \cdot \mathbf{l}) \mathbf{l} (1 - \cos \theta) \quad (6)$$

and the contribution to v from this atom is proportional to

$$\begin{aligned} \mathbf{r}' \cdot \mathbf{b} &= (\mathbf{r} \cdot \mathbf{b}) \cos \theta + (\mathbf{l} \times \mathbf{r} \cdot \mathbf{b}) \sin \theta + (\mathbf{r} \cdot \mathbf{l})(\mathbf{b} \cdot \mathbf{l})(1 - \cos \theta) \\ &= (\mathbf{r} \cdot \mathbf{b}) + \mathbf{l} \cdot (\mathbf{r} \times \mathbf{b}) \sin \theta \\ &\quad + [(\mathbf{r} \cdot \mathbf{l})(\mathbf{l} \cdot \mathbf{b}) - (\mathbf{r} \cdot \mathbf{b})](1 - \cos \theta). \end{aligned} \quad (7)$$

Substitution into (4) gives the residual as

$$E' = E - G \sin \theta + H(1 - \cos \theta). \quad (8)$$

Here G and H can be expressed in terms of a vector \mathbf{g} and a matrix \mathbf{T} both derived from \mathbf{V} .

$$G = \mathbf{g} \cdot \mathbf{l}, \quad \mathbf{g} = \sum_n w_n (\mathbf{r}_n \times \mathbf{b}_n). \quad (9)$$

$$H = \sum_{ij} l_i T_{ij} l_j, \quad T_{ij} = v \delta_{ij} - \frac{1}{2}(V_{ij} + V_{ji}). \quad (10)$$

The components of \mathbf{g} come from the antisymmetric part of the \mathbf{V} matrix, with $g_1 = (V_{23} - V_{32})$, and so on. When θ is small the change of E becomes $\delta E = -G\theta + \frac{1}{2}H\theta^2$, so that G is the downhill gradient of E about the chosen axis and H is the second derivative. The problem of minimizing E is equivalent to searching for the rotation \mathbf{R} which makes G vanish and H positive for any further choice of movement. Thus the vector \mathbf{g} vanishes, the \mathbf{V} matrix becomes symmetric and \mathbf{T} must be positive definite. \mathbf{g} has a simple physical interpretation as the couple which would act on the atoms in set A if each atom at \mathbf{r}_n was attracted to its guide point \mathbf{b}_n by an elastic restoring force $-w_n(\mathbf{r}_n - \mathbf{b}_n)$.

An important consequence of (8) is that the unique minimum of E around a given axis is obtained in only one step from the conditions

$$\begin{aligned} \sin \theta &= G/(G^2 + H^2)^{1/2}, \\ \cos \theta &= H/(G^2 + H^2)^{1/2}, \end{aligned} \quad (11)$$

$$E' - E = H - (G^2 + H^2)^{1/2} \leq 0. \quad (12)$$

The normal method of steepest descents reduces E iteratively in a series of rotations which are about axes parallel to the couples \mathbf{g} at the start of each cycle. The process converges slowly. The standard conjugate gradients procedure (Walsh, 1975) chooses the successive rotation axes to be 'conjugate directions' in the space of three-dimensional rotations and should ideally reach the minimum in just three steps. This would be true if E were a strictly quadratic function and if finite rotations could be treated as vector displacements in a suitable three-dimensional axis space.

The conjugate axes are chosen by taking each vector **1** parallel to a path vector **s** for the step. In the first step the rotation is about the axis of steepest descent, defined by the couple **g**:

$$\mathbf{s}_1 = \mathbf{g}_1. \quad (13)$$

Later paths each depend on the previous path and couple according to the relation

$$\mathbf{s}_{p+1} = \mathbf{g}_{p+1} + (\mathbf{g}_{p+1}^2 / \mathbf{g}_p^2) \mathbf{s}_p. \quad (14)$$

After each group of three successive paths the axis is once again chosen parallel to the path of steepest descent. The process terminates when the couple vanishes or the last angle of rotation falls below a set value.

In practice *E* is not a simple quadratic function. Furthermore, although infinitesimal rotations commute and form a vector space, finite rotations do not. There are however two good reasons for expecting that conjugate gradients should yield a rapidly converging solution in spite of these difficulties. The first is that every finite rotation applied, according to (11), leads to the exact minimum of *E* about that axis in just one step. The second is that when the orientation is close to the correct solution *E* does become a well-behaved quadratic function of the small rotation angles, and the concept of conjugate axes becomes a very good approximation.

Tests with typical sets of atomic coordinates show that five to eight iterations are usually sufficient to reduce the last rotation below 10^{-10} rad. Given the original **U** matrix, the calculation of **R** takes only 0.0032 s and 32 K bytes of store on an IBM 370/165. This is about one-third of the time taken by the previous method (McLachlan, 1979). A version of Kabsch's method, programmed by Dr Arthur Lesk, took 0.0050 s for the same task.

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Non-zero values of odd mixed moments in intensity statistics. By F. FOSTER, *Department of Mathematics, University of Manchester Institute of Science and Technology, Manchester M60 1QD, England*, A. HARGREAVES, *Department of Pure and Applied Physics, University of Manchester Institute of Science and Technology, Manchester M60 1QD, England*, U. SHMUELI, *Department of Chemistry, University of Tel Aviv, Ramat Aviv, 69978 Tel Aviv, Israel*, and A. J. C. WILSON, *Department of Physics, University of Birmingham, Birmingham B15 2TT, England*

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Abstract

Foster & Hargreaves [*Acta Cryst.* (1963), **16**, 1127], in discussing partial mixed moments of structure amplitudes, remark in passing 'For the triclinic, monoclinic and orthorhombic space groups the partial moments m_{pq} are zero when either *p* or *q* is odd, but for higher symmetries non-zero moments exist for *p* odd and *q* even'; the remark is repeated without comment by Srinivasan & Parthasarathy [*Some Statistical Applications in X-ray Crystallography* (1976).

Oxford: Pergamon Press]. Shmueli & Wilson failed to find any such non-zero moments among the general reflexions for any space group, and the problem has therefore been re-examined. Non-zero odd mixed moments are often found to occur in the *plane* groups with threefold or sixfold rotors, and hence in the *hk0*, but not the *hkl*, reflexions in *space* groups with trigonal or hexagonal symmetry. Details will be given in a forthcoming paper by Shmueli & Kaldor.

All information is given in the *Abstract*.

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