

Rotation procedure in intrinsic reaction coordinate calculations

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A procedure for calculating the distance between two points on an intrinsic reaction coordinate (IRC) obtained from two separate runs is proposed. The procedure mainly involves the rotation of the geometrical configuration of one point in order to obtain a configuration not rotated relative to the other point.

Key words: Intrinsic reaction coordinate

The intrinsic reaction coordinate (IRC) [1, 2] is a coordinate lying on the energy gradient vector curve linking the transition state, the reactant, and the product in the mass-weighted Cartesian coordinate system. The IRC value is defined as the distance along the gradient vector curve relative to the transition state. An algorithm for the calculation of the IRC has been proposed [2].

When the reactant (or the product) includes more than one molecule, its IRC value is infinity. When it includes only one molecule, its IRC value is a finite value and is necessary for a complete description of the reaction path. The geometry of the reactant is often calculated on a separate run prior to the calculation of the IRC, then the distance between the last point on the IRC and the reactant should be calculated.

The distance between two points in the mass-weighted coordinate superspace depends upon the displacement and the rotation of their configurations in the real space. In a run of an IRC calculation, each point is obtained from the last point according to the effect of the energy gradient, i.e. from the internal forces; this does not lead to displacement or rotation. However, it is inevitable that there

will exist some displacement and rotation of a point relative to another point from a separate run of calculation. We should move and rotate one of the molecules before calculating the distance in order that there is no displacement and rotation of the points relative to each other.

The problem of displacement is easy to solve by simply moving the center of mass to the origin of coordinates. The problem of rotation is discussed here in detail.

When two points with different geometrical configurations exist without displacement and rotation relative to each other, the distance between them in the mass-weighted superspace is minimum. Displacement or rotation will lengthen the distance. We can thus rotate the molecule to minimize the distance.

Let us call the points the initial and the end points. The Cartesian coordinates of the end point are denoted by $x_i, y_i, z_i, i = 1, \dots, n$, where n is the number of atoms in the system. In the following discussion, the subscript i will be omitted for simplicity, and the sum over i will simply be expressed by \sum . The Cartesian coordinates of the initial point are denoted by x^0, y^0, z^0 . The center of mass of the points is placed on the origin of coordinates. We will rotate the end point by a three-dimensional rotation matrix $R(\alpha, \beta, \gamma)$ into a new point denoted by x', y', z' to minimize the distance:

$$R \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}. \quad (1)$$

The square of the distance is

$$Q = \sum M[(x' - x^0)^2 + (y' - y^0)^2 + (z' - z^0)^2] \quad (2)$$

where M (M_i) is the mass of the atom i . The condition of minimization, i.e. the irrotational condition, is

$$\partial Q / \partial \alpha = 0, \quad \partial Q / \partial \beta = 0, \quad \partial Q / \partial \gamma = 0, \quad (3)$$

where α, β , and γ are rotation angles in independent directions. The usual three-dimensional rotation angles are the Euler angles in which the first and the third angles are on the old and the new z -axes. Such angles are not suitable for establishing the irrotational condition, as the first and the third angle become dependent when the second angle vanishes. We adopt the x, y , and z axes as the directions of the rotations, so the rotation matrix is

$$R = \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos \beta & 0 & -\sin \beta \\ 0 & 1 & 0 \\ \sin \beta & 0 & \cos \beta \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \gamma & -\sin \gamma \\ 0 & \sin \gamma & \cos \gamma \end{pmatrix}. \quad (4)$$

The concrete irrotational condition (Eckart condition) is thus derived from (3):

$$\sum M(y'x^0 - x'y^0) = \sum M(z'x^0 - x'z^0) = \sum M(z'y^0 - y'z^0) = 0. \quad (5)$$

The condition has been applied previously to some aspects of reaction dynamics [3].

An iteration algorithm is proposed to find the angles. Let X , Y , and Z be approximations of $\sin \alpha$, $\sin \beta$, and $\sin \gamma$. $\cos \alpha$, $\cos \beta$, and $\cos \gamma$ are approximated by 1, as the angles are usually small. Substituting Eqs. (1), (2), and (4) into (3) and omitting all non-linear terms, we obtain a set of linear equations:

$$\begin{aligned} a_1 X + b_1 Y + c_1 Z &= d_1 \\ a_2 X + b_2 Y + c_2 Z &= d_2 \\ a_3 X + b_3 Y + c_3 Z &= d_3 \end{aligned} \quad (6)$$

where

$$\begin{aligned} d_1 &= \sum M(yx^0 - xy^0) \\ d_2 &= \sum M(zx^0 - xz^0) \\ d_3 &= \sum M(zy^0 - yz^0) \\ a_1 &= \sum M(-xx^0 - yy^0) \\ a_2 &= \sum M(-zy^0) \\ a_3 &= \sum M(zx^0) \\ b_1 &= \sum M(-zy^0) \\ b_2 &= \sum M(-xx^0 - zz^0) \\ b_3 &= \sum M(-yx^0) \\ c_1 &= \sum M(zx^0) \\ c_2 &= \sum M(-yx^0) \\ c_3 &= \sum M(-yy^0 - zz^0). \end{aligned} \quad (7)$$

In each cycle of iteration, we solve Eq. (6), set $\sin \alpha = X$, $\cos \alpha = \sqrt{1 - X^2}$, etc., and substitute them into Eq. (1) to obtain x' , y' , z' . If the result meets the condition (5) to a suitable tolerance, we stop. If not, set $x = x'$, etc., we repeat the procedure.

If the angles are not small enough, the iteration will not converge, as the neglect of the higher order terms is not a good approximation in such cases. When the absolute value of X , Y , or Z obtained from Eq. (6) is greater than 0.5, we change it into ± 0.5 to ensure convergence.

The inversion of ammonia is chosen as an example for testing the procedure. The geometries of the reactant, the transition state, and intermediate states along the IRC are calculated by the MNDO method. For the last calculated point on the IRC the bond length is 100.626 pm and the bond angle is 105.957°. For the reactant they are 100.724 pm and 105.288°. As the latter is not obtained by

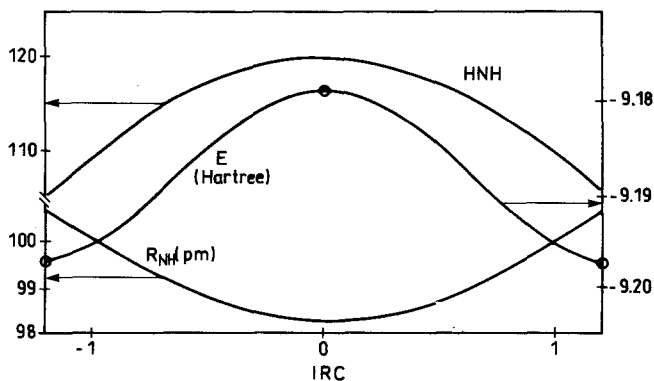


Fig. 1. Energy and geometry along the IRC of the inversion of ammonia

following the gradient from the former, the rotation technique is necessary for determining the distance between them. In order to test a large rotation, quite different orientations of the two points are chosen: for the former an NH bond is coincident with the x -axis, another NH bond lies in the xy -plane, while for the latter the symmetry axis is coincident with the x -axis. The iteration readily converges, resulting in a distance of $0.0316 (\text{g/mol})^{1/2}$ Bohr. The last point of the IRC has an IRC value of $-1.1803 (\text{g/mol})^{1/2}$ Bohr, so the reactant should have an IRC value of $-1.1803 - 0.0316 = -1.2119 (\text{g/mol})^{1/2}$ Bohr. Having obtained the IRC values of the reactant and the points on the IRC, we can plot various properties versus the IRC value to characterize the reaction path, as shown in Fig. 1.

The rotation procedure is also useful in the calculation of the IRC to correct the deviation from the irrotational condition due to calculation errors. It proved that the correction is meaningful, especially for comparatively large systems.

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References

1. Fukui K, Kato S, Fujimoto H (1975) *J Am Chem Soc* 97:1
2. Ishida K, Morokuma K, Komornicki A (1977) *J Chem Phys* 66:2153
3. For example, Miller WH, Handy NC, Adams JE (1980) *J Chem Phys* 72:99; Ehrenson S (1974) *J Am Chem Soc* 96:3778