

## CALCULATION OF THE LEAST ENERGY PATH ON THE ENERGY HYPERSURFACE

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In this paper an attempt was made to formulate mathematically a reaction coordinate as a valley on the energy hypersurface in  $n$ -dimensional space. A numerical procedure has been suggested which permits calculation of points lying in this valley. The calculated reaction path is demonstrated to satisfy boundary conditions demanded by the theory of absolute reaction rates. The procedure is amenable to any empirical, semiempirical and nonempirical method and can be applied to both unimolecular and bimolecular reactions.

At the present time two theoretical approaches to the reaction path are most widely used. These can be called static and dynamic ones. The latter which is physically more substantiated bears analogy to the classical collision theory. It involves solution of classical or quantum mechanical equations of motion for a given position and given momenta of reactants in the Hilbert coordinate space and construction of trajectories of particles as functions of time<sup>1-3</sup>. The use of the dynamic approach is inevitable if the velocity of reacting particles is high as *e.g.* in the case with reactions in crossed molecular beams. The applications to studies of reaction mechanisms encounter difficulties with most reactions because, ordinarily, the initial position and momenta of the reacting particles cannot be defined. Estimation of the rate constant then requires extensive computation for a large number of randomly chosen sets of initial parameters and a subsequent statistical treatment of results.

A considerably more effective treatment is provided by the methods of statistical thermodynamics. According to the theory of absolute reaction rates<sup>4</sup>, the rate constant can be determined from the thermodynamic functions of reactants and the activated complex. For a complete description of the reaction system it is necessary 1) to find the energy and the equilibrium geometry of reactants, 2) to find geometries and energies of all activated complexes, 3) to compare the rate constants and to select the one or several of the highest value. The task 1) is feasible on empirical<sup>5</sup>, semiempirical<sup>6-8</sup> and *ab initio*<sup>9</sup> levels. The task 2) has so far been solved only in part. The geometry of the activated complex has mostly been searched for by assuming the symmetry<sup>10</sup> or some plausible reaction course. In the simplest case only one or two internal coordinates were assumed to vary in the reaction. The activated complex was then identified with the highest point on the energy curve — one coordinate, or with a saddle point on the energy surface — two coordinates. The other coordinates were maintained fixed in the reaction process. Treatments of that type encounter difficulties with many reactions because sometimes the choice of the proper one or two reaction coordinates is *a priori* problematic or even impossible at all<sup>11</sup>. Considerable progress has been made since the introduction of minimization methods. The points on the reaction coordinate are calculated as local minima on the curves that are intersections

of the energy hypersurface with the hyperplanes perpendicular to an *a priori* chosen internal coordinate<sup>11-13</sup>. The pertinent coordinate is identified with the critical coordinate in the sense of the theory of absolute reaction rates. The actual applications of the procedure showed the phenomenon of chemical hysteresis<sup>11</sup>. This mathematical artefact manifests itself in the deviation of the calculated "reaction coordinate" from the least energy path. The greater the angle was between the direction along the chosen internal coordinate and that of the valley on the energy hypersurface, the more distinct was the effect.

The problem of finding the least energy path of unimolecular reactions in the vicinity of the reactant was discussed in refs<sup>3,14</sup>. The least energy motion was that which was parallel to the eigenvector of the matrix of force constants corresponding to the lowest eigenvalue. In chemical applications it is sometimes desirable to subject the search for the least energy path to certain restrictive conditions (*e.g.* to disregard hindered rotation or *cis-trans* isomeration if larger changes in structure are to be investigated). In such a case the least energy path is still parallel to some eigenvector of the matrix of force constants in the vicinity of the reactant.

In this paper a procedure is presented which permits a direct calculation of points lying on the least energy path. The reaction path calculated in this way will be demonstrated to satisfy all boundary conditions required by the theory of absolute reaction rates.

### THEORETICAL

First it is necessary to define necessary and sufficient conditions for a point, say  $\mathbf{x}$ , to lie on the least energy path, *i.e.* in the valley of the energy hypersurface. The case with the two-dimensional problem is outlined in Fig. 1. Obviously, the following requirements must be satisfied: 1) Energy must increase with all motions along the directions perpendicular to the direction of the valley. 2) The curvature of the energy surface along the direction of the valley must be lesser than the curvature along any other direction. Condition 1) implies there is no nonvanishing component of the

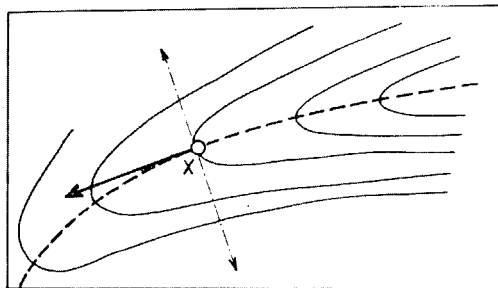


FIG. 1

The Valley in the Two-Dimensional Surface

----- Valley, ———→ direction of the gradient, - - - - - → direction perpendicular to the valley.

gradient in a direction perpendicular to the direction of the valley. In other words, the gradient is a tangent to the valley<sup>14</sup> at the point  $\mathbf{x}$ . Condition 2) implies the second derivative of energy along the reaction path must be lower than the second derivative of energy along any other direction. From this the following conclusion results about the eigenvectors of the matrix of second derivatives of energy with respect to coordinates: the eigenvector corresponding to the lowest eigenvalue is that which must be a tangent to the valley at the point  $\mathbf{x}$ .

As stated in the introduction, sometimes it is convenient to lower the number of degrees of freedom by disregarding some motions. In such a case a tangent to the valley is an eigenvector belonging to the lowest eigenvalue in a subspace spanned by the degrees of freedom of interest. To summarize the conditions 1) and 2), the gradient in a valley of the energy hypersurface must be parallel to one particular eigenvector of the matrix of force constants.

To calculate the position of the point  $\mathbf{x}_\mu$  lying on the reaction path it is convenient to use a recursive procedure. Once a point  $\mathbf{x}_{\mu-1}$  lying in the valley of the energy hypersurface is known, the shape of the energy function in the vicinity of  $\mathbf{x}_{\mu-1}$  permits one to arrive at the point  $\mathbf{x}'_\mu$ , which is a suitable approximation to  $\mathbf{x}_\mu$ . Let us note that with unimolecular reactions the coordinates of  $\mathbf{x}_1$  are the internal coordinates of the reactant. The next task of the procedure is to find such a vector  $\mathbf{r}$ , which on adding to  $\mathbf{x}'_\mu$  gives  $\mathbf{x}_\mu$  satisfying all requirements mentioned above for a point lying in the valley of the energy hypersurface.

For finding a point  $\mathbf{x}'_\mu$  use may be made of the fact that the gradient  $\mathbf{g}_{\mu-1}$  and one among the eigenvectors of the matrix of second derivatives of energy,  $\mathbf{c}_{n,\mu-1}$ , is a tangent to the valley on the energy hypersurface at the point  $\mathbf{x}_{\mu-1}$ . Generally, passage from  $\mathbf{x}_{\mu-1}$  to  $\mathbf{x}'_\mu$  along the gradient direction is preferable, as the gradient is computed usually with a higher precision than the matrix of second derivatives of energy.

On denoting

$$g_{\mu-1} = (\mathbf{g}_{\mu-1}^T \mathbf{g}_{\mu-1})^{1/2}$$

and

$$\mathbf{s}_{\mu-1} = \mathbf{x}_{\mu-1} - \mathbf{x}_{\mu-2},$$

the following equation holds

$$\mathbf{x}'_\mu = \mathbf{x}_{\mu-1} + \text{sign}(\mathbf{g}_{\mu-1}^T \mathbf{s}_{\mu-1}) \mathbf{g}_{\mu-1} \frac{s}{g_{\mu-1}}, \quad (1)$$

where  $s$  is an appropriately chosen scalar. If  $g_{\mu-1}$  is vanishingly small, it is necessary

to carry out the step along the direction of the eigenvector  $\mathbf{c}_{n,\mu-1}$ . This occurs, for example, in the first step of unimolecular reactions.

In the calculation of the vector  $\mathbf{r}$  we assume that the distance between  $\mathbf{x}'_{\mu}$  and  $\mathbf{x}_{\mu}$  is so small that the energy hypersurface between the two points can be approximated by a surface of second order. Let  $W'$ ,  $\mathbf{g}'$ , and  $\mathbf{H}$  be the energy, gradient and the matrix of second derivatives of energy with respect to coordinates at the point  $\mathbf{x}'_{\mu}$ . One can then write the energy  $W$  at the point  $\mathbf{x}_{\mu}$  in the form of a Taylor series

$$W = W' + \sum_i g'_i r_i + \frac{1}{2} \sum_i \sum_j H_{ij} r_i r_j, \quad (2)$$

The components of the gradient  $\mathbf{g}$  at the point  $\mathbf{x}_{\mu}$  are as follows

$$g_i = g'_i + \sum_j H_{ij} r_j. \quad (3)$$

Let  $\mathbf{c}_n$  be the eigenvector which is parallel to the gradient. Then it must hold at the point  $\mathbf{x}_{\mu}$

$$g'_i + \sum_j H_{ij} r_j = \lambda c_{in} \quad (4)$$

or in the matrix form

$$\mathbf{g}' + \mathbf{H}^T \mathbf{r} = \lambda \mathbf{c}_n, \quad (5)$$

where  $\lambda$  is a till now undetermined scalar. For  $\mathbf{r}$  it follows

$$r_i = \sum_j H_{ij}^{-1} (\lambda c_{jn} - g'_j) \quad (6)$$

where  $H_{ij}^{-1}$  is an element of the matrix which is inverse to the  $\mathbf{H}$  matrix. Since the expansion (2) lacks terms of the third and higher orders, the matrices of second derivatives at the points  $\mathbf{x}'_{\mu}$  and  $\mathbf{x}_{\mu}$  are identical. Therefore it is possible to write

$$H_{ij} = \sum_k E_k c_{ik} c_{jk} \quad (7)$$

and also

$$H_{ij}^{-1} = \sum_k E_k^{-1} c_{ik} c_{jk}, \quad (8)$$

where  $\mathbf{E}$  is the vector of eigenvalues of the  $\mathbf{H}$  matrix. By introducing (8) into (6)

one gets after some manipulation

$$r_i = \lambda E_n^{-1} c_{in} - \sum_k E_k^{-1} c_{ik} s_k, \quad (9)$$

where  $s_k$  is defined as a scalar product of the gradient at the point  $\mathbf{x}_\mu$  with the  $k$ -th eigenvector of the matrix of second derivatives of energy. Hence

$$s_k = \sum_j c_{jk} g'_j. \quad (10)$$

For any  $\lambda$  one then gets from (9) one vector  $\mathbf{r}$  and consequently one point  $\mathbf{x}_\mu$ . From the expression (9) it is easy to deduce that all calculated points  $\mathbf{x}_\mu$  will lie on the straight line colinear with the vector  $\mathbf{c}_n$ . For our purpose only that point  $\mathbf{x}_\mu$  is of interest which is nearest to  $\mathbf{x}'_\mu$ . In that case the neglect of terms of higher order in the expansion (2) is most justifiable. Accordingly, it is advantageous to choose  $\mathbf{r}$  in such a way as to be perpendicular to  $\mathbf{c}_n$ . Thus we get

$$\sum_i r_i c_{in} = 0. \quad (11)$$

By introducing  $\mathbf{r}$  according to (9), we obtain

$$\lambda E_n^{-1} \sum_i c_{in}^2 - \sum_i \sum_k E_k^{-1} c_{ik} s_k c_{in} = 0. \quad (12)$$

From this it follows

$$\lambda = s_n. \quad (13)$$

If we insert (13) in (9), we obtain the final relationship for  $\mathbf{r}$

$$r_i = - \sum_{k \neq n} E_k^{-1} c_{ik} s_k. \quad (14)$$

## DISCUSSION

Before discussing the formula (14) in more detail, let us note the corrective operation of the  $\mathbf{r}$  vector. If the points  $\mathbf{x}'_\mu$  and  $\mathbf{x}_\mu$  coincide, then all  $s_k$  vanish unless  $k = n$  (all  $\mathbf{c}_k$  eigenvectors are mutually orthogonal and  $\mathbf{c}_n$  is colinear with  $\mathbf{g}$ ). According to (14) all  $r_i$  therefore vanish. From that it follows that  $\mathbf{r} = 0$  is a necessary condition for a point  $\mathbf{x}_\mu$  to lie in the valley of the energy hypersurface. For the stationary points, *i.e.* stable isomers and activated complexes, all gradient components vanish. By using

(10) and (14) it is easy to find that  $\mathbf{r} = 0$  is valid in this case, too, and that the stationary points satisfy the above mentioned condition.

Eq. (14) is meaningful only if the vector  $\mathbf{r}$  is finite; with the exception of  $E_n$  no eigenvalue  $E_k$  of the matrix  $\mathbf{H}$  may be zero. If the energy and its second derivatives are continuous, then in the case of unimolecular reactions it must hold that only one eigenvalue can be negative. This follows from the fact that with the reactant all eigenvalues of the matrix of second derivatives are positive (the  $\mathbf{H}$  matrix is positive definite) and the passage to a negative value is allowed only for the eigenvalue  $E_n$ . The same conclusion concerning one negative eigenvalue must apply to the activated complex, too, which conforms to what was required for the behaviour of the activated complex in ref.<sup>15</sup>.

Since the calculation only gives us a series of equidistant points lying on the reaction path, the obtained points  $\mathbf{x}_\mu$  lie most likely before or behind a stationary point. The best way how to arrive at the latter is to apply Eq. (14) to points  $\mathbf{x}_\mu$  by performing the summation over all eigenvectors  $\mathbf{c}_k$ . In that case Eq. (14) becomes equivalent to the equation

$$\mathbf{r} = -\mathbf{H}^{-1}\mathbf{g}, \quad (15)$$

which is widely used for searching for the stationary point on a quadratic surface. For actual calculations, however, the form of Eq. (14) is more suitable.

If the eigenvector  $\mathbf{c}_n$  is degenerate with any vector  $\mathbf{c}_k$ , Eq. (14) cannot be applied directly. If the gradient is nonvanishing, the degeneracy is most likely accidental. In such a case the most effective procedure was found to be that of performing the correction according to Eq. (14) by making use of  $\mathbf{c}_i$  vectors that are not degenerate with  $\mathbf{c}_n$ ; the next step is made along the gradient direction. Degeneracy of eigenvectors in the case of stationary points implies mostly that the vectors belong to a highly symmetric representation; this will be discussed in the next paper.

Finally, we note the possibility to apply the procedure presented to bimolecular reactions. It is possible to consider the two reactants to constitute one supersystem and to apply Eq. (14) without change. The only difference lies in the first step. As one does not start from the geometry of the stationary point, some experience is needed to guess, at least roughly, the initial orientation of reactants. By multiple application of Eq. (14) one arrives at the valley which is nearest to the starting geometry assumed. This will be discussed in detail in a later paper.

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