

Original Investigations

Reactive Domains of Energy Hypersurfaces and the Stability of Minimum Energy Reaction Paths

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Special properties of the Riemannian metric for energy hypersurfaces, defined within the framework of the Born–Oppenheimer approximation, are utilized in devising a partitioning scheme for domains of nuclear coordinates. The chemically important coordinate domains are distinguished from domains of lesser importance by their curvature properties. Conditions are derived for the stability of minimum energy reaction paths, and the effects of instability regions are investigated. Instability domains along minimum energy paths may allow small vibrational perturbations to alter the outcome of the chemical reaction.

Key words: Potential energy surfaces – Reaction paths – Transition states

1. Introduction

In the Born–Oppenheimer approximation [1] a unique energy hypersurface may be assigned to any electronic state of a given molecule. In this approximation the molecular total energy, E_t , is the sum of a classical Coulomb term E_n , describing the nuclear repulsion of the fixed nuclei, and a quantum mechanical term E_e , representing the electronic energy of the given electronic state of the system. The total energy depends parametrically on the nuclear coordinates \mathbf{r} :

$$E_t = E_t(\mathbf{r}).$$

This $E_t(\mathbf{r})$ function is well defined for most nuclear configurations, although within the Hartree–Fock and related approximations neither $E_n(\mathbf{r})$ nor $E_e(\mathbf{r})$ is adequately defined for points \mathbf{r} where the coordinates of two or more of the nuclei become identical (processes leading to such points would involve nuclear reactions). These points, however, are of little chemical significance, and $E_t(\mathbf{r})$ is well defined over all chemically realistic values of the internal coordinates. After excluding all the above “unrealistic” points, together with their immediate neighbourhoods, for all the

allowed r points function $E_t(r)$ is continuous and differentiable. Consequently, $E_t(r)$ may be represented geometrically as an energy hypersurface over the nuclear coordinates r .

Although the basic assumption of the Born–Oppenheimer approximation, i.e. the separability of nuclear and electronic motion, is not strictly valid, the resulting error is usually small. Consequently, chemical reactions and conformational changes may be studied in terms of energy hypersurfaces, that correspond to potential functions for the nuclear motion.

Critical points of $E(r)$ ¹, i.e. points where the gradient vector is zero, $g(r) = 0$, are of particular importance. Minima correspond to most favoured nuclear arrangements that belong to reactant or product structures. First order saddle points [2], i.e. critical points where the Hessian matrix H of the second derivatives has exactly one negative eigenvalue, correspond to transition state structures.

Those curves P on the hypersurface that interconnect two minima, correspond to reaction paths. Among the reaction paths particularly important are those for which the energy barrier is minimum. Certain paths P that fulfill this condition are called minimum energy paths and are defined by the following properties: Minimum energy paths follow the direction of steepest descent from the transition state toward both minima. The definition of minimum energy reaction path P , in the form as given for the “intrinsic reaction coordinate” by Fukui [3, 4] will be the most useful for our purposes: P is a curve that interconnects two minima, passes through a transition state and is orthogonal to any equipotential contour surface crossed. These minimum energy paths correspond to idealized, vibrationless rearrangements of the nuclei. While this model is clearly a gross oversimplification, it is nevertheless reasonable to assume that a real chemical process can be approximated by reaction paths that do not deviate much from the minimum energy path, at least at low temperatures. What deviation is to be regarded small or large, however, requires a clear definition.

The classical image of a mass point moving along a potential surface suggests that those coordinate domains that contain the minimum energy paths and their close neighbourhoods are likely to be of the greatest chemical importance. Criteria for the specification and determination of these chemically important coordinate domains are clearly of some interest. Alternatively, one may attempt to specify domains of the nuclear coordinates r that correspond to unlikely nuclear arrangements. It has been demonstrated that no minimum energy path may pass through a finite neighbourhood of non-degenerate critical points of index $\lambda \geq 2$, where index λ is the number of negative eigenvalues of the Hessian matrix, since these points correspond to local maxima of a λ dimensional projection of the energy hypersurface [2]. Consequently, these coordinate domains are of little chemical importance provided that the chemical process is confined to a single surface. If criteria for the determination of such domains can be established, one may disregard them when investigating conformational phenomena or chemical reactions that do not

¹ In the following discussion subscript t will be omitted.

involve electronic excitations, i.e. transitions between different energy surfaces. On the other hand, if such surface to surface transition occurs, e.g. in a photochemical reaction, the point describing the new state of the system may very well fall into a coordinate region that is usually avoided by ordinary reaction paths on the given surface.

In the present study we shall address the following problems:

- 1) What are those domains of nuclear coordinates \mathbf{r} that are likely to contain the most probable reaction paths on a given energy hypersurface?
- 2) In what coordinate domains are minimum energy paths stable with respect to displacements orthogonal to the steepest descent direction?
- 3) What is the likelihood that actual reaction paths show large deviations from the minimum energy path in a given coordinate domain?
- 4) Under what conditions can one assign a minimum energy path (as defined above) to a unique reaction mechanism?

Whenever convenient, we shall use a tensor formalism that is not affected by the choice of internal coordinates. For the concepts of tensor calculus used in this paper the reader is referred to standard texts on Riemannian geometry [5, 6] and to recent reviews of the relevant aspects of hypersurfaces and differential geometry [2, 4].

2. Discussion

We shall assume that the nuclear arrangements of the molecular system are specified by position vectors \mathbf{r} of dimension $n = 3N - 6$, where N is the number of nuclei. Vector \mathbf{r} may be given in terms of contravariant components r^i or covariant components r_i , that are interrelated by the equation

$$r_i = g_{ij}r^j \quad (1)$$

In Eq. (1) g_{ij} is the Riemannian metric tensor, characteristic to the given coordinate representation of the n -dimensional space R [5, 6]. Throughout this paper the usual summation convention is used (following Einstein): any index which occurs twice in the same term is to be summed. The infinitesimal distance ds , a scalar quantity, is connected with the metric tensor g_{ij} by

$$ds^2 = g_{ij} dr^i dr^j \quad (2)$$

The scalar product of two vectors \mathbf{r} and \mathbf{p} , the norm $|\mathbf{r}|$, and the angle α between two vectors are defined the usual way [6], by

$$\mathbf{r} \cdot \mathbf{p} = g_{ij}r^i p^j = r^i p_i \quad (3)$$

$$|\mathbf{r}| = (r^i r_i)^{1/2} \quad (4)$$

and

$$\cos \alpha = \frac{\mathbf{r} \cdot \mathbf{p}}{|\mathbf{r}| |\mathbf{p}|}, \quad (5)$$

respectively.

We shall use a left superscript m for quantities in an m -dimensional space ${}^m R$, e.g. ${}^m \mathbf{r}$, ${}^m g_{ij}$. The summation convention will not apply for this index, and whenever

$m = n$, it will be omitted. It is convenient to consider energy $E(\mathbf{r})$ itself as the $n + 1$ st component [2, 4, 7] and define vector ${}^{n+1}\mathbf{r}$ by contravariant (covariant) components as

$${}^{n+1}r^k = r^k \quad ({}^{n+1}r_k = r_k) \quad \text{for } k = 1, \dots, n, \quad (6a)$$

$${}^{n+1}r^{n+1} = {}^{n+1}r_{n+1} = E(\mathbf{r}) \quad (6b)$$

As it has been pointed out earlier [2, 4] the transformation properties of the energy component are fundamentally different from that of the internal coordinates and the Riemannian metric ${}^{n+1}g_{ij}$ of ${}^{n+1}R$ is special:

$${}^{n+1}g_{n+1,i} = {}^{n+1}g_{i,n+1} = \delta_{i,n+1}. \quad (7)$$

This property of ${}^{n+1}g_{ij}$ is not affected by coordinate transformations in the n -dimensional space if the Jacobian determinant of the transformation is non-zero. Consequently, the distance ${}^{n+1}s$ in the $n + 1$ dimensional space ${}^{n+1}R$ can be generated as the Pythagorean distance of components ds and dE :

$${}^{n+1}ds^2 = ds^2 + dE^2 \quad (8)$$

This relation is very useful when comparing purely geometrical displacements of the nuclei and the generated displacements along the energy hypersurface. Naturally, component ds itself is not a Pythagorean distance in general, as it is evident from Eq. (2). If $dE = 0$ for an infinitesimal interval, we shall call the curve *horizontal* in this interval.

The terms reaction path and reaction coordinate are frequently used interchangeably, although by three-dimensional geographical analogy the common interpretation of path (a geometrical object) is different from that of a coordinate (a numerical measure). Indeed, the intrinsic reaction coordinate, as defined originally [3, 4], is a curve and one may refer to this curve as "intrinsic reaction path".

In fact, there are four different concepts we are concerned with:

- 1) *The curve ${}^{n+1}P$, describing the reaction in the $n + 1$ -dimensional space ${}^{n+1}R$.* This curve is analogous to a three-dimensional path on a relief map in the usual, geographic sense, energy taking the role of elevation. In the present paper we shall refer to curve ${}^{n+1}P$ as the $n + 1$ dimensional relief path or total reaction path.
- 2) *A numerical measure, how far the reaction has progressed along the ${}^{n+1}P$ curve in $n + 1$ dimensions.* A suitable measure is the ${}^{n+1}s$ arc length, measured from the minimum of the reactants:

$${}^{n+1}s = \int_{n+1P} {}^{n+1}ds \quad (9a)$$

where

$${}^{n+1}ds^2 = {}^{n+1}g_{ij} {}^{n+1}dr^i {}^{n+1}dr^j \quad (9b)$$

Arc length ${}^{n+1}s$ will be referred to as the *relief path coordinate* or *total reaction coordinate* of total reaction path ${}^{n+1}P$.

- 3) *The projection P of the above ${}^{n+1}P$ curve onto the n -dimensional coordinate space R . P corresponds to the actual physical displacements of the nuclei as described by the nuclear coordinates. The resulting curve is analogous to the curve on a two-dimensional map, representing a real geographical path of three dimensions. P is the projected image of the relief path ${}^{n+1}P$ on a “horizontal” hyperplane, with no reference to elevation, i.e. to energy. In the present paper we shall refer to curve P as the *reaction path*.*
- 4) *A numerical measure, how far the reaction has progressed along the above P curve in n dimensions. A suitable measure is the s arc length, measured from the coordinate point corresponding to the minimum of the reactants. For a given P curve we shall call s the *reaction coordinate*.*

$$s = \int_P ds \tag{10}$$

The relation between these curves, as represented by a three-dimensional example, is shown in Fig. 1.

The total variation of function $E(r)$ along curve P is defined [8] as

$$\nu(E) = \sup_k \sum_k |E(r_k) - E(r_{k+1})|, \tag{11}$$

$r_k \in P$ and $\{r_k\} : s(r_k) < s(r_{k+1})$

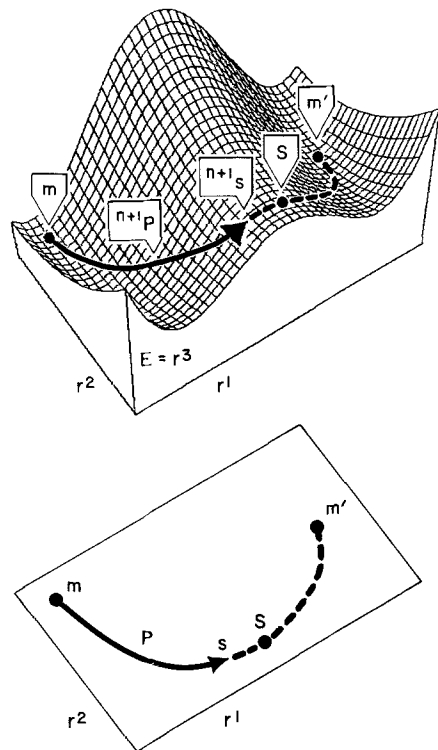


Fig. 1. The relations between relief path ${}^{n+1}P$, reaction path P , relief path coordinate ${}^{n+1}s$ and reaction coordinate s . Symbols m and S stand for minima and saddle points, respectively

If in an interval $I \subset P$ ($\partial E/\partial s$) does not change sign, then within I the total variation $\nu(E)$ is equal to the maximum variation $\tau(E)$,

$$\tau(E) = \nu(E) \quad (12)$$

where $\tau(E)$ is defined as

$$\tau(E) = \max |E(\mathbf{r}_1) - E(\mathbf{r}_2)|, \quad \mathbf{r}_1, \mathbf{r}_2 \in I \quad (13)$$

The maximum variation $\tau(E)$ and the total variation $\nu(E)$ of energy may be used to characterize segments of the reaction path and it can be shown that in a set of reaction paths interconnecting two minima $\nu(E)$ is minimum for the minimum energy path [9]. Due to the special properties (7) of Riemannian metric tensor ${}^{n+1}g_{ij}$, the total variation $\nu(E)$ of the energy along the reaction path may be expressed as

$$\nu(E) = \int_{n+1P} \left| \frac{dE}{{}^{n+1}ds} \right| {}^{n+1}ds \quad (14a)$$

where

$$|dE| = ({}^{n+1}ds^2 - ds^2)^{1/2} \quad (14b)$$

If P is a minimum energy reaction path, then the corresponding relief path ${}^{n+1}P$ follows the direction of steepest descent, i.e. the negative gradient $-\mathbf{g}$ on the hypersurface. This property of minimum energy paths, and the fact that at the critical points the gradient is zero,

$$\mathbf{g}(\mathbf{r}) = \mathbf{0}, \quad (15)$$

suggests that the properties of gradient vectors $\mathbf{g}(\mathbf{r})$ may be used to characterize various domains of energy hypersurfaces.

For each point $\mathbf{r} \in R$ an $n - 1$ -dimensional subspace ${}^{n-1}R(\mathbf{r})$ may be defined with the following properties:

$${}^{n-1}R(\mathbf{r}) = \{\mathbf{x}(\mathbf{r}) : \mathbf{x}(\mathbf{r}) \cdot \mathbf{a}(\mathbf{r}) = 0\} \quad (16)$$

that is, the elements $\mathbf{x}(\mathbf{r}) \in {}^{n-1}R(\mathbf{r})$ are orthogonal to a reference vector $\mathbf{a}(\mathbf{r})$ in the sense defined by Eqs. (3) and (5). If \mathbf{r} is an ordinary point with a non-vanishing gradient, i.e. $\mathbf{g}(\mathbf{r}) \neq \mathbf{0}$, then $\mathbf{a}(\mathbf{r})$ is taken as the normalized gradient vector

$$\mathbf{a}(\mathbf{r}) = \tilde{\mathbf{g}}(\mathbf{r}) = \frac{\mathbf{g}(\mathbf{r})}{|\mathbf{g}(\mathbf{r})|}. \quad (17)$$

Consequently, for such ordinary points \mathbf{r} , $\mathbf{g}(\mathbf{r}) \neq \mathbf{0}$, the ${}^{n-1}R(\mathbf{r})$ subspace is uniquely defined as the one orthogonal to the gradient.

If $\mathbf{g}(\mathbf{r}) = \mathbf{0}$, i.e. $\mathbf{r} = \mathbf{r}_C$, a critical point, then there is no unique $n - 1$ -dimensional subspace orthogonal to $\mathbf{g}(\mathbf{r}_C)$, i.e., to the $\mathbf{0}$ vector. Nevertheless, for any given steepest descent path P a unique ${}^{n-1}R_P(\mathbf{r}_C)$ subspace may be defined by assuming

continuous changes in reference vector $\mathbf{a}(\mathbf{r})$. Let us select infinite point series $\{\mathbf{r}_k\}$ on the steepest descent path P with the following properties:

$$\mathbf{r}_k \in P \quad (18a)$$

$$s(\mathbf{r}_k) < s(\mathbf{r}_C) \quad (18b)$$

$$\mathbf{g}(\mathbf{r}_1) \neq \mathbf{0} \quad (18c)$$

$$\lim_k \mathbf{r}_k = \mathbf{r}_C \quad (18d)$$

For the given steepest descent path P reference vector $\mathbf{a}(\mathbf{r}_C)$ may be chosen as

$$\mathbf{a}(\mathbf{r}_C) = \mathbf{a}_P(\mathbf{r}_C) = \lim_k \mathbf{a}(\mathbf{r}_k) \quad (19)$$

where index P refers to the given path P . For steepest descent paths at ordinary points and for minimum energy paths at both ordinary and critical points unit vector $\mathbf{a}(\mathbf{r})$ is tangent to P . Vector $\mathbf{a}(\mathbf{r})$ will be referred to as the *path vector*.

A unique subspace ${}^{n-1}R_P(\mathbf{r}_C)$ may be defined in terms of $\mathbf{a}(\mathbf{r}_C) = \mathbf{a}_P(\mathbf{r}_C)$ as

$${}^{n-1}R_P(\mathbf{r}_C) = \{\mathbf{x}(\mathbf{r}_C) : \mathbf{x}(\mathbf{r}_C) \cdot \mathbf{a}_P(\mathbf{r}_C) = 0\} \quad (20)$$

As condition (18b) on the reaction coordinates implies, the sign of $\mathbf{a}_P(\mathbf{r}_C)$ depends on the orientation of the path P , i.e. on the assignment of labels “reactant” and “product” to the minima. In this sense $\mathbf{a}_P(\mathbf{r}_C)$ is not unique. Nevertheless, ${}^{n-1}R_P(\mathbf{r}_C)$ is unique, since it is orthogonal to both $\mathbf{a}_P(\mathbf{r}_C)$ and $-\mathbf{a}_P(\mathbf{r}_C)$. Two further comments are in order here. Several different steepest descent paths P may pass through a critical point \mathbf{r}_C and subspace ${}^{n-1}R_P(\mathbf{r}_C)$ depends on the path P , as well as on point \mathbf{r}_C . By contrast, at ordinary points \mathbf{r} where $\mathbf{g}(\mathbf{r}) \neq \mathbf{0}$, there is only one steepest descent path passing through \mathbf{r} and ${}^{n-1}R(\mathbf{r})$ is unique for every point $\mathbf{r} \neq \mathbf{r}_C$. It is also noteworthy that definitions (19) and (20) are applicable to degenerate as well as non-degenerate critical points, since only the first point \mathbf{r}_1 of point series $\{\mathbf{r}_k\}$ is required explicitly to be a non-critical point.

At a critical point \mathbf{r}_C an ${}^{n-1}R(\mathbf{r}_C)$ subspace may also be defined in terms of the curvature properties of the hypersurface itself, rather than in terms of various steepest descent paths P . At a critical point \mathbf{r}_C the Hessian matrix $\mathbf{H}(\mathbf{r})$ may be diagonalized by a suitable coordinate transformation [2]. Reference vector $\mathbf{a}_H(\mathbf{r}_C)$ may be chosen as the eigenvector belonging to the *lowest* eigenvalue of $\mathbf{H}(\mathbf{r})$. If the lowest eigenvalue is k -fold degenerate ($k > 1$) then any vector $\mathbf{a} \neq \mathbf{0}$ from the k -dimensional degenerate subspace may be selected. A path-independent subspace ${}^{n-1}R(\mathbf{r}_C)$ may then be defined at a critical point \mathbf{r}_C as

$${}^{n-1}R(\mathbf{r}_C) = \{\mathbf{x}(\mathbf{r}_C) : \mathbf{x}(\mathbf{r}_C) \cdot \mathbf{a}_H(\mathbf{r}_C) = 0\} \quad (21)$$

The definition of minimum energy reaction path implies that whenever P is such a path and \mathbf{r}_C is a first-order critical point, i.e. $\lambda(\mathbf{r}_C) = 1$, then

$${}^{n-1}R(\mathbf{r}_C) = {}^{n-1}R_P(\mathbf{r}_C) \quad (22)$$

that is, Eqs. (20) and (21) define the same subspace. In the forthcoming discussion it is assumed that for critical points \mathbf{r}_C with indices $\lambda(\mathbf{r}_C) = 0$ or $\lambda(\mathbf{r}_C) = 1$ definition

(20) is applied with reference to a *minimum energy reaction path* P , unless otherwise stated, and indices P and C are usually omitted.

Along any steepest-descent reaction path P the subspace ${}^{n-1}R(\mathbf{r})$ depends parametrically on vector $\mathbf{a}(\mathbf{r})$, consequently on position vector \mathbf{r} . That is, to each point \mathbf{r} of a (generally non-linear) reaction path P a different but fixed ${}^{n-1}R(\mathbf{r})$ subspace may be assigned. One may then investigate displacements within each subspace ${}^{n-1}R(\mathbf{r})$, keeping in mind that the entire subspace belongs to a given point \mathbf{r} of the reaction path P . In general, ${}^{n-1}R(\mathbf{r})$ is a hyperplane tangent to the equipotential contour surface at point \mathbf{r} . In general, however, ${}^{n-1}R(\mathbf{r})$, being a hyperplane, is not identical to the equipotential contour surface passing through point \mathbf{r} , generally they are merely in contact at point \mathbf{r} . The cross section of the hypersurface over subspace ${}^{n-1}R(\mathbf{r})$ [i.e. excluding variations along $\mathbf{a}(\mathbf{r})$] is locally horizontal at \mathbf{r} , since ${}^{n-1}R(\mathbf{r})$ is either orthogonal to the gradient (Eq. (16)) or is a subspace defined at a critical point where the hypersurface itself is horizontal (Eq. (20)). Consequently, the above cross section of the hypersurface over ${}^{n-1}R(\mathbf{r})$ must have a critical point at \mathbf{r} . This property greatly simplifies the analysis of minimum energy reaction paths, since it ensures that the important curvature properties near the reaction path may be studied in terms of the conventional concept of the Hessian matrix

One may select a set of basis vectors $\{{}^{n-1}\mathbf{y}_k(\mathbf{r})\}$ in ${}^{n-1}R(\mathbf{r})$ with the following properties:

$${}^{n-1}\mathbf{y}_k(\mathbf{r}) \cdot \mathbf{a}(\mathbf{r}) = 0 \quad (23a)$$

and

$${}^{n-1}\mathbf{y}_k(\mathbf{r}) \cdot {}^{n-1}\mathbf{y}_l(\mathbf{r}) = \delta_{kl} \quad (23b)$$

Any vector ${}^{n-1}\mathbf{x}(\mathbf{r}) \in {}^{n-1}R(\mathbf{r})$ can be expressed as a linear combination of vectors ${}^{n-1}\mathbf{y}_k(\mathbf{r})$

$${}^{n-1}\mathbf{x}(\mathbf{r}) = x^k {}^{n-1}\mathbf{y}_k(\mathbf{r}) \quad (24)$$

where the x^k contravariant coordinates refer to the given $\{{}^{n-1}\mathbf{y}_k(\mathbf{r})\}$ basis.

Within the ${}^{n-1}R(\mathbf{r})$ subspace an infinitesimal displacement from point \mathbf{r} does not change the energy in first order. The second-order changes are described by the $n - 1$ -dimensional Hessian matrix ${}^{n-1}\mathbf{H}(\mathbf{r})$, with elements

$${}^{n-1}H(\mathbf{r})_{kl} = \frac{\partial^2 E}{\partial x^k \partial x^l} \quad (25)$$

When restricted to subspace ${}^{n-1}R(\mathbf{r})$, the general expression of the extended Hessian matrix [4],

$${}^{n-1}H_{kl} = \frac{\partial^2 E}{\partial x^k \partial x^l} - \Gamma_{kl}^i \frac{\partial E}{\partial x^i}, \quad (26)$$

where Γ_{kl}^i is the Christoffel symbol of the second kind [6], reduces to Eq. (25). Indeed, in our case the second term in Eq. (26) is zero, since at point \mathbf{r} the gradient has no non-zero component within subspace ${}^{n-1}R(\mathbf{r})$.

At each point \mathbf{r} the $\{n^{-1}\mathbf{y}_k(\mathbf{r})\}$ basis may be chosen as one, on which the $n^{-1}\mathbf{H}(\mathbf{r})$ Hessian matrix is diagonal:

$$n^{-1}\mathbf{H}(\mathbf{r})_{kl} = \frac{\partial^2 E}{\partial x^{k2}} \delta_{kl} = \alpha_k \quad (27)$$

(no summation for k)

where the α_k scalar is the k th eigenvalue of $n^{-1}\mathbf{H}(\mathbf{r})$.

This diagonal form of $n^{-1}\mathbf{H}(\mathbf{r})$, implicitly depending on gradient $\mathbf{g}(\mathbf{r})$ or on vector $\mathbf{a}(\mathbf{r})$, will be used for the characterization of points $\mathbf{r} \in R$. It is clear from the definition of subspace $n^{-1}R(\mathbf{r})$ that at a critical point \mathbf{r}_c the following relation holds for indices λ of $\mathbf{H}(\mathbf{r}_c)$ and μ of $n^{-1}\mathbf{H}(\mathbf{r}_c)$:

$$\mu \leq \lambda \quad (28)$$

Minima and first-order saddle points are the only non-degenerate critical points that may fall on a minimum energy path P . If \mathbf{r}_c is a minimum, $\mu = \lambda = 0$, while for a first-order saddle point $\lambda = 1$ and $\mu = 0$, that is, $\mu = 0$ for both types of critical points.

The choice of \mathbf{a} ensures that $n^{-1}R(\mathbf{r})$ will change continuously with \mathbf{r} along minimum energy path P . Furthermore, since the transformation involved in the diagonalization of $n^{-1}\mathbf{H}(\mathbf{r})$ is also continuous, the eigenvalues of $n^{-1}\mathbf{H}(\mathbf{r})$ must depend continuously on \mathbf{r} . Consequently, index μ must be zero for a set of infinite number of points in the neighbourhood of \mathbf{r}_c , i.e. in a coordinate domain D , $\mathbf{r}_c \in D$.

The continuous dependence of $\mathbf{g}(\mathbf{r})$ and $n^{-1}\mathbf{H}(\mathbf{r})$ on \mathbf{r} along minimum energy path P implies that by utilizing definition (10) both $\mathbf{g}(\mathbf{r})$ and $n^{-1}\mathbf{H}(\mathbf{r})$ may be parametrized for the given path P in terms of reaction coordinate s :

$$\mathbf{g}_{(P)}(\mathbf{r}) \rightarrow \mathbf{g}(s_P) \quad (29)$$

$$n^{-1}\mathbf{H}_{(P)}(\mathbf{r}) \rightarrow n^{-1}\mathbf{H}(s_P) \quad (30)$$

Vector $\mathbf{g}(s_P)$ and matrix $n^{-1}\mathbf{H}(s_P)$ give a complete description of the directional and curvature properties of minimum energy path P .

In the following analysis we shall ignore those coordinate domains that have been termed chemically unimportant at the outset: domains where the distance between two nuclei approaches zero. We may always assume that these domains are open sets. The excluded domain D_{excl} may then be defined as the union of open balls, $G(\mathbf{r}_\gamma, \rho)$, centered at points \mathbf{r}_γ , i.e. at points where the coordinates of two or more nuclei become identical:

$$D_{\text{excl}} = \bigcup_{\gamma} G(\mathbf{r}_\gamma, \rho) \quad (31)$$

where the ρ radius is a suitably chosen small positive value.

It is clear that for a small enough ρ value the omission of D_{excl} from our analysis is perfectly permissible: no chemical reaction path may possibly enter domain D_{excl} . It is also easy to show that whenever two disjoint (non-connected) coordinate

domains D_A and D_B are separated by D_{excl} , then D_A and D_B must have equivalent subdomains, as a consequence of the symmetry properties of one or more of the coordinates. A simple example for this case is the (fixed bond length) pyramidal inversion of NH_3 , carried to the extreme of three collapsing H atoms (closed umbrella). Beyond this point the H atoms would part again, and the remainder of the process would be symmetrically equivalent to the first part before the collapse.

A connected coordinate domain D_μ may be defined as the collection of all points r with the following two properties:

- 1) if $r \in D_\mu$ then $\mu(r) = \mu$
- 2) if $r_1, r_2 \in D_\mu$, then there is a P path interconnecting r_1 and r_2 , such, that for every $r \in P$ $\mu(r) = \mu$, that is, P lies entirely in D_μ .

Space R of nuclear coordinates may be partitioned into a set of $\{D_\mu^i\}$ domains, that may include several disjoint domains with the same index μ . This partitioning reflects the curvature properties of the energy hypersurface, since the D_μ^i domains are defined in terms of the Hessian ${}^{n-1}\mathbf{H}(r)$ of the local "horizontal" subspace ${}^{n-1}R(r)$ at each point r . The connectedness property within each D_μ^i is ensured by the continuity of point series consisting of points r where $\mathbf{g}(r) \neq \mathbf{0}$. Critical points r_c , $\mathbf{g}(r_c) = \mathbf{0}$, are special, since continuity is guaranteed only along a minimum energy path.

The significance of various D_μ domains of energy hypersurfaces is illustrated by the model surface shown in Fig. 2. For sake of simplicity we shall assume that this model surface is given in terms of rectilinear coordinates. Minimum energy path P interconnects m , the minimum of the reactants and m' , the minimum of the

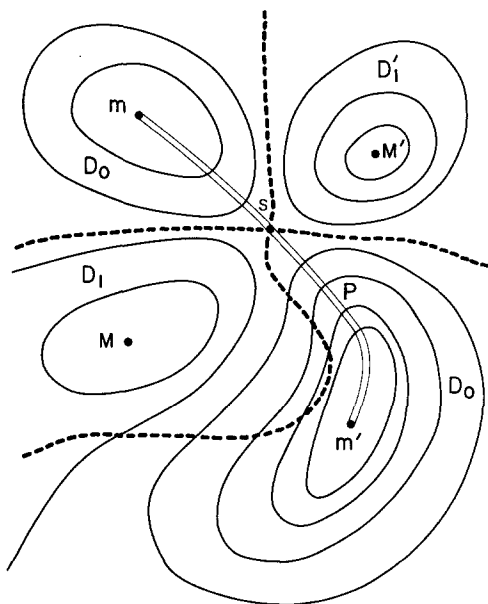


Fig. 2. Typical energy surface partitioning into D_μ domains. Minimum energy path P is stable with respect to displacements orthogonal to path vector \mathbf{a} . Symbols m , M and S stand for minima, maxima and saddle point, respectively

products. Saddle point S lies on the ridge between maxima M and M' . P intersects the equipotential contour lines perpendicularly, the broken lines show the boundaries of various D_μ domains. The two minima may appear to belong to two distinct D_0 domains, however, the two segments are connected: by definition, for first-order saddle point S $\mu(r_S) = 0$, that is, $r_S \in D_0$. On the other hand, maxima M and M' are located in two disjoint domains, in D_1 and D'_1 , respectively. The most important feature of the above model is that the *entire minimum energy path P is contained in a single domain D_μ with index $\mu = 0$* . We shall see that this is indeed the most common case and D_0 domains play a predominant role in the energy hypersurface representation of chemical reactions.

The energy hypersurface is “concave from above” in a domain D_0 : since $\mu(\mathbf{r}) = 0$ for all $\mathbf{r} \in D_0$, these points \mathbf{r} represent minima along any coordinate direction orthogonal to the gradient $\mathbf{g}(\mathbf{r})$ (or to vector $\mathbf{a}(\mathbf{r})$, if \mathbf{r} is a critical point, $\mathbf{r} = \mathbf{r}_C$). That is, any local variation ΔP , i.e. any displacement of a steepest descent path, orthogonal to the gradient, would result in an *increase* of the energy. Consequently, at point \mathbf{r} , a steepest descent path is *stable* with respect to any displacement orthogonal to the path, whenever $\mu(\mathbf{r}) = 0$. By contrast, whenever $\mu(\mathbf{r}) > 0$, there are just $\mu(\mathbf{r})$ linearly independent coordinate directions (hence for $\mu > 1$ infinite number of linear combinations) all orthogonal to $\mathbf{g}(\mathbf{r})$, along which a displacement of the path would result in an actual lowering of the energy. Consequently, if a steepest descent path passes through a point \mathbf{r} with $\mu(\mathbf{r}) > 0$, then it is *unstable* with respect to certain displacements orthogonal to $\mathbf{g}(\mathbf{r})$. An example for the latter, unstable path is the steepest descent lava flow on the surface of a conical volcano.

At any ordinary point $\mathbf{r} \neq \mathbf{r}_C$ a minimum energy path P is a steepest descent path, and all the above applies. In addition, a minimum energy path P is always stable with respect to displacements orthogonal to path vector $\mathbf{a}(\mathbf{r}_C)$ at a non-degenerate critical point \mathbf{r}_C . This is trivially true if \mathbf{r}_C is a minimum, i.e. $\lambda(\mathbf{r}_C) = 0$. If \mathbf{r}_C is a first-order saddle point, i.e. $\lambda(\mathbf{r}_C) = 1$, then path vector $\mathbf{a}(\mathbf{r}_C)$ is the eigenvector of $\mathbf{H}(\mathbf{r}_C)$, belonging to the single negative eigenvalue, hence within the subspace ${}^{n-1}R(\mathbf{r}_C)$, orthogonal to $\mathbf{a}(\mathbf{r}_C)$, the curvature is positive along any direction. Consequently, minimum energy path P is stable with respect to any displacement within ${}^{n-1}R(\mathbf{r}_C)$. For both minima ($\lambda = 0$) and first order saddle points ($\lambda = 1$) index $\mu = 0$, and higher order saddle points with index $\lambda(\mathbf{r}_C) > 1$ do not occur along minimum energy paths [2].

We may summarize the above observations in

Theorem 1: If $P \subset D_\mu$ is a segment of a steepest descent path or that of a minimum energy path, then P is stable with respect to displacements within D_μ in any direction orthogonal to path vector $\mathbf{a}(\mathbf{r})$ if and only if $\mu = 0$.

Theorem 1 represents the link between the intuitively plausible concaveness of chemically important “reactive domains” of energy hypersurfaces, and the stability of minimum energy reaction paths. A minimum energy reaction path can be regarded as an idealized guideline for real chemical processes only if it is stable with respect to displacements orthogonal to the gradient.

The special properties (7) of Riemannian metric tensor ${}^{n+1}g_{ij}$ and the positive definiteness of ${}^{n-1}H(\mathbf{r})$ for interior points \mathbf{r} of D_0 imply a simple rule, interrelating equipotential contour surfaces, gradients and tangent planes. An equipotential contour surface ($E = \text{const}$) for any fixed $E(\mathbf{r})$ value may be defined as the point set

$$F_{E=\text{const}} = \{\mathbf{r}' : E(\mathbf{r}') = E(\mathbf{r})\} \tag{32}$$

A neighbourhood $G_E(\mathbf{r}, \rho)$ of point \mathbf{r} on such an equipotential contour surface F may be given as the intersection

$$G_F(\mathbf{r}, \rho) = G(\mathbf{r}, \rho) \cap F_{E=E(\mathbf{r})} \tag{33}$$

where $G(\mathbf{r}, \rho)$ is a ball of radius $\rho > 0$ around point \mathbf{r} . The hyperplane ${}^{n-1}R(\mathbf{r})$ at point \mathbf{r} divides the space R into two parts. For interior points of D_0 , $\mathbf{r} \in D_0$, $\mathbf{r} \notin B_{D_0}$, where B_{D_0} is the boundary of D_0 , the negative gradient $-\mathbf{g}(\mathbf{r})$ (the steepest descent direction) and a neighbourhood $G_F(\mathbf{r}, \rho)$ of equipotential contour surface $F_{E=E(\mathbf{r})}$ fall on the same side of hyperplane ${}^{n-1}R(\mathbf{r})$, i.e. into the same one of the two segments of R . For any other domain D_μ , $\mu > 0$, there is no such $G_F(\mathbf{r}, \rho)$ neighbourhood of any $\mathbf{r} \in D_\mu$ that would not have points falling on the side of ${}^{n-1}R(\mathbf{r})$ hyperplane opposite to $-\mathbf{g}(\mathbf{r})$. This “ D_0 domain rule” is trivially true and is easily visualized for the $n = 2$ case, as is shown in Fig. 3. In this case the equipotential contour surfaces and the ${}^{n-1}R(\mathbf{r})$ hyperplane become contour lines and tangent lines, respectively. For points $\mathbf{r} \in D_0$, vector $-\mathbf{g}(\mathbf{r})$ and the $E = \text{const}$ curve [$E = E(\mathbf{r})$] appear on the same side of tangent line ${}^{n-1}R(\mathbf{r})$, while for points $\mathbf{r} \in D_1$ they appear on opposite sides. For points \mathbf{r} falling on a minimum energy path P , this D_0 domain

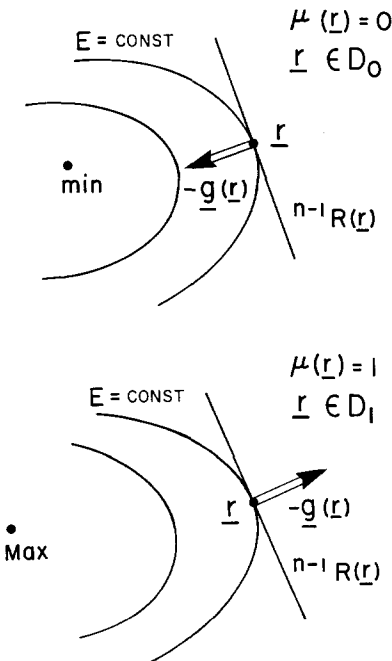


Fig. 3. Illustration of the “ D_0 domain rule”. In a D_0 domain equipotential contour line $E = \text{const.}$, and vector $-\mathbf{g}(\mathbf{r})$ fall on the same side of tangent ${}^{n-1}R(\mathbf{r})$, by contrast to a D_1 domain (instability region), where they fall on opposite sides

rule is equivalent to the stability condition derived earlier. Since only the steepest descent property of minimum energy reaction paths has been utilized in the above derivations, the results hold true for steepest descent paths in general. Domains and equipotential contour lines shown in Fig. 2 clearly follow this rule. It is also evident that minimum energy path P on this model surface is a stable path, since any displacement of the path, orthogonal to the gradient $\mathbf{g}(\mathbf{r})$, causes an increase in energy.

Domains D_0 are the reactive domains of primary importance on energy hypersurfaces. In order to utilize the special properties of domains D_0 , it is essential to determine the extent and the boundaries of these domains. At a boundary point \mathbf{r} of a domain D_μ , where a $\mu \rightarrow \mu \pm 1$ change occurs, the number of negative eigenvalues of ${}^{n-1}\mathbf{H}(\mathbf{r})$ changes by one. With the exception of critical points \mathbf{r}_C , matrix ${}^{n-1}\mathbf{H}(\mathbf{r})$ and eigenvalues $\alpha_k(\mathbf{r})$ depend continuously on \mathbf{r} along *any* path P . This implies that at a boundary point \mathbf{r} of D_μ , $\mathbf{r} \neq \mathbf{r}_C$, at least one eigenvalue α_k becomes zero. This result may be generalized for any $\Delta\mu > 0$ change at a boundary:

Theorem 2: If \mathbf{r} is a boundary point of domain D_μ and $\mathbf{g}(\mathbf{r}) \neq \mathbf{0}$, then ${}^{n-1}\mathbf{H}(\mathbf{r})$ is singular. If \mathbf{r} lies on a B_{D_μ/D_ν} boundary, then at least $|\mu - \nu|$ eigenvalues of ${}^{n-1}\mathbf{H}(\mathbf{r})$ become zero at point \mathbf{r} .

As the definition of domain D_μ implies, point \mathbf{r} on a B_{D_μ/D_ν} boundary ($\mu < \nu$) belongs to D_μ . That is, a D_μ point set is closed at a B_{D_μ/D_ν} boundary if $\mu < \nu$; D_μ is open at a B_{D_μ/D_ν} boundary if $\mu > \nu$.

A general D_μ domain may have several different types of boundary segments, some of them closed, others open. Points on the boundary of more than two domains belong to the domain of the smallest index μ .

The smallest possible index is $\mu = 0$, that indicates some further special properties of domains D_0 .

A D_0 domain may extend to infinity if it contains points representing infinite nuclear separation. Alternatively, D_0 may be bounded, i.e. the entire D_0 domain may be surrounded by other D_μ domains, $\mu \neq 0$. In the latter case D_0 is a *closed set*. In general, a bounded domain D_μ is a closed set if the indices ν of all neighbouring domains D_ν are larger than μ , $\mu < \nu$.

Theorem 2 provides a simple scheme for the partitioning of energy hypersurfaces, and for the partitioning of the underlying R space into a set of disjoint D_μ domains. The union T of all points \mathbf{r} where ${}^{n-1}\mathbf{H}(\mathbf{r})$ is singular,

$$T = \{\mathbf{r} : \det [{}^{n-1}\mathbf{H}(\mathbf{r})] = 0\} \quad (34)$$

contains all boundary points that are not critical points. Point set T may be visualized as a shell system of $n - 1$ -dimensional hypersurfaces partitioning the R space into various D_μ domains.

In Fig. 2 the $B_{D_0/D_1} \subset T$ boundaries are shown as broken lines. As a consequence of the D_0 domain rule, the B_{D_0/D_1} boundary lines intersect the equipotential contour lines $F_{E=\text{const}}$ at inflection points.

As this example shows, the region around the saddle point S is of particular interest. At point S the region of stability for a reaction path reduces to a single point, that is

equivalent to the condition set in the definition of minimum energy paths: it must pass through the saddle point. The energy surface shown is nearly quadratic in a relatively large neighbourhood of S as is indicated by the near linearity of boundaries B_{D_0/D_1} close to point S . Elementary algebraic treatment shows that for the simplest quadratic saddle surface $E(x, y) = x^2 - y^2$ the B_{D_0/D_1} boundaries are indeed straight lines, $y = x$ and $y = -x$. For this ideal saddle surface the (x, y) plane is partitioned into three domains by these boundaries:

$$D_0 = \{(x, y) : |y| \geq |x|\}$$

$$D_1 = \{(x, y) : |y| < -x, x < 0\}$$

$$D'_1 = \{(x, y) : |y| < x, x > 0\}$$

and a steepest descent path is stable only in D_0 .

While the example shown in Fig. 2 is typical for most chemical reactions, and a D_0 domain of stable steepest descent paths is sufficient in most instances to describe minimum energy reaction processes, nevertheless, a minimum energy path is not necessarily confined to a D_0 domain. In Fig. 4 a model of such an irregular, although probably not rare, process is shown. (Notations in this figure are the same as in Fig. 2.) Although most of the P minimum energy path falls into domain D_0 , it also enters domain D'_1 , that is, a domain of index $\mu = 1$. This domain D'_1 may be visualized best as a local protrusion on the otherwise smooth slope, that is not prominent enough to give rise to a local maximum. The progress along the minimum energy relief path ${}^{n+1}P$ over D'_1 is similar to the motion of a drop of water on the surface of a ball. By stretching this analogy somewhat further, if the ball is trans-

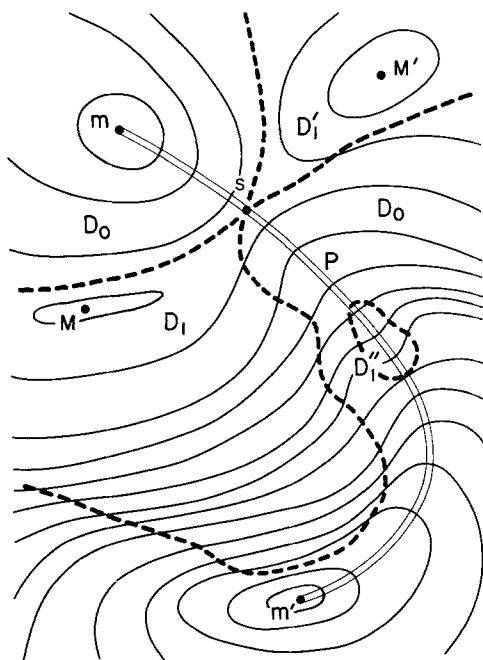


Fig. 4. Model surface with unstable minimum energy path in domain D'_1 . Instability region D'_1 does not influence the outcome of the chemical reaction

parent and placed on a horizontal plane, and one observes the motion of the shadow of the drop at noon, the shadow follows the direction of steepest descent. However, a displacement orthogonal to the gradient would also lower the potential energy of the drop, that is, the steepest descent path of the shadow on the plane is not a stable path. In the example of Fig. 4, the minimum energy reaction path P is also unstable in domain D'_1 . An important difference between D'_1 and the other two domains of index $\mu = 1$, D_1 and D'_1 , is the fact that D'_1 does not contain a local maximum point, while D_1 and D'_1 do. Such protrusions and in general, points $r \in D_\mu$, $\mu > 0$ are not likely to occur regularly along minimum energy paths, nevertheless, they may be present for certain paths. Such "built in" instability may be quite significant for real reaction paths that involve contributions from various vibrational modes, linearly independent of the steepest descent direction. Extensive instability regions along minimum energy paths may invalidate the claim that real reaction paths are approximately centered on minimum energy paths. Due to a small perturbation the minimum energy path may undergo large shifts, accompanied by an actual *lowering* of the energy for the same reaction coordinate value s . It is possible that such a shift causes the actual path to enter a D'_0 domain, different from domain D_0 that contains the minimum of products for the original minimum energy path. That is, an extensive instability domain D_μ , $\mu > 0$, along the minimum energy path may allow small perturbations to divert the path to a minimum of different products in D'_0 , thus the net result of the process may be an entirely different compound. In general, the presence of D_μ , $\mu > 0$ instability regions enhances the possibility of large deviations from an ideal minimum energy path.

On the model surface shown in Fig. 5, the minimum energy path P enters domain

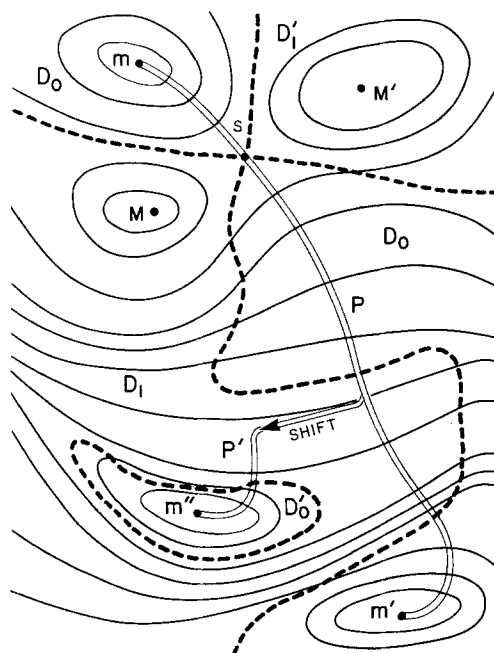


Fig. 5. Model surface with extensive instability region. Small perturbation may cause large shift in the minimum energy path P , associated with the lowering of energy. Path P' leads to a product m'' , different from product m'

D_1 , where due to the instability of the path a small perturbation may cause an extensive shift tangential to the equipotential contour line. It is clear that the actual shift shown causes a *lowering* of energy. Even if the ideal steepest descent resumes after this shift, the new path P' would lead to minimum m'' instead of minimum m' , thus to a different product.

Small contributions from various vibrational modes to the actual reaction path and small perturbations do not alter the outcome of the reaction if the entire minimum energy path falls into a D_0 domain. Consequently, such a *stable* minimum energy path, subject to small perturbations, may be associated with a *single* reaction mechanism as the example shown in Fig. 2 indicates.

Under fortuitous circumstances an unstable minimum energy path may also correspond to a single reaction mechanism, as shown by the model in Fig. 4. Here domain of instability D'_1 is embedded in domain D_0 and a shift within D'_1 cannot produce a path that would lead to a different minimum. However, as the model surface of Fig. 5 shows, this is not always the case, and a shift within the instability domain D_1 may lead to a product at m'' instead of one at m' . Although in the strict sense the ideal minimum energy path does lead to m' , the effect of the instability region cannot be predicted with certainty within the Born–Oppenheimer energy hypersurface model. Consequently, such an *unstable* minimum energy path, subject to small perturbations, may lead to more than one minimum, i.e. it may be associated with several actual reaction mechanisms.

A sufficient but not necessary condition of a one-to-one correspondence between reaction mechanisms and minimum energy paths is that the latter are entirely contained within D_0 domains.

An illustrative example is the motion of a bobsled over a convex terrain. If at the instance of leaving the concave route (D_0) and entering the convex terrain (D_1) the bobsled has the slightest momentum orthogonal to the steepest descent path, then over this convex terrain it may get hopelessly off-course. A similar momentum in a concave route (D_0) would cause only a “vibration” of negligibly small amplitude across the ideal path.

3. Conclusions

Partitioning of the R coordinate space of energy hypersurfaces into mutually exclusive $\{D_\mu^i\}$ connected point sets generates a hierarchy of coordinate domains in terms of their chemical importance. D_0 domains are of primary importance, since all minima and first-order saddle points necessarily fall into such D_0 domains. In addition, the stable regions of steepest descent paths coincide with the D_0 domains, as is established by Theorem 1. Domains D_μ with $\mu > 0$ may also occur along a minimum path and in these domains the minimum energy path, in fact any steepest descent path, is unstable. ${}^{n-1}\mathbf{H}(\mathbf{r})$ is necessarily positive definite at $\lambda = 0$ and $\lambda = 1$ type critical points, that is, $\mu = 0$ at these points of the path. Since the greater the index μ , the more eigenvalues of ${}^{n-1}\mathbf{H}(\mathbf{r})$ must become negative, D_μ domains with large index μ are not likely to fall near the $\lambda = 0$ and $\lambda = 1$ type critical points.

Consequently, the larger the index μ , the less likely that a D_μ domain would occur along a minimum energy path.

It is evident that large perturbations along a reaction path in any coordinate domain may alter the outcome of the reaction. Small perturbations, e.g. small vibrational contributions, on the other hand, will not change the outcome of the reaction, as long as the minimum energy path is contained in a D_0 domain. An instability region D_μ , $\mu > 0$, however, may allow small perturbations to cause large shifts of actual reaction paths, that may also alter the outcome of the reaction. In the latter case the Born–Oppenheimer energy hypersurface model is unable to predict the reaction products if small perturbations are allowed. Consequently, several sets of products and several sets of actual reaction paths (reaction mechanisms) may be associated with a single ideal minimum energy path passing through an instability domain D_μ , $\mu > 0$.

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References

1. Born, M., Oppenheimer, J. R.: *Ann. Phys.* **84**, 457 (1927)
2. Mezey, P. G.: Analysis of conformational energy hypersurfaces, in: *Progr. Theoret. Org. Chem.* **2**, 127 (1977)
3. Fukui, K.: *J. Phys. Chem.* **74**, 4161 (1970)
4. Tachibana, A., Fukui, K.: *Theoret. Chim. Acta (Berl.)* **49**, 321 (1978)
5. Einstein, A.: *The meaning of relativity*. Princeton: University Press 1950
6. Eisenhart, L. P.: *Riemannian geometry*. Princeton: University Press 1963
7. Tachibana, A., Fukui, K.: *Theoret. Chim. Acta (Berl.)* **51**, 189 (1979)
8. Klambauer, G.: *Real analysis*. New York: Elsevier 1973
9. Mezey, P. G.: *Chem. Phys. Letters* **47**, 70 (1977)

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