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Differential Geometry of Chemically Reacting Systems

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This paper is a detailed differential geometrical study of chemically reacting systems. In particular the following coordinate-free properties of chemically reacting systems are obtained: 1) the general solution of the intrinsic reaction coordinate (IRC) (henceforth referred to as meta-IRC), 2) "extended" definitions of the Hessian matrix and normal vibrations at any non-equilibrium point on the surface, and 3) clarification of the close connection between the geometry of meta-IRC and the geography of the surface at a transition point. The theory is elucidated using a model potential surface.

Key words: Reaction coordinate – Intrinsic reaction coordinate (IRC) approach – Chemically reacting systems, differential geometrical study of ~

1. Introduction

The picture of reaction coordinates has been conveniently utilized to abstract the essential nature of chemical reactions and many models of reaction processes have been proposed within the framework of reaction coordinates; the pioneering transition state theory [1] has paved the way for rationalization of reaction coordinates.

With the advent of quantum mechanical treatments describing the intrinsic forces governing the stability and interaction of atoms and molecules, new light was thrown on the theoretical treatments of chemical reactions. The major goal in this area of research is to calculate the adiabatic potential energy surfaces of reacting systems and to correlate the characteristics of the electronic structure of systems with the favorable reaction path in terms of reaction coordinates (see, for example, [2]). Recent works [3, 4] have tried to obtain geometrical images of the transition state on multi-dimensional potential energy surfaces in conjunction with reaction

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coordinates. In this connection, with the development of high-speed computers, one has come to be able to analyze with reasonable accuracy the adiabatic potential energy surfaces of chemically reacting systems.

Although the reaction coordinate had been used as a convenient and qualitative concept, Fukui [5] proposed the concept of intrinsic reaction coordinate (IRC) as a quantitative one based on a firm theoretical foundation, and Fukui *et al.* [6–8] have developed the reaction ergodography in terms of the IRC. The IRC defines for chemically reacting systems an idealized locus of nuclei on the adiabatic potential energy surface; the IRC is a curve passing from the initial to the final basin (or valley) by way of the transition point on the surface. Further recent studies have confirmed the utility of the concept of IRC [9, 10].

In this paper, we make a detailed differential geometrical study of adiabatic potential energy surfaces and reaction coordinates in the same manner that has proved so successful in analyzing the geometrical properties of visual 2-dimensional surfaces embedded in 3-dim. Euclidean space. We obtain various properties of geometrical importance about the adiabatic potential energy surface and IRC. In particular, special attention is given to the geometrical properties of the surface and IRC in the neighbourhood of the transition point. We also extend the notion of IRC in order that one may apply the notion of IRC to any reaction that may occur on a fixed adiabatic potential energy surface; from any point on the surface, one will be able to follow the idealized locus of chemical reaction by tracing the unique IRC along the gradient field of the adiabatic potential. This extended version of IRC will be referred to as meta-IRC. It will be clarified in the text that these geometrical properties are invariant under any coordinate transformation; consequently, we overcome the difficulty, pointed out by Stanton and McIver [3], that the use of curvilinear coordinates in the description of potential energy surfaces and reaction coordinates does not allow coordinate-free interpretation.

2. Geometry of Chemically Reacting Systems

One can trace the motion of the constituent nuclei of a chemically reacting system by the locus of an Euclidean multidimensional vector $\boldsymbol{x}$:

$$\boldsymbol{x}=(x^1,\ldots,x^{3N}) \tag{2.1}$$

where we suppose that the system is composed of N nuclei and the x^i $(i=1,\ldots,3N)$ are mass-weighted Cartesian coordinates. Let us introduce now an augmented $3N+1-$dim. Euclidean space E_{3N+1}, the $3N+1$'th coordinate x^{3N+1} of which is referred to as the energy-coordinate.[1] Since the dynamical motion of any chemically reacting system is characterized by a constant of motion, i.e., the total energy E of the system, the locus of $\boldsymbol{x}$ is then represented by a plane curve $\boldsymbol{r}$ in E_{3N+1} (see Fig. 1):

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[1] The $3N+1$'th coordinate x^{3N+1} is supposed to represent the total energy and adiabatic potential energy of the chemically reacting system.

$$r = (\boldsymbol{x}, x^{3N+1});\ x^{3N+1} = E = \text{const.}^2 \tag{2.2}$$

Although, in principle, the dynamical motion of the system is fully described by tracing the locus of r, one may often conveniently introduce n generalized coordinates $q^1, \ldots, q^n$ ($n \leqq 3N-6$) and trace the motion of the system in terms of a restricted number of coordinates; particularly for systems containing large molecules such as biological systems, it may be tractable to analyze only a few vibrational modes of interest rather than a huge number of normal vibrations at a time. Then, the vector r is described by $n+1$ coordinates (see Fig. 1):

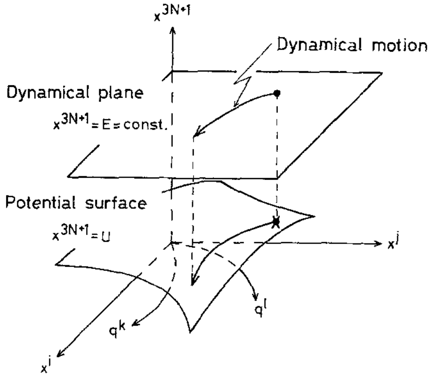

Fig. 1. Dynamical motion of the chemically reacting system in terms of the flight level of an airplane (marked with $\cdot$) and its shadow on the adiabatic potential energy surface U (marked with $\times$) in the framework of a mass-weighted Cartesian coordinate system $\{x^1 \cdots x^{3N} x^{3N+1}\}$ and a curvilinear coordinate system $\{q^1 \cdots q^n x^{3N+1}\}$

$$\begin{aligned} r &= r(q^i) \\ &= (x^1(q^1, \ldots, q^n), \ldots, x^{3N}(q^1, \ldots, q^n), x^{3N+1}); \\ & x^{3N+1} = E = \text{const.} \end{aligned} \tag{2.3}$$

These $n+1$ coordinates define a finite-dimensional Riemannian space, that is, an $n+1$-dim. $q^1 \ldots q^n x^{3N+1}$-space. The first fundamental form of this Riemannian space is given by using the line element ds of the underlying Euclidean space E_{3N+1} as follows:

$$\begin{aligned} ds^2 &= (dx^1)^2 + \cdots + (dx^{3N})^2 + (dx^{3N+1})^2 \\ &= \sum_{i,j=1}^{n} a_{ij}\, dq^i\, dq^j + (dx^{3N+1})^2 \end{aligned} \tag{2.4}$$

where

$$a_{ij} = \sum_{t=1}^{3N} (\partial x^t / \partial q^i)(\partial x^t / \partial q^j). \tag{2.5}$$

This $n+1$-dim. Riemannian space is apparently positive definite, and the Riemannian space will be referred to as R_{n+1}.

Now, we immerse the adiabatic potential energy surface $U(\boldsymbol{x})$ firstly in the $3N+1$-dim. Euclidean space E_{3N+1}; then, the surface U becomes a $3N$-dim.

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[2] The unit of the total energy and adiabatic potential energy is scaled so as to be equal to the mass-weighted coordinates.

hypersurface in E_{3N+1}. Likewise, when we describe $\boldsymbol{x}$ in terms of the n generalized coordinates, the adiabatic potential energy surface U is considered to be an n-dim. hypersurface in the $n+1$-dim. Riemannian space R_{n+1}.

In this case, any point on U is also represented by the position vector $\boldsymbol{r}$ as

$$\boldsymbol{r}=(\boldsymbol{x}(q^1,\ldots,q^n),x^{3N+1});x^{3N+1}=U(\boldsymbol{x}(q^1,\ldots,q^n)). \tag{2.6}$$

Now, let us follow the dynamical motion of the chemically reacting system. Metaphorically speaking, the locus $\boldsymbol{r}$ of motion may be interpreted as the locus of an airplane flying horizontally at fixed altitude over a range of mountains U (see Fig. 1). Then, the usual description of reaction coordinates on the potential energy surface U is nothing but the shadow of the airplane on the mountains U, as is illustrated in Fig. 1. The airplane may experience complicated rollings on account of air streams created by the characteristic geographical features of U and consequently vibrational (de-)excitations may frequently occur; for example, the bobsled effect, the whirlpool effect [11], or the mechanism of chemical laser [12, 13] are most typical. If other dynamical systems or other degrees of freedom of motion in the system disturb the flight of the airplane, they may 1) alter the shape of the mountains U, or 2) bring about pitching of the airplane; such cases are not treated in this paper.

We first investigate the geometrical (invariant under coordinate transformations) properties of the hypersurfaces, a) $x^{3N+1}=E$, and b) $x^{3N+1}=U(\boldsymbol{x}(q^1,\ldots,q^n))$ in the $n+1$-dim. Riemannian space R_{n+1}. These hypersurfaces themselves are n-dim. Riemannian surfaces. One of our major goals of this and succeeding sections is to formulate the differential geometry of such n-dim. Riemannian surfaces embedded in $n+1$-dim. Riemannian space R_{n+1}. The usual theory of hypersurfaces is concerned with n-dim. Riemannian surfaces embedded in $n+1$-dim. Euclidean spaces [14, 15]. More general theories deal with n-dim. Riemannian surfaces embedded in m-dim. Euclidean spaces [14]. However, these general theories will not be directly applied to the present problem; as far as the authors are aware, there is no detailed theory that deals with the particular case of the present problem where the $3N+1$'th coordinate of the underlying Euclidean space E_{3N+1} is preserved in $n+1$-dim. Riemannian space R_{n+1} and is used to define unique hypersurfaces in R_{n+1}.

Clearly from the definition, these n-dim. Riemannian surfaces are positive definite. The first fundamental forms are described by a) for $x^{3N+1}=E$ case:[3]

$$ds_a^2=a_{ij}\,dq^i\,dq^j \tag{2.7}$$

where a_{ij} is given by (2.5), and b) for $x^{3N+1}=U(\boldsymbol{x}(q^1,\ldots,q^n))$ case:

$$ds_b^2=b_{ij}\,dq^i\,dq^j \tag{2.8}$$

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[3] We use the very convenient summation convention introduced by Einstein. If an index occurs twice in a term, once as a superscript and once as a subscript, summation over that index is thereby indicated [14]: specifically, in the present theory of n-dim. Riemannian surfaces, from 1 through n. Note that n is not the dummy index to be summed over.

where

$$b_{ij}=a_{ij}+(\partial U/\partial q^i)(\partial U/\partial q^j). \tag{2.9}$$

One refers to ds_a and ds_b as the elements of arc length on the corresponding surfaces. The metric tensors a_{ij} and b_{ij} are symmetric covariant tensors of the second order, satisfying

$$a_{ij}=a_{ji},\ b_{ij}=b_{ji} \tag{2.10}$$

$$a_{ii},\ b_{ii}>0. \tag{2.11}$$

The metric forms are of course invariant under any coordinate transformation whose Jacobian is non-zero. We shall refer to the Riemannian surfaces constructed a) on the $x^{3N+1}=E$-plane as $R_n(a)$, and b) on the $x^{3N+1}=U$-surface as $R_n(b)$. It should be noted that at any equilibrium point P_{eq} on U, we have

$$b_{ij}=a_{ij}. \tag{2.12}$$

In other words, the Riemannian surface $R_n(b)$ is brought into contact with $R_n(a)$ at an equilibrium point P_{eq}. This property is very useful, as is clarified below, if one wishes to investigate the dynamical motion of chemically reacting systems in terms of the geometrical properties of U.

3. Geometrical Properties of the Riemannian Surfaces, $R_n(a)$ and $R_n(b)$

In this section, we concentrate mainly on the local differential geometry of the adiabatic potential energy surface U, that is, $R_n(b)$. However, the differential geometry of $R_n(a)$ is the same as $R_n(b)$ because they differ only in their first fundamental forms (2.7), (2.8). Therefore, unless otherwise specified, we shall develop the general theory of differential geometry of an n-dim. Riemannian surface R_n $(=R_n(a), R_n(b))$ embedded in an $n+1$-dim. Riemannian space R_{n+1}. The first fundamental forms (2.7), (2.8) can be written in the form

$$ds^2=g_{ij}\,dq^i\,dq^j \tag{3.1}$$

where the metric tensor g_{ij} represents a_{ij} or b_{ij}.

We show that a "unit normal vector" to the n-dim. Riemannian surface R_n can be successfully introduced in the $n+1$-dim. Riemannian space R_{n+1} (see (3.15)–(3.18)). This allows one to extend the theory of usual 2-dim. surfaces embedded in 3-dim. Euclidean space [14] to the present problem as will be clarified below. Therefore, the corresponding formulae and notation in the theory of 2-dim. surfaces are also used here in order to describe the special geometrical properties of R_n.

3.1. *Vector Space Properties*

A curve r lying on an n-dim. Riemannian surface R_n is described by its arc length s on the surface:

$$r=r(q^i(s)). \tag{3.2}$$

The direction of the tangent to the surface curve (3.2) is that of the vector

$$d\boldsymbol{r}/ds=\boldsymbol{r}_i\, dq^i/ds \tag{3.3}$$

where

$$\boldsymbol{r}_i=\partial \boldsymbol{r}/\partial q^i. \tag{3.4}$$

If one constructs all the possible curves on the surface that pass through a fixed point P_0 on the surface, then one sees from (3.3) that their tangent vectors point from P_0 into all the possible directions within the plane spanned by the n vectors $\boldsymbol{r}_i(P_0)$ $(i=1, \ldots, n)$. This plane is referred to as the tangent plane of the surface at the point P_0. The vector $\boldsymbol{r}_i$ is the tangent vector at P_0 on the curve

$$q^i(s)=s, \qquad q^j(s)=\text{fixed for } j\neq i. \tag{3.5}$$

A curve is referred to as a parametric curve; a curve given by (3.5) is referred to as a q^i-curve. Conversely, if one fixes q^i and allows all the other coordinates to vary freely, then one obtains a surface which is referred to as a q^i-surface. For the covariant counterparts, q_i-curves and q_i-surfaces are similarly defined.

In n-dim. Riemannian vector space R_n, the basis vectors $\boldsymbol{e}_i$ $(i=1, \ldots, n)$ of the coordinate system $\{q^1 \cdots q^n\}$ are given in terms of vectors of the underlying $3N+1$-dim. Euclidean space E_{3N+1} by[4]

$$\boldsymbol{e}_i=\boldsymbol{r}_i. \tag{3.6}$$

Also, we define the inner product of vectors in R_n by considering them as vectors in the underlying vector space E_{3N+1}.

Now, we introduce a basis $\boldsymbol{e}^i$ dual to $\boldsymbol{e}_i$ by

$$\boldsymbol{e}^i=g^{ij}\, \boldsymbol{e}_j. \tag{3.7}$$

The following biorthonormal relationship holds for the two kinds of basis sets:

$$\boldsymbol{e}_i\cdot \boldsymbol{e}^j=\delta_i^j, \qquad \boldsymbol{e}^i\cdot \boldsymbol{e}_j=\delta_j^i. \tag{3.8}$$

This relationship shows that the dual basis $\boldsymbol{e}^i$ is perpendicular to the q^i-surface, while $\boldsymbol{e}_i$ is tangent to the q^i-curve. Likewise, $\boldsymbol{e}_i$ is perpendicular to the q_i-surface, while $\boldsymbol{e}^i$ is tangent to the q_i-curve. Any vector $\boldsymbol{v}$ in R_n is then represented in two ways by

$$\boldsymbol{v}=v^i\boldsymbol{e}_i=v_i\boldsymbol{e}^i \tag{3.9}$$

where v^i/v_i are the contravariant/covariant components of the vector. Using properties (3.6)–(3.9), the angle θ between a pair of non-null vectors $\boldsymbol{u}$, $\boldsymbol{v}$ in R_n is defined by [16, 17]

$$\cos\theta=\boldsymbol{u}\cdot \boldsymbol{v}/|\boldsymbol{u}|\;|\boldsymbol{v}| \tag{3.10}$$

where the inner product and the norm are written as

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[4] It is assumed in this paper that the vectors $\boldsymbol{r}_i$ $(i=1, \ldots, n)$ are linearly independent.

$$\boldsymbol{u}\cdot\boldsymbol{v}=g_{ij}u^i v^j=u^i v_i \tag{3.11}$$

$$|\boldsymbol{u}|^2=u^i u_i. \tag{3.12}$$

In particular, the angle between $\boldsymbol{e}^i$ and $\boldsymbol{e}_i$ is given by

$$\cos\theta=|g^{ii}g_{ii}|^{-1/2}\quad\text{(not summed over } i\text{)}. \tag{3.13}$$

It should be noted that the angle θ thus defined is *independent of any coordinate transformation*

$$q'^i=q'^i(q^1,\ldots,q^n)$$

whose Jacobian is non-zero.

3.2. Curvature Properties

Now, the curvature vector of the curve on R_n is given by

$$d^2\boldsymbol{r}/ds^2. \tag{3.14}$$

Obviously, the vector may lie out of the tangent plane. Then, let us introduce a unit normal vector $\boldsymbol{n}$ to the tangent plane as

$$\boldsymbol{n}=\boldsymbol{N}/N,\qquad \boldsymbol{n}\cdot\boldsymbol{n}=1 \tag{3.15a}$$

$$\boldsymbol{N}=(-\partial x^{3N+1}/\partial x^1,\ldots,-\partial x^{3N+1}/\partial x^{3N},1) \tag{3.15b}$$

$$N^2=1+\sum_{i=1}^{3N}(\partial x^{3N+1}/\partial x^i)^2. \tag{3.15c}$$

This vector satisfies

$$\boldsymbol{n}\cdot\boldsymbol{e}_i=0\quad(i=1,\ldots,n), \tag{3.16}$$

which shows that the vectors $\boldsymbol{e}_i$ $(i=1,\ldots,n)$ together with $\boldsymbol{n}$ are linearly independent. It follows that any vector $\boldsymbol{r}$ in the $n+1$-dim. vector space R_{n+1} can be represented using mutually independent vectors $\boldsymbol{e}_i$ $(i=1,\ldots,n)$, $\boldsymbol{n}$ as follows:

$$\boldsymbol{r}=(\boldsymbol{r})^i\boldsymbol{e}_i+(\boldsymbol{r})^{n+1}\boldsymbol{n} \tag{3.17a}$$

where each component of the basis vector is defined by

$$(\boldsymbol{r})^i=\boldsymbol{e}^i\cdot\boldsymbol{r} \tag{3.17b}$$

$$(\boldsymbol{r})^{n+1}=\boldsymbol{n}\cdot\boldsymbol{r}. \tag{3.17c}$$

Particularly in $R_n(a)$, we have

$$\boldsymbol{n}=(0,\ldots,0,1) \tag{3.18a}$$

$$N=1. \tag{3.18b}$$

Note that the success of the introduction of the normal vector $\boldsymbol{n}$ by the explicit form (3.15), (3.18) is peculiar to the particular structure of the presented n-dim. Riemannian surfaces $R_n(a)$, $R_n(b)$ where the $3N+1$'th coordinate for energy is free from any coordinate transformation.

By using the unit normal vector $\boldsymbol{n}$ and the unit tangent vector $\boldsymbol{t}$, which is obtained as a linear combination of $\boldsymbol{e}_i$ $(i=1,\ldots,n)$, one may write the curvature vector (3.14) in the form

$$d^2\boldsymbol{r}/ds^2=\rho\boldsymbol{n}+\kappa_G\boldsymbol{t}. \tag{3.19}$$

In this representation, 1) the magnitude ρ of the normal component of the curvature vector is referred to as the normal curvature, and 2) the magnitude κ_G of the tangent component is referred to as the geodesic curvature of the curve. The curvature κ of the curve is then given by

$$\kappa^2=|d^2\boldsymbol{r}/ds^2|^2=\rho^2+\kappa_G^2. \tag{3.20}$$

We now study in more detail the two kinds of curvatures ρ, κ_G which characterize the geometry of R_n itself. To this purpose, one may easily find and utilize the formula of Gauss

$$\partial\boldsymbol{e}_j/\partial q^k=\Gamma^i_{jk}\boldsymbol{e}_i+L_{jk}\boldsymbol{n} \tag{3.21}$$

and the formula of Weingarten

$$\partial\boldsymbol{n}/\partial q^k=-g^{ij}L_{jk}\boldsymbol{e}_i. \tag{3.22}$$

In these formulae, 1) Γ^i_{jk} is the Christoffel symbol of the second kind, which is obtained from the Christoffel symbol of the first kind $[jk, l]$ as follows:

$$\Gamma^i_{jk}=g^{il}[jk, l] \tag{3.23}$$

$$\begin{aligned}[jk, l]&=(1/2)(\partial g_{kl}/\partial q^j+\partial g_{lj}/\partial q^k-\partial g_{jk}/\partial q^l)\\&=\sum_{t=1}^{3N}(\partial^2 x^t/\partial q^j\partial q^k)(\partial x^t/\partial q^l)+(\partial^2 x^{3N+1}/\partial q^j\partial q^k)(\partial x^{3N+1}/\partial q^l).\end{aligned} \tag{3.24}$$

and 2) L_{jk} is the coefficient of the second fundamental form of the surface R_n:

$$L_{jk}=(\partial^2 x^{3N+1}/\partial q^j\partial q^k-\sum_{t=1}^{3N}(\partial x^{3N+1}/\partial x^t)(\partial^2 x^t/\partial q^j\,\partial q^k))/N \tag{3.25}$$

where N is given by (3.15c). In $R_n(a)$, all the L_{jk} are zero. Using the formula of Gauss, we can reduce (3.14) to

$$d^2\boldsymbol{r}/ds^2=L_{jk}(dq^j/ds)(dq^k/ds)\boldsymbol{n}+(d^2q^i/ds^2+\Gamma^i_{jk}(dq^j/ds)(dq^k/ds))\boldsymbol{e}_i \tag{3.26}$$

and therefore we obtain

$$\rho=L_{jk}(dq^j/ds)(dq^k/ds) \tag{3.27}$$

$$\kappa_G\boldsymbol{t}=(d^2q^i/ds^2+\Gamma^i_{jk}(dq^j/ds)(dq^k/ds))\boldsymbol{e}_i. \tag{3.28}$$

In $R_n(a)$, the normal curvature ρ is identically zero.

Using these results, one can analyze in detail the locus of curves on the surface R_n. Of these, geodesic curves and lines of curvature are particularly important as we explain in turn.

1) Geodesic curves: A geodesic curve satisfies [14]

$$d^2q^i/ds^2+\Gamma^i_{jk}(dq^j/ds)(dq^k/ds)=0 \tag{3.29}$$

and therefore

$$\kappa_G = 0. \tag{3.30}$$

A geodesic curve gives the shortest distance measured on the surface R_n, provided that the two end points are located close to each other. In other words, a geodesic curve defines the intrinsic distance between any two points on R_n. Along the geodesic curve we have

$$d^2\boldsymbol{r}/ds^2 = \rho\boldsymbol{n}. \tag{3.31}$$

In $R_n(a)$, the geodesic curve satisfies

$$d^2\boldsymbol{r}/ds_a^2 = 0 \tag{3.32}$$

and the solution is of course a straight line in the underlying Euclidean space E_{3N+1}.

2) Lines of curvature: We define the principal directions [16] of the Riemannian surface $R_n(b)$ by extremizing ρ, that is,

$$\delta\rho = 0. \tag{3.33}$$

Then, we have the secular equation

$$(L_{jk} - \rho b_{jk})\xi^k = 0; \quad \xi^k = dq^k/ds_b. \tag{3.34}$$

This equation defines n principal directions $\xi^i_{(\alpha)}$ $(\alpha = 1, \ldots, n)$ associated with n principal normal curvatures ρ_α $(\alpha = 1, \ldots, n)$. The lines of curvature are the curves which are everywhere tangent to the principal directions. The solutions satisfy

$$L_{jk}\xi^j_{(\alpha)}\xi^k_{(\beta)} = \rho_\alpha\delta_{\alpha\beta} \tag{3.35}$$

$$b_{jk}\xi^j_{(\alpha)}\xi^k_{(\beta)} = \delta_{\alpha\beta} \tag{3.36}$$

where we assume that there is no degeneracy: $\rho_\alpha \neq \rho_\beta$ for $\alpha \neq \beta$. The line of curvature itself satisfies Rodrigues formula

$$d\boldsymbol{n}/ds_b = -\rho\, d\boldsymbol{r}/ds_b \tag{3.37}$$

which can be obtained from (3.22) and (3.34).

It should be noted that at any equilibrium point P_{eq} on U, we have from $\operatorname{grad} U = 0$ that

$$L_{jk} = \partial^2 U/\partial q^j\,\partial q^k \tag{3.38}$$

$$b_{jk} = a_{jk}, \qquad ds_b = ds_a \tag{3.39}$$

and then, the principal direction satisfies

$$(\partial^2 U/\partial q^j\,\partial q^k - \rho a_{jk})\xi^k = 0; \quad \xi^k = dq^k/ds_a. \tag{3.40}$$

Here, L_{jk} at P_{eq} is nothing but the jk-element of the Hessian matrix $\|\partial^2 U/\partial q^j\,\partial q^k\|$ [4] which defines the normal vibrations of the system. In the usual definition, the Hessian matrix $\|\partial^2 U/\partial q^j\,\partial q^k\|$ is not a covariant tensor of the second order at normal points on U. It follows that the normal vibrations that are obtained by diagonalizing the Hessian matrix at normal points on U are not invariant under coordinate transformations. Therefore, we extend the definition of Hessian matrix in Sect. 4.2. and find *extended normal vibrations* which are invariant under coordinate transformations. Also, the relation between the line of curvature and the meta-IRC is given in Sect. 4.1. (B) and discussed in more detail in Sect. 4.2. (B).

3.3. Particular Solution of the Line of Curvature

If the line of curvature is also geodesic, then using a fixed constant vector $\boldsymbol{l}$ the locus $\boldsymbol{r}$ is given as

$$\boldsymbol{l}\cdot\boldsymbol{r}=\text{const.} \tag{3.41}$$

This equation shows that the curve is a plane curve (see Fig. 2). The proof is given in the Appendix.

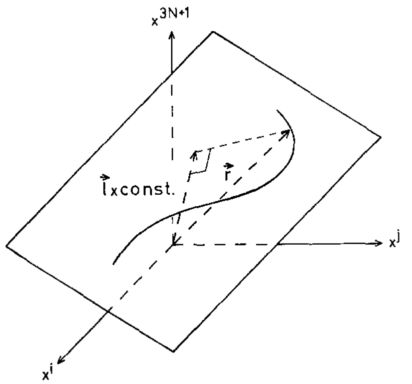

Fig. 2. The locus $\boldsymbol{r}$ of the geodesic line of curvature. This curve lies entirely on a plane perpendicular to the vector $\boldsymbol{l}$ given in (3.41) of the text

3.4. Dupin Indicatrix

We show in this subsection another useful character of the Riemannian surface R_n; namely the notion of Dupin indicatrix, which has been established in the usual theory of 2-dim. surfaces [14], and is also applicable in the study of the local geometrical character of U in the neighborhood of an arbitrary point on U in R_n.

The concept of Dupin indicatrix emerges as a result of employing a device that is helpful for obtaining some geometrical insight into curvature relations near a point P_0 on U. The device consists in carrying out a small parallel translation of the tangent plane at P_0 and then investigating its curve of intersection with the surface U. The locus in the translated tangent plane is represented by

$$L_{ij}(P_0)\eta^i\eta^j=\pm 1 \tag{3.42}$$

where η^i is the local coordinate chosen in place of q^i, which is obtained by magnification of the curve of intersection in the ratio $1:(2d)^{1/2}$, d being the length of the parallel translation. This locus is referred to as the Dupin indicatrix at P_0. Here, the principal directions of curvature coincide with the directions of the axes of the Dupin indicatrix and the lengths of the half-axes are given by

$$|\rho_1|^{-1/2}, \ldots, |\rho_n|^{-1/2}. \tag{3.43}$$

The Dupin indicatrix is classified as follows.

1) An ellipsoid with center zero if the second fundamental form is definite; in this case, P_0 is referred to as elliptic point.

The stable equilibrium point corresponds to the elliptic point. In the case $n=2$, the Dupin indicatrix is illustrated in Fig. 3(a).

2) Conjugate hyperboloids if the form is indefinite; in this case, P_0 is referred to as hyperbolic point. The tangent plane at P_0 intersects the surface U in cones which are tangent at P_0 to the asymptotic cones of the indicatrix. The cones of intersection satisfy

$$L_{ij}(P_0)(dq^i/ds_b)(dq^j/ds_b)=0 \tag{3.44}$$

and are referred to as asymptotic cones of the surface.

An unstable equilibrium point, a saddle, corresponds to a hyperbolic point. A transition point P_{tr} is a saddle possessing only one negative principal curvature. In the case $n=2$, the Dupin indicatrix is illustrated in Fig. 3b; *the asymptotic cone of the indicatrix retrogresses to a pair of asymptotic curves and the angle between them is bisected by the principal directions.* This property is very important when one considers the solution of meta-IRC at the transition point P_{tr} (see Sect. 4.1. (B)), and the relation with the normal coordinates at P_{tr} (see Sect. 4.2 (B)).

The other trivial cases are 3) the rank of L_{ij} is less than $n-1$ (P_0 is referred to as parabolic point), and 4) all L_{ij} vanish (P_0 is referred to as flat point; it is noted that R_n is embedded in a flat space).

Thus, we have obtained the intimate relationships between the geometry of any curve on the adiabatic potential energy surface U and the geometry of the surface itself. This will facilitate the dynamical study of chemically reacting systems in terms of the locus of trajectories cast on the surface U by the shadow of the airplane.

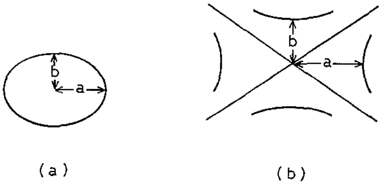

Fig. 3. The Dupin indicatrix of 2-dim. surfaces at a) an elliptic point, b) a hyperbolic point. The lengths of the half-axes are given by $a, b = |\rho_1|^{-1/2}, |\rho_2|^{-1/2}$

4. Dynamical Motions on U and the Meta-IRC

In this section, we shall analyze the dynamical properties of chemically reacting systems in terms of the reaction coordinate. The major results obtained in this section are 1) the general solution of IRC is given and will be referred to as meta-IRC, and permits the definition of a unique reaction coordinate starting from any non-equilibrium point on U, 2) the Taylor expansion of the potential energy U is defined for application to curvilinear coordinate systems, 3) by defining an "extended" Hessian matrix at any point on U, coordinate-transformation-invariant normal vibrations are given, 4) at any equilibrium point P_{eq} on U, the line of curvature exactly coincides with the normal coordinate and meta-IRC, and 5) particularly at the transition point P_{tr}, from a 2-dim. cross-sectional viewpoint, the meta-IRC exactly bisects the asymptotic lines which are just the curves of intersection between U and the equi-energy plane $x^{3N+1} = U(P_{\mathrm{tr}}) = \mathrm{const.}$ on which plane the airplane can narrowly fly across the transition point.

Now the Lagrangian L of the chemically reacting system is given by

$$L = (1/2)\dot{\boldsymbol{x}}^2 - U \tag{4.1}$$

where $\cdot$ signifies the derivative with respect to time. If we limit the degrees of freedom of the system to n ($n \leqq 3N-6$), then (4.1) is reduced by using generalized coordinates $q^1, \ldots, q^n$ to

$$L = (1/2) a_{ij} \dot{q}^i \dot{q}^j - U. \tag{4.2}$$

This is considered to be a Lagrangian in the Riemannian surface $R_n(a)$. In this Riemannian surface $R_n(a)$, the vector $\boldsymbol{r} = (\boldsymbol{x}, x^{3N+1})$ ($x^{3N+1} = E = \mathrm{const.}$) is essentially represented by, and therefore replaced by $\boldsymbol{x}$. Hence, we shall use the vector $\boldsymbol{x}$ in place of $\boldsymbol{r}$ unless confusion arises.

Lagrange's equation of motion is then given by

$$\ddot{q}^i + \Gamma^i_{jk} \dot{q}^j \dot{q}^k = -\partial U / \partial q_i. \tag{4.3}$$

The r.h.s. of this equation is the contravariant component of the gradient field created by the adiabatic potential energy U. Generally speaking, the gradient field may depend on some external parameters which are now disregarded; such as the contribution from the other degrees of freedom or from other systems. Thom's beautiful theory of catastrophes [18] may be useful in studying this kind of problem[5].

4.1. Gradient Field and the General Solution of Meta-IRC

Now, we shall solve the equation of meta-IRC. The meta-IRC is defined as the locus of the dynamical motion of the system the direction of which is always tangent to the gradient field. The starting point of the dynamical motion can be chosen at *any non-equilibrium point on U*; the system may attain to the equilibrium point by tracing the locus of meta-IRC. If one further searches for the allowable mode of chemical reaction starting at the equilibrium point, then one can follow the locus of IRC which is nothing but the particular solution of meta-IRC. The differential equation of meta-IRC is now represented in the covariant form as

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[5] After this work was completed, nice work of Collard and Hall [21] appeared, where the orthogonal trajectories of the electron density are discussed in terms of 1) the theory of virial partitioning of Bader [22] and Srebrenik and Bader [23], and 2) the catastrophe theory of Thom [18].

$$dq_1/(\partial U/\partial q^1) = \cdots = dq_n/(\partial U/\partial q^n). \tag{4.4}$$

It should be noted that the covariant component dq_i of the displacement vector $\boldsymbol{dr} = \boldsymbol{dx}$ relates with the generalized momentum p_i in the form

$$p_i = dq_i/dt = \dot{q}_i. \tag{4.5}$$

Therefore, we can rewrite (4.4) as

$$p_1/(\partial U/\partial q^1) = \cdots = p_n/(\partial U/\partial q^n). \tag{4.6}$$

This equation may allow a new interpretation for the dynamical motion along the meta-IRC on $R_n(a)$ that the direction of the generalized momentum along the meta-IRC is always tangent to the gradient field. This interpretation is inherent in the present particular problem where the adiabatic potential depends only on q^i and not on $\dot{q}^i$ $(i = 1, \ldots, n)$ (the explicit dependence of L on the time is of course not considered in this paper).

The solution of meta-IRC will be given A) at a normal point on U, and B) at an equilibrium point on U, in turn. A) At a normal point on U: There exist $n-1$ solutions of (4.4) which will be expressed by using $n-1$ parameters c_j $(j = 1, \ldots, n-1)$ as follows:

$$\phi_j(q_1, \ldots, q_n) = c_j \quad (j = 1, \ldots, n-1) \tag{4.7}$$

where ϕ_j $(j = 1, \ldots, n-1)$ are the solutions of

$$(\partial U/\partial q^i)(\partial \phi_j/\partial q_i) = 0 \quad (j = 1, \ldots, n-1). \tag{4.8}$$

Note that solutions of this kind are considered to be covariant versions of the solutions which are usually obtained for the differential equation written in terms of contravariant components [16]. In the present case, the contravariant version of (4.4) is given by

$$dq^1/(\partial U/\partial q_1) = \cdots = dq^n/(\partial U/\partial q_n). \tag{4.9}$$

The solutions ϕ^j $(j = 1, \ldots, n-1)$ of this differential equation may be equivalent to those of (4.4) and therefore one may start the following analysis by taking (4.9) as the fundamental differential equation; however, we shall choose (4.4) as the basic equation of meta-IRC because the covariant gradient field is more familiar and tractable to chemists rather than the contravariant one.

Then, let us choose these parametric curves as the $n-1$ new coordinates q'_j $(j = 1, \ldots, n-1)$ as

$$q'_j = \phi_j(q_1, \ldots, q_n) \quad (j = 1, \ldots, n-1). \tag{4.10}$$

Moreover, let us choose the n'th new coordinate q'_n as

$$q'_n = \phi_n(q_1, \ldots, q_n) \tag{4.11}$$

where the condition satisfied by ϕ_n is that the Jacobian of the coordinate transformation does not vanish:

$$\det \|\partial\phi_j/\partial q_k\| = \begin{Vmatrix} \partial\phi_1/\partial q_1 & \cdots & \partial\phi_n/\partial q_1 \\ \vdots & & \vdots \\ \partial\phi_1/\partial q_n & \cdots & \partial\phi_n/\partial q_n \end{Vmatrix} \neq 0. \tag{4.12}$$

By using this new coordinate system, the new covariant components of the displacement vector and gradient field will be represented by

$$dq'_j = (\partial\phi_j/\partial q_k)\, dq_k \quad (j=1, \ldots, n) \tag{4.13}$$

$$\partial U/\partial q'^j = (\partial\phi_j/\partial q_k)(\partial U/\partial q^k) \quad (j=1, \ldots, n). \tag{4.14}$$

Note that, on account of (4.8), all but one of the new covariant components of the gradient field are zero:

$$\partial U/\partial q'^n \neq 0, \qquad \partial U/\partial q'^j = 0 \quad (j=1, \ldots, n-1). \tag{4.15}$$

Therefore, the differential equation (4.4) is transformed into

$$dq'_1/0 = \cdots = dq'_{n-1}/0 = dq'_n/(\partial U/\partial q'^n). \tag{4.16}$$

Thus, we obtain the solution of meta-IRC as

$$dq'_n \neq 0, \qquad dq'_j = 0 \quad (j=1, \ldots, n-1). \tag{4.17}$$

This shows that *the meta-IRC is nothing but the* q'_n*-curve.* This solution includes the extension of the original IRC and defines a unique reaction coordinate that starts from any non-equilibrium point on the potential surface. This extension of the notion of IRC will prove effective not only for ground-state chemical reactions but also for excited-state chemical reactions where the starting nuclear configuration is usually far away from equilibrium. The dynamical motion along the meta-IRC is characterized by the one-dimensional displacement vector

$$d\boldsymbol{x}\,(=d\boldsymbol{r}) = dq'_n \boldsymbol{e}'^n. \tag{4.18}$$

The direction of this vector coincides with that of the generalized momentum p'_n. Then, one may say that the meta-IRC is nothing but the p'_n-curve. On the other hand, the contravariant components of the displacement vector and gradient field, which do not in general vanish for $j \neq n$, are given by

$$dq'^j = a'^{jn}\, dq'_n \quad (j=1, \ldots, n) \tag{4.19a}$$

$$\partial U/\partial q'_j = a'^{jn}\, \partial U/\partial q'^n \quad (j=1, \ldots, n). \tag{4.19b}$$

The geometrical interpretation of the solution is illustrated in Fig. 4. As is easily seen from Fig. 4, in the q'^n-surface, the potential remains constant along each q'^j-curve $(j \neq n)$: $\partial U/\partial q'^j = 0\,(j \neq n)$. This shows that the q'^n-surface represents the equi-potential surface, and hence the meta-IRC is orthogonal to the equipotential surface. But it should be noted that, although the increase or decrease of the equi-potential q'^n-surface is measured by the q'^n-curve and hence the q'^n-curve may be interpreted as the "promoting mode" of the chemical reaction, the meta-IRC is not identical with the q'^n-curve but with the q'_n- (or p'_n-) curve. This kind of incompatible relationship between the meta-IRC and the q'^n-curve stems from the non-orthogonality of the q'^n-curve to the other parametric q'^j-curves

($j=1,\ldots,n-1$). If the q'^n-curve is orthogonal to the other parametric curves, then we have

$$a'^{nj}=a'_{nj}=0 \quad (j=1,\ldots,n-1) \tag{4.20a}$$

and hence

$$\det \|a'_{ij}\| \neq 0 \quad (i,j=1,\ldots,n-1). \tag{4.20b}$$

In this case, (4.20b) shows that the equi-potential q'^n-surface is considered to be an $n-1$-dim. Riemannian surface in terms of the metric tensor a'_{ij} ($i,j=1,\ldots,n-1$); the q'^n-curve becomes orthogonal to this equi-potential surface. Then, the q'^n-curve becomes tangent to the meta-IRC and therefore the meta-IRC can be identified with the "orthogonal coordinate" q'^n; we shall refer to this coordinate q'^n as the normal meta-IRC. To summarize these results, we conclude that the coordinate q^n, which may be interpreted as the "promoting mode" of the chemical reaction, is identified with the meta-IRC when (4.20) holds; in this case, the coordinate is referred to as the normal meta-IRC.

Along the normal meta-IRC, we have from (4.19) that all but one of the contravariant components of the displacement vector and gradient field are zero:

$$dq'^n=a'^{nn}\,dq'_n\neq 0, \qquad dq'^j=0 \quad (j=1,\ldots,n-1). \tag{4.21}$$

$$\partial U/\partial q'_n=a'^{nn}\,\partial U/\partial q'^n\neq 0, \qquad \partial U/\partial q'_j=0 \quad (j=1,\ldots,n-1). \tag{4.22}$$

Now, if the meta-IRC becomes a geodesic curve on $R_n(a)$, then we have

$$a'^{nn}=a'_{nn}=1, \qquad a'^{nj}=a'_{nj}=0 \quad (j=1,\ldots,n-1) \tag{4.23}$$

which guarantees that *the geodesic meta-IRC is a normal meta-IRC*. In this case, we find from (3.13) that the angle between $\boldsymbol{e}'^n$ and $\boldsymbol{e}'_n$ is zero (mod 2π), which shows

$$\boldsymbol{e}'_n=\boldsymbol{e}'^n \tag{4.24}$$

and we finally obtain

$$dq'^n=dq'_n \tag{4.25}$$

accompanied by

$$\partial U/\partial q'_n=\partial U/\partial q'^n. \tag{4.26}$$

Now, (4.25) shows that both the direction and magnitude of the generalized velocity $\dot{q}'^n$ exactly coincide with those of generalized momentum p'_n. Moreover, Lagrange's equation of motion along the geodesic meta-IRC is reduced from (4.3) to the classical Newtonian equation of motion as if it were a one-dimensional motion in flat space:

$$\ddot{q}'^n=-\partial U/\partial q'^n. \tag{4.27}$$

(B) At an equilibrium point P_{eq} on U: In this case, one has

$$\partial U/\partial q^1=\cdots=\partial U/\partial q^n=0.$$

Then, the solution of (4.4) satisfies

$$(\partial^2 U/\partial q^i\,\partial q^j-\lambda a_{ij})\,dq^j/ds_a=0. \tag{4.28}$$

This is nothing but the equation of line of curvature at the equilibrium point P_{eq} with $\lambda=\rho$ that is given by (3.40). Also, we show in Sect. 4.2. (B) that the normal coordinate at P_{eq} coincides with the line of curvature and hence with meta-IRC, and we discuss the relationships in more detail in Sect. 4.2. (B).

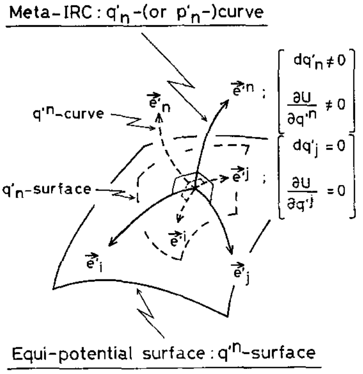


Fig. 4. Geometry of the reaction path

4.2. *Normal Vibrations and the Relationship with the Meta-IRC*

The normal vibrations of chemically reacting systems are usually obtained by diagonalizing the Hessian matrix. However, the so-called Hessian matrix $\|\partial^2 U/\partial q^i\,\partial q^j\|$ is not, as pointed out in Sect. 3.2., a covariant tensor of the second order at normal points on U so the normal vibrations thus obtained are not invariant under coordinate transformations. We shall give in this section the "extended" definition of the Hessian matrix $\|H_{ij}\|$ which is a covariant tensor of the second order, and find "extended" normal vibrations which are invariant under any coordinate transformation in $R_n(a)$.

The Hessian matrix has in principle been given by examining the Taylor expansion of the adiabatic potential. Now we define the Taylor expansion of the adiabatic potential U which is applicable to any curvilinear coordinate system as follows:

$$U(\boldsymbol{x}+\Delta\boldsymbol{x})=U(\boldsymbol{x})+U_i^{(1)}(\boldsymbol{x})\,\Delta u^i+(1/2)U_{ij}^{(2)}(\boldsymbol{x})\,\Delta u^i\,\Delta u^j+0((\Delta\boldsymbol{x})^3) \tag{4.29a}$$

where the local distance vector $\Delta\boldsymbol{x}$ ($|\Delta\boldsymbol{x}|$ is supposed to be sufficiently small) is represented on $R_n(a)$ as (see Fig. 5)

$$\Delta\boldsymbol{x}\;(=\Delta\boldsymbol{r})=\Delta u^i\boldsymbol{e}_i(\boldsymbol{x})\,; \qquad \Delta u^i=\boldsymbol{e}^i(\boldsymbol{x})\cdot\Delta\boldsymbol{x} \tag{4.29b}$$

and where the $U_i^{(1)}$ and $U_{ij}^{(2)}$ are defined by the covariant derivatives of U:

$$U_i^{(1)}=\partial U/\partial q^i \tag{4.29c}$$

$$U_{ij}^{(2)}=\partial^2 U/\partial q^i\,\partial q^j-\Gamma_{ij}^k\,\partial U/\partial q^k. \tag{4.29d}$$

By using covariant derivatives of U for the coefficients of each order of $\Delta\boldsymbol{x}$, we have obtained the required form of the Taylor expansion which has the superior property of invariance under coordinate transformations. Now we define an *extended* Hessian matrix $\|H_{ij}\|$ using $U_{ij}^{(2)}$ as

$$H_{ij}=U_{ij}^{(2)}=\partial^2 U/\partial q^i\,\partial q^j-\Gamma_{ij}^k\,\partial U/\partial q^k. \tag{4.30}$$

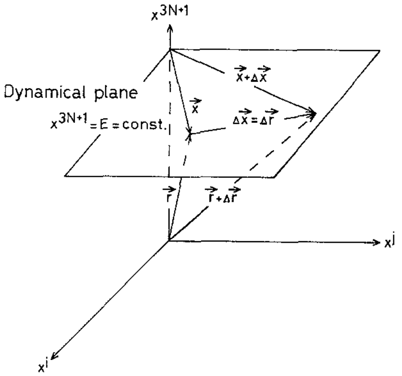


Fig. 5. The local distance vector $\Delta r = \Delta x$ on the dynamical plane $x^{3N+1} = E = \mathrm{const}$

This differs from the usual definition of the Hessian matrix by the term $-\Gamma^k_{ij}\,\partial U/\partial q^k$; this term ensures $\|H_{ij}\|$ to be a symmetric covariant tensor of the second order. Then, we define *extended normal vibrations* by diagonalizing the Hessian matrix as

$$(H_{ij} - \mu a_{ij})v^j = 0; \qquad v^j = dq^j/ds_a. \tag{4.31}$$

The n solutions of this equation define the vectors of normal vibrations $\boldsymbol{v}_{(\alpha)} = v^i_{(\alpha)}\boldsymbol{e}_i$ ($\alpha = 1, \ldots, n$). The explicit forms are given by

$$(H_{ij} - \mu_\alpha a_{ij})v^j_{(\alpha)} = 0 \tag{4.32a}$$

$$H_{ij}v^i_{(\alpha)}v^j_{(\beta)} = \mu_\alpha\,\delta_{\alpha\beta} \tag{4.32b}$$

$$a_{ij}v^i_{(\alpha)}v^j_{(\beta)} = \delta_{\alpha\beta}. \tag{4.32c}$$

The vectors of normal vibrations thus defined are invariant under any coordinate transformation:

$$\boldsymbol{v}_{(\alpha)} = v'^i_{(\alpha)}\boldsymbol{e}'_i = v^i_{(\alpha)}\boldsymbol{e}_i \tag{4.33}$$

where $v'^i_{(\alpha)}$ is the transformed vector component in terms of the transformed basis $\boldsymbol{e}'_i$. Also, the eigenvalue μ_α is of course invariant. The normal coordinates may be defined by the orthogonal curves that are everywhere tangent to the vectors of normal vibrations.

Using the above, we estimate the Taylor expansion of U; in particular, along the meta-IRC.

(A) At a normal point on U: Using the solutions of (4.31), the Taylor expansion of U is reduced from (4.29a) to a diagonalized form as follows:

$$U(\boldsymbol{x} + \Delta\boldsymbol{x}) = U(\boldsymbol{x}) + U^{(1)}_i(\boldsymbol{x})\,\Delta u^i + (1/2)\sum_{\alpha=1}^{n} \mu_\alpha(\Delta y^\alpha)^2 + 0((\Delta\boldsymbol{x})^3) \tag{4.34a}$$

$$U^{(1)}_i(\boldsymbol{x})\,\Delta u^i = \sum_{\alpha=1}^{n} U^{(1)}_i(\boldsymbol{x})v^i_{(\alpha)}\,\Delta y^\alpha \tag{4.34b}$$

where Δy^α is the weight of $v^i_{(\alpha)}$ in Δu^i:

$$\Delta u^i = \sum_{\alpha=1}^{n} v^i_{(\alpha)} \Delta y^\alpha \tag{4.34c}$$

$$\Delta y^\alpha = v_{(\alpha)i} \Delta u^i. \tag{4.34d}$$

Note that the coefficients Δy^α ($\alpha = 1, \ldots, n$) themselves may be referred to as the "local normal coordinates" that are 1) defined at each point $\boldsymbol{x}$, and 2) used as the local coordinates which describe the normal vibrations at the point. At the same time, the kinetic energy $(1/2)(\dot{\boldsymbol{x}} + \Delta\dot{\boldsymbol{x}})^2 = (1/2)\Delta\dot{\boldsymbol{x}}^2$ is also diagonalized at the point $\boldsymbol{x}$ as

$$(1/2)\,\Delta\dot{\boldsymbol{x}}^2 = \frac{1}{2}\sum_{\alpha=1}^{n} (\Delta\dot{y}^\alpha)^2. \tag{4.35}$$

If we employ the coordinate system which is given along the meta-IRC by (4.16), then we have only one linear term of $\Delta\boldsymbol{x}$ in the Taylor expansion:

$$U(\boldsymbol{x} + \Delta\boldsymbol{x}) = U(\boldsymbol{x}) + U'^{(1)}_n\, \Delta u'^n + \frac{1}{2}\sum_{\alpha=1}^{n} \mu_\alpha (\Delta y'^\alpha)^2 + 0((\Delta\boldsymbol{x})^3) \tag{4.36a}$$

$$U'^{(1)}_n\, \Delta u'^n = \sum_{\alpha=1}^{n} U'^{(1)}_n v'^n_{(\alpha)}\, \Delta y'^\alpha. \tag{4.36b}$$

Also, in this case, the kinetic energy is diagonalized at $\boldsymbol{x}$ as

$$(1/2)\,\Delta\dot{\boldsymbol{x}}^2 = \frac{1}{2}\sum_{\alpha=1}^{n} (\Delta\dot{y}'^\alpha)^2. \tag{4.37}$$

These formulas (4.36), (4.37) are the most fundamental representation of the Lagrangian of the system along meta-IRC in terms of the local normal coordinates $\Delta y'^\alpha$ ($\alpha = 1, \ldots, n$).

Furthermore, it may be more appropriate to block-diagonalize the Hessian matrix in the equi-potential q'^n-surface (see Fig. 4): because, from chemical intuition, it is supposed to be useful to separate the promoting mode of the chemical reaction along the meta-IRC from the residual $n-1$ normal vibrations in the equi-potential surface. We can do this with ease if the equi-potential q'^n-surface is considered to be an $n-1$-dim. Riemannian surface, that is, if

$$\det \|a'_{ij}\| \neq 0 \quad (i, j = 1, \ldots, n-1) \tag{4.38}$$

holds. Then, we obtain the Taylor expansion in the reduced diagonal form as

$$\begin{aligned} U(\boldsymbol{x} + \Delta\boldsymbol{x}) = {} & U(\boldsymbol{x}) + U'_n\, \Delta u'^n + (1/2) H'_{nn} (\Delta u'^n)^2 \\ & + \frac{1}{2}\sum_{\alpha=1}^{n-1} \bar{\mu}_\alpha (\Delta\bar{y}'^\alpha)^2 + \sum_{\alpha=1}^{n-1} H'_{nj} \bar{v}'^j_{(\alpha)} \Delta u'^n\, \Delta\bar{y}'^\alpha + 0((\Delta\boldsymbol{x})^3) \end{aligned} \tag{4.39}$$

where $\bar{\mu}_\alpha$, $\bar{v}'^i_{(\alpha)}$, $\Delta\bar{y}'^\alpha$ are the corresponding quantities of μ_α, $v'^i_{(\alpha)}$, $\Delta y'^\alpha$, which are obtained in the $n-1$-dim. q'^n-surface. We have a simple estimate of the off-diagonal component of the Hessian matrix as

$$H'_{nj} = \partial^2 U / \partial q'^n\, \partial q'^j - \Gamma'^n_{nj}\, \partial U / \partial q'^n \tag{4.40}$$

Also, the kinetic energy is obtained in the reduced diagonal form as

$$(1/2)\Delta\dot{\boldsymbol{x}}^2=(1/2)a'_{nn}(\Delta\dot{u}'^n)^2+\frac{1}{2}\sum_{\alpha=1}^{n-1}(\Delta\dot{\bar{y}}'^\alpha)^2 + \sum_{\alpha=1}^{n-1} a'_{nj}\bar{v}'^j_{(\alpha)}\,\Delta\dot{u}'^n\,\Delta\dot{\bar{y}}'^\alpha. \tag{4.41}$$

In these fundamental formulas (4.39), (4.41), the local coordinate $\Delta u'^n$ corresponds to the promoting mode of the chemical reaction, and the local coordinates $\Delta\bar{y}'^\alpha$ $(\alpha=1,\ldots,n-1)$ correspond to the residual normal vibrations in the equipotential q'^n-surface. These reduced diagonal forms of the potential and kinetic energies are supposed to be characteristic of chemical reactions proceeding along curvilinear reaction coordinates. Interestingly, *along the normal meta-IRC*, we have from (4.20) that 1) the condition (4.38) is satisfied, and 2) the kinetic energy is exactly diagonalized at each point:

$$(1/2)\Delta\dot{\boldsymbol{x}}^2=(1/2)a'_{nn}(\Delta\dot{u}'^n)^2+\frac{1}{2}\sum_{\alpha=1}^{n-1}(\Delta\dot{\bar{y}}'^\alpha)^2. \tag{4.42}$$

Regrettably, the off-diagonal term H'_{nj} in the potential energy does not vanish even though the chemical reaction proceeds along the normal meta-IRC:

$$H'_{nj}=-(1/2a'_{nn})(\partial a'_{nn}/\partial q'^j)(\partial U/\partial q'^n) \quad (j\neq n). \tag{4.43}$$

These results are useful for separating the promoting mode of nuclear rearrangements corresponding to the change of reacting system along the meta-IRC from the residual normal vibrations.

Furthermore, particularly in the case when the meta-IRC is also a geodesic curve on $R_n(a)$, which is of course a normal meta-IRC, we have $\Gamma'^n_{nn}=\Gamma'^j_{nn}=\Gamma'^n_{nj}=0$ $(j=1,\ldots,n-1)$ and (4.38). Then, the off-diagonal component of the Hessian matrix becomes zero:

$$H'_{nj}=0 \quad (j\neq n). \tag{4.44}$$

It follows that the Taylor expansion of U is reduced from (4.39) to a diagonalized form:

$$U(\boldsymbol{x}+\Delta\boldsymbol{x})=U(\boldsymbol{x})+U'^{(1)}_n\,\Delta u'^n+(1/2)H'_{nn}(\Delta u'^n)^2 +\frac{1}{2}\sum_{\alpha=1}^{n-1}\bar{\mu}_\alpha(\Delta\bar{y}'^\alpha)^2+0((\Delta\boldsymbol{x})^3). \tag{4.45}$$

The correspondence with the results of (4.34) is as follows

$$\mu_n=H'_{nn}=\partial^2U/(\partial q'^n)^2 \tag{4.46a}$$

$$\mu_\alpha=\bar{\mu}_\alpha \quad (\alpha=1,\ldots,n-1) \tag{4.46b}$$

$$\Delta y'^n=\Delta u'^n, \quad \text{i.e., } v'_{(n)i}=\delta_{ni} \text{ for } \boldsymbol{v}_{(n)} \tag{4.46c}$$

$$\Delta y'^\alpha=\Delta\bar{y}'^\alpha \quad (\alpha=1,\ldots,n-1). \tag{4.46d}$$

Then, we obtain the Lagrangian of the chemically reacting system proceeding along the geodesic meta-IRC as follows:

$$L(\boldsymbol{x}+\Delta\boldsymbol{x})=\frac{1}{2}\sum_{\alpha=1}^{n}(\Delta\dot{y}'^{\alpha})^2-U(\boldsymbol{x}+\Delta\boldsymbol{x}) \tag{4.47a}$$

$$U(\boldsymbol{x}+\Delta\boldsymbol{x})=U(\boldsymbol{x})+U_n'^{(1)}\,\Delta y'^n+\frac{1}{2}\sum_{\alpha=1}^{n}\mu_\alpha(\Delta y'^{\alpha})^2+0((\Delta\boldsymbol{x})^3). \tag{4.47b}$$

We may say therefore that one of the normal coordinates, which is locally represented by $\Delta y'^n$, indicates the promotion of the chemical reaction along the geodesic meta-IRC.

(B) At an equilibrium point P_{eq} on U: Here, the linear terms of $\Delta\boldsymbol{x}$ vanish from the Taylor expansion of U. Also, the Hessian matrix becomes a simple form as

$$H_{ij}=\partial^2 U/\partial q^i\,\partial q^j. \tag{4.48}$$

Then, the normal coordinates satisfy

$$(\partial^2 U/\partial q^i\,\partial q^j-\mu a_{ij})v^j=0; \quad v^j=dq^j/ds_a. \tag{4.49}$$

This is nothing but 1) the equation of lines of curvature at P_{eq} with $\mu=\rho$ that is given by (3.40), and 2) the equation of meta-IRC at P_{eq} with $\mu=\lambda$ that is given by (4.28). It follows that the three kinds of unique curves are tangent with each other at P_{eq}. In this case, we have from (3.15) that the unit normal vector of the potential energy surface U becomes

$$\boldsymbol{n}=(0,\ldots,0,1). \tag{4.50}$$

This property is particularly useful when we consider the local geometry of U and meta-IRC in the neighborhood of the transition point P_{tr}; the tangent plane of U at P_{tr} is nothing but the equi-energy plane $x^{3N+1}=U(P_{\mathrm{tr}})=\mathrm{const.}$ on which plane the airplane can narrowly fly across P_{tr}. Note that the path of the airplane goes along the meta-IRC and is confluent with the line of negative curvature at P_{tr}. Therefore, we can say that *the meta-IRC goes along the axis of the Dupin indicatrix at P_{tr} and passes the vertex, P_{tr}, of the asymptotic cone which, in the neighborhood of the transition point P_{tr}, is described by the cone of intersection between the equi-energy plane $x^{3N+1}=U(P_{\mathrm{tr}})=\mathrm{const.}$ and U.* In this case, the promoting mode of the chemical reaction at P_{tr} corresponds to one of the normal vibrations which is characterized by a negative force constant.

Clearly, the achievement of this geometrical property indicates the effectiveness of our particular choice of Riemannian surfaces $R_n(a)$ and $R_n(b)$. Moreover, we show in Sect. 5 that this property facilitates the pattern recognition of chemical reactions.

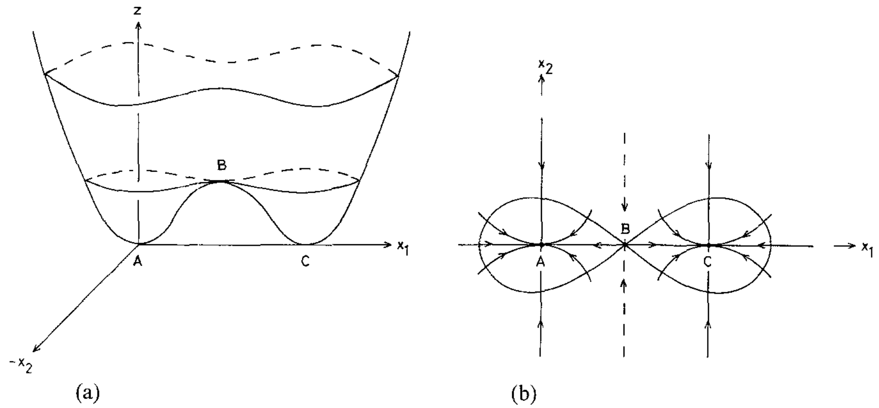
5. Example

We shall illustrate a model potential surface, which represents a typical pattern of isomerization reactions, and some of the results of the presented theory will be elucidated.

Let us consider the model potential energy surface as a function of two mass-weighted Cartesian coordinates which will be conveniently denoted by x_1 and x_2:

$$U(x_1, x_2)=(1/a^2)x_1^2(x_1-1)^2+(1/b^2)x_2^2; \quad a>b. \tag{5.1}$$

Here, the generalized coordinates are also chosen as x_1 and x_2. The x^{3N+1}'th coordinate for energy is now written as z. The shape of this model potential surface is depicted in Fig. 6(a). The $a=b$ case is also found in [19].



(a) (b)

Fig. 6. a) The shape of the model potential surface U given by (5.1) of the text. b) The solutions of meta-IRC (denoted by arrows) and the line of intersection between U and the equi-energy plane $z=U(B)$

There are three equilibrium points A, B, and C on this surface. The Dupin indicatrix at A, B, C is obtained by using magnified local coordinates η_1 and η_2 as follows:

A: Stable equilibrium point = elliptic point

$$(1/a^2)\eta_1^2+(1/b^2)\eta_2^2=1. \tag{5.2}$$

B: Transition point = saddle = hyperbolic point

$$-(1/2a^2)\eta_1^2+(1/b^2)\eta_2^2=\pm 1. \tag{5.3}$$

C: Stable equilibrium point = elliptic point

$$(1/a^2)\eta_1^2+(1/b^2)\eta_2^2=1. \tag{5.4}$$

Now, the distribution of hyperbolic points is confined to a domain $\alpha_- < x_1 < \alpha_+$ ($\alpha_\pm=(3\pm\sqrt{3})/6$), which is illustrated as the shaded region in Fig. 7. In this domain, a pair of asymptotic curves are found. Let θ be a parameter satisfying

$$-\pi/2<\theta<\pi/2. \tag{5.5}$$

Then, the asymptotic curves of the surface at B are given by

$$x_1=1/2+(\sqrt{12}/12)\sin\theta \tag{5.6}$$

$$x_2=\pm(\sqrt{6}/48)(b/a)(\sin 2\theta+2\theta). \tag{5.7}$$

The crossing point of this pair of asymptotic curves corresponds to $\theta = 0$ and is nothing but the saddle B. Then, in the neighborhood of B, we have

$$x_1 \sim 1/2 + (\sqrt{12}/12)\theta$$
$$x_2 \sim \pm(\sqrt{6}/12)(b/a)\theta$$

and therefore, in the limit as $\theta \rightarrow 0$ we have

$$-(1/2a^2)[(x_1 - 1/2)/\theta]^2 + (1/b^2)(x_2/\theta)^2 = 0 \tag{5.8}$$

which shows that this is nothing but the equation for the asymptotic curves of the Dupin indicatrix (5.3) with $\eta_1 \propto (x_1 - 1/2)/\theta$ and $\eta_2 \propto x_2/\theta$.

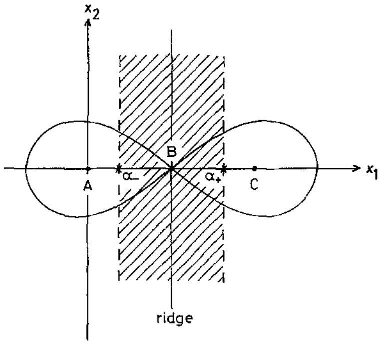


Fig. 7. The shaded region $\alpha_- < x_1 < \alpha_+$ ($\alpha_\pm = (3 \pm \sqrt{3})/6$) describes the distribution of hyperbolic points of the model potential surface

The solutions of meta-IRC are now obtained in closed form:

$$\begin{aligned} &x_1 = 0,\ 1/2,\ 1 \\ &x_2 = c \times [|x_1| \times |x_1 - 1| \times |x_1 - 1/2|^{-2}]^{a^2/b^2} \end{aligned} \tag{5.9}$$

where c is a constant. In the neighborhood of A, B, C, the allowed solutions of meta-IRC are given by

$$A\colon \quad \begin{aligned} &x_1 = 0 \\ &x_2 \sim c \times (4|x_1|)^{a^2/b^2} \end{aligned} \tag{5.10}$$

$$B\colon \quad \begin{aligned} &x_1 = 1/2 \\ &x_2 \sim c \times (4|x_1 - 1/2|^2)^{-a^2/b^2} \end{aligned} \tag{5.11}$$

$$C\colon \quad \begin{aligned} &x_1 = 1 \\ &x_2 \sim c \times (4|x_1 - 1|)^{a^2/b^2}. \end{aligned} \tag{5.12}$$

Some of the solutions of meta-IRC are shown in Fig. 6(b) by arrows. The direction of an arrow indicates that of the gradient field. In particular, at the transition point B, the allowed meta-IRC corresponding to the critical motion on the ridge is denoted by a broken line. Now, let us consider the IRC which traces the mode of isomerization from A through B to C. The solution of the IRC appropriate for the isomerization reaction is

$$x_2 = 0 \tag{5.13}$$

which corresponds to $c=0$ in (5.9). Note that this IRC is a geodesic line of curvature and therefore a plane curve (see, Sect. 3.3.), where the equation of this plane is also $x_2=0$ in the Euclidean 3-dim. x_1x_2z-space. In this case, the vectors of normal vibrations at each equilibrium point are the same and are given by

$$\boldsymbol{v}_{(1)}=(1, 0), \qquad \boldsymbol{v}_{(2)}=(0, 1) \tag{5.14}$$

and the eigenvalues (force constants) are given by

$$A: \quad \rho_1=2/a^2, \qquad \rho_2=2/b^2 \tag{5.15}$$

$$B: \quad \rho_1=-1/a^2, \qquad \rho_2=2/b^2 \tag{5.16}$$

$$C: \quad \rho_1=2/a^2, \qquad \rho_2=2/b^2. \tag{5.17}$$

Note that there are many solutions of meta-IRC which are confluent at the stable equilibrium points A and C. This ensures that any reaction starting at a non-equilibrium point on U in the neighborhood of some stable equilibrium point finally reaches that equilibrium point along the unique meta-IRC. Also, at the stable equilibrium points, every meta-IRC is tangent to only one vector $\boldsymbol{v}_{(1)}$, along the IRC $x_2=0$, which corresponds to the normal vibration of the weaker force constant $\rho_1=2/a^2$. It may be said therefore that the normal mode corresponding to the weaker force constant at the stable equilibrium point has a flexibility of accepting any promoting mode of the chemical reaction proceeding along the meta-IRC; conversely, the weaker normal vibration may have a flexibility of leading any mode of chemical reaction which starts at the stable equilibrium point (except those reactions proceeding along the isolated meta-IRC which is tangent to the normal vibration of the stronger force constant at the stable equilibrium point).

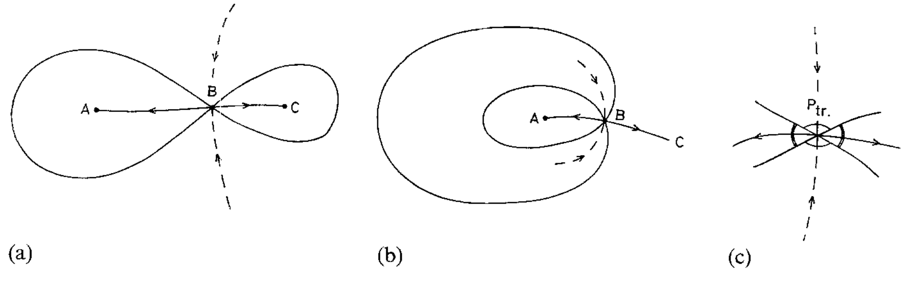


Fig. 8a–c. Pattern recognition of chemical reactions from the 2-dim. cross-sectional viewpoint. Fundamental patterns of a) isomerization reaction, and b) fragmentation reaction from A through B to C. c) shows that the meta-IRC should bisect a pair of asymptotic curves at any transition point P_{tr}. The "knot" pattern itself represents the dual geography of the potential surface $\bar{U}$ obtained by reversing the orientation of U: $U \rightarrow \bar{U} \equiv -U$

Furthermore, it should be noted that the line of intersection between U and the equi-energy plane $z=U(P_{tr})=\text{const.}$ allows the recognition of patterns in chemical reactions. The pattern of Fig. 8(a) is a generalization of Fig. 6 and describes the isomerization reaction $A \rightarrow B \rightarrow C$, and the pattern of Fig. 8(b) describes the fragmentation reaction $A \rightarrow B \rightarrow C$. These patterns may be considered to be the most fundamental patterns of chemical reactions. By folding, twisting, indenting, piling these patterns, one may obtain any kind of reaction pattern and may also classify the modes of complicated reactions (see Fig. 9). In this connection, the work of Krivoshey and Sleta [20] may be helpful for this kind of pattern recognition. Essential information needed to draw the patterns are 1) at any transition point, the curves of intersection between U and the equi-energy plane merge into a pair of asymptotic curves, and therefore, 2) the meta-IRC should bisect the two asymptotic curves (see Fig. 8(c)). Further discussion of these points will appear elsewhere.

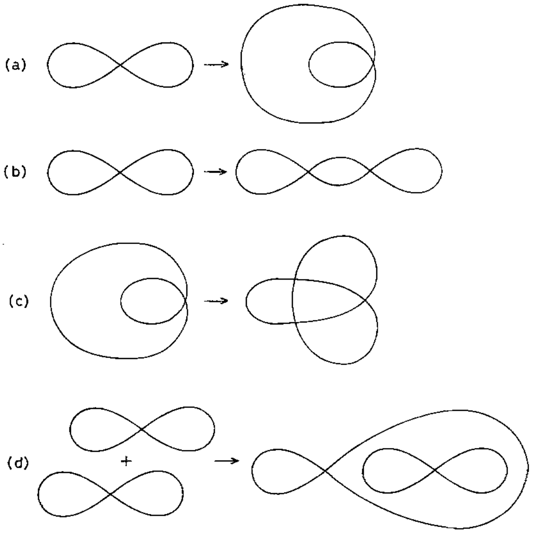


Fig. 9a–d. Basic operations to the fundamental patterns of Fig. 8a and b, yielding complicated patterns of chemical reactions from the 2-dim. cross-sectional viewpoint. a) Folding; note that this operation converts the pattern of isomerization reaction of Fig. 8a into that of fragmentation reaction of Fig. 8b. b) Twisting. c) Indenting. d) Piling; note that in this case as pattern may be disconnected we do not require that all levels of P_{tr}'s should be the same. Trivial operations such as shrinking (of several saddles) are omitted

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Appendix

In this Appendix, we prove the following theorem.
Theorem: A geodesic line of curvature $\boldsymbol{r}$ is a plane curve in R_{n+1}:

$$\boldsymbol{l}\cdot\boldsymbol{r}=\text{const.} \tag{A1}$$

where $\boldsymbol{l}$ is a fixed non-null vector:

$$\boldsymbol{l}=(\boldsymbol{l})_i\,\boldsymbol{e}^i+(\boldsymbol{l})_{n+1}\boldsymbol{n}. \tag{A2}$$

This is an extension of the well-known result for a curve in 3-dim. Euclidean space [14]. We shall prove this theorem in $n+1$-dim. Riemannian space R_{n+1}.

The proof proceeds in two steps. 1) First, we prove the following lemma.

Lemma: The necessary and sufficient condition that the curve $\boldsymbol{r}$ should obey in order to satisfy (A1), which is now written as

$$(\boldsymbol{l})_i(\boldsymbol{r})^i+(\boldsymbol{l})_{n+1}(\boldsymbol{r})^{n+1}=\text{const.}, \tag{A3}$$

is

$$\det \begin{Vmatrix} (\dot{\boldsymbol{r}})^1 & \cdots & (\boldsymbol{r}^{(n+1)})^1 \\ \vdots & & \vdots \\ (\dot{\boldsymbol{r}})^n & \cdots & (\boldsymbol{r}^{(n+1)})^n \\ (\dot{\boldsymbol{r}})^{n+1} & \cdots & (\boldsymbol{r}^{(n+1)})^{n+1} \end{Vmatrix} = \det \begin{Vmatrix} (\boldsymbol{e}^1 \cdot \dot{\boldsymbol{r}}) & \cdots & (\boldsymbol{e}^1 \cdot \boldsymbol{r}^{(n+1)}) \\ \vdots & & \vdots \\ (\boldsymbol{e}^n \cdot \dot{\boldsymbol{r}}) & \cdots & (\boldsymbol{e}^n \cdot \boldsymbol{r}^{(n+1)}) \\ (\boldsymbol{n} \cdot \dot{\boldsymbol{r}}) & \cdots & (\boldsymbol{n} \cdot \boldsymbol{r}^{(n+1)}) \end{Vmatrix} = 0 \tag{A4}$$

where · signifies the derivative with respect to the arc length s of the curve.

Proof: 1) Necessary condition. By successively differentiating (A1) $n+1$ times, we have

$$\begin{gathered} (\boldsymbol{l})_i(\dot{\boldsymbol{r}})^i + (\boldsymbol{l})_{n+1}(\dot{\boldsymbol{r}})^{n+1} = 0 \\ \vdots \\ (\boldsymbol{l})_i(\boldsymbol{r}^{(n+1)})^i + (\boldsymbol{l})_{n+1}(\boldsymbol{r}^{(n+1)})^{n+1} = 0. \end{gathered} \tag{A5}$$

Then, by eliminating $(\boldsymbol{l})_i$ and $(\boldsymbol{l})_{n+1}$, we obtain (A4). 2) Sufficient condition. If (A4) holds, one can choose a non-null vector $\tilde{\boldsymbol{l}}$ satisfying

$$\begin{gathered} \tilde{\boldsymbol{l}} \cdot \dot{\boldsymbol{r}} = 0, \quad \text{i.e.,}\ (\tilde{\boldsymbol{l}})_i(\boldsymbol{e}^i \cdot \dot{\boldsymbol{r}}) + (\tilde{\boldsymbol{l}})_{n+1}(\boldsymbol{n} \cdot \dot{\boldsymbol{r}}) = 0 \\ \vdots \\ \tilde{\boldsymbol{l}} \cdot \boldsymbol{r}^{(n+1)} = 0, \quad \text{i.e.,}\ (\tilde{\boldsymbol{l}})_i(\boldsymbol{e}^i \cdot \boldsymbol{r}^{(n+1)}) + (\tilde{\boldsymbol{l}})_{n+1}(\boldsymbol{n} \cdot \boldsymbol{r}^{(n+1)}) = 0. \end{gathered} \tag{A6}$$

By differentiating the first n equations of (A6), one has

$$\begin{gathered} \dot{\tilde{\boldsymbol{l}}} \cdot \dot{\boldsymbol{r}} = 0, \quad \text{i.e.,}\ (\dot{\tilde{\boldsymbol{l}}})_i(\boldsymbol{e}^i \cdot \dot{\boldsymbol{r}}) + (\dot{\tilde{\boldsymbol{l}}})_{n+1}(\boldsymbol{n} \cdot \dot{\boldsymbol{r}}) = 0 \\ \vdots \\ \dot{\tilde{\boldsymbol{l}}} \cdot \boldsymbol{r}^{(n)} = 0, \quad \text{i.e.,}\ (\dot{\tilde{\boldsymbol{l}}})_i(\boldsymbol{e}^i \cdot \boldsymbol{r}^{(n)}) + (\dot{\tilde{\boldsymbol{l}}})_{n+1}(\boldsymbol{n} \cdot \boldsymbol{r}^{(n)}) = 0. \end{gathered} \tag{A7}$$

Now, let us suppose that the determinant D^n defined by

$$D^n = \det \begin{Vmatrix} (\boldsymbol{e}^1 \cdot \dot{\boldsymbol{r}}) & \cdots & (\boldsymbol{e}^1 \cdot \boldsymbol{r}^{(n)}) \\ \vdots & & \vdots \\ (\boldsymbol{e}^{n-1} \cdot \dot{\boldsymbol{r}}) & \cdots & (\boldsymbol{e}^{n-1} \cdot \boldsymbol{r}^{(n)}) \\ (\boldsymbol{n} \cdot \dot{\boldsymbol{r}}) & \cdots & (\boldsymbol{n} \cdot \boldsymbol{r}^{(n)}) \end{Vmatrix} \tag{A8}$$

is non-zero (assumption 1). Then, by introducing a set of determinants $\{D^n(a \leftrightarrow n)\}$ which are the same as D^n except that the a'th column is replaced by the vector $((\boldsymbol{e}^n \cdot \dot{\boldsymbol{r}}), \ldots, (\boldsymbol{e}^n \cdot \boldsymbol{r}^{(n)}))$:

$$D^n(a \leftrightarrow n) = \det \begin{Vmatrix} (\boldsymbol{e}^1 \cdot \dot{\boldsymbol{r}}) & \cdots & (\boldsymbol{e}^1 \cdot \boldsymbol{r}^{(n)}) \\ \vdots & & \vdots \\ (\boldsymbol{e}^n \cdot \dot{\boldsymbol{r}}) & \cdots & (\boldsymbol{e}^n \cdot \boldsymbol{r}^{(n)}) \\ \vdots & & \vdots \\ (\boldsymbol{e}^{n-1} \cdot \dot{\boldsymbol{r}}) & \cdots & (\boldsymbol{e}^{n-1} \cdot \boldsymbol{r}^{(n)}) \\ (\boldsymbol{n} \cdot \dot{\boldsymbol{r}}) & \cdots & (\boldsymbol{n} \cdot \boldsymbol{r}^{(n)}) \end{Vmatrix} \begin{matrix} \\ \\ \leftarrow a\text{'th}, \\ \\ \\ \\ \end{matrix} \tag{A9}$$

we obtain the solutions of (A6) and (A7) as follows:

$$(\tilde{\boldsymbol{l}})_a = -(\tilde{\boldsymbol{l}})_n D^n(a \leftrightarrow n)/D^n; \quad a = 1, \ldots, n-1, n+1 \equiv n \tag{A10}$$

$$(\dot{\tilde{\boldsymbol{l}}})_a = -(\dot{\tilde{\boldsymbol{l}}})_n D^n(a \leftrightarrow n)/D^n; \quad a = 1, \ldots, n-1, n+1 \equiv n. \tag{A11}$$

Here, it is assumed that there exists a coordinate system $\{q^1 \cdots q^n x^{3N+1}\}$ in R_{n+1} which ensures that all the $D^n(a \leftrightarrow n)$ are non-zero (assumption 2). Therefore, for the a'th component associated with non-zero $D^n(a \leftrightarrow n)$, we have

$$(\dot{\tilde{\boldsymbol{l}}})_a/(\tilde{\boldsymbol{l}})_a = (\dot{\tilde{\boldsymbol{l}}})_n/(\tilde{\boldsymbol{l}})_n. \tag{A12}$$

If we set (A12) equal to $\sigma(s)$ and integrate we have

$$\tilde{\boldsymbol{l}}(s) = \boldsymbol{l} \exp\left[\int \sigma(s)\, ds\right] \tag{A13}$$

where $\boldsymbol{l}$ is a fixed non-null vector. Thus, by substituting (A13) into the first equation of (A6), we obtain

$$\boldsymbol{l} \cdot \dot{\boldsymbol{r}} = 0 \tag{A14}$$

and finally (A1).

Apparently, when $D^n = 0$ (when assumption 1) breaks down), the curve retrogresses to a plane curve in a lower-dimensional Riemannian space, that is, n-dim. $q^1 \cdots q^{n-1} x^{3N+1}$-space, which may be proved with ease by using mathematical induction. Likewise, if assumption 2) does not hold, then it can easily be shown that assumption 1) also breaks down for some coordinate system; in this case, the curve also retrogresses to a plane curve in a lower-dimensional Riemannian space.

(2) Second, a geodesic curve satisfies (3.31). Moreover, it follows from (3.37) that the geodesic line of curvature satisfies

$$\boldsymbol{r}^{(3)} = \dot{\rho} \boldsymbol{n} - \rho^2 \dot{\boldsymbol{r}}. \tag{A15}$$

Then, $\boldsymbol{r}^{(3)}$ is represented by a linear combination of $\dot{\boldsymbol{r}}$ and $\ddot{\boldsymbol{r}}$ as

$$\boldsymbol{r}^{(3)} = (\dot{\rho}/\rho)\ddot{\boldsymbol{r}} - \rho^2 \dot{\boldsymbol{r}} \quad (\rho = 0 \text{ case is trivial}). \tag{A16}$$

By combining (A16) and the lemma, we can prove the theorem.

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