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Novel Variational Principles of Chemical Reaction

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Minimum principles of chemical reaction coordinates are established. IRC (intrinsic reaction coordinate) draws the path of minimum distance from reactant to product. The distance is measured in the rigged configuration Riemannian space whose metric is determined by the distribution of the adiabatic potential energy. Moreover, minimum property of the intrinsic principle of least action is established for the intrinsic dynamism of chemical reaction. Minimum principle of the path connecting intercell boundary with cell is also discussed.

Key words: Minimum principle – Intrinsic reaction coordinate (IRC) approach – Geodesic law – Intrinsic principle of least action.

1. Introduction

Since the establishment of Eyring's absolute rate theory [1], the notion of "reaction coordinate" has been useful for the transparent description of the complex structure of chemical reaction mechanism. The chemical reaction process along reaction coordinate may be designated "quasistatic". The "quasistatic" process of chemical reaction is either exothermic or endothermic. In the case of exothermic process, the potential energy decreases along reaction coordinate, and in the case of endothermic process, the potential energy increases conversely. In both cases, the promotion of chemical reaction is measured along reaction coordinate by the variation of the potential energy. A unique definition of the reaction coordinate has been given by Fukui in 1970 [2] and designated IRC (intrinsic reaction coordinate). Various methods for the detailed analysis of the electronic and nuclear structure of chemically reacting system along IRC have been developed by Fukui et al. [3–6] and Morokuma et al. [7, 8] in terms of the advanced theory of chemical reactivity [9].

In the study of chemical reaction theory, the Born–Oppenheimer adiabatic approximation has been indispensable. In the Born–Oppenheimer adiabatic approximation, the constituent nuclei of chemically reacting system are momentarily clamped and then the adiabatic potential energy of the electronic state is obtained. If we solve the nuclear Lagrange's equation of motion on the adiabatic potential energy surface under the condition of momentarily clamped nuclei, then we have IRC as the solution. We have presented the differential geometrical study of chemically reacting systems, in particular, the differential equation satisfied by IRC [10]. The general solution of the differential equation, called the IRC equation, is referred to as meta-IRC; in this connection, IRC is classified as a particular meta-IRC which leads chemical reaction from reactant to product through transition state on the adiabatic potential energy surface [10].

On the other hand, dynamical studies of chemical reaction have widely developed in terms of classical mechanics; we follow the locus of classical trajectory of constituent nuclei on the adiabatic potential energy surface. For all that, it is certainly a matter of course that the theoretical background of the fundamental principle of chemical reaction dynamics is quantum mechanics. In the quantum mechanical treatment of chemical reaction dynamics, each classical trajectory has less physical reality. Quantum mechanically, every admissible dynamical state is described by a wavefunction. The wavefunction of a chemically reacting system spreads over the configuration Riemannian space; then, how reactant and product are to be recognized? In other words, how on the configuration Riemannian space should we draw the boundary in order to distinguish reactant and product? This problem is solved by introducing the cell structure of a chemically reacting system; this is based on the differential geometrical study of meta-IRC [10, 11]. The boundary of cell distinguishes reactant and product on the configuration Riemannian space. Transition state in the course of chemical reaction is then given as saddle point P_{tr} on the intercell boundary, through which point IRC connects reactant cell and product cell [11]. Meta-IRC's themselves serve as the generalized coordinates for the description of chemical reaction dynamics in terms of quantum mechanics [11].

Now, we have presented geodesic variational principle of reaction coordinates confined in a cell [12], the optimum reaction coordinate being meta-IRC: this is referred to as the geodesic law of meta-IRC. According to the geodesic law of meta-IRC (see (2.13) of [12]), we can associate with the "quasistatic" process of chemical reaction along meta-IRC the motion of a point along a geodesic curve in the rigged configuration Riemannian space R_n^* whose metric is determined by the distribution of the adiabatic potential energy [12]. Likewise, we have presented the intrinsic principle of least action with respect to the intrinsic dynamism of chemical reaction [12]: the intrinsic dynamism represents the "quasistatic" nuclear motion which obeys the IRC equation.

In this connection, the most successful variational principle in the development of chemical reaction theory has been the Rayleigh–Ritz variational principle. The Rayleigh–Ritz variational principle guarantees for the variational treatment of an eigenvalue problem the minimum property of real eigenvalues (upper bound property of trial eigenvalues). Using this property, many approximate models of chemically reacting systems have been developed: for example, the independent particle model (concept of orbital) of many-electron problem has been a very straightforward, successful one.

In the present paper, first, we shall establish 1) the minimum property of the geodesic law of meta-IRC as shown in Theorems G1 and G2, and using this, 2) a novel geodesic law of IRC having minimum property as shown in Theorems G3, G4, G5, and G6. Secondly, with respect to the intrinsic principle of least action also, the minimum property is proved as shown in Theorems A1 and A2. Thirdly, the minimum principle of the path connecting intercell boundary with cell is discussed. The novel variational principles thus established are characterized by their minimum property with respect to the optimum reaction coordinate. This property may play an important role for the application of the variational treatment of reaction coordinates, and further, a useful concept may be developed for the many-dimensional problems of chemical reaction theory.

2. Minimum Principles of Reaction Coordinates

2.1. Geodesic Law

Let us consider the following "quasistatic" process in a cell. A chemical reaction proceeds and arrives at a point P (see Fig. 1). Let an external work be exerted on the system to change the potential energy by a small amount $\Delta > 0$. For example, through the endothermic process, we arrive at a point $\tilde{P}^+$ on the equi-potential surface of $U = U(P) + \Delta$ (see Fig. 1). Also, through the exothermic process, we arrive at a point $\tilde{P}^-$ on the equi-potential surface of $U = U(P) - \Delta$ (see Fig. 1). Moving $\tilde{P}^+$ and $\tilde{P}^-$ independently, we find the meta-IRC which passes P, i.e. $P \rightarrow P^+$ and $P \rightarrow P^-$ (see Fig. 1). In what manner will the meta-IRC be selected as the optimum reaction coordinate to the "quasistatic" process of this kind? Here,

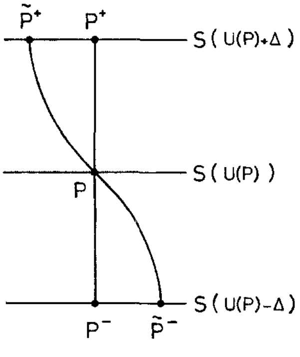

Fig. 1. Meta-IRC ($P^- \rightarrow P \rightarrow P^+$) penetrates equi-potential surfaces $S(U(P)-\Delta)$, $S(U(P))$, $S(U(P)+\Delta)$. Also shown is the curve of virtual reaction path ($\tilde{P}^- \rightarrow P \rightarrow \tilde{P}^+$)

we shall elucidate the minimum property of the geodesic law of meta-IRC and obtain the answer to this question: Theorems G1 and G2.

Theorem G1. Meta–IRC draws the path of minimum distance (hereafter in the present paper, the distance is measured in R_n^* and is referred to as s_g; the metric tensor g_{ij} of R_n^* is given by (2.11) and (2.12) of [12]) between a pair of termini of chemical reaction in a cell:

$$s_g\,(\text{virtual curve}) > s_g\,(\text{meta-IRC}). \tag{2.1}$$

Theorem G2. In a cell, meta-IRC draws the path of minimum distance from a point to an equi-potential surface.

Proof of Theorem G1. Let the geodesic law of meta-IRC be represented by

$$s_g = \int F\,d\theta = \text{extremum}, \tag{2.2}$$

$$F^2 = g_{ij}\dot{q}^i\dot{q}^j \tag{2.3}$$

where $\dot{q}^i$ is the ith contravariant component of the "velocity" vector with respect to the variation of $\theta = s_g$:

$$\dot{q}^i = dq^i/d\theta. \tag{2.4}$$

Using the Weierstrass E-function [13], the increment of s_g with respect to the virtual displacement of integral path is represented by

$$\Delta s_g \equiv s_g\,(\text{virtual curve}) - s_g\,(\text{meta-IRC})$$
$$= \int E\,d\theta, \tag{2.5}$$

where the path of integration goes along the curve of virtual reaction path. The E-function is now given by

$$E = |\mathbf{w}|\,(1-\cos\omega), \tag{2.6a}$$

$$\cos\omega = \langle \mathbf{w}|\text{grad}\ U\rangle / |\mathbf{w}| \cdot |\text{grad}\ U|, \tag{2.6b}$$

where $\mathbf{w}$ is the "velocity" vector along the virtual curve and ω is the angle between $\mathbf{w}$ and grad U. Since

$$1 \geq \cos\omega, \tag{2.7}$$

the E-function is non-negative definite:

$$E \geq 0. \tag{2.8}$$

This shows that

$$\Delta s_g \geq 0, \tag{2.9}$$

where the equal sign holds only when the virtual curve becomes identical to the meta-IRC. This proves Theorem G1.

Note that, by virtue of (2.20) of [12], the distance s_g of meta-IRC is measured by the difference of the adiabatic potential energy between a pair of termini of chemical reaction:

$$s_g = |\Delta U|. \tag{2.10}$$

Proof of Theorem G2. Suppose a stable equilibrium point A_i and the cell of A_i, which is referred to as Cell(A_i); A_i is referred to as the center of Cell(A_i) [11]. Consider an exothermic process in Cell(A_i). (The case of an endothermic process is similarly proved.) We shall use *reductio ad absurdum*. Assume that the distance between P and $\tilde{P}^-$ along a virtual curve is shorter than the distance between P and P^- along the meta-IRC:

$$s_g(\tilde{P}^- \to P;\ \text{virtual curve}) < s_g(P^- \to P;\ \text{meta-IRC}). \tag{2.11}$$

This will lead to contradiction. First, using Theorem G1 and (2.10), it is found that the curves of minimum distance from A_i to $\tilde{P}^-$ and P^- are given by the corresponding meta-IRC's, and the distances are equal to each other:

$$s_g(A_i \to \tilde{P}^-;\ \text{meta-IRC}) = s_g(A_i \to P^-;\ \text{meta-IRC}) = (U(P) - \Delta) - U(A_i). \tag{2.12}$$

Then, we have a pair of alternative paths from A_i to P: one is the meta-IRC via P^- and another is the succession of 1) meta-IRC from A_i to $\tilde{P}^-$, and 2) virtual curve from $\tilde{P}^-$ to P. Using (2.11) and (2.12), we have

$$\begin{aligned}
&s_g(A_i \to \tilde{P}^- \to P;\ \text{virtual curve})\\
&\quad = s_g(A_i \to \tilde{P}^-;\ \text{meta-IRC}) + s_g(\tilde{P}^- \to P;\ \text{virtual curve})\\
&\quad = s_g(A_i \to P^-;\ \text{meta-IRC}) + s_g(\tilde{P}^- \to P;\ \text{virtual curve})\\
&\quad < s_g(A_i \to P^-;\ \text{meta-IRC}) + s_g(P^- \to P;\ \text{meta-IRC})\\
&\quad = s_g(A_i \to P^- \to P;\ \text{meta-IRC}).
\end{aligned}$$

This shows that the distance from A_i to P along a virtual curve is shorter than that along the meta-IRC; this contradicts Theorem G1. This proves Theorem G2.

We have examined the minimum principles of the "quasistatic" process along meta-IRC in a cell. We shall now examine the "quasistatic" process along IRC between a pair of neighboring cells, Cell(A_i) and Cell(A_j). Then we should examine many curves of virtual reaction paths which pass through the intercell boundary, which is referred to as ((A_i, A_j)) [11]. In what manner will the IRC be singled out as the optimum reaction coordinate from among these reaction paths passing through ((A_i, A_j))? We shall find the answer to this question as follows.

Theorem G3. IRC is the path of minimum distance from the center of cell to the intercell boundary.

Theorem G4. IRC is the path of minimum distance between a pair of centers of neighboring cells through the intercell boundary.

Proof of Theorems G3 and G4. A set of points which are separated from A_i by an equal distance $\Delta > 0$ constitute the equi-potential surface of $U = U(A_i) + \Delta$. Since the "quasistatic" process from A_i to $((A_i, A_j))$ is endothermic, any set of points with Δ smaller than the minimum excitation energy $E_{ex} = U(P_{tr}) - U(A_i)$ have no intersection with $((A_iA_j))$. If Δ becomes as large as E_{ex}, then the intersection appears: this is nothing but the transition point P_{tr}. Clearly, the path of minimum distance from A_i to P_{tr} is IRC. This proves Theorem G3, and as a corollary, we have Theorem G4 (see Fig. 2(a)).

Note that the distance s_g of IRC is equal to the sum of the minimum excitation energies from both cells:

$$s_g(A_i \to A_j;\ \mathrm{IRC}) = (U(P_{tr}) - U(A_i)) + (U(P_{tr}) - U(A_j)). \tag{2.13}$$

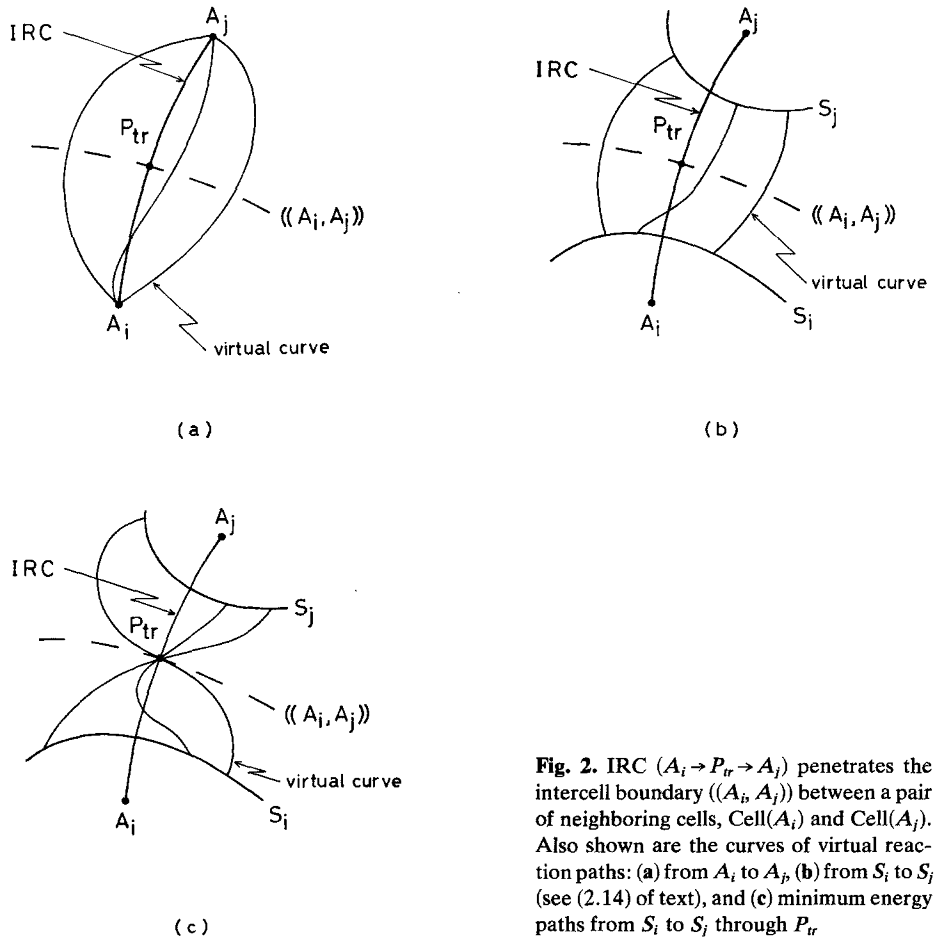

Fig. 2. IRC $(A_i \to P_{tr} \to A_j)$ penetrates the intercell boundary $((A_i, A_j))$ between a pair of neighboring cells, Cell(A_i) and Cell(A_j). Also shown are the curves of virtual reaction paths: (**a**) from A_i to A_j, (**b**) from S_i to S_j (see (2.14) of text), and (**c**) minimum energy paths from S_i to S_j through P_{tr}

Theorems G3 and G4 can be extended to intermediate reaction processes. Suppose an intermediate chemical reaction: the starting point lies on an equi-potential surface S_i activated by a certain amount $\Delta_i > 0$ from A_i, and the ending point lies on an equi-potential surface S_j activated by a certain amount $\Delta_j > 0$ from A_j, respectively, in such a way that

$$S_i = \{P_i | P_i \in \mathrm{Cell}(A_i),\ U(P_i) = U(A_i) + \Delta_i < U(P_{tr})\}, \tag{2.14a}$$

$$S_j = \{P_j | P_j \in \mathrm{Cell}(A_j),\ U(P_j) = U(A_j) + \Delta_j < U(P_{tr})\}. \tag{2.14b}$$

Since the minimum distances from A_i to any points $\{P_i\}$ on S_i are measured by corresponding meta-IRC's and are all equal, and the same is true for the case of j, we have extended the versions of Theorems G3 and G4 as follows (see Fig. 2(b)).

Theorem G5. IRC is the path of minimum distance from an equi-potential surface $S(U < U(P_{tr}))$ of the cell to the intercell boundary.

Theorem G6. IRC is the path of minimum distance between a pair of equi-potential surfaces $S(U < U(P_{tr}))$'s of neighboring cells through the intercell boundary.

The minimum principles of IRC thus obtained open the way for the variational optimization of IRC: with no recourse to the prescribed procedure of finding the steepest descent path from the transition point P_{tr}. Indeed, if we use Theorems G4 or G6 for the variational optimization of IRC, then it is unnecessary to locate P_{tr} in advance, because P_{tr} is obtained in consequence of the variational calculation itself. Moreover, since the geodesic curve of IRC gives the shortest distance from reactant to product, IRC can be considered to be suited to the object of chemical reaction which is to proceed from reactant to product through transition state. The teleological nature of this kind established for IRC has not been obtained by usual reaction coordinate approaches of qualitative and conventional nature.

2.2. Intrinsic Principle of Least Action

In [12], it has been shown that the intrinsic dynamism of chemical reaction along meta-IRC is provided with the extremum property, i.e. the intrinsic principle of least action (see Appendix):

$$A(\text{extended action}) = \text{extremum}. \tag{2.15}$$

The extremum value is measured by the distance s_g of meta-IRC (see (2.10) and (2.20) of [12]).

We shall show that the "action" A takes the minimum value along meta-IRC in conformity with the minimum character of s_g along meta-IRC.

Theorem A1. The "action" A takes the minimum value along meta-IRC between a pair of termini of chemical reaction in a cell:

$$A(\text{virtual curve}) > A(\text{meta-IRC}). \tag{2.16}$$

Theorem A2. In a cell, a meta-IRC from a point P to an equi-potential surface gives the path of minimum "action" from P to the surface.

Proof of Theorems A1 and A2. Consider an endothermic process. (The case of exothermic process is similarly proved.) Let the functional be represented by (see Appendix)

$$A = \int L\, d\tau, \tag{2.17}$$

$$L = (\tfrac{1}{2})(a_{ij}\dot{q}^i\dot{q}^j + \Delta_1 U), \tag{2.18}$$

where $\dot{q}^i$ is the ith contravariant component of the "velocity" vector with respect to the variation of τ (AT: accumulation time of reaction [11]):

$$\dot{q}^i = dq^i/d\tau. \tag{2.19}$$

Using the Weierstrass E-function [13], the increment of the "action" is represented by

$$\begin{aligned}\Delta A &\equiv A(\text{virtual curve}) - A(\text{meta-IRC})\\ &= \int E\, d\tau,\end{aligned} \tag{2.20}$$

where the path of integration goes along the virtual curve. The E-function for the present problem is represented by

$$E = (\tfrac{1}{2})|\mathbf{w} - \text{grad } U|^2 \geq 0. \tag{2.21}$$

Unless $\mathbf{w} = \text{grad } U$, the E-function is positive definite. This shows that

$$\Delta A \geq 0, \tag{2.22}$$

where the equal sign holds only when the virtual curve becomes identical to the meta-IRC. This proves Theorem A1. Theorem A1 for the intrinsic principle of least action corresponds to Theorem G1 for the geodesic law. Likewise, as the counterpart of Theorem G2, we have Theorem A2.

Furthermore, by considering τ as a time-like strictly monotone increasing parameter which describes the path of the endothermic process from the inside of cell to the intercell boundary, it is easy to obtain the counterpart theorems of Theorems G3, G4, G5, and G6 in a similar manner.

3. Minimum Principle of the Path Connecting Intercell Boundary with Cell

It has been shown by Theorems G3 and G5 that IRC is the optimum reaction coordinate of minimum distance from the inside of cell to the intercell boundary. Now, we shall fix a non-equilibrium point P located on the intercell boundary $((A_i, A_j))$ in the neighborhood of P_{tr} and examine the path of minimum distance from the inside of Cell(A_i) to P. Since P is a non-equilibrium point which belongs to the boundary of cell, we have no smooth meta-IRC which connects P with a point in the cell [11]. Then, to which point should the meta-IRC which starts from P converge? This is P_{tr}. In other words, P belongs to Cell(P_{tr}) on the intercell boundary if P is located in a sufficiently small neighborhood of P_{tr}. We shall show that the path of minimum distance from P to the center A_i of Cell(A_i) is the succession of 1) meta-IRC from P to P_{tr}, and 2) IRC from P_{tr} to A_i. The generalized version of this is given as follows.

Theorem. The path of minimum distance from a non-equilibrium point P on the intercell boundary $((A_i, A_j))$ to an equi-potential surface S_i (2.14a) is the succession of 1) meta-IRC from P to P_{tr}, and 2) IRC from P_{tr} to S_i. This is also the path of minimum "action".

Proof. Consider a curve C connecting Cell(A_i) and Cell(A_j) through the intercell boundary $((A_i, A_j))$ (see Fig. 3). Let a series of non-equilibrium points $\{P_k\}_{k=1,2,\ldots}$ be chosen near P on C in Cell(A_i). This series is assumed to converge to P from the inside of Cell(A_i):

$$\lim_{k \to \infty} P_k = P; \qquad P_k \in \mathrm{Cell}(A_i).$$

Since P_k lies in the inside of Cell(A_i), it is clear that meta-IRC which starts from P_k converges to S_i and this is the path of minimum distance from P_k to S_i. In the limit as $P_k \to P$, the meta-IRC converges to the succession of 1) meta-IRC from P to P_{tr} on $((A_i, A_j))$, and 2) IRC from P_{tr} to S_i (see Fig. 3). This is the path of minimum distance from P to S_i. Indeed, the value of the minimum distance between P_k and S_i is equal to the difference of the adiabatic potential energy, $U(P_k) - U(S_i)$; in the limit as $P_k \to P$, this value converges to the sum of 1) the minimum excitation energy from S_i to P_{tr} as given by the minimum distance between S_i and $((A_i, A_j))$, and 2) the minimum excitation energy from P_{tr} to P as given by the minimum distance between P_{tr} and P. It is clear that this is the path of minimum "action", as deduced from Theorems A1 and A2.

Thus, we have shown that a non-equilibrium point on the intercell boundary is connected with the cell using IRC as the path of minimum distance.

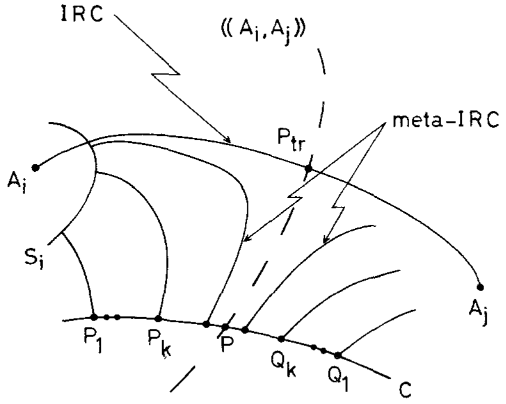

Fig. 3. IRC intersects the intercell boundary $((A_iA_j))$ at the transition point P_{tr}, and a curve C intersects $((A_i, A_j))$ at a fixed point P. A series of points $\{P_k\}_{k=1,2\ldots}$ on C converges to P from the inside of Cell(A_i). Also shown are the equi-potential surface S_i and the series of meta-IRC's from $\{P_k\}_{k=1,2,\ldots}$ to S_i. Likewise, a series of points $\{Q_k\}_{k=1,2,\ldots}$ on C converge to P from the inside of Cell(A_j), being accompanied by corresponding meta-IRC's

4. Discussion

There supposed to be pointed out two immediate applications of the present theory. One is the problem of determining the optimum reaction coordinate of "minimum energy paths". The minimum energy paths, which pass transition state, are visualized as a set of curves in Fig. 2(c). These paths are special cases of those virtual reaction paths in Fig. 2(b); the special character of the present problem is that we get the same minimum excitation energy E_{ex} $(=U(P_{tr})-U(S_i)$, or $U(P_{tr})-U(S_j))$ along each path as we need along IRC. We can follow a kind of "quasistatic" process along each path, but the solution of Lagrange's equation of motion under the "quasistatic" condition is uniquely given by IRC. Moreover IRC is found from Theorems G4 and G6 to have the teleological nature of providing the minimum distance from reactant to product. Thus IRC may be selected as the optimum reaction coordinate of "minimum energy paths". The variational calculation of IRC is then available using Theorems G4 or G6.

Another problem is the determination of transition state P_{tr} on the adiabatic potential energy surface; the electronic and nuclear structure of transition state itself has been the major subject of the development of chemical reaction theory. Now let us re-examine the Theorem obtained in Sect. 3. Suppose a series of non-equilibrium points $\{Q_k\}_{k=1,2,\ldots}$ be chosen on C in Cell(A_j), such that this series converges to P from the inside of Cell(A_j) (see Fig. 3):

$$\lim_{k\to\infty} Q_k = P; \qquad Q_k \in \mathrm{Cell}(A_j).$$

According to the Theorem, if sufficiently large k is given, then we have for $k'>k$ meta-IRC's starting from $P_{k'}$ or $Q_{k'}$ which pass sufficiently small the neighborhood of P_{tr}. In the limit as $k'\to\infty$, we have P_{tr} as well as P in due course.

5. Example

Let us take Theorem G6 and examine the minimum principle of IRC, which is the major result of the present theory. As a clear and simple example, we shall use the model potential:

$$U=-x^2+y^2. \tag{5.1}$$

The x-axis goes along the IRC. The origin is the transition point and the y-axis serves as the intercell boundary which divides the configuration space into two cells: one cell of $x=+\infty$ and another cell of $x=-\infty$.

Suppose a pair of equi-potential surfaces $S(U_1)$ and $S(U_2)$ which are connected by virtual reaction paths of type a:

$$y=\varepsilon x, \tag{5.2}$$

and type b:

$$y=\varepsilon, \tag{5.3}$$

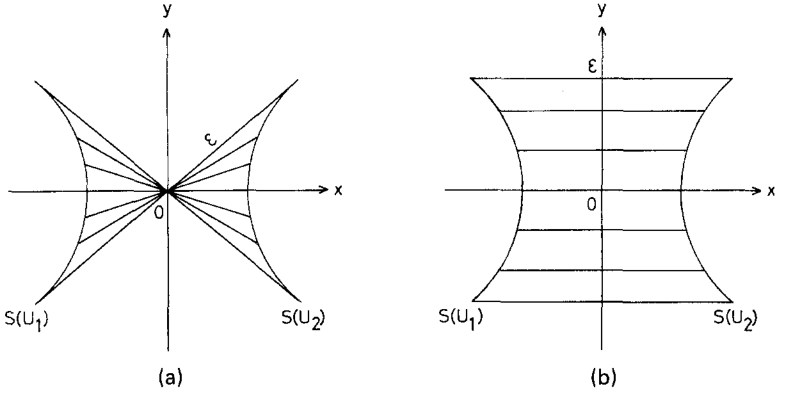

Fig. 4. A pair of equi-potential surfaces $S(U_1)$ and $S(U_2)$ on the model potential, and the virtual reaction paths of (**a**) type a and (**b**) type b (see Eqs. (5.1)–(5.3) of text)

where ε is a real parameter which characterizes the individual reaction path (see Fig. 4(a) and 4(b), respectively). The reaction paths of type a are minimum energy paths as discussed in Sect. 4 (see Fig. 2(c)). Mathematically, the minimum energy paths of type a are restricted to pass the transition point. On the other hand, the reaction paths of type b are free from such restriction and hence are supposed to be the simplified representatives of general reaction paths (see Fig. 2(b)).

Let the length of reaction path of each type measured in the rigged configuration space be designated as $s_g(\varepsilon)$, then we have

$$s_g(\varepsilon)=\{(1+\varepsilon^2)/(1-\varepsilon^2)\}(|\Delta U_1|+|\Delta U_2|) \tag{5.4}$$

for type a, and

$$\begin{aligned} s_g(\varepsilon) &= x_1\sqrt{x_1^2+\varepsilon^2}+x_2\sqrt{x_2^2+\varepsilon^2}+\varepsilon^2 \ln z; \\ x_1 &= \sqrt{\varepsilon^2+|\Delta U_1|}, \\ x_2 &= \sqrt{\varepsilon^2+|\Delta U_2|}, \\ z &= (x_1+\sqrt{x_1^2+\varepsilon^2})(x_2+\sqrt{x_2^2+\varepsilon^2})/\varepsilon^2 \end{aligned} \tag{5.5}$$

for type b of reaction paths, where

$$\Delta U_1 = U(0)-U_1, \qquad \Delta U_2 = U(0)-U_2. \tag{5.6}$$

The IRC corresponds to the path of $\varepsilon=0$ for both types of reaction paths, and satisfies the minimum principle of Theorem G6:

$$s_g(\varepsilon) \geq s_g(0). \tag{5.7}$$

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Appendix

In this Appendix, a note on the principle of least action is given. First, using the metric tensor a_{ij} of the configuration Riemannian space and the time parameter t, Maupertuis' principle of least action states that the action integral

$$A = \int 2T\,dt \tag{A1}$$

with

$$2T = a_{ij}\dot{q}^i\dot{q}^j, \tag{A2}$$

$$\dot{q}^i = dq^i/dt \tag{A3}$$

should have extremum value along real trajectory compared with that along virtual trajectory:

$$\delta A = 0; \qquad \text{along real trajectory.} \tag{A4}$$

It should be noted that along virtual trajectory also the conservation of energy should be satisfied:

$$T + U = E = \text{const.} \tag{A5}$$

The relationship of energy conservation brings about an intimate functional relationship between q^i and $\dot{q}^i$. If we consider the condition (A5) explicitly, then the variational problem (A4) can be rewritten as

$$\begin{aligned} \delta A &= \delta \int 2T\,dt; \qquad T = E - U \\ &= \delta \int (T + E - U)\,dt \\ &= \delta \int (T - U)\,dt. \end{aligned} \tag{A6}$$

This is equivalent to the variational problem

$$\delta A = 0 \tag{A7}$$

with the functional

$$A = \int L\,dt, \tag{A8}$$

where

$$L = T - U. \tag{A9}$$

Likewise, using the metric tensor a_{ij} of the configuration Riemannian space and the time-like parameter τ (AT: accumulation time of reaction [11]), the intrinsic principle of least action states that the extended action integral

$$A = \int 2T\,d\tau \tag{A10}$$

with

$$2T = a_{ij}\dot{q}^i\dot{q}^j, \tag{A11}$$

$$\dot{q}^i = dq^i/d\tau \tag{A12}$$

should have extremum value along meta-IRC [12]:

$$\delta A = 0; \qquad \text{along meta-IRC.} \tag{A13}$$

Note that the time-like parameter τ grows in the direction of endothermic process [11]; hence, the sign of A may be changed along exothermic process in order to ensure the chronological order of τ. As the counterpart of (A5), the functional relationship between q^i and $\dot{q}^i$ is represented by [12]

$$T - (\tfrac{1}{2})\Delta_1 U = 0, \tag{A14a}$$

where $\Delta_1 U$ is Beltrami's differential parameter of the first kind with respect to U:

$$\Delta_1 U = a^{ij}(\partial U/\partial q^i)(\partial U/\partial q^j). \tag{A14b}$$

Hence, if we consider the condition (A14) explicitly, then the variational problem (A13) can be rewritten as

$$\begin{aligned} \delta A &= \delta \int 2T\,d\tau; \qquad T = (\tfrac{1}{2})\Delta_1 U \\ &= \delta \int (T + (\tfrac{1}{2})\Delta_1 U)\,d\tau. \end{aligned} \tag{A15}$$

This is equivalent to the variational problem

$$\delta A = 0 \tag{A16}$$

with the functional

$$A = \int L\,d\tau, \tag{A17}$$

where

$$L = T + (\tfrac{1}{2})\Delta_1 U. \tag{A18}$$

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