Intrinsic Field Theory of Chemical Reactions*

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An intrinsic principle of least action is presented for the intrinsic dynamism of chemical reactions. Then, as the stationary trajectory, a meta-IRC (intrinsic reaction coordinate) draws a geodesic curve in a rigged Riemannian space. This establishes a geodesic law for the intrinsic dynamism. Moreover, a diagrammatic perturbation theory is formulated for the intrinsic dynamism, and a dynamical interaction between a chemically reacting system and a background system is investigated. Then, the structural stability of the system is discussed using a new concept of the dynamical potential field. An example is given in order to elucidate the present theory.

Key words: Intrinsic field theory – Intrinsic reaction coordinate (IRC) approach – Intrinsic principle of least action – Geodesic law – Structural stability – Dynamical potential field

1. Introduction

The ultimate goal of modern theoretical chemistry is supposed to be the establishment and examination of the foundation of the principle of chemical reactions. Quantum chemistry provides not only a theoretical framework for this activity, but it also provides a scheme of calculation to make a quantitative assessment of the theory. In particular, recent developments in computational quantum chemistry have acquired an outstanding progress in the computation of the adiabatic potential hypersurfaces of chemically reacting systems, and the development of molecular beam experiments has added direction and impetus. The determination of the hypersurface itself is one of the most difficult computational problems, but there

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* Dedicated to Prof. Hermann Hartmann on the occasion of his 65th birthday.

still remains the problem of how the chemically reacting system evolves through it. In this connection, a significant advance came with the introduction of the frontier orbital theory [1] and the Woodward–Hoffmann rules [2] with respect to stereo-selection and orientation of chemical reactions.

In the present paper, however, we shall direct our attention at another approach to chemical reactions. This is the IRC approach presented by Fukui [3] and developed by Fukui et al. [4–7] and Morokuma et al. [8, 9]; with a potential surface established, we seek the IRC through it, and arrive at the reaction rate constant by a suitable computational technique. Since the differential equation postulated by Fukui for the definition of the IRC is based on the gradient field of the potential [3], study on the geometrical properties of the chemically reacting system is central to the theoretical foundation of the IRC approach. Recently, from the detailed geometrical study of the adiabatic potential hypersurface, the intrinsic dynamism inherent to the IRC approach has been developed [10, 11]. In particular, by introducing a concept of meta-IRC, it has been clarified that a stable equilibrium point, that is the point of an equilibrium structure of the system, is realized as an accumulation point of the meta-IRC's which tie in its neighborhood a set of non-equilibrium points of the potential. This leads to a natural concept of cell structure of the chemically reacting system, where an intercell boundary appears by which an initial reactant cell and a final product cell are discriminated [11]. The IRC is then given by a particular meta-IRC which smoothly connects the terminal cells of the chemical reaction through the transition point located on the intercell boundary [11]. Stable limit theorems with respect to the intrinsic nature of the normal vibrations at the equilibrium point are also characteristic of the intrinsic dynamism [11].

On the other hand, as is well known, the fundamental principles of mechanics are formulated in terms of variational principles. The most famous one is the principle of least action presented by Maupertuis, who originally attempted to obtain for the corpuscular theory of light a theorem analogous to Fermat's principle of least time [12]. Maupertuis' principle of least action provides a real dynamical trajectory with a stationary character: for holonomic conservative system, an action integral evaluated along a real trajectory has the stationary value against deformation of the integral path with respect to a virtual trajectory adjacent to the real trajectory, with the time being correlated to the coordinates in such a way as to satisfy the conservation law of energy [12]. Maupertuis' principle of least action can be reformulated into Hamilton's principle, where, for a virtual trajectory, the time has the same terminal values as the real trajectory [12].

Likewise, from a geometrodynamical viewpoint, a locus of a trajectory satisfies a geodesic law: a trajectory draws a geodesic curve in a rigged Riemannian space. For example, Einstein's geodesic variational principle for the world line is the most famous; in the relativistic theory of gravitation, the world line draws a geodesic curve in a rigged Riemannian space whose metric is determined by the distribution of the source of gravitation [13]. Also, in the non-relativistic limit, Jacobi's geodesic principle is available; note that this is a reformulation of Maupertuis'

principle of least action [12]. In this connection, Einstein's geodesic variational principle for the world line can be considered to be a reformulation of a relativistic principle of least action [13].

In the first part of the present paper, we attempt to establish two kinds of fundamental variational principles for the intrinsic dynamism of chemical reactions. One is the *intrinsic principle of least action*, (2.5), and the other is the *geodesic variational principle*, (2.13). The former "dynamical" variational principle states that the "extended" action integral as defined by (2.2) has a stationary value for any part of an actual meta-IRC in the cell, as compared with neighboring paths which have the same terminal points and the same accumulation time (AT) τ [11] as the actual meta-IRC. The latter "geometrical" variational principle states that a meta-IRC is a geodesic curve in a rigged Riemannian space: this space is hereafter referred to as R_n^*. The relationship between these "dynamical" and "geometrical" variational principles is also shown, as in (2.20).

On the other hand, everything in the universe is interconnected and correlated with everything else. If we single out a chemically reacting system, we have divided the universe into two parts. All we have not singled out will be called the environment or the background. The background dependence of a chemically reacting system may be measured as a distortion of the rigged Riemannian space R_n^*, because a meta-IRC should draw a geodesic curve in R_n^* even under the influence of the background effect. (A particular perturbation may destroy the geodesic law, but such a case is not treated in the present paper.) Since the metric tensor g_{ij} of R_n^* is determined by the adiabatic potential U and the metric tensor a_{ij} of the primordial Riemannian space R_n, as is shown in (2.11) and (2.12), it may be of primary importance how to correlate the background effect into the perturbation of U and a_{ij} in terms of the intrinsic dynamism.

Thus, in the second part of the present paper, we shall develop a perturbation theory of the intrinsic dynamism of chemical reactions, which allows the perturbational treatment of U and a_{ij}. Then, a diagrammatic perturbation series is found for the perturbed solution of meta-IRC. Using this perturbation theory, a mechanism of dynamical energy transfer between a chemically reacting system and a background system will be discussed in terms of a new concept of the dynamical potential field, where the distortion of the metric tensor a_{ij} plays an important role. The dynamical potential field is found to be intimately related with the stability criterion of a chemically reacting system.

2. Variational Principles

2.1. Intrinsic Principle of Least Action

Let the "extended" action A with respect to a time-like parameter θ be defined by

$$A = \int 2T(q^i, dq^i/d\theta) \, d\theta \tag{2.1}$$

with

$$2T = a_{ij}(dq^i/d\theta)(dq^j/d\theta),\tag{2.2}$$

where $q^i(i = 1, \ldots, n)$ are the n generalized coordinates in the configuration Riemannian space R_n which describes the nuclear geometry of the system as a function of θ, T is the "extended" kinetic energy in terms of the "extended" velocities $dq^i/d\theta$ $(i = 1, \ldots, n)$, and a_{ij} is the metric tensor of R_n. The extended action A can be interpreted as the classical "action" if we multiply an appropriate scaling factor, if necessary.

As is well known, Maupertuis' principle of least action states that, along a real trajectory, the action is stationary with respect to virtual variation of the trajectory [12]:

$$\delta A = 0 \text{ along non-relativistic trajectory with } \theta = t,\tag{2.3}$$

where t is the realistic time. Likewise, Einstein's geodesic variational principle for the world line can be put into a form of relativistic principle of least action [13]:

$$\delta A = 0 \text{ along the world line with } \theta = s_w,\tag{2.4}$$

where s_w is the length of the world line chosen as a parameter of the world line.

Now, in the case of the intrinsic dynamism with respect to the AT τ, we can show that an "intrinsic" principle of least action holds as

$$\delta A = 0 \text{ along the meta-IRC with } \theta = \tau.\tag{2.5}$$

More precisely, the extended action A has a stationary value for any part of a meta-IRC in the cell, as compared with neighboring paths between the same termini for which the AT is correlated to the coordinates in such a way as to have same terminal values.

Proof of the intrinsic principle of least action. First, we shall prove that the extended kinetic energy T relates with the AT-dependent behavior of the adiabatic potential U along a meta-IRC in the form:

$$2T = dU/d\tau \text{ along the meta-IRC.}\tag{2.6}$$

Proof. The AT-dependence of U is represented by

$$dU/d\tau = (\partial U/\partial q^i)(dq^i/d\tau).\tag{2.7}$$

Using the IRC equation, of the form (3.19) in [11], the first derivative of U is given by

$$\partial U/\partial q^i = a_{ij} \, dq^j/d\tau.\tag{2.8}$$

Substituting (2.8) into (2.7), we have (2.6). Second, we shall prove that a meta-IRC satisfies the Euler equation of the variational problem (2.5) as

$$(d/d\tau)[\partial(2T)/\partial(dq^i/d\tau)] - \partial(2T)/\partial q^i = 0 \text{ along the meta-IRC.}\tag{2.9}$$

Proof. Using (2.6) and (2.7), we have $2T = (\partial U/\partial q^i)(dq^i/d\tau)$, and then we obtain (2.9) immediately:

$$(d/d\tau)[\partial(2T)/\partial(dq^i/d\tau)] = (d/d\tau)[\partial U/\partial q^i]$$
$$= (\partial^2 U/\partial q^i \, \partial q^j)(dq^j/d\tau)$$
$$= \partial(2T)/\partial q^i.$$

As a whole, the intrinsic principle of least action is proved.

Moreover, we have obtained from (2.1) and (2.6) the stationary value of the extended action A along meta-IRC; this is the increment of the potential energy from the initial terminus to the final terminus:

$$A = \Delta U \text{ along the meta-IRC.} \tag{2.10}$$

2.2. Geodesic Variational Principle

Here, we shall show that a meta-IRC is a geodesic curve in the rigged Riemannian space R_n^* whose metric tensor is given by

$$g_{ij} = \Delta_1 U a_{ij} \tag{2.11}$$

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

$$\Delta_1 U = a^{ij}(\partial U/\partial q^i)(\partial U/\partial q^j). \tag{2.12}$$

Then, a meta-IRC satisfies the geodesic variational principle:

$$\delta \int ds_g = 0 \text{ along the meta-IRC,} \tag{2.13}$$

where the line element ds_g of the meta-IRC is represented by using the first fundamental form of R_n^* as

$$ds_g^2 = g_{ij} \, dq^i \, dq^j. \tag{2.14}$$

Note that the relationship with the primordial configuration Riemannian space R_n is found to be

$$ds_g^2 = \Delta_1 U \, ds^2, \tag{2.15}$$

where ds^2 is the first fundamental form of R_n:

$$ds^2 = a_{ij} \, dq^i \, dq^j. \tag{2.16}$$

The conspicuous property of the meta-IRC as a stationary curve is illustrated in Fig. 1.

Proof of the geodesic variational principle. First, we shall prove that Beltrami's differential parameter of the first kind (2.12) is given along a meta-IRC by

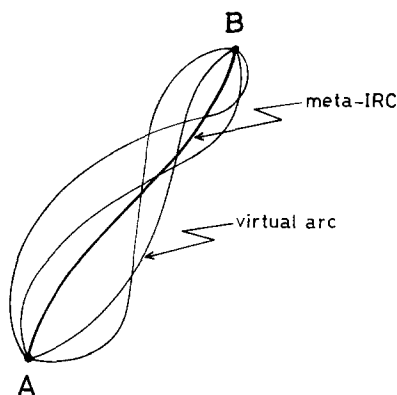$$\Delta_1 U = (dU/ds)^2 \text{ along the meta-IRC.} \tag{2.17}$$

Fig. 1. Meta-IRC draws a geodesic curve $(A \to B)$ in the rigged Riemannian space R_n^*

Proof. Using the IRC equation, of the form (3.10) in [11], we have

$$\partial U/\partial q^i = (dU/ds)a_{ij}(dq^j/ds).$$ (2.18)

Substituting (2.18) into (2.12) and using (2.16), we have (2.17). Second, we shall prove

$$ds_g^2 = (2T\,d\tau)^2 \text{ along the meta-IRC.}$$ (2.19)

Proof. Substituting (2.17) into (2.15) and using (2.6), we have (2.19). This proves that the variational principles (2.5) and (2.13) are identical along the meta-IRC in the cell; and therefore, the meta-IRC satisfies the geodesic variational principle, (2.13), as well as the intrinsic principle of least action, (2.5).

It should be noted that this geometrical variational principle, (2.13), is not merely a reformulation of the dynamical principle, (2.5). The two variational principles are presented independently. But, interestingly, the absolute values of the two kinds of functionals become the same along a meta-IRC in the cell:

$$|A| = \int ds_g = |\Delta U|.$$ (2.20)

Note that the intrinsic principle of least action and the geodesic variational principle are valid in the interior of a cell, where the stationary curve, that is a meta-IRC, is given as a smooth function of AT. Of course, it is possible to apply these variational principles for the intrinsic dynamism confined in the boundary of a cell excluding the equilibrium points. Also, by an appropriate limiting technique of the integration, it may be possible to extend the variational principles in order to allow the equilibrium points to be the termini of the integral. However, in order to establish the stationary nature of an IRC, which is nothing but a particular meta-IRC, a subtle problem arises; since an IRC crosses an intercell boundary, from a reactant cell to a product cell, a difficulty about the variational problem through the boundary of a cell should be overcome. Here, it should be remembered that an IRC has an accumulation point, that is a transition point, on the intercell boundary from either cell [11]. Hence, a remedy for this kind of difficulty may be given by

separating the integrand into two parts: from a reactant cell to a transition point, and from a transition point to a product cell. Then, the variational principles may be applicable in due course.

A clear illustration of the applicability of the geodesic variational principle to the IRC will be shown in Sect. 4 using a model potential surface.

Thus, the stationary nature of the intrinsic dynamism of chemical reactions is found to be governed by the variational principles. One may say that this establishes a teleological character of the intrinsic dynamism.

3. Perturbation Theory

In this section, we shall develop a perturbation theory of the intrinsic dynamism.

3.1. General Theory

3.1.1. IRC Equation

The IRC equation has been given in a compact form as [11]

$$dq^i(\tau)/d\tau = v^i(\tau) \quad (i = 1, \ldots, n) \tag{3.1}$$

where v^i $(i = 1, \ldots, n)$ are the contravariant components of the gradient field of the adiabatic potential U:

$$v^i = a^{ij} \, \partial U/\partial q^j. \tag{3.2}$$

The general solution of the IRC equation, that is the meta-IRC, constitutes a one-parameter continuous group G_1. Using the generator X of G_1, namely

$$X = v^i \, \partial/\partial q^i, \tag{3.3}$$

the locus of the meta-IRC can be represented by [11]

$$q^i(\tau) = R(\tau, \tau_0)q^i(\tau_0), \qquad q_i(\tau) = R(\tau, \tau_0)q_i(\tau_0) \tag{3.4}$$

with

$$R(\tau, \tau_0) = e^{X(\tau - \tau_0)}. \tag{3.5}$$

Here, R is an operator which governs the time (AT)-evolution of the reacting system along the meta-IRC: this operator is now referred to as the intrinsic reaction operator.

Now, it should be noted that the IRC equation can be reduced from (3.1) to an alternative form using the generator X of G_1 as

$$dq^i(\tau)/d\tau = Xq^i(\tau), \qquad dq_i(\tau)/d\tau = Xq_i(\tau). \tag{3.6}$$

The analogy of this form (3.6) with the form of the well-known time-dependent Schrödinger equation is remarkable:

$$d|\Psi(t)\rangle/d(-it/\hbar) = H|\Psi(t)\rangle, \tag{3.7}$$

where $\Psi(t)$ is the time-dependent wave vector and H is the Hamiltonian. Then, the following correspondence is found between the IRC equation (3.6) and the time-dependent Schrödinger equation (3.7):

$$\tau \leftrightarrow -it/\hbar \tag{3.8}$$

$$q^i(\tau) \text{ or } q_i(\tau) \leftrightarrow |\Psi(t)\rangle \tag{3.9}$$

$$X \leftrightarrow H. \tag{3.10}$$

Likewise, we obtain the following correspondence between the intrinsic reaction operator and the quantum mechanical evolution operator U:

$$R(\tau, \tau_0) \leftrightarrow U(t, t_0). \tag{3.11}$$

It follows that the intrinsic reaction operator satisfies the basic equations, analogous to those with respect to the quantum mechanical evolution operator, as follows: 1) the differential equation,

$$dR(\tau, \tau_0)/d\tau = XR(\tau, \tau_0), \tag{3.12}$$

and 2) the integral equation,

$$R(\tau, \tau_0) = 1 + \int_{\tau_0}^{\tau} XR(\tau', \tau_0) \, d\tau'. \tag{3.13}$$

Now, let us consider a perturbation of a meta-IRC. Suppose a perturbation of the gradient field in the form

$$v^i = v^{(0)i} + \tilde{v}^i, \tag{3.14}$$

where $v^{(0)i}$ $(i = 1, \ldots, n)$ are the unperturbed components and $\tilde{v}^i$ $(i = 1, \ldots, n)$ are the components of the perturbation. Then, the generator X is represented by

$$X = X^{(0)} + \tilde{X}, \tag{3.15}$$

where

$$X^{(0)} = v^{(0)i} \, \partial/\partial q^i, \tag{3.16}$$

$$\tilde{X} = \tilde{v}^i \, \partial/\partial q^i. \tag{3.17}$$

We assume that the unperturbed solution of the intrinsic reaction operator is available:

$$R^{(0)}(\tau, \tau_0) = e^{X^{(0)}(\tau - \tau_0)} \tag{3.18}$$

and that the unperturbed solution is obtained as

$$q^{(0)i}(\tau) = R^{(0)}(\tau, \tau_0)q^i(\tau_0),$$

$$q_i^{(0)}(\tau) = R^{(0)}(\tau, \tau_0)q_i(\tau_0). \tag{3.19}$$

Then, let R be given by

$$R = R^{(0)}\tilde{R}, \tag{3.20}$$

where $\tilde{R}$ is the intermediate reaction operator. The intermediate reaction operator satisfies the following differential equation:

$$d\tilde{R}/d\tau = \tilde{X}_I \tilde{R},\tag{3.21}$$

where $\tilde{X}_I$ is the intermediate generator defined by

$$\tilde{X}_I = R^{(0)-1} \tilde{X} R^{(0)}.\tag{3.22}$$

Also, the intermediate reaction operator satisfies the integral equation

$$\tilde{R}(\tau, \tau_0) = 1 + \int_{\tau_0}^{\tau} \tilde{X}_I(\tau') \tilde{R}(\tau', \tau_0) \, d\tau'\tag{3.23}$$

and the solution may be given by an iterative procedure as

$$\tilde{R}(\tau, \tau_0) = 1 + \sum_{m=1}^{\infty} \tilde{R}^{(m)}(\tau, \tau_0),\tag{3.24a}$$

where

$$\tilde{R}^{(m)}(\tau, \tau_0) = \int_{\tau > \tau_m > \cdots > \tau_1 > \tau_0} d\tau_m \ldots d\tau_1 \, \tilde{X}_I(\tau_m) \cdots \tilde{X}_I(\tau_1).\tag{3.24b}$$

Using (3.20), (3.22), (3.24), and Dyson's chronological operator P [14], the intrinsic reaction operator is found to be

$$R(\tau, \tau_0) = R^{(0)}(\tau, \tau_0) P \exp \left[\int_{\tau_0}^{\tau} d\tau' \, \tilde{X}_I(\tau') \right]\tag{3.25a}$$

or

$$R(\tau, \tau_0) = R^{(0)}(\tau, \tau_0) + \sum_{m=1}^{\infty} R^{(m)}(\tau, \tau_0),\tag{3.25b}$$

where

$$R^{(m)}(\tau, \tau_0) = \int_{\tau > \tau_m > \cdots > \tau_1 > \tau_0} d\tau_m \ldots d\tau_1 \, R^{(0)}(\tau, \tau_m) \tilde{X}(\tau_m)$$

$$\times \cdots \times R^{(0)}(\tau_2, \tau_1) \tilde{X}(\tau_1) R^{(0)}(\tau_1, \tau_0).\tag{3.25c}$$

Each term in this expansion (3.25b) describes the individual contribution from the perturbation of the gradient field as is shown in Fig. 2. For example, the zeroth-order diagram found in Fig. 2a describes the unperturbed path, and the first-order diagram found in Fig. 2b describes the sequence of 1) the unperturbed reaction path from τ_0 to τ_1, 2) the application of the perturbation at τ_1, and 3) the unperturbed reaction path from τ_1 to τ under the change of direction caused by the perturbation. If we evaluate the $m + 1$ terms $R^{(0)}, R^{(1)}, \ldots, R^{(m)}$ in (3.25b), then the meta-IRC is represented in terms of the mth degree of accuracy with respect to the perturbation.
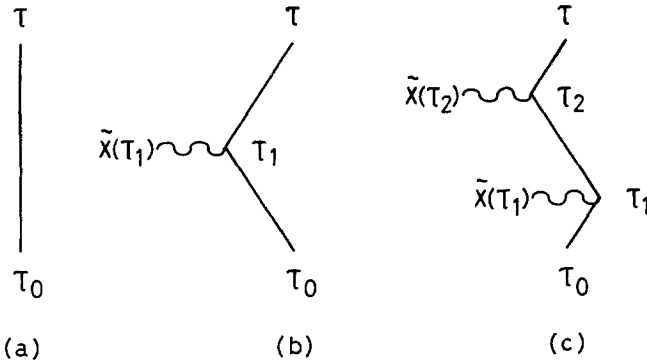
Fig. 2. Diagram of a perturbed meta-IRC: a) zeroth-order, b) first-order, c) second-order diagram. Solid line shows an unperturbed path, and wavy line shows a perturbation caused by a perturbation generator $\tilde{X}$ at each AT

Furthermore, it may be more tractable to obtain first, the unperturbed solution (3.19), and second, the deviation from the unperturbed solution using an alteration operator A in the form:

$$q^i(\tau) = A(\tau, \tau_0)q^{(0)i}(\tau), \qquad q_i(\tau) = A(\tau, \tau_0)q_i^{(0)}(\tau). \tag{3.26}$$

In this case, the alteration operator is represented by

$$A = RR^{(0)-1} \tag{3.27}$$

or

$$A = R^{(0)}\tilde{R}R^{(0)-1}. \tag{3.28}$$

For small value of $\Delta\tau \equiv \tau - \tau_0$, the series expansion of the alteration operator with respect to $\Delta\tau$ may be useful:

$$A(\tau, \tau_0) = \sum_{m=0}^{\infty} (\Delta\tau^m/m!)f_m, \tag{3.29a}$$

where

$$f_m = \sum_{r=0}^{m} (-1)^r {}_m C_r [X^{(0)} + \tilde{X}]^{m-r}[X^{(0)}]^r. \tag{3.29b}$$

For example, we have

$$f_0 = 1, \tag{3.29c}$$

$$f_1 = \tilde{X}, \tag{3.29d}$$

$$f_2 = X^{(0)}\tilde{X} - \tilde{X}X^{(0)} + \tilde{X}^2. \tag{3.29e}$$

Provided that the operators $X^{(0)}$ and $\tilde{X}$ commute, then we have

$$f_m = \tilde{X}^m \tag{3.30}$$

and the alteration operator is given in a simple form

$$A(\tau, \tau_0) = e^{\mathcal{R}(\tau - \tau_0)}. \tag{3.31}$$

3.1.2. Hessian Matrix

Using a Dirac bracket representation, the inner product in R_n [10] is conveniently represented by

$$\langle e^i \mid e_j \rangle = \delta^i_j, \qquad \langle e_i \mid e_j \rangle = a_{ij}. \tag{3.32}$$

Then, introducing a Hessian operator $\mathcal{H}$ in the form,

$$\mathcal{H} = |e^i\rangle H_{ij} \langle e^j|, \tag{3.33}$$

the eigenvalue equation of the normal vibrations [10] can be represented by

$$\mathcal{H}|v_{(\alpha)}\rangle = \mu_\alpha |v_{(\alpha)}\rangle \qquad (\alpha = 1, \ldots, n) \tag{3.34}$$

with

$$\langle v_{(\alpha)}|\mathcal{H}|v_{(\beta)}\rangle = \mu_\alpha \delta_{\alpha\beta}, \tag{3.35}$$

$$\langle v_{(\alpha)} \mid v_{(\beta)} \rangle = \delta_{\alpha\beta}, \tag{3.36}$$

where

$$|v_{(\alpha)}\rangle = v^i_{(\alpha)}|e_i\rangle. \tag{3.37}$$

The formal manipulation of the perturbational treatment with respect to the normal vibrations is analogous to that of the quantum mechanical eigenvalue problem of the Hamiltonian H, with H replaced by $\mathcal{H}$.

These perturbational treatments of the meta-IRC and the Hessian matrix are general, and therefore, the perturbation of 1) the metric tensor a_{ij} of the Riemannian space R_n, as well as 2) the potential function U can be treated on an equal theoretical footing.

We shall apply the present perturbation theory for a particular problem in Sect. 3.2.

3.2. Application to a New Concept of the Dynamical Potential Field

3.2.1. Dynamical Perturbation

Consider a chemically reacting system A composed of N_A nuclei and a background system M composed of N_M nuclei as is schematically illustrated in Fig. 3. Then, the Lagrangian of the total system A + M is given by

$$L = (1/2)\dot{x}(A)^2 + (1/2)\dot{x}(M)^2 - U_A - U_M - U_{AM}, \tag{3.38}$$

where $U_{A,M}$ is the potential function of each system A, M, and U_{AM} is the interaction potential function between A and M (such as intermolecular potential).
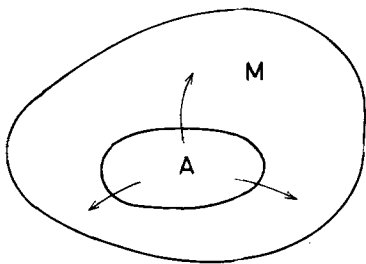
Fig. 3. Chemically reacting system A and initially frozen background system M. An arrow indicates dynamical energy flow

The configuration vectors are represented in the $3(N_A + N_M)$-dimensional Euclidean space as

$$x = (x(A), x(M)) \tag{3.39}$$

with

$$x(A) = (x^1, \ldots, x^{3N_A}), \tag{3.40}$$

$$x(M) = (x^{3N_A+1}, \ldots, x^{3N_A+3N_M}). \tag{3.41}$$

Of course, the configuration space of each of the individual systems A and M itself constitutes the $3N_A$- or $3N_M$-dimensional Euclidean space, respectively. The line element ds in each space is given by the first fundamental form as

$$ds(A)^2 = \sum_{t=1}^{3N_A} (dx^t)^2, \tag{3.42}$$

$$ds(M)^2 = \sum_{t=3N_A+1}^{3N_A+3N_M} (dx^t)^2. \tag{3.43}$$

The kinetic energy is then given by

$$(1/2)\dot{x}(A)^2 = (1/2)(ds(A)/dt)^2, \tag{3.44}$$

$$(1/2)\dot{x}(M)^2 = (1/2)(ds(M)/dt)^2. \tag{3.45}$$

Now, provided that the interaction U_{AM} is very weak,

$$U_{AM} = \text{weak}, \tag{3.46}$$

then we may consider that there exists only the isolated system A, and that the presence of the background system M may be neglected. In this case, suppose that the system A is described by the n generalized coordinates q^i ($i = 1, \ldots, n$) then the first fundamental form (3.42) is written as

$$ds(A)^2 = a_{ij}^{(0)} \, dq^i \, dq^j \tag{3.47}$$

with

$$a_{ij}^{(0)} = \sum_{t=1}^{3N_A} (\partial x^t/\partial q^i)(\partial x^t/\partial q^j). \tag{3.48}$$

Note that the generalized coordinate system constitutes the n-dimensional Riemannian space $R_n^{(0)}$ whose metric tensor is given by (3.48). As a whole, the Lagrangian of the total system can be approximated to be

$$L \simeq L^{(0)} \equiv (1/2)a_{ij}^{(0)}\dot{q}^i\dot{q}^j - U^{(0)}, \qquad (3.49)$$

where

$$U^{(0)} = U_A. \qquad (3.50)$$

This is the starting point to the succeeding treatment.

We shall treat the perturbation theory of $L^{(0)}$ in a particular case. The treatment proceeds in three stages as the accuracy of the treatment improves. In the third stage of the treatment, a new concept of the dynamical potential field will appear.

I) First stage. Let us consider the case where the system A is selectively activated under the condition (3.46), and where the background system M is held fixed as if the zero-point vibrational motions were frozen. This case may occur, for example, when a) a molecular system A in a large molecular aggregate (such as a molecular crystal) is activated by a laser beam, or b) in a molecular system, a set of normal modes A are selectively activated by a laser beam (in this case, the separation of A with the background system M may be performed with respect to the normal coordinates rather than the Cartesian coordinates), and c) a chemical reaction in a system A is initiated under a weak interaction with the solvent M. Then, the Lagrangian of the total system may be represented by that of the isolated system A under the perturbation of a field Φ:

$$L = L^{(0)} - \Phi. \qquad (3.51)$$

In this representation, the perturbation field is given by

$$\Phi = U_{AM} + \Phi_M, \qquad (3.52)$$

where Φ_M is brought about from the Lagrangian of the background system M:

$$\Phi_M = U_M - (1/2)\dot{x}(M)^2. \qquad (3.53)$$

Under the frozen condition for the dynamical motion of M, namely,

$$x(M) = \text{constant vector}, \qquad (3.54)$$

the field Φ_M is merely a constant:

$$\Phi_M(\text{frozen}) = U_M = \text{const.} \qquad (3.55)$$

Hence, the Lagrangian of the total system can be represented by

$$L = L^{[I]} \equiv (1/2)a_{ij}^{(0)}\dot{q}^i\dot{q}^j - U^{[I]}, \qquad (3.56)$$

where $U^{[I]}$ is the potential field of the system A under the static perturbation U_{AM}:

$$U^{[I]} = U_A + U_{AM} + \text{const.} \qquad (3.57)$$

Apparently, in this stage, the perturbation theory of Sect. 3.1 is applicable.

II) Second stage. Let us consider the second stage of approximation, where the dynamical motion of the background system M is almost fixed frozen but a slight configurational change may take place under the influence of the system A. In other words, the background system M is quasi-frozen and the time-evolution is brought about through the dynamics of A. This stage may correspond to a situation where a part of M which is most closely connected with A through the perturbation U_{AM} becomes slowly activated. In this stage, as the motion of the quasi-frozen configuration of M is slow, the kinetic energy part of the field Φ_M may be neglected:

$$\Phi_M(\text{quasi-frozen}) = U_M = \text{a function of } q^i. \tag{3.58}$$

Hence, the Lagrangian of the total system may be represented by

$$L = L^{[II]} \equiv (1/2)a_{ij}^{(0)}\dot{q}^i\dot{q}^j - U^{[II]}, \tag{3.59}$$

where $U^{[II]}$ is the potential field of the system A under the static perturbation $U_{AM} + U_M$:

$$U^{[II]} = U_A + U_{AM} + U_M = \text{a function of } q^i. \tag{3.60}$$

Also, at this stage, the perturbation theory of Sect. 3.1 is applicable without difficulty.

III) Third stage. Now, we shall consider the dynamical motion of the background system M. In this case, the dynamical part of the field Φ_M should be explicitly taken into account:

$$\Phi_M(\text{dynamical}) = U_M - (1/2)\dot{x}(M)^2. \tag{3.61}$$

It should be noted that the time-evolution of the system M is assumed to be brought about only through that of A; therefore, the dynamical part of Φ_M is given from (3.45) by

$$(1/2)\dot{x}(M; x(A))^2 = (1/2)(\partial s(M)/\partial q^i)(\partial s(M)/\partial q^j)\dot{q}^i\dot{q}^j, \tag{3.62}$$

where q^i $(i = 1, \ldots, n)$ are the generalized coordinates of A. Thus, the Lagrangian of the total system may be represented by

$$L = L^{[III]} \equiv (1/2)a_{ij}\dot{q}^i\dot{q}^j - U^{[III]}, \tag{3.63}$$

where a_{ij} and $U^{[III]}$ are given by

$$a_{ij} = a_{ij}^{(0)} + (\partial s(M)/\partial q^i)(\partial s(M)/\partial q^j), \tag{3.64}$$

$$U^{[III]} = U^{[II]} = U_A + U_{AM} + U_M. \tag{3.65}$$

Here, the $s(M) = s(M; q^i(A))$ in (3.62) and (3.64) will be referred to as the dynamical potential field. We have obtained now the Lagrangian in the n-dimensional Riemannian space R_n whose metric tensor is given in the modified form (3.64). Since the coordinate system is mass-weighted, the modification of the metric tensor implies that the dynamical perturbation results in renormalization of nuclear masses of the system A. In other words, under the dynamical perturbation of this kind, the "dressed-particle" having the effective mass appears (note that this kind

of perturbation is of purely dynamical nature, and hence, may in some cases compensate that of purely static nature such as U_{AM} and U_M).

To conclude, we may say that the dynamical motion of the system A disturbs the background field Φ, which finally affects the dynamism of A, yielding the dressed-particles.

In this connection, it is well-known, in the perturbation theory of the effective mass of an electron, that the interaction of electron with phonon affects the effective mass of the electron [15]; we have shown, in a closed form, a new type of the concept of effective mass that is of purely dynamical origin.

Since the dynamical potential is given by the length of the dynamical motion of the multidimensional vector $x(M)$, it is positive definite, and we can estimate the warming efficiency of the background system M in terms of the gradient of the dynamical potential.

In this stage, also, the perturbation theory of Sect. 3.1 will be applicable. Some of the results peculiar to the present stage of the dynamical perturbation will be discussed in detail in Sect. 3.2.2.

3.2.2. Application of the Perturbation Theory

I, II) First and second stages. In these stages, the perturbation field is of purely static origin. If we write

$$U = U^{(0)} + U^{(1)}, \tag{3.66}$$

where $U^{(1)}$ is the perturbation, then we have, for the solution of the alteration operator (3.29),

$$f_1 = a^{(0)ij}(\partial U^{(1)}/\partial q^j)\, \partial/\partial q^i, \tag{3.67}$$

$$
\begin{aligned}
f_2 = {}& a^{(0)ij}(\partial U^{(0)}/\partial q^j)(D_{ik}^{(0)}U^{(1)})a^{(0)kl}\,\partial/\partial q^l \\
& - a^{(0)ij}(\partial U^{(1)}/\partial q^j)(D_{ik}^{(0)}U^{(0)})a^{(0)kl}\,\partial/\partial q^l \\
& + a^{(0)ij}(\partial U^{(1)}/\partial q^j)(D_{ik}^{(0)}U^{(1)})a^{(0)kl}\,\partial/\partial q^l \\
& + a^{(0)ij}(\partial U^{(1)}/\partial q^j)a^{(0)kl}(\partial U^{(1)}/\partial q^l)D_{ik}^{(0)},
\end{aligned} \tag{3.68}
$$

where $D_{ij}^{(0)}$ is the second-order differential operator given in $R_n^{(0)}$ [11]:

$$D_{ij}^{(0)} = \partial^2/\partial q^i\,\partial q^j - \Gamma_{ij}^{(0)k}\,\partial/\partial q^k. \tag{3.69}$$

Note that the first-order correction of f_1 exactly vanishes on the surface perpendicular to the gradient field of $U^{(1)}$ in $R_n^{(0)}$. For the normal vibrations, we have the Hessian operator in the form

$$\mathscr{H} = \mathscr{H}^{(0)} + \mathscr{H}^{(1)}, \tag{3.70}$$

where

$$\mathscr{H}^{(0)} = |e^{(0)i}\rangle H_{ij}^{(0)}\langle e^{(0)j}|, \tag{3.71}$$

$$\mathscr{H}^{(1)} = |e^{(0)i}\rangle H_{ij}^{(1)}\langle e^{(0)j}|, \tag{3.72}$$

with

$$H_{ij}^{(0)} = D_{ij}^{(0)} U^{(0)}, \tag{3.73}$$

$$H_{ij}^{(1)} = D_{ij}^{(0)} U^{(1)}. \tag{3.74}$$

Then, following the usual procedure of the perturbed eigenvalue problem, we can easily obtain the perturbed solution of the eigenvalue equation for the Hessian operator in due course. Using the zeroth-order solutions,

$$\mathscr{H}^{(0)} |v_{(\alpha)}^{(0)}\rangle = \mu_\alpha^{(0)} |v_{(\alpha)}^{(0)}\rangle, \tag{3.75}$$

$$\langle v_{(\alpha)}^{(0)} \mid v_{(\beta)}^{(0)} \rangle = \delta_{\alpha\beta}, \tag{3.76}$$

we have the Rayleigh–Schrödinger type perturbation series as

$$v_{(\alpha)} = v_{(\alpha)}^{(0)} + v_{(\alpha)}^{(1)} + \cdots, \tag{3.77}$$

$$\mu_\alpha = \mu_\alpha^{(0)} + \mu_\alpha^{(1)} + \cdots. \tag{3.78}$$

For example, we obtain

$$v_{(\alpha)}^{(1)} = \sum_{\beta(\neq\alpha)} (\mu_\alpha^{(0)} - \mu_\beta^{(0)})^{-1} \cdot v_{(\beta)}^{(0)} \cdot \langle v_{(\beta)}^{(0)} | \mathscr{H}^{(1)} | v_{(\alpha)}^{(0)} \rangle, \tag{3.79}$$

$$\mu_\alpha^{(1)} = \langle v_{(\alpha)}^{(0)} | \mathscr{H}^{(1)} | v_{(\alpha)}^{(0)} \rangle. \tag{3.80}$$

III) Third stage. In this stage, the dynamical potential field disturbs the metric of the configuration Riemannian space itself. The basis vectors of R_n may then be given by

$$e_i = e_i^{(0)} + i\partial s(M)/\partial q^i \quad (i = 1, \ldots, n) \tag{3.81}$$

where i is a unit vector satisfying

$$\langle e_i^{(0)} \mid i \rangle = \langle i \mid e_i^{(0)} \rangle = 0, \qquad \langle i \mid i \rangle = 1. \tag{3.82}$$

Also, the contravariant components of the basis vectors and the metric tensor are given by

$$e^i = e^{(0)i} - [1 + \Delta_1^{(0)} s(M)]^{-1} a^{(0)ij} (\partial s(M)/\partial q^j)$$
$$\times (e^{(0)k} \partial s(M)/\partial q^k - i), \tag{3.83}$$

$$a^{ij} = a^{(0)ij} - [1 + \Delta_1^{(0)} s(M)]^{-1}$$
$$\times (a^{(0)ik} \partial s(M)/\partial q^k)(a^{(0)jl} \partial s(M)/\partial q^l), \tag{3.84}$$

where

$$\Delta_1^{(0)} s(M) = a^{(0)ij} (\partial s(M)/\partial q^i)(\partial s(M)/\partial q^j) \tag{3.85}$$

is Beltrami's differential parameter of the first kind with respect to $s(M)$ obtained in $R_n^{(0)}$. Likewise, the Christoffel symbols are obtained as

$$[ij, l] = [ij, l]^{(0)} + (\partial^2 s(M)/\partial q^i \partial q^j)(\partial s(M)/\partial q^l), \tag{3.86}$$

$$\Gamma_{ij}^k = \Gamma_{ij}^{(0)k} + [1 + \Delta_1^{(0)} s(M)]^{-1} (a^{(0)kl} \partial s(M)/\partial q^l) D_{ij}^{(0)} s(M). \tag{3.87}$$

Using the above, we shall analyze first the locus of the deformed meta-IRC, and second, the perturbed normal vibrations. Finally, we shall examine a mechanism of energy transfer between A and M in terms of the dynamical potential field.

First, let $\tilde{a}^{ij}$ be given by

$$\tilde{a}^{ij} \equiv a^{ij} - a^{(0)ij}, \tag{3.88}$$

then, for the solution of the alteration operator (3.29), we have

$$f_1 = (\tilde{a}^{ij} \, \partial U/\partial q^j) \, \partial/\partial q^i, \tag{3.89}$$

$$f_2 = (a^{(0)ij} \, \partial \tilde{a}^{kl}/\partial q^j)(\partial U/\partial q^i)(\partial U/\partial q^l) \, \partial/\partial q^k$$

$$\quad + a^{(0)ij}\tilde{a}^{kl}(D_{jl}^{(0)}U)[(\partial U/\partial q^i) \, \partial/\partial q^k - (\partial U/\partial q^k) \, \partial/\partial q^i]$$

$$\quad + a^{(0)ij}\tilde{a}^{kl}(\partial U/\partial q^j)\Gamma_{il}^{(0)m}[(\partial U/\partial q^m) \, \partial/\partial q^k + (\partial U/\partial q^k) \, \partial/\partial q^m]$$

$$\quad + \tilde{a}^{ij}(\partial \tilde{a}^{kl}/\partial q^j)(\partial U/\partial q^i)(\partial U/\partial q^l) \, \partial/\partial q^k$$

$$\quad + \tilde{a}^{ij}\tilde{a}^{kl}(\partial U/\partial q^j)[(D_{il}^{(0)}U) \, \partial/\partial q^k + (\partial U/\partial q^k)D_{il}^{(0)}]$$

$$\quad + \tilde{a}^{ij}\tilde{a}^{kl}(\partial U/\partial q^j)\Gamma_{il}^{(0)m}[(\partial U/\partial q^m) \, \partial/\partial q^k + (\partial U/\partial q^k) \, \partial/\partial q^m]. \tag{3.90}$$

For example, we obtain the perturbed solution of the meta-IRC up to the first order in $\Delta\tau$ as

$$q^i(\tau) = q^i(\tau_0) - \Delta\tau[1 + \Delta_1^{(0)}s(M)]^{-1}\langle \mathrm{grad}^{(0)}s(M) \mid \mathrm{grad}^{(0)}U\rangle$$

$$\quad \times \langle \mathrm{grad}^{(0)}s(M) \mid e^{(0)i}\rangle + 0(\Delta\tau^2), \tag{3.91}$$

where $\mathrm{grad}^{(0)}$ is the first-order differential operator given in $R_n^{(0)}$:

$$\mathrm{grad}^{(0)} = e^{(0)i} \, \partial/\partial q^i. \tag{3.92}$$

The first-order deviation of the meta-IRC vanishes when 1) the gradient field of the dynamical potential $s(M)$ is orthogonal to that of U in $R^{(0)}$, or, for the ith component, 2) the gradient field of the dynamical potential $s(M)$ lies entirely on the q^i-surface in $R_n^{(0)}$.

Second, let us analyze the dynamical background effect to the normal vibrations. In the present stage, the perturbed Hessian operator is represented by the infinite series expansion:

$$\mathscr{H} = \mathscr{H}^{(0)} + \mathscr{H}^{(1)} + \mathscr{H}^{(2)} + \cdots \tag{3.93}$$

where the perturbation parameter is that for the dynamical potential $s(M)$. For example, we have

$$\mathcal{H}^{(0)} = |e^{(0)i}\rangle H_{ij}^{(0)}\langle e^{(0)j}|, \tag{3.94}$$

$$\begin{aligned}\mathcal{H}^{(1)} = \; &|e^{(0)i}\rangle H_{ij}^{(0)}\langle ia^{(0)jk}\,\partial s(M)/\partial q^k| \\ &+ |ia^{(0)ik}\,\partial s(M)/\partial q^k\rangle H_{ij}^{(0)}\langle e^{(0)j}|, \end{aligned} \tag{3.95}$$

$$\begin{aligned}\mathcal{H}^{(2)} = \; &-|e^{(0)i}\rangle H_{ij}^{(0)}\langle a^{(0)jk}(\partial s(M)/\partial q^k)(\partial s(M)/\partial q^l)e^{(0)l}| \\ &- |a^{(0)ik}(\partial s(M)/\partial q^k)(\partial s(M)/\partial q^l)e^{(0)l}\rangle H_{ij}^{(0)}\langle e^{(0)j}| \\ &- |e^{(0)i}\rangle\Gamma_{ij}^{(2)k}\,\partial U/\partial q^k\langle e^{(0)j}| \\ &+ |ia^{(0)ik}\,\partial s(M)/\partial q^k\rangle H_{ij}^{(0)}\langle ia^{(0)jk}\,\partial s(M)/\partial q^k|, \end{aligned} \tag{3.96a}$$

with

$$\Gamma_{ij}^{(2)k} = a^{(0)kl}(\partial s(M)/\partial q^l)D_{ij}^{(0)}s(M). \tag{3.96b}$$

In this case, on account of the orthogonality relationship (3.82), all the first-order quantities are zero: [the intermediate normalization of the eigenvector is adopted: $\langle v_{(\alpha)}^{(0)} \mid v_{(\alpha)}^{(m)}\rangle = 0\;(m = 1, 2, \ldots)$]

$$v_{(\alpha)}^{(1)i} = 0, \tag{3.97}$$

$$\mu_\alpha^{(1)} = 0. \tag{3.98}$$

The second-order quantities are obtained as

$$v_{(\alpha)}^{(2)i} = \sum_{\beta(\neq\alpha)} (\mu_\beta^{(0)} - \mu_\alpha^{(0)})^{-1}v_{(\beta)}^{(0)i}c_{\beta\alpha} \tag{3.99a}$$

with

$$\begin{aligned}c_{\beta\alpha} = \; &\mu_\alpha^{(0)}\langle v_{(\alpha)}^{(0)} \mid \mathrm{grad}^{(0)}\,s(M)\rangle\langle v_{(\beta)}^{(0)} \mid \mathrm{grad}^{(0)}\,s(M)\rangle \\ &+ \langle \mathrm{grad}^{(0)}\,U \mid \mathrm{grad}^{(0)}\,s(M)\rangle \sum_\gamma \omega_\gamma\langle v_{(\alpha)}^{(0)} \mid w_{(\gamma)}\rangle\langle v_{(\beta)}^{(0)} \mid w_{(\gamma)}\rangle, \end{aligned} \tag{3.99b}$$

and

$$\begin{aligned}\mu_\alpha^{(2)} = \; &-\mu_\alpha^{(0)} \mid \langle v_{(\alpha)}^{(0)} \mid \mathrm{grad}^{(0)}\,s(M)\rangle|^2 \\ &- \langle \mathrm{grad}^{(0)}U \mid \mathrm{grad}^{(0)}\,s(M)\rangle \sum_\gamma \omega_\gamma|\langle v_{(\alpha)}^{(0)} \mid w_{(\gamma)}\rangle|^2. \end{aligned} \tag{3.100}$$

In these formulas, the contributions from the second derivatives of the dynamical potential $s(M)$ are simplified by diagonalizing the second-order terms as follows:

$$(D_{ij}^{(0)}s(M) - \omega_\gamma a_{ij}^{(0)})w_{(\gamma)}^j = 0 \quad (\gamma = 1, \ldots, n), \tag{3.101a}$$

$$a_{ij}^{(0)}w_{(\gamma)}^i w_{(\delta)}^j = \delta_{\gamma\delta} \quad (\gamma, \delta = 1, \ldots, n) \tag{3.101b}$$

with

$$w_{(\gamma)} = e_i^{(0)}w_{(\gamma)}^i \quad (\gamma = 1, \ldots, n). \tag{3.101c}$$

Now, let us examine a mechanism of energy transfer between A and M. In order to clarify the nature of the dynamical potential field $s(M)$ on the energy transfer, we shall classify two typical cases such as (A): $\text{grad}^{(0)} s(M)$ is parallel to the equi-potential surface, and (B): $\text{grad}^{(0)} s(M)$ is perpendicular to the equi-potential surface. Other cases may have a mixed nature of (A) and (B).

Case (A). In this case, vibrational motion on the equi-potential surface directly induces the variation of $s(M)$, and then the kinetic energy of the background system M will increase. A normal mode which has maximal overlap with $\text{grad}^{(0)} s(M)$ has a leading contribution to this kind of vibrational energy transfer.

Now, remember that a normal mode α confined on the equi-potential surface is characterized by the vibrational quantum number n_α. Since the dynamical inter-action with M is weak so as to be treated by perturbation theory, the quantum number n_α may be conserved during the dynamical process of energy transfer; that is, the vibrational quantum number n_α may be a good quantum number. Hence, in order to account for the energy outflow from A to M, the unit of quantum of the vibrational mode α should be reduced. In other words, softening of phonon should occur for the normal mode α. Clearly, the result of the perturbation theory deduced from (3.100) represents this mechanism of energy transfer in terms of the softening of phonon, that is the weakening of the normal mode α:

$$\mu_\alpha^{(2)} = -\mu_\alpha^{(0)} |\langle v_{(\alpha)}^{(0)} \mid \text{grad}^{(0)} s(M)\rangle|^2. \tag{3.102}$$

Case (B). In this case, promotion of chemical reaction along the meta-IRC produces kinetic energy of M through the coupling with $\text{grad}^{(0)} s(M)$. This kind of translational energy transfer is further classified according as $(B\text{-}1)$: $\text{grad}^{(0)} s(M)$ is parallel to $\text{grad}^{(0)} U$, and $(B\text{-}2)$: $\text{grad}^{(0)} s(M)$ is anti-parallel to $\text{grad}^{(0)} U$. Additionally, for the vibrational mode α on the equi-potential surface, we have

$$\mu_\alpha^{(2)} = -\langle \text{grad}^{(0)} U \mid \text{grad}^{(0)} s(M)\rangle \sum_\gamma \omega_\gamma |\langle v_{(\alpha)}^{(0)} \mid w_{(\gamma)}\rangle|^2. \tag{3.103}$$

Note that the factor $\langle \text{grad}^{(0)} U \mid \text{grad}^{(0)} s(M)\rangle$ in (3.103) changes its sign accordingly, which effect is significant when we consider an indirect scheme of vibrational energy transfer that may occur on the equi-potential surface.

Case $(B\text{-}1)$. In this case, as U increases along the meta-IRC, the dynamical potential $s(M)$ increases in the same direction. In other words, as the system A destabilizes, the increase of the net energy transfer from A to M is brought about. This mechanism of energy flow results in a lowering of the total energy of the system A, and finally inhibits the destabilizing motion of A. Conversely, as U decreases, the $s(M)$ decreases in the same direction. This mechanism shows that the approach of the system A to a stable equilibrium structure is supported by the positive energy supply from the background system M; finally, the system A reproduces its equilibrium structure. As a whole, the structural stability of the system A is guaranteed.

This is confirmed by another approach of analysis on the mechanism of energy transfer that may occur on the equi-potential surface. Since the gradient field

$\mathrm{grad}^{(0)} s(\mathrm{M})$ vanishes on the equi-potential surface, the direct mode of energy transfer in terms of the dynamical potential field $s(\mathrm{M})$ is not present. But an indirect scheme of vibrational energy transfer is present, being governed by the vibration-like mode γ of $s(\mathrm{M})$, as defined by (3.101), through the coupling with the vibrational mode α of the system A. Clearly, the mode of positive ω_γ governs the energy transfer from A to M, while the mode of negative ω_γ governs the energy transfer from M back to A in the reverse direction. Under the conservation law of vibrational quantum number with respect to the normal mode α, the allowable coupling scheme should be

$$\omega_\gamma > 0 \rightarrow \text{softening of normal mode } \alpha$$

$$\omega_\gamma < 0 \rightarrow \text{hardening of normal mode } \alpha. \tag{3.104}$$

These postulates are confirmed by the formula (3.103). Case (B-2). In this case, as U increases, the $s(\mathrm{M})$ decreases. This mechanism shows that the destabilizing motion of A is facilitated by the energy flow from M. Conversely, as U decreases, the $s(\mathrm{M})$ increases. This mechanism implies that the dynamics of A at the stable equilibrium structure becomes seriously disturbed by the dynamical perturbation with M, which may finally become so serious that the perturbational treatment may not be adequate. As a whole, the structural stability of the system A is not guaranteed.

Likewise, the vibration-like coupling of $s(\mathrm{M})$ with the normal mode of A on the equi-potential surface has completely opposite effect, as compared with (3.104), because of the negative contribution of the factor $\langle \mathrm{grad}^{(0)} U \mid \mathrm{grad}^{(0)} s(\mathrm{M}) \rangle$ in (3.103):

$$\omega_\gamma > 0 \rightarrow \text{hardening of normal mode } \alpha$$

$$\omega_\gamma > 0 \rightarrow \text{softening of normal mode } \alpha. \tag{3.105}$$

This kind of heterogeneous character of the coupling scheme may result in the growth of unbalanced distribution of the vibrational energy on the equi-potential surface. This, again, indicates the structural instability of A.

Note that, at an equilibrium point of A, we have the same situation as in the Case (A). However, since the dynamical event is somewhat of a global nature, the critical mode of dynamical energy transfer should be analyzed from a global coupling scheme as described above.

To summarize, a mechanism of dynamical energy transfer from a chemically reacting system A to a background system M is discussed. We have clarified the typical patterns of energy transfer for a structurally stable system and for a structurally unstable system; the former case is found in Case (A) and Case (B-1), and the latter case is found in Case (B-2). A structurally stable system allows an energy exchange with a background system and the structure of the system itself remains stable, while a structurally unstable system allows an amplification of the interaction mode with a background system and may finally undergo a fragmentation.

For a structurally stable system, 1) an energy outflow occurs in the Case (A) through a vibrational mode that lies in the direction of $\text{grad}^{(0)} s(M)$, and in the Case $(B\text{-}1)$ through the promoting mode of chemical reaction and a vibrational mode that couples with a vibration-like mode of positive ω_y, and 2) an energy inflow occurs in the Case $(B\text{-}1)$ through the promoting mode of chemical reaction and a vibrational mode that couples with a vibration-like mode of negative ω_y. This classification is exact if the requirement of the vibrational adiabaticity is fulfilled; for a general case where the vibrational coupling with the promoting mode of chemical reaction is present, the off-diagonal part of the Hessian matrix between the reduced normal modes on the equi-potential surface and the promoting mode lying along meta-IRC should be taken into account [10].

In the present paper we have laid great emphasis on chemically reacting systems. However, the potential applicability for the system having the Lagrangian of the form (3.38) and (3.51) is supposed to be universal. The intrinsic nature of the dynamical process of the system can be analyzed in terms of the intrinsic dynamism. The quantum mechanical formulation is also available [11].

4. Example

In this section, we shall elucidate the applicability of the fundamental principle of the intrinsic field theory of chemical reactions, that is the geodesic variational principle to an IRC, by using a model potential surface.

The shape of the model potential is illustrated in Fig. 6 of [10]. This model shows a typical pattern of isomerization reaction $A \rightarrow B \rightarrow C$, A and C being the minima and B the transition point. The IRC appropriate for the isomerization reaction is depicted in Fig. 4.

Suppose a variational parameter ε, being connected with a virtual trajectory as
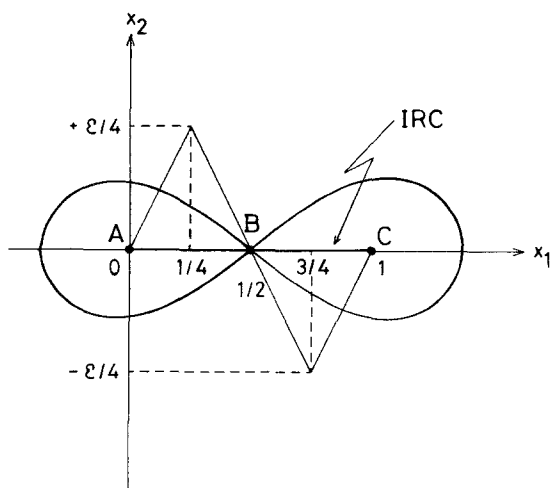

Fig. 4. Pattern of an isomerization reaction model $A \rightarrow B \rightarrow C$ [10]. Folded line from A through B to C shows a virtual trajectory used in (4.1) of the text

shown in Fig. 4. Then, we have the length of the trajectory in the rigged Riemannian space R_n^* as

$$\int_A^C ds_g \equiv \int_A^B ds_g + \int_B^C ds_g$$

$$= |\Delta U(A \to B)| + |\Delta U(B \to C)| + h\varepsilon^2 + 0(\varepsilon^3) \tag{4.1}$$

with

$$|\Delta U(A \to B)| = |\Delta U(B \to C)| = 1/16a^2, \tag{4.2}$$

$$h = (a^2/b^4) \ln (3\sqrt{3}/4) + 1/16a^2 \quad (>0), \tag{4.3}$$

where a and b are certain constants [10]. Clearly, the IRC corresponding to the locus of $\varepsilon = 0$ satisfies the geodesic variational principle (2.13), yielding the minimal value of the functional.

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