Theoret. Chim. Acta (Berl.) 51, 189–206 (1979)

THEORETICA CHIMICA ACTA

© by Springer-Verlag 1979

Intrinsic Dynamism in Chemically Reacting Systems

Akitomo Tachibana and Kenichi Fukui

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

The geometrical cell structure of the chemically reacting system is discussed. The boundary of the cell uniquely defines the dividing surface between the initial reactant side and the final product side. Introducing the concept of the intrinsic reaction time (IRT) and the accumulation time (AT) of reaction along the meta-IRC (intrinsic reaction coordinate), the intrinsic dynamism in the cell is discussed. Then, the stable limit theorems with respect to the intrinsic nature of the normal vibrations are derived. The theory is elucidated by using a model potential surface.

Key words: Intrinsic dynamism – Intrinsic reaction coordinate (IRC) approach – Chemically reacting systems, cell structure of ~ – Stable limit theorems

1. Introduction

Since the establishment of Eyring's absolute rate theory [1], the concept of reaction coordinates has been a guiding principle in studying the complicated modes of chemical reactions. The fundamental assumptions of this theory consist of E1) the presence of the activated complex (or transition state) B in the course of the chemical reaction $A \rightarrow C$:

$$A \rightarrow B \rightarrow C, \tag{1.1}$$

and E2) the chemical equilibrium between A and B. Usually, the location of the activated complex has been ascribed to the transition point, that is the saddle, on the adiabatic potential energy surface. In this connection, recent quantum mechanical calculations have succeeded in developing the efficient algorithms of searching for the transition point on the surface [2–4].

Recently, Miller [5–7] has devoted himself to the quantum mechanical reformulation of the absolute rate theory. In this case, the nuclear configuration of the

0040–5744/79/0051/0189/$03.60

activated complex itself is not the major subject; but the hypersurface S appears on which the flux of the trajectories in the phase space takes the minimal value [8, 5–7]. Then, the surface S defines the dividing surface by which the initial reactant side A and the final product side C are discriminated. Also, the classical rate formula of the absolute rate theory has been interpreted quantum mechanically by replacing the partition function of the activated complex with the flux integral on the dividing surface S [5–7]. But it should be noted that the flux integral itself is dependent on the total energy of the reacting system and hence, it is not guaranteed that the only one dividing surface S is determined for the given reaction (1.1). Also, the relation between the geometrical property of S and that of the adiabatic potential energy surface has not been clarified; for example, the transition point B is not necessarily located on the dividing surface S.

On the other hand, Hofacker and his collaborators [9–14] have directed their attention to the geometrical property of the reaction path and its relationship with the chemical dynamism in terms of the local quantum mechanics along the reaction path. Particularly, they have defined an unbranched reaction path and discussed the vibrational (non-)adiabaticity along the reaction path [9, 10]; the essential assumptions of their treatments are summarized as follows: H1) the reaction path is a curve of minimum Gaussian curvature, and H2) the first derivative of the adiabatic potential vanishes on the surface perpendicular to this path. The quantum mechanical developments of their theory have been based on the perturbational treatments of Podolsky's Hamiltonian [15, 16], where the following simplifications are adopted: H3) the kinetic energy operator is separable; that is, the sum of squares of individual linear momentum operators, and H4) harmonic oscillator approximation for the bound degrees of freedom perpendicular to the reaction path. The reaction path characterized by these simplifications has also been referred to as the dynamic reaction path [14]; in this connection, Marcus has utilized the concept of the dynamic reaction path for three-body reactions [14, 17–20]. Note, however, that there are some difficulties in the treatments described above. First, there has been no mathematical proof for the presence of the unbranched reaction path satisfying the criterions H1) and H2). Moreover, since the first derivative of the adiabatic potential energy completely vanishes at any equilibrium point, one cannot find the direction of the reaction path at the equilibrium point. Second, there is an unsatisfactory balance in the perturbational order inherent to the treatment of the dynamic reaction path: the simplification H3) is obtained by the zeroth-order perturbation theory of the kinetic energy operator in terms of the deviation of coordinates from the reaction path, while the simplification H4) is obtained by the second-order perturbation theory of the potential energy operator [9, 10, 12–14]. Although the first-order correction to the kinetic energy operator has been partly taken into account [9, 10, 12–14], the zeroth-order kinetic energy operator is supposed to be insufficient for the quantum mechanical description of the chemical dynamism in the region of finite volume.

Now, Fukui has introduced a concept of intrinsic reaction coordinate (IRC) as the reaction path from the initial A to the final C basin (or valley) by way of the transition point B on the adiabatic potential energy surface, and given the differential equation of the IRC [21]. Also, Fukui *et al.* [22–25] and Morokuma *et al.* [26, 27] have developed the reaction ergodography in terms of the IRC. The IRC possesses the outstanding properties that F1) this is the intrinsic solution of Lagrange's equation of motion [23] and F2) this converges to one of the stable normal coordinates of positive force constants at the stable equilibrium point and to the unstable normal coordinate of negative force constant at the transition point [21]. Likewise, the general solution of the IRC equation allows the unique definition of the reaction coordinate for the reaction starting from any non-equilibrium point on the potential energy surface: this solution has been referred to as the meta-IRC, and the IRC has been given as the particular case of the meta-IRC [28]. In this way, the utility of the IRC approach over the usual qualitative and convenient concept of reaction coordinates has been corroborated [21–28].

In the present paper, we discuss the dynamism of chemically reacting systems in terms of the IRC approach. Particularly, it is shown that the chemically reacting system has a cell structure as if the system were an organism. We can then tread the cell of A along the IRC, pass through the intercell boundary at the transition point B, and finally enter the cell of C along the IRC. The intercell boundary is uniquely determined in terms of the geometry of the adiabatic potential energy surface. Hence, the intercell boundary allows the unique and natural definition of the dividing surface S separating the initial reactant side A and the final product side C. Moreover, it should be noted that the solution of the meta-IRC satisfies the criterion H2) of the reaction path defined by Hofacker *et al.* [28]. But the meta-IRC cannot be always identified with the reaction path defined by Hofacker *et al.*, because the criterion H1) for the latter concerns the second-order derivative of the adiabatic potential energy surface U and the IRC equation concerns only the first derivative of U. Furthermore, it will be shown that in the IRC approach, the perturbation-free kinetic energy operator is obtained by the sum of squares of individual local momentum operators. This property may prove useful for one to overcome the difficulty inherent to the approach of the dynamic reaction path [14], as well as to improve the accuracy inherent to the approximate treatment of the IRC approach [25] and other approaches [17–20, 29–34] of the same kind.

The intrinsic dynamism of the chemically reacting system is formulated using a pair of time-like parameters: the intrinsic reaction time (IRT) and the accumulation time (AT) of reaction. The IRT is defined uniformly all over the configuration space as if it were the realistic time, while the AT is defined within the cell or the boundary excluding the equilibrium points. In particular, the IRC equation is simplified, as is shown in (3.19), if the intrinsic dynamism is represented with respect to the AT. Note that this simplified equation (3.19) is similar to the well-known differential equation of the dynamical system [35]. Different from the usual dynamical system described in the Euclidean space [35], 1) the intrinsic dynamism is formulated in the Riemannian space. Moreover, 2) from the definition (3.18), the AT diverges to infinity in the limit at the equilibrium point. The limiting property of the AT may represent the accumulating behavior of the meta-IRC at the equilibrium point; this limiting property of the AT is analogous to that of the time-like parameter used in the usual dynamical system [35]. However, it should be noted that the limiting property of the AT can be deduced logically from its definition, while the analogous property of the time-like parameter in the usual dynamical system is not provided with the *a priori* reasoning itself. As far as the authors are aware, there is no detailed theory that deals with the particular case of the intrinsic dynamism having the characteristics 1) and 2). Also shown are the stable limit theorems of the IRC approach, which describe an intrinsic nature of the normal vibrations at the stable equilibrium point.

2. Cell Structure in Chemically Reacting Systems

Let us consider the chemical reaction (1.1) where the reaction proceeds from the reactant side A through the transition point B to the product side C. In the case of isomerization reaction, the structure of the reacting system is illustrated in Fig. 1 using the reaction pattern [28]: A and C correspond to the minima of the potential energy surface and B corresponds to the saddle. The isomerization reaction is described by the idealized locus of nuclei, namely the IRC, as is illustrated in Fig. 1; note that we consider in this simple reaction scheme that there are no other minima on the potential energy surface. Then, any non-equilibrium point on the path AB of the IRC corresponds to the nuclear configuration on the reactant side; conversely, any non-equilibrium point on the path BC of the IRC corresponds to the nuclear configuration on the product side. Hence, the discrimination of the nuclear configuration according to the reactant side and the product side is very clear on the IRC. However, in the actual dynamical processes of the chemical reaction, the system may take other nuclear configurations bypassing the transition point B. Then, the definition for the vague notion of the reactant "side" and the product "side" should be firmly established.

It should be noted here that the vague entity of the "atomic region" in a molecule has become firmly established on a solid theoretical foundation by Bader *et al.* [36–43]; a certain atomic region (or atomic group region) in a molecule is circumscribed in terms of the distribution of the electron density [36–40], and the regional quantum mechanics has been formulated [41–43].

Now, in the chemically reacting system, we shall utilize the geometrical property of the adiabatic potential energy surface in order to obtain the discernment of the reactant side and the product side. In this case, in terms of the mathematical treatments of abstract gradient vector fields, a manifold is found in the neighborhood of the stable equilibrium point of the potential and is often referred to as a basin [35, 44]. Since the sophisticated mathematical treatments are forbidding, we shall conveniently interpret for the chemically reacting system the concept of the purely mathematical object, namely the basin, as the cell, and analyze the intrinsic dynamism of the chemical reaction (1.1) in terms of the cell structure of the system. In our previous paper [28], we have shown that any reaction starting from a non-equilibrium point in the neighborhood of the stable equilibrium point, say A, finally reaches A by following the unique meta-IRC. So we have the cell of the stable equilibrium point A as follows: the cell of A, or the Cell (A) to be short, is a set of the non-equilibrium points on the meta-IRC along which the direction of the gradient force field $\boldsymbol{F} = -\text{grad}\ U$ does not vanish and finally converges to the stable equilibrium point A. Thus, for any stable equilibrium point A_i, we have the unique Cell (A_i). Within the cell, the progress of any intrinsic reaction is described by the meta-IRC, being accompanied by the vibrational degrees of freedom on the equi-potential surface which is perpendicular to the meta-IRC [28]; in terms of the contravariant character of coordinates, the promoting mode of the intrinsic chemical reaction itself is measured by the normal meta-IRC [28]. Then, as a natural extension of the notion of the transition point, the intercell boundary $((A_i, A_j))$ between a pair of the stable equilibrium points A_i and A_j can be defined by the intersection of the boundaries as

$$((A_i, A_j)) = \partial\ \text{Cell}\ (A_i) \cap \partial\ \text{Cell}\ (A_j) \tag{2.1}$$

where ∂ Cell (A_i) denotes the boundary of the Cell (A_i). The IRC which connects A_i and A_j has the unique accumulation point in the intercell boundary $((A_i, A_j))$ from either cell, Cell (A_i) or Cell (A_j). This point is nothing but the transition point. In other words, any *idealized* flux of particles which leave A_i for A_j along the meta-IRC becomes a minimum at the intercell boundary $((A_i, A_j))$. In this connection, the intercell boundary may serve the minimum-of-flux criterion for the definition of the dividing surface S [8, 5] in terms of the *intrinsic dynamism* of a reaction.

Let us obtain the quantum mechanical expression of the rate constant $k_{C \leftarrow A}$ for the reaction (1.1). The general formula has been shown by Miller as follows [5, 6]:

$$k_{C \leftarrow A}(T) = Q_A^{-1}\ \text{tr}\ [e^{-\beta H}\ \delta(f(\boldsymbol{q}))(\partial f(\boldsymbol{q})/\partial \boldsymbol{q}) \cdot \boldsymbol{p} m^{-1} \mathscr{P}], \tag{2.4a}$$

where $\beta = (kT)^{-1}$, $(\boldsymbol{p}, \boldsymbol{q})$ are the vectors of the nuclear momenta and coordinates of the system, Q_A is the partition function per unit volume of the reactant, H is the total Hamiltonian of the system, $\mathscr{P}$ projects onto all the states that have evolved in the infinite past from the reactant, and $f(\boldsymbol{q})$ is a function which defines the dividing surface S via

$$f(\boldsymbol{q}) = 0; \quad \text{on S}. \tag{2.4b}$$

Here, the dividing surface S is given by the intercell boundary:

$$S = ((A, C)) \tag{2.4c}$$

(of course, we consider now the simplified example of the isomerization reaction (see Fig. 1), where the transition point B is isolated on the adiabatic potential energy surface and there are no intermediates in the course of the reaction). From the definition, the intercell boundary is energy-independent. Moreover, the IRC crosses the intercell boundary at right angles and the critical promoting mode of negative force constant at the transition point is exactly isolated from the stable normal modes of positive force constants lying on the intercell boundary [28].

From the 2-dimensional cross-sectional viewpoint, the cell and the intercell boundary are directly visualized using the pattern of reaction [28] as in Fig. 2.

3. Intrinsic Dynamism in the Cell

3.1. The Intrinsic Reaction Time (IRT) *and the Accumulation Time* (AT) *of Reaction*

Suppose the n generalized coordinates q^i ($i = 1, \ldots, n$) which describe the variation of the nuclear geometry of the chemically reacting system: the mass-weighted Cartesian coordinates x^t ($t = 1, \ldots, 3N$), N being the number of the nuclei, are then described by

$$x^t = x^t(q^1, \ldots, q^n) \quad (t = 1, \ldots, 3N). \tag{3.1}$$

Using the multidimensional vector [28]

$$\boldsymbol{x} = (x^1, \ldots, x^{3N}), \tag{3.2}$$

the infinitesimal displacement vector of the chemical reaction is given by

$$d\boldsymbol{x} = \boldsymbol{e}_i\, dq^i \tag{3.3}$$

(Einstein's summation convention is adopted in this paper) where

$$\boldsymbol{e}_i = \partial \boldsymbol{x}/\partial q^i \quad (i = 1, \ldots, n). \tag{3.4}$$

The covariant components are found to be

$$d\boldsymbol{x} = \boldsymbol{e}^i\, dq_i. \tag{3.5}$$

The relationship with the contravariant components are represented by

$$dq_i = a_{ij}\, dq^j \quad (i = 1, \ldots, n) \tag{3.6}$$

and hence

$$\boldsymbol{e}_i = a_{ij} \boldsymbol{e}^j \quad (i = 1, \ldots, n), \tag{3.7}$$

where

$$a_{ij} = \boldsymbol{e}_i \cdot \boldsymbol{e}_j = \sum_{t=1}^{3N} (\partial x^t/\partial q^i)(\partial x^t/\partial q^j) \quad (i, j = 1, \ldots, n). \tag{3.8}$$

Likewise, the gradient vector field of U is defined in terms of the generalized coordinate system by

$$\text{grad } U = \boldsymbol{e}^i\, \partial U/\partial q^i = \boldsymbol{e}_i\, \partial U/\partial q_i. \tag{3.9}$$

Note that all these vectors are considered to be the vectors in the n-dimensional Riemannian space R_n whose metric tensor is a_{ij} (3.8) [28]. Using the above, the IRC equation [28] is now rewritten as

$$dq_i/ds = (\partial U/\partial q^i)/(dU/ds) \quad (i = 1, \ldots, n), \tag{3.10}$$

where ds is the infinitesimal line element of the meta-IRC, which is represented by the first fundamental form of R_n as

$$ds^2 = a_{ij}\, dq^i\, dq^j, \tag{3.11}$$

and where dU/ds is given by

$$dU/ds = (\partial U/\partial q^i)(dq^i/ds). \tag{3.12}$$

On the other hand, let the intrinsic rate of the chemical reaction along the meta-IRC be $\mathbf{c}(x)$ and the intrinsic reaction time (IRT) be t' (the IRT is a measure of the idealized locus of motion along the meta-IRC, which is not identified with the realistic time t), then the infinitesimal vector of the chemical reaction is $\mathbf{c}\, dt'$:

$$dx = \mathbf{c}\, dt' \tag{3.13}$$

and we have

$$dq_i = c_i\, dt' \quad (i = 1, \ldots, n), \tag{3.14}$$

where

$$c_i = \mathbf{e}_i \cdot \mathbf{c} \quad (i = 1, \ldots, n). \tag{3.15}$$

Thus, we obtain from (3.10) and (3.14)

$$dq_i/dt' = c_i = (\partial U/\partial q^i)(ds/dt')/(dU/ds) \quad (i = 1, \ldots, n) \tag{3.16}$$

and the locus of the meta-IRC has the form

$$q_i(t') = q_i(t'; x(t'_0)) \quad (i = 1, \ldots, n) \tag{3.17a}$$

$$q^i(t') = q^i(t'; x(t'_0)) \quad (i = 1, \ldots, n), \tag{3.17b}$$

where t'_0 is the initial value of the IRT. This form defines the point transformation using the IRT as the parameter, which forms a one-parameter continuous group of transformations [45]. This group is referred to as G_1.

Now, let us introduce a new time-like parameter τ of G_1 by

$$\tau = \int^{t'} [(ds/dt')/(dU/ds)]\, dt' = \int^{s(t')} ds/(dU/ds), \tag{3.18}$$

which will be referred to as the accumulation time (AT) of reaction. Clearly, the AT is singular at any equilibrium point, where $dU/ds = 0$; hence, we can use the AT as the continuous parameter of G_1 only within the cell or the boundary excluding the equilibrium points. Using the AT, the fundamental equation of G_1 is simplified as

$$dq_i(\tau)/d\tau = \partial U/\partial q^i(\tau) \quad (i = 1, \ldots, n) \tag{3.19}$$

and then, we have the locus of the meta-IRC in the form

$$q_i(\tau) = e^{X(\tau-\tau_0)} q_i(\tau_0) \quad (i = 1, \ldots, n) \tag{3.20a}$$

or

$$q^i(\tau) = e^{X(\tau-\tau_0)} q^i(\tau_0) \quad (i = 1, \ldots, n), \tag{3.20b}$$

where τ_0 is the initial value of the AT, and where X is the generator of G_1 [45]:

$$X = (\partial U/\partial q^i)\, \partial/\partial q_i = (\partial U/\partial q_i)\, \partial/\partial q^i. \tag{3.21}$$

Now, it should be remembered that the IRT may change uniformly along the meta-IRC, while the AT directly depends on the reaction path, which is not uniform in general. In particular, at the stable equilibrium point P_{eq}, we have the limiting value

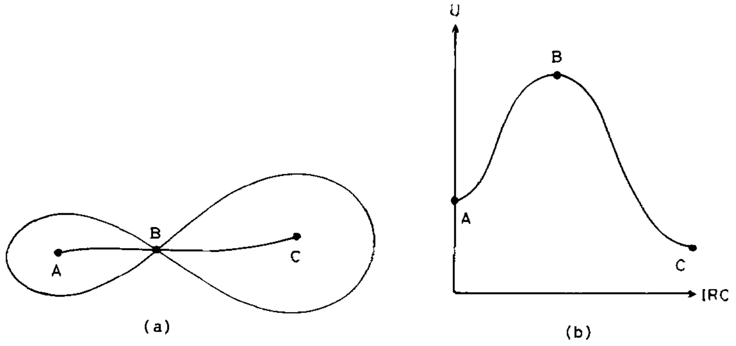

Fig. 1. (a) Pattern of isomerization reaction [28]: A (reactant) → B (transition point) → C (product). (b) Potential barrier along the IRC

of the AT as $\tau = -\infty$ irrespective of the direction of the meta-IRC which accumulates at the P_{eq}. At the transition point, however, we have $\tau = +\infty$ along the IRC and $\tau = -\infty$ along the meta-IRC which belongs to the intercell boundary. This is easily realized by examining the model reaction system undergoing the isomerization reaction (1.1) as is illustrated in Figs. 1, 3. Moreover, at any equilibrium point P_{eq}, the intrinsic rate $\mathbf{c}$ of the reaction is given with respect to the IRT by

$$dx/dt' = \mathbf{c} = \boldsymbol{v}\, ds/dt'; \quad \text{at } P_{eq}, \tag{3.22}$$

where $\boldsymbol{v}$ is the vector of the normal vibration [28]. On the other hand, in terms of the AT, the "rate" becomes zero at the P_{eq} as is clear from (3.19):

$$dx/d\tau = 0; \quad \text{at } P_{eq}. \tag{3.23}$$

The heterogeneous behavior of (3.23) is characteristic of the intrinsic reaction dynamism with respect to the AT.

It should be remarked here that the limiting property of the AT at the equilibrium point will play an important role when we discuss the stable limit theorems in Sect. 5.

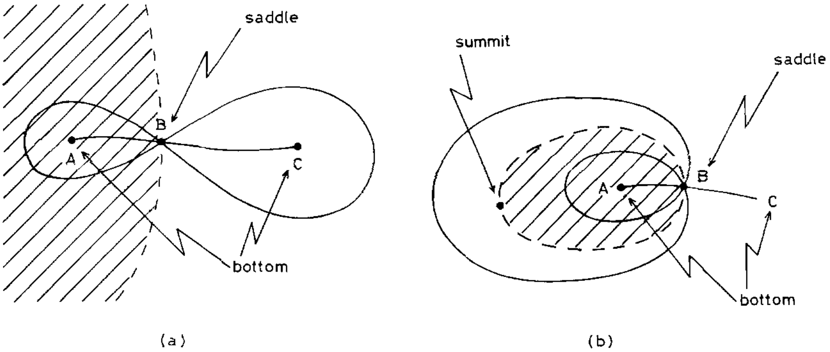

Fig. 2. Cell (A) (shaded region), Cell (C) (plain region), and intercell boundary ((A, C)) (dashed curve) in terms of the patterns of (a) isomerization reaction, and (b) fragmentation reaction [28]

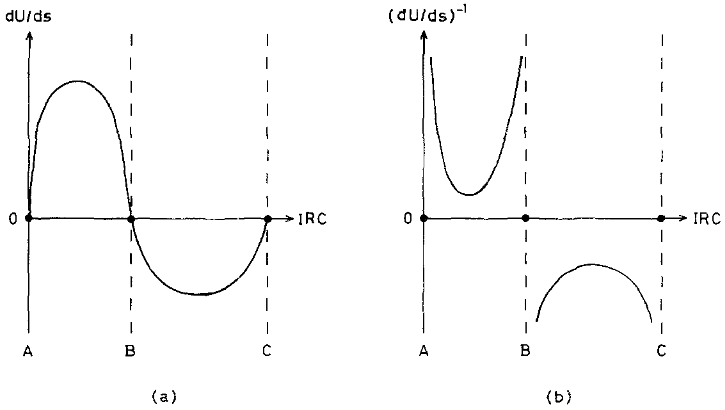

Fig. 3. Path-dependent values of (a) dU/ds, and (b) $(dU/ds)^{-1}$ along the IRC given in Fig. 1

3.2. *The Accumulation Time of Reaction and the Meta*-IRC

In this subsection, we investigate the relationship between the AT, the solution of the meta-IRC, and the adiabatic potential U.

Performing a coordinate transformation, we have the solution of the meta-IRC as [28]

$$dq'_n \neq 0, \qquad dq'_j = 0 \quad (j = 1, \ldots, n-1), \tag{3.24}$$

$$\partial U/\partial q'^n \neq 0, \qquad \partial U/\partial q'^j = 0 \quad (j = 1, \ldots, n-1). \tag{3.25}$$

In other words, the displacement vector along the meta-IRC has the one-dimensional form [28]

$$dx = e'^n \, dq'_n. \tag{3.26}$$

Furthermore, let the succeeding coordinate transformation be

$$q''_n = \int^{q'_n} dq'_n/(\partial U/\partial q'^n), \qquad q''_j = q'_j \quad (j = 1, \ldots, n-1). \tag{3.27}$$

In this q''-coordinate system, we have

$$\partial U/\partial q''^n = 1, \qquad \partial U/\partial q''^j = 0 \quad (j = 1, \ldots, n-1) \tag{3.28}$$

This shows that the q''^n is equivalent to the potential U itself:

$$q''^n = U + \text{const} \tag{3.29}$$

where const is an additive constant.

Now, differentiating

$$U = \text{const}$$

we have

$$0 = dq^i \, \partial U/\partial q^i.$$

This shows that a displacement vector $dx = e_i\, dq^i$ lying on the $U =$ const surface is orthogonal to the gradient vector field grad $U = e^i\, \partial U/\partial q^i$ of U. Therefore, we can choose a coordinate system q''' by making the $n - 1$ coordinates span the equi-potential surface and hence be orthogonal to the q''^n-curve:

$$q'''^n = q''^n = U + \text{const} \quad , \quad q'''^k\,(k = 1, \ldots, n - 1) \tag{3.30}$$

span the equi-potential surface.

In this coordinate system, we have

$$a'''_{kn} = a'''^{kn} = 0 \quad (k = 1, \ldots, n - 1) \tag{3.31}$$

and the first fundamental form of R_n becomes

$$ds^2 = a'''_{kl}\, dq'''^k\, dq'''^l + a'''_{nn}(dq'''^n)^2 \quad (k, l = 1, \ldots, n - 1). \tag{3.32}$$

This shows that the q'''^n-curve is nothing but the normal meta-IRC [28] (see Fig. 4). Then, we have

$$\partial U/\partial q'''^n = 1, \qquad \partial U/\partial q'''^k = 0 \quad (k = 1, \ldots, n - 1). \tag{3.33}$$

In this case, the generator X becomes

$$X = \partial/\partial q'''_n \tag{3.34}$$

and the finite equations of the group G_1 are found to be

$$\begin{aligned} q'''_n(\tau) &= q'''_n(\tau_0) + \tau - \tau_0, \\ q'''_k(\tau) &= q'''_k(\tau_0) \quad (k = 1, \ldots, n - 1) \end{aligned} \tag{3.35}$$

or, the infinitesimal components are

$$dq'''_n = d\tau, \qquad dq'''_k = 0 \quad (k = 1, \ldots, n - 1). \tag{3.36}$$

The meta-IRC is now represented by the q'''_n-curve and is equivalent to the AT itself; indeed, (3.26) is written as

$$dx = e'''^n\, d\tau, \tag{3.37}$$

where e'''^n is the tangent vector of the meta-IRC. Also, using the relationship for the normal meta-IRC [28], we have

$$dq'''^n = a'''^{nn}\, dq'''_n = a'''^{nn}\, d\tau, \qquad dq'''^k = 0 \quad (k = 1, \ldots, n - 1). \tag{3.38}$$

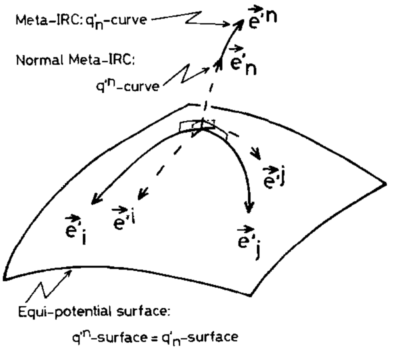

Fig. 4. Geometry of the reaction path represented in terms of the normal coordinate system

On the other hand, we have from (3.30)

$$dq'''^{n} = dU. \tag{3.39}$$

Hence, we obtain the functional relationship of U with τ as

$$dU = a'''^{nn}\, d\tau. \tag{3.40}$$

4. Quantum Mechanical Representation of the Local Intrinsic Dynamism

In [28], we have introduced the local coordinates Δu^{i} $(i = 1, \ldots, n)$ in order to describe the local structure of the chemically reacting system and besides, as the more convenient local coordinates, the local normal coordinates Δy^{α} $(\alpha = 1, \ldots, n)$ or the reduced local normal coordinates $\Delta \bar{y}'^{\alpha}$ $(\alpha = 1, \ldots, n)$; remark that $(a'_{nn})^{1/2}\Delta u'^{n}$ in [28] is now conveniently written as $\Delta \bar{y}'^{n}$ in terms of the normal coordinate system in which the q'^{n}-coordinate is the normal meta-IRC (see Fig. 4). By considering the Δy^{α} or $\Delta \bar{y}'^{\alpha}$ $(\alpha = 1, \ldots, n)$ as the independent variables, the quantum mechanical Hamiltonian H of the system will be locally given by

$$H(\boldsymbol{x} + \Delta \boldsymbol{x}) = (1/2) \sum_{\alpha=1}^{n} p_{\alpha}^{2} + U(\boldsymbol{x} + \Delta \boldsymbol{x}) \tag{4.1a}$$

$$= (1/2) \sum_{\alpha=1}^{n} \bar{p}_{\alpha}'^{2} + U(\boldsymbol{x} + \Delta \boldsymbol{x}) \tag{4.1b}$$

where

$$p_{\alpha} = -i\hbar\, \partial/\partial \Delta y^{\alpha} \tag{4.2a}$$

or

$$\bar{p}'_{\alpha} = -i\hbar\, \partial/\partial \Delta \bar{y}'^{\alpha}. \tag{4.2b}$$

It should be noted that, unlike the global Hamiltonian obtained by Podolsky [15], these local Hamiltonians (4.1a) or (4.1b) have *separable kinetic energy operators*. Then, the adiabatic potential is also represented in the alternative forms as follows.

A) Δy-coordinate system. In this case, we have

$$U(\boldsymbol{x} + \Delta \boldsymbol{x}) = \sum_{r=0}^{\infty} (1/r!) \sum_{\alpha_1, \cdots, \alpha_r = 1}^{n} \Delta y^{\alpha_1} \cdots \Delta y^{\alpha_r} D^{(y)}_{\alpha_1 \cdots \alpha_r} U \tag{4.3a}$$

where the $(r = 0)$-term is nothing but $U(\boldsymbol{x})$ and the others are given by

$$D^{(y)}_{\alpha_1 \cdots \alpha_r} = v^{i_1}_{(\alpha_1)} \cdots v^{i_r}_{(\alpha_r)} D_{i_1 \cdots i_r}. \tag{4.3b}$$

In this expression, $D_{i_1 \cdots i_r}$ is the differential operator, satisfying

$$D_{i_1 \cdots i_r i_{r+1}} = \partial D_{i_1 \cdots i_r}/\partial q^{i_r+1} - \sum_{p=1}^{r} \Gamma^{k}_{i_p i_{r+1}} D_{i_1 \cdots i_{p-1} k i_{p+1} \cdots i_r}, \tag{4.4}$$

where Γ^k_{ij} is the Christoffel symbol of the second kind [28]. For example, we have [28]

$$D_i = \partial/\partial q^i, \tag{4.5a}$$

$$D_{ij} = \partial^2/\partial q^i\,\partial q^j - \Gamma^k_{ij}\,\partial/\partial q^k. \tag{4.5b}$$

The explicit form of (4.3) has been given in [28] up to the second order of the expansion.

B) $\Delta\bar{y}'$-coordinate system. In this case, we have

$$U(x + \Delta x) = \sum_{r=0}^{\infty} (1/r!) \sum_{\alpha_1,\cdots,\alpha_r=1}^{n} \Delta\bar{y}'^{\alpha_1}\cdots\Delta\bar{y}'^{\alpha_r} D^{(\bar{y}')}_{\alpha_1\cdots\alpha_r} U, \tag{4.6a}$$

$$D^{(\bar{y}')}_{\alpha_1\cdots\alpha_r} = \bar{v}'^{i_1}_{(\alpha_1)}\cdots\bar{v}'^{i_r}_{(\alpha_1)} D'_{i_1\cdots i_r}, \tag{4.6b}$$

where the reduced vector components $\bar{v}'^{i}_{(\alpha)}$ $(\alpha, i = 1, \ldots, n-1)$ are given by diagonalizing the Hessian matrix in the equi-potential surface [28] and the others are now defined by

$$\bar{v}'^{n}_{(\alpha)} = \bar{v}'_{(\alpha)n} = 0 \qquad (\alpha = 1, \ldots, n-1), \tag{4.6c}$$

$$\bar{v}'^{i}_{(n)} = (a'_{nn})^{-1/2}\delta_{ni} \quad (i = 1, \ldots, n), \tag{4.6d}$$

$$\bar{v}'_{(n)i} = (a'_{nn})^{1/2}\delta_{ni} \quad (i = 1, \ldots, n). \tag{4.6e}$$

Neglecting the higher-order terms, we have

$$\begin{aligned} U(x + \Delta x) = {} & U(x) + \Delta\bar{y}'^{n} D^{(\bar{y}')}_{n} U + (1/2) \sum_{\alpha=1}^{n} \bar{\mu}_a (\Delta\bar{y}'^{\alpha})^2 \\ & + \sum_{\alpha=1}^{n-1} \Delta\bar{y}'^{n}\Delta\bar{y}'^{\alpha} D^{(\bar{y}')}_{n\alpha} U + 0((\Delta\bar{y}')^3). \end{aligned} \tag{4.7}$$

In this case, although the off-diagonal parts of the second-order terms cannot be eliminated, we have only one linear term of $\Delta\bar{y}'^{n}$ in the expansion (4.7). Thus, the Hamiltonian in terms of the $\Delta\bar{y}'$-coordinate system is more appropriate for the description of 1) the one-dimensional promotion of the chemical reaction along the meta-IRC, and 2) the residual vibrations confined in the equi-potential surface which is perpendicular to the meta-IRC. If the requirement of the vibrational adiabaticity is fulfilled, then the two representations of the Hamiltonian, (4.1a) and (4.1b), of course become identical. As a whole, it should be emphasized that the perturbation-free separable kinetic energy operator is more tractable than Podolsky's Hamiltonian with respect to the description of the local quantum mechanics of the chemically reacting system.

5. Stable Limit Theorems

In this section, the limiting behavior of the meta-IRC at an equilibrium point P_{eq} is discussed.

From (3.10), we have by virtue of l'Hospital's theorem

$$dq_i/ds = (\partial^2 U/\partial q^i\,\partial q^j)(dq^j/ds)/(d^2U/ds^2); \quad \text{at } P_{\text{eq}} \tag{5.1}$$

and therefore

$$(\partial^2 U/\partial q^i\, \partial q^j - (d^2U/ds^2)a_{ij})\, dq^j/ds = 0; \quad \text{at } P_{\text{eq}}. \tag{5.2}$$

This shows that the motion along the meta-IRC should become one of the normal vibrations at the P_{eq}; then, the force constant is given by d^2U/ds^2.

Since the stable equilibrium point is the center of the cell where the idealized reaction may start or finish, it will be of primary importance to investigate which normal vibrational mode the meta-IRC should converge to, or which normal vibration the reaction may make useful for the initializing motion of the reaction.

We show that the weakest normal mode has the unique nature compared with the stronger normal modes in terms of the boundary condition with respect to the intrinsic dynamism at the stable equilibrium point.

In the present treatment, the characteristic limiting value of the AT plays an important role: τ become $-\infty$ if the meta-IRC converges to the stable mode of positive force constant, while τ becomes $+\infty$ if the meta-IRC converges to the unstable normal mode of negative force constant. This heterogeneous character of the AT has been clearly distinguished from the uniform character of the IRT in the text (see the discussions following (3.18)). Provided that we were working in an Euclidean space, the analogous situation is well known: in the usual textbook approach [35, 46] and recently in the study of the orthogonal trajectories of the electron density by Collard and Hall [47], one may find the infinite character of the AT-like parameter, though without showing the *ab initio* reasoning of the character itself.

Now, in terms of the local normal coordinates Δy^α $(\alpha = 1, \ldots, n)$, the IRC equation is reduced from (3.19) to

$$d\Delta y^\alpha/d\tau = \partial U(x + \Delta x)/\partial \Delta y^\alpha \quad (\alpha = 1, \ldots, n), \tag{5.3}$$

where the r.h.s. of this equation is evaluated by (4.3). In the neighborhood of the equilibrium point, the local IRC equation (5.3) can then be approximated to be

$$d\Delta y^\alpha/d\tau \sim \mu_\alpha \Delta y^\alpha \quad (\alpha = 1, \ldots, n). \tag{5.4}$$

Neglecting the higher order contributions of unharmonicity, the solution becomes

$$\Delta y^\alpha \sim c_\alpha \exp(\mu_\alpha \tau) \quad (\alpha = 1, \ldots, n), \tag{5.5}$$

where c_α $(\alpha = 1, \ldots, n)$ are the integral constants which govern the boundary condition of the meta-IRC at the equilibrium point. Then, we obtain

$$d\Delta y^\alpha/ds \sim c_\alpha \mu_\alpha \exp(\mu_\alpha \tau) \Bigg/ \left[\sum_{\beta=1}^{n} c_\beta^2 \mu_\beta^2 \exp(2\mu_\beta \tau)\right]^{1/2} \quad (\alpha = 1, \ldots, n). \tag{5.6}$$

Note that at the *stable* equilibrium point, τ becomes $-\infty$, and then, by omitting the orientation of the vector from our consideration, we have

$$d\Delta y^\alpha/ds \sim (c_\alpha \mu_\alpha / c_{\alpha=\min} \mu_{\alpha=\min}) \exp[(\mu_\alpha - \mu_{\alpha=\min})\tau] \quad (\alpha = 1, \ldots, n), \tag{5.7}$$

where $\alpha = \min$ designates *the normal mode of minimal force constant whose contribution is non-zero.* It follows that

$$d\Delta y^{\alpha}/ds = 1; \quad \text{if } \alpha = \min$$
$$= 0; \quad \text{otherwise.} \tag{5.8}$$

Hence, we have

$$dq^{i}/ds = v^{i}_{(\alpha=\min)}, \quad \text{i.e.,} \quad dx/ds = \boldsymbol{v}_{(\alpha=\min)}; \quad \text{at } \tau = -\infty. \tag{5.9}$$

This shows that any idealized locus of the chemical reaction proceeding along the meta-IRC should converge to *the weakest normal mode that is available* at the stable equilibrium point. Using this important property, we shall prove the theorem:

Theorem 1. It is *most probable* for any intrinsic chemical reaction promoting along the meta-IRC to converge to *the weakest normal mode* at the stable equilibrium point.

This is referred to as the stable limit theorem 1.

Proof. Any intrinsic chemical reaction in the Cell (P_{eq}) is represented by a point in the space spanned by c_{α} ($\alpha = 1, \ldots, n$) which specify the boundary condition at the stable equilibrium point P_{eq}: this space is referred to as V. Suppose the force constants at the P_{eq} be given in the sequence of $\mu_i > \mu_j$ if $i < j$:

$$\mu_1 > \mu_2 > \cdots > \mu_n > 0\,.$$

Then, it is found that the meta-IRC should converge to the weakest normal mode n unless $c_n = 0$. In other words, the meta-IRC cannot converge to the weakest normal mode n if the representative point of the meta-IRC belongs to the ($c_n = 0$)-hypersurface in V. Clearly, the ($c_n = 0$)-hypersurface has *measure zero* in V; therefore, we can find a meta-IRC which converges to the weakest normal mode n *almost everywhere* in V. This proves the theorem.

Moreover, using the property that the meta-IRC is perpendicular to the equipotential surface in the cell, we have

Theorem 2. It is *most probable* that the normal modes on the equi-potential surface along the meta-IRC should converge to *the non-weakest normal modes* at the stable equilibrium point.

This is referred to as the stable limit theorem 2. The proof is trivial.

To summarize, we conclude that almost all the intrinsic chemical reactions, in their idealized loci, start by using the weakest normal vibration at the stable equilibrium point, proceed along the IRC accompanying the stronger vibrations in the equi-potential surface (in the initial stage of the reaction), and reach the transition point to give the critical normal vibration of negative force constant; after overriding the transition point, the reaction along the IRC is most likely to converge to the weakest normal mode of the product.

Using a model potential surface, the applicability of the stable limit theorems will be clearly shown in the next section.

Furthermore, at any saddle, we have two kinds of normal modes: the ($\tau = -\infty$)-modes and the ($\tau = +\infty$)-modes corresponding to the positive force constants and the negative force constants, respectively (at the summit of the potential surface, we have only the ($\tau = +\infty$)-modes). If the converged normal mode belongs to the former set of ($\tau = -\infty$)-modes, then we have (5.9) in the same way. On the other hand, if the converged normal mode belongs to the latter set of ($\tau = +\infty$)-modes, then we have a quite different result:

$$dq^i/ds = v^i_{(\alpha=\max)}, \quad \text{i.e.,} \quad d\mathbf{x}/ds = \mathbf{v}_{(\alpha=\max)}; \quad \text{at } \tau = +\infty, \tag{5.10}$$

where $\alpha = \max$ designated the normal mode of *maximal* (remark that this mode is the *weakest* in the ($\tau = +\infty$)-modes) force constant whose contribution is nonzero. Note that at any unstable equilibrium point, these two kinds of mixed characters, (5.9) and (5.10), will be useful for the analysis of the intrinsic dynamism according as the meta-IRC lies on the intercell boundary or not; the mixed characters themselves may be arranged to be referred to as the unstable limit theorem.

In the study of chemical reactions that are selected by the excitation of a single normal mode at a stable equilibrium point [48], the implications of the stable limit theorems may play an important role. Also, then, the effect of the conservation of symmetry may be significant, particularly for the distribution of the initially activated vibrational modes [21, 49, 50]. Moreover, the detailed information with respect to the geometry of the adiabatic potential energy surface itself will be useful when we consider the nonadiabatic reactions where the state degeneracy gives the significant effect in the geometry of the surface. Finally, it should be noted that the force-theoretical arguments [51, 52] are helpful for the IRC approach; the electronic properties of the chemically reacting system are intimately related to the variation of the gradient field of the adiabatic potential energy surface.

6. Example

Here, we give a model of the isomerization reaction (1.1) and elucidate some of the results of the present theory.

The shape of the model potential is depicted in Fig. 6 of [28]. The solution of the meta-IRC is represented by [28]

$$\begin{aligned} x_1 &= 0, \tfrac{1}{2}, 1 \\ x_2 &= c \times [|x_1| \times |x_1 - 1| \times |x_1 - 1/2|^{-2}]^{a^2/b^2}; \quad a > b, \end{aligned} \tag{6.1}$$

where x_1 and x_2 are the generalized coordinates in an Euclidean coordinate space, and where c is a constant.

We shall examine the behavior of the reduced normal vibrations on the equipotential surface along the meta-IRC in Cell (A); in Cell (C), we have the mirror image of the situation in Cell (A). The eigenvector and the eigenvalue of the Hessian matrix on the equi-potential surface are obtained in Cell (A) as follows:

$$\bar{\mathbf{v}}_{(1)} = (f/(f^2 + g^2)^{1/2}, \qquad -g/(f^2 + g^2)^{1/2}), \tag{6.2}$$

$$\bar{\mu}_1 = [(12/a^2)(x_1 - \alpha_+)(x_1 - \alpha_-)f^2 + (2/b^2)g^2]/(f^2 + g^2), \tag{6.3}$$

where $\alpha_{\pm}$ are the certain constants [28], and where

$$f = (2/b^2)c/(2/a^2)x_1(x_1 - 1)(2x_1 - 1), \tag{6.4}$$

$$g = c/x_2. \tag{6.5}$$

Note that the orientation of the vector is omitted from our consideration. Now, at the center A of Cell (A), we have (see Fig. 5a)

$$\bar{v}_{(1)} = (0, 1); \quad \text{at A}, \tag{6.6}$$

$$\bar{\mu}_1 = 2/b^2; \quad \text{at A}. \tag{6.7}$$

This is the hardest normal mode at A, and hence this confirms the stable limit theorem 2. Interestingly, this normal mode is invariably transferred in a parallel way along the IRC (see Fig. 5b):

$$\bar{v}_{(1)} = (0, 1); \quad x_2 = 0, \tag{6.8}$$

$$\bar{\mu}_1 = 2/b^2; \quad x_2 = 0. \tag{6.9}$$

On the other hand, the isolated solution of the meta-IRC that converges smoothly to the hardest normal mode at A is

$$x_1 = 0. \tag{6.10}$$

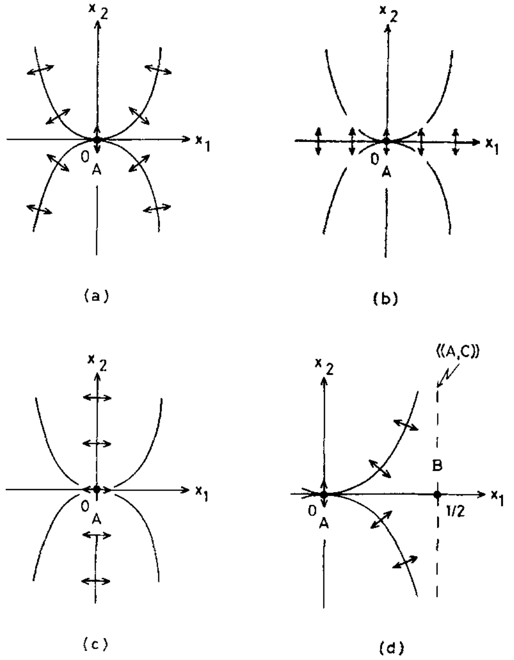

Fig. 5. Vectors ↔ of the reduced normal vibrations on the equi-potential surface along (**b**) the IRC, (**c**) the isolated meta-IRC which is rarely found on account of the stable limit theorem 2, and (**a, d**) all the other meta-IRC's in the Cell (A). Some of the representative meta-IRC's are drawn by solid curves and lines. Also, (**d**) shows the behavior of the reduced normal vibration in the limit at the intercell boundary ((A, C))

Along this meta-IRC, in order to make the value of x_2 finite, the constant c should formally diverge to infinite. Then we have (see Fig. 5c)

$$\bar{v}_{(1)} = (1, 0); \quad x_1 = 0, \tag{6.11}$$

$$\bar{\mu}_1 = 2/a^2; \quad x_1 = 0. \tag{6.12}$$

This is of course the weakest normal mode at A. Moreover, it may be worthwhile to examine the behavior of the reduced normal vibration in the limit at the intercell boundary ((A, C)). Along the IRC, we have (6.8) and (6.9), while the others satisfy (see Fig. 5d)

$$\bar{v}_{(1)} \to (1, 0); \quad x_1 \to 1/2, \quad x_2 \neq 0, \tag{6.13}$$

$$\bar{\mu}_1 \to -1/a^2; \quad x_1 \to 1/2, \quad x_2 \neq 0. \tag{6.14}$$

This is nothing but the critical normal mode of negative force constant at the transition point B [28]. This mode may act as the escaping mode of the intrinsic reactive flux that oozes from the Cell (A) to the adjacent Cell (C) through the intercell boundary ((A, C)).

Acknowledgement. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

References

1. Glasstone, S., Laidler, K., Eyring, H.: The theory of rate processes. New York: McGraw-Hill 1941
2. McIver, Jr., J. W., Komornicki, A.: Chem. Phys. Letters **10**, 303 (1971); J. Am. Chem. Soc. **94**, 2625 (1972)
3. Halgren, T. A., Pepperberg, I. M., Lipscomb, W. N.: J. Am. Chem. Soc. **97**, 1248 (1975)
4. Peterson, M. R., Csizmadia, I. G., in: Application of MO theory in organic chemistry, Csizmadia, I. G., ed. Amsterdam: Elsevier 1977
5. Miller, W. H.: J. Chem. Phys. **61**, 1823 (1974)
6. Miller, W. H.: Accounts Chem. Res. **9**, 306 (1976)
7. Miller, W. H.: J. Chem. Phys. **65**, 2216 (1976)
8. Keck, J. C.: Advan. Chem. Phys. **13**, 85 (1967)
9. Fischer, S. F., Hofacker, G. L., Seiler, R.: J. Chem. Phys. **51**, 3951 (1969)
10. Hofacker, G. L., Levine, R. D.: Chem. Phys. Letters **9**, 617 (1971)
11. Hofacker, G. L., Levine, R. D.: Chem. Phys. Letters **15**, 165 (1972)
12. Hofacker, G. L., Rösch, N.: Ber. Bunsenges. Physik. Chem. **77**, 661 (1973)
13. Hofacker, G. L., Michel, K. W.: Ber. Bunsenges. Physik. Chem. **78**, 174 (1974)
14. Hofacker, G. L., Levine, R. D.: Chem. Phys. Letters **33**, 404 (1975)
15. Podolsky, B.: Phys. Rev. **32**, 812 (1928)
16. Hofacker, G. L.: Z. Naturforsch. **18a**, 607 (1963)
17. Marcus, R. A.: J. Chem. Phys. **45**, 4493 (1966)
18. Marcus, R. A.: J. Chem. Phys. **45**, 4500 (1966)
19. Marcus, R. A.: J. Chem. Phys. **49**, 2610 (1968)
20. Marcus, R. A.: J. Chem. Phys. **49**, 2617 (1968)
21. Fukui, K.: J. Phys. Chem. **74**, 4161 (1970)
22. Fukui, K., in: The world of quantum chemistry, Daudel, R., Pullman, B. eds. Dordrecht, Holland: D. Reidel Publ. Co. 1974
23. Fukui, K., Kato, S., Fujimoto, H.: J. Am. Chem. Soc. **97**, 1 (1975)

24. Kato, S., Fukui, K.: J. Am. Chem. Soc. **98**, 6395 (1976)
25. Kato, S., Kato, H., Fukui, K.: J. Am. Chem. Soc. **99**, 684 (1977)
26. Ishida, K., Morokuma, K., Komornicki, A.: J. Chem. Phys. **66**, 2153 (1977)
27. Joshi, B. D., Morokuma, K.: J. Chem. Phys. **67**, 4880 (1977)
28. Tachibana, A., Fukui, K.: Theoret. Chim. Acta (Berl.) **49**, 321 (1978)
29. Brickmann, J.: Z. Naturforsch. **28a**, 1759 (1973)
30. Brickmann, J.: Intern. J. Quantum Chem. **S7**, 427 (1973)
31. Russegger, P., Brickmann, J.: Chem. Phys. **62**, 1086 (1975)
32. Russegger, P., Brickmann, J.: Chem. Phys. Letters **30**, 276 (1975)
33. Brickmann, J.: Z. Naturforsch. **30a**, 1730 (1975)
34. Russegger, P., Brickmann, J.: J. Chem. Phys. **66**, 1 (1977)
35. Hirsch, M. W., Smale, S.: Differential equations, dynamical systems, and linear algebra. New York: Academic Press 1974
36. Bader, R. F. W., Beddall, P. M.: J. Chem. Phys. **56**, 3320 (1972)
37. Bader, R. F. W., Beddall, P. M., Peslak, Jr., J.: J. Chem. Phys. **58**, 557 (1973)
38. Bader, R. F. W., Runtz, G. R.: Mol. Phys. **30**, 117 (1975)
39. Bader, R. F. W.: Accounts Chem. Res. **8**, 34 (1975)
40. Runtz, G. R., Bader, R. F. W., Messer, R. R.: Can. J. Chem. **55**, 3040 (1977)
41. Srebrenik, S., Bader, R. F. W.: J. Chem. Phys. **63**, 3945 (1975)
42. Srebrenik, S., Bader, R. F. W., Dang, T. T. N.: J. Chem. Phys. **68**, 3667 (1978)
43. Bader, R. F. W., Srebrenik, S., Dang, T. T. N.: J. Chem. Phys. **68**, 3680 (1978)
44. Thom, R.: Structural stability and morphogenesis. London: Benjamin 1975
45. Eisenhart, L. P.: Riemannian geometry. Princeton: Princeton Univ. Press 1963
46. Pontrjagin, L.: Ordinary differential equations. New York: Addison-Wesley 1962
47. Collard, K., Hall, G. G.: Intern. J. Quantum Chem. **12**, 623 (1977)
48. Ambartsumian, R. V., Letokhov, V. S., in: Chemical and biochemical applications of lasers, vol. 3, Moore, C. B. ed. New York: Academic Press 1977
49. Bader, R. F. W.: Mol. Phys. **3**, 137 (1960)
50. Bader, R. F. W.: Can. J. Chem. **40**, 1164 (1962)
51. Deb, B. M.: Rev. Mod. Phys. **45**, 22 (1973)
52. Nakatsuji, H.: J. Am. Chem. Soc. **96**, 24; **96**, 30 (1974)

Received August 29, 1978