

## The Path of Chemical Reactions — The IRC Approach

KENICHI FUKUI

*Department of Hydrocarbon Chemistry, Kyoto University, Kyoto, Japan*

*Received February 23, 1981 (Revised Manuscript Received August 27, 1981)*

The absolute rate theory of Eyring,<sup>1</sup> which provided a highly useful theoretical tool for studying chemical reactions, is essentially associated with the concept of "transition state", a unique state on the "potential energy surface" of the reacting system. To obtain the absolute rate theoretically involves the following steps: (i) calculating the potential energy function in terms of the atomic positions; (ii) obtaining the transition state and reactant and product points; (iii) unequivocally determining the reaction path connecting the relevant stable points and the transition state point; and (iv) calculating the absolute rate of the nuclear rearrangement along the reaction path by appropriate quantum statistical mechanical approaches.

Modern ab initio quantum-chemical methods are capable of calculating the total energy of a molecular system with a fixed nuclear arrangement—adiabatic potential,  $V$ —based on the Born–Oppenheimer approximation.<sup>2</sup> We represent the nuclear configuration of a chemically reacting system composed of  $N$  nuclei by a point in  $3N$ -dimensional configuration space with space-fixed  $3N$  Cartesian coordinates,  $X_\alpha, Y_\alpha, Z_\alpha$  ( $\alpha = 1, 2, \dots, N$ ). The potential energy function,  $V$ , can be represented in terms of  $X_\alpha, Y_\alpha, Z_\alpha$ , and we can obtain the equilibrium points as satisfying

$$\frac{\partial V}{\partial X_\alpha} = \frac{\partial V}{\partial Y_\alpha} = \frac{\partial V}{\partial Z_\alpha} = 0 \quad (\alpha = 1, 2, \dots, N)$$

Practical methods of calculating the energy gradient and of locating the equilibrium points have been developed.<sup>3</sup>

On the basis of results already established for steps i and ii, the present Account aims to discuss steps iii and iv. Molecules react with each other while vibrating about an equilibrium configuration, rotating as a whole around the center of mass, and exchanging energies in all degrees of freedom. The molecular changes in nuclear configuration are so varied that it is difficult to imagine a simple classical picture of the motion. On

Kenichi Fukui is Professor of Chemistry in the Faculty of Engineering of Kyoto University, Kyoto, Japan. He was born in Nara, the ancient imperial capital of Japan, and received his bachelor's and doctor's degrees from Kyoto University. Professor Fukui's research interests primarily involve the theory of chemical reactions. He is chiefly responsible for developing "frontier orbital theory" which is now widely used to treat orientation and stereoselection in chemical reactions. He is a Foreign Associate of the National Academy of Sciences and a Member of the International Academy of Quantum Molecular Science. He was awarded the 1981 Nobel Prize in Chemistry.

the other hand, the chemical reaction path is a concept which has a definite foundation from empirical observations. The problem of how to connect this empirical concept of a reaction path to a model relevant to theoretical treatment is a matter of deep concern in chemistry. A number of different approaches have been developed for defining the reaction path.<sup>4–7</sup> Here, the discussion is focused on our "intrinsic reaction coordinate" or "IRC" approach.

The IRC approach is based on the classical equations of motion, written as

$$\frac{d}{dt}(M_\alpha \dot{X}_\alpha) = -\frac{\partial V}{\partial X_\alpha} \quad \text{etc.}$$

Consider movement of the nuclei from a given point with an *infinitesimal* velocity. The velocity of nuclei is given by

$$M_\alpha \dot{X}_\alpha = -\frac{\partial V}{\partial X_\alpha} t + \text{constant, etc.}$$

for a small time interval. Since, by assumption, the nuclei start to move with an infinitesimal velocity, i.e.,

(1) (a) S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1941; (b) also see, e.g., K. J. Laidler and A. Tweedale, *Adv. Chem. Phys.*, **21**, 113 (1971); L. Hofacker, *Int. J. Quantum Chem.*, **35**, 33 (1969).

(2) (a) D. R. Yarkony, W. J. Hunt, and H. F. Schaefer, *Mol. Phys.*, **26**, 941 (1973), and references cited therein; (b) B. Liu, *J. Chem. Phys.*, **58**, 1924 (1973); (c) H. F. Schaefer in "Atom-Molecule Collision Theory: A Guide for the Experimentalists", R. B. Bernstein, Ed., Plenum, New York, 1979, p. 45.

(3) (a) J. W. McIver, Jr., and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972); (b) A. Komornicki, K. Ishida, K. Morokuma, R. Ditchfield, and M. Conrad, *Chem. Phys. Lett.*, **45**, 595 (1977).

(4) (a) R. A. Marcus, *J. Chem. Phys.*, **45**, 4493, 4500 (1966); **49**, 2610, 2617 (1968); (b) J. C. Light, *Adv. Chem. Phys.*, **19**, 1 (1971); (c) P. Russegger and J. Brickmann, *J. Chem. Phys.*, **66**, 1 (1977); P. Russegger, *Chem. Phys.*, **22**, 41 (1977); **34**, 329 (1978); **41**, 299 (1979).

(5) (a) R. A. Marcus, *J. Chem. Phys.*, **45**, 2138, 2630 (1966); (b) K. Morokuma and M. Karplus, *ibid.*, **55**, 63 (1971); (c) D. L. Bunker, *Methods Comput. Phys.*, **10**, 287 (1971); (d) R. N. Porter, *Annu. Rev. Phys. Chem.*, **25**, 317 (1974); (e) W. H. Millers, *J. Chem. Phys.*, **61**, 1823 (1974); (f) R. B. Walker and J. C. Light, *Annu. Rev. Phys. Chem.*, **31**, 401 (1980).

(6) R. F. Nalewajski, *Int. J. Quant. Chem.*, **12**, 87 (1978).

(7) (a) J. N. Murrell, *Struct. Bonding (Berlin)*, **32**, 93 (1977); (b) J. F. McNutt and R. E. Wyatt, *J. Chem. Phys.*, **70**, 5307 (1979); (c) K. Müller, *Angew. Chem., Int. Ed. Engl.*, **19**, 1 (1980); K. Müller and L. D. Brown, *Theor. Chim. Acta*, **53**, 75 (1979); (d) M. V. Basilevsky and V. M. Ryabov, *Chem. Phys.*, **50**, 231 (1980); (e) P. G. Mezey, *Theor. Chim. Acta*, **54**, 95 (1980); **58**, 309 (1981); (f) K. Jug, *ibid.*, **54**, 263 (1980); (g) M. Sana, G. Reckinger, and G. Leroy, *ibid.*, **58**, 145 (1981).

$\dot{X}_\alpha = 0$  at  $t = 0$ , the integration constant should be zero. This incremental change introduces the concept of "intrinsic motion".

In this way, we obtain the simultaneous equations<sup>8</sup>

$$\dots = \frac{M_\alpha dX_\alpha}{\partial V} = \frac{M_\alpha dY_\alpha}{\partial V} = \frac{M_\alpha dZ_\alpha}{\partial V} = \dots \quad (1)$$

If we adopt the "mass-weighted" cartesian coordinates  $x_i$  ( $i = 1, 2, \dots, 3N$ ) in which

$$M_\alpha^{1/2} X_\alpha = x_{3\alpha-2}, \quad M_\alpha^{1/2} Y_\alpha = x_{3\alpha-1}, \quad M_\alpha^{1/2} Z_\alpha = x_{3\alpha}$$

eq 1 becomes

$$\frac{dx_1}{\partial V} = \frac{dx_2}{\partial V} = \dots = \frac{dx_{3N}}{\partial V} \quad (2)$$

with the kinetic energy expression

$$T = \frac{1}{2} \sum_{i=1}^{3N} \dot{x}_i^2$$

The basic idea of this formalism was proposed in 1970,<sup>9</sup> and the solution of this equation which reaches a transition-state point from a stable equilibrium point was named as "intrinsic reaction coordinate (IRC)".<sup>10</sup> Equation 1 as well as eq 2 may be called the "IRC equation". These are regarded as the fundamental equations which determine the "center line" of the reaction path region, since the IRC represents the vibrationless-rotationless motion path of the reacting system. The IRC equation has an infinite number of solutions in addition to the IRC. These solutions are generally called "meta-IRC's".<sup>11</sup>

### Nature of the IRC

We designate the infinitesimal distance of the mass-weighted cartesian configuration space as  $ds$ . If we denote each side of eq 2 as  $d\tau$ , we have the relation

$$ds^2 = \sum_{i=1}^{3N} dx_i^2 = \sum_{i=1}^{3N} \left( \frac{\partial V}{\partial X_i} \right)^2 d\tau^2$$

which is valid on a meta-IRC. Also it should be noticed that on a meta-IRC the useful relation

$$d\tau = \frac{ds}{\frac{\partial V}{\partial s}} \quad (3)$$

holds with respect to the parameter  $\tau$ , since on a meta-IRC we have

$$dV = \sum_{i=1}^{3N} \frac{\partial V}{\partial x_i} dx_i = \sum_{i=1}^{3N} \left( \frac{\partial V}{\partial x_i} \right)^2 d\tau$$

(8) K. Fukui, "The World of Quantum Chemistry. Proceedings of the First International Congress of Quantum Chemistry, Menton, 1973", R. Daudel and B. Pullman, Eds., D. Reidel, Dordrecht, Holland, 1974, p 113.

(9) K. Fukui, *J. Phys. Chem.*, **74**, 4161 (1970); also see ref 13 in ref 14.

(10) Why the term "intrinsic" was used here was to introduce the concept of "intrinsic motion"—a quasistatic nuclear displacement. The term "intrinsic path" was suggested by Mezey<sup>6</sup> instead of "intrinsic coordinate". This may be reasonable since an IRC is a mathematical curve, but this curve has been obtained through a number of too simplified assumptions to be named "path" of a chemical reaction.

(11) A. Tachibana and K. Fukui, *Theor. Chim. Acta*, **49**, 321 (1978).

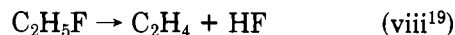
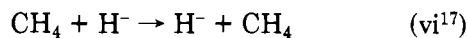
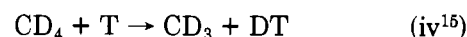
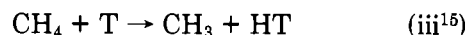
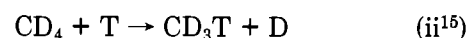
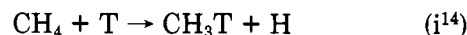
Therefore, we can express the IRC equation in another compact form as

$$\frac{dx_i}{ds} = \frac{\frac{\partial V}{\partial x_i}}{\frac{\partial V}{\partial s}} \quad (i = 1, 2, \dots, 3N) \quad (4)$$

If the space is provided with the metric  $ds^2 = 2Tdt^2$ , the IRC is then shown to be the path for which the gradient of the potential energy,  $dV/ds$ , is an extremum.<sup>9,12</sup> In this sense, the IRC descending from the transition-state point may be called the "steepest descent path". It is evident from eq 3 that the symmetry, if any exist in the geometry of the reacting system, is conserved along the IRC, so that the orbital symmetry is also conserved along the IRC.<sup>9,13</sup>

### Reaction Ergodography

Equation 1 or 2 comprises a set of differential equations. As stated before, they have an infinite number of solution curves. The particular solution which corresponds to the IRC is easily obtained if we start from the transition-state point and successively plot the neighboring points by a numerical gradient calculation along the direction given by the IRC equation. The following examples have been considered in several papers<sup>14-19</sup> in which the change in geometry of the reacting molecules along the IRC was given:



The procedure of plotting the IRC for a chemical reaction is called "reaction ergodography".<sup>15</sup>

The IRC calculation determines the energy as well as the geometry of the reacting system. The energy change along the IRC gives the potential barrier shape. In this case the width of the barrier provides information about the isotope effect.<sup>15</sup> For instance, the effect of deuteration in the methane-tritium reactions was studied.<sup>15</sup> In the abstraction mode ((iii) and (iv)) the barrier broadening was remarkable *before* reaching the

(12) (a) K. Fukui, A. Tachibana, and K. Yamashita, *Int. J. Quantum Chem.*, in press; (b) K. Fukui, *ibid.*, in press, and many papers cited therein.

(13) K. Fukui, *Recl. Trav. Chim. Pays-Bas*, **98**, 75 (1979).

(14) K. Fukui, S. Kato, and H. Fujimoto, *J. Am. Chem. Soc.*, **97**, 1 (1975).

(15) S. Kato and K. Fukui, *J. Am. Chem. Soc.*, **98**, 6395 (1976).

(16) K. Ishida, K. Morokuma, and A. Komornicki, *J. Chem. Phys.*, **66**, 2153 (1977).

(17) B. D. Joshi and K. Morokuma, *J. Chem. Phys.*, **67**, 4880 (1977).

(18) K. Morokuma, S. Kato, and K. Hirao, *J. Chem. Phys.*, **72**, 6800 (1980).

(19) S. Kato and K. Morokuma, *J. Chem. Phys.*, **73**, 3900 (1980).

transition state, whereas for the substitution mode ((i) and (ii)) it occurred, even more remarkably than the abstraction case, *after* the transition state. These results suggest that the mass effect mainly relates to the C-H stretching mode. The effect in the abstraction is reduced by that on the H-T bond to be formed, whereas in the substitution case the effect in the CH<sub>3</sub> inversion adds.

Once the geometry along the IRC has been determined, we can discuss the force acting on atoms to displace them.<sup>14</sup> The potential energy gradient is partitioned by dividing the electron density into several terms, including exchange, delocalization, and polarization terms.<sup>20</sup> By such treatments the origin of favorableness and unfavorableness of a given reaction path is discussed in terms of orbital interactions.<sup>21</sup> In the case of methane-tritium reaction i, for instance, the importance of 3a<sub>1</sub> → 4a<sub>1</sub> local excitation configuration in methane was quantitatively pointed out.<sup>14</sup>

If desired, we can combine the IRC approach with the considerations of the interaction of particular orbitals<sup>8,21</sup>—the interaction of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)—to discuss the nature of reaction paths and the detailed mechanism of that reaction. With each geometry along the reaction path, the importance of a particular orbital interaction can be identified.<sup>22-25</sup> A recent study to visualize the phase pattern of one single “interaction frontier orbital”<sup>26</sup> or “interactive hybrid MO”<sup>27</sup> for each reactant molecule helps to elucidate the mechanism of a chemical reaction. An animated picture displaying the essential features of a chemical reaction would be a powerful heuristic device.

### The IRC Equation with Internal Coordinates

Although the use of 3*N* Cartesian coordinates encounters essentially no significant difficulty in the reaction ergodography, it is obviously not suitable for discussing the potential energy surface, since these coordinates include translational and rotational motion. Thus, it is worthwhile to reduce the number of variables to 3*N* - 6 by eliminating the translation and the rotation of the reacting system as a whole.

Consider any set of internal coordinates which is sufficient to uniquely describe the nuclear arrangement of the reacting system. Denote these by *q*<sub>1</sub>, *q*<sub>2</sub>, ... *q*<sub>*n*</sub> (*n* = 3*n* - 6), which are expressible in terms of 3*N* Cartesian coordinates *X*<sub>α</sub>, *Y*<sub>α</sub>, *Z*<sub>α</sub>. Then, the following relations are obtained.

(20) H. Fujimoto and K. Fukui, *Israel J. Chem.*, **19**, 317 (1980).

(21) K. Fukui, “Theory of Orientation and Stereoselection”, Springer, Berlin, 1970, 1975; *Acc. Chem. Res.*, **4**, 57 (1971).

(22) K. Fukui, “23rd International Congress of Pure and Applied Chemistry”, Vol. 1, Butterworths, London, 1971, p 65.

(23) H. Fujimoto, S. Yamabe, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **45**, 1556, 2424 (1972); H. Fujimoto, S. Yamabe, T. Minato, and K. Fukui, *J. Am. Chem. Soc.*, **94**, 9205 (1972); S. Kato, H. Fujimoto, S. Yamabe, and K. Fukui, *ibid.*, **96**, 2024 (1974); S. Yamabe, T. Minato, H. Fujimoto, and K. Fukui, *Theor. Chim. Acta*, **32**, 187 (1974); H. Fujimoto, S. Kato, S. Yamabe, and K. Fukui, *J. Chem. Phys.*, **60**, 572 (1974).

(24) H. Fujimoto and K. Fukui in “Chemical Reactivity and Reaction Paths”, G. Klopman, Ed., Wiley, New York, 1974, p 23.

(25) T. Minato, S. Yamabe, H. Fujimoto, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **51**, 1 (1978); S. Yamabe, T. Minato, H. Fujimoto, and K. Fukui, *ibid.*, **52**, 3243 (1979).

(26) K. Fukui, N. Koga, and H. Fujimoto, *J. Am. Chem. Soc.*, **103**, 196 (1981).

(27) H. Fujimoto, N. Koga, M. Endo, and K. Fukui, *Tetrahedron Lett.*, **22**, 1263 (1981); *ibid.*, in press; H. Fujimoto, N. Koga, and K. Fukui, *J. Am. Chem. Soc.*, in press.

$$dq_i = \sum_{\alpha=1}^N \left( \frac{\partial q_i}{\partial X_\alpha} dX_\alpha + \frac{\partial q_i}{\partial Y_\alpha} dY_\alpha + \frac{\partial q_i}{\partial Z_\alpha} dZ_\alpha \right) \quad (i = 1, 2, \dots, n) \quad (5)$$

We add the following six relations after Eckart:<sup>28</sup>

$$\sum_{\alpha} M_{\alpha} dX_{\alpha} = \sum_{\alpha} M_{\alpha} dY_{\alpha} = \sum_{\alpha} M_{\alpha} dZ_{\alpha} = 0$$

$$\sum_{\alpha} M_{\alpha} (Y_{\alpha} dZ_{\alpha} - Z_{\alpha} dY_{\alpha}) = \sum_{\alpha} M_{\alpha} (Z_{\alpha} dX_{\alpha} - X_{\alpha} dZ_{\alpha}) = \sum_{\alpha} M_{\alpha} (X_{\alpha} dY_{\alpha} - Y_{\alpha} dX_{\alpha}) = 0 \quad (6)$$

which assures a zero total momentum and zero total angular momentum motion. Note that the increments given by eq 1 satisfy the relation of eq 6.<sup>8</sup> Then, we get 3*N* linear simultaneous equations with respect to 3*N* unknowns *dX*<sub>α</sub>, *dY*<sub>α</sub>, *dZ*<sub>α</sub>, from which we obtain

$$dX_{\alpha} = \sum_{i=1}^n \frac{\partial X_{\alpha}}{\partial q_i} dq_i, \quad dY_{\alpha} = \sum_{i=1}^n \frac{\partial Y_{\alpha}}{\partial q_i} dq_i, \quad dZ_{\alpha} = \sum_{i=1}^n \frac{\partial Z_{\alpha}}{\partial q_i} dq_i \quad (7)$$

If we put these relations into the kinetic energy formula, we obtain

$$T = \frac{1}{2} \sum_{i,j=1}^n a_{ij} \dot{q}_i \dot{q}_j \quad (8)$$

in which

$$a_{ij} = \sum_{\alpha=1}^N M_{\alpha} \left( \frac{\partial X_{\alpha}}{\partial q_i} \frac{\partial X_{\alpha}}{\partial q_j} + \frac{\partial Y_{\alpha}}{\partial q_i} \frac{\partial Y_{\alpha}}{\partial q_j} + \frac{\partial Z_{\alpha}}{\partial q_i} \frac{\partial Z_{\alpha}}{\partial q_j} \right)$$

can be represented in terms of *internal* coordinates *q*<sub>*i*</sub>'s.<sup>12</sup> In actuality the direct calculation of the elements *a*<sub>*ij*</sub> is never an easy task. But the inverse of the matrix (*a*<sub>*ij*</sub>), denoted by (*a*<sup>-1</sup><sub>*ij*</sub>), can easily be obtained from

$$a^{-1}_{ij} = \sum_{\alpha=1}^N M_{\alpha}^{-1} \left( \frac{\partial q_i}{\partial X_{\alpha}} \frac{\partial q_j}{\partial X_{\alpha}} + \frac{\partial q_i}{\partial Y_{\alpha}} \frac{\partial q_j}{\partial Y_{\alpha}} + \frac{\partial q_i}{\partial Z_{\alpha}} \frac{\partial q_j}{\partial Z_{\alpha}} \right)$$

The proof that this is an element of the inverse matrix of (*a*<sub>*ij*</sub>) was established by Wilson.<sup>29</sup> Therefore, *a*<sub>*ij*</sub> can be obtained by calculating the inverse matrix of (*a*<sup>-1</sup><sub>*ij*</sub>).

We can follow the same procedure which was used to derive eq 1 to derive the IRC equation with internal motion,

$$\frac{\sum_{j=1}^n a_{1j} dq_j}{\frac{\partial V}{\partial q_1}} = \frac{\sum_{j=1}^n a_{2j} dq_j}{\frac{\partial V}{\partial q_2}} = \dots = \frac{\sum_{j=1}^n a_{nj} dq_j}{\frac{\partial V}{\partial q_n}} \quad (9)$$

or, alternatively, if written in terms of *a*<sup>-1</sup><sub>*ij*</sub>

$$\frac{dq_1}{\sum_{j=1}^n a^{-1}_{1j} \frac{\partial V}{\partial q_j}} = \frac{dq_2}{\sum_{j=1}^n a^{-1}_{2j} \frac{\partial V}{\partial q_j}} = \dots = \frac{dq_n}{\sum_{j=1}^n a^{-1}_{nj} \frac{\partial V}{\partial q_j}} \quad (10)$$

It is easy to prove that the trace of geometry of the

(28) C. Eckart, *Phys. Rev.*, **47**, 552 (1935).

(29) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, “Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra”, McGraw-Hill, New York, 1955.

reacting molecules given by eq 9 agrees with that obtained by eq 1.

For the purpose of deriving various analytical relations, one of the most convenient sets of internal coordinates is the following. If we denote the internuclear distance between two nuclei  $\alpha$  and  $\beta$  as  $R_{\alpha\beta}$ , we can take as the variables  $q_1, q_2, \dots, q_n$ .

$$q_1 = R_{23}, \quad q_2 = R_{31}, \quad q_3 = R_{12}$$

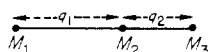
$$q_{3r+m} = R_{m,3+r} \quad (r = 1, 2, \dots, N-3; m = 1, 2, 3)$$

This set of coordinates is, for brevity, referred to as "internal  $F$  coordinates".<sup>12b</sup> If we adopt the internal  $F$ -coordinate system, all elements of the matrix  $(a^{-1}_{ij})$  are conveniently and explicitly expressed in terms of  $q_1, q_2, \dots, q_n$ .<sup>30</sup>

Perhaps the simplest illustration of the internal IRC is for the collinear triatomic reaction. Here, the IRC equation is

$$dq_1/dq_2 = \frac{(M_2^{-1} + M_3^{-1})\partial V/\partial q_1 - M_2^{-1}\partial V/\partial q_2}{-M_2^{-1}\partial V/\partial q_1 + (M_1^{-1} + M_2^{-1})\partial V/\partial q_2}$$

with the nuclear arrangement



This corresponds to a kinetic energy expression with constant  $a_{ij}$ 's

$$T = 2^{-1}(M_1 + M_2 + M_3)^{-1}\{M_3(M_1 + M_2)q_1^2 + 2M_1M_3q_1q_2 + M_1(M_2 + M_3)q_2^2\}$$

Since this quadratic form is converted to a diagonal one by a linear transformation of  $q_1$  and  $q_2$ , the IRC can be discussed in cartesian space by the use of skewed coordinate axes taken by Eyring.<sup>1a</sup>

### Complete Classical Hamiltonian of a Reacting System

Recently, the kinetic energy formula for large amplitude motions in nonrigid molecules has attracted the attention of theoreticians. Several papers have been published which discuss the Hamiltonian appropriate for these problems.<sup>31-33</sup>

One of the least rigid molecules is the chemically reacting system regarded as a supermolecule. An exact kinetic energy formula pertinent to this system is represented by<sup>12a,32</sup>

$$T = (1/2) \sum_{i,j=1}^{3N-6} a_{ij} \dot{q}_i \dot{q}_j + (M/2)(\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2) + (1/2)(I_1\sigma_1^2 + I_2\sigma_2^2 + I_3\sigma_3^2) + (1/2)(I_1^{-1}m_1^2 + I_2^{-1}m_2^2 + I_3^{-1}m_3^2) + (\sigma_1m_1 + \sigma_2m_2 + \sigma_3m_3) \quad (11)$$

in which the first term on the right-hand side is the internal motion within the conditions of eq 6, the second is the translational energy of the center of mass,  $M$  being the total mass,  $X, Y, Z$  are the space-fixed cartesian coordinates of the center of mass, and the

(30) See, however, the remarks mentioned in Appendix 1 of ref 12a.

(31) R. Meyer and Hs. H. Günthard, *J. Chem. Phys.*, **49**, 1510 (1968).

(32) H. M. Pickett, *J. Chem. Phys.*, **56**, 1715 (1972).

(33) (a) P. R. Bunker, *J. Chem. Phys.*, **47**, 718 (1967); **48**, 2832 (1968); J. T. Hougen, P. R. Bunker, and J. W. C. Jons, *J. Mol. Spectros.*, **34**, 136 (1970); (b) A. Sayvetz, *J. Chem. Phys.*, **7**, 383 (1939); J. K. G. Watson, *Mol. Phys.*, **15**, 479 (1968); **19**, 465 (1970); C. R. Quade, *J. Chem. Phys.*, **65**, 700 (1976); (c) D. C. Moule and Ch. V. S. Ramachandra Rao, *J. Mol. Spectros.*, **45**, 120 (1973); J. C. D. Brand and Ch. V. S. Ramachandra Rao, *ibid.*, **61**, 360 (1976); P. G. Mezey and V. S. Ramachandra Rao, *J. Chem. Phys.*, **72**, 121 (1980); (d) F. Jørgensen, *Int. J. Quantum Chem.*, **14**, 55 (1978).

remaining terms originate from nonzero total angular momentum. The third term is the usual rotational energy,  $\sigma_r$  ( $r = 1, 2, 3$ ) being the components of angular velocity about the instantaneous principal axes of inertia with instantaneous principal moments of inertia  $I_r$  ( $r = 1, 2, 3$ ). The angular velocity components  $\sigma_r$  are given by the Eulerian angles  $\theta, \phi, \psi$ <sup>34</sup> and their time derivatives as

$$\sigma_1 = (\sin \psi)\dot{\theta} - (\sin \theta \cos \psi)\dot{\phi}$$

$$\sigma_2 = (\cos \psi)\dot{\theta} + (\sin \theta \sin \psi)\dot{\phi}$$

$$\sigma_3 = \dot{\psi} + (\cos \theta)\dot{\phi}$$

The fourth term arises from the internal rotational motion of each nucleus around the center of mass with respect to the principal axes of inertia. The  $m_r$  ( $r = 1, 2, 3$ ) are given by

$$m_1 = \sum_{\alpha=1}^N M_{\alpha}(\xi_{2\alpha}\xi_{3\alpha} - \xi_{3\alpha}\xi_{2\alpha}), \text{ etc.}$$

in which  $\xi_{1\alpha}, \xi_{2\alpha}, \xi_{3\alpha}$  are the Cartesian coordinates of nucleus  $\alpha$  whose axes are coincident with the three principal axes of inertia. The  $I_r$  as well as  $\xi_{r\alpha}$  are obtained as functions of the internal coordinates  $q_i$  by use of the equations

$$q'_i = q'_i(q_1, q_2, \dots, q_{3N-6}) \quad (i = 1, 2, \dots, 3N-6)$$

$$(q'_i)^2 = (\xi_{1\alpha} - \xi_{1\beta})^2 + (\xi_{2\alpha} - \xi_{2\beta})^2 + (\xi_{3\alpha} - \xi_{3\beta})^2$$

$$\sum_{\alpha} M_{\alpha}\xi_{1\alpha} = \sum_{\alpha} M_{\alpha}\xi_{2\alpha} = \sum_{\alpha} M_{\alpha}\xi_{3\alpha} = 0$$

$$\sum_{\alpha} M_{\alpha}\xi_{2\alpha}\xi_{3\alpha} = \sum_{\alpha} M_{\alpha}\xi_{3\alpha}\xi_{1\alpha} = \sum_{\alpha} M_{\alpha}\xi_{1\alpha}\xi_{2\alpha} = 0$$

in which  $q_i$  denote any set of internal coordinates and  $q'_i$  are the internal  $F$  coordinates. The last term of the right-hand side of eq 11 stands for the interaction between the rotation "as a whole" and the internal (vibrational) rotation of each nucleus.

The utility of eq 11 is that it is a general expression of kinetic energy for a reacting system and is represented in terms of  $3N$  coordinates  $X, Y, Z, \theta, \phi, \psi, q_i$  ( $i = 1, 2, \dots, 3N-6$ ) and their time derivatives. Accordingly, we can easily set up Lagrange's equations of motion to discuss the classical dynamics. Also the momenta conjugate to these coordinates, and the classical Hamiltonian, may be obtained by the usual procedures<sup>12,32</sup> which leads to the quantum-mechanical operator form.<sup>35</sup>

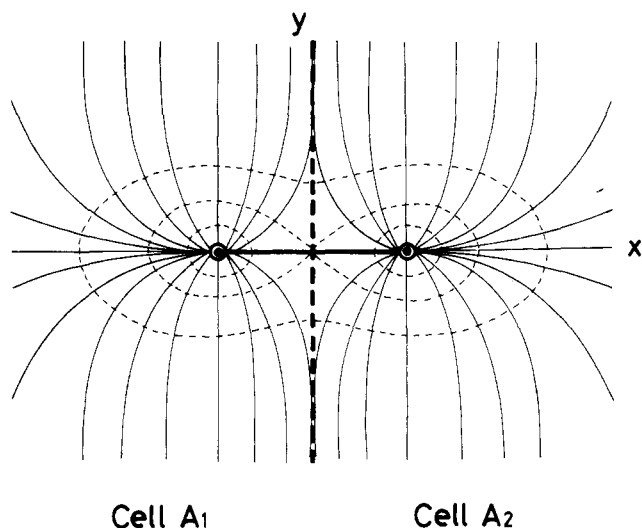
### The Cell Structure of the Configuration Space

One of the most important features of the IRC approach with internal coordinates comes about in connection with the cell structure of the internal configuration space.<sup>36</sup> The whole space is divided into cells by each set of meta-IRC's, each containing one stable equilibrium point normally. Each meta-IRC belonging to a cell starts from the equilibrium point and runs toward the cell boundary. The intercell boundary is composed of  $(n-1)$ -dimensional subspaces, each containing normally one transition-state point which connects that cell to another. The stable equilibrium point of a cell is called the "cell center". When we discuss

(34) E. T. Whittaker, "A Treatise on the Analytical Dynamics of Particles and Rigid Bodies", Cambridge University Press, Cambridge, 1937.

(35) B. Podolsky, *Phys. Rev.*, **32**, 812 (1928).

(36) A. Tachibana and K. Fukui, *Theor. Chim. Acta*, **51**, 189 (1979).



**Figure 1.** The cell structure indicated by a simple model. (○) Cell center; (×) transition-state point; (---) equipotential surface (line; (—) meta-IRC: A heavy dashed line represents the intercell boundary and a heavy straight line the IRC.  $y = \text{const.} [|x^2 - 1|^{1/2}/|x|]^{b^2/2a^2}$  ( $b^2 > 2a^2$ ).

a chemical reaction between two points corresponding to initial and final states, the cell containing the initial state is named the initial cell and that containing the final state, the final cell.

The characteristics of the cell structure are most tangibly understood by adopting the following simple model:<sup>11</sup>

$$ds^2 = dx^2 + dy^2 = 2Tdt^2$$

$$V = a^2(1 - x^2)^2 + b^2y^2$$

It is seen in Figure 1 that meta-IRC's are perpendicular to equipotential surfaces. This is a general feature of IRC. It is possible that on the cell boundary surrounding one cell there may exist more than one transition state point. An illustrative model is

$$ds^2 = dr^2 + r^2d\phi^2 = 2Tdt^2$$

$V =$

$$(r - a)^2 + a^2[\sin^2(n/2)]\phi \quad (r, \phi: \text{polar coordinates})$$

The result is given in Figure 2.

The cell structure is characteristic of a given reacting system. The cell concept is essential for a wave-mechanical interpretation of a chemical reaction between two neighboring cells. As might be anticipated, it has been shown that techniques from differential geometry<sup>37</sup> are effective in developing the IRC approach.<sup>11,36,38-40</sup> Several interesting mathematical results have been obtained concerning the IRC.<sup>11,12,36,38-40</sup>

### Absolute Rate of Chemical Reactions

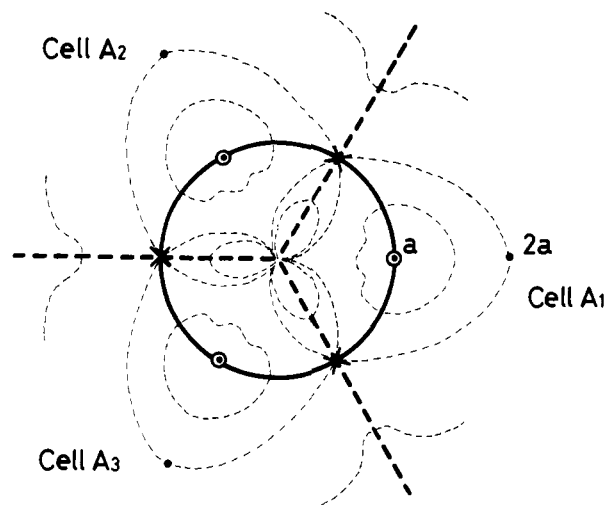
The cell structure of configuration space is essentially important for the wave-mechanical evaluation of the absolute rate of chemical reactions. The chemical reaction is regarded as a large-amplitude nuclear motion in the internal configuration space. The amplitude may in many cases be infinitely large. Here, however, we imagine the atomic rearrangement only between finite cells, corresponding to intramolecular reactions.

(37) J. L. Synge, *Philos. Trans. R. Soc. London, Ser. A*, **226**, 31 (1926); also see any textbook available on differential geometry.

(38) A. Tachibana and K. Fukui, *Theor. Chim. Acta*, **51**, 275 (1979).

(39) A. Tachibana and K. Fukui, *Theor. Chim. Acta*, **57**, 81 (1980).

(40) A. Tachibana, *Theor. Chim. Acta*, **58**, 301 (1981).



**Figure 2.** A model for the two-dimensional  $n$ -cell space. (The case  $n = 3$  is indicated.) See Figure 1 for identification of symbols.

Consider one of the cells as the initial cell. Let the Hamiltonian operator for the internal motion of the reacting system be  $\mathcal{H}$ . As has been mentioned before, we can assume that the classical expression of Hamiltonian of the form

$$\mathcal{H} = \frac{1}{2} \sum_{ij} a^{-1}_{ij} P_i P_j + V$$

is known, in which  $a^{-1}_{ij}$  is a function of coordinates  $q_i$  ( $i = 1, 2, \dots, n$ ) and  $P_i$  is the momentum which conjugates to  $q_i$ . Then, the quantum-mechanical expression of Hamiltonian operator given by Podolsky<sup>36</sup>

$$\mathcal{H} = \frac{1}{2} \sum_{ij} a^{-1/4} \left( -i\hbar \frac{\partial}{\partial q_i} \right) a^{-1}_{ij} a^{1/2} \left( -i\hbar \frac{\partial}{\partial q_j} \right) a^{-1/4} + V(q_1, q_2, \dots, q_n)$$

is applicable, where  $a = \det(a_{ij})$ . If the Hamiltonian is applicable to more than one cell region, we call it the "global" Hamiltonian. In this expression,  $\mathcal{H}$  is taken so that the integral

$$\int \dots \int \Psi^*(q_1, q_2, \dots, q_n) \Psi(q_1, q_2, \dots, q_n) dq_1 dq_2 \dots dq_n$$

in which  $\Psi(q_1, q_2, \dots, q_n)$  is a global wavefunction, becomes unity. If the global wavefunction were known, a full description of dynamics of nuclear rearrangement from one cell to another would be easy in the framework of the general wave-mechanical treatment for time-dependent processes.<sup>41</sup> The method consists of<sup>12</sup> (a) obtaining the cell Hamiltonian and its eigenfunctions with respect to the initial cell which is surrounded by a hypothetical wall of infinitely high potential, (b) constructing the initial density function for the initial cell by use of the cell wavefunctions obtained in (a) and the initial statistical distribution, (c) obtaining the time development of the cell wavefunctions obtained in (b) in terms of global wavefunctions, and finally (d) calculating the time-dependent population of the initial cell from the time-dependent density function. However, owing to the great deal of computational difficulties involved in the procedure, no actual calculation has yet been done. Certainly, a recourse to some

(41) E.g., see D. N. Zubarev, "Nonequilibrium Statistical Thermodynamics", Consultants Bureau, New York, 1974.

physically reasonable simplification is needed.

One way of making the rate calculation practicable is to reduce the problem to one dimension. The first such attempt was made in the absolute rate calculation of proton migration in the enol-form malonaldehyde.<sup>42</sup> We can imagine a picture of a large-amplitude nuclear motion in which the reacting system proceeds along the IRC with normal vibrational motions in the plane perpendicular to the direction of IRC. We assume in this approximation a "vibrational adiabaticity"<sup>43</sup> with regard to the large amplitude "translational" motion along the IRC.

The result<sup>42</sup> for malonaldehyde proton migration did not agree with experiment, although the adiabatic approach illustrated the one-dimensional reduction. The rate constant obtained ( $\sim 10^{14} \text{ s}^{-1}$ ) was  $10^2$ – $10^3$  times larger than that estimated from experimental studies ( $\sim 10^{11} \text{ s}^{-1}$ ). Obviously, this result was partially caused by the small potential barrier, less than 1 kcal/mol, adopted in the calculation. The numerical result could have been no doubt improved by taking the barrier height to be 11 kcal/mol which was recently obtained by theoretical calculations.<sup>44</sup> Such a presumption is actually ascertained by a simpler tunneling calculation.<sup>12a</sup>

The Hamiltonian valid for a narrow region along the IRC is called the IRC Hamiltonian. The effect of vibrational *nonadiabaticity*<sup>45</sup> can be taken into account

(42) S. Kato, H. Kato, and K. Fukui, *J. Am. Chem. Soc.*, **99**, 684 (1977).

(43) R. A. Marcus, *J. Chem. Phys.*, **43**, 1598 (1966); **46**, 959 (1967); M. Quack and J. Troe, *Ber. Bunsen ges. Phys. Chem.*, **78**, 240 (1974); **79**, 170 (1975).

(44) G. Karlström, H. Wennerström, B. Jönsson, and S. Forsén, *J. Am. Chem. Soc.*, **97**, 4188 (1975); E. M. Fluder and J. R. de la Vega, *ibid.*, **100**, 5265 (1978); J. Catalán, M. Yáñez, and J. I. Fernández-Alonso, *ibid.*, **100**, 6917 (1978).

in the IRC Hamiltonian. A calculation of the tunneling rate of the reaction  $\text{HNC} \rightarrow \text{HCN}$  was carried out<sup>46a</sup> by the use of the IRC Hamiltonian of Miller and co-workers,<sup>46b</sup> obtaining the interesting result that the rate constant value  $\sim 10^5 \text{ s}^{-1}$  was achieved about 8 kcal/mol below the classical threshold.

### Concluding Remarks

The IRC approach in chemodynamical studies has just begun to take shape. The present stage of the theory is mainly to establish a framework. With this in mind the theory has been formulated to be as broadly applicable as possible. At this stage, it may be tolerable to sacrifice pragmatism because of the shortage of efficient computing procedures. It is expected that in the near future, however, actual calculations will become feasible using a new generation of computers. In anticipation of these advances, the theory should be armed with mathematical foundations.

In particular, the *global* character of configuration space should be clarified by the use of global coordinates. The solution of the multidimensional Schrödinger equations, the rate problem in general nonadiabatic cases, the intercell tunneling rate involving infinite cells, the treatment of the nonzero angular momentum case using the general kinetic energy formula of eq 11, and IRC approach for excited state reactions, and so forth will be explored by mathematical methods.

*It is a pleasure to acknowledge the reviewers of the manuscript and the editors for their suggestions and comments.*

(45) R. A. Marcus and M. E. Coltrin, *J. Chem. Phys.*, **67**, 2609 (1977); R. A. Marcus, *J. Phys. Chem.*, **83**, 204 (1979).

(46) (a) S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, III, *J. Chem. Phys.*, **73**, 2733 (1980); (b) W. H. Miller, N. C. Handy, and J. E. Adams, *ibid.*, **72**, 99 (1980).

## The Semiclassical Way to Molecular Spectroscopy

ERIC J. HELLER

*Department of Chemistry, University of California, Los Angeles, California 90024,  
and Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

*Received June 22, 1981*

This Account deals with a new perspective on the interaction of light with molecules. Although much of chemistry may take place in the dark (literally and figuratively), our knowledge of fundamental molecular and chemical processes is often greatly enhanced when we shed light on the subject! Light of various wavelengths and intensities can be used as a probe of molecular structure and dynamics, and sometimes light acts as a reagent or product in a chemical reaction.

Very often, we can profit from a classical or semiclassical picture of the interaction of light with molecules. It is easy, for example, to imagine a heteronuclear

diatomic molecule as two partially charged masses connected by a spring, oscillating and absorbing energy due to a resonantly oscillating electric field. This picture enhances our understanding of infrared vibrational transitions.

In electronic absorption and emission spectra, we also have a classical picture of sorts, namely, the Franck-Condon idea of a vertical transition in which the sluggish nuclei retain their position and momentum while the electrons quickly make a transition. After the electrons have made a transition, the nuclei experience new forces; they find themselves displaced relative to the equilibrium geometry of the new potential surface, and interesting dynamics should ensue. Unfortunately, most discussions of electronic transitions cut short any allusions to dynamics and explain the absorption spectrum in terms of Franck-Condon overlaps of the

Eric Heller is Professor of Chemistry at University of California, Los Angeles. He received his B. S. degree from the University of Minnesota in 1968 and the Ph.D. at Harvard University in 1973, with W. P. Reinhardt. He joined the faculty at UCLA following 2 years of postdoctoral work with S. A. Rice at the University of Chicago.