

반응 경로의 일의적 함수 (제 1 보), 정의 및 근사

金鎮濂¹ · 張孝元

서울대학교 자연과학대학 화학과

(1987. 12. 18 접수)

A Unique Function of Reaction Path (I). Definition and Approximation

Hojing Kim¹ and Hyo Weon Jang

Department of Chemistry, College of Natural Sciences, Seoul National University,
Seoul 151-742 Korea

(Received December 18, 1987)

요 약. principle of least motion의 정량적 표현을 제시하였다. potential energy surface 상의 주어진 반응 경로에 대하여 전자 위치 변수의 함수, 그 함수의 norm 과 반응 경로 평균 에너지를 일의적으로 정의하였고, 그들의 성질을 검토하였다. 함수의 norm 과 평균 에너지를, 일분자 이성질체화 반응의 허용된 경로를 판별하는 척도로 사용할 수 있음을 제안하였다. 대칭성을 가진 분자에 대해서 계산하지 않고 허용된 경로를 판별하였으며 Woodward-Hoffmann 규칙의 적용과 같은 결과를 얻었다.

ABSTRACT. A quantitative description of the principle of least motion is suggested. The reaction path function of electronic variables, its norm and the reaction path average energy, which are unique for a given reaction path on a potential energy surface of a reacting system, are defined and their characteristics are discussed. It is postulated that the norm of the function and the average energy can be used as a criterion for identification of the preferred path of a unimolecular isomerization reaction. For a molecule with a certain symmetry, the preferred path, with which Woodward-Hoffmann rule agrees, is immediately identified without laborious computation.

INTRODUCTION

The basic idea of the principle of least motion about the favored reaction path was formalized,¹⁻⁵ considering the displacements of the nuclear positions of the reacting system along a path, and was tested on several kinds of elementary reactions. However, the theory has failed for the justification of some specific reaction path.⁴ This deficiency may result from the inherent attitude that only nuclear positions are essential. Although the geometry of the

nuclear configuration may reflect its potential energy, it may not be sufficient to rationalize all the energetics of the reaction, which are delicately dependent on electronic distribution via electronic wave function. One has to consider the wave functions of the reacting system for a more precise description about the allowedness of a path.

On the other hand, a topological view of electronic wave function was introduced to rationalize the favored path by Trindle⁶ and later by Kelsey⁷. The basic idea is that the allowed

path transforms the wave function of reactant to the wave function of product as a topological identity. They devised methods for practical use.

In the present work, two above ideas are hybridized. A function and a scalar, which are unique for a given reaction path, are introduced. The function is an integrated electronic wave function with respect to an abstract reaction coordinate from reactant to product, and is one of electron position vectors. Its norm measures the extent of deformation of the electronic wave function along the path. It is postulated that the preferred path accompanies the least deformation of the electronic configuration of the reacting system. Then the square of the norm, a weighted average of wave function overlaps between all the points of the path, should be the largest for the preferred path. The scalar quantity is a weighted average of potential energies along the path, and may also be used as a criterion for the preferred path. That is, one can conjecture that a path should be likely allowed if the path maintains potential energy of the reacting system relatively low throughout the path. If one is to calculate the overlap integral of two electronic wave functions, one should choose a common coordinate frame, since the overlap integral of two wave functions corresponding to two different nuclear configurations depends on the relative positions of the two nuclear frameworks. In this work principal axis frame,^{8,9} one of molecule-fixed frames, is taken as the common coordinate frame. Due to the very use of the frame, present method can be applied nominally to intramolecular isomeric rearrangement.

DEFINITION OF THE REACTION PATH FUNCTION AND THE REACTION PATH AVERAGE ENERGY

According to the Born-Oppenheimer approximation, the time independent total molecular wave function may be separated into the product of nuclear wave function and electronic wave function. The electronic wave function is the eigenfunction of electronic Hamiltonian,

$$H_{el}\psi_{el} = E_{el}\psi_{el}. \quad (1)$$

But, in space-fixed frame, ψ_{el} is not yet uniquely determined because ψ_{el} is parametrically dependent on nuclear coordinates,

$$\psi_{el} = \psi_{el}(\{r_i\}, \{R_A\}), \quad (2)$$

where r_i is electron position vector and R_A is nucleus position vector in space-fixed frame. Consequently when the molecule translates and rotates, ψ_{el} in space-fixed frame is varied, even though the nuclear configuration of the molecule is not changed.

Therefore molecule-fixed frame must be used in description of ψ_{el} in the study of chemical reaction, which involves deformation of nuclear configuration. In the present work, principal axis frame,^{8,9} which has its origin at the center of mass of the nuclear configuration and whose orientations of axes diagonalize the moment of inertia tensor of the nuclear configuration, is used. From now on, a wave function, ψ , means a real normalized ground electronic wave function, ψ_{el} , above.

Let the reacting system (nuclear configurations along a reaction path) be composed of M nuclei.

And one may define

$$r = (x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_M, y_M, z_M), \quad (3)$$

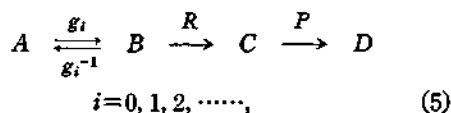
where x_i, y_i, z_i are coordinates of i -th nucleus in principal axis frame.

And let

$$r_0 = r \text{ of reactant nuclear configuration}$$

$r_1=r$ of product nuclear configuration. (4)

One considers the following scheme



where A is a closed interval $[0, 1]$, B is a set of r (r denotes nuclear configuration along a reaction path), C is a set of ψ (wave functions along a reaction path), D is a set of E (ground state potential energies along a reaction path).

g_i , R and P are defined as follows.

g_i : one to one, onto, continuous function on domain A and satisfies $g_i(0)=r_0$, $g_i(1)=r_1$

R : one to one, onto, continuous or piecewise continuous function on domain B which maps r to its corresponding ψ

P : one to one, onto, continuous function on domain C which maps ψ to its corresponding E

(specific r determines uniquely an electronic Hamiltonian and its solutions $H_{el}\psi_{el}=E_{el}\psi_{el}$). For arbitrarily small deformation of nuclear configuration, ψ is also deformed slightly, which means a small change in r induces a small change in ψ . Therefore R is continuous. But, if the reacting system conserves some symmetry, R can be discontinuous at some point along the reaction path (e.g., single Slater determinant description of the disrotatory ring opening of cyclobutene). Similarly, a small change in ψ induces a small change in E , therefore P is continuous.

A one to one function has its inverse function and an inverse function of a continuous function is also a continuous function,¹⁰ so g_i^{-1} can be defined as the inverse function of g_i ,

g_i^{-1} : one to one, onto, continuous function on domain B , then

$$g_i^{-1}(r_0)=0, \quad g_i^{-1}(r_1)=1. \quad (6)$$

Now $h_i(x)$ is defined as follows.

$$h_i(x) \equiv g_i^{-1}(g_0(x)) \text{ on domain } A, \quad (7)$$

then

$$\begin{aligned} h_0(x) &= g_0^{-1}(g_0(x)) = x \\ h_i(0) &= g_i^{-1}(g_0(0)) = g_i^{-1}(r_0) = 0 \\ h_i(1) &= g_i^{-1}(g_0(1)) = g_i^{-1}(r_1) = 1. \end{aligned} \quad (8)$$

$h_i(x)$ is a one to one, onto, continuous function because g_i^{-1} and g_0 are one to one, onto, continuous functions.¹¹

Since,

$$\begin{aligned} h_i(x) &= g_i^{-1}(g_0(x)) = g_i^{-1}(r), \\ g_i^{-1}(r) &\in [0, 1], \end{aligned} \quad (9)$$

then

$$0 \leq h_i(x) \leq 1 \quad (10)$$

holds. Furthermore $h_i(x)$ is a strictly monotonic function on A because $h_i(x)$ is a real-valued and one to one function on A .¹²

For

$$h_i(0)=0 < 1 = h_i(1), \quad (11)$$

$h_i(x)$ is a strictly monotonic increasing function on A .

Next, the definite integrals are defined as follows:

$$f_i \equiv \int_0^1 R(g_i(x)) dx \quad (i=1, 2, \dots). \quad (12)$$

They are integrals of ψ , from a reactant to a product along a given reaction path, and functions of electron position vectors, of course. Since the integrand $R(g_i(x))$, which is a real normalized wave function, is continuous or piecewise continuous on the integration interval, then the integral f_i exists.¹³

In particular,

$$f_0 = \int_0^1 R(g_0(x)) dx. \quad (13)$$

Using eq. (8),

$$f_i = \int_0^1 R(g_i(y)) dy = \int_{x=0}^{x=1} R(g_i(h_i(x))) dh_i(x)$$

$$\begin{aligned}
&= \int_0^1 R(g_i(g_i^{-1}(g_0(x)))) dh_i(x) \\
&= \int_0^1 R(g_0(x)) dh_i(x), \quad (14)
\end{aligned}$$

where variable y is replaced by $h_i(x)$ in f_i . One should remind that $h_i(x)$ is a strictly monotonic continuous function.¹⁴

$R(g_0(x))$, the integrand of f_i , is equal to that of f_0 , but $h_i(x)$, the integrator of f_i , replaces x of f_0 .

f_i has following characteristics. The norm of f_i is

$$\|f_i\| = (\langle f_i | f_i \rangle)^{1/2} \geq 0 \quad (15)$$

and

$$\begin{aligned}
\|f_i\|^2 &= \int_0^1 \int_0^1 \langle R(g_0(x)) | R(g_0(y)) \rangle dh_i(x) dh_i(y) \\
&\leq \int_0^1 \int_0^1 dh_i(x) dh_i(y) = [h_i(1) - h_i(0)]^2 = 1
\end{aligned} \quad (16)$$

because $R(g_0(x))$ is a real normalized wave function and therefore $\langle R(g_0(x)) | R(g_0(y)) \rangle \leq 1$. That is,

$$0 \leq \|f_i\| \leq 1. \quad (17)$$

Now the reaction path function, F , is defined as f_k of the smallest norm:

$$F \equiv f_k = \int_0^1 R(g_0(x)) dh_k(x) \equiv \int_0^1 \mathbf{R}(x) dh_k(x), \quad (18)$$

where for brevity

$$\mathbf{R}(x) \equiv R(g_0(x)). \quad (19)$$

For all f_i 's, it does hold that

$$\|F\| \leq \|f_i\|. \quad (20)$$

Finally, the reaction path average energy is defined as

$$\begin{aligned}
E_{RP} &\equiv \int_0^1 P(\mathbf{R}(x)) dh_k(x) \\
&\equiv \int_0^1 \mathbf{E}(x) dh_k(x), \quad (21)
\end{aligned}$$

where $h_k(x)$ is the integrator of the reaction path function, and

$$\mathbf{E}(x) \equiv P(\mathbf{R}(x)). \quad (22)$$

Since F is one of f_i 's, obviously $0 \leq \|F\| \leq 1$. However the lower bound is not zero at least for the case of closed shell single Slater determinant description of wave function. First, one should prove that $\langle \mathbf{R}(x) | \mathbf{R}(y) \rangle$, which is the overlap integral of wave functions, is not negative for closed shell.

The reacting system is assumed to have $2N$ electrons in closed shell electronic configuration. The wave functions may be described as single Slater determinants,¹⁵

$$\begin{aligned}
\mathbf{R}(x) &= \{(2N)!\}^{-1/2} \det \{\psi_1 \psi_2 \cdots \psi_N \bar{\psi}_1 \bar{\psi}_2 \cdots \bar{\psi}_N\} \\
\mathbf{R}(y) &= \{(2N)!\}^{-1/2} \det \{\phi_1 \phi_2 \cdots \phi_N \bar{\phi}_1 \bar{\phi}_2 \cdots \bar{\phi}_N\},
\end{aligned} \quad (23)$$

where spatial orbitals are same for ψ_i and $\bar{\psi}_i$, with α, β spin respectively, also for $\phi_i, \bar{\phi}_i$.

Then the overlap integral is

$$\begin{aligned}
\langle \mathbf{R}(x) | \mathbf{R}(y) \rangle &= \det \{ \langle \psi_1 | \phi_1 \rangle \langle \psi_2 | \phi_2 \rangle \cdots \langle \psi_N | \phi_N \rangle \} \\
&\quad \{ \langle \bar{\psi}_1 | \bar{\phi}_1 \rangle \langle \bar{\psi}_2 | \bar{\phi}_2 \rangle \cdots \langle \bar{\psi}_N | \bar{\phi}_N \rangle \} \\
&= [\det \{ \langle \psi_1 | \phi_1 \rangle \langle \psi_2 | \phi_2 \rangle \cdots \langle \psi_N | \phi_N \rangle \}]^2 \geq 0.
\end{aligned} \quad (24)$$

In general, when the reacting system has no symmetry $\langle \mathbf{R}(x) | \mathbf{R}(y) \rangle$ is non-zero. Therefore in this case $\langle \mathbf{R}(x) | \mathbf{R}(y) \rangle > 0$. So the square of the norm of the reaction path function satisfies the relation,

$$\begin{aligned}
\|F\|^2 &= \int_0^1 \int_0^1 \langle \mathbf{R}(x) | \mathbf{R}(y) \rangle dh_k(x) dh_k(y) \\
&\geq \int_0^1 \int_0^1 S_{\min} dh_k(x) dh_k(y) = S_{\min} > 0,
\end{aligned} \quad (25)$$

where

$$0 < S_{\min} \leq \langle \mathbf{R}(x) | \mathbf{R}(y) \rangle. \quad (26)$$

On the other hand, when the reacting system conserves some symmetry, it is possible that the

irreducible representations of occupied MO's change at some point along the reaction path. In such situation, it follows that,

$$\begin{aligned} \langle R(x; x \in X) | R(y; y \in Y) \rangle &= 0 \\ \langle R(x; x \in Y) | R(y; y \in X) \rangle &= 0 \\ \langle R(x; x \in X) | R(y; y \in X) \rangle &> 0 \\ \langle R(x; x \in Y) | R(y; y \in Y) \rangle &> 0, \end{aligned} \quad (27)$$

where

$$X = [0, a], \quad Y = [a, 1], \quad 0 < a < 1, \quad (28)$$

corresponds to the orbital crossing point.

Therefore

$$\begin{aligned} \|F\|^2 &= \int_0^a \int_0^a \langle R(x) | R(y) \rangle dh_k(x) dh_k(y) \\ &\quad + \int_a^1 \int_a^1 \langle R(x) | R(y) \rangle dh_k(x) dh_k(y) \\ &\geq S_{\min, 1} h_k(a)^2 + S_{\min, 2} \{h_k(1) - h_k(a)\}^2 \\ &> 0, \end{aligned} \quad (29)$$

where

$$\begin{aligned} 0 < S_{\min, 1} &\leq \langle R(x; x \in A) | R(y; y \in A) \rangle \\ 0 < S_{\min, 2} &\leq \langle R(x; x \in B) | R(y; y \in B) \rangle. \end{aligned} \quad (30)$$

Consequently, the inequality,

$$\|F\| > S, \quad S > 0, \quad (31)$$

holds for closed shell single Slater determinant wave functions whether or not the reacting system conserves symmetry.

In general, if $\langle R(x) | R(y) \rangle > 0$ along the reaction path, then definitely eq. (31) holds.

APPROXIMATE FORM OF THE REACTION PATH FUNCTION

A Riemann-Stieltjes integral, f_i (eq. (14)), can be rewritten by a limit of Riemann-Stieltjes sum¹⁶

$$\begin{aligned} f_i &= \lim_{N \rightarrow \infty} \sum_{j=1}^N R(x_j) \Delta h_i^N(j), \\ x_j &\in \left[\frac{j}{N}, \frac{j-1}{N} \right], \end{aligned} \quad (32)$$

where

$$\Delta h_i^N(j) \equiv h_i\left(\frac{j}{N}\right) - h_i\left(\frac{j-1}{N}\right) > 0 \quad (33)$$

because $h_i(x)$ is a strictly monotonic increasing function as emphasized earlier.

Then

$$\begin{aligned} \sum_{j=1}^N \Delta h_i^N(j) &= h_i\left(\frac{N}{N}\right) - h_i\left(\frac{0}{N}\right) \\ &= h_i(1) - h_i(0) = 1. \end{aligned} \quad (34)$$

Naturally, F is now one of f_i 's, with the smallest norm,

$$F = \lim_{N \rightarrow \infty} \sum_{j=1}^N R(x_j) \Delta h_i^N(j). \quad (35)$$

For the purpose of approximation, one may define,

$$\bar{F}_N \equiv \sum_{j=1}^N R(x_j) \bar{A}_j, \quad (36)$$

where \bar{A}_j 's are numbers so chosen that

$$\sum_{j=1}^N \bar{A}_j \equiv 1, \quad \bar{A}_j > 0. \quad (37)$$

Picking F_N with the smallest norm out of \bar{F}_N functions:

$$\|F_N\| \leq \|\bar{F}_N\|, \quad (38)$$

one may define

$$F_N \equiv \sum_{j=1}^N R(x_j) A_j, \quad \sum_{j=1}^N A_j = 1, \quad A_j > 0. \quad (39)$$

Then

$$\begin{aligned} \lim_{N \rightarrow \infty} F_N &= F \\ \lim_{N \rightarrow \infty} A_j &= \lim_{N \rightarrow \infty} \Delta h_i^N(j). \end{aligned} \quad (40)$$

So it is reasonable to use F_N as the approximate reaction path function.

For the reaction path average energy, the corresponding approximation would be

$$E_{RP}(N) \equiv \sum_{j=1}^N E(x_j) A_j, \quad (41)$$

where A_j is the one appeared in the approximate

reaction path function (eq. (39)). And $E_{RP}(N)$ approaches E_{RP} as N goes infinite.

One may define

$$dh_m(x) \equiv \sum_{j=1}^N \Delta_j \delta(x_j - x) dx, \quad h_m(0) \equiv 0, \quad (42)$$

where the domain of $h_m(x)$ is A , that is $[0, 1]$. $\delta(x)$ denotes Dirac delta function and Δ_j is the one appeared in eq. (39).

Then

$$h_m(x) = \int_0^x \sum_{j=1}^N \Delta_j \delta(x_j - y) dy. \quad (43)$$

For $x=1$,

$$h_m(1) = \int_0^1 \sum_{j=1}^N \Delta_j \delta(x_j - y) dy = \sum_{j=1}^N \Delta_j = 1. \quad (44)$$

$h_m(x)$ is a step function, but a step function can be regarded as the limiting function of a sequence of continuous, one to one, onto, strictly monotonic increasing functions (Fig. 1).

So, in practical manner, $h_m(x)$ satisfies the conditions of $h_i(x)$ which is the integrator of f_i (eq. (14)).

Therefore

$$\begin{aligned} \|F\| &\leq \|f_m\| \\ f_m &= \int_0^1 R(x) dh_m(x). \end{aligned} \quad (45)$$

On the other hand,

$$\begin{aligned} f_m &= \int_0^1 R(x) dh_m(x) = \int_0^1 R(x) \sum_{j=1}^N \Delta_j \delta(x_j - x) dx \\ &= \sum_{j=1}^N R(x_j) \Delta_j = F_N. \end{aligned} \quad (46)$$

Therefore

$$\|F\| \leq \|F_N\|. \quad (47)$$

It is shown that the lower bound of the norm of the approximate reaction path function is the norm of the exact reaction path function. As the approximate reaction path function converges to the exact reaction path function, the norm of the approximate reaction path function approaches to the norm of the exact reaction path

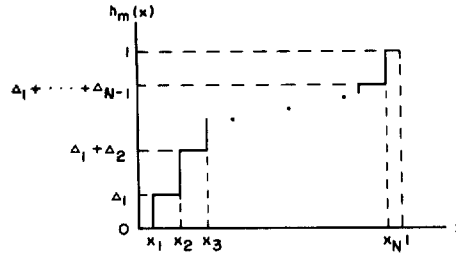


Fig. 1. Graph of $h_m(x)$.

function, from above.

To find F_N means to find Δ_k 's, because $R(x_k)$ is a wave function and must be calculated in advance. Since \bar{F}_N may be regarded as a function of $\bar{\Delta}_k$'s, minimization of $\|\bar{F}_N\|^2$ with respect to $\bar{\Delta}_k$'s would give $\|F_N\|^2$. When $\text{grad}\|\bar{F}_N\|^2=0$, $\|\bar{F}_N\|^2$ as well as $\|\bar{F}_N\|$ is an extremum. And if the extremum is not a maximum then it is a minimum. Therefore the minimum $\|\bar{F}_N\|$ is the norm of the approximate reaction path function, $\|F_N\|$, and the corresponding $\bar{\Delta}_k$'s give F_N for a given set of $R(x_k)$'s.

The square of the norm of F_N is given by

$$\|F_N\|^2 = \sum_{i=1}^N \sum_{j=1}^N \langle R(x_i) | R(x_j) \rangle \Delta_i \Delta_j \quad (48)$$

with

$$\Delta_j > 0, \quad \sum_{j=1}^N \Delta_j = 1, \quad (49)$$

so that

$$\Delta_N = 1 - \sum_{j=1}^{N-1} \Delta_j. \quad (50)$$

If real normalized wave functions are used,

$$S_{ij} \equiv \langle R(x_i) | R(x_j) \rangle, \quad S_{ii} = 1, \quad S_{ij} = S_{ji}, \quad (51)$$

then

$$\begin{aligned} \|F_N\|^2 &= \sum_{i=1}^N \sum_{j=1}^N S_{ij} \Delta_i \Delta_j \\ &= \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} S_{ij} \Delta_i \Delta_j + 2 \sum_{i=1}^{N-1} S_{iN} \Delta_i \Delta_N + \Delta_N^2 \\ &= \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} S_{ij} \Delta_i \Delta_j + 2 \sum_{i=1}^{N-1} S_{iN} \Delta_i \left(1 - \sum_{j=1}^{N-1} \Delta_j\right) \\ &\quad + \left(1 - \sum_{j=1}^{N-1} \Delta_j\right)^2. \end{aligned} \quad (52)$$

To find \mathcal{A}_k 's at $\text{grad}\|F_N\|^2=0$, one has to differentiate $\|F_N\|^2$ with respect to \mathcal{A}_k 's ($k=1, 2, \dots, N-1$) and set the derivatives equal to zero.

$$\begin{aligned} \frac{\partial\|F_N\|^2}{\partial\mathcal{A}_k} &= \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} \{S_{ij}(\delta_{ik}\mathcal{A}_j + \delta_{jk}\mathcal{A}_i)\} \\ &+ 2\sum_{i=1}^{N-1} S_{iN}\delta_{ik}\left(1 - \sum_{j=1}^{N-1} \mathcal{A}_j\right) \\ &- 2\sum_{i=1}^{N-1} S_{iN}\mathcal{A}_i \sum_{j=1}^{N-1} \delta_{jk} - 2\left(1 - \sum_{j=1}^{N-1} \mathcal{A}_j\right) \sum_{j=1}^{N-1} \delta_{jk} \\ &= 2\left\{\sum_{j=1}^{N-1} S_{kj}\mathcal{A}_j + S_{kN}\left(1 - \sum_{i=1}^{N-1} \mathcal{A}_i\right) - \sum_{i=1}^{N-1} S_{iN}\mathcal{A}_i\right. \\ &\quad \left. - \left(1 - \sum_{i=1}^{N-1} \mathcal{A}_i\right)\right\} = 0 \end{aligned} \quad (53)$$

There results a simultaneous equation,

$$\begin{aligned} \sum_{i=1}^{N-1} (1 + S_{ki} - S_{kN} - S_{iN}) \mathcal{A}_i &= 1 - S_{kN}, \\ k &= 1, 2, \dots, N-1. \end{aligned} \quad (54)$$

And \mathcal{A}_N is given by eq. (50). Because maximum of $\|F_N\|^2$ is 1, if the extremum is not 1, this extremum is a minimum.

If one or more of \mathcal{A}_k 's are negative, then the solution of eqs. (50, 54) does not give the minimum which one is seeking for. The point of \mathcal{A}_k 's, which gives an acceptable extremum for $\|F_N\|^2$, locates on the boundary of a region,

$$S = \left\{ \mathcal{A}_i ; \mathcal{A}_i > 0, \sum_{i=1}^N \mathcal{A}_i = 1 \right\}. \quad (55)$$

Since, inside S , $\text{grad}\|F_N\|^2 \neq 0$, there is no extremum point inside S . Therefore the extremum point is on the boundary of S , i. e., one or more \mathcal{A}_k 's are arbitrary small positive numbers.

APPLICATION TO REACTIONS WITH SYMMETRY

For a reacting system with a certain symmetry it can be shown immediately which reaction path has larger norm, without computation. By constructing orbital correlation diagram, one can notice that the allowed reaction path cons-

erves symmetry of occupied MO's, while the forbidden reaction path does not.¹⁷ Consequently, for the allowed reaction path, the overlap integral between the wave functions of any two nuclear configurations along the reaction path does not vanish in principal axis frame, because of symmetry reason. And for the forbidden reaction path, however, the overlap integral between a nuclear configuration at the former half of the reaction path and that at the latter half is necessarily zero, because of symmetry reason. As generally known, a symmetry axis is a principal axis and a reflection plane is a plane on which the principal axes are located. One describes a reacting system with real normalized closed shell wave functions. By definition of the reaction path function, one has

$$\begin{aligned} F &= \int_0^1 R(x) dh_k(x) = \int_0^1 R(g_0(x)) dh_k(x) \\ &= \int_0^1 R(g_k(x)) dx. \end{aligned} \quad (56)$$

For the symmetry allowed path, the square of the norm of the reaction path function is

$$\begin{aligned} \|F\|_a^2 &= \int_0^1 \int_0^1 \langle R(g_k(x)) | R(g_k(y)) \rangle dx dy \\ &= \int_0^a \int_0^a \langle R(g_k(x)) | R(g_k(y)) \rangle dx dy \\ &\quad + 2 \int_0^a \int_a^1 \langle R(g_k(x)) | R(g_k(y)) \rangle dx dy \\ &\quad + \int_a^1 \int_a^1 \langle R(g_k(x)) | R(g_k(y)) \rangle dx dy \\ &\equiv S_1 + 2S_2 + S_3, \end{aligned} \quad (57)$$

where $0 < a < 1$, and S_1, S_2, S_3 are defined as follows.

$$\begin{aligned} S_1 &\equiv \int_0^a \int_0^a \langle R(g_k(x)) | R(g_k(y)) \rangle dx dy \\ S_2 &\equiv \int_0^a \int_a^1 \langle R(g_k(x)) | R(g_k(y)) \rangle dx dy \\ S_3 &\equiv \int_a^1 \int_a^1 \langle R(g_k(x)) | R(g_k(y)) \rangle dx dy, \end{aligned} \quad (58)$$

then

$$S_1 > 0, \quad S_2 > 0, \quad S_3 > 0 \quad (\text{Fig. 2}). \quad (59)$$

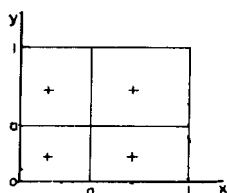


Fig. 2. $\langle R(g_k(x)) | R(g_k(y)) \rangle$ of the symmetry allowed path.

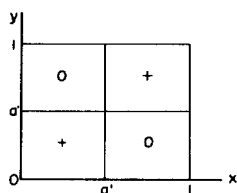


Fig. 3. $\langle R(g_k(x)) | R(g_k(y)) \rangle$ of the symmetry forbidden path.

And for the symmetry forbidden path,

$$\|F\|_f^2 = S_1' + 2S_2' + S_3', \quad (60)$$

where

$$\begin{aligned} S_1' &= \int_0^{a'} \int_0^{a'} \langle R(g_k(x)) | R(g_k(y)) \rangle dx dy \\ S_2' &= \int_0^{a'} \int_{a'}^1 \langle R(g_k(x)) | R(g_k(y)) \rangle dx dy \\ S_3' &= \int_{a'}^1 \int_{a'}^1 \langle R(g_k(x)) | R(g_k(y)) \rangle dx dy \\ 0 < a' < 1, \end{aligned} \quad (61)$$

a' corresponds to the point where orbital crossing occurs. ($g_k(x)$ is not necessarily same for both paths)

Then

$$S_1' > 0, S_2' = 0, S_3' > 0 \quad (\text{Fig. 3}). \quad (62)$$

If $S_1 + S_3 \approx S_1' + S_3'$, then

$$\begin{aligned} \|F\|_a &= (S_1 + 2S_2 + S_3)^{1/2} \\ &> (S_1' + S_3')^{1/2} = \|F\|_f. \end{aligned} \quad (63)$$

Therefore it can be concluded that the norm of the reaction path function of the symmetry allowed path is larger than that of the symmetry forbidden path. So the reaction path function can be applied to the reacting system with sym-

metry in non-calculative manner. For a closed shell symmetric reacting system, the result of the reaction path function method is equivalent to that of Woodward-Hoffmann rule.

At least, for thermal electrocyclic reaction of cyclobutene, the disrotatory path has no transition state and *cis*-butadiene is not a minimum on potential energy surface, so the disrotatory path is not a true reaction path.¹⁸ But this path and *cis*-butadiene can be considered as an approximate reaction path and an approximate nuclear configuration of product molecule.

CONCLUSION

The unique quantities for a given reaction path, i. e., the reaction path function, its norm and the reaction path average energy, are defined, and their characteristics are clarified. For practical use, their approximate forms are suggested and the characteristics of the approximate reaction is discussed in relation to the exact function. Applications of these quantities to some thermal electrocyclic reactions are presented in accompanying paper to show that the path with larger norm of the function and lower average energy is more preferred to others.

REFERENCES

1. J. Hine, *J. Org. Chem.*, **31**, 1236 (1966).
2. J. Hine, *J. Am. Chem. Soc.*, **88**, 5525 (1966).
3. O. S. Tee, *ibid.*, **91**, 7144 (1969).
4. O. S. Tee and K. Yates, *ibid.*, **94**, 3074 (1972).
5. J. Hine, "Advances in Physical Organic Chemistry", Vol. 15, P. 1ff, V. Gold and D. Bethell, Ed., Academic Press, London, 1977.
6. C. Trindle, *ibid.*, **92**, 3251, 3255 (1970).
7. D. R. Kelsey, *J. Comput. Chem.*, **1**, 3, 21 (1980).
8. G. S. Ezra, "Symmetry Properties of Molecules", P. 25ff, Springer, Berlin, 1982.
9. B. Buck, L. C. Biedenharn and R. Y. Cusson, *Nucl. Phys.*, **A317**, 205 (1979).
10. R. C. Buck, "Advanced Calculus", 3rd Ed., P. 114.

- McGraw-Hill, New York, 1978.
11. Ref. 10, P. 78.
 12. Ref. 10, P. 96.
 13. T. M. Apostol, "Mathematical Analysis", 2nd Ed., P. 159, Addison-Wesley, Massachusetts, 1974.
 14. Ref. 13, P. 144.
 15. A. Szabo and N. S. Ostlund, "Modern Quantum Chemistry", P. 74ff, Macmillan, New York, 1982.
 16. Ref. 13, P. 141.
 17. R. A. Y. Jones, "Physical and Mechanistic Organic Chemistry", Chapter 15, Cambridge University Press, Cambridge, 1979.
 18. J. Breulet and H. F. Schaefer III, *J. Am. Chem. Soc.*, **106**, 1221 (1984).