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Classically forbidden nonadiabatic transitions in multidimensional chemical dynamics

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An accurate method is proposed to deal with such nonadiabatic transitions as those energetically inaccessible, namely, classically forbidden transitions. This is formulated by using the corresponding Zhu–Nakamura formulas and finding the optimal paths in the classically forbidden tunneling regions that maximize the overall transition probabilities. This can be done for both the nonadiabatic tunneling type (so-called normal case in electron transfer) in which two diabatic potentials have opposite signs of slopes and the Landau–Zener type (inverted case) in which two diabatic potentials have the same sign of slopes. The method is numerically demonstrated to be useful for clarifying chemical and biological dynamics.

I. Introduction

Nonadiabatic transition presents a very basic mechanism of state and phase change in various branches of science.[1,2] As is well known, in the case of chemical and biological dynamics, for instance, this transition is ubiquitous and occurs through the conical intersection of adiabatic potential energy surfaces.[1–3] In the one-dimensional picture, there are two types of transitions; nonadiabatic tunneling (NT) type and Landau–Zener (LZ) type, which correspond to the normal and inverted cases in the electron transfer problems as Marcus named.[4]

For these two types of transitions, the analytical Zhu–Nakamura formulas are available for the whole energy region and the whole electronic coupling strength.[1,2,5] Although the Zhu–Nakamura theory has been formulated for one-dimensional problems, the formulas are actually applicable to multidimensional dynamics, since the nonadiabatic transition occurs predominantly along the direction of nonadiabatic coupling vector. Multidimensional

potential energy surfaces are cut along this direction and the formulas are employed along these one-dimensional potential curves. Practical applications have been made successfully to real chemical and biological systems, not only to triatomic reaction systems but also to reactions in the environment.[1,2,6–8] The electron transfer processes can also be treated for the whole range of electronic coupling strengths.[9–12] In such a way, a semiclassical molecular dynamics simulation method can be developed with quantum mechanical effects taken into account.[13] The quantum mechanical effects meant here are nonadiabatic transition, quantum mechanical tunneling, and phases associated with these transitions.

The above mentioned reduction to the one-dimensional system is a good approximation in the case that the corresponding nonadiabatic transition, *i.e.*, conical intersection position, is located in the energetically accessible, namely, classically allowed region. It naturally becomes less accurate in the case of classically forbidden transitions, since the quantum mechanical tunneling in the multidimensional space occurs simultaneously. What is the best way to use the Zhu–Nakamura formulas in this case? This is the main theme of this paper. Our basic strategy is as follows: (1) run a classical trajectory. (2) When a caustic is detected, draw a straight line tunneling path (blue line in Fig. 1) from the caustic and calculate the nonadiabatic transition probability. (3) Optimize the tunneling path (the purple line) to achieve the maximum transition probability. (4) Run the classical trajectory to find the next caustic. Owing to the localizability of nonadiabatic transitions in the adiabatic state representation, the dynamics along a tunneling path can be decomposed into localized nonadiabatic transition and adiabatic tunneling processes, the former of which can be treated nicely with Zhu–Nakamura formulas, and the latter is treated by calculating the tunneling action. The methods of finding caustics and calculating tunneling action were proposed by us in ref. 13 for multi-dimensional pure tunneling. In this paper, we combine the two theories of nonadiabatic transition and multi-dimensional tunneling to develop a new theory for multi-dimensional classically forbidden nonadiabatic transitions.

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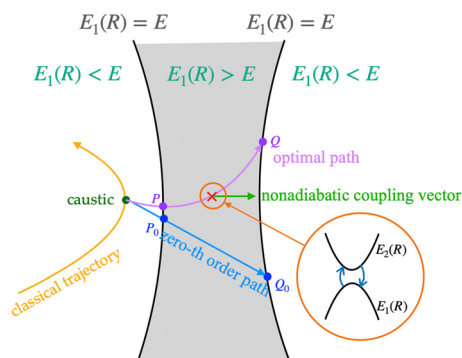† Present address: Nakamura Institute of Chemical Dynamics, 3-10-20 Tatsumi Higashi, Okazaki, Japan.

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Fig. 1 Schematic view of the zero-th order and the optimal nonadiabatic tunneling path.

This paper is organized as follows: Section II presents the main formulation of this paper, namely, it describes how to treat the classically forbidden transitions in multidimensional space. In Section III, the method presented in Section II is numerically demonstrated to work well by using a two-dimensional model system. Our conclusions and future perspectives are given in Section IV.

II. Method

A. Basic idea

Let us consider a general system composed of n atoms with masses $m_k(k = 1 \sim n)$. First, the mass-scaled relative internal coordinates and momenta $\{q_j, p_j\}(j = 1 \sim 3n - 3)$ are introduced. Then the Hamiltonian is given by

$$H = \frac{1}{2}\mathbf{p} \cdot \mathbf{p} + V(\mathbf{q}) \tag{1}$$

In the Zhu–Nakamura trajectory surface hopping (ZN-TSH) method the following two approximations are employed:[1,2] (i) the minimum energy separation between two relevant adiabatic potential energy surfaces $E_j(\mathbf{q})(j = 1,2)$ is detected along each classical trajectory, which is used as the transition point, and (ii) the nonadiabatic coupling vector is evaluated there, along which direction the potential energy surfaces are cut to define two potential energy curves that are used to calculate the transition probability. This method has been proven to work well.[1,2,7,8] In the case of classically forbidden transitions, however, this method becomes naturally less accurate, since the quantum mechanical tunneling in a multidimensional space is involved and the straight line path does not necessarily provide the optimal path. First, we have to detect caustics along each classical trajectory, since the caustics define the boundary between classically allowed and forbidden regions. It is also easily conjectured that the optimal tunneling path in the classically forbidden region is not just a straight line.

In Zhu–Nakamura theory, there are two basic parameters, σ_{ZN} and δ_{ZN}, which represent the effects of nonadiabatic transition and the tunneling, respectively, can be evaluated separately.[1,2] This scheme of separate evaluation of σ_{ZN} and δ_{ZN} is guaranteed by the fact that the nonadiabatic transition is

localized in the vicinity of the avoided crossing point. The parameter σ_{ZN} can be estimated locally at the minimum energy separation position and the parameter δ_{ZN} can be given by the action integral along the tunneling path. This theory has been demonstrated to work well in the various one-dimensional potential systems.[1,2] Thus what we have to do is to determine the optimal tunneling path in multi-dimensional space that maximizes the overall transition probability. This can be done by using a method similar to the one that we have proposed before to treat multidimensional tunneling (see ref. 13–16). Besides, the Zhu–Nakamura theory provides the explicit analytical expressions of the overall transition probabilities P_{ZN} for both NT and LZ types. The main objective of this paper is to propose an accurate method usable in multi-dimensional nonadiabatic chemical dynamics.

The detection of caustics is made by propagating the matrix

$$A_{ij} = \frac{\partial p_i(t)}{\partial q_j(t)}(i, j = 1 \sim N_I) \tag{2}$$

along the classical trajectory, where $p_i(q_j)$ is the i-th (j-th) component of the momentum vector $p(\mathbf{q})$ in the N_I-dimensional space. At the caustics the maximum absolute value of the eigenvalues of this matrix diverges,

$$\text{Max}_j|\text{Diag}(A)_{jj}| = \infty \text{ or } \text{Min}_j|\text{Diag}(B)_{jj}| = 0, \tag{3}$$

where Diag(X) means the diagonalized matrix of X and $B = A^{-1}$.

Depending on the types of the nonadiabatic transition, we have different ways of representing the tunneling path, basically because the trajectory runs on the same adiabatic potential surface in the NT type, while the LZ type induces a jump from one potential surface to another. This indicates that it is necessary to have *a priori* knowledge about the potential topography, *i.e.*, NT type or LZ type, before starting the dynamics calculation. Hereafter, our treatments for the two types are explained, respectively.

B. In the case of NT-type

Starting from the caustic, the tunneling path runs through the potential barrier of the adiabatic potential $E_1(\mathbf{q})$. It is noted that the overall tunneling is affected by the nonadiabatic coupling as explained below. In order to determine the optimal tunneling path, we can employ basically the same method used in ref. 13. The optimal path is determined variationally by maximizing the probability P_{ZN} given by the Zhu–Nakamura theory (see, for instance, eqn (8.119) of ref. 2). As the zero-th order approximation to start with, two straight lines, one in the steepest ascent direction and the other in the direction of the nonadiabatic coupling vector at the caustic (C) are employed. Then the one providing the larger probability is selected to start with. This enables the computation time for optimization to be reduced, but it is possible to start with any linear path in principle.

The tunnel action in the m-th order approximation is expressed as

$$S^{(m)} = S_m^{CP} + S_m^{PQ} \tag{4}$$

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where $P(Q)$ is the crossing point of the path with the equipotential surface at the entrance to (exit from) the tunneling region (see ref. 13). The tunneling path $\{q_j^{(m)}\}$ is expressed geometrically as a function of parameter $z \in (0,1)$ as

$$q_j^{(m)} = q_j^C + \sum_{k=1}^{N_b} C_{jk}^{(m)} z^k \tag{5}$$

where q_j^C represents the coordinate at the caustic C, N_b is a certain number to guarantee the convergence, the parameter z runs from $z = 0$ at C to $z = 1$ at Q, and $C_{jk}^{(m)}$ are the expansion coefficients to be determined.

The procedure to determine the optimal path is summarized as follows:

(1) When the trajectory enters the reaction zone, the first caustic is detected and the straight line is drawn from there. This straight line is extended and the crossing point P_0 with the equipotential surface, *i.e.* the entrance to the tunneling region, should be detected. The zero-th order action integral along this line is denoted as

$$S_0^{SA}(\xi) \equiv S_0^{CP_0} + S_0^{P_0}(\xi), \tag{6}$$

where $S_0^{CP_0}$ is the action from $C(\xi = 0)$ to $P_0(\xi = P_0)$. The action $S_0^{P_0}(\xi)$ from the point P_0 is evaluated step by step up to ξ. When the total action S_0^{SA} becomes bigger than a certain criterion,

$$S_0^{SA}(\xi) \geq \text{Bigact}, \tag{7}$$

then the tunneling there is not carried out and the trajectory is further propagated. If the straight line reaches the equipotential surface in the exit channel at $\xi = \xi_{Q_0}$ and the total action is smaller than the above criterion, then the determination of the optimal tunneling path is carried out.

On this straight line, the minimum adiabatic energy difference position $R_0(z = z_0)$ is detected and the normalized nonadiabatic coupling vector $\mathbf{e}_{nad}$ is evaluated there. Along the direction of this vector two adiabatic potentials are calculated and the basic parameter σ_{ZN} is evaluated. The negative kinetic energy K_{tr} in this direction is given by

$$K_{tr}^{(m=0)} = E_{eff} - E_1(\mathbf{q}) \tag{8}$$

with

$$E_{eff} = \frac{1}{2}\left(\sum_j \frac{dq_j}{dz} e_j\right)^2 (\dot{z})^2 + E_1(\mathbf{q}),$$
$$(\dot{z})^2 = -\frac{2(E_1 - E)}{\sum_j \left(\frac{dq_j}{dz}\right)^2}, \tag{9}$$

where E is the total energy, e_j is the j-th component of the coupling vector $\mathbf{e}_{nad}$, and E_{eff} represents the effective total energy along the transition direction. This is employed to evaluate the parameter b^2. The overall Zhu–Nakamura transition probability $P_{ZN}^{(0)}$ is calculated, where $\delta_{ZN} = S^{(0)} \equiv S_0^{SA}(\xi_{Q_0})$. The parameter σ_{ZN} originally defined by the complex phase integral up to the complex crossing point from the real axis is

given by the simple analytical expression by using the linear potential model (see ref. 1 and 2). If this probability is smaller than a certain critical value, say ε,

$$P_{ZN}^{(0)} \leq \varepsilon, \tag{10}$$

then the search of the optimal path is stopped and the classical trajectory is further propagated to detect the next caustic. If $P_{ZN}^{(0)}$ is larger than ε, then we proceed to find the optimal path.

(2) The tunneling path $\{q_j^{(m)}\}$ in the m-th order approximation is obtained by slightly modifying the coefficients $C_{jk}^{(m-1)}$ in the $(m - 1)$th order approximation in the direction of increasing $P_{ZN}^{(m-1)}$. The pure imaginary actions S_m^{CP} and S_m^{PQ} are calculated separately: S_m^{CP} is the action along the steepest ascent direction and S_m^{PQ} is the action along the tunneling path from P to Q. Then δ_{ZN} is given by $S_m(=S_m^{CP} + S_m^{PQ})$. The minimum energy separation position $R_0(z = z_0)$ is detected along the path and the parameter σ_{ZN} is evaluated as mentioned above, where the negative kinetic energy $K_{tr}^{(m)}$ at R_0 is calculated by eqn (8).

(3) The above procedure to find the optimal path is repeated until the required convergence of the probability $P_{ZN}^{(m)}$ is attained. Then the overall nonadiabatic tunneling probability is determined in the same way as that in ref. 13 by

$$P_{ZN} = 1 - \prod_{i=i_{min}}^{i=i_{max}} [1 - P_{ZN}^{(i)}], \tag{11}$$

where i designates the i-th caustic in the reaction zone (see eqn (122) of ref. 13).

(4) After a sufficient number of trajectories is run, the final reaction probability p_{react} is calculated by taking the average of the probabilities over the total number of trajectories satisfying a given quantum mechanical initial condition.

C. In the case of LZ type

The situation in this case is a bit more complicated than in the case of NT type, since the tunneling path jumps from $E_1(\mathbf{q})$ to $E_2(\mathbf{q})$ at R_0, giving rise to the non-smoothness of the tunneling path at the crossing point. In the semiclassical Zhu–Nakamura theory, the transition is assumed to occur locally at the avoided crossing point and thus the tunneling processes before and after the transition can be treated separately. This means that the second portion of the whole tunneling path, namely the path from R_0 to Q, can be determined separately from the first one in each iteration process. Such a separated treatment for before and after the crossing point makes it possible to represent the non-smooth path, which climbs (descends) the potential $E_1(\mathbf{q})$ ($E_2(\mathbf{q})$) before (after) passing the crossing point. This treatment for the LZ type relies on the localizability of nonadiabatic transition the same as the NT type. Owing to the usefullness of the Zhu–Nakamura formulas both for the NT and the LZ types, we expect that our method for the LZ type should work as well as the NT type.

In the zero-th order approximation, the straight line from the caustic $C(z_1 = 0)$ on $E_1(\mathbf{q})$ is extended to $R_0(z_1 = 1)$ and the second one is a straight line in the steepest descent direction from $R_0(z_2 = 0)$ on $E_2(\mathbf{q})$ to the exit $Q_0(z_2 = 1)$. In the higher order

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approximations, the second path from R_0 to the exit Q is determined so that the total transition probability P_{ZN} is maximized. The first path from C to R_0 gives the action,

$$S_1 = S_1^{CP} + S_1^{PR_0} \tag{12}$$

and the second path from R_0 to Q provides the action,

$$S_2 = S_s^{R_0 Q}. \tag{13}$$

The basic parameters σ_{ZN} and δ_{ZN} are given by (see ref. 1 and 2)

$$\sigma_{ZN} = \sigma_0^{ZN} \text{ and } \delta_{ZN} = -S_1 + S_2 + \delta_0^{ZN}, \tag{14}$$

where

$$\sigma_0^{ZN} + i\delta_0^{ZN} = \int_{R_0}^{R_*} [K_1(R) - K_2(R)]\mathrm{d}R, \tag{15}$$

where R_* is the complex crossing point and

$$K_j(R) = \sqrt{2[E - E_j(R)]}, \tag{16}$$

The overall transition probability P_{ZN} is given in the analytical form in terms of σ_{ZN} and δ_{ZN} (see, for instance, eqn (8.90) of ref. 2).

III. Numerical demonstration

As mentioned above, the nonadiabatic transition and the multi-dimensional tunneling can be treated separately once the tunneling path is given. The nonadiabatic transitions are well localized in the vicinity of avoided crossing points and the Zhu–Nakamura theory has been demonstrated to work well even for the energetically inaccessible transitions in one-dimensional systems.[1,2,5] The method to determine the optimal tunneling path in the multi-dimensional space, on the other hand, has been well tested to work well.[13–16] Thus, the method proposed here is supposed to be accurate. In this section it is numerically demonstrated that the Zhu–Nakamura formulas of P_{ZN} in the linear approximation can be very much improved by using the present method with the use of the same analytical expressions of P_{ZN}. In the linear approximation, the tunneling path is assumed to be linear along the direction of the nonadiabatic coupling vector at the caustic.

Here, the NT-type two-dimensional model reaction system A + BC → AB + C proposed in ref. 17 is used.‡ The adiabatic potentials $E_1(r,R)$ and $E_2(r,R)$ are given as follows:

$$E_1 = \frac{1}{2}\left[(V_R + V_P) - \sqrt{(V_R - V_P)^2 + 4V_C^2}\right], \tag{17}$$

$$E_2 = \frac{1}{2}\left[(V_R + V_P) + \sqrt{(V_R - V_P)^2 + 4V_C^2}\right], \tag{18}$$

with

$$V_R = D\{1 - \exp[-\beta(r - r_e)]\}^2 - \frac{1}{2}D$$
$$+ \frac{1}{2}D\left\{1 + \exp\left[-\beta\left(R + \frac{1}{2}r - 2r_e\right)\right]\right\}^2, \tag{19}$$
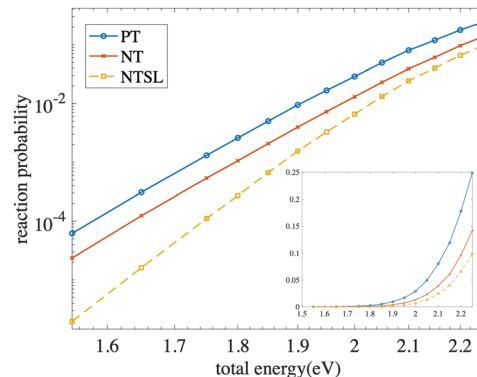

Fig. 2 Nonadiabatic tunneling probability against energy. PT: optimized pure tunneling through $E_1(r,R)$, NT: optimized nonadiabatic tunneling, NTSL: nonadiabatic tunneling along a straight line. The saddle point energy of the lower adiabatic potential is $E_{sp} = 2.275$ eV.

$$V_P = D\left\{1 - \exp\left[-\beta\left(R + \frac{1}{2}r - r_e\right)\right]\right\}^2 - \frac{1}{2}D$$
$$+ \frac{1}{2}D\left\{1 + \exp\left[-\beta\left(R + \frac{1}{2}r - 2r_e\right)\right]\right\}^2, \tag{20}$$

$$V_C = A \exp\{-\gamma[(r - r_C)^2 + (R - R_C)^2]\} \tag{21}$$

where r and R are the distance between B and C and the distance of A from the center of mass of BC, respectively. The various parameters are $D = 4.9$ eV, $\beta = 1.877$ Å, $r_e = 0.7417$ Å, $r_C = 1.5707 r_e$, $R_C = 1.5 r_C$, $A = 0.3$ eV, and $\gamma = 1.0$ Å^{-2}, which are the same as ref. 17 except A. The coupling strength A is taken to be smaller than the original one in order to emphasize the difference between the pure and nonadiabatic tunneling. The smaller the parameter A, the larger the difference, naturally.

Fig. 2 shows the numerical result of tunneling probability against total energy. It is clearly seen that the present optimized nonadiabatic tunneling probability improves the one in the linear approximation. The difference is emphasized naturally in the low energy region.

IV. Concluding remarks

A method has been proposed to treat energetically inaccessible, namely, classically forbidden, nonadiabatic transitions in multi-dimensional space for both NT and LZ types of transitions. Since the nonadiabatic transition itself is localized, it can be treated by the Zhu–Nakamura formulas along the direction of the nonadiabatic coupling vector at the minimum energy separation position in the tunneling region.[1,2] The multi-dimensionality effect, on the other hand, comes from the tunneling, namely, the optimal tunneling path is not a straight line in general. Determination of the optimal tunneling path can be achieved by the method proposed by the authors.[13] The caustics are detected along a classical trajectory and the optimal path up to and from the nonadiabatic transition position

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can be determined geometrically. The simple linear approximation in which the tunneling path is assumed to be linear from the caustic can be very much improved by using the present method. The method proposed in this paper properly takes into account the effect of multi-dimensionality and is expected to be usefully utilized to clarify the classically forbidden nonadiabatic chemical dynamics. For instance, the spin crossover of thiophosgene is a good example.[18,19] The detailed description of the method together with applications to real reaction systems will be reported in a full paper.

Conflicts of interest

The authors declare no competing financial interest.

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‡ The potential functions given in ref. 17 do not agree with the potential contours depicted there. Instead, the contours seem to be consistent with the potentials used here. However, the tunneling probabilities given in ref. 17 cannot be reproduced by these potentials.

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