Wentzel-Kramers-Brillouin theory of multidimensional tunneling: General theory for energy splitting

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A general Wentzel-Kramers-Brillouin (WKB) theory of multidimensional tunneling is formulated and an illuminating physical picture of the effects of multidimensionality is provided. Two basic problems are solved: (i) Maslov's semiclassical wave function in the classically accessible region is connected to the wave function in the classically inaccessible region and (ii) the latter is propagated into the deep tunneling region. It is found that there exist two distinct types of tunneling: pure tunneling and mixed tunneling. The former is the usual one in which the tunneling path can be defined by a certain classical trajectory on the inverted potential and its associated action is pure imaginary. In the latter case, no tunneling path can be defined and the Huygens-type wave propagation should be carried out. In this case, tunneling is always accompanied by classical motion in the transversal direction and the associated action is complex. A general procedure is presented for the evaluation of energy splitting \( \Delta E \) in the double well. Moreover, under the locally separable linear approximation, a simple and convenient formula for \( \Delta E \) is derived and is confirmed to work well by comparison with the exact numerical calculations.

I. INTRODUCTION

Quantum mechanical tunneling is a very interdisciplinary concept, being an important phenomenon in the fields of physics, chemistry, and biology.\(^1\) This represents one of the most important quantum mechanical effects, together with interference, quantization, resonance, and non-adiabatic transition.\(^2\)\(^3\) Multidimensional tunneling has been extensively studied in a variety of fields, such as false vacuum states in quantum field theory,\(^6\)\(^-\)\(^8\) fission of atomic nuclei in nuclear physics,\(^9\)\(^-\)\(^10\) scanning tunneling microscope and mesoscopic device in solid state physics,\(^11\)\(^-\)\(^12\) and proton transfer and chemical reaction in chemical physics.\(^12\)\(^-\)\(^31\) In chemical physics, for instance, bimolecular reactions such as

\[
\text{Cl} + \text{HCl} \rightarrow \text{ClH} + \text{Cl}, \tag{1.1}
\]

molecular dissociations such as

\[
\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}, \tag{1.2}
\]

and intramolecular conversions such as

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{O} \\
\text{H} \\
\text{H}\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{II} \\
\text{O} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array} \tag{1.3}
\]

are the most typical examples. Although the one-dimensional theory of tunneling has been well developed, multidimensionality is now known to be crucial in many cases and a good theory of multidimensional tunneling is strongly required.

For instance, the intramolecular conversion of malonaldehyde (1.3) has recently been investigated in detail. Using microwave and far infrared spectroscopic data, the tunneling energy splitting \( \Delta E_0 \) of the ground vibrational state has been estimated to be 21.6 cm\(^{-1}\) by Baughcum et al.\(^20\) Several quantum mechanical calculations have been made\(^23\)\(^-\)\(^26\)\(^-\)\(^28\) the one by Shida, Barbara, and Almlöf\(^6\) is the most exhaustive. They calculated the three-dimensional potential energy surface with high accuracy by using the \textit{ab initio} method and estimated the energy splitting \( \Delta E_0 \) by direct diagonalization of the Hamiltonian matrix. Their value is 9 cm\(^{-1}\), which is about 40% of the experimental value. Since we cannot expect the accuracy to be less than \( \sim 0.3 \) kcal mol\(^{-1}\) for the potential energy of such a big molecule, this agreement seems to be satisfactory. On the other hand, \( \Delta E_0 \) estimated by the one-dimensional potential along the intrinsic reaction coordinate (IRC) gives a few-orders-of-magnitude-smaller value.\(^28\) A more crucial example that demonstrates the conceptual insufficiency of the one-dimensional tunneling path will be given here.

Our purpose is to answer the following questions and to get a better chemical and physical picture of multidimensional tunneling: What are the essential differences between multidimensional tunneling and one-dimensional tunneling? Can we always define a unique tunneling path? How is it defined, if it exists? To answer these questions, the semiclassical approximation is the most desirable method, because it enables us to treat the problem analytically; while quantum mechanical calculations almost always give only numerical values.

Quite a few microscopic studies of multidimensional tunneling have been made so far based on the semiclassical approximation.\(^6\)\(^-\)\(^12\)\(^14\)\(^-\)\(^15\)\(^29\)\(^-\)\(^32\) Among them, the work of Banks, Bender, and Wu (BBW)\(^6\) in the study of quantum field theory was one of the most fundamental breakthroughs. They introduced the concept of the most probable escape path (MPEP), a classical trajectory that gives the minimum action on the inverted potential and perpen-
dicular approaches the boundary between the classically accessible and inaccessible regions. Another famous theory is the instanton theory, which also was invented in quantum field theory and which has been applied to various problems such as macroscopic tunneling. Both of these theories utilize classical trajectories on the inverted potential and claim that multidimensional tunneling proceeds along a certain particular path (or, at most, several paths). The exponent of the tunneling amplitude is always given by the Gamow factor along the path. Multidimensionality affects how the most appropriate tunneling path is determined and how to take into account the thickness of the tunneling path. The latter is incorporated into the preexponential factor.

Some attempts have also been made in chemical reaction dynamics to incorporate the effects of multidimensionality, mainly within the spirit of the transition state theory. The Marcus–Coltrin tunneling path has often been used in practical calculations for its convenience. This is the path emanating from the inner turning point of the ground state vibrational motion transversal to the IRC. This is basically an adiabatic approximation with respect to the translational motion and is not so bad for a system with large skew angle (small curvature of the IRC). For systems with large curvature such as reaction (1.1), the corner cutting direct path is intuitively assumed, or more legitimately the hyperspherical coordinates are employed to reduce the problem to one dimension along the hyper-radius to be dealt with by the analytical theories in one dimension. The periodic-orbit transition state theory devised by Miller is more versatile as far as the total (not the state to state) reaction rate constant is concerned. This can be shown to be equivalent to the instanton theory.

Our basic standpoint is quite different from those in the above-mentioned theories in the following sense. As easily conceived, there are two fundamental problems to be solved in multidimensional tunneling theory: (i) connection of the wave functions between the classically accessible and inaccessible regions, and (ii) wave propagation in the classically inaccessible region. In our viewpoint, the connection and the propagation of wave functions. We have succeeded in deriving a simple, convenient formula for energy splitting. This formula is confirmed to work well by comparison with the exact numerical calculations. It should be noted here that our formulation is carried out in real coordinate space, being different from that of Wilkinson, who formally considered the analytical continuation into the complex coordinate space. We are afraid that the latter treatment would inevitably encounter the difficulties of the Stokes phenomenon in multidimensional space.

This paper is organized as follows: In Sec. II, our general formalism is described for the two basic problems, i.e., the connection of wave functions between the classically accessible and inaccessible regions and wave propagation in the classically inaccessible region. Section III presents a global picture and physical interpretation of multidimensional tunneling using several typical examples. On the basis of these qualitative arguments, the next two sections (IV and V) clarify the two quite different types of tunneling. First, Sec. IV discusses the case where pure tunneling mainly contributes to $\Delta E$. A simple, convenient formula is derived under the LSLA approximation and is examined numerically to demonstrate the usefulness of the formula. Second, in Sec. V, a simple model, the shifted parabola potential, is employed to demonstrate the importance of mixed tunneling. Not only are the analytical expressions derived, but a numerical comparison with the exact numerical calculations is also made. Discussions and the conclusion are provided in Sec. VI.

II. THEORY

In this section, a general procedure is formulated for the connection and the propagation of wave functions. We confine ourselves to the case where classical motion is not chaotic. Explicit expressions are given only for the two-dimensional symmetric double well potential (SDWP), but generalization to a general $N$-dimensional case is rather straightforward.

Tunneling energy splitting $\Delta E$ in SDWP can be given by a simple formula derived by Herring as described below. The Hamiltonian is assumed to be $H = -\left(\nabla^2/2\right) + V$, where mass-weighted coordinates are used. Let $\Psi_1$ and $\Psi_2$ be the quasidegenerate eigenfunctions with energies $E_1$ and $E_2$ ($E_1 < E_2$). Inserting the Schrödinger equations into Green's theorem,

$$\int_{\Sigma} d\sigma \cdot (\Psi_2 \nabla \Psi_1 - \Psi_1 \nabla \Psi_2) = \int_{\Sigma} d\sigma \cdot (\Psi_2 \nabla \Psi_1 - \Psi_1 \nabla \Psi_2),$$

we obtain

$$\int \nabla \Psi_1 \cdot \nabla \Psi_2 = \int \nabla \Psi_2 \cdot \nabla \Psi_1.$$
where the surface $\Sigma$ divides the whole space into two equivalent regions and the volume $V$ represents one of them. Let us introduce wave functions localized in either the left or right well by taking the symmetric and antisymmetric linear combinations of $\Psi_1$ and $\Psi_2$:

$$\Psi^L = \frac{1}{\sqrt{2}} (\Psi_1 + \Psi_2) \quad (2.3)$$

$$\Psi^R = \frac{1}{\sqrt{2}} (\Psi_1 - \Psi_2). \quad (2.4)$$

Using Eqs. (2.2)-(2.4), we obtain

$$\Delta E = \frac{h^2}{2} \int_{\Sigma} d\sigma \cdot \left( \Psi^L \nabla \Psi^R - \Psi^R \nabla \Psi^L \right) \quad (2.5)$$

under the assumption that the tail of $\Psi^L$ ($\Psi^R$) in the right (left) well is sufficiently small and therefore the integral in the left-hand side of Eq. (2.2) is $\frac{1}{2}$. As seen from Eq. (2.5), what we need to estimate $\Delta E$ are the values of the wave functions $\Psi^L$ and $\Psi^R$ and their derivatives in the deep tunneling region. Hereafter, we concentrate only on one of the half-spaces separated by $\Sigma$ and accordingly omit the suffixes $L$ and $R$.

A. Semiclassical quantization

Let us start with the semiclassical dynamics in the classically accessible region. Here, we assume that the classical motion is not chaotic and the KAM torus exists according to the Kolmogorov-Arnold-Moser (KAM) theorem $^{36,37}$ (Fig. 1). It is well known that integrable systems can be quantized by the Einstein-Brillouin-Keller (EBK) quantization rule $^{37,38}$ as follows:

$$I_j \equiv \oint_{\mathcal{C}_j} \mathbf{p} \cdot d\mathbf{x} = 2\pi \hbar \left( n_j + \frac{1}{4} \beta_j \right), \quad j = 1, 2, \quad (2.6)$$

where $n_j$ is a quantum number corresponding to the action variable $I_j$, $\mathcal{C}_j$ is an irreducible circle on the KAM torus (see Fig. 1, for example), and $\beta_j$ is the Maslov index to represent the topology of $\mathcal{C}_j$. In particular, $\beta_j$ is equal to $2$ in the case of vibrational motion and $0$ in the case of rotational motion. The quantized eigenvalue is just equal to the Hamiltonian expressed in terms of the $I_j$'s,

$$E_{n_1 n_2} = H(I_1, I_2). \quad (2.7)$$

It is generally believed that the KAM torus can also be quantized by the same procedure. The fact that most of low-lying vibrational states can be assigned to a set of quantum numbers $n = (n_1, n_2, \ldots)$ suggests the existence of the quantized KAM torus for these states.

The semiclassical wave function for the EBK quantized state has been successfully formulated by Maslov and his co-workers. $^{39,40}$ Since the primitive semiclassical wave function diverges at the boundary of the classically accessible region (caustics), their main problem was to avoid this singularity. This is briefly explained here for later convenience by taking an example of two-dimensional nonlinear coupled oscillators. $^{41}$ Figure 2 illustrates a configuration space in which the projection of the KAM torus becomes a distorted rectangular. In the inner region (I) (see Fig. 2) the primitive semiclassical wave function is nonsingular and given by

$$\Psi_n = \sum_{\nu=1}^{4} (\rho_n)^{1/2} \exp \left( \frac{i}{\hbar} W_{\nu} \right), \quad (2.8)$$

where $W_{\nu}(x, y, I)$ and $\rho_n(x, y, I)$ are the solutions of the Hamilton Jacobi (HJ) equation

$$\frac{1}{2} (\nabla W_{\nu})^2 + V(x) = E_n \quad (2.9)$$

and the continuity equation

$$\nabla \cdot (\rho_n \nabla W_{\nu}) = 0. \quad (2.10)$$

Although the action $W$ and, accordingly, the density $\rho$ are single-valued functions on the torus in phase space, they become multivalued after being projected onto configuration space. Subscript $\nu$ ($=1, \ldots, 4$) classifies trajectories according to the sign of the momenta $p_x = \partial W/\partial x$ and $p_y = \partial W/\partial y$. The branches $\nu = 1, 2, 3, 4$ correspond to $p_x = +, -, +, -$ respectively. The HJ equation (2.9) can be solved by the method of characteristics: $^{42}$ the solution $W_{\nu}$ can be evaluated by the integral

$$W_{\nu}(x) = \int^x p_{\nu}(x) \cdot dx$$
from the classical trajectories on the quantized torus. In region (II) of Fig. 2, which contains the caustics of classically accessible region, the wave function (2.8) cannot be utilized because of its divergence on the caustics. There, the wave function in the mixed \((p_x, y)\) representation

\[
\Psi_a(p_x, y) = \sum_{v=1}^{4} \left[ \tilde{p}_v(p_x, y, I) \right]^{1/2} \exp \left( i \int W_v(p_x, y, I) \right)
\]

(7.11)
can be used. The action \(\tilde{W}_v\) and the density \(\tilde{p}_v\) are given by the solutions of the HJ equation and the continuity equation expressed in terms of \(p_v\) and \(y\) This wave function is nonsingular in region (II) and the corresponding wave function \(\Psi_a(x, y)\) in the coordinate representation can be obtained by Fourier transformation. Similarly, in region (III), which contains the caustics in both the \(x\) and \(y\) directions, the variables \((p_x, p_y)\) should be chosen to construct a primitive semiclassical wave function \(\Psi_a(p_x, p_y)\). Finally, the wave functions \(\Psi_a(x, y)\) defined in regions (I)- (III) are matched in each overlapping region to form a global uniform semiclassical wave function. The result of this matching can be summarized as the simple statement that the wave function (2.8) loses its phase by \(\pi/2\) each time when the corresponding classical trajectory touches the caustics. For instance, in the case of the trajectory depicted in Fig. 2 we have a relation \(W_4 = W_1 - \pi \phi/2\). Moreover, we can obtain other trivial relations, \(p_1 = \nabla W_1 = \nabla W_4 = -\nabla W_2 = -\nabla W_3\) at the right caustic curve. Using these relations, we obtain Table I, which gives all the necessary interrelations among the \(W_v\)'s on the caustics. Because of the local separability, the wave function near the caustics can be reduced locally to the form \(43\) in region (II) of Fig. 2, for instance

\[
\Psi_a(x) \propto \text{Ai}(\alpha \xi) \cos[w(\eta)/H]
\]

(2.12)
where \(\text{Ai}\) means the Airy function \(43\) and \((\xi, \eta)\) is the local coordinate system: \(\eta\) is the arclength along the caustics and \(\xi\) is the deviation perpendicular to the caustics. The parameter \(\alpha\) represents the potential gradient in the \(\xi\) direction, weakly dependent on \(\eta\), and \(w(\eta)\) represents the action along the caustics, also weakly dependent on \(\xi\). Finally, near the corner \(\text{HU}\) (called the “hyperbolic umbilic” point in catastrophe theory) the wave function is locally expressed as

\[
\Psi_a(x) \propto \text{Ai}(\alpha \xi) \text{Ai}(\beta \eta)
\]

(2.13)
where the origin of \((\xi, \eta)\) is at the \(\text{HU}\) point. This wave function (2.13) plays a key role in Sec. II B.

**TABLE I. Interrelations among \(W_v\)'s on the caustics.**

<table>
<thead>
<tr>
<th>Caustics</th>
<th>Relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Right</td>
<td>(W_1 = -W_2 + (\pi \phi/2) = -W_3 = W_4 + \pi \phi/2)</td>
</tr>
<tr>
<td>Left</td>
<td>(W_1 = -W_2 - (\pi \phi/2) = -W_3 = W_4 - \pi \phi/2)</td>
</tr>
<tr>
<td>Top</td>
<td>(W_1 = W_2 + (\pi \phi/2) = -W_3 = W_4 + \pi \phi/2)</td>
</tr>
<tr>
<td>Bottom</td>
<td>(W_1 = W_2 - (\pi \phi/2) = -W_3 = W_4 - \pi \phi/2)</td>
</tr>
</tbody>
</table>

**B. Wave function in tunneling region and connection between two regions**

Let us move into the tunneling region near the \(\text{HU}\) point. With use of the asymptotic expansions of the Airy,

\[
\text{Ai}(X) = \begin{cases} 
\frac{1}{2} \pi^{-1/2} X^{-1/4} \exp(-\frac{1}{2} \pi^{3/2}), & X \gg 1, \\
\frac{1}{2} \pi^{-1/2} |X|^{-1/4} \sin(\frac{1}{2} |X|^{3/2} + \pi/4), & X \ll -1,
\end{cases}
\]

(2.14)
the asymptotic behavior of the wave function (2.13) in the region of \(\xi > 0\) and \(\eta < 0\) can be obtained, to exponential accuracy, as

\[
\Psi_a \propto \exp[-\frac{1}{6}(\alpha \xi)^{3/2}] \exp[i \frac{1}{6} \beta \eta^{3/2} + (\pi/4)i] + c.c.
\]

(2.15)
This expression in comparison with Eq. (2.8) indicates that the action \(W\) is complex,

\[
W_{\pm}(x) = \pm W_R(\eta) + i W_I(\xi),
\]

(2.16)
where the subscript \(\pm\) specifies the branch mentioned before. In the first quadrant \(\xi, \eta > 0\), on the other hand, the wave function (2.13) becomes

\[
\Psi_a(x) \propto \exp[-\frac{1}{6}(\alpha \xi)^{3/2} - \frac{1}{3}(\beta \eta)^{3/2}],
\]

(2.17)
which indicates that the action is pure imaginary,

\[
W(x) = i W_I(\xi, \eta).
\]

(2.18)
Thus, as was suggested by Wilkinson,\(^{33}\) there are three distinct regions around the \(\text{HU}\) point: The \(R\) region (classically accessible region), the \(C\) region, and the \(I\) region, where action is real, complex, and pure imaginary, respectively (cf. Fig. 2). Note that the four branches in the \(R\) region connect to two branches in the \(C\) region and the latter connect to one branch in the \(I\) region. Accordingly, the wave function of the excited state can have nodal lines in the \(C\) region, but not in the \(I\) region. The boundaries between the \(C\) and \(I\) regions form caustics in the classically inaccessible region.

Let us first consider the connection from the \(R\) region to the \(C\) region and wave propagation in the latter. The basic equation for the action is still the HJ equation (2.9). If we insert Eq. (2.16) into Eq. (2.9), we obtain

\[
(\nabla W_R)^2 - (\nabla W_I)^2 = 2[E_a - V(x)] = F(x)
\]

(2.19)
and

\[
\nabla W_R \cdot \nabla W_I = 0.
\]

(2.20)
These equations are first-order nonlinear coupled partial differential equations. The conventional classical trajectory technique cannot be used to solve these equations. The Huygens-type wave propagation devised by Huang et al.,\(^{12}\) however, can be applied to this problem. Its essential idea is to propagate the \(W_I\) equisurface step by step (see Fig. 3; the equisurface in the two-dimensional case is just a curve). For convenience, we use the following notation:
FIG. 3. \(j\)th and \((j+1)\)st \(W_I\) equisurfaces in the Huygens-type wave propagation.

\[
\rho_R = \left| \nabla W_R \right|, \quad \rho_I = \left| \nabla W_I \right|, \quad \epsilon_R = \nabla W_R / \left| \nabla W_R \right|, \quad \epsilon_I = \nabla W_I / \left| \nabla W_I \right|,
\]

and

\[
\epsilon_j = \nabla W_j / \left| \nabla W_j \right|.
\]

Then the HJ equations (2.19) and (2.20) reduce to

\[
(2.19') \quad \rho_R^2 \cdot \rho_I^2 = F(x)
\]

and

\[
(2.20') \quad \epsilon_R \cdot \epsilon_I = 0.
\]

Assuming that \(\rho_R, \rho_I, \epsilon_R, \) and \(\epsilon_I\) are known on the \(W_I\) equisurface in the \(j\)th step, we can construct the next \((j+1)\)st equisurface by the equation

\[
x_{j+1} = x_j + (\Delta W_I / \rho_I^{(j+1)}) \epsilon_I^{(j+1)},
\]

where \(x_{j+1}\) and \(x_j\) designate positions of the \((j+1)\)st and \(j\)th equisurface, and \(\Delta W_I\) is an increment of \(W_I\) by that step. The unit vectors \(\epsilon_I^{(j+1)}\) and \(\epsilon_I^{(j+1)}\) on the new surface can be estimated from the data on \(x_{j+1}\). To obtain \(\rho_I^{(j+1)}\) on the new surface, we now need to estimate \(\Delta \rho_I / \Delta \xi\), which gives the directional derivative in the \(\epsilon_I\) direction in the limit \(\Delta \xi \to 0\). The difference of \(\rho_R\) at positions A and B (see Fig. 3) is given by

\[
\Delta \rho_R = \frac{\Delta W_R}{\Delta \eta} = \frac{\Delta W_R}{\Delta \eta} \frac{\Delta \rho_I}{\Delta \eta} = - \frac{\Delta \rho_R}{\Delta \eta} \rho_I \kappa + O(\Delta \xi^2).
\]

In the limit \(\Delta \xi \to 0\), this leads to

\[
\frac{\partial \rho_R}{\partial \xi} = - \rho_R \kappa,
\]

where \(\kappa = \partial \theta / \partial \eta\) is the curvature of the \(W_I\) equisurface, which is assumed to be positive when the \(W_I\) equisurface is convex. Using this equation and the directional derivative of Eq. (2.19'), we obtain

\[
\frac{\partial \rho_I}{\partial \xi} = \frac{\rho_R}{\rho_I} \kappa - \frac{1}{2} \frac{\partial F(x)}{\partial \xi},
\]

which finally gives the increment of \(\rho_I\) to lowest order as

\[
\rho_I^{(j+1)} = \rho_I^{(j)} + \frac{\partial \rho_I}{\partial \xi} \left( \Delta W_I / \rho_I \right).
\]
According to Table I, the wave function near the right caustics in the R region can be expressed as

$$
\Psi_n(\xi, \eta) = 4c \frac{1}{\sqrt{p_x p_\eta}} \cos \left( \frac{W_R(0, \eta)}{\hbar} - \frac{\pi}{4} \right) \times \cos \left( \frac{1}{\hbar} \int_\xi^0 |p_x| d\xi' \frac{\pi}{4} \right).
$$

(2.37)

Applying the one-dimensional connection formula in the $\xi$ direction, we obtain the wave function in the C region as

$$
\Psi_n(\xi, \eta) = \frac{2c}{\sqrt{p_x p_\eta}} \cos \frac{W_R(\eta)}{\hbar} \exp \left( -\frac{1}{\hbar} W_I(\xi) \right)
$$

$$
= \frac{c}{\sqrt{p_x p_\eta}} \left( \exp \frac{i}{\hbar} \left[ W_R(\eta) + iW_I(\xi) \right] + \exp \frac{i}{\hbar} \left[ -W_R(\eta) + iW_I(\xi) \right] \right).
$$

(2.38)

where

$$
W_R(\eta) = W_I(0, \eta) - \pi \eta / 4,
$$

(2.39)

$$
W_I(\xi) = \int_0^\xi d\xi' \sqrt{2[V(\xi', \eta) - V(0, \eta)]},
$$

(2.40)

$p_R = p_\eta$, and $p_I = \partial W_I / \partial \xi$. It should be noted that, under the separable approximation, Eq. (2.40) does not depend on $\eta$. This connection can provide the initial $W_I$ equisurface to start the Huygens-type wave propagation in the C region.

The connection between the C and I regions is essentially the same as above. The wave function near the boundary in the C region again has the form of Eq. (2.38) with $\xi$ and $\eta$ slightly modified: $\xi$ represents the arclength along the boundary (measured from the HU point), while $\eta$ is a perpendicular deviation from the boundary. Obviously, Eqs. (2.39) and (2.40) cannot be used, and $W_R$ and $W_I$ should be obtained by the Huygens wave propagation.

With use of the connection formula at the boundary between the C and I regions we can write the wave function near the boundary in the I region as

$$
\Psi_n(\xi, \eta) = \frac{c'}{\sqrt{p_x p_\eta}} \exp \left( -\frac{1}{\hbar} [W_I(\eta) + W_I(\xi)] \right)
$$

$$
= \frac{c'}{\sqrt{p_x p_\eta}} \exp \left( -\frac{1}{\hbar} W_I(\eta) \right).
$$

(2.41)

where

$$
W_I(\xi) = W_I(\xi),
$$

(2.42)

$$
W_I(\eta) = \int_0^\eta d\eta' \sqrt{2[V(\xi, \eta') - V(\xi, 0)]},
$$

(2.43)

$$
p_\eta = \frac{\partial W_I}{\partial \eta},
$$

(2.44)

and $p_x = p_I$. Equation (2.44) determines the initial condition of classical trajectory in the I region; since $p_\eta = 0$ on the boundary, the trajectory leaves tangentially to the boundary.

III. GLOBAL PICTURE AND PHYSICAL INTERPRETATION

In this section, three typical models are discussed in order to elucidate the physical picture of multidimensional tunneling. In particular, some qualitatively new aspects are clarified.

A. Case of symmetric mode coupling

First, let us consider the Hamiltonian,

$$
\hat{H}_{SMC} = 3^2 + V_{SMC}
$$

$$
= -\frac{g^2}{2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{8} (x-1)^2 (x+1)^2
$$

$$
+ \frac{\omega_y^2}{2} \left( y + \frac{\gamma}{\omega_y} (x^2 - 1) \right)^2,
$$

(3.1)

where all quantities are scaled to be dimensionless; $g$, $\omega_y$, and $\gamma$ play the role of the Planck constant $\hbar$, relative frequency in the $y$ direction, and coupling strength, respectively. Potential contour is depicted in Fig. 4 for $(\omega_y, \gamma) = (0.5, 0.25)$. This potential $V_{SMC}(x, y)$ has been widely used, $^{24,28}$ especially as a model of proton tunneling. One of the most typical examples is that of malonaldehyde [Eq. (1.3)], in which the coordinate $x$ mainly represents the motion of the hydrogen atom transferring from O to O, while $y$ roughly represents the scissors-like motion of the O-C-C-C-O frame. Since the mutual approach of two oxygen atoms makes it easier for the hydrogen to hop, the saddle point $(0, \gamma/\omega_y)$ of $V_{SMC}$ is shifted to positive $y$. In fact, Bosch et al. $^{28}$ fitted this potential function to the data.
obtained by ab initio calculations for malonaldehyde. The parameters determined by them are, in terms of our notation, \((\omega_0, \gamma, g) = (0.48, 0.39, 0.10)\). In general, when the \(\alpha_1\) symmetric mode (as a nonrigid molecule\(^{25}\)) couples to the tunneling coordinate to assist the hydrogen tunneling, Eq. (3.1) may be the simplest model among those that keep the symmetry of the system.

Figure 5 shows a numerical example of the Huygens type wave propagation in the C region around the potential well in the left half of \(V_{SMC}\) in Fig. 4. Parameters \((\omega, \gamma, g)\) are chosen to be \((0.8, 0.16, 0.04)\). Unfortunately, this numerical wave propagation in the C region is not very easy and requires more experience. This is because the caustics in the classically inaccessible region must be determined self-consistently by the wave propagation in the C region itself. That is to say, the problem of solving Eqs. (2.19) and (2.20) is a sort of initial value problem with free boundary.\(^{45}\) The following self-consistent procedure has been used here to get the converged result: First, the boundaries are assumed and the wave is propagated with the fixed boundaries. Then new boundaries are determined so that they satisfy the condition [see Eq. (2.32)]

\[
\frac{\partial W_R}{\partial \eta} = 0,
\]

and the same procedure is repeated until the converged result is attained. A more detailed explanation of the numerical method will be given elsewhere.

More importantly, we can obtain a global picture of multidimensional tunneling without doing any more accurate calculations as explained below. The most typical picture of tunneling is depicted in Fig. 6(a), which is a case of the values of the coupling strength \(\gamma\) and the frequency \(\omega_0\) being so modest that the main contribution comes from the I region. Using Herring's formula [Eq. (2.5)], we have an expression for the energy splitting,

\[
\Delta E = g \int_{\Sigma} dy \left( p_L^2 - p_R^2 \right) \left( \rho_L^{1/2} \rho_R^{1/2} \right) \times \exp \left[ -\frac{1}{g} \left[ W_L^f(x) + W_R^f(x) \right] \right],
\]

up to semiclassical accuracy. The stationary phase approximation to the surface integration leads to

FIG. 5. Huygens-type wave propagation around the potential well in the left half of \(V_{SMC}\) (numerical results). Parameters are chosen to be \((\omega_0, \gamma, g) = (0.8, 0.16, 0.04)\) and the interval of the equisurfaces is \(0.002\).
This means that the two [left (L) and right (R)] classical trajectories smoothly connect with each other [solid curve in Fig. 6(a)]. Namely, the tunneling path is defined as the path starting tangentially from the left caustics and arriving again tangentially at the right caustics.

The intuitive picture of the above tunneling is as follows: Starting from the R region, tunneling first proceeds in the C1 region [see Fig. 6(a)] for a while. In principle, at any point on the edge of this C1 region, the tunneling trajectory can enter into the I region. Because of condition (3.4), however, only the trajectory taking off from the C1 region at a certain position \( x_0 \) [see Fig. 6(a)] contributes to \( \Delta E \). In the C1 region the motion in the \( \eta \) direction is non-classical, while the motion in the \( \xi \) direction is still classical. Therefore we call tunneling through the C region "mixed tunneling." On the other hand, in the I region no classical motion exists in any direction and the tunneling there is called "pure tunneling." It should be noted that the work of BBW is concerned only with the latter case. Existence of mixed tunneling is one of the most remarkable characteristics of multidimensional tunneling.

If the coupling strength \( \gamma \) becomes small, the global picture of tunneling changes quite drastically to one like in Fig. 6(b). In this case, tunneling proceeds mainly through the C2 region and tunneling path cannot be defined any more. Naturally, the present theory becomes essentially different from that of BBW. In the limit of small \( \gamma \), the potential \( V_{\text{SMC}} \) becomes separable and tunneling proceeds most widely in the C region. Interestingly, this separable case exemplifies the new characteristics of multidimensional tunneling, i.e., the broad mixed tunneling in the C region. It is shown in the Appendix that the present theory can give a consistent result with that obtained from one-dimensional WKB theory in the separable regime.

Finally, Fig. 6(c) shows schematically the case of large \( \omega_y \), in which tunneling mainly goes through the C1 region with a small final journey in the I region. For the calculation of the energy splitting, the boundary between the C1 and I regions plays the essential role.

### B. Case of antisymmetric mode coupling

As a second example, let us consider

\[
\hat{H}_{\text{ASMC}} = \hat{T} + V_{\text{ASMC}}
\]

\[
= -\frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{8} (x-1)^2(x+1)^2
\]

\[
+ \frac{\omega_x^2 (y - \gamma \omega_y x)^2}{2},
\]

where \( \hbar, \omega_x, \) and \( \gamma \) have the same meanings as in Eq. (3.1). A potential contour map is given in Fig. 7 for the parameters \((\omega_x, \gamma) = (0.2, 0.02)\). This model has also been used widely, especially in the study of proton tunneling. For instance, in the case of malonaldehyde, the coordinate \( x \) again represents the motion of transferring hydrogen, while \( y \) may represent the C-O stretching mode.

Here, the pictures are quite similar to the different cases in the previous model: In the case of modest \( \omega_y \) and \( \gamma \), tunneling mainly goes through the I region and the tunneling path can be defined uniquely. If the coupling strength \( \gamma \) becomes small, two C regions tend to overlap with each other on the symmetry surface and mixed tunneling in the C region plays an essential role (see Fig. 8). It should be noted that in the present model the C regions overlap only partly with each other, being different from Fig. 6(b). Therefore, it can be expected that the energy splitting in the vibrationally excited state becomes small or even close to zero because of the out-of-phase matching of the nodes of the vibrational wave functions.

![FIG. 7. Contours of the antisymmetric mode coupling (ASMC) potential [Eq. (3.5)] for the parameters \((\omega_x, \gamma) = (0.2, 0.02)\). The other conditions are the same as in Fig. 4.](image)

![FIG. 8. Schematic picture of tunneling in the case of antisymmetric mode coupling with small coupling, in which the C_2 region plays a key role.](image)
C. Squeezed double well

Our final example is

\[ \hat{H}_{\text{SQZ}} = \hat{T} + V_{\text{SQZ}} \]

\[ = -\frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{8} (x-1)^2(x+1)^2 \]

\[ + \frac{1}{2} [\omega^2 + \gamma(x^2 - 1)^2]y^2, \]

(3.6)

where again the dimensionless parameters \( \omega, \gamma \), and \( \gamma \) play the same roles as in the preceding two models. Figure 9 is the potential contour map for \((\omega, \gamma) = (1.5, 5)\). The local frequency \( \omega(x) \) along the \( y \) axis, defined as \( \omega_x(x) = \omega^2 + \gamma(x^2 - 1)^2 \), increases as \( x \) approaches zero. This potential is a good example to emphasize the role of the first term of Eq. (2.28).

For this purpose it may be helpful to discuss the effect of potential squeezing using the adiabatic viewpoint of Auerbach and Kivelson. Suppose \( \omega \) to be large enough so that the tunneling motion along \( x \) can be described by the renormalized one-dimensional potential

\[ V_{\text{ren}}(x) = V_{\text{SQZ}}(x,0) + g\omega_x(x)(n_x + \frac{1}{2}), \]

(3.7)

where \( n_x \) is a vibrational quantum number in the \( y \) direction. The potential \( V_{\text{ren}} \) is depicted in Fig. 10 by dashed lines. If we use the one-dimensional WKB theory, \( \Delta E_0 \) is obtained as

\[ \Delta E_0 = \frac{g}{\pi} \exp \left( -\frac{1}{g} \int_{x_-}^{x_+} dx \sqrt{2[V_{\text{ren}}(x) - E]} \right), \]

(3.8)

where the \( x_{\pm} \) are the solutions of \( V_{\text{ren}}(x) - E = 0 \). It should be noted that the effect of potential squeezing is found in the exponent. On the other hand, if we use directly the imaginary-time Green's function for this multidimensional problem, the squeezing effect appears only in the preexponential factor. This overestimates the tunneling amplitude and is inappropriate.

Returning back to the present theory, on the other hand, let us discuss the role of \( \kappa \) in Eq. (2.28). When the \( \mathcal{W}_x \) equisurface is concave, as drawn in Fig. 11(a), \( \kappa \) in Eq. (2.28) is negative by definition and, thus, it makes \( \partial \rho \partial \xi \) larger. As a result \( \mathcal{W}_x \) increases. If the \( \mathcal{W}_y \) equisurface is convex, as drawn in Fig. 11(b), then \( \mathcal{W}_y \) decreases. Thus, this kind of nonlocal effect is incorporated in the exponent, as desired.

In the case of a squeezed potential (3.6) with large \( \omega \), the \( \mathcal{W}_x \) equisurfaces in the \( C \) region are expected to become like Fig. 12. This can be explained as follows. Since the boundary between the \( C \) and \( I \) regions is, by definition, a

---

FIG. 9. Contours of the squeezed potential [Eq. (3.6)] for the parameters \((\omega, \gamma) = (1.5, 5)\). The other conditions are the same as in Fig. 4.

FIG. 10. Renormalized one-dimensional potential curve \( V_{\text{ren}}(x) \) [Eq. (3.7)]. Dashed lines represent \( V_{\text{ren}}(x) \), while the solid line is the bare potential \( V_{\text{SQZ}}(x,0) \).

FIG. 11. \( \mathcal{W}_x \) equisurfaces [(a) concave and (b) convex] and wave propagation. Arrows represent the direction of wave propagation.
FIG. 12. Schematic picture of tunneling in the case of squeezed potential with large $\omega_x$. Curvature of $W_i$ equisurfaces plays an important role.

$W_R$ equisurface, we have $W_R(P) - W_R(Q) = W_R(P') - W_R(Q')$ (see Fig. 12). If we note that $W_y(x)$ increases as $x$ approaches zero, we can easily say that the arclength $P'Q'$ is shorter than that of PQ. Preliminary numerical calculations support this conjecture. Considering this fact together with the above discussions about the role of $K$, we can conclude that the potential squeezing makes $W_I$ larger, as desired. In this way the present theory can explain the squeezing effect, also.

IV. LOCALLY SEPARABLE LINEAR APPROXIMATION (LSLA)

In this section, we confine ourselves to the case in which tunneling occurs mainly through the I region as in the case of Fig. 6(a). This enables us to introduce an approximation called the LSLA in which the potential is assumed to be separable in between the HU point and the taking-off point $x_0$; thus, the extended caustics are straight lines (see Fig. 13). Moreover, we also assume that the potential is linear near the HU point and $x_0$. These simplifications enable us to connect the wave function directly from the R region to the I region without explicitly passing through the C region. As seen from Eq. (2.13), the wave function around the HU point can be written as

$$\Psi_a(x) = 4c a_i(\xi) a_i(\eta),$$

where the normalized Airy function $a_i(x)$ is defined by

$$a_i(x) = \pi^{1/2} (2\beta x)^{-1/6} \text{Ai}[(2\beta x^2)^{1/3}],$$

where $\beta$ represents the potential gradient at turning point $x=0$. Using the one-dimensional WKB theory, we can show that near $x_0$ in the I region, Eq. (4.1) becomes

$$\Psi_a(x) = \frac{c}{\sqrt{\rho_x \rho_\eta}} \exp\left[ -\frac{1}{\beta} \left( \int_0^x p_x d\xi + \int_0^{x_0} p_\eta d\eta \right) \right].$$

On the other hand, from Eq. (2.35) we can express the corresponding wave function deep inside the I region as

$$\Psi_a(x) = a[-(1/\beta) W_I(x_0 \to x)],$$

where $W_I(x_0 \to x)$ is the imaginary action along the classical trajectory from $x_0$ to $x$, and

$$\bar{J} \equiv \frac{\partial x_0}{\partial (p^0_{\eta \eta})} f^0_{\eta}. \tag{4.5}$$

Here the caustic line from which the classical trajectory takes off is taken to be the $\eta$ axis, $f^0_{\eta}$ is the potential gradient in the $\eta$ direction at $x_0$, and $w_0$ in the Jacobian (2.36) is chosen to be the initial momentum $p^0_{\eta}$. In the overlap region where Eqs. (4.3) and (4.4) hold, we can derive the relation

$$\bar{J} = \left( \frac{\partial \xi}{\partial \eta} \frac{\partial \eta}{\partial \xi} \right) f^0_{\eta} = p_{\xi} p_{\eta}, \tag{4.6}$$

and accordingly

$$a = c \exp\left[ -(1/\beta) W_I(HU \to x_0) \right], \tag{4.7}$$

where $W_I(HU \to x_0)$ means the action from the HU point to $x_0$ along the caustic line. Inserting Eq. (4.7) into Eq. (4.4), we obtain the wave function deep inside the I region as

$$\Psi_a(x) = c[-(1/\beta) W_I(HU \to x_0 \to x)], \tag{4.8}$$

where $W_I(HU \to x_0 \to x)$ is a sum of $W_I(HU \to x_0)$ and $W_I(x_0 \to x)$.

Let us consider an energy splitting in the SDWP like the one shown in Fig. 13, where the symmetry line is chosen to be the $y$ axis. As denoted in Eq. (3.4), the wave function on the symmetry line $x=0$ should satisfy

$$\frac{1}{\Psi^L_n} \frac{\partial \Psi^L_n}{\partial y}(x,y) \big|_{x=0} = -\frac{1}{\Psi^R_n} \frac{\partial \Psi^R_n}{\partial x}(x,y) \big|_{x=0}. \tag{4.9}$$

Thus, Herring’s formula (2.5) [see, also, Eq. (3.3)] can be reduced to

$$\Delta E = 2\hbar \int_{x=0} dy \rho_Y \Psi^L_n(0,y) \Psi^R_n(0,y). \tag{4.10}$$
TABLE II. Energy splittings in the case of the symmetric mode coupling Hamiltonian (3.1). Parameter $g$ is set to 0.04 except for the final column, where $g$ is taken to be 0.08. Figures in parentheses are the power of 10 by which the entry is to be multiplied.

<table>
<thead>
<tr>
<th>Energy splittings</th>
<th>$(\omega_{p,1,0})$</th>
<th>$(\omega_{p,0,2})$</th>
<th>$(\omega_{p,0,3})$</th>
<th>$(\omega_{p,0,16})$</th>
<th>$(\omega_{p,1,125})$</th>
<th>$(\omega_{p,2,125})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{0M}$</td>
<td>5.73(-9)</td>
<td>1.66(-8)</td>
<td>4.55(-9)</td>
<td>1.49(-8)</td>
<td>2.15(-8)</td>
<td>1.75(-8)</td>
</tr>
<tr>
<td>$\Delta E_{SLA}$</td>
<td>5.8(-9)</td>
<td>1.5(-8)</td>
<td>6.8(-9)</td>
<td>1.6(-8)</td>
<td>2.1(-8)</td>
<td>2.9(-8)</td>
</tr>
<tr>
<td>$\Delta E_{act}$</td>
<td>6.4(-9)</td>
<td>1.9(-8)</td>
<td>5.2(-9)</td>
<td>1.7(-8)</td>
<td>2.5(-8)</td>
<td>2.0(-8)</td>
</tr>
<tr>
<td>$\Delta E_{ARC}$</td>
<td>0.015(-9)</td>
<td>0.065(-8)</td>
<td>0.021(-9)</td>
<td>0.12(-8)</td>
<td>0.50(-8)</td>
<td>0.19(-8)</td>
</tr>
<tr>
<td>$\Delta E_{Height}$</td>
<td>0.016(-9)</td>
<td>0.29(-8)</td>
<td>4.7(-15)</td>
<td>0.016(-8)</td>
<td>0.61(-8)</td>
<td>2.0(-14)</td>
</tr>
</tbody>
</table>

*Distance between $HU^L$ and $x_5^L$.

Inserting Eq. (4.8) into Eq. (4.10) and using the stationary phase approximation, we can finally obtain

$$\Delta E = (2\hbar)^{3/2} 2^{3/2} c_L c_R \Delta \times \exp\left[-\left(1/\hbar\right) W_f(HU^L \rightarrow HU^R)\right], \quad (4.11)$$

where $W_f(HU^L \rightarrow HU^R)$ represents the Gamow factor, which is calculated first along the caustic line from $HU^L$ to $x_5^L$, then along the classical trajectory from $x_5^L$ to $x_5^R$, and finally along the caustic line from $x_5^R$ to $HU^R$. The factor $\Delta$ is defined by

$$\Delta = \left| \frac{\partial^2 (W_I + W_R)}{\partial y^2} \right|^{-1/2} \left( x_5 = (0,0) \right), \quad (4.12)$$

where $(0,0)$ represents the position at which the stationary phase condition (3.4) is satisfied. It should be noted that these formulas [(4.11) and (4.12)] hold also for the antisymmetric mode-coupling Hamiltonian (3.5), too, in that the tunneling proceeds mainly through the I region.

The above results can be easily generalized to an $N$-dimensional problem. Actually, if we denote the wave function around the corner of classically accessible region as

$$\Psi_0(x) = 2^N c a_i(x) \prod_{j=1}^{N-1} a_i(\eta_j), \quad (4.13)$$

the energy splitting is given by

$$\Delta E = 2\hbar (2\pi \hbar)^{(N-1)/2} c_L c_R \Delta \times \exp\left[-\left(1/\hbar\right) W_f(HU^L \rightarrow HU^R)\right], \quad (4.14)$$

where

$$\Delta = \left| \frac{\partial^2 (W_I + W_R)}{\partial y^2} \right|^{-1/2} \left( x_5 = (0,0) \right), \quad (4.15)$$

and

$$\tilde{J}^L \equiv \frac{\partial^2 \tilde{x}_{ij}^L (p_{\eta^L}, y)}{\partial (p_{\eta^L})^2} \prod_{j=1}^{N-1} \int_{\eta_j}^{\eta_j^L}, \quad (4.16)$$

Here $y = (y_1, y_2, ..., y_{N-1})$ and $\eta = (\eta_1, \eta_2, ..., \eta_{N-1})$ define the symmetry plane and the caustic plane from which the classical trajectory takes off, respectively. In particular, if $N$ is equal to unity, we can reduce the above equation to the well-known formula

$$\Delta E = \frac{\hbar^2}{\pi} \exp\left[-\frac{1}{\hbar} \int_{x_-}^{x_+} |p| dx\right], \quad (4.17)$$

where the $x_\pm$ represent the classical turning points.

The numerical algorithm we have employed is quite simple. First, the EBK quantized torus is constructed by the adiabatic switching method. The caustic curve is extended into tunneling region by a straight line, and then the classical path that satisfies the boundary conditions is searched. Equation (4.12) is employed to calculate $\Delta$, in which derivatives are replaced by finite differences. As for the normalization factor $c$ in Eq. (4.1), we simply estimated that by comparing Eq. (4.1) with an approximate numerical quantum mechanical result at the $HU^L$ point. The latter is calculated by diagonalizing the $10 \times 10$ Hamiltonian matrix with the harmonic oscillator basis set. The determination of $c$ can also be made by using the semiclassical function. To compare the present result with the quantum mechanically exact one, we also diagonalized a $70 \times 70$ Hamiltonian matrix by the discrete variable representation (DVR) method.

Table II lists the numerical results of energy splitting for the symmetric mode-coupling model [Eq. (3.1)]. To examine the LSLA approximation itself, the parameter $g$ should be chosen as small as possible. The value 0.04 used here (except for the final column) is slightly smaller than the value 0.1 appropriate for the model of malonaldehyde. More realistic model calculations will be reported elsewhere. It can easily be seen from this table that the LSLA works better as the taking-off point $x_5^L$ comes closer to the $HU^L$ point. This is quite reasonable, because the separable approximation should be better when $x_5^L$ is close to the $HU^L$ point. Furthermore, the LSLA works reasonably well even when $x_5^L$ is quite far from $HU^L$. It is thus expected that the general WKB theory presented in Sec. II could give satisfactory results even when $x_5^L$ is far from $HU^L$.

For comparison, we have also calculated $\Delta E$ by the instanton theory, this result is also shown in Table II. As seen from this table, the instanton theory gives a good estimate. Thus, the following natural question arises:
Which is more accurate, the present WKB theory or the instanton theory? This seems to be a subtle question. When \( x_0 \) is close to the HU point, however, the LSLA works better than the instanton theory, because a straight line is a good approximation to the caustic curve near the HU point. When \( x_0 \) is far away from the HU point, the instanton theory is slightly better than the LSLA. The more general WKB theory described in Sec. II should be employed there to improve the LSLA. Second, as was reported by Hontscha, Honggi, and Pollak\(^4^9\) for the one-dimensional case, the WKB theory is expected to work better than the instanton theory as the parameter \( g \) increases. The last column of Table II, where \( g \) is taken to be 0.08, shows this tendency. In any case, more exhaustive comparison should be made in a wide range of parameters.

Finally, and more importantly, the present WKB theory can be applied directly to the case of vibrationally excited states; while the instanton theory is applicable only to the ground states. Table II includes also \( \Delta E \) estimated from the one-dimensional formula along the IRC and along the straight line path shown in Fig. 13. Both give values that are too small.

V. MIXED TUNNELING—SHIFTED PARABOLA POTENTIAL

Using a simple model, this section demonstrates the peculiarities of the mixed tunneling. As is clarified in Sec. III [cf. Figs. 6(b) and 8], when the coupling becomes weak, a drastic change occurs and tunneling proceeds mainly through the C region. To study this case more deeply, let us consider the following simple potential (shifted parabola):

\[
\hat{H}_{\text{SP}} = \hat{f} + V_{\text{SP}}(x,y),
\]

with

\[
V_{\text{SP}}(x,y) = \begin{cases} 
\frac{1}{2}(x+1)^2 + \frac{1}{2}y_0^2(y+y_0)^2, & \text{for } x < 0, \\
\frac{1}{2}(x-1)^2 + \frac{1}{2}y_0^2(y-y_0)^2, & \text{for } x > 0,
\end{cases}
\]

where \( g \) and \( \omega_p \) are the same as those of Eq. (3.1) and \( y_0 \) represents the distance between the two parabolas in the \( y \) direction. Obviously, this model can be viewed as a simplification of the case of antisymmetric mode coupling [Eq. (3.5)]. We employ this potential in spite of its discontinuity at \( x=0 \), since the problem can be treated analytically and, thus, the peculiarities of mixed tunneling can be grasped easily. These qualitative characteristics of mixed tunneling are not affected by this discontinuity, as demonstrated at the end of this section. As seen from Fig. 15, the sign of the factor \( \alpha^2 = y_0^2 - g/\omega_p \) classifies the tunneling in the ground state basically into two cases: pure tunneling (\( \alpha^2 > 0 \)) and mixed tunneling (\( \alpha^2 < 0 \)).

Since this potential is separable on each side (\( x > 0 \) and \( x < 0 \)) and the present WKB theory gives the same results as those obtained from one-dimensional theory (see the Appendix), it is straightforward to obtain the energy splitting formula. On the symmetry surface (\( x = 0 \)), the wave function localized on the left side is given as

\[
\Psi_0^L(0,y) = \phi_1^L(0)\phi_2^L(y),
\]

where \( \phi_1^L(x) \) and \( \phi_2^L(y) \) are the wave functions in \( x \) and \( y \) coordinates, respectively. This leads to the following explicit expression for the ground state energy splitting:

\[
\Delta E_0 = c_1 \Delta,
\]
results when $a^*$ is close to zero, as expected. It is found that formula (5.6) works well. Formula (5.8) gives reasonable calculated in the same way as in the case of the symmetric quantum mechanical results. The latter results have been calculated by the present methods together with the exact semiclassically excited states in the case of the shifted parabola model (5.1). Parameter $g$ is set to 0.07.

Table III shows the ground state energy splittings calculated quantum mechanically (WKB results are essentially the same), both in the case where tunneling mainly passes through the I region and in the case of tunneling through the C region. Table IV shows the results for vibrational excitation in the $y$ direction. Vibrational excitation in the $x$ direction does not give any particularly new effect and obviously makes tunneling more probable. Note that, although the tunneling in the I region (see the left column in Table IV) is always promoted by the vibrational excitation, the tunneling in the C region (right column in Table IV) is either promoted or suppressed by the excitation. This is because the wave functions in the C region have nodal lines (parallel to the $x$ axis) and, thus, the overlap integration in Eq. (5.5) can become very small because of phase cancellation. This is another manifestation of qualitative differences between the two types of tunneling. It should be noted that this kind of cancellation does not occur in the case of $V_{SMC}$ [Fig. 6(b)]. Symmetry of the mode coupling plays a key role in this sense.

Before closing this section, it may be appropriate to demonstrate that the discontinuity of the model potential [Eq. (5.1)] at $x=0$ does not affect the above-mentioned characteristics of multidimensional tunneling. To do so, we made a quantum mechanical numerical calculation of the energy splitting for the case of antisymmetric mode coupling [Eq. (3.5)]. The numerical results are shown in Table IV.

### Table III. Energy splittings in the case of the shifted parabola model (5.1). Parameter $g$ is set to 0.07.

<table>
<thead>
<tr>
<th>Energy splittings</th>
<th>$(a^<em>,b^</em>)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{QM}$</td>
<td>$(0.3,0.2)$</td>
</tr>
<tr>
<td>$\Delta E_{WKB}$</td>
<td>1.58(-7)</td>
</tr>
<tr>
<td>$\Delta E_{Eq}$</td>
<td>1.45(-7)</td>
</tr>
<tr>
<td>$\Delta E_{QO}$</td>
<td>...</td>
</tr>
<tr>
<td>$\Delta E_{C}$</td>
<td>...</td>
</tr>
</tbody>
</table>

where

$$\epsilon_i = (2\sqrt{g/\pi})e^{-i\alpha - b/x}$$

and

$$\Delta = \int dy \phi_x^2(y)\phi_y^2(y)$$

represent the energy splitting for the $x$ direction and the overlap factor in the $y$ direction, respectively.

Let us consider the overlap $\Delta$ for the following three cases. First, when $\alpha^2 > 0$, tunneling proceeds mainly through the I region and, thus, the integral in Eq. (5.5) can be performed by the stationary phase approximation. After simple manipulations, we obtain the explicit expression for $\Delta$ as

$$\Delta = \left[ \frac{\omega_x}{2 \pi g D} \frac{1}{\alpha} \frac{1}{\alpha + g \omega_x} \right]$$

where

$$D = \frac{g \omega_x}{\alpha^2} \left[ \frac{2 \phi_0^2 - 3 g \omega_x}{\alpha^2} \right]$$

The tunneling path can be drawn explicitly and is the same as that of Benderskii, Goldanskii, and Makarov.30 Second, if $\alpha^2$ is close to zero, the boundary between the C and I regions plays an essential role and, thus, both wave functions $\phi_x^2(y)$ and $\phi_y^2(y)$ may be approximated by the Airy function. Integrating directly the product of the two Airy functions, we can write down the expression for $\Delta$ as

$$\Delta = \left[ 1 - 2(1 - \sqrt{g} \omega_x) \right]$$

Finally, in the case of negative $\alpha^2$, unfortunately, we cannot obtain any simple analytical formula and we have to perform numerical integration. For simplicity, we have used the Airy function near the caustics and primitive semiclassical wave function elsewhere. The Airy function is used only when its argument is smaller than unity.

Table III shows the ground state energy splittings calculated by the present methods together with the exact quantum mechanical results. The latter results have been calculated in the same way as in the case of the symmetric mode-coupling model. The WKB results calculated numerically agree with the quantum mechanical ones within 10%. When tunneling goes mainly through the I region, formula (5.8) works well. Formula (5.8) gives reasonable results when $\alpha^2$ is close to zero, as expected. It is found that, in the case where the I region plays an essential role, $\Delta E_{QO}$ depends more strongly on $\omega_y$ than in the case where tunneling proceeds mainly through the C region. This is one of the manifestations of qualitative differences between pure tunneling and mixed tunneling.

Tunneling energy splittings for vibrationally excited states are calculated quantum mechanically (WKB results are essentially the same), both in the case where tunneling mainly passes through the I region and in the case of tunneling through the C region. Table IV shows the results for vibrational excitation in the $y$ direction. Vibrational excitation in the $x$ direction does not give any particularly new effect and obviously makes tunneling more probable. Note that, although the tunneling in the I region (see the left column in Table IV) is always promoted by the vibrational excitation, the tunneling in the C region (right column in Table IV) is either promoted or suppressed by the excitation. This is because the wave functions in the C region have nodal lines (parallel to the $x$ axis) and, thus, the overlap integration in Eq. (5.5) can become very small because of phase cancellation. This is another manifestation of qualitative differences between the two types of tunneling. It should be noted that this kind of cancellation does not occur in the case of $V_{SMC}$ [Fig. 6(b)]. Symmetry of the mode coupling plays a key role in this sense.

### Table IV. Energy splittings calculated quantum mechanically for vibrationally excited states in the case of the shifted parabola model (5.1). Parameter $g$ is equal to 0.07. $\Delta E_{a,b}$ indicates the energy splitting for the ground and the $n$th excited vibrational states for the $x$ and $y$ direction, respectively.

<table>
<thead>
<tr>
<th>Energy splittings</th>
<th>$(a^<em>,b^</em>)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{a,b}$</td>
<td>$(0.8,0.9)$</td>
</tr>
<tr>
<td>$\Delta E_{w}$</td>
<td>1.5(-11)</td>
</tr>
<tr>
<td>$\Delta E_{w'}$</td>
<td>31.1(-11)</td>
</tr>
<tr>
<td>$\Delta E_{w''}$</td>
<td>240.2(-11)</td>
</tr>
<tr>
<td>$\Delta E_{C}$</td>
<td>1063(-11)</td>
</tr>
</tbody>
</table>

Tunneling regions

| Tunneling regions | C-C | C-C | boundary | I-I | C-C | I-I |

Table V. Energy splittings calculated quantum mechanically for vibrationally excited states in the case of antisymmetric mode coupling (3.5).

<table>
<thead>
<tr>
<th>Energy splittings</th>
<th>( \omega_r \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E_{00} )</td>
<td>(0.5,0.25)</td>
</tr>
<tr>
<td>( \Delta E_{01} )</td>
<td>1.4(-10)</td>
</tr>
<tr>
<td>( \Delta E_{02} )</td>
<td>60.5(-10)</td>
</tr>
<tr>
<td>( \Delta E_{03} )</td>
<td>1316.5(-10)</td>
</tr>
<tr>
<td>( \Delta E_{04} )</td>
<td>18920.0(-10)</td>
</tr>
</tbody>
</table>

Table V. Energy splittings calculated quantum mechanically for vibrationally excited states in the case of antisymmetric mode coupling (3.5).

V. The left column represents the case where tunneling mainly passes through the I region, while the right column corresponds to the case where tunneling goes through the C region. As expected, the same feature as in the case of shifted parabola can be seen: Pure tunneling is always promoted by vibrational excitation, while mixed tunneling is either promoted or suppressed by the excitation.

VI. DISCUSSIONS AND CONCLUSION

Let us elucidate the relations between the theory presented in this work and those proposed previously by other authors in chemical reaction dynamics in the context of transition state theory (TST). Among the latter, we discuss the following three representative works: the Marcus-Coltrin (MC) method, 17-19 Ovchinnikova's method, 15 and Miller's periodic orbit (PO) TST. 15

The MC method is based on the adiabatic approximation, in which tunneling motion along the IRC is assumed to be much slower than the perpendicular vibrational motion. Therefore, tunneling is assumed to occur along the effective one-dimensional potential, that is, the bare potential along the IRC plus the vibrational ground state energy. The MC tunneling path is defined as a set of classical turning points of vibration. It has been shown 22 that this MC method gives a reasonable description only when the curvature of the IRC is small. Noting that the adiabatic approximation is alright for a large frequency of vibration, we can easily guess that our Fig. 6(c) corresponds to the situation where the MC method works. Naturally, the boundary between the C and I regions in the present theory can be viewed as a generalization of the MC tunneling path. It should be noted, however, that the present theory does not require any assumption about adiabaticity.

Ovchinnikova's method may be reasonable in the limit opposite to the case of the MC method. That is to say, this is based on the sudden approximation and corresponds to the case of large curvature of the IRC. Tunneling is assumed to be a sudden hopping from a reactant valley to a product valley. The total tunneling amplitude is estimated by summing up such one-dimensional amplitudes over the initial points of hopping. In the present theory the similar situation occurs in the case of Fig. 6(b), where tunneling occurs mainly in the C region. In other words, the tunneling in the C region in the present context gives a generalization of Ovchinnikova's picture; the present theory does not rely on any sudden approximation and is more general.

Miller's POTST, derived from the semiclassical TST formulated by Miller, 50 is more general than the other two and is more legitimate from a theoretical viewpoint. The final expression, however, can be shown to be exactly the same as that of the instanton theory. The tunneling path can be defined as a periodic orbit on the inverted potential with the period \( \hbar/kT \), where \( k \) is the Boltzmann constant. This picture is quite close to our Fig. 6(a).

As is clear from the above discussions, the present theory can give a unified description of multidimensional tunneling and, thus, is quite versatile for describing the effects of multidimensionality. It should be noted, however, that the above-mentioned three theories assume bimolecular reactions in canonical ensemble, while the present theory is formulated for a quantum state with intramolecular conversion.

Quite recently, theories similar to ours have been analyzed by Huang et al. 12 and Bowcock and Gregory. 31 They used the complex action only for the scattering problem, because they claim there is a difference between tunneling in the scattering problem and tunneling from a well. In the present paper, we have clarified that both complex and pure imaginary actions must be taken into account even for the tunneling in the double well. Thus, an extension of the present theory to multidimensional collision and decay of the metastable state is highly desired.

Next, we comment on the extension of the theory to the three-dimensional problem. Around the corner of the classically accessible region, there exist eight distinct regions, each of which is separated by the caustic surface: the R region, the I region, and six C regions. Moreover, mixed tunneling in the C regions can be classified into two types—one-dimensional tunneling with two-dimensional classically accessible motion and two-dimensional tunneling with one-dimensional classically accessible motion. Starting from the R region, tunneling first proceeds through the first type of C region. Then a part of this wave enters into the second type of C region and after that arrives at the I region.

Wave propagation in the C region can be performed by essentially the same method as that in the two-dimensional case discussed here, although slightly new complications arise. In the I region the same procedure, i.e., the classical trajectory method, can be used. In the same way, the present theory can, in principle, be extended to the general N-dimensional problem.

In this paper, a general WKB theory of multidimensional tunneling has been formulated and the qualitative characteristics of multidimensionality have been clarified by using simple models. The most remarkable thing is that there are two distinct types of tunneling: mixed tunneling accompanied by classical motion, which occurs in the C region where action is complex; and pure tunneling, which occurs in the I region where action is pure imaginary. Generally speaking, tunneling starting from classically accessible region proceeds first through the C region and then enters the I region. Corresponding to these two types of tunneling, energy splitting in the symmetric double well...
potential (SDWP) can also be classified into two cases in which the main contribution comes from the I or C regions. The tunneling path can be defined uniquely in the former case, while in the latter case tunneling proceeds very broadly. The LSLA proposed in Sec. IV gives a simple and promising way of numerical estimation for the former case. The shifted parabola model is used in Sec. V to elucidate qualitative differences between pure tunneling and mixed tunneling, and it is found that the tunneling in the I region is always promoted by the vibrational excitation, while that in the C region is either promoted or suppressed by the excitation.

Obviously, the more comprehensive numerical treatment based on the general theory presented in Sec. II is required in order to demonstrate the generality of the present theory. It is also important to treat more realistic models and to demonstrate the capability of estimating energy splittings for vibrationally excited states. This is because the present theory is applicable to the case of a vibrationally excited state in a straightforward way. These works are actually now in progress, and will be reported in subsequent publications.

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APPENDIX: SEPARABLE CASE

Here we prove that in the separable case the present two-dimensional WKB wave function naturally reduces to a product of one-dimensional wave functions. As noted in Sec. III, tunneling proceeds mainly through the C region in the separable case. Therefore, we can concentrate on the wave function in the C region.

The separable Hamiltonian is assumed to be

$$\hat{H}_{\text{SEPA}} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + v_1(x) + v_2(y). \quad (A1)$$

Let $x_+$ and $y_-$ represent the four boundaries of the rectangular region where the classical motion is allowed. If the connection from the R to the right C region is carried out by Eqs. (2.37)–(2.40), the first $W_R$ equisurface is clearly a straight line parallel to the y axis and $p_x$ is constant on that surface. Therefore, in the next step, Eq. (2.28) reduces to

$$\frac{\partial p_x}{\partial x} = -\frac{1}{2p_x} \frac{\partial F}{\partial x} = -\frac{1}{2p_x} \frac{\partial v_1}{\partial x}. \quad (A2)$$

Since the right-hand side of this equation does not depend on y, the next $W_R$ equisurface and $p_x$ are again a straight line parallel to the y axis and a constant on the surface, respectively. Iterating this procedure, we can see that these properties are preserved anywhere in the C region. Then, integrating Eq. (A2), we obtain

$$p_x(x) = \sqrt{2[v_1(x) - \epsilon_1]} \quad (A3)$$

and

$$W_R(x) = \int_{x_+}^{x} dx \sqrt{2[v_1(x) - \epsilon_1]}, \quad (A4)$$

where $\epsilon_1 = v_1(x_+)$ is the energy component in the x direction. Using Eq. (2.19), we can write down $p_R$ and $W_R$ as

$$p_R(y) = \sqrt{2[\epsilon_2 - v_2(y)]} \quad (A5)$$

and

$$W_R(y) = \int_{y_-}^{y_+} dy \sqrt{2[\epsilon_2 - v_2(y)] + W_R(y_-)} \quad (A6)$$

where $\epsilon_2$ is equal to $v_2(y_-)$. The above two equations are just the same as those in the one-dimensional WKB theory. As for the preexponential factor, it is clear that the separable form

$$\rho = 1/p_B\rho_R \quad (A7)$$

is the solution of the continuity equation (2.10). This completes the proof.

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