Nonadiabatic dynamics: Transitions between asymptotically degenerate states

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(Received 1 May 2000; published 16 April 2001)

Nonadiabatic transitions between asymptotically degenerate potential curves are discussed. Both crossing and noncrossing two-coupled-Morse-potential systems are studied semiclassically as well as quantum mechanically. Conditions for the appearance of a nonadiabatic transition are clarified. The case of inverse power potentials at infinity is also analyzed. Expressions of nonadiabatic transition probability are obtained.

DOI: 10.1103/PhysRevA.63.052710 PACS number(s): 03.65.Nk

I. INTRODUCTION

Nonadiabatic transitions are usually classified into two cases: the curve crossing case and noncurve-crossing case. The Landau-Zener-Stueckelberg (LZS) type curve crossing and the Rosen-Zener-Demkov (RZD) type noncrossing problems represent the most important and well-studied cases [1–7]: Especially, the LZS type of curve crossing problem has recently been completely solved [8–10]. As an interesting intermediate case, there is an exponential potential model, which was first investigated by Nikitin within the time-dependent straightline trajectory framework [1]. After that quite a few investigations have been carried out in attempt to generalize it [11–14]. There is another type of nonadiabatic transition, i.e., the nonadiabatic transition between two tangentially touching potentials. If that occurs at a finite distance, this is nothing but the Renner-Teller type of transition [15]. In this report we analyze the touching at infinity, i.e., a nonadiabatic transition at infinity between asymptotically degenerate potential curves. The transition between asymptotically degenerate curves induced by Coriolis coupling is such an example. The degeneracy limit of the RZD model is the so-called symmetrical resonance case and does not belong to this category, because there is no nonadiabatic coupling between the two adiabatic potentials in the symmetrical resonance case. If the diabatic potentials have a certain dependence on the coordinate, however, the nonadiabatic coupling exists, such as in the nondegenerate RZD model, although that coupling goes to zero at infinity. In this paper we will consider this problem more deeply, and make clear the conditions for the appearance of such nonadiabatic transition at infinity, depending on the functionalities of the diabatic potentials and coupling there. This paper is organized as follows: in the next section the semiclassical analysis (high-energy approximation) is carried out for two Morse potentials coupled by an exponential function. Both crossing and noncrossing cases are discussed and a new expression for the asymptotic nonadiabatic transition is derived. In Sec. III quantum-mechanical solutions for a special case is discussed to confirm the semiclassical result. The origin of the appearance of such nonadiabatic transition is clarified in Sec. IV by considering different decreasing rates of the potentials and coupling at infinity within the framework of the perturbation theory. Some specific generalizations will be considered in Sec. V.

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II. SEMICLASSICAL SOLUTION OF COUPLED MORSE POTENTIALS

First, we will consider the following coupled Morse potential model:

$$\left(-\frac{\hbar^2}{2M}\frac{d^2}{dx^2}+V-E\right)\Psi=0, \tag{2.1}$$

where

$$\Psi=\begin{pmatrix}\Psi_1\\ \Psi_2\end{pmatrix},$$

$$V=\begin{pmatrix}Ae^{-\alpha x}+Be^{-2\alpha x} & Ge^{-\alpha x}\\ Ge^{-\alpha x} & Ce^{-\alpha x}+De^{-2\alpha x}\end{pmatrix},\quad E>0. \tag{2.2}$$

In the asymptotic region,

$$x\to\infty,\quad V\to e^{-\alpha x}\begin{pmatrix}A & G\\ G & C\end{pmatrix}. \tag{2.3}$$

This matrix can be diagonalized by the constant angle rotation, which indicates that there is no nonadiabatic coupling at infinity. When the diabatic potentials cross at a certain finite distance, we can easily guess that the Landau-Zener type transition occurs there and the Massey type parameter δ, defined below, plays a role,

$$\delta=\frac{MG^2}{\hbar\alpha\sqrt{2ME}|D-B|}. \tag{2.4}$$

Because of the asymptotic degeneracy, however, the situation even for the noncrossing potentials cannot be foretold simply, and actually the parameter δ also controls the dynamics at infinity, as we will see. Let us consider here the high-energy approximation to the model potential given by Eq. (2.2), which is introduced by the following representation of the wave vector

$$\Psi=\psi e^{i\sqrt{2ME}/\hbar x}. \tag{2.5}$$

The amplitude ψ is considered to be a slowly varying function that satisfies the first-order differential equation,

$$\left(-i\frac{\hbar\sqrt{2ME}}{M}\frac{d}{dx}+V\right)\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}=0, \tag{2.6}$$

which is in fact the eikonal approximation for the two state system. Substituting the variable

$$z=e^{-\alpha x}, \tag{2.7}$$

we get the system of coupled differential equations well known in the time-dependent linear potential model [1,2,6,7]:

$$\left(i\frac{d}{dz}+a+bz\right)\psi_1+g\psi_2=0,$$
$$\left(i\frac{d}{dz}+c+dz\right)\psi_2+g\psi_1=0. \tag{2.8}$$

The new lower case parameters are defined by the relation

$$a,b,c,d,g=M\frac{A,B,C,D,G}{\alpha\hbar\sqrt{2ME}}. \tag{2.9}$$

For the physical model under consideration the coupled equations (2.8) have to be solved in the half $(0,\infty)$ of the whole z axis. Interestingly, such a seemingly simple difference from the ordinary situation of the full axis will lead to an essentially new nonadiabatic dynamics. It should also be noted that the same reduction can be made with use of the Stueckelberg variable $T=(V_{22}-V_{11})/2V_{12}$ [16,17], but here we have to deal with boundary conditions different from the ordinary ones such as those in Ref. [17].

Eliminating ψ_2 from the system of equations and then replacing ψ_1 with $\varphi(z)$ defined by

$$\psi_1(z)=e^{i\zeta(z)}\varphi(z) \tag{2.10}$$

with

$$\zeta(z)=\frac{1}{2}(a+c)z+\frac{1}{4}(b+d)z^2, \tag{2.11}$$

we obtain the following second-order differential equation

$$\frac{d^2\varphi}{dZ^2}+\left(-\frac{Z^2}{4}+i\alpha^2\frac{d-b}{2}+\alpha^2g^2\right)\varphi=0, \tag{2.12}$$

in which the following new variable and parameter are introduced,

$$Z=\frac{1}{\alpha}\left(z-\frac{a-c}{d-b}\right),\quad \alpha^4=-(d-b)^{-2}. \tag{2.13}$$

Without losing generality we can assume

$$D\leqslant B \tag{2.14}$$

and

$$\alpha=e^{i(\pi/4)}(d-b)^{-1/2}. \tag{2.15}$$

The linearly independent solutions to Eq. (2.12) are the parabolic cylinder functions [18] $D_{-1+i\delta}(Z)$ and $D_{-i\delta}(iZ)$, where in terms of the new parameters given in Eq. (2.9), the parameter δ [see Eq. (2.4)] is rewritten as

$$\delta=\frac{g^2}{d-b}. \tag{2.16}$$

Using the recurrence relation of D functions, we obtain two linearly independent solutions to the system (2.12) for the diabatic amplitudes in the following form:

$$\begin{pmatrix}\psi_1^{(1)}\\ \psi_2^{(1)}\end{pmatrix}=e^{i\zeta(z)}\begin{pmatrix}D_{-1+i\delta}(Z)\\ \delta^{-1/2}e^{i\pi/4}D_{i\delta}(Z)\end{pmatrix}, \tag{2.17}$$

$$\begin{pmatrix}\psi_1^{(2)}\\ \psi_2^{(2)}\end{pmatrix}=e^{i\zeta(z)}\begin{pmatrix}\delta^{-1/2}e^{3\pi i/4}D_{-i\delta}(iZ)\\ D_{-1-i\delta}(iZ)\end{pmatrix}. \tag{2.18}$$

The adiabatic states can be obtained as usual by the transformation

$$\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix}=\begin{pmatrix}\cos\Theta & -\sin\Theta\\ \sin\Theta & \cos\Theta\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}. \tag{2.19}$$

The rotation angle Θ is defined by the following expressions:

$$\sin 2\Theta(z)=-\frac{2G}{\sqrt{[(A-C)+(B-D)z]^2+4G^2}},$$

$$\cos 2\Theta(z)=\frac{(A-C)+(B-D)z}{\sqrt{[(A-C)+(B-D)z]^2+4G^2}}. \tag{2.20}$$

The correlations

$$\begin{pmatrix}\varphi_1^{(1)}\\ \varphi_2^{(1)}\end{pmatrix}\to\begin{pmatrix}-\psi_2^{(1)}\\ 0\end{pmatrix},\quad \begin{pmatrix}\varphi_1^{(2)}\\ \varphi_2^{(2)}\end{pmatrix}\to\begin{pmatrix}0\\ \psi_1^{(2)}\end{pmatrix},\quad z\to\infty,$$

$$\begin{pmatrix}\varphi_1^{(k)}\\ \varphi_2^{(k)}\end{pmatrix}\to\begin{pmatrix}\cos\eta & -\sin\eta\\ \sin\eta & \cos\eta\end{pmatrix}\begin{pmatrix}\psi_1^{(k)}\\ \psi_2^{(k)}\end{pmatrix},\quad z\to 0 \tag{2.21}$$

with

$$\eta=\Theta(0),\quad k=1,2 \tag{2.22}$$

enable us to construct the nonadiabatic transition matrix N, which connects the asymptotic adiabatic amplitudes in the following way:

$$\begin{pmatrix}A_1^{(k)}\\ A_2^{(k)}\end{pmatrix}=N\begin{pmatrix}B_1^{(k)}\\ B_2^{(k)}\end{pmatrix}, \tag{2.23}$$

where

$$\varphi_{1,2}^{(k)}(z\to\infty)=B_{1,2}^{(k)}\exp\left(i\int_0^z U_{1,2}(z)\,dz\right),$$

$$\varphi_{1,2}^{(k)}(z\to 0)=A_{1,2}^{(k)}, \tag{2.24}$$

and

$$U_{1,2}=\frac{(a+c)}{2}+\frac{(b+d)z}{2}\pm\sqrt{\left(\frac{a-c}{2}+\frac{b-d}{2}z\right)^2+g^2}. \tag{2.25}$$

We finally find

$$N=-e^{-\pi\delta/4}\begin{pmatrix}\cos\eta & -\sin\eta\\ \sin\eta & \cos\eta\end{pmatrix}\begin{pmatrix}e^{-i\pi/4}\delta^{1/2}D_{-1+i\delta}(e^{-i\pi/4}\Delta) & -D_{-i\delta}(e^{i\pi/4}\Delta)\\ D_{i\delta}(e^{-i\pi/4}\Delta) & e^{i\pi/4}\delta^{1/2}D_{-1-i\delta}(e^{i\pi/4}\Delta)\end{pmatrix}\begin{pmatrix}e^{-i\xi} & 0\\ 0 & e^{i\xi}\end{pmatrix}, \tag{2.26}$$

where the new real parameter Δ is introduced,

$$\Delta=\frac{c-a}{\sqrt{d-b}} \tag{2.27}$$

and the matching phase ξ is defined as

$$\xi=-\frac{\delta}{2}+\frac{\Delta\sqrt{\Delta^2+4\delta}}{4}+\delta\ln\left(\frac{\Delta+\sqrt{\Delta^2+4\delta}}{2}\right). \tag{2.28}$$

It should be noted that $\Delta<0$ (>0) corresponds to the potential crossing (noncrossing) case. In terms of the principal parameters δ and Δ, the rotation angle η given by Eq. (2.22) can be rewritten as

$$\eta=\frac{1}{2}\arctan\frac{2\delta^{1/2}}{\Delta}. \tag{2.29}$$

The transition matrix N in Eq. (2.26) is unitary because of the Wronskian of the D functions,

$$\delta|D_{-1\pm i\delta}(e^{\mp i\pi/4}\Delta)|^2+|D_{\pm i\delta}(e^{\mp i\pi/4}\Delta)|^2=e^{\pi\delta/2} \tag{2.30}$$

and leads to the following principal expression for the overall nonadiabatic transition probability,

$$P\equiv|N_{12}|^2=|N_{21}|^2$$
$$=\frac{1}{2}-\left(p-\frac{1}{2}\right)\cos 2\eta+\sqrt{p(1-p)}\cos S\sin 2\eta, \tag{2.31}$$

where

$$p=1-e^{-\pi\delta/2}|D_{i\delta}(e^{-i\pi/4}\Delta)|^2 \tag{2.32}$$

has the meaning of the overall diabatic-diabatic transition probability,

$$p=\frac{|\psi_{1,2}^{(1,2)}(x\to+\infty)|^2}{|\psi_{2,1}^{(1,2)}(x\to-\infty)|^2}. \tag{2.33}$$

It should be noted that Eq. (2.31) is the result under the high-energy approximation, Eq. (2.6), and thus represents the transition probability for one passage from $x=\infty$ to $x=-\infty$ [see Eq. (2.23)]. The phase S represents the interference effect, namely, the phase difference between the two paths in one passage of the two transition regions: one at the crossing and the other at infinity, and is given by

$$S=\frac{\pi}{4}+\arg D_{i\delta}(e^{-i\pi/4}\Delta)-\arg D_{-1+i\delta}(e^{-i\pi/4}\Delta). \tag{2.34}$$

The above general expression of P depicts the simple behavior in the high-energy limit as

$$P=\cos^2\eta,\quad E\to\infty, \tag{2.35}$$

since in this limit $p\to 0$. The other limit for $\delta\to 0$ is given by

$$P=H(-\Delta), \tag{2.36}$$

where $H(X)$ is the Heaviside step function and represents the boundary between the crossing ($\Delta<0$) and noncrossing ($\Delta>0$) cases. Another interesting limit is $E\to 0$, in which δ and $\Delta\to\infty$ with $\delta^{1/2}/\Delta=\text{const}$. With use of the asymptotic expression of the parabolic cylinder function $D_{i\delta}(e^{-\pi/4}\Delta)$ in this limit, Eq. (2.32) leads to

$$p=\cos^2\eta. \tag{2.37}$$

This indicates that the diabatic states here are mixed with each other even at $E=0$, and that the diabatic state representation considered in Sec. 10.1 of Ref. [1] is not appropriate.

The expression (2.31) is very sensitive to the limit of the parameters δ and Δ, and depends crucially on the sign of Δ. Nevertheless, we can find some explicit expressions of N_{12} by using the asymptotic expansions of the D functions and their recurrence relations. Particularly, we can obtain the following expressions for $|\Delta|\to\infty$ with δ fixed:

$$-N_{12}^{*}=N_{21}=(A_+e^{i\Phi}+A_-e^{-i\Phi})e^{-i\xi} \tag{2.38}$$

with

$$\Phi=\frac{\Delta^2}{4}+\delta\log|\Delta|. \tag{2.39}$$

For $\Delta\to-\infty$, we have

$$A_+=-e^{-\pi\delta}[1+O(\Delta^{-2})],$$
$$A^-=\frac{(2\pi)^{1/2}e^{-(1/2)\pi\delta}}{\Gamma(-i\delta)|\Delta|^3}e^{-(1/4)i\pi}. \tag{2.40}$$

On the other hand, when $\Delta\to\infty$, we have

$$A_+=\frac{\delta^{1/2}}{\Delta^3}e^{(1/2)i\pi},$$
$$A_-=0. \tag{2.41}$$

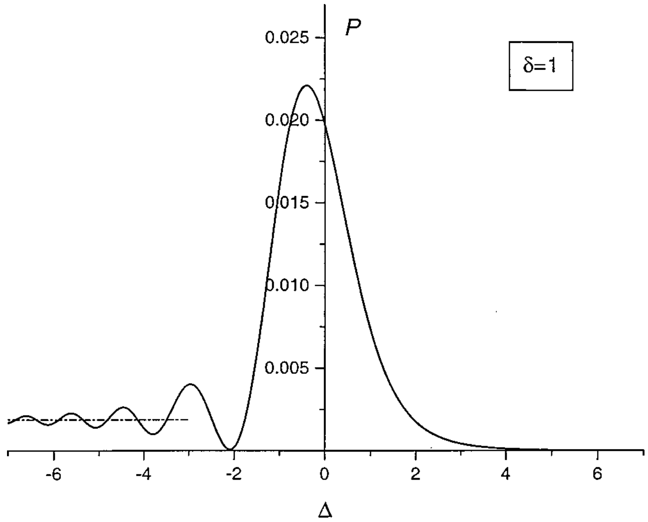

FIG. 1. The overall nonadiabatic transition probability P as a function of Δ for $\delta=1.0$. Solid line: results of Eq. (2.31), dash-dot line: result of the Landau-Zener formula.

From these expressions the probability P in the limit $\Delta\to-\infty$ for the crossing case takes the form

$$P=e^{-2\pi\delta}[1+O(\Delta^{-2})]-2e^{-\pi\delta}(1-e^{-2\pi\delta})^{1/2}\times\frac{\delta^{1/2}}{\Delta^3}[1+O(\Delta^{-2})]\cos\Omega+(1-e^{-2\pi\delta})\frac{\delta}{\Delta^6}. \tag{2.42}$$

The phase Ω represents the interference phase between the asymptotic region and the crossing region, and includes also the difference of the dynamical phases φ_c at the crossing point and $\varphi_a=\pi/2$ at infinity,

$$\Omega=\mathrm{Re}\int_{\zeta^*}^{\Delta}(\zeta^2+4\delta)^{1/2}d\zeta+\varphi_c-\varphi_a,\quad \zeta=e^{(1/4)i\pi}Z \tag{2.43}$$

with $\zeta^*=2i\sqrt{\delta}$ and

$$\varphi_c=\frac{\pi}{4}-\delta+\delta\log\delta-\arg\Gamma(1+i\delta), \tag{2.44}$$

$$\varphi_a=\frac{\pi}{2},\quad \Delta\to-\infty.$$

In the case of noncrossing, we have

$$P=\frac{\delta}{\Delta^6},\quad \Delta\to\infty. \tag{2.45}$$

The above result clearly indicates that there are two types of nonadiabatic transitions: one is the Landau-Zener type transition represented by the first term in Eq. (2.42) and the second is a new one in the asymptotic region represented by the third term in Eq. (2.42) or Eq. (2.45). These two appear naturally only in the case of crossing. Figures 1 and 2 show

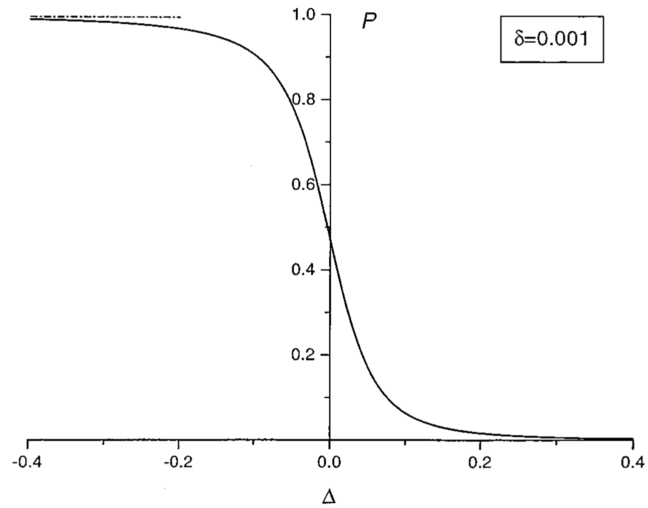

FIG. 2. The same as Fig. 1 except for $\delta=0.001$.

P given by Eq. (2.31) as a function of Δ for $\delta=1.0$ (Fig. 1) and $\delta=0.001$ (Fig. 2). The dash-dot line shows the simple Landau-Zener result.

The physical picture of the transitions expressed by Eqs. (2.42) and (2.45) can be comprehended by using the perturbation theory, which yields

$$|N_{12}|=\delta^{1/2}\left|\int_{\Delta}^{\infty}\frac{e^{i\int^{\zeta}\sqrt{\zeta^2+4\delta}d\zeta}}{\zeta^2+4\delta}d\zeta\right|. \tag{2.46}$$

In this expression, we can easily see that two regions in the complex ζ plane, $\zeta\sim\zeta^*$ and $\zeta\sim\Delta$, bring about the essential contributions. The proper deformation of the integration contour reproduces both types of transitions, in a certain limit of which Eqs. (2.42) and (2.45) are obtained. The Landau-Zener transition looks like the penetration of complex classical trajectories into the ''deep shadow'' region and the transition of the type Eq. (2.45) looks like the diffraction effect at edge [19].

The Δ end contribution to the integral Eq. (2.46) leads to

$$P=\frac{\delta}{(\Delta^2+4\delta)^3}, \tag{2.47}$$

which agrees with Eq. (2.45) in the limit $\Delta\to\infty$. Figure 3 shows P given by Eq. (2.47) for $\delta>4$, which is actually indistinguishable from the accurate result. This is rather amazing, because the simple perturbation theory usually does not work for nonadiabatic transitions, as is well known. The simple perturbation theory works well in the present case, because the exponential factor, which dominates in the usual cases, does not appear and the higher-order terms become smaller. Demkov, Ostrovskii, and Solov'ev have also pointed out that when adiabatic potentials cross on the real axis, the coupling has no pole and the perturbation theory gives the exact result in the small velocity limit [20]. However, they did not discuss such a degeneracy case as was presented here. It is also interesting to note that the

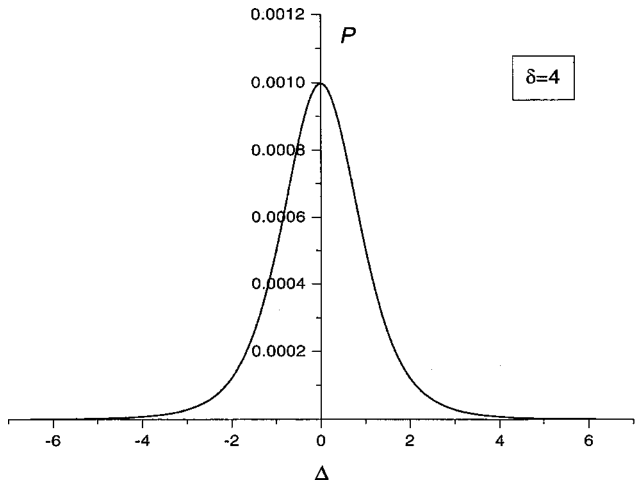

FIG. 3. The same as Fig. 1 except for $\delta=4$. The result of Eq. (2.42) is indistinguishable from the accurate one by Eq. (2.31).

asymptotic nonadiabatic transition, given by Eq. (2.47) gives the energy dependence at $E\to 0$ qualitatively correctly as

$$P=2\frac{\alpha^2\hbar^2}{m}\frac{G^2(D-B)^2}{[(C-A)^2+4G^2]^3}E,\quad E\to 0,\qquad(2.48)$$

although in the close vicinity of the quantum-mechanical threshold region, this cannot quantitatively correctly represent the energy dependence because of the semiclassical approximation (see the discussions in the next section). The behavior of quantum systems within the framework of adiabatic perturbation has been studied in the classical paper by Born and Fock [21]. Particularly, they have given the estimate of the nonadiabatic transition probability for the finite time interval without any accidental adiabatic potential crossing on the real axis in the form, $P=O(T^{-2})$, where T is the large characteristic time. The linear behavior $P\sim E$, given by Eq. (2.48), is consistent with this result, because mathematically the model considered here has the boundary at $z=0$ and does not contain the adiabatic crossing on the real z.

Before closing this section, let us clarify the connection of the above N matrix to the Landau-Zener type nonadiabatic transition matrix and derive the corresponding matrix for the asymptotic nonadiabatic transition. For that we use the following asymptotic expressions of the parabolic cylinder functions valid at $\Delta^2+4\delta\gg 1$ with τ, $\upsilon\leqslant 1$. For $\Delta<0$,

$$D_{-1+i\delta}(e^{-i\pi/4}\Delta)=e^{i\tau}\cos\eta\frac{\sqrt{2\pi}}{\Gamma(1-i\delta)}e^{-\pi\delta/4}e^{i\zeta}+e^{i\upsilon}\sin\eta\,\delta^{-1/2}e^{-3\pi\delta/4}e^{i\pi/4-i\zeta},\qquad(2.49)$$

$$D_{i\delta}(e^{-i\pi/4}\Delta)=-e^{-i\upsilon}\sin\eta\frac{\sqrt{2\pi}}{\Gamma(1-i\delta)}\delta^{1/2}e^{-\pi\delta/4}e^{-i\pi/4+i\zeta}+e^{-i\tau}\cos\eta\, e^{-3\pi\delta/4}e^{-i\zeta},\qquad(2.50)$$

and for $\Delta>0$,

$$D_{-1+i\delta}(e^{-i\pi/4}\Delta)=e^{i\tau}\cos\eta\,\delta^{-1/2}e^{\pi\delta/4}e^{i\pi/4+i\zeta},\qquad(2.51)$$

$$D_{i\delta}(e^{-i\pi/4}\Delta)=-e^{-i\upsilon}\sin\eta\, e^{\pi\delta/4}e^{i\zeta},\qquad(2.52)$$

where

$$\tau=\frac{(d\eta/d\Delta)}{\delta^{1/2}}\sin^2(\eta)-\int\frac{(d\eta/d\Delta)^2}{2\delta^{1/2}}\sin(2\eta)d\Delta\qquad(2.53)$$

and

$$\upsilon=\frac{(d\eta/d\Delta)}{\delta^{1/2}}\cos^2(\eta)+\int\frac{(d\eta/d\Delta)^2}{2\delta^{1/2}}\sin(2\eta)d\Delta.\qquad(2.54)$$

In both cases of $\Delta<0$ and $\Delta>0$, we have

$$D_{-1-i\delta}(e^{i\pi/4}\Delta)=D^*_{-1+i\delta}(e^{-i\pi/4}\Delta),\qquad(2.55)$$

$$D_{-i\delta}(e^{i\pi/4}\Delta)=D^*_{i\delta}(e^{-i\pi/4}\Delta),\qquad(2.56)$$

and

$$\tau+\upsilon=-\frac{1}{\Delta^2+4\delta}\ll 1.\qquad(2.57)$$

In the case of $\Delta<0$ from Eq. (2.26) we have

$$N(\Delta<0)=-\begin{pmatrix}\cos\eta & -\sin\eta\\ \sin\eta & \cos\eta\end{pmatrix}\begin{pmatrix}e^{i\tau}\cos\eta & e^{i\upsilon}\sin\eta\\ -e^{-i\upsilon}\sin\eta & e^{-i\tau}\cos\eta\end{pmatrix}\times\begin{pmatrix}e^{i\omega/2} & 0\\ 0 & e^{-i\omega/2}\end{pmatrix}I_X^{LZ}\begin{pmatrix}e^{-i\omega/2} & 0\\ 0 & e^{i\omega/2}\end{pmatrix}=N_\infty I^{LZ},\qquad(2.58)$$

where

$$I_X^{LZ}=\begin{pmatrix}\sqrt{1-e^{-2\pi\delta}}e^{i\phi_S} & -e^{-\pi\delta}\\ e^{-\pi\delta} & \sqrt{1-e^{-2\pi\delta}}e^{-i\phi_S}\end{pmatrix},\qquad(2.59)$$

$$\omega=\xi+(\delta-\delta\ln\delta)/2=\int_0^\Delta(\zeta^2+4\delta)^{1/2}d\zeta.\qquad(2.60)$$

$$N_\infty=-\begin{pmatrix}\cos\eta & -\sin\eta\\ \sin\eta & \cos\eta\end{pmatrix}\begin{pmatrix}e^{i\tau}\cos\eta & e^{i\upsilon}\sin\eta\\ -e^{-i\upsilon}\sin\eta & e^{-i\tau}\cos\eta\end{pmatrix},\qquad(2.61)$$

$$I^{LZ}=\begin{pmatrix}\sqrt{1-e^{-2\pi\delta}}e^{i\phi_S} & -e^{-\pi\delta}e^{i\omega}\\ e^{-\pi\delta}e^{-i\omega} & \sqrt{1-e^{-2\pi\delta}}e^{-i\phi_S}\end{pmatrix},\qquad(2.62)$$

and

$$\phi_S=\delta-\delta\ln\delta+\pi/4+\arg\Gamma(i\delta).\qquad(2.63)$$

The matrix I_X^{LZ} is nothing but the Landau-Zener type nonadiabatic transition matrix at the avoided crossing and I^{LZ} represents the similar matrix including the adiabatic wave propagation from infinity to the crossing point represented by the phase ω (see Refs. [8–10]). For $\Delta>0$ we have from Eq. (2.26)

$$N(\Delta>0)=N_\infty, \tag{2.64}$$

which gives the asymptotic nonadiabatic transition matrix and is naturally identical to that in the crossing case ($\Delta<0$). For small values of τ, v the following simple expression can be obtained:

$$N_\infty=\begin{pmatrix} \left(1-\dfrac{1}{4(\Delta^2+4\delta)^2}\right)^{1/2}+i\,\dfrac{\Delta}{2(\Delta^2+4\delta)^{3/2}} & i\,\dfrac{\delta^{1/2}}{(\Delta^2+4\delta)^{3/2}} \\ i\,\dfrac{\delta^{1/2}}{(\Delta^2+4\delta)^{3/2}} & \left(1-\dfrac{1}{4(\Delta^2+4\delta)^2}\right)^{1/2}-i\,\dfrac{\Delta}{2(\Delta^2+4\delta)^{3/2}} \end{pmatrix}. \tag{2.65}$$

The above finding is quite useful, because the nonadiabatic transition matrices describe the transitions in local regions and thus can be used in other general even multichannel problems. Furthermore, the matrices I_X^{LZ} and I^{LZ} can be replaced by the far more accurate ones obtained recently [8–10].

III. QUANTUM-MECHANICAL SOLUTION OF A SPECIAL CASE

In this section we present the quantum-mechanically exact solution of a special case and discuss the validity of the semiclassical approximation given in the previous section. If we set $A=C=B=0$ in Eq. (2.2), we can solve Eq. (2.1) exactly by using the method of Osherov and Nakamura [12]. The physically independent solutions of Eq. (2.1) for diabatic wave functions are obtained as

$$\psi_1^{(1)}=G_{2,4}^{4,1}\left(Kz^2e^{i\pi}\Big|_{b_q}^{a_1,a_2}\right), \tag{3.1}$$

$$\psi_1^{(2)}=G_{2,4}^{4,1}\left(Kz^2e^{i\pi}\Big|_{b_q}^{a_2,a_1}\right), \tag{3.2}$$

$$\psi_1^{(3)}=G_{2,4}^{4,0}\left(Kz^2\Big|_{b_q}^{a_1,a_2}\right), \tag{3.3}$$

$$\begin{aligned}\psi_2^{(1)}=\frac{1}{Lz}\Bigg\{&G_{2,4}^{4,1}\left(Kz^2e^{i\pi}\Big|_{b_q}^{a_1,a_2-2}\right)-(2a_2-3)\\ &\times G_{2,4}^{4,1}\left(Kz^2e^{i\pi}\Big|_{b_q}^{a_1,a_2-1}\right)+\left[(a_2-1)^2+\left(\frac{q}{2}\right)^2\right]\\ &\times G_{2,4}^{4,1}\left(Kz^2e^{i\pi}\Big|_{b_q}^{a_1,a_2}\right)\Bigg\},\end{aligned} \tag{3.4}$$

$$\begin{aligned}\psi_2^{(2)}=\frac{1}{Lz}\Bigg\{&G_{2,4}^{4,1}\left(Kz^2e^{i\pi}\Big|_{b_q}^{a_2,a_1-2}\right)-(2a_1-3)\\ &\times G_{2,4}^{4,1}\left(Kz^2e^{i\pi}\Big|_{b_q}^{a_2,a_1-1}\right)+\left[(a_1-1)^2+\left(\frac{q}{2}\right)^2\right]\\ &\times G_{2,4}^{4,1}\left(Kz^2e^{i\pi}\Big|_{b_q}^{a_2,a_1}\right)\Bigg\},\end{aligned} \tag{3.5}$$

$$\begin{aligned}\psi_2^{(3)}=\frac{1}{Lz}\Bigg\{&G_{2,4}^{4,0}\left(Kz^2\Big|_{b_q}^{a_1,a_2-2}\right)-(2a_2-3)G_{2,4}^{4,0}\left(Kz^2\Big|_{b_q}^{a_1,a_2-1}\right)\\ &+\left[(a_1-1)^2+\left(\frac{q}{2}\right)^2\right]G_{2,4}^{4,0}\left(Kz^2\Big|_{b_q}^{a_1,a_2}\right)\Bigg\},\end{aligned} \tag{3.6}$$

where $G_{2,4}^{4,1}$ and $G_{2,4}^{4,0}$ are the Meijir's G functions [22] and the various parameters are defined as

$$\begin{gathered}K=\frac{MD}{2\hbar^2\alpha^2},\quad L=\frac{MG}{2\hbar^2\alpha^2},\\ a_{1,2}=1\pm\frac{ir}{2},\quad b_{1,2}=\frac{1}{2}\pm\frac{iq}{2},\quad b_{3,4}=\pm\frac{iq}{2}.\end{gathered} \tag{3.7}$$

The principal parameters r and q are the dimensionless momenta in the asymptotic regions of the adiabatic potentials,

$$r=\frac{\sqrt{2M\left(E+\dfrac{G^2}{D}\right)}}{\hbar\alpha},\quad q=\frac{\sqrt{2ME}}{\hbar\alpha}. \tag{3.8}$$

The diabatic wave functions given by Eqs. (3.1)–(3.6) have the following asymptotic behavior:

$$\begin{aligned}\psi_{1,2}^{(k)}&=\tilde{B}_{1,2}^{(k)}\overleftarrow{q}+\tilde{A}_{1,2}^{(k)}\vec{q}\quad\text{for}\quad z\to 0,\\ \psi_1^{(k)}&=\tilde{B}_3^{(k)}\vec{r}+\tilde{A}_3^{(k)}\overleftarrow{r},\\ \psi_2^{(k)}&=0\quad\text{for}\quad z\to\infty,\end{aligned} \tag{3.9}$$

where

$$\overleftarrow{q},\ \vec{q},\ \overleftarrow{r},\ \vec{r}=\frac{1}{\sqrt{q,r}}e^{\pm i(q,r)\alpha x} \tag{3.10}$$

and the amplitudes $\tilde{A}_i^{(k)}$ and $\tilde{B}_j^{(k)}$ are connected by the transition matrix $\tilde{N}_{i,j}$ as

$$\tilde{A}_i^{(k)}=\tilde{N}_{i,j}\tilde{B}_j^{(k)}. \tag{3.11}$$

The matrix elements $\tilde{N}_{ij}$ can be obtained as

$$\tilde{N}_{11}=K^{b_4-b_3}\frac{\Gamma(b_1-b_4)\Gamma(b_2-b_4)\Gamma(b_3-b_4)}{\Gamma(b_1-b_3)\Gamma(b_2-b_3)\Gamma(b_4-b_3)} \times\frac{\Gamma(a_2-b_3)\Gamma(a_1-b_3)}{\Gamma(a_2-b_4)\Gamma(a_1-b_4)} \times\frac{\sin\pi(b_4-b_1)\sin\pi(b_3-a_1)}{\sin\pi(b_4-a_1)\sin\pi(b_3-a_1)}, \tag{3.12}$$

$$\tilde{N}_{12}=K^{b_4-b_1}\frac{L}{b_1^2-b_3^2}\frac{\Gamma(b_1-b_4)\Gamma(b_2-b_4)\Gamma(b_3-b_4)}{\Gamma(b_2-b_1)\Gamma(b_3-b_1)\Gamma(b_4-b_1)} \times\frac{\Gamma(a_2-b_1)\Gamma(a_1-b_1)}{\Gamma(a_2-b_4)\Gamma(a_1-b_4)} \times\frac{\sin\pi(b_3-b_4)\sin\pi(b_1-a_1)}{\sin\pi(b_3-b_1)\sin\pi(b_4-a_1)}, \tag{3.13}$$

$$\tilde{N}_{13}=-\sqrt{\frac{r}{q}}K^{a_1-1-b_3} \times\frac{\Gamma(1+b_1-a_1)\Gamma(1+b_2-a_1)\Gamma(1+b_3-a_1)}{\Gamma(1+a_2-a_1)\Gamma(b_1-b_3)} \times\frac{\Gamma(1+b_4-a_1)\Gamma(a_2-b_3)\Gamma(a_1-b_3)}{\Gamma(b_4-b_3)} \times\frac{\sin\pi(b_3-a_1)\sin\pi(b_1-a_1)}{\pi\sin\pi(b_3-b_1)}, \tag{3.14}$$

$$\tilde{N}_{22}=K^{b_2-b_1}\frac{b_2^2-b_4^2}{b_1^2-b_3^2}\frac{\Gamma(b_1-b_2)\Gamma(b_3-b_2)}{\Gamma(b_2-a_1)\Gamma(b_3-b_1)} \times\frac{\Gamma(b_4-b_2)\Gamma(a_2-b_1)\Gamma(a_1-b_1)}{\Gamma(b_4-b_1)\Gamma(a_2-b_2)\Gamma(a_1-b_2)} \times\frac{\sin\pi(b_3-b_2)\sin\pi(b_1-a_1)}{\sin\pi(b_2-a_1)\sin\pi(b_3-b_1)}, \tag{3.15}$$

$$\tilde{N}_{23}=\sqrt{\frac{r}{q}}K^{a_1-1-b_1}\frac{L}{b_1^2-b_3^2}\frac{\Gamma(1+b_1-a_1)\Gamma(1+b_2-a_1)}{\Gamma(1+a_2-a_1)\Gamma(b_2-b_1)} \times\frac{\Gamma(1+b_3-a_1)\Gamma(1+b_4-a_1)\Gamma(a_2-b_1)\Gamma(a_1-b_1)}{\Gamma(b_3-b_1)\Gamma(b_4-b_1)} \times\frac{\sin\pi(b_3-a_1)\sin\pi(b_1-a_1)}{\pi\sin\pi(b_3-b_1)}, \tag{3.16}$$

$$\tilde{N}_{33}=K^{a_1-\alpha_2}\frac{\Gamma(1+b_1-a_1)\Gamma(1+b_2-a_1)\Gamma(1+b_3-a_1)}{\Gamma(1+b_1-a_2)\Gamma(1+b_2-a_2)\Gamma(1+b_3-a_2)} \times\frac{\Gamma(1+b_4-a_1)\Gamma(1+a_1-a_2)\Gamma(a_1-b_1)}{\Gamma(1+b_4-a_2)\Gamma(1+a_2-a_1)} \times\frac{\sin\pi(b_3-b_1)\sin\pi(b_1-a_1)}{\sin\pi(a_2-b_3)\sin\pi(a_2-b_1)}. \tag{3.17}$$

The adiabatic wave functions have the asymptotic behavior,

$$\varphi_{1,2}^{(k)}=B_{1,2}^{(k)}\overleftarrow{q}+A_{1,2}^{(k)}\vec{q}\quad\text{for } z\to 0,$$
$$\varphi_1^{(k)}=0, \tag{3.18}$$
$$\varphi_2^{(k)}=B_3^{(k)}\vec{r}+A_3^{(k)}\overleftarrow{r}\quad\text{for } z\to\infty,$$

which define the principal transition matrix $N_{i,j}$ connecting the adiabatic channels as

$$A_i^{(k)}=N_{i,j}B_j^{(k)}. \tag{3.19}$$

For the model under consideration the formulas Eqs. (2.19) and (2.20) with $A=B=C=0$, lead to

$$\begin{pmatrix}\varphi_1^{(k)}\\ \varphi_2^{(k)}\end{pmatrix}\to\begin{pmatrix}0 & -1\\ 1 & 0\end{pmatrix}\begin{pmatrix}\psi_1^{(k)}\\ \psi_2^{(k)}\end{pmatrix},\quad z\to\infty, \tag{3.20}$$

$$\begin{pmatrix}\varphi_1^{(k)}\\ \varphi_2^{(k)}\end{pmatrix}\to\frac{1}{\sqrt{2}}\begin{pmatrix}-1 & -1\\ 1 & -1\end{pmatrix}\begin{pmatrix}\psi_1^{(k)}\\ \psi_2^{(k)}\end{pmatrix},\quad z\to 0. \tag{3.21}$$

Using Eqs. (3.9), (3.11), (3.18–3.21), we obtain

$$N=T\tilde{N}T^{-1}, \tag{3.22}$$

where

$$T=\begin{pmatrix}-\frac{1}{\sqrt{2}}, & -\frac{1}{\sqrt{2}}, & 0\\ \frac{1}{\sqrt{2}}, & -\frac{1}{\sqrt{2}}, & 0\\ 0, & 0, & 1\end{pmatrix}. \tag{3.23}$$

The overall nonadiabatic transition probability P_0 takes the form

$$P_0=|N_{13}|^2=\frac{1}{2}|\tilde{N}_{13}+\tilde{N}_{23}|^2. \tag{3.24}$$

Using Eqs. (3.11)–(3.17), we finally obtain

$$P_0=\frac{1}{2}\sinh(2\pi q)\frac{\sinh\pi r}{\sinh\pi(r+q)}\left(\frac{\cosh\pi\left(\frac{r-q}{2}\right)}{\sinh\pi\left(\frac{r+q}{2}\right)}+\frac{\sinh\pi\left(\frac{r-q}{2}\right)}{\cosh\pi\left(\frac{r+q}{2}\right)}+2\sqrt{\frac{\sinh\pi(r-q)}{\sinh\pi(r+q)}}\cos(S_{0Q})\right), \tag{3.25}$$

and

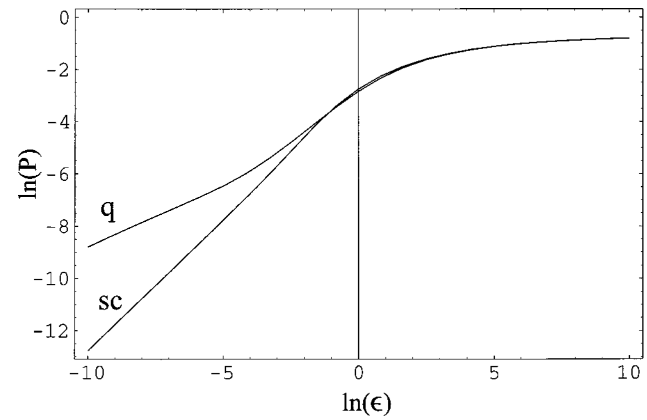

FIG. 4. The overall nonadiabatic transition probability P in the special case of exponential potential discussed in Sec. II as a function of $\epsilon = 2ME/\hbar^2\alpha^2$ for the case of $r_0 = 1$. The ordinate is equal to $\ln(P)$ and the abscissa is equal to $\ln(\epsilon)$. The line ''q'' is the result of the exact quantum formula Eq. (2.31) and the curve ''sc'' is the result of the semiclassical approximation, Eq. (2.42).

$$S_0 = \pi - \arg\Gamma\left(\frac{1}{2} + i\frac{r-q}{2}\right) + \arg\Gamma\left(i\frac{r-q}{2}\right) + \arg\Gamma\left(\frac{1}{2} + i\frac{r+q}{2}\right) - \arg\Gamma\left(i\frac{r+q}{2}\right). \qquad (3.26)$$

In the eikonal semiclassical approximation, $1 \ll r,q$ and $G^2/D \ll |E|$, the above result accurately reduces to

$$P_0 = \frac{1}{2}\left(1 - \sqrt{1 - e^{-2\pi\delta}}\cos S_0\right), \qquad (3.27)$$

$$S_0 = \frac{\pi}{4} + \arg\Gamma\left(1 - \frac{i\delta}{2}\right) - \arg\Gamma\left(\frac{1}{2} - \frac{i\delta}{2}\right), \qquad (3.28)$$

which coincide with the semiclassical results of Eq. (2.31) in the limits $A = C$ and $\Delta \to 0$. At the threshold $q \ll 1$, $q \ll r_0$ the above result, Eq. (3.25), gives the energy dependence as

$$P_0 = \frac{4\pi}{e^{2\pi r_0} - 1}\,\frac{\sqrt{2ME}}{\hbar\alpha} \qquad (3.29)$$

with

$$r_0 = \frac{\sqrt{2M\dfrac{G^2}{D}}}{\hbar\alpha}. \qquad (3.30)$$

The comparison between the quantum results, Eq. (3.25), and the semiclassical results, Eq. (3.27), is given in Fig. 4 and Fig. 5. This demonstrates good accuracy of the semiclassical approximation. It is interesting to note that Eq. (3.27) takes a rather unusual form in the limit $\delta \to \infty$,

$$P_0 \to \frac{1}{(8\delta)^2}, \qquad (3.31)$$

which actually agrees with Eq. (2.47) with $\Delta = 0$.

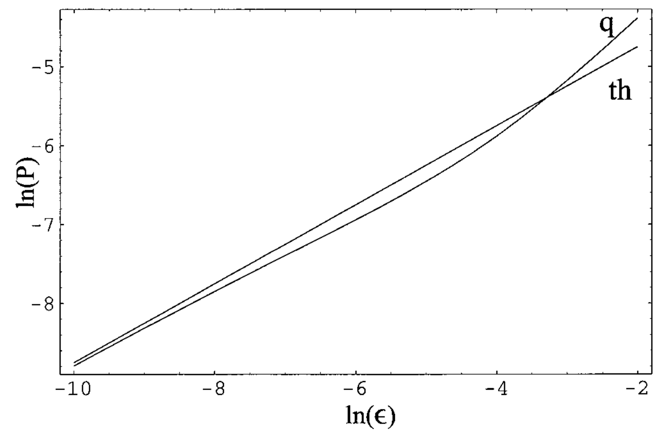

FIG. 5. The same as Fig. 4 except that the threshold region is emphasized. The line ''th'' is the result of the approximation Eq. (3.29).

IV. ORIGIN OF THE ASYMPTOTIC NONADIABATIC TRANSITIONS

In this section we will try to analyze, in more detail, the physical origin of the asymptotic nonadaiabatic transition within the high-energy approximation. Let us consider the following system of two asymptotically degenerate states:

$$\left(i\frac{d}{dx} + \begin{pmatrix} u_1 & v \\ v & u_2 \end{pmatrix}\right)\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = 0 \qquad (4.1)$$

with

$$u_{1,2}, v = -M\frac{U_{1,2}, V}{\hbar\sqrt{2ME}} \qquad (4.2)$$

and

$$U_{1,2}, V \to 0 \quad \text{for} \quad x \to \infty. \qquad (4.3)$$

Transforming Eq. (4.1) into the adiabatic representation by

$$\sin 2\Theta = -\frac{2v}{\sqrt{(u_1-u_2)^2 + 4v^2}}, \qquad \cos 2\Theta = \frac{u_1 - u_2}{\sqrt{(u_1-u_2)^2 + 4v^2}}, \qquad (4.4)$$

we obtain

$$\left[i\frac{d}{dx} + \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} + i\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\frac{d\Theta}{dx}\right]\begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} = 0, \qquad (4.5)$$

where

$$\epsilon_{1,2} = \frac{1}{2}\left(u_1 + u_2 \pm \sqrt{(u_1-u_2)^2 + 4v^2}\right). \qquad (4.6)$$

Now, we expand $U_1 - U_2$ and V in terms of certain basis functions $f_n(x)$, which satisfy the limit Eq. (4.3),

$$U_1-U_2=\sum_{n=1} A_n f_n(x), \quad V=\sum_{m=1} B_m f_m(x). \quad (4.7)$$

In accordance with Eqs. (4.3), (4.4), (4.6), and (4.7), the following limits hold true

$$\epsilon_{1,2}, \frac{d\Theta}{dx}\to 0 \quad \text{for} \quad x\to\infty. \quad (4.8)$$

Depending on the decreasing rates of the potential difference and the coupling, we will consider the following two cases separately.

A. The case where the nonadiabatic coupling decreases not slower than the energy splitting

The adiabatic solutions of Eq. (4.5) take the form

$$\begin{pmatrix}\varphi_1^0\\ \varphi_2^1\end{pmatrix}=\begin{pmatrix} C_1 \exp\left(i\int^x \epsilon_1(x)dx\right)\\ C_2 \exp\left(i\int^x \epsilon_2(x)dx\right)\end{pmatrix}, \quad (4.9)$$

where $C_{1,2}$ are arbitrary constants. Assuming that the Massey parameter δ is much larger than unity, we use the perturbation theory for simplicity. Choosing $C_2=0$, we obtain

$$\psi_2=-C_1 \sin\Theta \exp\left(i\int^x \epsilon_1(x)dx\right),$$
$$\psi_1=\frac{C_1}{v}\left((u_2-\epsilon_1)\sin\Theta+i\frac{d\Theta}{dx}\cos\Theta\right)\exp\left(i\int^x \epsilon_1(x)dx\right). \quad (4.10)$$

With use of Eqs. (2.19), (4.4), (4.6), and (4.10) the adiabatic wave function φ_2 can be expressed as

$$\varphi_2=\frac{iC_1}{2v}\frac{d\Theta}{dx}\sin 2\Theta \exp\left(i\int^x \epsilon_1(x)dx\right), \quad (4.11)$$

which leads to the expression of the *asymptotic nonadiabatic transition* probability,

$$P=\left|\frac{\varphi_2(\infty)}{\varphi_1^0(X)}\right|^2=\lim_{x\to\infty}\frac{1}{(\epsilon_1-\epsilon_2)^2}\left(\frac{d\Theta}{dx}\right)^2, \quad (4.12)$$

where X is located outside the asymptotic transition region. In terms of the basis functions $f_n(x)$ we have

$$P=\lim_{x\to\infty}\frac{2\hbar^2\left[\sum_{n,m=1}(A_nB_m-A_mB_n)f_n(x)f_m'(x)\right]^2}{M\left[\sum_{n,m=1}(A_nA_m+4B_nB_m)f_n(x)f_m(x)\right]^3}E. \quad (4.13)$$

As can be seen from the derivation of Eq. (4.12), this expression can be formally used to reveal the *asymptotic nonadiabatic transitions* even for the models without asymptotic degeneracy. Particularly, this gives $P=0$ for the linear potential model, Nikitin model, and Demkov model. On the other hand, if we use $f_n(x)=e^{-\alpha nx}$, we can recover Eq. (2.46) and Eq. (2.47). If we use the power basis set $f_n(x)=(\rho/x)^n$, Eq. (4.13) leads to the following expressions:

$$P=0 \quad \text{for} \quad A_1 \quad \text{or} \quad B_1\neq 0, \quad (4.14)$$

$$P=\frac{2\hbar^2}{M\rho^2}\frac{(A_2B_3-A_3B_2)^2}{(A_2^2+4B_2^2)^3}E \quad \text{for} \quad A_1, B_1=0, \quad (4.15)$$

and

$$P=\frac{2^3\hbar^2}{M\rho^2}\frac{(A_3B_5-A_5B_3)^2}{(A_3^2+4B_3^2)^3}E \quad \text{for} \quad A_1,B_1,A_2,B_2,A_4,B_4=0. \quad (4.16)$$

The formula (4.15) applies to the Coriolis coupling and charge-dipole potentials and the formula (4.16) for the charge-dipole and charge-quadrupole potentials.

B. The case that the adiabatic potential energy splitting decreases faster

In this case Eq. (4.12) loses meaning, because the denominator, $(\epsilon_1-\epsilon_2)^2$, goes to zero faster than the nominator. Since we cannot discuss the general cases, let us consider a particular case with $A_1=A_2=B_1=B_2=0$ and $f_n(x)=(\rho/x)^n$. The adiabatic potentials are given by

$$\epsilon_{1,2}=\frac{1}{2}\left(v_1+v_2\pm\sqrt{A_3^2+4B_3^2}\left(\frac{\rho}{x}\right)^3\frac{\sqrt{M}}{\hbar\sqrt{2E}}\right)=\frac{(v_1+v_2)}{2}\pm\frac{L}{x^3}, \quad (4.17)$$

and

$$\frac{d\Theta}{dx}=-\frac{A_3B_4-A_4B_3}{A_3^2+4B_3^2}\frac{\rho}{x^2}=-\frac{R}{x^2} \quad \text{for} \quad x\to\infty. \quad (4.18)$$

In this case, it is possible to find the exact solution as follows:

transforming the wave function by

$$\tilde{\varphi}_{1,2}=\varphi_{1,2}e^{-i\int^x\epsilon_{1,2}dx}, \quad (4.19)$$

we obtain

$$\frac{d\tilde{\varphi}_1}{dt}+\mathrm{R}e^{iLt^2}\tilde{\varphi}_2=0,$$

$$\frac{d\tilde{\varphi}_2}{dt}-\mathrm{R}e^{-iLt^2}\tilde{\varphi}_1=0, \quad (4.20)$$

$$\text{with} \quad t=\frac{1}{x},$$

which can be solved again in terms of the parabolic cylinder functions. The general solution is given by

$$\tilde{\varphi}_1 = e^{iL/2x^2} e^{i\pi/4}\left[c_1 \nu^{1/2} D_{-1+i\nu}\left(e^{-i\pi/4}\frac{\sqrt{2L}}{x}\right) - c_2 \nu^{-1/2} D_{-i\nu}\left(e^{i\pi/4}\frac{\sqrt{2L}}{x}\right)\right], \quad (4.21)$$

$$\tilde{\varphi}_2 = e^{-iL/2x^2}\left[c_1 D_{i\nu}\left(e^{-i\pi/4}\frac{\sqrt{2L}}{x}\right) + c_2 D_{-1-i\nu}\left(e^{i\pi/4}\frac{\sqrt{2L}}{x}\right)\right], \quad (4.22)$$

where

$$\nu = \frac{R^2}{2L} = \frac{\hbar}{\rho}\frac{(A_3B_4 - A_4B_3)^2}{(A_3^2 + 4B_3^2)^{5/2}}\frac{\sqrt{2E}}{\sqrt{M}}. \quad (4.23)$$

The nonadaiabatic transition matrix N connecting the amplitudes of adiabatic waves at $x \to 0$ and $x \to \infty$, is given by

$$N = \sqrt{\pi} e^{-\pi\nu/4}\begin{pmatrix} \dfrac{1}{\Gamma\left(\dfrac{1}{2} + \dfrac{i\nu}{2}\right)} & \dfrac{(i\nu)^{1/2}}{2^{1/2}\Gamma\left(1 - \dfrac{i\nu}{2}\right)} \\ -\dfrac{(-i\nu)^{1/2}}{2^{1/2}\Gamma\left(1 + \dfrac{i\nu}{2}\right)} & \dfrac{1}{\Gamma\left(\dfrac{1}{2} - \dfrac{i\nu}{2}\right)} \end{pmatrix}. \quad (4.24)$$

The *asymptotic nonadiabatic transition* probability can be expressed as

$$P = \frac{1}{2}(1 - e^{-\pi\nu}). \quad (4.25)$$

From this expression we obtain again the power-law behavior of the probability at low energy, i.e., $P \propto \sqrt{E}$, which is the principal characteristic feature of the asymptotic nonadiabatic transition. This indicates that the asymptotic degeneracy of the potential-energy curves creates a new type of nonadiabatic dynamics with respect to the analytical dependence of the probability on the collision energy.

V. GENERALIZATIONS

In this section we will investigate three kinds of generalizations.

A. Case (1)

First, let us consider the following potential system:

$$V = \begin{pmatrix} Ae^{-\alpha x} + Be^{-2\alpha x} & Ge^{-\alpha x} + \Lambda e^{-2\alpha x} \\ Ge^{-\alpha x} + \Lambda e^{-2\alpha x} & Ce^{-\alpha x} + De^{-2\alpha x} \end{pmatrix}. \quad (5.1)$$

This can be transformed into other diabatic potential systems by a constant angle (ω) rotation defined by

$$V_R = RVR^{-1} \quad (5.2)$$

with

$$R = \begin{pmatrix} \cos\chi & \sin\chi \\ -\sin\chi & \cos\chi \end{pmatrix}. \quad (5.3)$$

If we choose χ as

$$\tan^2 2\chi = \frac{2\Lambda}{B - D}, \quad (5.4)$$

we can transform Eq. (5.1) to the form of Eq. (2.2) with the replacement of the parameters

$$A, C \to \frac{1}{2}\left(A + C \pm \frac{(D-B)(A-C) - 4\Lambda G}{[(D-B)^2 + 4\Lambda^2]^{1/2}}\right), \quad (5.5)$$

$$B, D \to \frac{1}{2}\{B + D \mp [(D-B)^2 + 4\Lambda^2]^{1/2}\}, \quad (5.6)$$

and

$$G \to \frac{G(D-B) - \Lambda(C-A)}{[(D-B)^2 + 4\Lambda^2]^{1/2}}. \quad (5.7)$$

Redefining the basic parameters δ and Δ by

$$\delta = \frac{[G(D-B) - \Lambda(C-A)]^2}{[(D-B)^2 + 4\Lambda^2]^{3/2}} \quad (5.8)$$

and

$$\Delta = \frac{(D-B)(C-A) + 4\Lambda G}{[(D-B)^2 + 4\Lambda^2]^{3/4}}, \quad (5.9)$$

we can employ the previous results given in Sec. II. The above analysis makes it possible to consider the two limiting cases, $A = C = \Lambda = 0$ and $D = B = G = 0$, which represent faster decay of the diabatic potential-energy difference and the diabatic coupling, respectively.

B. Case (2)

Let us consider the system described by Eq. (4.1) with the following potential matrix elements:

$$U_1 - U_2 = A_n e^{-n\alpha x} + A_m e^{-m\alpha x}, \quad V = B_n e^{-n\alpha x} + B_m e^{-m\alpha x} \quad (5.10)$$

with $n, m > 0$ and $m > n$, which do not lead to any loss of generality. We can further assume $B_m = 0$, since a constant angle rotation can eliminate this term without losing generality in the same way as in the previous case. Transforming the wave function by

$$\psi_{1,2} = e^{-i\int^x \epsilon_{1,2} dx}\tilde{\psi}_{1,2}, \quad (5.11)$$

and changing the variable by

$$X = e^{-n\alpha x}, \quad (5.12)$$

we obtain the following equation:

$$\frac{d^2\tilde{\psi}_1}{dX^2}-\frac{i}{n\alpha}(\widetilde{A_n}+\widetilde{A_m}X^{m-n/n})\frac{d\tilde{\psi}_1}{dX}+\frac{\widetilde{B_n}^2}{n^2\alpha^2}\tilde{\psi}_1=0, \tag{5.13}$$

where

$$\tilde{A},\tilde{B}=-M\frac{A,B}{\hbar\sqrt{2ME}}. \tag{5.14}$$

The special case of $m=2n$ leads to the type discussed in Sec. II and can be solved exactly.

C. Case (3)

Using the same method as above, we can solve some cases of the following potential system:

$$U_1-U_2=A_k\left(\frac{\rho}{x}\right)^k+A_l\left(\frac{\rho}{x}\right)^l,\ \ V=B_k\left(\frac{\rho}{x}\right)^k+B_l\left(\frac{\rho}{x}\right)^l, \tag{5.15}$$

with $k,l>0$ and $l>k$. In the same way as above, the term containing B_l can be absorbed by a constant angle rotation and thus we can assume $B_l=0$ without loss of generality. Using the same transformation given by Eq. (5.11) and the variable change,

$$X=\left(\frac{\rho}{x}\right)^{k-1}, \tag{5.16}$$

we can obtain

$$\frac{d^2\tilde{\psi}_1}{dX^2}-\frac{i\rho}{k-1}(\widetilde{A_k}+\widetilde{A_l}X^{l-k/k-1})\frac{d\tilde{\psi}_1}{dX}+\frac{\widetilde{B_n}^2\rho^2}{(k-1)^2}\tilde{\psi}_1=0, \tag{5.17}$$

where $\tilde{A}$ and $\tilde{B}$ are defined in the same way as above by Eq. (5.14). In this model, the special case of $l=2k-1$ leads to the same equation as Eq. (5.13) with the correspondences $\alpha\to 1/\rho$ and $n\to k-1$. In particular, the cases with $k=2$, $l=3$ and $k=3$, $l=5$ can be solved not only exactly in terms of the N matrix given by Eq. (2.26), but also perturbatively by the formulas (4.15) and (4.16).

The model with $k=1$ should be considered separately. Using the variable transformation,

$$X=\left(\frac{\rho}{x}\right)^{l-1}, \tag{5.18}$$

we obtain

$$\frac{d^2\tilde{\psi}_1}{dX^2}+\left(\frac{1-ia_1}{X}-ia_2\right)\frac{d\tilde{\psi}_1}{dX}+\frac{b_1}{X^2}\tilde{\psi}_1=0, \tag{5.19}$$

where the following abbreviations are used:

$$a_1,a_2,b_1=\frac{(\widetilde{A_1},\widetilde{A_l},\widetilde{B_1})\rho}{l-1}. \tag{5.20}$$

The above differential equation can be solved exactly in terms of the confluent hypergeometric functions. We choose the following particular solution

$$\tilde{\psi}_1=X^a\Psi(a,c,ia_2X), \tag{5.21}$$

where

$$a=\frac{i}{2}(a_1+\sqrt{a_1^2+4b_1^2}),\ \ c=1+i\sqrt{a_1^2+4b_1^2} \tag{5.22}$$

and the function $\Psi(a,c,ia_2X)$ is the Ψ-confluent hypergeometric function [18]. The solution (5.21) has the suitable asymptotic behavior as

$$\lim_{X\to\infty}|\tilde{\psi}_1|^2=\exp\left[\frac{\pi}{2}(a_1+\sqrt{a_1^2+4b_1^2})\right]. \tag{5.23}$$

The second diabatic function takes the form

$$\tilde{\psi}_2=ib_1X^{-ia_1+a}e^{-ia_2X}\Psi(a+1,c,ia_2X), \tag{5.24}$$

which satisfies the following boundary condition:

$$\lim_{X\to\infty}\tilde{\psi}_2=0. \tag{5.25}$$

The above boundary conditions given by Eqs. (5.23) and (5.25) enable us to write the nonadiabatic transition probability as

$$\begin{aligned}P=&\exp\left[-\frac{\pi}{2}(a_1+\sqrt{a_1^2+4b_1^2})\right]\\&\times\lim_{X\to\infty}\left|\sin\Theta(X)\Psi(a,c,ia_2X)+ib_1\cos\Theta(X)\right.\\&\left.\times\Psi(a+1,c,ia_2X)\right|^2,\end{aligned} \tag{5.26}$$

which, with the help of the asymptotic formula of the Ψ-confluent hypergeometric function [18], leads to the following final compact expression:

$$P=\exp\left[-\frac{\pi}{2}(a_1+\sqrt{a_1^2+4b_1^2})\right]\frac{\sinh\frac{\pi}{2}(\sqrt{a_1^2+4b_1^2}-a_1)}{\sinh\pi\sqrt{a_1^2+4b_1^2}}. \tag{5.27}$$

This formula gives the nonadiabatic transition probability for the crossing ($a_1<0$) and noncrossing ($a_1>0$) diabatic potentials. However, the probability P is exponentially small when the collision energy tends to zero. This indicates that the *asymptotic nonadiabatic transition* is absent in this model in accordance with the discussion in Sec. IV A.

The inverse power potential models that satisfy the condition of Sec. IV B and induce the *asymptotic nonadiabatic transitions*, are given by the condition

$$l=\frac{3k-1}{2}, \tag{5.28}$$

which can be solved in terms of the parabolic cylinder type functions.

VI. CONCLUSION

A new type of nonadiabatic transition between two asymptotically degenarate potentials has been found, analyzed, and formulated semiclassically and quantum mechanically. The conditions for the appearance of this type of transition were clarified. The model of the Morse type potentials coupled by an exponential function was mainly utilized for the analysis, but some other potential forms were also employed to formulate the general conditions. It was shown that the transition depicts an interesting power-law type of energy dependence at low energies. This is quite a unique property in contrast with the ordinary types of nonadiabatic transitions. Probably, more attention should be paid to this type of transition in various practical collision processes. The explicit expression of the asymptotic nonadiabatic transition matrix was obtained. This describes the localized transition between two degerate states in asymptotic region and thus, as for the similar matrices for the other types of transitions [8,9,10], this can be used for other general even multichannel problems. It is, however, more desirable to express this matrix in a more general form, namely, not in terms of the particular parameters of model potentials but in terms of adiabatic potentials. This requires a further study.

ACKNOWLEDGMENTS

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area ''Molecular Physical Chemistry'' and Grant No. 10440179 from The Ministry of Education, Science, Culture, and Sports of Japan.

[1] E. E. Nikitin and S. Ya. Umanski, *Theory of Slow Atomic Collisions* (Springer-Verlag, Berlin, 1984).
[2] M. S. Child, *Molecular Collision Theory* (Academic, London, 1974).
[3] M. S. Child, *Semiclassical Mechanics with Molecular Applications* (Oxford University, London, 1991).
[4] D. S. F. Crothers, Adv. Phys. **20**, 405 (1971).
[5] E. S. Medvedev and V. I. Osherov, *Radiationless Transitions in Polyatomic Molecules*, Springer Series in Chemical Physics Vol. 57 (Springer-Verlag, Berlin, 1994).
[6] H. Nakamura, Int. Rev. Phys. Chem. **10**, 123 (1991).
[7] H. Nakamura, Adv. Chem. Phys. **82**, 243 (1992).
[8] H. Nakamura, in *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. Zhang (Marcel-Dekker, New York, 1996).
[9] H. Nakamura and C. Zhu, Comments At. Mol. Phys. **32**, 249 (1996).
[10] C. Zhu, Y. Teranishi, and H. Nakamura, Adv. Chem. Phys. **117**, 127 (2001).
[11] V. I. Osherov and H. Nakamura, J. Chem. Phys. **105**, 2770 (1996).
[12] V. I. Osherov and H. Nakamura, Phys. Rev. A **59**, 2486 (1999).
[13] V. I. Osherov, V. G. Ushakov, and H. Nakamura, Phys. Rev. A **57**, 2672 (1997).
[14] L. Pichl, V. I. Osherov, and H. Nakamura, J. Phys. A **33**, 3361 (2000).
[15] H. C. Longuet-Higgins, Adv. Spectrosc. (N.Y.), **2**, 429 (1961).
[16] A. Barany and D. S. F. Crothers, Proc. R. Soc. London, Ser. A **385**, 129 (1983).
[17] D. S. F. Crothers, J. Phys. B **9**, 635 (1976).
[18] A. Erdelyi, *Higher Transendental Functions* (Krieger, Malabar, 1981).
[19] L. Felsen and N. Marcuvitz, *Radiation and Scattering of Waves* (IEEE Press, New Jersey, 1994) Vol. 2.
[20] Yu. N. Demkov, V. N. Ostrovskii, and E. A. Solov'ev, Phys. Rev. A **18**, 2089 (1978).
[21] M. Born and V. Fock, Z. Phys. **51**, 165 (1928).
[22] Y. Luke, *Mathematical Functions and Their Applications* (Academic, New York, 1975).