NONADIABATIC TRANSITIONS DUE TO CURVE CROSSINGS: COMPLETE SOLUTIONS OF THE LANDAU–ZENER–STUECKELBERG PROBLEMS AND THEIR APPLICATIONS

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CONTENTS

I. Introduction

II. Physical Significance of Level Crossing

III. Complete Solutions of the Two-State Landau–Zener–Stueckelberg Problems
   A. Brief Historical Survey
   B. Complete Solutions
      1. Landau–Zener Case
      2. Nonadiabatic Tunneling Case

IV. How to Deal with Multichannel and Multidimensional Problems
   A. Multichannel Processes
      1. General Framework
      2. Numerical Applications
   B. Multidimensional Problems

V. Other Models
   A. Exponential Potential Model
   B. Rosen–Zener–Demkov Model ($\beta_1 = \beta_2 = 0$)
   C. Special Cases of Exponential Potential Model ($\beta_1 = (1/\beta_2)$)
   D. Remarks

VI. Time-Dependent Level Crossings
   A. Complete Solutions of the Quadratic Model
   B. Generalizations and Applications
   C. Other Models

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I. INTRODUCTION

As will be explained in more detail in Section II, nonadiabatic transition due to potential curve crossing presents a very important fundamental mechanism of state and/or phase changes in various fields of natural sciences. Without nonadiabatic transition, this world would have been dead, because no basic chemical and biological processes, such as electron and proton transfer, could have occurred. Nonadiabatic transition is certainly an origin of mutability of this world. Because of the importance of nonadiabatic transition in all branches of natural sciences, a lot of theoretical studies have been carried out to formulate this phenomenon. The pioneering work was done independently by Landau [1], Zener [2], and Stueckelberg [3] for the two-state curve crossing problem in the same year of 1932. Interestingly, the basic theory for the two-state noncurve crossing problem was also first formulated by Rosen and Zener (RZ) [4] in the same year. These pioneering works initiated the subsequent big flow of theoretical studies of nonadiabatic transitions covering a lot of quantum mechanical, semiclassical, and numerical investigations. Readers should refer to recent books and review articles [5–11].

In spite of these numerous efforts in the last 60 years some essential problems have remained unsolved. First of all, no good formulas were available to evaluate nonadiabatic transition probabilities at energies near or lower than the crossing point that represents the physically and chemically important region. In that energy region, the nonadiabatic transition probability takes the value of the order 0.5 in many cases. The celebrated Landau–Zener formula cannot work in this energy region and behaves correctly only in high energies. Second, no theory could work well for the entire region of coupling strength and actually no good theory was available at all in the region of strong diabatic coupling. Third, in the conventional theory nonunique diabatization procedure and the inconvenient complex contour integral, which is quite annoying for nonspecialist users, were required. Furthermore, various phases, which play important roles in many cases, were not necessarily provided properly.

Starting with the most basic linear potential model, in which the two diabatic potentials are linear functions of the spatial coordinate and the diabatic coupling
is a constant, Zhu and Nakamura [12–23] have solved all the above mentioned problems for the first time in 60 years since the pioneering works was done by Landau, Zener, and Stuckelberg [1–3]. They have not only obtained the quantum mechanically exact analytical solutions for the two-state linear potential model [12, 13], but also carried out the semiclassical analysis carefully to derive a useful set of compact semiclassical analytical solutions for the linear potential model [14–16]. Based on these solutions, they further extended the theory to present a complete set of compact analytical solutions that are applicable to general two-state curved potential systems. The theory can cover both the Landau–Zener (LZ) case [17, 18], in which the two diabatic potentials cross with the same sign of slopes, and the nonadiabatic tunneling (NT) case [19, 20], in which the two diabatic potentials cross with the opposite slope signs and create a potential barrier. In the LZ case, the whole energy range is divided into two regions: (1) higher and (2) lower than the crossing energy, for each of which compact analytical formulas are obtained not only for the nonadiabatic transition probability but also for the various phases. In the NT case, three energy regions are considered (1) higher than the bottom of the upper adiabatic potential, (2) lower than the top of the lower adiabatic potential, and (3) the region in between. All necessary quantities are expressed in terms of real-phase integrals along adiabatic potentials on the real axis. The two basic parameters designated as $a^2$ and $b^2$, which were originally defined in terms of the diabatic coupling and slopes of the diabatic potentials, can be determined in the final version of the theory from shapes of the adiabatic potentials on the real axis in the vicinity of the avoided crossing. The theory is not only very simple but also very accurate and should be very useful for practical applications. The parameter $a^2$ represents the effective coupling strength and turns out to be a very important parameter to judge the overall significance of the nonadiabatic transition. The parameter $b^2$ represents the energy effectively; $b^2 = 0$ corresponds to the crossing point. Very interestingly, the theory does not require any information on the nonadiabatic coupling and everything can be estimated only from the adiabatic potentials on the real axis. Furthermore, the following semiclassical idea has been confirmed to work well [17, 19, 21–23]: the whole molecular process, whatever it is, involving nonadiabatic transitions, can be decomposed into a series of basic phenomena that include nonadiabatic transition at avoided crossing, wave propagation along the adiabatic potential, reflection at the turning point, potential barrier penetration, and so on. The present theory presents, of course, the transition probability amplitude including phases at the avoided crossing. We know how to deal with the other elements mentioned above and the corresponding matrices can be easily incorporated. In the case of inelastic scattering, we can formulate the scattering matrix by incorporating the nonadiabatic transition matrix that we call the $I$ matrix. In the case of elastic scattering with resonance due to nonadiabatic transition, the elastic scattering phase shift can be
formulated. In the case of the bound state problem involving nonadiabatic transition, a secular matrix equation can be obtained. That is to say, whenever nonadiabatic transitions are involved in whatever the problem, the present theory can be nicely incorporated into the framework and should work well. These achievements are summarized in recent review articles [21–23].

The next natural question is whether this new theory can be applied to general multichannel and even multidimensional problems, since this is very important in view of the applications to various practical problems in chemical dynamics beyond simple diatomic systems. As can be easily conjectured from the above explanation, in the case of multichannel problems each avoided crossing is treated independently by the two-state theory and the whole problem can be formulated by combining all of them. Namely, by incorporating the two-state $I$ matrices, any problem such as elastic or inelastic scattering with or without resonances and multichannel bound state problems can be formulated. Zhu and Nakamura [24, 25] actually demonstrated that their theory works very well in multichannel problems, nicely reproducing even heavily overlapping resonances in the NT case. This means that not only the nonadiabatic transition probability but also the various phases can be accurately estimated by the theory. The theory works surprisingly well even when two avoided crossings lie very close together and the nonadiabatic couplings overlap significantly on the real axis. This is because the new two-state theory takes into account the analytical structure of the problem correctly. The next challenging application is, of course, treatment of multidimensional problems. There are two possible ways of treating multidimensional problems: (1) reduction of the problem into a one-dimensional (1D) multichannel system by expanding the total wave function in terms of appropriate internal state wave functions, and (2) direct treatment of the problem by using classical trajectories in an appropriate way. The first one is more accurate naturally, because we do not rely on classical trajectories. But, from the view point of applications to a variety of chemical dynamical processes such as electronically nonadiabatic chemical reactions in higher dimensions, the second method with inclusion of important quantum mechanical effects such as interference and tunneling would be much more promising. As an example of the first method, Zhu et al. [26] analyzed the electronically adiabatic three-dimensional (3D) chemical reactions, $O(^3\text{P}) + \text{HCl} \rightarrow \text{OH} + \text{Cl}$ and $\text{Cl} + \text{HBr} \rightarrow \text{HCl} + \text{Br}$, fully analytically with use of the Zhu–Nakamura theory within the framework of the hyperspherical coordinate approach. They treated $> 100$ channels and almost 1000 avoided crossings. The parameter $a^2$ can be usefully utilized to pick up important avoided crossings; actually $\sim 100$ avoided crossings are found to be important and are treated analytically by the theory. The cumulative reaction probabilities are nicely reproduced by the theory. For the more important second method, theoretical studies have just started. The nonadiabatic transition matrix $I$ can be
incorporated into various semiclassical propagation schemes such as trajectory surface hopping (TSH), the semiclassical method based on initial value representation (IVR), and cellular frozen Gaussian wave packet propagation (CFGW) method [27–30]. In the case of TSH, only the probabilities are required, but in the other methods, phases also play important roles. Since the new theory of nonadiabatic transition is very simple and accurate, it is expected that the combination of the second or the third semiclassical propagation method with the new theory could present a nice practically useful methodology to attack large chemical dynamical systems.

Based on the exponential potential model of Nikitin [6], which can cover the LZ and RZ formulas in certain limits, further studies of various exponential potential models have been carried out in an attempt to hopefully formulate a unified theory [31–34].

So far, we have been discussing the time-independent framework of nonadiabatic transitions. In view of the recent remarkable progress of laser technology, however, a time-dependent version of nonadiabatic transitions has attracted much attention and is gaining importance more and more than before. Since it is possible to create new curve crossings by shifting energy levels up and down with use of the time-dependent external fields and also to vary the diabatic coupling strength there by changing the field strength, it is probably easily understood that various versions of time-dependent nonadiabatic transitions become very important in this sense. The importance is more emphasized because of the possibility of controlling molecular processes by manipulating external fields. Time-dependent theory of nonadiabatic transitions is, however, simpler than the time-independent one. This is simply because time is unidirectional and the time-dependent Schrödinger equation is just a first-order differential equation. Since the Zener's treatment of the time-dependent linear potential model [2], various types of time-dependent nonadiabatic transition models have been proposed and solved such as Demkov–Osherov multilevel problem, band-crossing model, Demkov–Kunike model, exponential model, and bowtie model [35–43]. The new time-independent theory developed by Zhu and Nakamura can also be transferred to the time-dependent version. Actually, the exact solution of the time-independent linear potential model can provide the exact solution for the time-dependent quadratic potential model, and thus the whole set of the Zhu–Nakamura theory can be easily transferred to the time-dependent framework [44]. Corresponding to the fact that the theory can deal with the energy region near and lower than the crossing point, the time-dependent version can treat the cases of tangential touching and diabatic avoided crossing of two diabatic potentials. These time-dependent theories can be nicely used to control molecular processes based on the dressed or Floquet state representation [45]. Actually, Teranishi and Nakamura [45, 47] proposed a new idea of controlling nonadiabatic processes by sweeping the frequency and/or the intensity of the external
field. The control conditions can be formulated analytically with the help of the theory of time-dependent nonadiabatic transitions.

In this chapter, we will explain in more detail what has been outlined above. In Section II, the significance of nonadiabatic transitions in natural sciences are emphasized more. In Section III, the complete solutions of the two-state Landau–Zener–Stueckelberg (LZS) problems by Zhu and Nakamura are summarized together with a brief description of history. The final set of practically useful formulas are presented. Applications of the theory to multichannel and multidimensional problems are discussed in Section IV. Other types of nonadiabatic transitions are explained in Section V. Time-dependent theories of nonadiabatic transitions are presented in Section VI, and a new way of controlling molecular processes by time-dependent external fields is discussed in Section VII. Future perspectives are mentioned in Section VIII.

II. PHYSICAL SIGNIFICANCE OF LEVEL CROSSING

As was briefly mentioned in the introduction, it is needless to say that nonadiabatic transitions due to energy level or curve crossings play very crucial roles in various branches of natural sciences, representing an origin of mutability of this universe. Especially, the nonadiabatic transitions in the NT type curve crossing, in which two diabatic potentials cross with opposite signs of slope and create a potential barrier in the lower adiabatic potential curve, must play a significant role in various fields, inducing changes of state, conformation, and phase.

The best known examples are, of course, collision and spectroscopic processes in atomic and molecular physics, which occur most effectively through potential curve crossings. Needless to say, all kinds of chemical dynamics proceed effectively only through potential energy surface crossings. Even organic chemical reactions are tried to be classified in terms of curve crossing schemes [48]. Electron and proton transfer, which play significant roles in chemical and biological systems, are nothing but a curve crossing problem in which the ordinate is not the ordinary potential energy but free energy [49, 50]. In solid-state physics, there are also many examples such as desorption of molecules from a solid surface [51], ion neutralization in collision with a solid surface [52], quenching of color center [53, 54], self-trapped localized state of exciton [55], and many other nonradiative energy relaxation processes in solids [56]. In many of these processes in condensed medium, the abscissa is some sort of renormalized coordination coordinate. Nuclear collision and reaction mechanisms are also often clarified in terms of potential curve crossings based on the picture of a nuclear molecular orbital [57]. Curve crossings represent, on the other hand, one of the causes to create quantum chaotic behavior [58].
If we assume the adiabatic parameter (which is usually a certain nuclear coordinate in the above examples) to be a classical time-dependent variable, then the nonadiabatic transition processes are transformed into time-dependent problems. On the other hand, when we explicitly apply time-dependent external fields to various systems, there arise a variety of intrinsically time-dependent nonadiabatic transition problems. Molecular processes in laser fields are one of the most typical examples. Within the picture of the dressed or Floquet state, dynamic processes due to artificially created curve crossings can be induced and thus it becomes possible to control those dynamic processes by manipulating the external fields. Controlling molecular processes by lasers has actually become an attractive and important subject nowadays. There are many other examples of time-dependent nonadiabatic transitions induced by external fields such as quantum mechanical effects in current driven Josephson junctions in a magnetic field and Zener transitions in flux-driven normal metallic rings or current biased tunnel junctions in a magnetic field, and quantum spin tunneling in a magnetic field. Even electron spin resonance (ESR) and nuclear magnetic resonance (NMR) can be considered as time-dependent nonadiabatic transitions. The neutrino conversion among various kinds of neutrinos is a subject attracting much attention recently in elementary particle physics. This is again an example of time-dependent nonadiabatic transition in which the ordinate is the neutrino mass squared specifying different kinds of neutrinos and the abscissa is a time-dependent electron density in the matter through which the neutrinos fly.

As explained above, nonadiabatic transitions appear in all branches of the natural sciences and actually play crucial roles there. The concept of nonadiabatic transition is very deep and multidisciplinary. The concept can also be applied to social sciences, for instance, to economics. We can find and encounter many examples of nonadiabatic transitions even in daily life.

III. COMPLETE SOLUTIONS OF THE TWO-STATE LANDAU–ZENER–STUECKELBERG PROBLEMS

A. Brief Historical Survey

The simplest two-state curve crossing model was discussed independently, for the first time, by Landau, Zener, and Stueckelberg. Landau dealt with the time-independent problem by using the perturbation theory and the complex integral method through which the exponent of the nonadiabatic transition probability was expressed. This complex integral method is now called the Landau method. The simplest linear potential model in the time domain was solved exactly by Zener. When we apply various approximations such as linear diabatic potentials, constant diabatic coupling, and the straight-line trajectory with
constant velocity for the relative motion to Landau's expression of nonadiabatic
transition probability, then we can get the same probability expression as that of
Zener, which is now known as the Landau–Zener formula. Stueckelberg ana-
lyzed the general two-state time-independent problem by using the WKB
(Wentzel–Kramers–Brillouin) type semiclassical phase-integral method. He
obtained the overall transition probability for the whole collision process, which
includes the phase interference effect due to the two possible paths. This phase
is now called the Stueckelberg phase. The LZS theory has been reviewed and
further extended by many authors since their pioneering works in 1932. In spite
of such numerous efforts, however, the semiclassical theory has not been com-
plete and has many problems, as mentioned in the introduction [5–11].

B. Complete Solutions

Let us start with the basic coupled equations for the two-state curve crossing
problems in the diabatic representation:

\[
\left( \frac{\hbar^2}{2\mu} \right) \frac{d^2\psi_1(R)}{dR^2} + [E - V_{11}(R)]\psi_1(R) = V_{12}(R)\psi_2(R) \tag{3.1}
\]

and

\[
\left( \frac{\hbar^2}{2\mu} \right) \frac{d^2\psi_2(R)}{dR^2} + [E - V_{22}(R)]\psi_2(R) = V_{21}(R)\psi_1(R) \tag{3.2}
\]

where \( \mu \) is the reduced mass of the system and \( R \) is a spatial coordinate defined
in the region \( 0 < R < +\infty \). This region is not essential, because the most
important quantity is the nonadiabatic transition matrix at the avoided crossing,
which can be used even if the potentials extend to \(-\infty\). The coupling terms are
symmetric, \( V_{12}(R) = V_{21}(R) \). In this chapter, we present our semiclassical the-
ory in adiabatic representation. For this purpose, what we need is just the
following two adiabatic potentials,

\[
E_2(R) = \frac{1}{2}[V_{22}(R) + V_{11}(R)] + \frac{1}{2}\sqrt{[V_{22}(R) - V_{11}(R)]^2 + 4V_{12}^2(R)} \tag{3.3}
\]

and

\[
E_1(R) = \frac{1}{2}[V_{22}(R) + V_{11}(R)] - \frac{1}{2}\sqrt{[V_{22}(R) - V_{11}(R)]^2 + 4V_{12}^2(R)} \tag{3.4}
\]

As explained before, there are two types of avoided crossings shown in
Figure 1: one is the LZ type and the other is the NT type.
Figure 1. (a) Schematic two-state adiabatic potentials for inelastic scattering in the LZ case. (b) Schematic two-state adiabatic potentials for transmission and reflection in the NT case.
In the LZ case we choose \( R_0 \), which corresponds to the minimum separation between the two adiabatic potentials as a reference point. The WKB type of wave functions for Eqs. (3.1) and (3.2) can be written in the form,

\[
\psi_1 (R) = \frac{A_1}{\sqrt{K_1 (R)}} e^{i \int_{r_1}^R K_1 (R) dR - i (\pi/4)} + \frac{B_1}{\sqrt{K_1 (R)}} e^{-i \int_{r_1}^R K_1 (R) dR + i (\pi/4)}
\]

(3.5)

and

\[
\psi_2 (R) = \frac{A_2}{\sqrt{K_2 (R)}} e^{i \int_{r_2}^R K_2 (R) dR - i (\pi/4)} + \frac{B_2}{\sqrt{K_2 (R)}} e^{-i \int_{r_2}^R K_2 (R) dR + i (\pi/4)}
\]

(3.6)

at \( R \gg R_0 \) [see Fig. 1(a)], where \( T_i (i = 1, 2) \) is the turning point on the adiabatic potential \( E_i (R) \) and

\[
K_i (R) = \frac{\sqrt{2 \mu}}{\hbar} \sqrt{E - E_i (R)} \quad i = 1, 2
\]

(3.7)

The reduced \( S \) matrix, \( S^R \), can be defined by

\[
\begin{pmatrix}
A_1 \\
A_2
\end{pmatrix}
= \begin{pmatrix}
S^R_{11} & S^R_{12} \\
S^R_{21} & S^R_{22}
\end{pmatrix}
\begin{pmatrix}
B_1 \\
B_2
\end{pmatrix} \equiv S^R \begin{pmatrix}
B_1 \\
B_2
\end{pmatrix}
\]

(3.8)

which includes all the necessary information about nonadiabatic transitions. A simple manipulation can prove that \( S^R \) satisfies [71, 72]

\[
S^R_{11} = (S^R_{22})^* \quad \text{and} \quad S^R_{12} = (S^R_{21})^* = \text{pure imaginary}
\]

(3.9)

The scattering matrix \( S \) in the semiclassical theory is written as [73]

\[
S_{mn} = S^R_{mn} \exp [i (\eta_m + \eta_n)] \quad n, m = 1, 2
\]

(3.10)

where \( \eta_n \) represents the WKB phase shift for elastic scattering in the channel \( n \), and is well defined as

\[
\eta_n = \lim_{R \to \infty} \left[ \int_{r_i}^R K_1 (R) dR - K_1 (R) R + \frac{\pi}{4} \right]
\]

(3.11)
and

\[ \eta_2 = \lim_{R \to \infty} \left[ \int_{R}^{\infty} K_2(R)dR - K_2(R)R + \frac{\pi}{4} \right] \] (3.12)

Under the two-state linear curve crossing model, Zhu et al. [13] for the first time, derived the exact quantum mechanical solution, which is expressed in terms of one parameter, \( U_1 \), called the Stokes constant in mathematics [74],

\[ S^R = \begin{pmatrix} (1 + U_1 U_2)e^{-2\sigma} & -U_2 \\ -U_2 & (1 - U_1^* U_2)e^{2i\sigma} \end{pmatrix} \] (3.13)

where

\[ U_2 = \frac{U_1 - U_1^*}{1 + |U_1|^2} \] (3.14)

with

\[ U_1 = U_1(a^2, b^2; \sigma, \delta) \] (3.15)

The overall nonadiabatic transition probability is given by

\[ P_{12} = |S_{12}^R|^2 = \frac{4(\text{Im } U_1)^2}{(|U_1|^2 + 1)^2} = 4p(1 - p) \sin^2 \psi \] (3.16)

with

\[ \psi = \arg(U_1) \] (3.17)

and

\[ p = \frac{1}{1 + |U_1|^2} \] (3.18)

The exact quantum solution for \( U_1 \) was obtained as a convergent infinite series as a function of the two parameters \( a^2 \) and \( b^2 \) defined below, but its form is not very convenient for practical applications to the general two-state curve crossing problems (an explicit expression of \( U_1 \) is not given here [13]). In the case of the two-state linear model, they can be expressed only in terms of \( a^2 \) and \( b^2 \). In order to generalize the theory so as to be applicable to general curved potentials,
we have carefully analyzed the expression of $U_1$ and divided the roles of the
parameters into two parts: a portion directly responsible for nonadiabatic
transition and a portion responsible for phases. In the case of general curved
potentials, the first part can still be expressed in terms of $a^2$ and $b^2$, and the
second part was rewritten in terms of phase integrals $\sigma$ and $\delta$, whose definitions
are given below. By generalizing the expressions of $\sigma$ and $\delta$ as phase integrals
along curved adiabatic potentials, the theory became applicable to general
cases.

The two dimensionless parameters $a^2$ and $b^2$ are originally defined as follows
in terms of diabatic potentials:

$$a^2 = \left( \frac{\hbar^2}{2m} \right) \frac{F(F_1 - F_2)}{8V_X^3}$$

(3.19)

and

$$b^2 = (E - E_X) \frac{F_1 - F_2}{2FV_X}$$

(3.20)

with $F = \sqrt{|F_1 F_2|}$, where $F_i$ ($i = 1, 2$), $V_X$, and $E_X$, all of which are defined at
the crossing point, represent the slope of $V_i(R)$, diabatic coupling, and energy,
respectively. In our semiclassical theory, however, these parameters can be
reexpressed in terms of adiabatic potentials $[17]$

$$a^2 = \sqrt{d^2 - 1} \frac{\hbar^2}{\mu(T_2^0 - T_1^0)^2[E_2(R_0) - E_1(R_0)]}$$

(3.21)

and

$$b^2 = \sqrt{d^2 - 1} \frac{E - [E_2(R_0) + E_1(R_0)]/2}{[E_2(R_0) - E_1(R_0)]/2}$$

(3.22)

where

$$d^2 = \frac{[E_2(T_2^0) - E_1(T_1^0)] [E_2(T_2^0) - E_1(T_2^0)]}{[E_2(R_0) - E_1(R_0)]^2}$$

(3.23)

This means that the theory does not require diabatization. Here, $a^2$ represents
effective nonadiabatic coupling strength; $a^2 \to 0(\infty)$ corresponds to the adia-
batic (diabatic) limit. These two limiting cases are dynamically not interesting,
because everything proceeds either adiabatically or diabatically. The most
effective range for nonadiabatic transition lies in $0.01 \leq a^2 \leq 100$. The parameter $b^2$ in Eq. (3.22) represents effective collision energy, and when $b^2 > 0 (b^2 < 0)$ corresponds to the energy higher (lower) than the crossing point: thus $b^2 < 0$ is a nonadiabatic transition accompanied by tunneling. Definitions of $T_1^{(0)}$ and $T_2^{(0)}$ are given by [see Fig. 1(a)]

$$E_X = \frac{[E_2(R_0) + E_1(R_0)]}{2} = E_2(T_2^{(0)}) = E_1(T_1^{(0)})$$  

(3.24)

where $E_X$ represents the crossing energy as mentioned above.

In the NT case, the WKB type of wave function on the lower adiabatic potential $E_1(R)$ [see Fig. 1(b)] can be written as

$$\psi_1(R) = \frac{A_1}{\sqrt{K_1(R)}} e^{i \int_{R_1}^{R} K_i(R) dR - i(\pi/4)} + \frac{B_1}{\sqrt{K_1(R)}} e^{-i \int_{R_1}^{R} K_i(R) dR + i(\pi/4)}$$  

(3.25)

and

$$\psi_2(R) = \frac{B_2}{\sqrt{K_2(R)}} e^{i \int_{R_1}^{R} K_i(R) dR + i(\pi/4)} + \frac{A_2}{\sqrt{K_2(R)}} e^{-i \int_{R_1}^{R} K_i(R) dR - i(\pi/4)}$$  

(3.26)

where $K_i(R)$ ($i = 1, 2$) is defined in Eq. (3.7). Two reference points in Eqs. (3.25) and (3.26) are chosen as turning points $t_1'$ and $t_1''$ on the lower adiabatic potential $E_1(R)$ at $E \leq E_t$, where $E_t$ represents the top of the lower adiabatic potential. If $E \geq E_t$, the reference points are fixed at $R = R_t$. Now, let us define the reduced scattering matrix as

$$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} S_{11}^R & S_{12}^R \\ S_{21}^R & S_{22}^R \end{pmatrix} \begin{pmatrix} B_1 \\ B_2 \end{pmatrix} \equiv S^R \begin{pmatrix} B_1 \\ B_2 \end{pmatrix}$$  

(3.27)

Again, the simple manipulation proves [75]:

$$|S_{11}^R| = |S_{22}^R| \quad \text{and} \quad S_{12}^R = S_{21}^R$$  

(3.28)

under the two-state linear curve crossing model. Note that Eq. (3.9) for the LZ case differs from Eq. (3.28) for the NT case. It should be noted that the $S$ matrix here represents the transmission amplitude on the lower adiabatic potential.
Exact quantum solution was found again to be expressed in terms of one Stokes constant $U_1$ [13]:

$$S^R = \frac{1}{1 + U_1 U_2} \left( \begin{array}{cc}
U_1 e^{i\Delta_1} & U_2 e^{i\Delta_2} \\
U_2 e^{i\Delta_1} & e^{i\Delta_2} 
\end{array} \right)$$  (3.29)

where

$$U_2 = \frac{U_1 - U_1^*}{|U_1|^2 - 1}$$  (3.30)

with

$$U_1 = U_1(a^2, b^2; \sigma, \delta)$$  (3.31)

The additional phases $\Delta_1, \Delta_2$, and $\Delta_1$ are defined later. As in the LZ case, $U_1$ is expressed only in terms of $a^2$ and $b^2$ in the linear potential model, but was generalized by introducing $\sigma$ and $\delta$. The overall transmission probability is given by

$$P_{12} = |S^R_{12}|^2 = \frac{4(\text{Im } U_1)^2}{(|U_1|^2 - 1)^2 + 4(\text{Im } U_1)^2} = \frac{4\cos^2 \psi}{4\cos^2 \psi + p^2/(1 - p)} \quad \text{for } b^2 \geq 1$$  (3.32)

with

$$p = 1 - |U_1|^2 \quad \text{for } b^2 \geq 1$$  (3.33)

and

$$\psi = \text{arg}(U_1) - \pi/2$$  (3.34)

The scattering matrix $S$ in the semiclassical theory is written as [73]

$$S_{nm} = S^R_{nm} \exp[i(\eta_m + \eta_n)] \quad n, m = 1, 2$$  (3.35)

where $\eta_n$ represents the WKB phase shift for elastic scattering in the channel $n$, and is given by

$$\eta_n = \lim_{R \to R_n} \left[ \int_{R_n}^R K_1(R) dR - K_1(R)R + \frac{\pi}{4} \right]$$  (3.36)
and

\[
\eta_2 = \lim_{R \to t_i'} R \left[ - \int_{t_i}^{R} K_1(R) dR + K_1(R) R + \frac{\pi}{4} \right] \quad (3.37)
\]

Note that \( t_i' \) and \( t_i' \) must be replaced by \( R_i \) if \( E \geq E_i \). The original definitions of the two basic dimensionless parameters \( a^2 \) and \( b^2 \) are the same as before in diabatic representation; but in our semiclassical theory these are again re-expressed in terms of the adiabatic potentials as \([19]\)

\[
a^2 = \frac{(1 - \gamma^2) \hbar^2}{\mu (R_b - R_i)^2 (E_b - E_i)} \quad (3.38)
\]

and

\[
b^2 = \frac{E - (E_b + E_i)/2}{(E_b - E_i)/2} \quad (3.39)
\]

where

\[
\gamma = \frac{E_b - E_i}{E_2 \left( \frac{R_b + R_i}{2} \right) - E_1 \left( \frac{R_b + R_i}{2} \right)} \quad (3.40)
\]

Definitions of \( R_b, R_i \) and \( E_b, E_i \) are shown in Fig. 1(b). The physical meaning of \( a^2 \) and \( b^2 \) are the same as in the LZ case mentioned before. In the two-state linear curve crossing model, the exact quantum solution of the Stokes constant \( U_1 \) is again obtained in an infinite series and is not very convenient for general cases; but it still provides a unique basis for generalization and for checking the validity of the semiclassical solution. The LZS type of nonadiabatic transition corresponds to the Stokes phenomenon in the four-transition-point asymptotic expansion problem in mathematics \([13, 74]\). Although we have solved this problem exactly in the case of the linear potential model, the final expression is not simple and not very convenient as mentioned above. In the semiclassical approximation, we have treated the four transition points as two pairs of two transition points, since the two-transition-point problem is exactly solved in terms of the Weber function. The semiclassical theory thus derived by Zhu and Nakamura \([19]\) works very well even when the two pairs come close together, but naturally does not work well when the two-pair structure disappears and the four points almost coalesce. This extreme situation occurs at \( a^2 \gg 1 \) at \( b^2 \sim 0 \). In order to cover even this kind of situation uniformly, we have introduced certain empirical corrections. In Section III.B.1, we present our
compact semiclassical solutions directly applicable to the two-state general curved potentials.

1. Landau–Zener Case

a. $E \geq E_X(b^2 \geq 0)$. The Stokes constant $U_1$ in Eq. (3.15) can be written in the form

$$U_1 = \sqrt{\frac{1}{p} - 1} e^{i\psi}$$  \hspace{1cm} (3.41)

where $p$ is the nonadiabatic transition probability for one passage of the crossing point and is given as

$$p = \exp \left[ -\frac{\pi}{4a} \left( \frac{2}{b^2 + \sqrt{b^4 + 0.4a^2 + 0.7}} \right)^{1/2} \right]$$  \hspace{1cm} (3.42)

The phase $\psi$ is given by

$$\psi = \sigma + \phi_s = \sigma - \delta + \frac{\delta}{\pi} \ln \left( \frac{\delta}{\pi} \right) - \arg \left( \frac{i}{\pi} \right) - \frac{\pi}{4}$$  \hspace{1cm} (3.43)

where the parameters $a^2$ and $b^2$ are defined in Eqs. (3.21) and (3.22), and two other parameters $\sigma$ and $\delta$ originally defined as the real and the imaginary part of the complex phase integral can now be expressed by the simple real quantities as follows [18]:

$$\sigma + i\delta = \left[ \int_{R_0}^{R_0} K_-(R)dR - \int_{R_0}^{R_0} K_+(R)dR \right] + \sigma_0 + i\delta_0$$  \hspace{1cm} (3.44)

with

$$\sigma_0 + i\delta_0 \equiv \int_{R_0}^{R_0} [K_-(R) - K_+(R)]dR \simeq \frac{1}{\sqrt{a^2}} \frac{\sqrt{2\pi}}{4} \frac{1}{F^2_+ + F^2_-} [F_- + iF_+]$$  \hspace{1cm} (3.45)

where

$$F_{\pm} = \sqrt{\sqrt{(b^2 + \gamma_1)^2 + \gamma_2 \pm (b^2 + \gamma_1)} + \sqrt{(b^2 - \gamma_1)^2 + \gamma_2 \pm (b^2 - \gamma_1)}}$$  \hspace{1cm} (3.46)
NONADIABATIC TRANSITIONS DUE TO CURVE CROSSINGS

\[ F^c_+ = F_+ [b^2 \rightarrow (b^2 - b^2_c)] \quad \text{with} \quad b^2_c = \frac{0.16b_x}{\sqrt{b^2 + 1}} \quad (3.47) \]

\[ F^c_- = F_- (\gamma_2 \rightarrow \gamma'_2) \quad \text{with} \quad \gamma'_2 = \frac{0.45}{1 + 1.5e^{2.2b_x|b_1|^{0.57}}} \quad (3.48) \]

\[ b_x = b^2 - 0.9553 \quad (3.49) \]

and

\[ \gamma_1 = 0.9\sqrt{d^2 - 1} \quad \text{and} \quad \gamma_2 = \frac{7}{16}\sqrt{d^2} \quad (3.50) \]

where \(d^2\) is defined by Eq. (3.23). In deriving Eq. (3.45), \(R_0\) was found to be better as the reference point [18] than \(T_j^{(0)} (j = 1, 2)\) [see Fig. 1(a)], which was used previously [17]. In order to cover the very strong coupling region well, \(a^2 \leq 0.05\) at \(|b^2| < 1\), some empirical corrections are introduced as can be seen in Eqs. (3.47)-(3.50).

b. \(E \leq E_X (b^2 \leq 0)\). The reduced \(S\) matrix is given in the same way as before in terms of Stokes constant \(U_1\), but \(U_1\) itself is now given by

\[ \text{Re} \ U_1 = \cos (\sigma) \left\{ \sqrt{B(\sigma/\pi)}e^\delta - g_1 \sin^2 (\sigma) \frac{e^{-\delta}}{\sqrt{B(\sigma/\pi)}} \right\} \quad (3.51) \]

and

\[ \text{Im} \ U_1 = \sin (\sigma) \left\{ B(\sigma/\pi)e^{2\delta} - g_1^2 \sin^2 (\sigma) \cos^2 (\sigma) \frac{e^{-2\delta}}{B(\sigma/\pi)} + 2g_1 \cos^2 (\sigma) - g_2 \right\}^{1/2} \quad (3.52) \]

The nonadiabatic transition probability for one passage of the crossing point and the phase \(\psi\) are given by

\[ p = \left[ 1 + B(\sigma/\pi)e^{2\delta} - g_2 \sin^2 (\sigma) \right]^{-1} \quad (3.53) \]

and

\[ \psi = \arg (U_1) \quad (3.54) \]
where

\[ g_1 = 1.8(a^2)^{0.23} e^{-\delta} \]  \hspace{1cm} (3.55)

\[ g_2 = \frac{3\sigma}{\pi \delta} \ln(1.2 + a^2) - 1/a^2 \]  \hspace{1cm} (3.56)

and

\[ B(X) = \frac{2\pi X^{2X} e^{-2X}}{\Gamma^2(X)} \]  \hspace{1cm} (3.57)

where \( \Gamma(X) \) is the gamma function. The two parameters \( \sigma \) and \( \delta \) are given by Eq. (3.44).

c. \textit{I Matrix (for Both} \( b_2^2 \geq 0 \text{ and} \ b_2^2 \leq 0 \)). The reduced scattering matrix in Eq. (3.8) represents a full scattering process that actually includes both incoming and outgoing segments of the propagation. In order to apply the two-state theory to multichannel curve crossing problems, we can semiclassically extract the incoming part of propagation that is called the \( I \) matrix given by

\[
I = \begin{pmatrix}
\sqrt{1-p} e^{-i(\sigma-\Psi)} & -\sqrt{p} e^{i\sigma} \\
\sqrt{p} e^{-i\sigma} & \sqrt{1-p} e^{i(\sigma-\Psi)}
\end{pmatrix}
\]  \hspace{1cm} (3.58)

in the adiabatic representation. In the case of the two-state linear curve crossing model, we can directly compare the present Zhu–Nakamura formula for \( p \) in Eqs. (3.42) and (3.53) with the LZ formula in Figure 2. The Zhu–Nakamura formulas are much better than the LZ formula. In terms of the above \( I \) matrix, the reduced scattering matrix \( S^R \) can be rewritten as

\[ S^R = I^t I \quad (t = \text{transposed}). \]  \hspace{1cm} (3.59)

The nonadiabatic transition matrix \( I_X \) at the avoided crossing is given by

\[
I_X = \begin{pmatrix}
\sqrt{1-p} e^{i\phi, -(\Psi-\sigma)} & -\sqrt{p} e^{i\sigma_0} \\
\sqrt{p} e^{-i\sigma_0} & \sqrt{1-p} e^{-i\phi, -(\Psi-\sigma)}
\end{pmatrix}
\]  \hspace{1cm} (3.60)
In terms of this matrix, the total scattering matrix $S$ is expressed as

$$S = P_{\infty X} O_X P_{XTX} I_X P_{X\infty}$$  \hspace{1cm} (3.61)$$

where $P_{A\rightarrow B}$ is a diagonal matrix, representing the adiabatic wave propagation from B to A, and is defined as
\[(P_{\infty})_{nm} = (P_{\infty})_{nm} = \delta_{nm} \exp \left\{ i \int_{R_0}^{\infty} [K_n(R) - K_n(\infty)]dR - iK_n(\infty)R_0 \right\} \]  
\[(3.62)\]

and

\[(P_{\text{TX}})_{nm} = \delta_{nm} \exp \left[ 2i \int_{T_n}^{R_0} K_n(R)dR + \frac{i\pi}{2} \right] \]  
\[(3.63)\]

where \(T_n\) is the turning point on the \(n\)th adiabatic potential. Since the \(I_X\) matrix describes the transition locally at the avoided crossing, this would be useful in applications to multidimensional problems.

### 2. Nonadiabatic Tunneling Case

This case was treated in [19, 20].

\(a.\ E \geq E_h(b^2 \geq 1)\). The Stokes constant \(U_1\) in Eq. (3.31) is given by

\[U_1 = i\sqrt{1 - p} \ e^{i\psi} \]  
\[(3.64)\]

where the nonadiabatic transition probability for one passage of the crossing point takes the form

\[p = \exp \left[ -\frac{\pi}{4a} \left( \frac{2}{b^2 + \sqrt{b^4 - 0.72 + 0.62a^{1.43}}} \right)^{1/2} \right] \]  
\[(3.65)\]

and the phase \(\psi\) is given by

\[\psi = \sigma - \phi_s = \sigma + \frac{\delta}{\pi} - \frac{\delta}{\pi} \ln \left( \frac{\delta}{\pi} \right) + \arg \Gamma \left( \frac{\delta}{\pi} \right) + \frac{\pi}{4} \]  
\[(3.66)\]

in which \(\sigma\) and \(\delta\) are estimated from

\[\sigma = \int_{T_1}^{T_2} K_2(R)dR \]  
\[(3.67)\]
and

\[
\delta = \frac{\pi}{8ab} \frac{1}{2} \sqrt{6 + 10 \sqrt{1 - (1/b^4)}} \left( \frac{1}{1 + \sqrt{1 - (1/b^4)}} \right) \tag{3.68}
\]

Note that \(a^2\) and \(b^2\) in above equations are now defined in Eqs. (3.38) and (3.39). The additional phases appearing in Eq. (3.29) take the form

\[
\Delta_{11} = 2 \int_{T_1}^{R_b} K_2(R) dR - 2\sigma_0
\]

\[
\Delta_{22} = 2 \int_{T_2}^{R_b} K_2(R) dR + 2\sigma_0 \tag{3.69}
\]

and

\[
\Delta_{12} = \sigma \tag{3.70}
\]

with

\[
\sigma_0 = \left( \frac{R_b - R_t}{2} \right) \left\{ K_1(R_t) + K_2(R_b) + \frac{1}{3} \frac{[K_1(R_t) - K_2(R_b)]^2}{K_1(R_t) + K_2(R_b)} \right\} \tag{3.71}
\]

Note that the \(I\) matrix for the NT case can be defined only for \(b^2 \geq 1\) (i.e., \(E \geq E_b\)), and is given by

\[
I = \begin{pmatrix}
\sqrt{1 - \tilde{p}} e^{i\phi_1} & \sqrt{\tilde{p}} e^{i\sigma} \\
-\sqrt{\tilde{p}} e^{-i\sigma} & \sqrt{1 - \tilde{p}} e^{-i\phi_1}
\end{pmatrix} \tag{3.72}
\]

Here, it should be noted that the sign in off-diagonal elements of Eqs. (3.58) and (3.72) differ.

The \(I_X\) matrix is given in the same way as before [see Eq. (3.60)] as

\[
I_X = \begin{pmatrix}
\sqrt{1 - \tilde{p}} e^{i\phi_1} & \sqrt{\tilde{p}} e^{i\sigma_0} \\
-\sqrt{\tilde{p}} e^{-i\sigma_0} & \sqrt{1 - \tilde{p}} e^{-i\phi_1}
\end{pmatrix} \tag{3.73}
\]
The overall transmission probability is given by

\[ P_{12} = |\beta_{12}^R|^2 = \frac{4\cos^2\psi}{4\cos^2\psi + p^2/(1 - p)} \]  (3.74)

This indicates that an interesting phenomenon of complete reflection \( (P = 0) \) occurs at energies that satisfy \( \psi = (n + 1/2)\pi \) \( (n = 0, 1, 2, \ldots) \) and gives a possibility of molecular switching [76–78].

b. \( E_b \geq E \geq E_f \) \( (|b^2| \leq 1) \). In this case, the energy \( E \) is in between the two adiabatic potentials [see Fig. 1(b)]. The Stokes constant \( U_1 \) is given by

\[ U_1 = i\left[ \sqrt{1 + W^2e^{i\phi}} - 1 \right]/W \]  (3.75)

where

\[ \phi = \sigma + \arg\Gamma \left( \frac{1}{2} + i\frac{\delta}{\pi} \right) - \frac{\delta}{\pi} \ln \left( \frac{\delta}{\pi} \right) + \frac{\delta}{\pi} - g_3 \]  (3.76)

with

\[ g_3 = 0.34 \frac{a^{0.7}(a^{0.7} + 0.35)}{a^{2.1} + 0.73} \left( \frac{0.42 + b^2}{\frac{100b^2}{100 + a^2}} \right)^{0.25} \]  (3.77)

The quantity \( W \) in Eq. (3.75) is defined by

\[ W = \frac{1 + g_5}{a^{2/3}} \int_0^\infty \cos \left[ \frac{t^3}{3} - \frac{b^2}{2a^{2/3}t} - \frac{g_4}{0.61\sqrt{2 + b^2 + a^{1/3}t}} \right] dt \]  (3.78)

where

\[ g_4 = \frac{\sqrt{a^2 - 3b^2}}{\sqrt{a^2 + 3}} \sqrt{1.23 + b^2} \]  (3.79)

and

\[ g_5 = 0.38(1 + b^2)^{1.2 - 0.4b^2}/a^2 \]  (3.80)
The two parameters $\sigma$ and $\delta$ can be written in terms of $a^2$ and $b^2$ as

$$\sigma = -\frac{1}{\sqrt{a^2}} \left[ 0.057(1 + b^2)^{0.25} + \frac{1}{3} \right] (1 - b^2) \sqrt{5 + 3b^2} \quad (3.81)$$

and

$$\delta = \frac{1}{\sqrt{a^2}} \left[ 0.057(1 - b^2)^{0.25} + \frac{1}{3} \right] (1 + b^2) \sqrt{5 - 3b^2} \quad (3.82)$$

The additional phases $\Delta_{ij}$ in Eq. (3.29) have the form

$$\Delta_{11} = \sigma - 2\sigma_0$$

$$\Delta_{22} = \sigma + 2\sigma_0 \quad (3.83)$$

and

$$\Delta_{12} = \sigma \quad (3.84)$$

with

$$\sigma_0 = -\frac{1}{3}(R_i - R_b)K_1(R_i)(1 + b^2) \quad (3.85)$$

The overall transmission probability takes the form,

$$P_{12} = \frac{W^2}{1 + W^2} \quad (3.86)$$

c. \quad E \leq E_t \ (b^2 \leq -1). \quad \text{The Stokes constant } U_1 \text{ is given by}

$$\text{Re } U_1 = \sin (2\sigma_c) \left\{ \frac{0.5\sqrt{a^2}}{1 + \sqrt{a^2}} \sqrt{B(\sigma_c/\pi)} e^{-\delta} + \frac{e^\delta}{\sqrt{B(\sigma_c/\pi)}} \right\} \quad (3.87)$$

and

$$\text{Im } U_1 = \cos (2\sigma_c) \sqrt{\frac{(\text{Re } U_1)^2}{\sin^2(2\sigma_c)} + \frac{1}{\cos^2(2\sigma_c)} - \frac{1}{2 \sin (\sigma_c)}} \left| \frac{\text{Re } U_1}{\cos (\sigma_c)} \right| \quad (3.88)$$
where $B(X)$ is defined in Eq. (3.57), and

$$\sigma_c = \sigma(1 - g_6) \quad (3.89)$$

$$g_6 = 0.32 \times 10^{-2/a^2} e^{-\delta} \quad (3.90)$$

with

$$\sigma = \frac{\pi}{8a|b|} \frac{1}{2} \frac{\sqrt{6 + 10 \sqrt{1 - (1/b^2)}}}{1 + \sqrt{1 - (1/b^2)}} \quad (3.91)$$

and

$$\delta = \int_{r_1}^{r_f} |K_1(R)|dR \quad (3.92)$$

The additional phases in this case are quite simple as

$$\Delta_{11} = \Delta_{22} = \Delta_{12} = -2\sigma \quad (3.93)$$

For one passage of transition probability we can define $p$ in Eq. (3.65) at $b^2 \geq 1$, but this loses the meaning completely at $b^2 < 1$ because of the tunneling process that can never be separated from the nonadiabatic transition. It should be emphasized, however, that $p$ in the LZ case can be mathematically extended to $b^2 < 0$. Equation (3.59) with the $I$ matrix given by Eq. (3.58) still holds at $b^2 < 0$, although $p$ is not physically the same as in the case of $b^2 \geq 0$. In the NT case, $p$ in Eq. (3.65) cannot be mathematically extended to the region $b^2 \leq 1$. However, it is interesting to note that the quantity

$$Q = \frac{1}{1 + |U_1|^2} \quad (3.94)$$

and $p$ in Eq. (3.65) approach each other at $b^2 = 1$ as the effective coupling constant $a^2$ gets larger (see Fig. 3). This indicates that the quantity $Q$ in Eq. (3.94) might be considered as a mathematical extension of $p$ in Eq. (3.65) for the NT case. Figure 3 also demonstrates good agreement between the exact quantum results and the semiclassical calculations. Discussions here actually address an important fact that nonadiabatic transition cannot be easily separated from
Figure 3. Nonadiabatic transition probability $p$ for $b^2 > 1$ and the quantity $Q$ for $b^2 \leq 1$, which might be interpreted as the nonadiabatic transition probability in the NT type of two-state linear curve crossing. Dashed line: exact numerical result, solid line: the present semiclassical result for $p$ in Eq. (3.65), and for $Q$ in Eq. (3.94).

Tunneling whenever tunneling is involved. How to approximately separate these two transitions is still a big problem in the multidimensional case. The present semiclassical theory based on the two-state model can be considered as a nice illustration for studying this problem.

The overall transmission (nonadiabatic tunneling) probability is explicitly expressed as

$$P_{12} = |S_{12}^R|^2 = \frac{B(\sigma_c/\pi)e^{-2\delta}}{[1 + (0.5\sqrt{a^2}/(1 + \sqrt{a^2}))B(\sigma_c/\pi)e^{-2\delta}]^2 + B(\sigma_c/\pi)e^{-2\delta}}$$

(3.95)

It should be noted that this naturally contains both effects of quantum tunneling ($e^{-2\delta}$ is the Gamov factor) and nonadiabatic transition. This transmission probability is always smaller than the corresponding potential barrier penetration probability because of the nonadiabatic coupling effect. When the diabatic coupling is infinitely strong, that is, $a^2 \to 0$, Eq. (3.95) naturally goes to the ordinary tunneling probability [$= e^{-2\delta}/(1 + e^{-2\delta})$].
IV. HOW TO DEAL WITH MULTICHANNEL AND MULTIDIMENSIONAL PROBLEMS

A. Multichannel Processes

A diatomic system is a typical example for multichannel curve crossing problems, in which the adiabatic potential curves, obtained with the internuclear coordinate $R$ fixed, may show many avoided crossings. The present two-state semiclassical theory can present not only physically meaningful interpretation about those avoided crossings, but also a nice computational tool to calculate physical quantities such as scattering matrix, resonance width, and bound state energies. When avoided crossings are well separated from each other, nonadiabatic transitions well localized at each avoided crossing can be treated as in a pure two-state problem. Even when some of the avoided crossings come close together and their nonadiabatic couplings overlap with each other, the present semiclassical theory can still work surprisingly well. This is because the present semiclassical theory can take multistate coupling effects into consideration by using adiabatic potentials and also the underlying analytical structure of the problem is most properly taken into account. Actually, the important two parameters $a^2$ and $b^2$, which are defined in terms of the two adiabatic potential curves at one avoided crossing, include all the interaction information coming from the other neighboring avoided crossings; namely, when two avoided crossings come close together, the corresponding $a^2$ and $b^2$ change from the corresponding values when they are far apart. This is simply because the adiabatic potentials are obtained by diagonalizing the whole multichannel electronic Hamiltonian matrix. In the diabatic representation the interactions among other states are completely neglected, so that the theory cannot work better than in the adiabatic representation [25].

In a certain special multichannel curve crossing model, Demkov and Osherov [35] proved that the overall state-to-state transition probabilities can be exactly expressed in terms of an appropriate multiplication of the LZ probabilities at crossings, and any phase is not necessary. Later, many people thought that in general phases may not be as important. This is not correct, of course. For example, oscillation and resonance structure of overall nonadiabatic transition probabilities depend on various phases strongly. The $I$ matrix propagation method developed by Nakamura [79, 80] made an important step to properly take phases into consideration. The present version of the $I$ matrix propagation scheme [24, 25] enables us to deal with multichannel curve crossing problems more conveniently by absorbing all adiabatic phases between avoided crossings into the redefined $I$ matrix. Generally speaking, the better the two-state theory is, the more accurate results we can obtain for multichannel curve crossing problems. We will first present a general framework for multichannel processes
in which the transitions considered can be either LZ or NT, and then give a couple of examples to demonstrate the accuracy of the present theory. Actually, this general framework can be used for any type of transition other than LZ and NT as far as the corresponding $I$ matrix is known. The RZ type noncurve crossing and the exponential potential models are such examples.

1. General Framework

The multichannel WKB wave function can be defined almost anywhere for both incoming and outgoing branches, and the internal reduced scattering matrix can be defined at a certain finite distance $R = R_0$, where all channels are energetically open. This is a connection matrix that connects the coefficients associated with incoming WKB solutions to the coefficients associated with outgoing WKB solutions. Then, we further propagate the solutions to the asymptotic region where the final $S$ matrix is defined. As is well known, the exact quantum mechanical close-coupling calculations have to be carried out far into the asymptotic region to obtain converged solutions. In the semiclassical propagation method, however, we can terminate the propagation at the position just beyond the outmost avoided crossing.

Let us assume that we consider a general multichannel system that contains totally $n + m$ states, in which $n$ represents the number of asymptotically open channels and $m$ is the number of closed channels (see Fig. 4). Of course, $n$ and $m$ vary as the collision energy changes.

a. Case of No Closed Channel ($m = 0$). In this case, all channels ($n$) are open, and the avoided crossings are assumed to be distributed in the order,

$$R_N < R_{N-1} < \cdots < R_1$$

(4.1)

where $R_N$ represents the innermost avoided crossing and $R_1$ is the outermost avoided crossing. Each avoided crossing at $R_i$ ($i = 1, 2, \ldots, N$) is identified by the channel indexes $\alpha$ and $\beta$ ($\alpha < \beta = 1, 2, \ldots, n$), and the $n \times n$ $I_{R_i}$ matrix is given by

$$(I_{R_i})_{\alpha\alpha} = I_{11} \quad (I_{R_i})_{\alpha\beta} = I_{12}$$

$$(I_{R_i})_{\beta\alpha} = I_{21} \quad \text{and} \quad (I_{R_i})_{\beta\beta} = I_{22}$$

(4.2)

with the other elements

$$(I_{R_i})_{\nu\gamma} = \delta_{\nu\gamma} \quad (\nu, \gamma) \neq (\alpha\alpha), (\beta\beta), (\alpha\beta), (\beta\alpha)$$

(4.3)
Figure 4. Schematic \((n + m)\)-state potential curves with \(n\) open and \(m\) closed channels. The turning points \(T_a (\alpha = 1, 2, \ldots, n + m)\) and \(T_b (\beta = n + 1, n + 2, \ldots, n + m)\) mentioned in the text (omitted in this figure) are, respectively, the leftmost and rightmost turning points on the \(\alpha\)th and \(\beta\)th adiabatic potentials. \(1, \ldots, n, n + 1, \ldots, n + m - 1, n + m\) correspond to the adiabatic potentials \(E_1(R) \ldots E_n(R), E_{n+1}(R) \ldots E_{n+m-1}(R), E_{n+m}(R)\). (a) In the case of energy higher than the bottom of \(E_{n+m}(R)\). (b) In the case of energy lower than the bottom of \(E_{n+m}(R)\).
where $I_{11}$, $I_{12}$, $I_{21}$, and $I_{22}$ are the matrix elements of the two-by-two $I$ matrix defined in Eq. (3.58) for the LZ case and Eq. (3.72) for the NT case. The final reduced scattering matrix can be expressed as

$$S^R = (I_{R_n} I_{R_{n-1}} \cdots I_{R_1})^t (I_{R_n} I_{R_{n-1}} \cdots I_{R_1})$$

(4.4)

When there are closed channels, that is, $m \neq 0$, this matrix gives the internal reduced scattering matrix $\chi$. We will always denote it as $\chi$ in order to distinguish it from the final reduced scattering matrix $S^R$.

b. Case of $m \neq 0$ With Energies Higher Than the Bottom of the Highest Adiabatic Potential. In this case $m$ channels are closed, as is shown in Figure 4(a). Although in Figure 4(a), we have chosen the NT type avoided crossing at $R = R_j$ for the highest one, it can be the LZ type or any other type as far as we know its $I$ matrix. We first find the $\chi$ matrix at $R = R_0$, where all $n + m$ channels are open. Actually, $\chi$ can be obtained exactly in the same way as in Eq. (4.4), but now it becomes $(n + m) \times (n + m)$. It should be noted that this $\chi$ matrix may now also include contributions from the other avoided crossings, if any, lying in the region $R > R_0$. This means that $R_i$ does not have to be a definite single value, but can designate different positions depending on channels.

Let us write the $\chi$ matrix as

$$\chi = \begin{bmatrix} \chi_{oo}(n \times n) & \chi_{oc}(n \times m) \\ \chi_{co}(m \times n) & \chi_{cc}(m \times m) \end{bmatrix}$$

(4.5)

where $o(c)$ means open (closed). Then, the final $n \times n$ reduced $S^R$ matrix can be found as

$$S^R = \chi_{oo} - \chi_{oc} D^{-1} \chi_{co}$$

(4.6)

with

$$D_{\alpha\beta} = \delta_{\alpha\beta} e^{-i2\theta_{\alpha}} + [\chi_{cc}]_{\alpha\beta} \quad (\alpha, \beta = 1, 2, \ldots, m)$$

(4.7)

where the additional adiabatic phase $\theta_{\alpha}$ in Eq. (4.7) represents the WKB phase integral on the $\alpha$-th adiabatic potential,

$$\theta_{\alpha} = \int_{T_{n+\alpha}}^{T_{n+\alpha+1}} K_{n+\alpha}(R) dR \quad \alpha = 1, 2, \ldots, m$$

(4.8)
which is an ordinary-phase integral on a single adiabatic potential well. The derivation of the \( S^R \) matrix is essentially the same as that of the multichannel quantum defect theory [8, 81], and actually has been used in the heavy particle scattering theory [80, 82]. But now we have compact analytical expressions for all elements.

Equation (4.6) indicates that resonance information is totally included in the \( D \) matrix given by Eq. (4.7), and actually the complex zeros of \( \det(D) \) provide positions and widths of resonances. It can be easily checked that the \( D \) matrix goes to the correct adiabatic limit when all avoided crossings turn to be adiabatic, \( a^2 \rightarrow 0 \).

c. Case of \( m \neq 0 \) With Energies Lower Than the Bottom of the Highest Adiabatic Potential. Now we turn to the situation shown in Figure 4(b) in which the highest avoided crossing \( j \) is assumed to be the NT type and energy \( E \) is lower than the bottom of the highest adiabatic potential. The NT and LZ cases require different approaches. In the case of LZ, we can still use the \( I \) matrix even if energies are lower than the corresponding avoided crossing, and thus the whole procedure is the same as in section IV.A.1.b. But in the case of NT, the \( I \) matrix no longer exists at energies lower than the corresponding avoided crossing, and we must use the transfer matrix \( N^R \) [renamed from \( S^R \) in Eq. (3.29) for the reason that it represents the local transmission phenomenon]. This \( N^R \) matrix represents nonadiabatic tunneling through the avoided crossing \( j \) in Figure 4(h), since the highest state \( E_{n+m}(R) \) is closed everywhere. Now the propagation scheme becomes a little bit complicated because of this nonadiabatic tunneling process. We have to divide avoided crossings into three regions: A, B, and C in Figure 4(b);

Avoided crossings in A: \( R_\alpha < R_i \)

Avoided crossings in B: \( R_i < R_\alpha < R_k \)

and

Avoided crossings in C: \( R_k < R_\alpha \)

where \( \alpha \) is a running index that covers all avoided crossings in the corresponding region. Thus, we can define the \( I \) matrices for these three regions as

\[
I_A = I_{R_N} I_{R_{N-1}} \cdots I_{R_i}
\]

\[
I_B = I_{R_{i-1}} \cdots I_{R_{j-1}} I_{R_{j+1}} \cdots I_{R_{k+1}}
\]
and

\[ I_C = I_{R_l} I_{R_{l-1}} \cdots I_{R_1} \]  
(4.11)

where \( R_N < R_{N-1} \cdots < R_l < R_{l-1} < R_{j-1} < R_{j+1} \cdots < R_{k+1} < R_k \cdots < R_1 \), and each \( I_{R_x} \) (\( x \neq j \)) can be calculated in the same way as shown in Eqs. (4.2) and (4.3).

Let us define the internal \((n + m - 1) \times (n + m - 1)\) matrix at \( R \leq R_{01} \) as

\[ \chi^{[1]} = (I_A I_B)' (I_A I_B) \]  
(4.12)

where \( R_{01} > R_l \) (\( R_{02} < R_k \)) is a certain position in the left (right) well of \( E_{n+m-1}(R) \) [see Fig. 4(b)]. Here, we have combined \( I_B \) with \( I_A \), since the tunneling through \( j \) can commute with nonadiabatic transitions in region B. Next, we consider the WKB wave function \( \psi_{n+m-1}(R) \) in the region of tunneling through the top barrier (crossing \( j \)) from \( R_{01} \) to \( R_{02} \), and then we have the internal \((n + m - 1) \times (n + m - 1)\) matrix, \( \chi^{[2]} \):

\[ \chi^{[2]}_{\alpha \beta} = \chi^{[1]}_{\alpha \beta} - \frac{\chi^{[1]}_{\alpha(n+m-1)\beta}}{D_b} N_{22}^R N_{12}^{R_{n+m-1}} \]  
(4.13)

\[ \chi^{[2]}_{\alpha(n+m-1)} = \frac{iN_{21}^R e^{-i2\theta_b}}{D_b} \chi^{[1]}_{\alpha(n+m-1)} \]  
(4.14)

\[ \chi^{[2]}_{(n+m-1)\beta} = \chi^{[2]}_{\beta(n+m-1)} \]  
(4.15)

and

\[ \chi^{[2]}_{(n+m-1)(n+m-1)} = N_{11}^R \frac{\chi^{[1]}_{(n+m-1)(n+m-1)} (N_{12}^R)^2}{D_b} \]  
(4.16)

where \( \alpha, \beta = 1, 2, \ldots, (n + m - 2) \), and \( D_b \) is given by

\[ D_b = e^{-i2\theta_b} + \chi^{[1]}_{(n+m-1)(n+m-1)} N_{22}^R \]  
(4.17)
with

\[ \theta_b = \int_{T_{n,m-1}}^{t_0} K_{n,m-1}(R) dR \]  \hspace{1cm} (4.18)

which is the phase integral along the left well of \( E_{n+m-1}(R) \) [see Fig. 4(b)]. \( N_{11}^R, \ N_{22}^R, \) and \( N_{12}^R \) are evaluated from Eq. (3.29). The third step is to propagate the WKB wave functions to \( R \sim R_{03} \) where all avoided crossings in region C contribute to give

\[ \chi^{[3]} = I'_C \chi^{[2]} I_C \equiv \left[ \frac{\chi_{\infty}(n \times n)}{\chi_{\infty}(m-1) \times n} \right] \left[ \frac{\chi_{\infty}(n \times (m-1))}{\chi_{\infty}([m-1] \times (m-1))]} \right] \]  \hspace{1cm} (4.19)

The final step is to propagate the WKB wave functions from \( R_{03} \) to \( R \), where the asymptotic region is reached, and we finally obtain the \( S^R \) matrix \((n \times n)\) as

\[ S^R = \chi_{\infty} - \chi_{\infty} D^{-1} \chi_{\infty} \]  \hspace{1cm} (4.20)

with

\[ D_{\alpha\beta} = \delta_{\alpha\beta} e^{-i2\theta_\alpha} + [\chi_{cc}]_{\alpha\beta} \] \hspace{1cm} \( (\alpha, \beta = 1, 2, \ldots, m - 1) \)  \hspace{1cm} (4.21)

where the phase integrals along adiabatic potentials are defined by

\[ \theta_\alpha = \int_{T_{n+\alpha}}^{t_{n+\alpha}} K_{n+\alpha}(R) dR \] \hspace{1cm} \( (\alpha = 1, 2, \ldots, m - 1) \)  \hspace{1cm} (4.22)

Note that

\[ \theta_{m-1} \equiv \theta_\alpha = \int_{t_\alpha}^{t_{n+(m-1)}} K_{n+(m-1)}(R) dR \]  \hspace{1cm} (4.23)

which is the phase integral on the right well along \( E_{n+m-1}(R) \) in Figure 4(b). Note that the turning points \( t_\alpha \) and \( t_b \) in Figure 4(b) must be replaced by \( R_j \) when the energy is located in the gap of the top avoided crossing \( j \). Now, resonances come from the following two parts: one is from the complex zeros of \( D_{\alpha\alpha} = 0 \) in Eq. (4.16) and the other is from the complex zeros of \( \det D = 0 \) in Eq. (4.20). The great advantage of the present semiclassical method is that the resonance part can be completely separated from the other transition processes and thus can be easily analyzed.
When the energy goes down further, lower than the bottom of the adiabatic potential \( E_{n+m-1}(R) \) in Figure 4(b), the present semiclassical theory cannot take the highest \( j \)-th crossing contribution into consideration. However, when energy is very low, the nonadiabatic tunneling at \( j \) almost coincides with single potential barrier tunneling. In that case, we can neglect the adiabatic potential \( E_{n+m}(R) \), or we can treat the effect of the highest avoided crossing perturbatively. Then, the present \( I \)-matrix propagation method can still be formulated in a similar way as above. In this way, the present semiclassical theory can deal with multichannel curve crossing problems without any restriction for energy and the number of channels, as long as all avoided crossings are relatively separated from each other.

2. Numerical Applications

We choose a model system of two Morse potentials crossed with two repulsive exponential potentials to demonstrate the accuracy of our semiclassical theory [25]. The model potentials in diabatic representation are given by

\[
V_1(R) = 0.037e^{-1.3(R-3.25)} - 0.034
\]

\[
V_2(R) = 0.037e^{-1.3(R-3.25)} - 0.012
\]

\[
V_3(R) = 0.4057[1 - e^{-0.344(R-3)}]^2 - 0.03
\]

and

\[
V_4(R) = 0.4057[1 - e^{-0.344(R-3)}]^2
\]

(4.24)

Coupling terms are given as

\[
V_{13}(R) = V_{14}(R) = V_{23}(R) = V_{24}(R) = \frac{2V_0}{1 + e^{R-3}}
\]

and

\[
V_{12}(R) = V_{34}(R) = 0
\]

(4.25)

All quantities are in atomic units, and the reduced mass of the system is chosen to be that of an oxygen molecule \((m = 29,377.3)\). This model system was taken from some states of \( O_2 \) and the coupling represents the spin–orbit interaction among vibrational states of the oxygen molecule [83]. We have chosen \( V_0 = 0.002 \) at which any perturbation theory does not work at all, as it is realized as the strong coupling regime [83]. Figure 5 shows an adiabatic potential diagram
with $V_0 = 0.002$ from which we estimate all effective coupling constants $a^2$ for four nonzero coupling terms from Eq. (3.38) as

$$V_0 = 0.002 \Rightarrow (a_1^2, a_2^2, a_3^2, a_4^2) = (7.88, 4.5, 3.61, 1.8) \quad (4.26)$$

Note that although the diabatic coupling constant $V_0$ is the same, their corresponding effective coupling parameters $a^2$ are very different from crossing to crossing. Actually, that $0.1 \gtrsim a^2 \gtrsim 10$ corresponds to the most significant region for nonadiabatic transition, and in this region any attempt to use perturbation method will fail. Figure 6 show an excellent agreement between exact quantum results [Fig. 6(a)] and the present semiclassical results [Fig. 6(b)] for a wide range of energy. Even very detailed resonance structures are very well reproduced by the present semiclassical theory. More examples can be seen in [25].

**Figure 5.** Four-state potential diagram of Eqs. (4.24) and (4.25) with $V_0 = 0.002$. Solid lines for adiabatic potentials $E_i(R)$ and dashed lines for diabatic potentials $V_i(R)(i = 1, 2, 3, 4)$. 
Figure 6. Overall transition probability $P_{12}$ against energy for the potential system given in Figure 5. (a) Quantum mechanically exact numerical solution of coupled equations. (b) Present semiclassical theory in the adiabatic representation. The starting energy and the energy step used in both calculations are exactly the same.

B. Multidimensional Problems

Since most of chemical dynamical processes in reality proceed in multidimensional configuration space, a very natural question arises as to whether the simple 1D two-state theory can deal with such problems. Unfortunately, it is almost impossible to develop any intrinsically multidimensional analytical theory; and thus it is better to figure out some useful methods with the help of accurate 1D theories. In this sense, there are two ways: one is to reduce any multidimensional problem to a 1D multichannel problem by expanding the total wave function in terms of appropriate internal states, as is usually done in the quantum mechanical numerical solutions of the Schrödinger equation. The
second, which is more approximate but may be practically more useful, is to use classical trajectories that define curvilinear 1D space and try to incorporate quantum mechanical effects as much as possible. The ordinary multidimensional semiclassical mechanics [84–90] belongs to this category. The present semiclassical theory of nonadiabatic transition can be incorporated in either way.

As for the first example, here we consider reactive scattering that presents a very interesting example, since different rearrangement channels are associated with different coordinates. The most convenient method within the framework of the collision theory is to use the hyperspherical coordinate approach in which all arrangement channels can be treated on equal footing. The hyperspherical coordinate approach implemented for tri- and tetraatomic reaction systems has shown remarkable progress recently [86–90]. Especially, in the 3D heavy–light–heavy (HLH) reactions on a single potential energy surface, a newly
introduced coordinate system called "hyperspherical elliptic coordinate system" has made it possible to define the vibrationally adiabatic ridge lines and clarified the reaction mechanisms nicely in terms of the concept of vibrationally non-adiabatic transitions [89, 90]. Zhu et al. [26] treated, for the first time, such 3D HLH reactions analytically with the use of the present semiclassical theory. Needless to say, the conventional understanding of nonadiabatic transition is a transition between two electronically adiabatic states. This traditional adiabatic separation is, of course, based on the big mass disparity between the electron and the nucleus. This idea may be extended to reactive scattering on a single electronically adiabatic potential energy surface. Especially in the case of 3D HLH systems, the light atom has some analogy to an electron, and the adiabatic separation becomes the separation between hyperradius and hyperangles.

The Schrödinger equation for a triatomic system in hyperspherical coordinates can be written as (in atomic units)

$$
\left[ \frac{1}{2\mu} \frac{\partial}{\partial \rho} \frac{\partial}{\partial \rho} + \frac{\Lambda^2(\omega)}{2\mu \rho^2} + V(\rho, \omega_H) - E \right] \Psi(\rho) = 0
$$

(4.27)

where $\Lambda^2(\omega)$ is the so-called grand angular momentum operator, $\rho$ is the hyperradius, $\omega$ represents the five hyperangles that are divided into three Euler angles $\omega_E$ [not appearing in the interaction potential $V(\rho, \omega_H)$], and two geometric angles $\omega_H$ of a triatomic system. The reduced mass $\mu$ is defined by

$$
\mu = \sqrt{\frac{m_A m_B m_C}{m_A + m_B + m_C}}
$$

(4.28)

where $m_A$, $m_B$, and $m_C$ are the masses of atoms A, B, and C, respectively.

The following expansion is used for solving Eq. (4.27):

$$
\Psi(\rho) = \rho^{-5/2} \sum_{\nu} F_{\nu}(\rho) \Phi_{\nu}(\omega : \rho)
$$

(4.29)

where the adiabatic channel functions $\Phi_{\nu}(\omega : \rho)$ satisfy the hyperspherical adiabatic eigenvalue problem,

$$
[H_{ad}(\omega, \rho) - \mu \rho^2 \hat{U}_{\nu}(\rho)] \Phi_{\nu}(\omega : \rho) = 0
$$

(4.30)

with

$$
H_{ad}(\omega, \rho) = \frac{1}{2} \Lambda^2(\omega) + \mu \rho^2 V(\rho, \omega_H)
$$

(4.31)
in which \( \hat{U}_v(p) \) is the eigenvalue to be determined at each fixed \( p \), since \( H_{ad}(\omega, p) \) depends on \( p \) parametrically. The scattering wave function \( F_v(p) \) in Eq. (4.29) turns out to satisfy

\[
\left\{ \frac{d}{dp^2} + 2\mu[E - U_v(p)] \right\} F_v(p) + \sum_{\mu} W_{v\mu}(p) F_\mu(p) = 0 \tag{4.32}
\]

with

\[
U_v(p) = \bar{U}_v(p) + \frac{15}{8\mu p^2} \tag{4.33}
\]

where \( W_{v\mu}(p) \) is the nonadiabatic coupling term (not given here explicitly; see [89]). Now the problem becomes an ordinary multichannel scattering problem in the same way as in Section IV.A. We need only \( U_v(p) \) in Eq. (4.33) to formulate the analytical solution of the reduced scattering matrix within the framework of the present semiclassical theory. Namely, we do not need any information about the nonadiabatic coupling \( W_{v\mu}(p) \). The scattering wave function \( F_v(p) \) in Eq. (4.32) can be written in the WKB form as

\[
F_v(p) = \frac{A_v}{\sqrt{K_v(p)}} e^{i \int_{T_v}^p K_v(p) dp - i(\pi/4)} + \frac{B_v}{\sqrt{K_v(p)}} e^{-i \int_{T_v}^p K_v(p) dp + i(\pi/4)} \tag{4.34}
\]

for \( \rho \to \infty \), where \( T_v \) is the rightmost turning point on the adiabatic potential \( U_v(p) \) and

\[
K_v(p) = \sqrt{2\mu[E - U_v(p)]} \tag{4.35}
\]

The reduced scattering matrix \( S^R \) is defined as

\[
\begin{pmatrix}
A_1 \\
A_2 \\
\vdots \\
A_n
\end{pmatrix} = S^R \begin{pmatrix}
B_1 \\
B_2 \\
\vdots \\
B_n
\end{pmatrix} \tag{4.36}
\]

where \( n \) represents the number of open channels at a given total collision energy \( E \).

The \( I \)-matrix propagation method is directly implemented to obtain the reduced scattering matrix,

\[
S^R = (I_1I_2 \cdots I_N)^t(I_1I_2 \cdots I_N) \tag{4.37}
\]
where $N$ is the number of avoided crossings that can be as many as a thousand among the massive number of adiabatic potential curves $U_v(\rho)$. Those avoided crossings represent rovibrationally nonadiabatic transitions that represent reactive as well as nonreactive transitions. For 3D HLH systems, vibrationally adiabatic ridge lines can be extracted and the most important avoided crossings that represent reactive transitions are found to be located along or near these ridge lines. The lowest (ground vibrational, $v = 0$) ridge line defines the boundary of reaction zone. The avoided crossings outside this ridge line represent only nonreactive inelastic transitions. Those avoided crossings that are distributed far inside the ridge line represent a mixture of reactive and nonreactive transitions.

The effective coupling parameter $a^2$ defined in Eq. (3.21) for the LZ type and Eq. (3.38) for the NT type provides a very nice quantitative index of nonadiabatic coupling strength at each avoided crossing. Most of thousands of avoided crossings correspond to $a^2 > 1000$, which represent very sharp avoided crossings, and do not play meaningful roles in dynamics. Only $\sim 100$ avoided crossings with $0.001 \leq a^2 \leq 1000$ among $100 \sim 200$ adiabatic potential curves contribute significantly to the reaction.

In the hyperspherical coordinate approach, all arrangement channels are treated equally and represented as adiabatic potential curves as a function of the hyperradius $\rho$. Therefore, important avoided crossings exist not only between adjacent adiabatic potentials, but can appear among nonadjacent adiabatic potentials. Besides, adiabatic potential curves belonging to physically separated arrangement channels avoid crossings very sharply outside the reaction zone and are better connected diabatically without any transitions. In order to extract these avoided crossings among nonadjacent adiabatic potentials, we have developed a certain diabatic decoupling method [26, 91]. We follow $U_v(\rho)$ inward from the asymptotic $\rho$, where each channel can be assigned. If avoided crossings between adjacent adiabatic potentials on the way in have $a^2 > a^2_0$, then we switch $U_v(\rho)$ to $U_{v-1}(\rho)$, or $U_{v+1}(\rho)$. By repeating this diabatic switching procedure even inside the reaction zone, we can finally obtain a diabatic potential manifold and pick up important avoided crossings between originally nonadjacent potential curves. The dependence of this decoupling procedure on the critical value $a^2_0$ is not as strong and $a^2_0 \approx 100$ was chosen. All the important avoided crossings are treated analytically to evaluate the scattering matrix. In [26], we studied the two examples of the 3D HLH reactions: $O(3P) + HCl \rightarrow OH + Cl$ and $Br + HCl \rightarrow HBr + Cl$. Figure 7 shows a magnification of the reaction zone of adiabatic potential curve diagram of OHCl. A comparison between the exact quantum calculation and the present semiclassical result is shown in Figure 8 for cumulative reaction probability.

We can see that the agreement is quite good, considering that the semiclassical one is a completely analytical treatment. Similar agreement has
Figure 7. Magnification of the reaction zone of the adiabatic potential curves of OHCl. The dashed line represents the \( v = 0 \) ridge line. Circles represent important avoided crossings among the adjacent adiabatic potentials and some of the circles assigned with the values of \( a^2 \) are the most important ones. The circle signed by letter A (B) indicates the avoided crossing responsible for the peak of certain vibrationally specified cumulative reaction probabilities (see [26]). The symbols \( \Box, \triangle, \triangledown, \times, \text{ and } \circ \) represent the avoided crossings among the nonadjacent adiabatic potentials. The symbols \( \Box, \triangle, \text{ and } \triangledown \) are from the diabatic potential manifolds with \( v = 0, 1, 2, \) respectively, for HCl + O arrangement (see [26]). The symbols \( \times \) and \( \circ \) are from the diabatic potential manifolds, respectively, for OH + Cl arrangement (see [26]).
Figure 8. Total cumulative reaction probability $N(E)$ as a function of the total energy $E$ measured from the ground state of the reactant in the case of OHCl system: solid line (exact numerical result); dash line (semiclassical calculation with the avoided crossings among adjacent adiabatic potentials); dotted line (semiclassical calculation with the avoided crossings among both adjacent and nonadjacent adiabatic potentials included).
been obtained for BrHCl. The state-to-state reaction probabilities are not quantitatively well reproduced, however. This is because nonreactive inelastic transitions are not necessarily well represented by avoided crossings.

The second more approximate way of treating multidimensional dynamics is to incorporate the present semiclassical theory into a certain semiclassical propagation scheme based on classical trajectories. The best example will be an electronically nonadiabatic chemical reaction. Since a classical trajectory defines nothing but a curvilinear 1D space, the nonadiabatic transition \( I \) matrix, actually \( I_X \) matrix given by Eq. (3.60), can be incorporated whenever the trajectory comes to a potential energy surface crossing region. We can actually utilize various types of semiclassical propagation schemes such as TSH [27], the semiclassical IVR [28], and CFGWP [29]. The TSH is actually an ordinary quasiclassical trajectory (QCT) method without any incorporation of phases, but the electronically nonadiabatic transition probability or the surface hopping probability can be very much improved by the present semiclassical theory. Numerical solutions of time-dependent Schrödinger equations required in the case of fewest switches trajectory surface hopping (TFSH) [30] are not necessary at all. A more sophisticated framework is the semiclassical propagation based on IVR, in which all phases associated with each trajectory are taken into account to evaluate the transition amplitude. The IVR was figured out to avoid the divergence of the Van Vleck determinant at caustics [28]. With use of the present semiclassical theory even the dynamical phases due to nonadiabatic transition are accurately incorporated. For systems bigger than triatomic ones, the CFGW method will probably be useful [29]. In this method, the initial wave function is represented as a superposition of small wave packets and all of them are propagated along the classical trajectory of its center with the Gaussian shape frozen. This method was successfully applied to a 15-dimensional (15D) eigenvalue problem [29]. In any case, whatever the semiclassical propagation method is, the present semiclassical theory, especially the \( I_X \) matrix, may be nicely incorporated into the framework in order to treat the electronically nonadiabatic transitions. Not only the phases but also the transition probability even at energies lower than the crossing point can be accurately and easily evaluated and incorporated.

V. OTHER MODELS

From the previous sections, we have seen how the solutions of the two-state linear curve crossing model is generalized to deal with the two-state general curve crossing problems, as well as multichannel and multidimensional problems. These generalizations are made possible thanks to the fact that the compact solutions have been obtained for the linear potential model in a generalizable form and also the positions of nonadiabatic
transitions can be easily identified as avoided crossings. As is well known, there is another kind of nonadiabatic transition generally termed as the noncurve crossing case. The RZ model is the most typical one in this category [4]. It is a very challenging subject to formulate a sort of unified theory that can cover both the curve crossing and noncurve crossing case in a unified way. The exponential potential model first studied by Nikitin [6] presents an interesting case in this sense, because the nonadiabatic transition probability contains two parameters and leads to either the LZ formula or the RZ formula in certain limits. Compared to the curve crossing case discussed in the previous sections, however, the theory of noncurve crossing case is actually far from complete.

A. Exponential Potential Model

For the noncrossing model, it is convenient to start with the following exponential model. Diabatic potentials in Eqs. (3.1) and (3.2) now read as

\[ V_{11}(x) = V_1 - \beta_1 V_0 e^{-\alpha x} \]
\[ V_{22}(x) = V_2 - \beta_2 V_0 e^{-\alpha x} \]

and

\[ V_{12}(x) = V_{21}(x) = V_0 e^{-\alpha x} \quad (V_0 > 0) \quad -\infty < x < \infty \quad (5.1) \]

where \( V_2 > V_1 \) is assumed without losing generality. Equation (5.1) actually includes both crossing (if \( \beta_2 > \beta_1 \)) and noncrossing (if \( \beta_2 < \beta_1 \)) cases. More generally, the three exponents in \( V_{11}, V_{22}, \) and \( V_{12} \) can all be different, of course. Analytical solutions obtained so far are, however, restricted to the above case. The exponential model here is more general than the linear crossing model previously discussed in the sense that this can cover both crossing and noncrossing cases and the avoided crossing point can significantly differ from the original crossing point of the diabatic potentials. This means that the localizability of nonadiabatic transition is much better in the two-state linear crossing case.

Adiabatic potentials of Eq. (5.1) can be easily written as

\[ E_2(x) = \frac{1}{2} [V_2 + V_1 - (\beta_2 + \beta_1) V_0 e^{-\alpha x}] + \frac{1}{2} \sqrt{[V_2 - V_1 - (\beta_2 - \beta_1) V_0 e^{-\alpha x}]^2 + 4V_0^2 e^{-2\alpha x}} \]
\[
E_1(x) = \frac{1}{2} [V_2 + V_1 - (\beta_2 + \beta_1)V_0e^{-\alpha x}] \\
- \frac{1}{2} \sqrt{(V_2 - V_1 - (\beta_2 - \beta_1)V_0e^{-\alpha x})^2 + 4V_0^2e^{-2\alpha x}} 
\]

(5.2)

There are an infinite number of complex zeros of \(E_2(x) = E_1(x)\), all of which have the same real part, in contrast with the two complex zeros in the linear curve crossing case. As we know, the configuration structure of complex zeros completely determine the connection problem associated with the Stokes phenomenon and thus the physical phenomenon. The two-state exponential model has not been solved exactly quantum mechanically except for some special cases. By applying the Bessel integral transformation, Osherov et al. [32] transformed the coupled equations of Eqs. (3.1) and (3.2) with the potentials Eq. (5.1) in coordinate space into momentum space to obtain

\[
\left[ \frac{d^2}{dp^2} + \frac{Q(p)}{p^2S(p)} \right] f(p) = 0
\]

(5.3)

where both \(Q(p)\) and \(S(p)\) are the fourth-order polynomials, whose explicit expressions can be found in [32]. The four transition points existing in \(Q(p)\) are symmetrically distributed with respect to the imaginary axis in the complex \(p\) plane, and the four poles (besides two at \(p = 0\)) in \(S(p)\) are also distributed symmetrically with respect to the imaginary axis. The exact solution of the basic equation (5.3) is unfortunately unknown; but in the high-energy approximation, certain semiclassical solutions have been obtained with the use of the complex phase integral method [32]. There are generally two approaches to solve the two-state exponential model with Eq. (5.1): one is the method used in [32] and the other is that some special cases of the exponential model of Eq. (5.1) are first solved exactly, and then the exact solutions are tried to be generalized to general cases with use of the comparison-equation method (see, e.g., [5]). In fact, the two approaches mentioned above give almost the same final semiclassical solutions [31, 32, 34, 92–94].

Although the localizability of nonadiabatic transition on the real axis is worse than the linear curve crossing case, the semiclassical idea of nonadiabatic transition and adiabatic wave propagation still holds well and the \(I_X\) matrix is given by

\[
I_X = \begin{pmatrix}
\sqrt{1 - pe^{i\phi}} & -\sqrt{pe^{i\gamma}} \\
\sqrt{pe^{-i\gamma}} & \sqrt{1 - pe^{-i\phi}}
\end{pmatrix}
\]

(5.4)
where $p$ is as usual the nonadiabatic transition probability for one passage of the transition region, and $\phi$ and $\psi$ are dynamical phases created by the nonadiabatic transition [32,34]. The nonadiabatic transition or this $I_x$ matrix should be assigned at the real part of the complex crossing point $X^*$. The probability $p$ and the dynamical phases $\phi$ and $\psi$ are explicitly given by [6,32,34]

\[
p = e^{-\pi \delta_2} \frac{\sinh(\pi \delta_1)}{\sinh(\pi \delta_2)} \tag{5.5}
\]

\[
\phi = \gamma(\delta_2) - \gamma(\delta) \tag{5.6}
\]

and

\[
\psi = \gamma(\delta_1) - \gamma(\delta) - 2 \left[ \sqrt{\delta \delta_2} + \frac{\delta_1}{2} \ln \frac{\sqrt{\delta - \sqrt{\delta_2}}}{\sqrt{\delta + \sqrt{\delta_2}}} \right] \tag{5.7}
\]

with

\[
\gamma(X) = X \ln(X) - X - \arg \Gamma(iX) \tag{5.8}
\]

and

\[
\delta = \delta_1 + \delta_2 \tag{5.9}
\]

The parameters $\delta_1$ and $\delta_2$ are given by

\[
\delta_1 = \frac{1}{\pi} \int_{\text{Re}X^*}^{X^*} \left| K_2(x) - K_1(x) \right| dx \tag{5.10}
\]

and

\[
\delta_2 = \frac{1}{2\pi i} \int_{\infty}^{X^*} \left| K_2(x) - K_1(x) \right| dx - \delta_1 \tag{5.11}
\]

where $K_j(x)$ ($j = 1,2$) are defined by Eq. (3.7). Equation (5.5) leads to the LZ probability $p = e^{-\pi \delta_2}$ in the limit $\delta_1 \to \infty$ or $\delta_2 \to 0$, and covers the RZ probability $p = (1 + e^{2\pi \delta_2})^{-1}$ in the limit $\delta_1 \to 2\delta_2$.

Three exactly solvable cases follow with the potentials given by Eq. (5.1):

1. Rosen–Zener–Demkov model with $\beta_1 = \beta_2 = 0$ (see [94])
2. Attractive potential model with $\beta_1 = (1/\beta_2) > 0$ (see [31])
3. Repulsive potential model with $\beta_1 = (1/\beta_2) < 0$ (see [92])
By directly transforming the coupled equations (3.1) and (3.2) into a single fourth-order differential equation, we can solve equations exactly in terms of the Meijer's G functions [95] under the three conditions mentioned above. From the exact solution of wave functions, we can extract the reduced scattering matrix. In Section V.B, the above three exponential models will be briefly discussed.

B. Rosen–Zener–Demkov Model ($\beta_1 = \beta_2 = 0$)

Two adiabatic potentials are shown in Figure 9(a). Channel 3 is divergent, but it does not make any trouble to define the reduced scattering matrix $S^R$ that is actually given by [94]

$$
S^R = \begin{pmatrix}
-N_1 e^{2\theta_1} & -\sqrt{N_1 N_2 - N_1 N_3 e^{i(\theta_1 + \theta_2)}} & -\sqrt{N_2 - N_1 N_3 e^{i(\theta_1 + \theta_3)}} \\
-\sqrt{N_1 N_2 - N_1 N_3 e^{i(\theta_1 + \theta_2)}} & -N_2 e^{2\theta_2} & \sqrt{N_1 - N_2 N_3 e^{i(\theta_2 + \theta_3)}} \\
-\sqrt{N_2 - N_1 N_3 e^{i(\theta_1 + \theta_2)}} & \sqrt{N_1 - N_2 N_3 e^{i(\theta_2 + \theta_3)}} & N_3 e^{2\theta_3}
\end{pmatrix}
$$

(5.12)

Figure 9. Adiabatic potentials for two special cases of the two-state (three-channel) exponential model. (a) Rosen–Zener–Demkov case with $\beta_1 = \beta_2 = 0$ in Eq. (5.1). (b) The repulsive case with $\beta_1 = 1/\beta_2 < 0$ in Eq. (5.1).
where the amplitudes are defined by

\[ N_1 = e^{-\pi q_1} \frac{\cosh \pi (q_1 + q_2)/2}{\cosh \pi (q_1 - q_2)/2} \]  

(5.13)

\[ N_2 = e^{-\pi q_2} \frac{\cosh \pi (q_1 + q_2)/2}{\cosh \pi (q_1 - q_2)/2} \]  

(5.14)

and

\[ N_3 = e^{-\pi q_1 - \pi q_2} \]  

(5.15)

with the phases given by

\[ \theta_1 = 4q_1 \ln(2) + \arg \Gamma \left[ \frac{1}{2} + i \frac{q_1 - q_2}{2} \right] - \arg \Gamma \left[ \frac{1}{2} - i \frac{q_1 + q_2}{2} \right] + \arg \Gamma[iq_1] \]  

(5.16)
\[ \theta_2 = 4q_2 \ln(2) - \arg \Gamma \left[ \frac{1}{2} + i \frac{q_1 - q_2}{2} \right] - \arg \Gamma \left[ \frac{1}{2} - i \frac{q_1 + q_2}{2} \right] + \arg \Gamma [i q_2] \]  
\hspace{2cm} (5.17)

and

\[ \theta_3 = \frac{\pi}{4} \]  
\hspace{2cm} (5.18)

It can be easily seen that the symmetrical SR matrix in Eq. (5.12) satisfies unitarity when \( N_1, N_2, \) and \( N_3 \) satisfy the following constraint:

\[ N_1 + N_2 = 1 + N_3 \]  
\hspace{2cm} (5.19)

The parameters \( q_1 \) and \( q_2 \) in the above equations are given by

\[ q_i = \frac{\sqrt{2\mu}}{\hbar x} \sqrt{E - V_i}, \quad (i = 1, 2) \]  
\hspace{2cm} (5.20)

In order to generalize this model so that we can deal with general two-state potentials in the noncrossing case, we have to close channel 3 in Figure 9(a) by putting a repulsive wall far from the interaction region \((x \ll x_0)\). In this way, we can have the following overall nonadiabatic transition probability:

\[ P_{12} = \frac{\sinh(\pi q_1) \sinh(\pi q_2) \cos^2(\sigma)}{\cosh^2(\pi(q_1 - q_2)/2) \left[ \cosh^2(\pi(q_1 + q_2)/2) - \cos^2(\sigma) \right]} \]  
\hspace{2cm} (5.21)

This formula is valid even in the threshold region where \( q_2 \to 0 \). If we apply the high-energy approximation, Eq. (5.21) turns to be

\[ P_{12} \approx \frac{\cos^2(\sigma)}{\cosh^2(\pi(q_1 - q_2)/2)} \equiv \frac{\cos^2(\sigma)}{\cosh^2 \delta} \]  
\hspace{2cm} (5.22)

This is nothing but the famous RZ formula in which \( \sigma \) and \( \delta \) can be generally evaluated by the complex phase integral,

\[ \sigma + i\delta = \int_{T_1}^{R} K_1(R) dR - \int_{T_2}^{R} K_2(R) dR \]  
\hspace{2cm} (5.23)
where $R^*$ is the complex crossing between two general noncrossing adiabatic potentials. The $I_X$ matrix for the RZ noncrossing problem can also be defined as

$$I_X = \begin{pmatrix} \sqrt{1-\rho e^{-i\phi}} & -\sqrt{\rho} e^{i\psi} \\ \sqrt{\rho} e^{-i\psi} & \sqrt{1-\rho e^{i\phi}} \end{pmatrix} \tag{5.24}$$

where

$$\phi = \gamma(\delta_{RZ}) - \gamma(2\delta_{RZ}) \tag{5.25}$$

$$\psi = \phi - \delta_{RZ} \left[ 2\sqrt{2} + \ln \frac{\sqrt{2} - 1}{\sqrt{2} + 1} \right] \tag{5.26}$$

$$\delta_{RZ} = \frac{\sqrt{\mu}}{\sqrt{2\hbar\alpha}} (\sqrt{E - V_1} - \sqrt{E - V_2}) \tag{5.27}$$

and one passage probability is given by

$$p = \frac{1}{1 + e^{2\delta}} \tag{5.28}$$

**C. Special Cases of Exponential Potential Model ($\beta_1 = 1/\beta_2$)**

First we discuss the repulsive case. In this case, channel 3 is not divergent [see Fig. 9(b)] and the reduced scattering matrix is given by [93]

$$S = \begin{pmatrix} N_1 e^{2\beta_1} & \sqrt{N_1} N_2 - N_3 e^{i(\theta_1 + \theta_2)} & \sqrt{N_2} - N_1 N_3 e^{i(\theta_1 + \theta_3)} \\ \sqrt{N_1} N_2 - N_3 e^{i(\theta_1 + \theta_2)} & N_2 e^{2\beta_2} & -\sqrt{N_2} - N_1 N_3 e^{i(\theta_2 + \theta_3)} \\ \sqrt{N_2} - N_1 N_3 e^{i(\theta_1 + \theta_3)} & -\sqrt{N_2} - N_1 N_3 e^{i(\theta_2 + \theta_3)} & -N_3 e^{2\beta_3} \end{pmatrix} \tag{5.29}$$

where the amplitude parts are defined by

$$N_1 = \frac{\sinh \pi(q_1 - q_3) \sinh \pi(q_1 + q_2)}{\sinh \pi(q_1 + q_3) \sinh \pi(q_1 - q_2)}$$

$$N_2 = \frac{\sinh \pi(q_3 - q_2) \sinh \pi(q_1 + q_2)}{\sinh \pi(q_3 + q_2) \sinh \pi(q_1 - q_2)}$$
and

\[ N_3 = \frac{\sinh \pi (q_1 - q_3) \sinh \pi (q_3 - q_2)}{\sinh \pi (q_1 + q_3) \sinh \pi (q_3 + q_2)} \quad (5.30) \]

and the phases are given by

\[ \theta_1 = -q_1 \ln(\gamma e^{-x_0}) + \arg \Gamma[2iq_1] + \arg \Gamma[i(q_1 - q_2)] + \arg \Gamma[i(q_1 + q_2)] - \arg \Gamma[i(q_1 - q_3)] - \arg \Gamma[i(q_1 + q_3)] \]

\[ \theta_2 = -q_2 \ln(\gamma e^{-x_0}) + \arg \Gamma[2iq_2] - \arg \Gamma[i(q_1 - q_2)] + \arg \Gamma[i(q_1 + q_2)] + \arg \Gamma[i(q_3 - q_2)] - \arg \Gamma[i(q_3 + q_2)] \]

and

\[ \theta_3 = q_3 \ln(\gamma e^{-x_0}) + \arg \Gamma[2iq_3] + \arg \Gamma[i(q_1 - q_3)] - \arg \Gamma[i(q_1 + q_3)] - \arg \Gamma[i(q_3 - q_2)] - \arg \Gamma[i(q_3 + q_2)] \quad (5.31) \]

Again, we can easily prove that \( S \) in Eq. (5.29) satisfies unitarity and \( N_1, N_2, \) and \( N_3 \) satisfies the following relation:

\[ N_1 + N_2 = 1 + N_3 \quad (5.32) \]

In the above equations, \( q_1 \) and \( q_2 \) are the same as in Eq. (5.20) with \( q_3 \) given by

\[ q_3 = \frac{\sqrt{2\mu}}{\hbar \alpha} \sqrt{E - V_3} \quad (5.33) \]

with

\[ V_3 = \frac{\beta_1 V_2 + V_1/\beta_1}{\beta_1 + 1/\beta_1} \quad (5.34) \]

The real part \( x_0 \) of the complex zero and \( \gamma \) in Eq. (5.31) are defined by

\[ x_0 = -\frac{1}{\alpha} \ln \left[ \frac{V_2 - V_1}{V_0(|\beta_1 + 1/\beta_1|)} \right] \quad (5.35) \]

and

\[ \gamma = \frac{2\mu V_0}{\hbar^2 \alpha^2 (|\beta_1 + 1/\beta_1|)} \quad (5.36) \]
It should be emphasized that the present repulsive model includes both the crossing case \((0 > \beta_1 > -1)\) and the noncrossing case \((\beta_1 < -1)\). In a similar way as carried out in Section V.B, we can generalize the present model to a general two-state problem with a repulsive wall. The overall transition probability is found as [93]

\[
P_{12} = \frac{4(1-N_1)(1-N_2)}{(1+N_3)^2} \frac{\sin^2(\theta + \theta_3)}{1 - (4N_3/(1+N_3))\sin^2(\theta + \theta_3)}
\] (5.37)

This formula is valid even in the threshold region \((q_2\to 0)\). Under the high-energy approximation Eq. (5.37) turns to be

\[
P_{12} \approx 4p(1-p)\sin^2(\sigma + \phi)
\] (5.38)

where the one passage nonadiabatic transition probability \(p\) is given by

\[
p = \frac{\sinh(d^2 - 1)\delta}{\sinh(d^2\delta)} e^{-\delta}
\] (5.39)

and the phase \(\phi\) by

\[
\phi = \phi_s \left(\frac{\delta}{\pi} \right) - \phi_s \left[(d^2 - 1)\frac{\delta}{\pi}\right]
\] (5.40)

where

\[
\phi_s(X) = X \ln(X) - X - \arg(\Gamma(iX)) - \frac{\pi}{4}
\] (5.41)

The two parameters \(\delta\) and \(\sigma\) are given by the complex phase integral as shown in Eq. (5.23). The probability expression given in Eq. (5.39) actually coincides with Eq. (5.5) and also with Nikitin’s formula [6]. Here, however, the important parameter \(d\) in the above equations, introduced by the comparison-equation method, represents a type of nonadiabatic transition in general two-state problems and is given by

\[
d = \sqrt{1 + \frac{4V_{12}^2(x_0)}{[V_1(x_0) - V_{22}(x_0)]^2}}
\] (5.42)

where \(x_0\) is the real part of the complex crossing point between the adiabatic potentials. In fact, it is easy to check that if we apply the two-state linear curve
crossing model to Eq. (5.42) in which the diabatic crossing point coincides with the real part of the complex crossing, we have

\[ d = \infty \] (5.43)

under which the formula goes back to the LZ case, and that if we apply the two-state RZ model to Eq. (5.42), we have

\[ d = \sqrt{2} \] (5.44)

which leads the formula to the RZ case. In general, we have \( 1 < d < \infty \) so that type of nonadiabatic transition can change continuously depending on the value of \( d \) in Eq. (5.42). In this way, a certain unified semiclassical theory for the general two-state problems can be formulated, but the theory is established only in the diabatic representation as is seen from Eq. (5.42). Some numerical calculations are presented in [93] in which the unified formula works very well especially for the case of \( d < \sqrt{2} \), which is neither the LZ nor RZ case.

In the attractive case \( (\beta_1 = \beta_2^{-1} > 0) \), we have four- \((E > V_1)\), three- \((V_1 > E > V_3)\), two- \((V_3 > E > V_2)\), and one- \((E < V_2)\) channel problems, where \( V_3 \) is given in Eq. (5.34) (see Fig. 10) [31]. Here we only give the exact expressions of nonadiabatic transition probabilities \( p_{ij} = |(I_{X})_{ij}|^2 \) in the four-channel case

\[
p_{11} = \left[ \frac{\sinh \pi (q_3 - q_1) \sinh \pi (q_2 + q_1)}{\sinh \pi (q_3 + q_1) \sinh \pi (q_2 - q_1)} \right]^2 e^{-4\pi q_1} \] (5.45)

\[
p_{12} = \frac{e^{-2\pi q_2 - 2\pi q_1}}{\sinh^2 \pi (q_2 - q_1)} \frac{\sinh \pi (q_3 - q_1) \sinh (2\pi q_2) \sinh (2\pi q_1) \sinh \pi (q_2 - q_3)}{\sinh \pi (q_3 + q_2) \sinh \pi (q_3 + q_1)} \] (5.46)

\[
p_{13} = 2 \frac{\sinh \pi (q_3 - q_1) \sinh \pi (q_2 + q_1) \sinh (2\pi q_1)}{\sinh \pi (q_3 + q_1) \sinh \pi (q_2 - q_1)} e^{-2\pi q_2 - 2\pi q_1} \] (5.47)

\[
p_{14} = \frac{e^{-2\pi q_3 - 2\pi q_1}}{\sinh^2 \pi (q_1 + q_3)} \frac{\sinh (2\pi q_3) \sinh \pi (q_2 + q_1) \sinh (2\pi q_1) \sinh \pi (q_2 - q_3)}{\sinh \pi (q_3 + q_2) \sinh \pi (q_2 - q_1)} \] (5.48)
Figure 10. Two diabatic potentials (dotted line) and corresponding two adiabatic potentials (solid line) for special attractive cases of the two-state (four-channel) exponential model. (a) Crossing case, (b) Noncrossing case.

\[ p_{22} = \frac{\sinh \pi (q_2 - q_3) \sinh \pi (q_2 + q_1)}{\sinh \pi (q_2 + q_3) \sinh \pi (q_2 - q_1)} \frac{2}{\sinh \pi (q_2 - q_1)} e^{-4\pi q_2} \]  
\[(5.49)\]

\[ p_{23} = \frac{\sinh (2\pi q_2) \sinh \pi (q_2 + q_1) \sinh \pi (q_2 - q_3)}{\sinh \pi (q_2 + q_3) \sinh \pi (q_2 - q_1)} e^{2\pi q_3 - 2\pi q_2 - 2\pi q_1} \]  
\[(5.50)\]

\[ p_{24} = \frac{\sinh (2\pi q_2) \sinh (2\pi q_3) \sinh \pi (q_2 + q_1) \sinh \pi (q_3 - q_1)}{\sinh \pi (q_3 + q_1) \sinh \pi (q_2 - q_1)} e^{4\pi q_1 - 2\pi q_2 - 2\pi q_3} \]  
\[(5.51)\]
Semiclassically, $p_{33}$ and $p_{34}$ represent the nonadiabatic transition probability for one passage of the transition region, and is nicely given by the following formula except at the threshold:

$$p_{33} = e^{4\pi(q_3 - q_2 - q_1)} \quad (5.52)$$

$$p_{34} = 2 \frac{\sinh(2\pi q_3) \sinh\pi(q_3 - q_1) \sinh\pi(q_2 - q_3)}{\sinh\pi(q_2 + q_3) \sinh\pi(q_1 + q_3)} e^{2nq_1 - 2nq_1 - 2nq_2} \quad (5.53)$$

$$p_{44} = \left( \frac{\sinh\pi(q_3 - q_1) \sinh\pi(q_3 - q_2)}{\sinh\pi(q_3 + q_1) \sinh\pi(q_3 + q_2)} \right)^2 e^{4\pi q_3} \quad (5.54)$$

Semiclassically, $p_{13}$ and $p_{24}$ represent the nonadiabatic transition probability for one passage of the transition region, and is nicely given by the following formula except at the threshold:

$$p = e^{-\pi(q_1 - q_3)} \frac{\sinh\pi(q_3 - q_1)}{\sinh\pi(q_2 - q_1)} \xrightarrow{\varepsilon \to \infty} \frac{V_1}{V_1 + V_2} \quad (5.55)$$
Other probabilities are zeros except for

\[ p_{14} = p_{23} = 1 - p \]  

(5.56)

The \( I_x \) matrix is given by Eq. (5.24) with \( p \) given by Eq. (5.55). This \( I_x \) matrix provides the nonadiabatic transition amplitude in the transition region and can be used even in multidimensional problems.

D. Remarks

There is an important difference between Eq. (5.37) and (5.38) [the same is true between Eq. (5.21) and (5.22)]. The amplitude part of the overall transition probability in Eq. (5.37) has two independent quantities \( N_1 \) and \( N_2 \), but in Eq. (5.38) it has only one \( p \). This means that Eq. (5.38) is not guaranteed to be valid in the threshold region \( (q_2 \to 0) \). Physically speaking, the overall transition process is always a mixture of nonadiabatic transition at avoided crossing and the threshold effect. It would be very good, if we could generalize both \( N_1 \) and \( N_2 \) for a general two-state problem; however, this generalization does not seem possible so far, since the threshold effect is not a localized transition at all. This fact can be seen more clearly from the special case of the exponential model. If we set \( \beta_1 = \beta_2 = 1 \) in Eq. (5.1), the formula Eq. (5.38) will turn to the RZ formula Eq. (5.22), which is obtained by applying \( \beta_1 = \beta_2 = 0 \) in Eq. (5.1). This is possible simply because we neglect the threshold effect completely. This is in good contrast with the fact that Eq. (5.37) with \( \beta_1 = \beta_2 = 1 \) will not become Eq. (5.21) with \( \beta_1 = \beta_2 = 0 \) due to the threshold effects. Fortunately, however, the threshold effects appear conspicuously only in a very small region, as was demonstrated in [31].

Another problem is the judgment of transition type when two adiabatic potentials are given. The parameter \( d \) in Eq. (5.42) can do this, if a certain diabatization can be reasonably carried out. It is more desirable if we could do this only with the information of two adiabatic potentials. This might be possible by introducing another kind of complex phase integral, but this has not been successful and is actually one of the basic motivations in trying to formulate a unified theory within the adiabatic representation. As discussed earlier in this section, the exponential model may be a good candidate for this purpose, since a certain unified semiclassical theory has been already established in the diabatic representation [93]. Some tests were also carried out by somehow extending the exponential potential model at least at relatively high energies [34]. In any case, this is a very challenging subject.

Finally, we would like to draw attention to Eq. (5.3) in which the four transition points in \( Q(p) \) correspond to definitely localized nonadiabatic transitions, and poles in \( S(p) \) may contain information about the nonadiabatic
transition type as well as the threshold effect. How to investigate the Stokes phenomenon of Eq. (5.3) more deeply without the high-energy approximation is still an unsolved problem. Moreover, Eq. (5.3) should also be a useful starting point for dealing with the case that energies are lower than the nonadiabatic transition points, which so far has never been attacked except for the linear curve crossing model.

VI. TIME-DEPENDENT LEVEL CROSSINGS

A. Complete Solutions of the Quadratic Model

As well as the time-independent nonadiabatic transitions, time-dependent ones play important roles in various fields of science. Examples are atomic and molecular dynamic processes in an external field [96], tunneling junctions of the Josephson element in an external electric field, metallic ring current in a magnetic field, and Zener transitions [60–66]. In these cases the external fields depend on time, and the processes are quantum mechanical time-dependent problems. Time-dependent and time-independent nonadiabatic transitions seem very different, but they are closely related to each other as easily conjectured from the fact that the latter can be reduced to the former by the classical approximation where the spatial coordinate is given by a function of time. The famous LZ formula, for example, is an exact solution of the linear potential model in the time domain, while it is a high-energy approximation in the time-independent linear potential model.

In this section, the complete solutions for time-independent curve crossing problems discussed in Sections II–IV are applied to time-dependent problems. It is shown that the exact solutions of the time-independent linear potential model can provide the exact solutions to the time-dependent quadratic potential model [44]. The compact semiclassical solutions developed for the general two-state time-independent potential curve crossing problems can be transferred to general time-dependent curve crossing problems. Time-dependent diabatically avoided crossing problems can also be accurately dealt with, since this case corresponds to the energy region lower than the crossing point in the time-independent curve crossing problem. Note that the NT type in the time-independent case does not show up in the time-dependent problems, since there is no bifurcation into transmission and reflection in the time-dependent case (time is unidirectional).

A general quadratic potential model of the time-dependent curve crossing problem in the diabatic representation is given by

\[
\frac{i\hbar}{\partial t} \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix} = \begin{bmatrix} \hat{\epsilon}_1(t) & V_0 \\ V_0 & \hat{\epsilon}_2(t) \end{bmatrix} \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix}
\]  

(6.1)
where $V_0$ is the constant diabatic coupling, $\hat{\epsilon}_1(t)$ and $\hat{\epsilon}_2(t)$ are quadratic diabatic energy levels given by

\[ \hat{\epsilon}_1(t) = \alpha_1 t^2 + \beta_1 \]  
\[ \hat{\epsilon}_2(t) = \alpha_2 (t - \gamma_2)^2 + \beta_2 \]

Equation (6.1) can be reduced to the following coupled equations:

\[
 i\hbar \frac{d}{dt} \begin{bmatrix} c_1(\tau) \\ c_2(\tau) \end{bmatrix} = \begin{bmatrix} 0 & \frac{1}{2} e^{i \int_0^\tau \Delta \epsilon(\tau') d\tau'} \\ \frac{1}{2} e^{-i \int_0^\tau \Delta \epsilon(\tau') d\tau'} & 0 \end{bmatrix} \begin{bmatrix} c_1(\tau) \\ c_2(\tau) \end{bmatrix} 
\]

where

\[ \tau = 2V_0 \left( t + \frac{\alpha_2 \gamma_2}{\alpha_1 - \alpha_2} \right) / \hbar \]

\[ \Delta \epsilon(\tau) \equiv \frac{[\hat{\epsilon}_1(\tau) - \hat{\epsilon}_2(\tau)]}{V_0} = \alpha \tau^2 - \beta \]

\[ \alpha \equiv \frac{(\alpha_1 - \alpha_2) \hbar^2}{8V_0^3} \]

and

\[ \beta \equiv \left( \beta_2 - \beta_1 + \frac{\alpha_1 \alpha_2 \gamma_2^2}{\alpha_1 - \alpha_2} \right) / 2V_0 \]

Note that this problem can be described in terms of only two parameters, $\alpha$ and $\beta$, and that the two diabatic curves cross (do not cross), if $\beta > 0$ ($\beta < 0$). The parameter $\alpha$ is taken to be positive, that is, $\alpha_1 > \alpha_2$.

Now, we introduce the evolution matrix $F(z, z_0)$ defined by the following equation:

\[
 \begin{bmatrix} c_1(z) \\ c_2(z) \end{bmatrix} = F(z, z_0) \begin{bmatrix} c_1(z_0) \\ c_2(z_0) \end{bmatrix} 
\]
where $z$ represents a complex variable with $\tau = \text{Re}(z)$. From the coupled equation (6.4), we can derive the following properties of $F(z, z_0)$:

$$\text{det} F(z, z_0) = 1 \quad (6.10)$$

and

$$F(z, z_0) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} F^*(z, z_0) \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad (6.11)$$

The transition matrix defined by

$$\begin{bmatrix} c_1(\infty) \\ c_2(\infty) \end{bmatrix} = T^R \begin{bmatrix} c_1(-\infty) \\ c_2(-\infty) \end{bmatrix} \quad (6.12)$$

is obviously equal to $F(\infty, -\infty)$. In addition to unitarity, the transition matrix $T^R$ satisfies the following symmetries, which are derived from the properties of the evolution matrix $F(z, z_0)$:

$$T^R_{11} = (T^R_{22})^* \quad (6.13)$$

and

$$T^R_{12} = T^R_{21} = \text{pure imaginary} \quad (6.14)$$

In order to derive the explicit expression of $T^R$, let us consider the following single differential equation derived from the coupled equations (6.4):

$$\frac{d^2 u(\tau)}{d\tau^2} + I(\tau)u(\tau) = 0 \quad (6.15)$$

where

$$u(\tau) = c_1(\tau) \exp \left[ -\frac{i}{2} \int_{y_0}^{\tau} A\varepsilon(\tau) d\tau \right] \quad (6.16)$$

and

$$I(\tau) = \frac{i}{2} A\varepsilon(\tau) + \frac{1}{4} [A\varepsilon(\tau)]^2 + \frac{1}{4} \quad (6.17)$$
A direct comparison of Eq. (6.15) with the corresponding differential equation in the time-independent linear potential model, see Eq. (2.3) of [13], can derive the following correspondence:

\[ a^2 \leftrightarrow \alpha \]  (6.19)

and

\[ b^2 \leftrightarrow \beta \]  (6.20)

It can also be confirmed that the transition matrix \( T^R \) corresponds to the reduced scattering matrix \( S^R \) of the time-independent case.

With this correspondence, the present time-dependent quadratic potential problem can be solved in exactly the same way as in the time-independent linear potential problem. Thus the transition matrix \( T^R \) exactly corresponds to the reduced scattering matrix \( S^R \) in the time-independent problem. It should be noted that since \( a^2 > 0 \), \( \alpha_1 \) and \( \alpha_2 \) must be chosen so that \( \alpha > 0 \), and that \( b^2 > 0 \) (crossing) corresponds to \( \beta > 0 \).

Following the solution method in the time-independent case, we briefly outline the procedure to obtain the exact solution of \( T^R \) from Eqs. (6.4). First, we introduce the general WKB solutions, with which the asymptotic solutions are given by

\[ u_1(z) = AI^{-1/4}(z) \exp \left[ i \int_{z_0}^{z} \frac{1}{2} I^{1/2}(z) dz \right] + BI^{-1/4}(z) \exp \left[ - i \int_{z_0}^{z} \frac{1}{2} I^{1/2}(z) dz \right] \]  (6.21)

and

\[ u_2(z) = CI^{-1/4}(z) \exp \left[ i \int_{-z_0}^{z} \frac{1}{2} I^{1/2}(z) dz \right] + DI^{-1/4}(z) \exp \left[ - i \int_{-z_0}^{z} \frac{1}{2} I^{1/2}(z) dz \right] \]  (6.22)

where \( A, B, C, \) and \( D \) are certain constants.

If we evaluate the phase integrals in Eqs. (6.21) and (6.22), we can rewrite them as

\[ u_1(z) \xrightarrow{z \to \infty} AI^{-1/4}(z) \exp \left[ iQ^+(z) \right] + BI^{-1/4}(z) \exp \left[ - iQ^+(z) \right] \]  (6.23)
and
\[ u_2(z) \xrightarrow{z \to \infty} CI^{-1/4}(z) \exp \left[ iQ^-(z) \right] + DJ^{-1/4}(z) \exp \left[ -iQ^-(z) \right] \] (6.24)

where
\[ i \int_{z_0}^z I_1(z) dz \xrightarrow{z \to \infty} iQ^+(z) \equiv iP(z) + i\ln(z) + i\delta_+(z_0) \] (6.25)

\[ -i \int_{-z_0}^z I_1(z) dz \xrightarrow{z \to \infty} iQ^-(z) \equiv iP(z) + i\ln(z) + i\delta_-(z_0) \] (6.26)

\[ P(z) = \frac{1}{2} \int_0^z \Delta \varepsilon dz \] (6.27)

and \( \delta_\pm(z_0) \) are constants dependent on the reference point \( z_0 \). Let us now introduce the standard WKB solutions [22] in which the lower limit of the phase integral is not specified,
\[ (\cdot, z) = z^{-1} \exp[iP(z) + i\ln z] \] (6.28)

and
\[ (z, \cdot) = z^{-1} \exp[-iP(z) + i\ln z] \] (6.29)

In terms of these solutions, \( u_1(z) \) and \( u_2(z) \) can be expressed as
\[ u_1(z) \xrightarrow{z \to \infty} A'(\cdot, z) + B'(z, \cdot) \] (6.30)

and
\[ u_2(z) \xrightarrow{z \to \infty} C'(\cdot, z) + D'(z, \cdot) \] (6.31)

From the analysis of the Stokes phenomenon, the following relation among the primed coefficients is obtained [13]:
\[ \begin{bmatrix} C' \\ D' \end{bmatrix} = \begin{bmatrix} 1 + U_2U_3 & U_1 + U_3 + U_1U_2U_3 \\ U_2 & 1 + U_3U_2 \end{bmatrix} \begin{bmatrix} A' \\ B' \end{bmatrix} \] (6.32)

\[ \equiv \begin{bmatrix} L'_{11} & L'_{12} \\ L'_{21} & L'_{22} \end{bmatrix} \begin{bmatrix} A' \\ B' \end{bmatrix} \]
where \( U_1 \sim U_3 \) are the Stokes constants that are functions of \( \alpha \) and \( \beta \). From Eqs. (6.23) and (6.24) with use of Eqs. (6.30)-(6.32), we can obtain the connection matrix \( L \) as

\[
\begin{bmatrix}
C \\
D
\end{bmatrix} = \begin{bmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{bmatrix} \begin{bmatrix}
A \\
B
\end{bmatrix}
\]

(6.33)

Thus, finally the transition matrix is given by

\[
T^R = \begin{bmatrix}
1 + U_1 U_2 & -(U_1 + U_3 + U_1 U_2 U_3) \frac{1}{2\alpha} \\
-2\alpha U_2 & 1 + U_2 U_3
\end{bmatrix}
\]

(6.34)

The following relations among the Stokes constants are obtained from the symmetries of \( T^R \):

\[
2\alpha U_2 = (U_1 + U_3 + U_1 U_2 U_3) \frac{1}{2\alpha} = \text{pure imaginary}
\]

(6.35)

and

\[
U_3 = -U_1^*
\]

(6.36)

These relations enable us to express \( T^R \) in terms of only one Stokes constant \( U_1 \),

\[
T^R = \begin{bmatrix}
1 + U_1 U_2 & -2\alpha U_2 \\
-2\alpha U_2 & 1 - U_1 U_2
\end{bmatrix}
\]

(6.37)

with

\[
U_2 = \frac{U_1 - U_1^*}{4\alpha^2 - U_1 U_1^*}
\]

(6.38)

The total transition probability \( P_{12} \) is expressed as,

\[
P_{12} = |T^R_{12}|^2 = \frac{16\alpha^2 (3U_1)^2}{(|U_1|^2 + 4\alpha^2)^2}
\]

(6.39)
The Stokes constant $U_1$ is exactly expressed in the form of convergent infinite series as shown in [13]. It also has a compact and accurate semiclassical expression, as presented in Section III.

B. Generalizations and Applications

The compact semiclassical formulas derived in the case of time-independent linear potential model can be transferred to the present time-dependent quadratic potential problem with the correspondences Eqs. (6.19) and (6.20). The overall nonadiabatic transition probability $P_{12}$ is given by

$$P_{12} = 4p(1 - p) \sin^2 \psi$$  \hspace{1cm} (6.40)

When the two diabatic potential curves cross as in Figure 11(a), the Stokes constant $U_1$, the nonadiabatic transition probability $p$ for one passage of the

![Diagram](image)

**Figure 11.** Schematic time-dependent quadratic potentials $\varepsilon_1(\tau)$ and $\varepsilon_2(\tau)$. (a) Crossing case. (b) Noncrossing case.
crossing, and the phase $\psi$, are the same as those given by Eqs. (3.41)-(3.43) with $\sigma$ and $\delta$ defined by

$$\sigma + i\delta = \frac{1}{\hbar} \int_{t_0}^{t'} \Delta E(t) dt$$  \hspace{1cm} (6.41)

with

$$\Delta E(t) \equiv E_+(t) - E_-(t)$$  \hspace{1cm} (6.42)

where $E_{\pm}(t)$ are the adiabatic potentials obtained from the diabatic potentials as usual by

$$E_{\pm}(t) = \frac{1}{2} \left\{ \left[ \varepsilon_1(t) + \varepsilon_2(t) \right] \pm \sqrt{\left[ \varepsilon_1(t) - \varepsilon_2(t) \right]^2 + 4V_0^2} \right\}$$  \hspace{1cm} (6.43)
The lower integral limit $t_0$ in Eq. (6.41) is the center of time between the two avoided crossings, and the upper limit $t^*$ is a complex solution of

$$\Delta E(t^*) = 0 \quad (6.44)$$

closest to the real axis.

In the case of general (nonquadratic) curve crossing problem, the parameters $\alpha$ and $\beta$ are given by

$$\alpha = \frac{\sqrt{d^2 - \hbar^2}}{2V_0(t_f^2 - t_b^2)} \quad (6.45)$$

$$\beta = -\sqrt{d^2 - 1} \left( \frac{t_f^2 + t_b^2}{(t_f^2 - t_b^2)} \right) \quad (6.46)$$

with

$$d^2 = \frac{[E_+(t_b) - E_-(t_b)][E_+(t_f) - E_-(t_f)]}{[E_+(t_x) - E_-(t_x)]^2} \quad (6.47)$$

and

$$V_0 = \frac{1}{2} [E_+(t_x) - E_-(t_x)], \quad (6.48)$$

where $t_x$ is the real position at which $E_+(t) - E_-(t)$ becomes minimum, and $t_b(t_f)$ is the bottom (top) of the potential $E_+(t)(E_-(t))$, that is, the point where $(dE_+(t)/dt)(dE_-(t)/dt)$ becomes zero. If it is annoying to evaluate Eq. (6.41) directly, $\sigma$ and $\delta$ can be evaluated from $\alpha$, $\beta$, and $E_\pm(t)$ on the real axis by

$$\sigma + \delta = \frac{1}{\hbar} \left[ \int_0^{t_0} E_-(t)dt - \int_0^{t_0} E_-(t)dt + \Delta \right] \quad (6.49)$$

with

$$\Delta = \frac{\sqrt{2\pi}}{4\sqrt{\alpha F_+^2 + F_-^2}} \left[ F_- + iF_+^c \right] \quad (6.50)$$
where $F^\pm$ are defined by Eqs. (3.46)–(3.50) with $a^2$ and $b^2$ replaced by $\alpha$ and $\beta$. The parameter $d^2$ is now given by Eq. (6.47). When the two crossings lie close together, $\alpha$ and $\beta$ are better estimated by the following expressions:

$$\alpha = \frac{\hbar^2 \sqrt{(\Delta E_M - \Delta E_m)(\Delta E_M + \Delta E_m)}}{(\Delta E_m)^3 t_m^2} \quad (6.51)$$

and

$$\beta = \frac{\sqrt{(\Delta E_M - \Delta E_m)(\Delta E_M + \Delta E_m)}}{\Delta E_m} \quad (6.52)$$

with

$$\Delta E_m = \frac{1}{2} \left[ \Delta E(t_m^{+}) + \Delta E(t_m^{-}) \right] \quad (6.53)$$

$$\Delta E_M = \Delta E(t_M) \quad (6.54)$$

and

$$t_m = \frac{1}{2} \left( t_m^{+} + t_m^{-} \right) \quad (6.55)$$

where $t_m^{(+)}$ are the positions at which $\Delta E(t) = E_2(t) - E_1(t)$ becomes minimum, and $t_M$ is the position at which $\Delta E(t)$ becomes maximum.

When, on the other hand, the two diabatic potentials do not cross as in Figure 11(b), we have to use the formulas that are valid at $E < E_X$, that is, Eqs. (3.51)–(3.57) with Eq. (6.41). Again, if it is difficult to evaluate Eq. (6.41), $\sigma$ and $\delta$ can be evaluated by Eq. (6.50) with $\beta < 0$.

The parameters $\alpha$ and $\beta$ are obtained by fitting the position of the minimum of $(\Delta E)^2$ by a quadratic polynomial as

$$\alpha = \hbar^2 \frac{XY}{(XZ - Y^2)^{3/2}} \quad (6.56)$$

and

$$\beta = -\frac{Y}{XZ - Y^2} \quad (6.57)$$
where

\[
X = \frac{1}{24} \left\{ \frac{d^4}{dt^4} [\Delta E(t)]^2 \right\}_{t=0} 
\]  
(6.58)

\[
Y = \left\{ \frac{d^2}{dt^2} [\Delta E(t)]^2 \right\}_{t=0} 
\]  
(6.59)

and

\[
Z = [\Delta E(t)]^2_{t=0} 
\]  
(6.60)

In the numerical examples shown below [44], \( \sigma \) and \( \delta \) are evaluated with the use of Eqs. (3.14)–(3.17) of [44], which correspond to Eqs. (3.2)–(3.8) in [17]. Equation (6.50) is, however, finally recommended, since this is better as mentioned before [18]. The numerical examples shown here are not affected, since the values of \( \alpha \) in the examples sit in the range where Eqs. (3.14)–(3.17) of [44] can work well. We would like to take this opportunity to show that Eq. (3.15) of [44] should contain \( \sqrt{\beta/\alpha} \) and the term corresponding to the first term of Eq. (3.4) of [17].

Let us now consider, as an example, the following model:

\[
\varepsilon_1(t) = -(A \cosh \omega t + B) 
\]  
(6.61)

and

\[
\varepsilon_2(t) = (A \cosh \omega t + B) 
\]  
(6.62)

The coupling \( V_0 \) is taken to be constant. The adiabatic potentials are given by

\[
E_\pm = \pm \left[ (A \cosh \omega t + B)^2 + V_0^2 \right]^{1/2} 
\]  
(6.63)

There are an infinite number of complex crossing points given by

\[
\omega^* = \ln \left[ \frac{-B \pm iV_0}{A} \pm \sqrt{\left( \frac{-B \pm iV_0}{A} \right)^2 - 1} \right] \pm 2\pi i 
\]  
(6.64)

but here the crossing point nearest to the real axis is taken. This means that the other complex crossing points do not contribute very much to the transition probability. Numerical comparisons between the exact results and the
semiclassical results are shown in Figure 12 for $A/V_0 = 1.0$ and $A/V_0 = 5.0$. The region $B/V_0 > -A/V_0$ corresponds to the non-crossing regime. This clearly demonstrates the usefulness of the present analytical formulas that cover nicely both crossing and noncrossing regimes even for nonquadratic problems.

As an additional example of general curved potentials with two crossing points, we take laser assisted surface ion neutralization (LASIN), which is a neutralization process induced by laser in the collision between an ion and a metal surface. We consider an electron transfer from a single valence bond state $\varepsilon_1$ of the surface to a state $\varepsilon_2$ of the atom. According to [52], this process can be described by the following coupled equations:

$$
\begin{bmatrix}
    i\hbar \dot{c}_1(t) \\
    i\hbar \dot{c}_2(t)
\end{bmatrix} =
\begin{bmatrix}
    E_2(t) & g(t) \\
    g(t) & E_1(t) + \hbar \eta
\end{bmatrix}
\begin{bmatrix}
    c_1(t) \\
    c_2(t)
\end{bmatrix}
$$

(6.65)

Figure 12. Transition probability in the case of hyperbolic cosine potential [$\Delta \varepsilon(\tau) = 2A/V_0 \cosh \tau + 2B/V_0$] against $B/V_0$. Solid line: exact numerical result, open circle: present semiclassical theory. (a) $A/V_0 = 1.0$ (b) $A/V_0 = 5.0$. 
with

\[ 2E_1(t) = \varepsilon_1 + \varepsilon_2 - [4V^2(t) + \omega^2]^{1/2} \quad (6.66) \]

\[ 2E_2(t) = \varepsilon_1 + \varepsilon_2 + [4V^2(t) + \omega^2]^{1/2} \quad (6.67) \]

and

\[ g(t) = \frac{1}{2} W_0 \omega f(\lambda t) / [4V_0^2(t) f^2(\lambda t) + \omega^2]^{1/2} \quad (6.68) \]

where

\[ V(t) = V_0 f(\lambda t) \quad (6.69) \]
\[ f(\lambda t) = \sech(\lambda t) \] (6.70)

and \( \omega \) is the energy defect defined by \( \omega = \varepsilon_2 - \varepsilon_1 > 0 \). The states \( E_1(t) \) and \( E_2(t) \) are the adiabatic states originating from \( \varepsilon_1 \) and \( \varepsilon_2 \) with the electronic hopping interaction potential \( V(t) \) diagonalized. The state \( E_1(t) \) is further dressed by one photon absorption to \( E_1(t) + \hbar \eta \), where \( \hbar \eta \) represents the photon energy. The quantity \( g(t) \), given by Eq. (6.68), represents the interaction with a laser field after the first diagonalization procedure is carried out. The rotating wave approximation is also used.

The parameters \( \sigma \) and \( \delta \) are determined by the following complex integral:

\[
\sigma + i\delta = \frac{1}{\hbar} \int_0^\prime dt [4g^2 + (E_2 - E_1 - \eta)^2]^{1/2} \quad (6.71)
\]

By introducing the following dimensionless parameters:

\[
X = \lambda t \quad (6.72)
\]

\[
r = \hbar \eta / 2V_0 \quad (6.73)
\]

\[
q = \hbar \omega / 2V_0 \quad (6.74)
\]

\[
\nu = 2V_0 / \lambda \quad (6.75)
\]

and

\[
E = W_0 / 2V_0 \quad (6.76)
\]

we can rewrite Eq. (6.71) as

\[
\sigma + i\delta = \nu \int_0^{X^\prime} dX \left[ \frac{E_2^2 q^2 f^2(X)}{f^2(X) + q^2} + \left\{ \left[ f^2(X) + q^2 \right]^{1/2} - r \right\}^2 \right]^{1/2} \quad (6.77)
\]

where \( X^\prime \) is the complex zero of the integrand, and is given by

\[
X^\prime = \ln \left[ \pm \frac{1}{\sqrt{x - q^2}} \pm \sqrt{\frac{1}{x - q^2} - 1} \right] \pm 2n\pi i \quad (n = 0, 1, \ldots) \quad (6.78)
\]
Here $x$ satisfies the following equation:

$$
x^4 + (2E^2q^2 - 2r^2)x^3 + (E^4q^4 + 2E^2q^2r^2 + r^4 - 2E^2q^4)x^2 
- (E^2q^6 + 2E^2q^4r^2)x + E^4q^8 = 0
$$

It can be shown that the substitution of the real solutions of Eq. (6.79) gives $X^*$ with a large imaginary part, and that we need a complex solution of Eq. (6.79) to find $X^*$ closest to the real axis.

In the case of a weak laser field discussed in [52], the parameter $\alpha$ is extremely large ($\approx 10^4$), and the ordinary simple perturbation theory with respect to $g$ works well. In order to demonstrate the effectiveness of the present semiclassical theory, we have chosen a much stronger laser field ($\alpha \approx 0.7$) for which the perturbation theory does not work at all. Figure 13 shows the results for $E = 0.25$, $q = 0.2923$, and $v = 23.585$. The present theory can nicely cover the diabatically avoided crossing region ($r > 1.042$). Note that when the parameter

![Graph showing transition probability as a function of the dimensionless laser photon energy $r$ in the case of LASIN. The parameters chosen are $v = 23.585$, $q = 0.29225$, and $E = 0.25$. The region $r > 1.04183$ corresponds to the diabatically avoided crossing.](image-url)
\( \alpha \) is extremely large \(( \alpha > 10^3 \) for which the perturbation theory works well, the present semiclassical theory produces an erroneous sharp peak near the point where the two diabatic potentials touch each other. This is because of the empirical correction, but the theory still gives an overall correct behavior if we neglect this sharp peak.

Multilevel problems and/or problems with more than two avoided crossings can be treated by dividing the total process into nonadiabatic transitions and adiabatic propagation, and total transition probability is given by the multiplication of transition matrices and adiabatic propagation matrices. This idea itself is not new at all. By utilizing our new formulas shown above, however, it is possible to treat diabatically avoided crossing and two closely lying avoided crossings as one unit. For isolated avoided crossing, the transition matrix \( I_X \) is given by

\[
I_X \equiv \begin{bmatrix}
\sqrt{1 - pe^{i\phi}} e^{i(\psi - \sigma)} & -\sqrt{pe^{i\phi}} e^{i\sigma_0} \\
\sqrt{pe^{-i\phi}} & \sqrt{1 - pe^{-i\phi}} e^{-(\psi - \sigma)}
\end{bmatrix}
\]  

(6.80)

where \( \psi, \sigma \) and \( p \) are given, respectively, by Eqs. (3.43), (3.44) and (3.42) or by Eqs. (3.54), (3.44) and (3.53), and \( \sigma_0 \) is given by

\[
\sigma_0 = \text{Re} \left[ \frac{1}{\hbar} \int_R^{t'} E_1(t) dt \right]
\]  

(6.81)

For an diabatically avoided crossing or a pair of two closely lying avoided crossings, the transition matrix is \( T_{12}^R \) given by Eq. (6.37). The adiabatic propagation matrix \( X \) is given by

\[
X \equiv \begin{bmatrix}
e^{-i \int_{\alpha}^{\beta} E_1(t) dt} & 0 \\
0 & e^{-i \int_{\alpha}^{\beta} E_2(t) dt}
\end{bmatrix}
\]  

(6.82)

As an example of a two state multicrossing problem, we take here the periodic crossing model in which the diabatic levels,

\[
\varepsilon_1 = -(A \sin \omega t + B)
\]  

(6.83)

and

\[
\varepsilon_2 = (A \sin \omega t + B)
\]  

(6.84)
are coupled by a constant coupling $V_0$. This model is frequently discussed for the systems with a periodic external field (Zener tunneling in a periodic external field is one of the examples). The adiabatic potentials of this model is given by

$$E_\pm = \pm [(A \sin \omega t + B)^2 + V_0]^{1/2} \quad (6.85)$$

and the complex crossing points closest to the real axis are expressed as

$$t' = \frac{i}{\omega} \ln \left[ \frac{V_0 - iB}{A} + \sqrt{\left( \frac{-iB \pm iV_0}{A} \right)^2 + 1} \right] \quad (6.86)$$

Finally, the total transition matrix is expressed as

$$T = I_X X I_X X \cdots \quad (6.87)$$

The matrix $X$ represents the adiabatic propagation between crossing points. When the diabatic potentials avoid crossing, we have

$$T = T^R X T^R X \cdots \quad (6.88)$$

The results are shown in Figure 14 for $A/V_0 = 15.0, B/V_0 = 0.0$ [Fig. 14(a)] and $B/V_0 = 18.0$ [Fig. 14(b)]. The region $B/V_0 > A/V_0$ corresponds to the noncrossing regime, and the famous LZ formula does not work at all there. Our theory, on the other hand, works well in all regions of $A/V_0$ and $B/V_0$. Even the time-evolution of the whole process can be well reproduced in the adiabatic representation.

The matrix multiplication method explained in Section IV.A can be easily extended to multilevel crossing problems. The matrices $I_x$, $T^R$, and $X$ become $N \times N$ matrices, where $N$ is the number of levels. From the analysis of the time-independent multi-channel curve crossing problems [24, 25], we can safely expect that this kind of two-by-two approximation works well, because our basic two-state theory is very accurate. The matrix $I_x$ (or $T^R$) contains a $2 \times 2$ submatrix given by Eq. (6.80) [or Eq. (3.60)], representing a transition at the relevant crossing; otherwise this matrix is diagonal. For the evaluation of the basic parameters $\sigma$ and $\delta$, the following three methods are possible. The first and the most accurate one is to diagonalize the whole $N \times N$ potential matrix to obtain fully adiabatic potentials and then evaluate the complex contour integral given by Eq. (6.41) for each relevant avoided crossing. This is quite difficult, unfortunately, because practically it is very hard to find complex crossing points accurately, especially when the number of states $N$ exceeds three. The simplest, yet still good method is the two-by-two diabatic approach, in which only the
Figure 14. Transition probability as a function of time in the case of $\Delta \epsilon(\tau) = 2A/V_0 \sin(\tau) + 2B/V_0$ with $A/V_0 = 15.0$. Solid line: exact, dashed line: present semiclassical theory. The region $B/V_0 > A/V_0$ corresponds to the noncrossing regime. (a) $B/V_0 = 0.0$, (b) $B/V_0 = 18.0$.

relevant two states are considered at each crossing. In the two-state case, it is, of course, not difficult to evaluate the integral in Eq. (6.41). If the couplings at other crossings are strong and affect the relevant crossing, however, this method naturally breaks down. The third method is to evaluate the parameters $\sigma$ and $\delta$ from fully adiabatic potentials on the real axis only [Eqs. (6.49)–(6.50)]. This method can avoid the annoying complex calculus and is quite convenient, being more accurate than the two-by-two diabatic approach.

Now we take the following three-level problem:

$$H = \begin{bmatrix}
-a_1t^2 + b_1 & V_{12} & V_{13} \\
V_{12} & a_2t^2 & 0 \\
V_{13} & 0 & a_3t^2 + b_3
\end{bmatrix}$$

(6.89)
where $V_{ij}$ are constant couplings and $a_1, a_2, a_3, b_1, b_3 > 0$. The dimensionless parameters defined as $\alpha_j \equiv \hbar^2 a_j / 8V_{12}^3$, $\beta_j \equiv b_j / 2V_{12}$ are taken to be $\alpha_1 = 0.05$, $\alpha_2 = 0.061$, $\alpha_3 = 0.111$, $\beta_1 = 1.66$, and $\beta_3 = 1.0$. Figure 15 depict the diabatic and adiabatic potentials for (a) $V_{13}/V_{12} = 1.0$ and $V_{13}/V_{12} = 0.2$. Figure 16(a)–(c) shows the results of the three methods mentioned in Section III.C in comparison with the exact results as a function of $V_{13}/V_{12}$. The method based on the complex crossing points in the full adiabatic representation works very well even in a strong coupling region [see Fig. 16(a)]. The two-by-two diabatic method, on the other hand, does not work well in a strong coupling region (see Fig. 16(b)). The third method, which employs the parameters given by Eqs. (6.45)–(6.50) evaluated from the full adiabatic potentials on the real axis, gives much better results than the two-by-two diabatic method, even though the required computational effort is not much at all. This method works well until the full adiabatic potentials become flat [as in Fig. 15(a)] and the
Figure 15. Diabatic (dashed line) and full adiabatic (solid line) potentials in the case of three-level problems of Eq. (6.89) with (a) $V_{13}/V_{12} = 1.0$ and (b) $V_{13}/V_{12} = 0.2$. The ordinate and abscissa are the scaled energy, $\alpha_i \tau^2 + \beta_i$, and the scaled time, $\tau = 2V_{12}t/\hbar$, respectively [see the text below Eq. (6.89)].

parameters cannot be estimated. Since the search of complex crossing points becomes extremely difficult when the number of states exceeds three, the third method based on Eqs. (6.45)-(6.50) is recommended.

C. Other Models

Theoretical studies of time-dependent curve crossing problems naturally have a long history [6, 40, 41]. After the famous LZ and RZ models, various types of multilevel as well as two-state problems have been studied. Here, some important models are summarized.

Nikitin's exponential model [6] is a sort of mixture of LZ and RZ models, since it describes the nonadiabatic transition due to the time variations in both
diabatic energy and diabatic coupling. The Hamiltonian of this model in the diabatic representation is given by [cf. Eq. (133)]

\[
H_{\text{exp}} = \begin{bmatrix}
U_1 + V_1 e^{-\beta t} & Ve^{-\beta t} \\
Ve^{-\beta t} & U_2 + V_2 e^{-\beta t}
\end{bmatrix}
\] (6.90)

The Shrödinger equation for this model can be solved in terms of confluent hypergeometric function, and the nonadiabatic transition probability is given by

\[
p_{\text{exp}} = \exp(-\pi \delta_2) \frac{\sinh(\pi \delta_1)}{\sinh[\pi(\delta_1 + \delta_2)]}
\] (6.91)

where

\[
\delta_1 = \frac{U_1 - U_2}{2\hbar \beta} \left[ 1 + \frac{(V_1 - V_2)/2V}{\sqrt{1 + (\frac{V_1 - V_2}{2V})^2}} \right]
\] (6.92)
Figure 16. Transition probabilities against the coupling strength $V_{13}/V_{12}$ in the case of the three-level problem given in Eq. (6.89). Solid line: $P_{1,1}$ (exact), dash-dot line: $P_{1,2}$ (exact), dotted line: $P_{1,-1}$ (exact), solid circle: $P_{1,1}$ (semiclassical), solid rhomb: $P_{1,2}$ (semiclassical), solid triangle: $P_{1,-1}$ (semiclassical). (a) The semiclassical theory is based on the complex crossing points in the full adiabatic representation. (b) The semiclassical theory is based on the two-by-two diabatic approach. (c) The semiclassical theory is based on the parameter defined by Eqs. (6.45)-(6.50).

and

$$
\delta_2 = \frac{U_1 - U_2}{2\hbar\beta} \left[ 1 - \frac{(V_1 - V_2)/2V}{\sqrt{1 + (V_1 - V_2)^2/4V^2}} \right]
$$

Another important two-state model may be the one by Demkov–Kunike, in which two hyperbolic tangent diabatic levels are coupled by a hyperbolic secant potential [36].

The Demkov–Osherov model [35] is a generalization of the LZ model for multilevel problem. In this model, a band of flat parallel levels with an arbitrary
spacing cross another slant level. In this model, the various transition probabilities are simply expressed as a product of $p_{LZ}$ or $1 - p_{LZ}$, where $p_{LZ}$ is the LZ probability. This is exact because of the peculiarity of the model. The next step of generalization was proposed by Demkov and Ostrovsky [37]. In their model, two bands of parallel levels cross each other, namely, the diabatic levels are given by

$$H_{an,an} = \beta_at + \omega_{an}$$

where the index $a(= 1, 2)$ labels the band, and $n$ labels the states in each band, and the diabatic coupling is nonzero (constant) only between the levels belonging to different bands.

The bowtie model is another type of multilevel system, in which many linear potentials cross at one point. After the three-level case of this model was solved
by Carroll and Hioe [43], Ostrovsky and Nakamura [38] obtained the general solution for the $N$-level case where the Hamiltonian is given by

$$H_{0,0} = 0$$ \hspace{1cm} (6.95)

$$H_{i,i} = \beta_j t$$ \hspace{1cm} (6.96)

$$H_{j,0} = H_{0j} = V_j(j \neq 0)$$ \hspace{1cm} (6.97)

and

$$H_{j,k} = 0(k \neq 0, j \neq 0)$$ \hspace{1cm} (6.98)
where
\[ \ldots \beta_{-3} < \beta_{-2} < \beta_{-1} < \beta_0 < \beta_1 < \beta_2 < \ldots \]  
(6.99)

The probability \( P_{ij} \) of the transition from the diabatic state \( i \) to the diabatic state \( j \) is exactly obtained. For example, \( P_{00} \) is given by
\[ P_{00} = \left[ 1 - \prod_{n > 0} p_n - \prod_{n < 0} p_n \right]^2 \]  
(6.100)

where \( p_j \) is given by the LZ formula, namely,
\[ p_j = \exp \left[ -\frac{\pi V_j^2}{|\beta_j|} \right] \]  
(6.101)

The general transition probability \( P_{ij} \) for arbitrary \( i \) and \( j \) can also be written in terms of \( p_k \) and \( 1 - p_k \), and the physical interpretation can be provided [42]. It is interesting to note that the total transition probability for both the bowtie and Demkov–Osherov model can be simply given in terms of a product of the two-state LZ probability. This, however, does not hold for general multilevel problems because of the interference effect and deviation from the linear model. As described in the Section VLC, the present theory works well for the general case, since it not only contains the interference effect but also can deal with curved potentials.

VII. NEW WAY OF CONTROLLING MOLECULAR PROCESSES BY TIME-DEPENDENT EXTERNAL FIELDS

A. Basic Theory

In this section, being based on the developments in the theory of nonadiabatic transition discussed above, we propose a new idea [46,47] to control nonadiabatic processes so that an overall transition probability to any specified state in a multichannel curve crossing system becomes unity. This can be realized by periodically sweeping the external field in time at the crossing point. By periodically changing the field, either field strength or the frequency, we can use not only the nonadiabatic transition probability for one passage of crossing point but also the various phases and the number of sweeping periods as control parameters. By taking a simple two-state curve crossing as a function of time (see Fig. 17), we explain and formulate our basic idea. It should be emphasized that the theory proposed here can be applied to general multichannel problems as far as the crossings are relatively well separated.
The transition matrix $I$, which describes the transition from $F_a$ to $F_b$ (see Fig. 17), is given by

$$I = \begin{bmatrix} \sqrt{1-p}e^{i(\phi_0+\sigma_1/2+\sigma_2/2)} & \sqrt{p}e^{i(\sigma_0-\sigma_1/2+\sigma_2/2)} \\ -\sqrt{p}e^{-i(\sigma_0-\sigma_1/2+\sigma_2/2)} & \sqrt{1-p}e^{-i(\phi_0+\sigma_1/2+\sigma_2/2)} \end{bmatrix}$$  \hspace{1cm} (7.1)$$

while the transpose of this matrix, $I'$, describes the backward transition from $F_b$ to $F_a$. Here, $p$ represents the nonadiabatic transition probability by one passage.
of the crossing point $F_x$, $\phi_s$ is the Stokes phase, and $\sigma_0$, $\sigma_1$, and $\sigma_2$ are the phase factors which are defined, respectively, by

\[
\sigma_0 = \text{Re} \left( \int_{F_a}^{F_x} \frac{\Delta E(F)}{dF} dF \right) = \text{Re} \left[ \int_{t_a}^{t_x} \Delta E(t) dt \right] \quad (7.2)
\]

\[
\sigma_1 = \int_{F_a}^{F_x} \frac{\Delta E(F)}{dF} dF = \int_{t_a}^{t_x} \Delta E(t) dt \quad (7.3)
\]

and

\[
\sigma_2 = \int_{F_a}^{F_b} \frac{\Delta E(F)}{dF} dF = \int_{t_a}^{t_b} \Delta E(t) dt \quad (7.4)
\]

where $\Delta E(F)$ is the adiabatic energy difference at the field parameter $F$, $F_*$ is the solution of $\Delta E(F_*) = 0$, and $F_x$ is the field parameter corresponding to the diabatic crossing point. The time $t_a$ for $\alpha = a, b, x, \text{ and } *$ is the time at which $F(t_a) = F_x$ is satisfied. Since $\Delta E \neq 0$ on the real axis, $F_*$ and $t_*$ are complex numbers. Note that the compact analytical expressions of these quantities are available even for the cases where the two diabatic potentials tangentially touch each other ($F_b = F_x$) or avoid crossing ($F_b < F_x$).

The final overall transition matrix $T_n$ after $n$ periods of oscillation between $F_a$ and $F_b$ is expressed as

\[
T_n = T^n \quad (7.5)
\]

where $T$ is the transition matrix for one period, which is given by

\[
T \equiv I' I = \begin{bmatrix}
(p + (1 - p)e^{2i\psi})e^{-i\sigma} & -2i\sqrt{p(1-p)}\sin\psi \\
-2i\sqrt{p(1-p)}\sin\psi & (p + (1 - p)e^{-2i\psi})e^{i\sigma}
\end{bmatrix} \quad (7.6)
\]

with $\psi \equiv \phi_s + \sigma_0 + \sigma_2$ and $\sigma \equiv 2\sigma_0 + \sigma_2 - \sigma_1$.

In the case of $n$ and half periods of traversing the crossing point, the overall transition matrix is given by

\[
T_{n+1/2} = I'(I')^n = IT^n \quad (7.7)
\]

Note that the adiabatic potentials, and thus the parameters $p$, $\psi$, and $\sigma_i (i = 0 \sim 2)$, are dependent on the external field. Roughly speaking, the non-adiabatic transition probability $p$, the Stokes phase $\phi_s$, and the phase $\sigma_0$ are dependent on the local functionality of the adiabatic potentials around
NONADIABATIC TRANSITIONS DUE TO CURVE CROSSINGS

the crossing point, namely, the sweep velocity \((dF/dt)\) of the external field at the crossing point; while, the phase factors \(\sigma_1\) and \(\sigma_2\) are dependent on the global functionality of the adiabatic potentials in the range \((F_a, F_b)\) of the field. We try to find conditions for the parameters \((n, p, \psi, \sigma_i (i = 1 \sim 2))\) to satisfy

\[
P_{12}^{(n)} \equiv |(T_n)_{12}|^2 = 0 \text{ or } 1 \tag{7.8}
\]

or

\[
P_{12}^{(n+1/2)} \equiv |(T_{n+1/2})_{12}|^2 = 0 \text{ or } 1 \tag{7.9}
\]

By using the Lagrange–Sylvester formula, we obtain

\[
T_n = T^n = \frac{\lambda_+ \lambda_- (\lambda_-^{n-1} - \lambda_+^{n-1})}{\lambda_+ - \lambda_-} E + \frac{\lambda_+^n - \lambda_-^n}{\lambda_+ - \lambda_-} T \tag{7.10}
\]

where \(E\) is the unit matrix and \(\lambda_{\pm}\) are the eigenvalues of \(T\), which are given by

\[
\lambda_{\pm} = e^{\pm i\xi} \tag{7.11}
\]

where

\[
\cos \xi = (1 - p) \cos (2\psi - \sigma) + p \cos (\sigma) \tag{7.12}
\]

The unitarity of the matrix \(T\) requires \(\xi\) to be real. Equation (7.12) implies that the nonadiabatic transition probability \(p\) should satisfy

\[
\frac{1 - |\cos \xi|}{2} \leq p \leq \frac{1 + |\cos \xi|}{2} \tag{7.13}
\]

Then, the requirements of Eq. (7.8) lead, respectively, to

\[
P_{12}^{(n)} = \left| \frac{\lambda_+^n - \lambda_-^n}{\lambda_+ - \lambda_-} T_{12} \right|^2
= 4 \frac{\sin^2 (n\xi)}{\sin^2 \xi} p(1 - p) \sin \psi = 0 \tag{7.14}
\]

or

\[
P_{12}^{(n)} = 4 \frac{\sin^2 (n\xi)}{\sin^2 \xi} p(1 - p) \sin^2 \psi = 1 \tag{7.15}
\]
In the case of Eq. (7.14), we simply have the condition $\sin (n\xi) = 0$ or $\sin \psi = 0$. It is more interesting and worthwhile to consider Eq. (7.15). If $P_{12}^{(2n)} = 1$ holds for $n$ periods, then $P_{12}^{(2n)} = 0$ must be satisfied for $2n$ periods; thus Eq. (7.15) for $n$ may be divided into the following two conditions:

$$\sin (2n\xi) = 0 \quad (7.16)$$

and

$$4p(1-p)\sin^2 \psi = \sin^2 \xi \quad (7.17)$$

Since $\sin (n\xi) \neq 0$ in general because of Eq. (7.15), Eq. (7.16) leads to

$$\sin^2 (n\xi) = 1 \quad (7.18)$$

This equation determines $\xi$ for a given $n$, and Eq. (7.17) gives a condition for $p$ and $\psi$ for a given $\xi$. The phase $\sigma$ may be determined from Eq. (7.12). Equation (7.17) implies that $p$ must satisfy the following condition:

$$p(1-p) \geq \frac{1}{4} \sin^2 \xi \quad (7.19)$$

which is the same as Eq. (7.13).

The above analysis can be summarized as follows: (1) For a given system, the nonadiabatic transition probability $p$ is estimated as a function of the external field. (2) From Eq. (7.18), $\xi$ is determined for an appropriately specified $n$. If $p$ is not in the range of Eq. (7.13), the external field (mainly the sweep velocity) and/or $n$ should be modified so that this condition is satisfied. (3) The phase $\psi$ is controlled by changing $\sigma_1$ to satisfy Eq. (7.17), while $\sigma$ is controlled by changing $\sigma_2$ to satisfy Eq. (7.12). These can be realized by adjusting the oscillation period $n$ and the range $(F_a, F_b)$ of the field. When the above procedure is completed, then we can achieve $P_{12}^{(n)} = 1$. The required range of $p$ as a function of $\xi$ given by Eq. (7.13) can be easily known and be used to search for appropriate conditions for the parameters.

Let us next consider $n$ and half-periods of oscillation of the external field [see Eq. (7.9)]. This case together with the $n$ period case discussed above is useful to treat general multilevel problems, since this enables us to follow any specified path from any initial state to any desirable final state. If either one of the conditions of Eq. (7.9) is satisfied for $n$ and half-periods, then $P_{12}^{(2n+1)} = 0$ must be satisfied for $2n + 1$ periods. Then, from Eq. (7.14), we have

$$\sin^2 [(2n + 1)\xi] = 0 \quad (7.20)$$
Now, the condition $P_{12}^{(n+1/2)} = 0$ can be explicitly expressed as

$$4(1 - p) \sin^2(\psi - \sigma) = \frac{\sin^2 \xi}{\sin^2(n\xi)}$$

(7.21)

which tells

$$(1 - p) \geq \frac{\sin^2 \xi}{4 \sin^2(n\xi)}$$

(7.22)

On the other hand, the condition $P_{12}^{(n+1/2)} = 1$ can be reduced to the following equation:

$$4p \sin^2(\psi - \sigma) = \frac{\sin^2 \xi}{\sin^2(n\xi)}$$

(7.23)

which implies

$$p \geq \frac{\sin^2 \xi}{4 \sin^2(n\xi)}$$

(7.24)

From Eqs. (7.20), (7.22), and (7.24), we end up with the same condition for the range of $p$ as Eq. (7.13).

Search for the best condition of the parameters can be done in the same way as in the $n$-period case. In the case of the requirement $P_{12}^{(n+1/2)} = 0$, Eq. (7.18) in the above step (2) should be replaced by Eqs. (7.20), and (7.17) has to be replaced by Eq. (7.21). In the case of $P_{12}^{(n+1/2)} = 1$, on the other hand, Eqs. (7.20) and (7.23) take the place of Eqs. (7.18) and (7.17) in the procedure.

An example of multilevel crossing is shown in Figure 18, which is taken from the quantum tunneling of the magnetization of Mn12Ac in a time-dependent magnetic field [67, 97, 98]. Here, we consider the lowest three adiabatic states 1–3, and demonstrate control of the nonadiabatic processes by our idea presented above. The Hamiltonian is taken from Eq. (1) of [97]. In Figure 18, the energy is scaled by the anisotropy energy $D$. Figure 19 shows the time evolution of the state probability from the point “a” on state 1 to “b” on state 3 via two avoided crossings A and B. At the avoided crossing A(B) four-(five-) period oscillation of the field is applied. This is shown in Figure 19(a). The probability of the state $I(P_1)$ becomes zero after the four periods, as is seen in Figure 19(b). The probability $P_2$ reaches unity when $P_1$ becomes zero, and after five periods at B it becomes zero [Fig. 19(c)] at which time $P_3$ reaches unity [Fig. 19(d)]. Figure 20 demonstrates another path from “a” on state 1 to “c” on state 3.
Figure 18. Adiabatic spin states as a function of an external magnetic field, $g\mu_B H$: three lowest levels (scaled by the anisotropy energy $D$) are shown, where $g$ is the Landé $g$ factor, $\mu_B$ is the Bohr magneton, and $H$ is the magnetic field. The nonadiabatic probabilities $p$ at avoided crossings A–C are 0.039, 0.977, and 0.977, respectively.

via two avoided crossings A and C. In this case, we have applied four and half (five)-periods of oscillation of the field at the avoided crossing A(C). This example clearly demonstrates that we can choose any path to reach any specified final state with unity probability.

Figures 19 and 20 are the results of a numerical solution of the coupled Schrödinger equations; but we have confirmed that the semiclassical theory developed by the present authors [44] based on the present new theory for the time-dependent nonadiabatic transition gives the results almost indistinguishable from Figure 19(b)–(d) and Figure 20(b)–(d) except for the humps and dips that appear when the probability jumps abruptly. This guarantees that
Figure 19. Controlled nonadiabatic processes, starting from "a" on state 1 and ending at "b" on state 3 via avoided crossings A and B (see Fig. 18). (a) Variation of the external magnetic field as a function of time, $g\mu_B H/D$. The first four-period oscillation around $g\mu_B H/D = 0$ corresponds to the control at the avoided crossing A. The second five-period oscillation around $g\mu_B H/D = 1.0$ corresponds to the control at B. (b) Time evolution of the probability $P_1$ for the system to be staying on the state 1. (c) Time evolution of $P_2$. (d) Time evolution of $P_3$. 
we do not have to solve multichannel coupled equations numerically, and that we can formulate all necessary conditions of control analytically.

B. Control by Laser Field

With the help of nonadiabatic Floquet theory [45], our control theory is applicable to controlling by a laser field. In this case, the frequency and/or the
intensity can be the adiabatic parameter(s) to sweep. Sweeping the frequency induces the LZ type of nonadiabatic transition, while sweeping the intensity induces the RZ type. Utilizing such nonadiabatic transition several times, unit transition probability can be realized with a small laser intensity.

Let us take, as an example, a 1D model of a laser-induced ring-puckering isomerization of trimethylenimine, which was discussed by Sugawara and Fujimura [99]. This problem may be reduced to a double well problem in which the left (right) well corresponds to the isomer A (B), and the isomerization from A to B occurs through tunneling from the left well to the right well [see Fig. 21(a)]. We try to control this isomerization with use of the various types of laser pulses. All the parameters to determine the potential system are taken from [99].

The Floquet-state diagram as a function of laser frequency $\omega$ (cm$^{-1}$) with constant intensity [$I = 0.1$(TW/cm$^2$)] is shown in Fig. 21(b). A lot of avoided crossings appear, where the energy gap is proportional to the laser intensity $I$ and the square of the transition dipole moment between the corresponding two states. We can treat each avoided crossing separately unless the laser intensity is extremely strong and avoided crossings overlap with each other.

Nonadiabatic transitions among the Floquet states induced by the variation of intensity and/or frequency can be described by the nonadiabatic Floquet theory [45,100], and we can employ the various analytical theories of nonadiabatic transition to analyze them. Next, demonstrate the control of vibrational transitions and isomerization numerically with use of the various theoretical schemes.

1. **Landau–Zener Type of Nonadiabatic Transition**

If the system has a clear avoided crossing as a function of the adiabatic parameter, the LZS type transition can be utilized. The Hamiltonian of the simplest linear potential model of LZ, as is well known, is given by

$$H_{LZ} = \begin{bmatrix} \alpha_1t & V \\ V & \alpha_2t \end{bmatrix}$$

(7.25)

where $V$ is the constant diabatic coupling and $t$ is the time. In the case of a laser, this model corresponds to the constant intensity and linear sweeping of the frequency. This model is good enough to explain qualitative features of our control scheme. The nonadiabatic transition occurs at $t = 0$ with the transition probability $p$ given by

$$p_{LZ} = \exp \left(-2\pi \frac{V^2}{\hbar \alpha} \right) = \exp \left(-2\pi \frac{I \omega^2}{\hbar^2 |l - m| \omega} \right)$$

(7.26)

where $\alpha \equiv |\alpha_1 - \alpha_2|$; $l$ and $\omega$ are the laser intensity and the sweep velocity of the frequency at the avoided crossing, respectively; $l$ and $m$ (can be negative) are the
Figure 21. (a) A double well potential model of ring-puckering isomerization of trimethylenimine (see [99]). The origin of potential energy is taken at the barrier top. The horizontal solid line represents the main portion of the eigenfunction. (b) Floquet-state diagram, that is, vibrational levels in (a) as a function of laser frequency \( \omega [\text{cm}^{-1}] \) at fixed intensity \( I = 0.1 [\text{TW/cm}^2] \). The gap at each avoided crossing is proportional to the transition dipole moment between the corresponding two states.

photon numbers; and \( \epsilon \) is the dipole matrix element. The conventional adiabatic passage requires large laser intensity and small sweep velocity to make \( p_{LZ} \) very small. For instance, the adiabatic passage with \( p_{LZ} \leq 0.001 \) requires

\[
1.0994 \frac{\hbar \omega}{\epsilon} \leq I
\]

For the values \( \epsilon = 1.0 [\text{Åe}] \) and \( \omega = 0.5 [\text{cm}^{-1}/\text{ps}] \), \( I \) must be \( > 1.0 [\text{TW/cm}^2] \).
In order to accomplish the passage in a reasonably short timescale with relatively large $\dot{\omega}$, a large intensity $I$ or a large number of oscillation is required. If $p_{\text{LZ}} = 0.5$ can be attained without difficulty, then one period of oscillation enables us to achieve exactly zero or unit final transition probability. The required intensity in this case is given by

$$I = 0.1103\hbar\dot{\omega}/\varepsilon \quad (7.28)$$

Namely, one period of oscillation requires the intensity by one order smaller compared to the case of one passage for the same $\varepsilon$ and $\dot{\omega}$. Furthermore, 10 periods of oscillation require the following condition [see Eq. (7.15)]:

$$0.982 \times 10^{-3}\hbar\dot{\omega}/\varepsilon \leq I \leq 0.810\hbar\dot{\omega}/\varepsilon \quad (7.29)$$

This requires only 1000 of the intensity required in the case of one passage. Many periods of oscillation, however, requires high accuracy of $p$ and phases. When $p$ is large, it is sensitive to the error in the exponent that is proportional to the intensity. In the case of adiabatic passage, on the other hand, $p$ is relatively stable against the error in the exponent, since the exponent is large. When $p \approx 0.5$, 15% of error in the exponent yields the fluctuation in the range $0.45 < p_{\text{LZ}} < 0.65$.

So far, our discussion is based on the simple model Eq. (7.25). For finding the actual parameters, however, it is much better to use the new semiclassical theory based on the quadratic model because this theory is applicable to the general functionality of $\omega$, even if the two diabatic potentials touch each other or avoid crossing.

Let us first consider the vibrational transition $|0\rangle \rightarrow |1\rangle$ via the avoided crossing $A$ in Figure 21(b) with use of the LZS type curve crossing model. In this case, the complete control can be achieved by one period of oscillation with reasonable values of the laser intensity and the sweep velocity. Figure 22(b) and (c) show the frequency and intensity as a function of time. The frequency is taken to be a quadratic function of time, that is, $\omega(t) = at^2 + b$, and the analytical theory for quadratic model has been used. The resonance frequency $\omega_X$ corresponding to the avoided crossing is $\omega_X = 202.6 \text{ cm}^{-1}$. Two functional forms, constant(solid line) and $4A^2\text{sech}^2(\beta t)/\varepsilon^2$ (dash line), are assumed for the laser intensity [Fig. 22(c)]. The frequencies shown in Figure 22(b) are the solutions of our control theory corresponding to the intensities given in Figure 22(c). Figure 22(a) shows the time variation of the transition probability for the process $|0\rangle \rightarrow |1\rangle$ with use of the avoided crossing $A$ in Figure 21(b). Non-adiabatic transitions occur twice, and each time $p = 0.5$ is achieved. Unit transition probability is finally realized in the two cases. In the case of the intensity of pulse shape [dash line in Fig. 22(c)], not only the frequency but also the area of
Figure 22. Controlled nonadiabatic process from $|0\rangle$ to $|2\rangle$ with use of the LZS type nonadiabatic transition at the avoided crossing "A" at 202.6 cm$^{-1}$ in Figure 21(b). (a) Time evolution of the transition probability. (b) Variation of laser frequency as a function of time. (c) Variation of laser intensity as a function of time. Solid line is the case of constant intensity and quadratic variation of frequency, and dash line corresponds to pulse shape intensity and quadratic variation of frequency. In both cases, complete control is attained. The dotted line shows the sensitivity to the constant shift of frequency. The final probability is $\sim 0.975$ in this case.

The intensity pulse contribute to the phase. Thus the corresponding frequency in Figure 22(b) is slightly smaller than the solid line. In this LZS type of nonadiabatic transition, functionality of the intensity is not important, but the intensity at the avoided crossing is critical. This is the reason why the difference
in frequency is so small in the two cases. The dotted line is to show the effects of intensity variation on the final result. Although the nonadiabatic transition probability $p$ is reduced to 0.45 by a small shift in intensity, the final transition probability is not as bad, since the phase is accurate.

If we sweep the frequency more than once at the avoided crossing, we can naturally achieve the final unit transition probability with smaller intensity $I$, but it takes a longer time. It should be noted that the required peak intensity for the case of constant intensity is smaller than that required by a $\pi$ pulse (discussion will be made later in relation to Fig. 24). Note that the constant intensity can of course be cut off outside the transition region.

For a transition between two states with a small transition moment $\epsilon$, a larger intensity or a smaller sweep velocity is required to satisfy $p = 0.5$ [see Eq. (7.26)]. This means that the direct isomerization from $|0\rangle \rightarrow |1\rangle$ requires a very large intensity or a very long transition time (very slow sweeping). For the isomerization, it is thus better to use an indirect process that is composed of the transitions of relatively large transition moments [99]. Note that the square of the transition moment for the direct process $|0\rangle \rightarrow |1\rangle$ is about four orders of magnitude smaller than that for $|0\rangle \rightarrow |2\rangle$. Figure 23 shows an example of such indirect isomerization: $|0\rangle \rightarrow |2\rangle \rightarrow |4\rangle \rightarrow |3\rangle \rightarrow |1\rangle$, where four pulses are applied corresponding to these four transitions. That is to say, the first pulse achieves the complete transition $|0\rangle \rightarrow |2\rangle$, and the second one does $|2\rangle \rightarrow |4\rangle$, and so on.

Since the essential qualitative features such as the characteristics of various types of nonadiabatic transitions that we want to address here do not depend on the transitions, we consider the transition $|0\rangle \rightarrow |2\rangle$ for a while.

2. **Rosen–Zener Type of Nonadiabatic Transition**

The Hamiltonian of the Rosen–Zener–Demkov model in the diabatic representation is given by

$$H_{RZ} = \begin{bmatrix} \Delta/2 & A \exp(\beta t) \\ A \exp(\beta t) & -\Delta/2 \end{bmatrix}$$

(7.30)

This model describes the process with constant frequency and exponentially rising intensity in the case of a laser. The nonadiabatic transition occurs at $t = \log(\Delta/A)/\beta$, and the transition probability $p$ is given by

$$p_{RZ} = \frac{1}{1 + \exp(2\delta)}$$

(7.31)
Figure 23. Controlled isomerization process induced by the sequence of the LZS type transitions, \( |0> \to |2> \to |4> \to |3> \to |1> \). The corresponding avoided crossings are designated as A-D in Figure 21(b). The corresponding resonance frequencies are 202.6, 153.6, 82.6, and 185.2 cm\(^{-1}\), respectively. (a) Time evolution of the probability. At each stage complete transition is attained. Twelve Floquet states are taken into account for the calculation. The time variations of frequency and intensity are shown in (b) and (c), respectively.

where

\[
\delta = \frac{\pi \Delta}{2\hbar \beta}
\]  

(7.32)

As is clearly seen from Eqs. (7.31) and (7.32), the range of \( p \) is \( 0 \leq p \leq 0.5 \), and \( p \to 0 \) when \( \Delta/\beta \to \infty \); while \( p \to 0.5 \) when \( \Delta/\beta \to 0 \). Note that \( p_{RZ} \) does
depend only on $\Delta/\beta$ and not on the laser intensity $A$, and that $p \approx 0.5$ can be achieved even with very small intensity (small $A$) in short time with large $\beta$. Thus, by adjusting the phases, we can achieve the unit final transition probability with use of one laser pulse of the shape $E(t) = 2A\text{sech}(\beta t)/\epsilon$, namely, by one period of oscillation. This process of one pulse with $\Delta = 0$ corresponds to the $\pi$ pulse. The condition $\Delta = 0$ leads to $P_{\text{RZ}} = 0.5$ and thus $P_{12}^{(n)}$ given by Eq. (7.15) with $n = 1$ reduces to $\sin^2 \psi = 1$, which coincides with the condition of the area of $\pi$ pulse. Note that our theory is quite general, and that the condition for unit final transition probability can be attained for any frequency, if we use more than one pulse.

The sensitivity of $P_{\text{RZ}}$ against an error in $\delta$ is largest when $P_{\text{RZ}} = 0.5$, and decreases as $P_{\text{RZ}}$ decreases. In the case of $\pi$ pulse ($\Delta = 0$), a constant shift of the frequency $\Delta$ from zero yields a relatively large effect on $P_{\text{RZ}}$ when $\beta$ or the pulse width is small. If the pulse width is, say, several picoseconds, about several reciprocal centimeters of shift in $\Delta$ yields $P_{\text{RZ}} \approx 0.45$. It should be noted, however, that a small fluctuation of $\Delta$ in time (not a constant shift) causes a large error in the nonadiabatic transition probability $p$.

Figure 24 is an example of the so-called $\pi$ pulse (solid lines) with parameters chosen so that the overall transition time between the corresponding Floquet states becomes the same order as that in Figure 22. Again, nonadiabatic transitions occur twice with the transition probability $p = 0.5$, and the final overall transition probability is controlled to be unity with the use of the phase accumulated between the two transitions. In the case of the $\pi$ pulse, the condition of $p = 0.5$ is attained by fixing the frequency at the resonance frequency $\omega_X$, or the frequency at the avoided crossing. The phase condition is satisfied by adjusting the area of the intensity pulse. These conditions are relatively simple and seem to be easily realized compared to the LZS case.

It should be noted that a small variation of the frequency could cause unexpected transitions and errors if the frequency is close to the resonance. Dashed and dotted lines in Figure 24 demonstrate the sensitivity of the $\pi$-pulse method to frequency variations. The dashed line shows the effects of a constant shift of the frequency from the resonance. As discussed above, frequency can contain a constant shift error up to several reciprocal centimeters, if the phase due to the intensity variation is accurate, and the intensity can have a 10% error, and if the frequency is exactly at the resonance. More shocking is the large effect of a very small time-dependent fluctuation in frequency, as is demonstrated by the dotted line. This small fluctuation induces unexpected curve crossing type nonadiabatic transitions between the closely lying states effectively, and causes a big effect in the final result, as seen in Figure 24(a). In order to avoid this instability, it might be worthwhile to use the off-resonant case explicitly. In the case of off-resonance, the nonadiabatic transition probability $p$ is $< 0.5$, and more than one pulse, that is, more than one period of oscillation, is required. Figure 25 shows an example of two pulses. The frequency shift is kept constant at 5 cm$^{-1}$ (solid line) and the various parameters are chosen so that the transition time is...
Figure 24. The same as Figure 22 for the case of π pulse. (a) Time evolution of the transition probability. Time variations of frequency and intensity are shown in (b) and (c), respectively. The parameter $\Delta \omega$ represents the shift from the resonance frequency $\omega_K = 202.6$ cm$^{-1}$. The dashed line shows the case of constant shift in frequency. The solid line shows the case of exact one. The dotted line shows the large effect of small time variation of the frequency around resonance. Note that the small fluctuation of frequency in (b) gives a large effect on the transition probability [dotted line in (a)].

the same order as that in Figures 22 and 24. As seen from this figure in comparison with Figure 24, this scheme is very effective. The nonadiabatic transition probability for one passage is $\sim 0.2$, and after four nonadiabatic transitions the final transition probability reaches unity. This can be achieved
NONADIABATIC TRANSITIONS DUE TO CURVE CROSSINGS

Figure 25. The same as Figure 22 for the case of off-resonant two pulses. (a) Time evolution of the probability. Time variations of frequency and intensity are shown in (b) and (c), respectively. The parameter $\Delta \omega$ represents the shift from the resonance frequency $\omega_X = 202.6$ cm$^{-1}$. The solid line is the case of complete control. Dashed and dotted lines demonstrate the stability of the method against time variation of frequency (dashed line) and the constant shift in frequency (dotted line).

with a smaller peak intensity compared to the $\pi$ pulse. This is because the necessary phase can be accumulated not only by the intensity but also by the frequency because of the off-resonance. In the case of off-resonance, however, we should adjust not only the height and shape of the pulse $I(t)$ but also the interval of two pulses, because the nonadiabatic transition probability $p_{RZ}$
depends on the exponent of $I(t)$, that is, $\beta$ in Eq. (7.30) and the interval of two pulses determine the phase $\sigma_2$ (see Fig. 17). It might be difficult to adjust the shape of $I(t)$ accurately, but the control by off-resonant pulses is very attractive. It requires a small peak intensity. The stability against frequency fluctuation is also satisfactory, as demonstrated by the dashed and dotted lines in Figure 25.

We can choose either the LZS (oscillation of the frequency) or the RZD type (oscillation of the intensity) depending on the availability of the laser. One thing we should keep in mind is that the LZS type requires a large intensity to achieve $p = 0.5$, while the RZD (including the $\pi$ pulse) requires a large intensity to satisfy the phase condition. In other words, the LZS does not require large intensity to satisfy the phase condition and the RZD does not require that to satisfy $p = 0.5$. Thus we may think of a hybrid of LZS and RZD that enables us to achieve $p = 0.5$ by changing the intensity and to accumulate enough phase by changing the frequency.

3. Exponential Type of Nonadiabatic Transition

The well-known model that contains time variations in both diabatic energy and diabatic coupling is the exponential model [6, 31, 32]. The Hamiltonian of this model is given by

$$
H_{\text{exp}} = \begin{bmatrix}
U_1 + V_1 e^{-\beta t} & Ve^{-\beta t} \\
Ve^{-\beta t} & U_2 + V_2 e^{-\beta t}
\end{bmatrix}
$$

(7.33)

In the case of a laser, this model describes the process of exponentially changing intensity and frequency with the same exponent. The nonadiabatic transition probability in this model is given by [6, 32]

$$
p_{\text{exp}} = \exp(-\pi \delta_2) \frac{\sinh(\pi \delta_1)}{\sinh[\pi(\delta_1 + \delta_2)]}
$$

(7.34)

where

$$
\delta_1 = \frac{U_1 - U_2}{2h\beta} \left[ 1 + \frac{(V_1 - V_2)/2V}{\sqrt{1 + (V_1 - V_2/2V)^2}} \right]
$$

(7.35)

and

$$
\delta_2 = \frac{U_1 - U_2}{2h\beta} \left[ 1 - \frac{(V_1 - V_2)/2V}{\sqrt{1 + (V_1 - V_2/2V)^2}} \right]
$$

(7.36)

In the same way as in the RZD case, we can achieve $p = 0.5$ within a relatively short time with a small intensity. The necessary phase, on the other
hand, may be accumulated by changing the intensity as well as the frequency. This means that a large intensity is not necessary to accumulate the necessary phase, and we can achieve unit transition probability with a small intensity by one period of oscillation (one pulse). The control scheme with use of this exponential model may provide one of the most effective ones (rapid transition with small intensity). A model with different exponents for the diabatic energy and the diabatic coupling would be more versatile and useful, although there is no analytical theory available yet. It should, however, be noted that the transition probability $p_{\exp}$ is rather sensitive to the functionalities of both intensity and frequency as a function of time, and a small experimental error might affect the final overall transition probability. Comparative studies on the effectiveness and the stability of the various control schemes described here are made hereafter together with the presentation of numerical examples.

Figure 26 (solid line) shows the control of the transition $|0>\rightarrow|2>$ by one pulse (period) with two nonadiabatic transitions of the exponential type ($p = 0.5$). It should be noted that the required intensity for the same order of transition time as before is quite small and the frequency is not necessary to be kept at resonance; while, as demonstrated before, the LZS type requires the larger intensity and RZD requires the frequency to be close to resonance to achieve $p = 0.5$. Due to the off-resonance, small fluctuation of $\omega$ does not cause any appreciable errors as in the case of the $\pi$ pulse. The necessary phase can be accumulated by means of both frequency and intensity, which is the reason why the required intensity can be so small. Dashed and dotted lines in Figure 26 show the stability of the method against the variations of intensity and frequency. Thus, the exponential model may provide quite an efficient control method compared to LZS and RZD.

By taking the vibrational transition $|0>\rightarrow|2>$, we have explained the characteristics of various types of nonadiabatic transitions and proved that the exponential model presents the most effective way of control. As mentioned before, this does not depend on the transitions and thus is also true for the tunneling transition $|0>\rightarrow|1>$. Figure 27 demonstrates this. As is well known, it is far better to use the detour $|0>\rightarrow|2>\rightarrow|4>\rightarrow|3>\rightarrow|1>$ in the same way as in Figure 27 than to take the direct path $|0>\rightarrow|1>$, since the dipole moment for the latter is about two orders of magnitude smaller than that of $|0>\rightarrow|2>$. As is seen in Figure 27, the required intensity is much smaller than that in Figure 23. If the laser intensity could be kept constant, however, we could further reduce the necessary maximum intensity, as was demonstrated in Figure 22. Figure 28 shows this type of control of the isomerization.

A more general model, like an exponential model with different exponents for frequency and intensity, for which no analytical theory is unfortunately available yet, is expected to provide a more efficient scheme. Note, however, that the exponential model in general requires accurate shaping of both intensity and
frequency pulses, since the nonadiabatic transition probability $p_{\text{exp}}$ depends explicitly on the exponents of both intensity and frequency.

So far, we have discussed several control schemes with the help of analytical theories. We can choose one of them depending on the molecular process and availability of lasers. If accurate pulse shaping of both intensity and frequency is possible, the scheme with the exponential type of nonadiabatic transition is the best. If pulse shaping is available for intensity, but not for frequency, the RZD type works relatively well. In this case, the off-resonant RZD type is

Figure 26. The same as Figure 25 for the case of exponential model. The solid line is the case of complete control. Frequency is swept around the avoided crossing "A" at $\omega_n = 202.6 \text{ cm}^{-1}$. Dashed and dotted lines demonstrate the stability of the method against the error in the exponent of intensity (dashed line) and the constant shift in frequency from the solid line (dotted line).
Figure 27. The same as Figure 23, that is, control of the isomerization process $|0\rangle \rightarrow |2\rangle \rightarrow |4\rangle \rightarrow |3\rangle \rightarrow |1\rangle$. The exponential model is employed. Twelve Floquet states are taken into account to obtain (a). It should be noted that the intensity is reduced by ~ a factor of 3 compared to Figure 23. In (b), the frequency shift $\Delta \omega$ from the resonance is shown instead of $\omega$ itself in order to clearly show its exponential form. The shape is taken to be the same for the four transitions.

Generally speaking, molecular processes in a laser field can be considered to be a sequence of nonadiabatic transitions and adiabatic propagation as before, recommended. If accurate shaping of intensity is not attainable, the resonant RZD ($\pi$ pulse) or the LZS methods are recommended.
and we can treat the whole control problem analytically, if the nonadiabatic transitions are separated from each other in time. This indicates that we may construct a control scheme for a general shape of pulse, even if no analytical theory for each nonadiabatic transition is available. Once we know the phase

**Figure 28.** The same as Figure 23, that is, control of the isomerization process $|0\rangle \rightarrow |2\rangle \rightarrow |4\rangle \rightarrow |3\rangle \rightarrow |1\rangle$. The constant intensity and the quadratic variation of frequency are utilized.
change and the probability change by one pulse (one period of oscillation), we can design an efficient way of control based on the analytical scheme. The optimum conditions for one pulse, namely, the conditions to satisfy \( \sin^2 \psi = 1 \) and \( p = 0.5 \), may be found numerically or even experimentally.

In the present work, we have focused our attention mainly on the laser case, in which the diabatic coupling (energy) depends on the intensity (frequency) under the nonadiabatic Floquet formalism. By sweeping the adiabatic parameter(s) periodically, the unit transition probability can be achieved due to the interference effect among different passages of the nonadiabatic transition point. One pulse (or one period of oscillation) requires the nonadiabatic transition probability \( p \) for one passage to be 0.5. The required range of \( p \) becomes wider as the number of oscillation increases. The nonadiabatic transition can be any type such as LZS, RZD, and the type of exponential model. Even a transition for which no analytical theory is available might be used.

It is known that \( I \) (laser intensity) \( \approx 10 \) TW/cm\(^{-2}\) is the upper limit for us to safely focus on the vibrational transitions [10]. The maximum intensity required in some of the processes discussed in the present work is 1.0 TW/cm\(^{-2}\). The best way of control based on our new idea requires only 60 \( \approx 170 \) GW/cm\(^{-2}\) maximum intensity, two orders of magnitude smaller than the upper limit.

Since nonadiabatic transitions play important roles in various molecular processes in external fields, our idea of controlling nonadiabatic transitions would give a versatile control scheme of molecular processes. Magnetic resonance, ESR, or NMR can be another interesting example. With the help of analytical theories of time-dependent nonadiabatic transitions, various possibilities can be discussed. One can choose an appropriate one depending on the availability and quality of the lasers. The physical conditions of our controlling scheme are very clear, and the analysis can be done analytically without any heavy computations.

VIII. FUTURE PERSPECTIVES

In this chapter, we have presented an overview of the newly established theory for time-independent two-state curve crossing problems. The basic two-state theory is simple enough for the general users to utilize, and can still work well over the entire range of energy and coupling strength. The theory is further demonstrated to be applicable to multichannel and multidimensional problems. The time-dependent version of the theory has also been presented, and a new idea of controlling molecular processes by time-dependent external fields was discussed. These semiclassical theories are completely established in adiabatic representation, and there is no need for any diabatization and for any information about nonadiabatic coupling. In contrast, the semiclassical theory for the noncurve crossing case has not been complete yet; especially no theory is
available for energies lower than the transition region. This is a big challenge for the future. Formulation of a unified theory that can cover both crossing and noncrossing cases in a unified way would be a very challenging subject.

If we consider the fact that the LZS type potential surface crossings, including conical intersections, most commonly appear and play crucial roles in various real physical and chemical dynamic processes, it is very important and worthwhile to develop practically useful accurate methodologies to deal with multi-dimensional nonadiabatic transition problems. As was discussed in Section IV, the new semiclassical theory of nonadiabatic transition can be easily incorporated into the various frameworks such as the TSH method [27,30], the semiclassical propagation method based on the IVR [28], and the CFGWP method [29]. Accurate formulas not only for nonadiabatic transition probability but also for all necessary phases are available in present semiclassical theory; and even when the surface crossing is located in the classically forbidden region, the accurate treatment is possible with the present semiclassical theory. In the case of conical intersection, the geometrical phase [102] should just be added to the phase along each trajectory.

Controlling molecular processes by time-dependent external fields is one of the important modern subjects in chemical dynamics. Again, nonadiabatic transitions play a crucial role there. We have proposed a new idea of controlling nonadiabatic transitions that is summarized in Section VII. Various generalizations and applications of this idea can be thought of and should be carried out.

Acknowledgments

The present work is partly supported by a Grant-in-Aid for Scientific Research on Priority Area "Molecular Physical Chemistry" and also by a Research grant 10440179 from the Ministry of Education, Science, Culture and Sports of Japan.

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