

A statistical theory for the effect of nonadiabatic transitions on activated processes

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A simple statistical theory for calculating the effects of nonadiabatic transitions on activated barrier crossing is presented. It is based on the model of Cline and Wolynes which combines the impulsive BGK collisional model with the Landau-Zener theory for curve crossing to calculate rate constants for barrier crossing. We derive a closed analytical expression for the rate constant for nonadiabatic transitions which requires as input only the rate constant for barrier crossing on the adiabatic surface and the parameters for the Landau-Zener theory. Our theory gives excellent agreement with the numerical results of Cline and Wolynes.

I. INTRODUCTION

In most discussions of classical reaction rate theory^{1,2} it is assumed that (1) the temperature is high enough that tunneling is negligible in comparison with activated crossing of the barrier, and (2) the electronic state of the reacting molecule follows the motion of the nuclei adiabatically. The adiabatic potential surface corresponds to the ground state of the diagonalized Hamiltonian. These assumptions allow a simple description of nuclei moving on a Born-Oppenheimer potential surface according to Newton's equations of motion.

For those physical systems where the temperature is below a certain value, the "crossover temperature," tunneling will be the dominant reaction channel and the first assumption will be violated.³ The effect of a solvent on the tunneling frequency was first examined by Wolynes⁴ and has since been given much attention. A recent review of this work is given by Hänggi.⁵ Also, Pollak has unified many of these ideas under a single formalism, the multidimensional transition state theory.⁵

For those systems above the crossover temperature, the dominant contribution to the rate should be activated barrier crossing. However, when the splitting between the excited and ground state adiabatic potential energy surfaces is small compared to $k_B T$, the assumption of adiabatic curve crossing may be violated. For isolated systems, nonadiabatic effects have been incorporated in the semiclassical trajectory calculations of Tully and Preston,⁶ and Miller and George.⁷ These ideas and further applications have been reviewed by Tully.⁸ Recently, Cline and Wolynes have applied these techniques to study nonadiabatic effects in activated barrier crossing.⁹

A great deal is known about activated processes in adiabatic systems. Analytic theories exist for the prediction of rate constants for single and many degree of freedom systems for weak and strong collision models at both low and high friction or collision rate.^{1-3,10} In addition, an increasing number of numerical simulations have been performed on stochastic and molecular systems to test the validity and ap-

plicability of these theories.¹¹⁻¹⁴ Here we present a statistical theory which predicts the rate for activated barrier crossing in *nonadiabatic* systems simply in terms of the rate for barrier crossing in the *adiabatic* system and the Landau-Zener curve crossing probability. Our result may be readily applied to predict barrier crossing rates for any nonadiabatic system where the adiabatic rate constant is known from theory or simulation.

In Sec. II we review the model of Cline and Wolynes; in Sec. III we derive our primary result which relates the nonadiabatic rate constant to the adiabatic rate constant and the Landau-Zener probability; in Sec. IV we compare our prediction with the numerical simulation data of Cline and Wolynes; and in Sec. V we discuss the possible limitations of this model.

II. THE MODEL OF CLINE AND WOLYNES

Cline and Wolynes examined a system consisting of a nuclear reaction coordinate q , linearly coupled, by the parameter g , to a two-level system. The reaction coordinate moves in one of two electronic states which are modeled as harmonic wells centered at $q = \pm g/\omega^2$. The Hamiltonian is given by

$$H = \frac{1}{2}\dot{q}^2 + \frac{\omega^2}{2}q^2 + \frac{\Delta}{2}\sigma_x + gq\sigma_z + H_B, \quad (2.1)$$

where $\sigma_{x,z}$ are Pauli spin matrices, Δ is twice the matrix element which couples the two electronic states, and H_B is the bath Hamiltonian. The diabatic and adiabatic potential surfaces are shown schematically in Fig. 1. The transition state surface is chosen at the curve crossing point $q = 0$ which has energy $Q = g^2/2\omega^2$.

The bath was incorporated using a stochastic BGK model¹⁵ which thermalizes the velocity of the reaction coordinate on each collision while sampling collision times from a Poisson distribution with average collision frequency ζ .¹⁶

If the electronic state surfaces are strongly coupled, nonadiabatic effects are important. Cline and Wolynes used a surface hopping model to calculate nonadiabatic corrections to the adiabatic theory. They performed a trajectory calculation using the reactive flux formalism¹⁷ (also, see Sec. III); 10^4 trajectories were used for each rate constant calculation. Their method may be summarized as follows. Initial-

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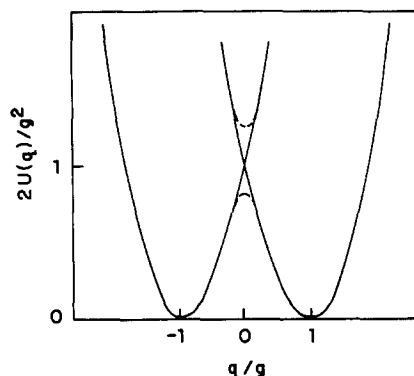


FIG. 1. Potential surface for the Cline-Wolynes model.

ly, all trajectories are placed on the left diabatic surface (Fig. 1). The trajectories begin at the transition state $q = 0$, and are propagated on the diabatic surface according to the BGK algorithm until they recross the transition state, at which point the probability of hopping to the other diabatic surface is calculated. The trajectory then either moves to the other diabatic surface, or continues on the present surface. Trajectories with initial velocity $\dot{q} > 0$ are immediately tested for curve crossing (as though they had started just to the left of the transition state) while those with initial velocity $\dot{q} < 0$ are moved away from the surface and are only tested for crossing on return (as though they had started just to the left of the transition state).

The probability for curve crossing on a single passage through the curve crossing region is given approximately by the Landau-Zener formula^{8,18}

$$P_{LZ} = 1 - \exp(-\pi\Delta^2/2\hbar v|F_2 - F_1|), \quad (2.2)$$

where $F_{1,2}$ are the slopes of the diabatic potential surfaces at the point of curve crossing and v is the velocity of the trajectory which is assumed to be constant in the curve crossing region. Note that for small velocities, where the nuclei move very slowly, the probability of curve crossing will approach unity and the reaction coordinate will move on the adiabatic Born-Oppenheimer surface.

III. THEORY

In this section we will summarize the reactive flux method of Chandler.¹⁷ We then present a short discussion of an approximate version of the reactive flux method for adiabatic systems, the so-called absorbing boundary method.^{19,20} Finally, we generalize the absorbing boundary formalism to include nonadiabatic transitions and derive an analytical expression for the nonadiabatic rate constant expressed in terms of the adiabatic rate constant and the Landau-Zener curve crossing probability.

The reactive flux method consists of calculating the function^{16,21}

$$\hat{k}(t) = \langle \theta[q(t)] \rangle_+ - \langle \theta[q(t)] \rangle_-, \quad (3.1)$$

where $\theta(q)$ is the Heaviside step function, which is unity for $q > 0$ and zero otherwise, and $\langle \rangle_{\pm}$ indicate, respectively, averages over the normalized phase space distribution functions

$$P^{(\pm)}(\Gamma) = \frac{\dot{q}\theta(\pm\dot{q})\delta(q)e^{-\beta H(\Gamma)}}{\int d\Gamma \dot{q}\theta(\pm\dot{q})\delta(q)e^{-\beta H(\Gamma)}}, \quad (3.2)$$

q is the reaction coordinate, $\delta(q)$ defines the transition state, \dot{q} is the reaction coordinate velocity, and $H(\Gamma)$ is the Hamiltonian.

We restrict ourselves to a discussion of symmetric double wells. For a system consisting of two bound states separated by a barrier Q (Fig. 1) if $Q \gg k_B T$, $\hat{k}(t)$ will decay on two widely different times scale.¹⁷ There will be a fast transient decay from the initial value, followed by a very slow decay

$$\hat{k}(t) \rightarrow \kappa e^{-(k_f + k_b)t}, \quad (3.3)$$

where k_f and k_b are the forward and backward rate constants and κ is the "plateau value" of the reactive flux or the dynamical transmission coefficient

$$\kappa = \frac{k_f + k_b}{(k_f + k_b)_{\text{TST}}} = \frac{k}{k_{\text{TST}}}, \quad (3.4)$$

where $k = k_f + k_b$ is the exact kinetic rate constant, and $k_{\text{TST}} = (k_f + k_b)_{\text{TST}}$ is the transition state theory approximation to k .²²

We have proposed a simple and accurate method for the calculation of rate constants for chemical reactions, the absorbing boundary method,^{19,20} which is an approximate version of the reactive flux method. We observe that the separation of time scales required for a plateau in $\hat{k}(t)$, Eq. (3.3), implies that there are two types of trajectories, those which move into the wells and are trapped for long times, and those which rebound from the turning point of the potential, or are reversed by collisions, and recross the transition state in a short time. Therefore, if $P(t)$ is the probability that a trajectory, which starts at the transition state at $t = 0$, will remain in the well at time t having never crossed the transition state, then $P(t)$ will begin at unity and decay to a plateau value T_0 . [At long times, $P(t)$ must decay to zero as all trajectories will eventually cross the transition state.]

If one assumes that those trajectories which recross the transition state conform to the initial state distribution, Eq. (3.2), then, after each recrossing, the same fraction of trajectories will be trapped. Consider $\langle \theta[q(t)] \rangle_+$, the number of trajectories in the right well at time t , which begin with positive velocity, moving into the right well, at $t = 0$. Initially, a fraction of trajectories T_0 is trapped in the right well and the complementary fraction $1 - T_0$ moves into the left well where $T_0(1 - T_0)$ will be trapped and $(1 - T_0)^2$ will cross the transition state back into the right well, and so on. At intermediate times $\langle \theta[q(t)] \rangle_+ \approx T_0 + T_0(1 - T_0)^2 + \dots$. Similarly, at intermediate times $\langle \theta[q(t)] \rangle_- \approx T_0(1 - T_0) + T_0(1 - T_0)^3 + \dots$ and¹⁹

$$\begin{aligned} \kappa_A &= \langle \theta[q(t)] \rangle_+ - \langle \theta[q(t)] \rangle_- \\ &= \frac{T_0}{2 - T_0}, \end{aligned} \quad (3.5)$$

where the subscript A denotes that the reaction takes place on the ground adiabatic surface.

To calculate κ_A in practice, one samples points in phase

space from the distribution function $P^{(+)}(\Gamma)$ which places them at the transition state with positive velocity, heading into the product well. One then propagates the trajectories removing those which cross the transition state. If a separation of time scales exists, one may follow the trajectories in time until $P(t)$ reaches the plateau T_0 . A good rule of thumb is that $P(t)$ should remain constant over an order of magnitude in time. If $k \ll k_{\text{TST}}$, $\kappa_A \ll 1$, and $T_0 \ll 1$. Using the absorbing boundary method, only a small fraction of trajectories will have to be integrated for the full length of the simulation. In such cases, the absorbing boundary method is computationally much faster than a full reactive flux calculation which requires that all trajectories be integrated for the full length of the simulation.

In what follows, we apply the absorbing boundary formalism to the system of Cline and Wolynes, assuming only (1) that the distribution of those states recrossing the transition state is given by Eq. (3.2), and (2) that the velocity dependent probability for curve crossing [Eq. (2.2)] can be replaced by its average value \bar{P}_{LZ} .³²

Consider the two-dimensional column vector \mathbf{p} whose elements represent the population on the upper (excited) p_1 , and lower (ground) p_2 , electronic surfaces in a given well moving towards the transition state. We can then define the matrix

$$\mathbf{C} = \begin{pmatrix} \bar{P}_{\text{LZ}} & 1 - \bar{P}_{\text{LZ}} \\ 1 - \bar{P}_{\text{LZ}} & \bar{P}_{\text{LZ}} \end{pmatrix}, \quad (3.6)$$

such that $\mathbf{C}\mathbf{p}$ is the population having crossed the transition state. Curve crossing results in a redistribution of trajectories on the upper and lower electronic surfaces. The diagonal elements of \mathbf{C} correspond to the probability of remaining on the lower or upper electronic surface while the off-diagonal terms represent the probability of making a transition to the other surface.

We may similarly define the matrix

$$\mathbf{S} = \begin{pmatrix} 1 & 0 \\ 0 & 1 - T_0 \end{pmatrix} \quad (3.7)$$

such that $\mathbf{S}\mathbf{p}$ is the population returning to the transition state on a given electronic surface *without* being trapped in a well. That $S_{11} = 1$ expresses the fact that a trajectory cannot be trapped in a well while on the upper electronic surface while $S_{22} = 1 - T_0$ is the probability of surviving a passage in the well to recross the transition state.

Finally, we define the vector

$$\mathbf{d} = \begin{pmatrix} T_0(1 - \bar{P}_{\text{LZ}}) \\ T_0\bar{P}_{\text{LZ}} \end{pmatrix} \quad (3.8)$$

such that $\mathbf{d}^T\mathbf{p}$ is the population of trajectories which are trapped in a given well before they can recross the transition state. d_1 gives the probability that when a trajectory is on the upper electronic surface it must first cross to the lower surface with probability $1 - \bar{P}_{\text{LZ}}$ before it can be trapped with probability T_0 , while d_2 corresponds to the fact that a trajectory on the lower electronic surface must remain on the lower surface to be trapped.

With these vectors and matrices we follow the adiabatic calculation described above and compose the averages $\langle \theta[q(t)] \rangle_+$ and $\langle \theta[q(t)] \rangle_-$ at intermediate times. Then,

using Eqs. (3.1) and (3.3) we calculate the transmission coefficient κ for the nonadiabatic system.

Translating the scheme of Cline and Wolynes: initially those trajectories starting at the transition state with velocity $\dot{q} > 0$ will reside on the left diabatic state of the reactant, so that the initial state vector is

$$\mathbf{i}_+ = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (3.9)$$

Trajectories will cross the transition state where they will be trapped in the product, right diabatic, well with probability $\mathbf{d}^T\mathbf{i}_+$ or recross the transition state with population $\mathbf{S}\mathbf{C}\mathbf{i}_+$. The population $\mathbf{S}\mathbf{C}\mathbf{i}_+$ recrosses the transition state with $\dot{q} < 0$ where a fraction $\mathbf{d}^T\mathbf{S}\mathbf{C}\mathbf{i}_+$ will be trapped in the reactant well while the population $(\mathbf{S}\mathbf{C})^2\mathbf{i}_+$ will recross the transition state. Continuing, we may write the fraction of trajectories which begin in the reactant well with $\dot{q} > 0$ and are trapped in the product well as

$$\begin{aligned} \langle \theta[q(t)] \rangle_+ &= \mathbf{d}^T \sum_{N=0}^{\infty} (\mathbf{S}\mathbf{C})^{2N} \mathbf{i}_+ \\ &= \mathbf{d}^T [1 - (\mathbf{S}\mathbf{C})^2]^{-1} \mathbf{i}_+. \end{aligned} \quad (3.10)$$

We may similarly find $\langle \theta[q(t)] \rangle_-$. Initially, those trajectories starting at the transition state with velocity $\dot{q} < 0$ will reside on the left diabatic surface, corresponding to the ground state of the reactant. A fraction T_0 of the trajectories will be trapped in the reactant well while the remaining fraction $1 - T_0$ will cross the transition state on the left diabatic surface with $\dot{q} > 0$. The analysis for $\langle \theta[q(t)] \rangle_+$ may then be applied where the initial state vector \mathbf{i}_+ is replaced by

$$\mathbf{i}_- = \begin{pmatrix} 0 \\ 1 - T_0 \end{pmatrix}. \quad (3.11)$$

It follows that

$$\begin{aligned} \langle \theta[q(t)] \rangle_- &= \mathbf{d}^T [1 - (\mathbf{S}\mathbf{C})^2]^{-1} \mathbf{i}_- \\ &= (1 - T_0) \langle \theta[q(t)] \rangle_+. \end{aligned} \quad (3.12)$$

Combining Eqs. (3.1), (3.10), and (3.12) we may write the transmission coefficient for the nonadiabatic system as

$$\kappa = T_0 \mathbf{d}^T [1 - (\mathbf{S}\mathbf{C})^2]^{-1} \mathbf{i}_+. \quad (3.13)$$

After some algebra, one finds that the nonadiabatic transmission coefficient can be expressed in terms of the adiabatic transmission coefficient κ_A [Eq. (3.5)] and the averaged Landau-Zener curve crossing probability \bar{P}_{LZ} [Eq. (2.2)] as

$$\kappa = \frac{k_f + k_b}{k_{\text{TST}}} = \frac{2\bar{P}_{\text{LZ}}\kappa_A}{\kappa_A + \bar{P}_{\text{LZ}}(2 - \kappa_A)}. \quad (3.14)$$

This is an explicit relationship between the nonadiabatic transmission coefficient and the adiabatic one for the same collision rate. Further, Eq. (3.14) can be transformed into

$$\kappa^{-1} = \frac{1 - \bar{P}_{\text{LZ}}}{2\bar{P}_{\text{LZ}}} + \kappa_A^{-1} \quad (3.15)$$

which neatly separates the adiabatic and nonadiabatic contributions to the rate constant. Equation (3.15) can also be derived for asymmetric potentials where the trapping probabilities of the reactant and product states differ.

It is worth noting that when κ_A is approximated by the

small step diffusion limit of Kramers theory of adiabatic activated barrier crossing, and the term $(1 - \bar{P}_{LZ})/2\bar{P}_{LZ}$ is expanded to second order in Δ , Eq. (3.15) reduces to something very similar to Eq. (3.38) in a recent paper of Rippes and Jortner³⁶ (and Refs. 10, 35, and 36 cited therein).

Deviations from transition state theory are normally described in terms of recrossings of the transition state surface. Equation (3.15) may be understood as a sum of the number of recrossings of the transition state where the first term on the right-hand side varies as the number of recrossings due to nonadiabatic curve crossing while κ_A^{-1} varies as the number of recrossings due to inertial recrossings of the barrier at low collision frequency or spatial diffusion in the barrier region at high collision frequency.

In the adiabatic limit, $\bar{P}_{LZ} = 1$ and $\kappa = \kappa_A$. In the strongly nonadiabatic limit, $\bar{P}_{LZ} \ll 1$ and if κ_A is not far from unity then $\kappa \approx 2\bar{P}_{LZ}/(1 + \bar{P}_{LZ})$, while if $\kappa_A \ll \bar{P}_{LZ}$ then $\kappa \approx \kappa_A$ which is the asymptotic adiabatic result.²³ The largest deviations from the adiabatic theory should occur for intermediate collision frequency where the maximum in the rate constant is reduced by nonadiabatic effects. The maximum in our transmission coefficient for a given \bar{P}_{LZ} is found for $\kappa_A = 1$, where $\kappa = 2\bar{P}_{LZ}/(1 + \bar{P}_{LZ})$ which, for $\bar{P}_{LZ} \ll 1$, reduces to $\kappa = 2\bar{P}_{LZ}(1 - \bar{P}_{LZ})$.⁸

IV. COMPARISON WITH SIMULATION DATA

It is straightforward to apply Eq. (3.15). One needs only the adiabatic transmission coefficient κ_A and the average curve crossing probability \bar{P}_{LZ} [Eq. (2.2)].³³

Cline and Wolynes carried out BGK simulations for the system defined by Eq. (2.1) (see Fig. 1) on (1) the lowest electronic (ground) state potential³⁴ and (2) the diabatic potential surfaces where curve crossing was allowed. The parameters defining system 1 (2), chosen to approximate ligand binding to hemoproteins,⁹ are $\Delta/\hbar\omega = 0.6(0.8486)$, $g/\hbar\omega = 1.87(4.1195)$, and $\beta Q = 21.0(4.0)$.

The adiabatic rate constants are defined as follows. The rate constant at low collision frequency was first given by Skinner and Wolynes.²⁴ They determined the rate at which a particle, whose dynamics correspond to the BGK model, escapes from a harmonic well. For a symmetric double well potential, the rate for energy activation is given approximately by

$$k_{EA} \sim \frac{1}{2}\zeta [e^{-\beta Q} - \text{erfc}(\sqrt{\beta Q})/2], \quad (4.1)$$

where ζ is the collision frequency and $\text{erfc}(x)$ is the complementary error function.²⁵ At high collision frequency, the rate for energy activation is fast and spatial diffusion across the barrier top will be rate limiting. For a cusped barrier the rate for spatial diffusion is given by²⁶

$$k_{SD} \sim k_{TST}(\omega/\zeta)(\pi\beta Q)^{1/2}. \quad (4.2)$$

The adiabatic theory predictions [Eqs. (4.1) and (4.2)] are combined with the connection formula

$$k^{-1} = k_{EA}^{-1} + k_{TST}^{-1} + k_{SD}^{-1}, \quad (4.3)$$

to predict the total rate constant at any collision frequency²⁷; $k_{TST} = \omega e^{-\beta Q}/2\pi$.

Figure 2 compares the numerical data of Cline and Wolynes, for (a) system 1 and (b) system 2, with the adiabatic

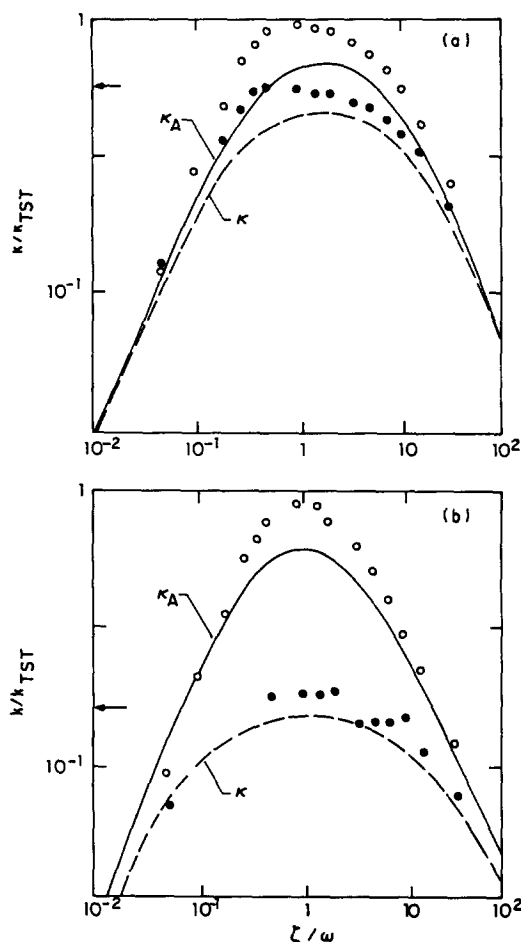


FIG. 2. A log-log plot of the transition state theory normalized rate constant as a function of the collision frequency ζ for the adiabatic theory (—) using the connection formula [Eq. (4.3)]; the nonadiabatic result (---) is calculated using Eq. (3.15). The simulation results are shown for the adiabatic (○) and nonadiabatic (●) reactive flux calculations of Cline and Wolynes for (a) system 1 and (b) system 2 (as defined in the text). The maximum nonadiabatic transmission coefficient, predicted by Eq. (3.15), is indicated by an arrow.

theory [Eq. (4.3)] and the nonadiabatic theory [Eq. (3.15)]. The adiabatic rate constants agree well with the theory of Skinner and Wolynes [Eq. (4.1)] at low collision frequency and with the spatial diffusion rate constant for a cusped barrier [Eq. (4.2)] at high collision frequency. The connection formula [Eq. (4.3)] consistently underestimates the simulation results at intermediate collision frequency. For intermediate collision frequency, there is often a maximum in the transmission coefficient close to unity. Our result [Eq. (3.15)] predicts a maximum of $\kappa = 2\bar{P}_{LZ}/(1 + \bar{P}_{LZ})$. Frauenfelder and Wolynes have proposed that the transmission coefficient should show a maximum of $\kappa = \bar{P}_{LZ}$.²⁸ [The simulation results show a maximum in the transmission coefficient of the diabatic rate data of approximately 0.552 (0.176) for system 1 (2). Averaging Eq. (2.2) over the distribution Eq. (3.2) to calculate \bar{P}_{LZ} produces 0.407 (0.090) which corresponds to a prediction based on Eq. (3.15) of a maximum in κ of 0.578 (0.165). Therefore, our estimate of the maximum in the transmission coefficient is accurate, showing good agreement with the

simulation results. These values are marked by arrows in Fig. 2.

The nonadiabatic rate constants show excellent agreement with our statistical theory, indicating that Eq. (3.15) accurately represents the dynamics of the stochastic simulation. The question of the physical validity of the model will be discussed in the section which follows.

V. DISCUSSION

While our theory accurately predicts the simulation results, it is not clear if the model of Cline and Wolynes, while an excellent first step, is a realistic one for measuring nonadiabatic curve crossing effects on activated barrier crossing. Below we focus on a number of specific problems.

(1) The Landau-Zener theory assumes that the velocity of particles in the curve crossing region is constant, or that the excess kinetic energy is large. This assumption is certainly a bad one for barrier crossing with reasonably high barriers. The average energy of those states crossing the barrier will be close to the barrier energy. It is likely that the barrier maximum will be located at the point of curve crossing which will be very close to the turning points of the diabatic surfaces. At high collision frequency, where the trajectory is diffusive, there are many reversals of the velocity in the crossing region. Zusman has extended the Landau-Zener analysis to treat such diffusive trajectories.³⁷

(2) The classical trajectory method assumes that there are no interference effects for trajectories which remain in the excited state and oscillate for long times. Child has calculated the probability of curve crossing for the case when the slopes of the diabatic surfaces at the point of crossing are of opposite sign. He finds that interference effects can be important.²⁹ Cline and Wolynes recognize this and have proposed a quantum mechanical model which attempts to include interference effects important in the crossing region.⁹ Of course, at high collision frequency it is likely that random collisions will wipe out this phase coherence.

Note that the Landau-Zener calculation is asymptotic in time. It involves the calculation of the probability that a wave function, initially at $q = +\infty$, will be at $q = -\infty$ at $t = +\infty$. In this application, the double well potential leads to bound states where the asymptotic limits used to separate states are not appropriate.

(3) Those trajectories which move in the curve crossing region should be propagated on the appropriate electronic surface. For nearly adiabatic systems, the best approximation would be to propagate the nuclei on the ground or excited state adiabatic surfaces.⁸ This surface hopping model may breakdown for strongly nonadiabatic systems as the adiabatic surfaces will not be a good representation of what the nuclei see. Also, all these models allow for surface hopping only at the transition state. A more accurate representation would allow for curve crossing over a transition region.³⁰

(4) This model ignores the effect of solvation on nonadiabatic transitions. This may well be an essential consideration in the calculation of the rate constant.³¹ A sound derivation is needed which incorporates the effects of solvation consistently in a dynamic calculation of the Landau-Zener type.

The main result of this paper, namely Eq. (3.15), allows one to determine the nonadiabatic transmission coefficient κ , in terms of the adiabatic transmission coefficient κ_A for symmetric and asymmetric potential energy surfaces. Since κ_A can be determined either by computer simulation, or from analytical theories such as the Kramers theory, the sudden collision model, or the Grote-Hynes theory for non-Markovian baths, it is now possible to determine the nonadiabatic rate constant for these models, using Eq. (3.15) and the simple Landau-Zener probability.

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- ³¹D. Chandler, *J. Stat. Phys.* **42**, 49 (1986).
- ³²Cline and Wolynes approximate \bar{P}_{LZ} by replacing v in Eq. (2.2) with the average velocity of the Maxwell distribution. A more accurate approximation is to replace v with the average velocity of the weighted distribution [Eq. (3.2)] corresponding to those trajectories crossing the transition state surface.
- ³³It is important to note that our theory is completely general and may be

applied to multidimensional systems where the Landau-Zener curve crossing probability is taken at a surface rather than a point in space.⁸

³⁴The adiabatic calculation of Cline and Wolynes propagated trajectories on the lowest energy diabatic surface rather than the ground state Born-Oppenheimer surface.

³⁵This connection formula can be understood as the sum of times for energy activation, to the barrier energy, and spatial diffusion, through the barrier region, added to the condition that the rate should not exceed the transi-

tion state theory value. For cusped barriers, the rate constant for spatial diffusion [Eq. (4.2)] is the inverse mean passage time for traveling from the reactant well minimum to the minimum of the product well (Ref. 26). Therefore, if the regions of spatial and energy diffusion overlap, Eq. (4.3) will overestimate the total reaction time and underestimate the total rate constant.

³⁶I. Rips and J. Jortner, *J. Chem. Phys.* **87**, 2090 (1987).

³⁷L. D. Zusman, *Chem. Phys.* **49**, 295 (1980).