

Tunneling dynamics in dissipative curve-crossing problems

Dmitrii E. Makarov and Nancy Makri

School of Chemical Sciences, University of Illinois, 505 S. Mathews Avenue, Urbana, Illinois 61801

(Received 25 June 1993)

We have studied the real-time dynamics of dissipative tunneling between two coupled diabatic surfaces. The interplay of tunneling, vibrational relaxation, dephasing, and resonances leads to various regimes of population dynamics, from coherent oscillations between the surfaces to exponential decay described by a rate constant. To describe these phenomena, we exploited recent efficient discretized-path-integral techniques; the two-surface system is treated exactly using a numerically constructed propagator, while the effects of the dissipative environment are incorporated through an influence functional. This procedure results in a low-dimensional integral, which is evaluated by quadrature. Use of a discrete-variable representation (DVR) allows us to replace continuous paths by paths that sample a small set of coordinate points; in particular, the conventional two-level-system approximation is shown to correspond to the limit of two DVR points. The specific features pertinent to nonadiabatic tunneling are discussed.

PACS number(s): 34.70.+e, 05.40.+j, 31.70.Hq, 73.40.Gk

I. INTRODUCTION

A chemical reaction is associated with a change in both electronic structure and positions of the reactants. The standard picture of such a process involves transition between diabatic surfaces of the initial and final states (see Fig. 1) induced by coupling between them, so the Hamiltonian reads as

$$H_0 = \frac{p^2}{2m} \mathbf{1} + \begin{bmatrix} V_1(s) & V_d(s) \\ V_d(s) & V_2(s) \end{bmatrix}, \quad (1)$$

where s is the reaction coordinate, and $\mathbf{1}$ is the 2×2 unit matrix. In many cases s does not have a direct meaning, for example, it may be some collective coordinate, such as the solvent polarization for electron transfer in solution. Diagonalizing the potential-energy term alone, one gets two adiabatic surfaces (Fig. 1)

$$V_{\pm}(s) = \frac{1}{2} [V_1(s) + V_2(s)] \pm \frac{1}{2} [4V_d^2(s) + (V_2(s) - V_1(s))^2]^{1/2}. \quad (2)$$

When the motion along the reaction coordinate is sufficiently slow and/or the separation $2V_d$ between the adiabatic surfaces is large enough, the influence of the upper surface can be neglected, and one arrives at the standard formulation of the problem of electronically adiabatic chemical reactions, where the electronic structure adiabatically follows the nuclear displacements. Many chemical reactions are believed to proceed according to an adiabatic mechanism; however, when long-range electron transfer is in question, which is associated with very small diabatic couplings, or when the transition is spin forbidden, the nonadiabatic regime is more likely.

For classical motion along the reaction coordinate, whether the transition is adiabatic or nonadiabatic depends on the parameter [1-3]

$$\delta = \frac{2\pi V_d(0)^2}{\hbar v |V_2'(0) - V_1'(0)|}, \quad (3)$$

where v is the velocity of the particle at the crossing point $s=0$. The exact solution of the classical curve-crossing problem has been given by Landau, Zener, and Stueckelberg [1-3] for the case where the diabatic coupling is constant and the potentials $V_1(s)$ and $V_2(s)$ are linear functions. This solution is a good approximation to the general case, Eq. (1), because nonadiabaticity is important only in the vicinity of the avoided crossing where the surfaces can usually be approximated by linear functions and V_d by a constant. It is also worth mentioning that several semiclassical [4,5] and purely classical [6,7] models have been developed for including nonadiabatic effects in molecular-dynamics simulations.

When nonclassical tunneling motion along the reaction coordinate is allowed, the problem becomes much more complicated. Ovchinnikova [8] and Holstein [9] extended the Landau-Zener-Stueckelberg theory [1-3] to the tunneling case using the WKB approximation and showed

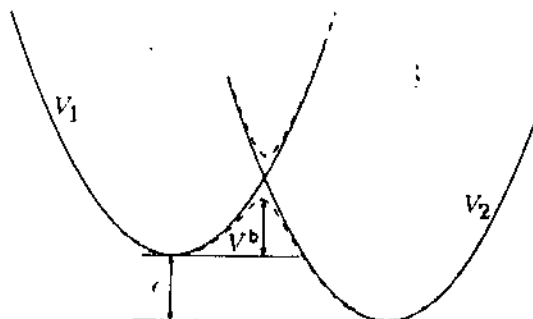


FIG. 1. Diabatic (V_1 and V_2) (solid lines) and adiabatic (V_{\pm}) (dashed lines) potential-energy surfaces. The barrier height, V^b , and the asymmetry ϵ are indicated.

that the velocity in Eq. (3) should be replaced by the absolute value of the underbarrier (instanton) velocity $v = \sqrt{2m(V^b - E)}$, where V^b is the height of the adiabatic barrier and E the energy. Since for a chemical reaction usually $V^b \gg kT$, this velocity is often greater than the thermal velocity $v_T = \sqrt{8k_B T / \pi m}$, so a reaction which proceeds classically in the adiabatic regime may happen to be nonadiabatic in the tunneling regime.

These theories were further refined by Coveney, Child, and Barany [10] and Nakamura [11], who showed that the Landau-Zener-Stueckelberg approximation breaks down when the energy is close to that of the crossing point (i.e., lies between the two adiabatic surfaces) and the transition probability may depend nonmonotonically on energy.

In a condensed-phase chemical reaction, where typically V_1 and V_2 are bound potentials, tunneling may manifest itself in two different ways: Having started on one of the surfaces (or, generally, from any nonequilibrium state), the probability to find the system on one of the surfaces may oscillate with time; these oscillations are associated with tunneling splittings of spectral lines that can be observed in the frequency domain. Or the reaction may exhibit an irreversible transition from the initial to a final equilibrium state, described by a rate constant.

A one-dimensional model cannot exhibit irreversible dynamics unless the potential is unbound. Standard theories for intramolecular radiationless transitions and electron transfer attribute the existence of a rate constant to fast vibrational relaxation on the "product" surface, which destroys phase coherence and renders the transition irreversible (see, e.g., [12,13]). In an exchange symmetric reaction, where the initial and final states are degenerate, relaxation within tunneling doublets may also be the origin of incoherent dynamics. If the vibrational relaxation is not too fast compared to the tunneling time scale, one may expect a rich variety of behaviors observed both in the frequency domain (as broadened spectral lines) and in the time domain (as damped oscillations or decay of probability). Of course, to incorporate the vibrational relaxation consistently, one should explicitly include in the Hamiltonian the terms that are responsible for it. One way to do this is to give up the collective-coordinate description and to replace the reaction coordinate s by the total set of modes the electronic state is coupled to. In general, among them there are slow and fast modes, so one cannot tell in advance whether the transition will be adiabatic, nonadiabatic, or intermediate.

Assuming that among these modes there is only one mode s that couples strongly the two electronic states, the remaining degrees of freedom can be treated using linear-response theory as a collection of harmonic oscillators. (Even if this is not the case, one may artificially choose the reaction coordinate s as a minimum energy path connecting reactant and product states in the full multidimensional space.) Thus the total Hamiltonian breaks up into the "system" Hamiltonian, Eq. (1), and a "bath" of harmonic oscillators coupled to it:

$$H = H_0 + \sum_j \frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 (x_j + C_j s / \omega_j)^2. \quad (4)$$

Note that the bath part $H - H_0$ includes standard counterterms [14] quadratic in s which ensure that if the bath relaxes to its equilibrium along the reaction coordinate s , the system potential is the same irrespective of the coupling parameters C_j . [This potential is usually referred to as the adiabatic potential, but we do not use this term in order to avoid confusion with *electronically* adiabatic surfaces, Eq. (2).] The integral characteristic of the bath is its spectral density

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{C_j^2}{\omega_j} \delta(\omega - \omega_j). \quad (5)$$

Classically, the effect of the harmonic bath is to introduce friction into the classical equation of motion for the s coordinate. In particular, in the Ohmic case, $J(\omega) = m \gamma \omega$, the classical motion on each surface satisfies the Langevin equation

$$m \ddot{s} + m \gamma \dot{s} + V'_{1(2)}(s) = f(t), \quad (6)$$

where $f(t)$ is a δ -correlated fluctuating force (see, e.g., [15]).

If the influence of the upper adiabatic term is neglected, the problem that results is well known in the literature as dissipative tunneling (see, e.g., [14–18]). In the purely incoherent case, successful studies have been performed using imaginary-time path-integral instanton methods, which give the rate of escape from the initial well. Studying the coherent tunneling case requires usually an additional simplification, i.e., truncation of the system Hamiltonian to a two-level system (TLS) corresponding to the lowest tunneling doublet in the double well. The resulting Hamiltonian of a TLS coupled to a harmonic bath (known as the spin-boson Hamiltonian) can be treated analytically [19–24]; in particular the so-called noninteracting blip approximation has proven very useful and helped to establish the criteria for localization and the coherent-incoherent transition [20]. The spin-boson treatment, however, takes into account only the dynamics within the lowest tunneling doublet and, therefore, entirely misses vibrational relaxation between different doublets. The inadequacy of the spin-boson treatment for describing chemical conversions in the condensed phase has been realized by several authors [22,25] who took higher tunneling doublets into consideration; however, the resulting problem is so complicated and difficult to treat analytically even after very strong additional assumptions (such as equidistant energy spectrum) are made, that it is hard to imagine obtaining in this way a theory so elaborate and exhaustive as that developed for the spin-boson model.

The full treatment of the two-surface problem presents an even more challenging task. Zusman [26] studied the case of a classical reaction coordinate and derived a Fokker-Planck equation. The qualitative picture of nonadiabatic reaction dynamics has been described by Frauenfelder and Wolynes [27]. Garg, Onuchic, and Ambegao-kar [28] and Wolynes [29] focused on the specific case where V_1 and V_2 are harmonic potentials with the same frequency and advanced further towards low temperatures, i.e., to the quantum regime, using Feynman's

path-integral influence-functional techniques [30]. In this case the reaction coordinate may be considered as part of the harmonic bath, and, after proper diagonalization, the problem reduces to the spin-boson Hamiltonian exactly. However, the use of the noninteracting blip approximation implies smallness of the off-diagonal matrix element responsible for the exchange; because this matrix element is the electronic coupling (rather than half the tunneling splitting, as in the traditional dissipative tunneling problem) and is not necessarily small, the powerful techniques of [20] prove useful only in the purely nonadiabatic limit of small V_d . This limit has also been studied using the golden rule by Wolynes [31], and also by Chandler and co-workers in a series of papers devoted to quantum simulations of aqueous Fe^{3+} - Fe^{2+} electron transfer, for which nuclear tunneling was noted to play an important role [13,32]. The significance of the large V_d case for charge-transfer reactions was also realized [33,34] and approximate theories interpolating between adiabatic and nonadiabatic electron transfer were proposed. Mak and Gehlen recently reported [35] some numerical calculations for the spin-boson model of electron transfer in the large-electronic-coupling case. The case of very low temperatures where tunneling from the ground state of the initial surface dominates has also been addressed using instanton techniques, based on the assumption that tunneling is an incoherent irreversible process [29,36].

The opposite case of reversible coherent oscillations between the surfaces has received much attention mostly in the context of spectroscopy [37]. Among the methods employed to study this case have been those based on Redfield theory [38], an influence-functional approach [39], and the extended adiabatic formalism for the spectroscopic spin-boson problem [40]. These approaches are approximate in that they either assume reduction of the problem to the spin-boson Hamiltonian thereby implying harmonicity of all nuclear coordinates, or rely on perturbation theory in the coupling to the bath modes, which is known to break down and be even qualitatively incorrect for strong enough friction [20].

In this paper we describe a numerical-path-integral technique designed to study the dynamics of a system described by the Hamiltonian of Eq. (4) in real time. This technique is free of all additional approximations and assumptions mentioned above. Our primary goal is to study the dynamics induced by the coupling between the surfaces on a long (tunneling) time scale and to observe how, when the friction increases, this dynamics changes from coherent probability oscillations to complete loss of phase coherence associated with rate dynamics, as well as effects specific to the two-surface problem not displayed by either single-surface adiabatic tunneling or the spin-boson problem.

Computation of real-time path integrals involves circumventing the so-called sign problem, i.e., the problem of oscillating integrand which does not allow use of standard Monte Carlo techniques for evaluating multidimen-

sional integrals. This problem has recently been attacked with a number of approaches [41–57] such as use of effective smooth propagators [45–47] and sampling around semiclassical stationary phase paths [48–52] which permits Monte Carlo sampling; for a review of these methods see [53]. Although quite successful at short times, the above methods proved impractical for calculating long-time dynamics because of additional phase interference inherent in quantum dynamics even in the strict semiclassical limit. A stochastic resummation method has also been proposed for the spin-boson problem [54].

A new numerical-path-integral technique has been proposed recently [55] and applied to single-surface system-bath problems [56,57]. This approach exploits one's ability to obtain an exact system propagator using basis-set methods; the numerically constructed system propagator is then supplemented with an influence functional that describes the multidimensional corrections due to the bath. Because the path integral constructed in this way starts from the exact dynamics of a one-dimensional system as a zeroth approximation, a much less fine time discretization is needed to obtain convergent results even for long times, and the resulting integral has such low dimensionality that it can be evaluated by quadrature.

In Sec. II we describe how these ideas can be implemented in the case of the two-surface Hamiltonian, Eq. (4). Section III discusses the discrete variable grid we adopt in order to evaluate the path-integral expressions obtained in Sec. II. In Sec. IV, numerical applications on model systems are presented, which illustrate the coherent-incoherent transition in dissipative tunneling between the surfaces, the effect of friction on destroying localization of the system in an asymmetric double well, as well as the promotion of tunneling by vibrational relaxation for a particle trapped in a quasidegenerate doublet. Finally, we conclude in Sec. V with some general remarks.

II. DISCRETIZED PATH-INTEGRAL WITH EXACT SYSTEM PROPAGATORS

Suppose that at $t=0$ all oscillators are in the ground state such that the initial wave function in the space of the reaction coordinate s , pseudospin index $\sigma=1,2$ indicating the surface, and all bath coordinates \mathbf{x} is factorized:

$$\psi(s, \sigma, \mathbf{x}; 0) = \phi(s, \sigma) \chi_0(\mathbf{x}). \quad (7)$$

This is the simplest initial condition adopted in [20,30]. As an alternative, one may study equilibrium correlation functions [51] or start with displaced oscillator wave functions. As long as the tunneling dynamics is being investigated rather than the details of vibrational relaxation on a single surface, the details of the initial preparation are usually insignificant. After time t the wave function becomes

$$\psi(s_f, \sigma_f, \mathbf{x}_f; t) = \sum_{\sigma_i} \int ds_i \int d\mathbf{x}_i \langle s_f \sigma_f \mathbf{x}_f | e^{-iHt/\hbar} | s_i \sigma_i \mathbf{x}_i \rangle \phi(s_i, \sigma_i) \chi_0(\mathbf{x}_i). \quad (8)$$

Since we are not interested in the details of the bath behavior, we square the absolute value of the wave function and integrate this quantity over all bath coordinates to obtain the probability density

$$P(s_f, \sigma_f; t) = \sum_{\sigma_1} \sum_{\sigma'_1} \int d\mathbf{x}_f \int ds_1 \int ds'_1 \int d\mathbf{x}_1 \int d\mathbf{x}'_1 \langle s_f \sigma_f \mathbf{x}_f | e^{-iHt/\hbar} | s_1 \sigma_1 \mathbf{x}_1 \rangle \times \langle s'_1 \sigma'_1 \mathbf{x}'_1 | e^{iHt/\hbar} | s_f \sigma_f \mathbf{x}_f \rangle \phi(s_1, \sigma_1) \phi(s'_1, \sigma'_1) \chi_0(\mathbf{x}_1) \chi_0(\mathbf{x}'_1). \quad (9)$$

To obtain a path-integral expression for this probability density, we divide the total time t into N time slices Δt so that

$$\langle s_f \sigma_f \mathbf{x}_f | e^{-iHt/\hbar} | s_1 \sigma_1 \mathbf{x}_1 \rangle = \sum_{\sigma_1} \cdots \sum_{\sigma_{N-1}} \int ds_1 \int d\mathbf{x}_1 \cdots \int ds_{N-1} \int d\mathbf{x}_{N-1} \times \langle s_f \sigma_f \mathbf{x}_f | e^{-iH\Delta t/\hbar} | s_{N-1} \sigma_{N-1} \mathbf{x}_{N-1} \rangle \cdots \langle s_1 \sigma_1 \mathbf{x}_1 | e^{-iH\Delta t/\hbar} | s_1 \sigma_1 \mathbf{x}_1 \rangle \quad (10)$$

and employ following [55] the short-time approximation for the time-evolution operator

$$e^{-iH\Delta t/\hbar} \approx e^{-i(H-H_0)\Delta t/2\hbar} e^{-iH_0\Delta t/\hbar} e^{-i(H-H_0)\Delta t/2\hbar}. \quad (11)$$

[Note that the system Hamiltonian H_0 involves the adiabatic (i.e., minimum energy) potential for each of the electronic surfaces, and the bath $H-H_0$ enters as harmonic oscillators whose equilibrium positions are adiabatically displaced along the minimum energy path. For this reason, in previous papers [55–57] on single-surface problems the splitting described by Eq. (11) has been referred to as a quasiadiabatic propagator. In the present paper, however, we refrain from using this term in order to avoid confusion with electronically adiabatic processes.] Substituting Eqs. (11) and (10) into (9) and integrating over the Gaussian bath variables [30] one arrives at the result

$$P(s_f, \sigma_f; t) = \sum_{\sigma_0^+} \cdots \sum_{\sigma_{N-1}^+} \sum_{\sigma_0^-} \cdots \sum_{\sigma_{N-1}^-} \int ds_0^+ \int ds_1^+ \cdots ds_{N-1}^+ \int ds_0^- \int ds_1^- \cdots ds_{N-1}^- \times \langle s_f \sigma_f | e^{-iH_0\Delta t/\hbar} | s_{N-1}^+ \sigma_{N-1}^+ \rangle \cdots \langle s_1^+ \sigma_1^+ | e^{-iH_0\Delta t/\hbar} | s_0^+ \sigma_0^+ \rangle \phi(s_0^+, \sigma_0^+) \times \phi(s_0^-, \sigma_0^-) \langle s_0^- \sigma_0^- | e^{iH_0\Delta t/\hbar} | s_1^- \sigma_1^- \rangle \cdots \langle s_{N-1}^- \sigma_{N-1}^- | e^{iH_0\Delta t/\hbar} | s_f \sigma_f \rangle \times I(s_0^+, s_1^+, \dots, s_{N-1}^+, s_0^-, s_1^-, \dots, s_{N-1}^-, s_f; \Delta t). \quad (12)$$

Here I is the bath influence functional given by [30]

$$I = \exp \left\{ -\frac{1}{\hbar} \int_0^t dt' \int_0^{t'} dt'' [s^+(t') - s^-(t')] \times [\alpha(t' - t'') s^+(t'') - \alpha^*(t' - t'') s^-(t'')] - \frac{i}{\hbar} \int_0^t dt' \sum_j \frac{C_j^2}{2\omega_j^2} [s^+(t')^2 - s^-(t')^2] \right\}, \quad (13)$$

where $\alpha(t)$ is the bath response function

$$\alpha(t) = \sum_j \frac{C_j^2}{2\omega_j} e^{-i\omega_j t}. \quad (14)$$

The path $s^\pm(t')$ that appears in Eq. (13) consists of constant s segments [$s^\pm(t') = s_0^+$ for $0 < t' < \Delta t/2$, $s^\pm(t') = s_1^\pm$ for $\Delta t/2 < t' < 3\Delta t/2$, . . . , $s^\pm(t') = s_f \equiv s_{N-1}^\pm$ for $t - \Delta t/2 < t' < t$] arranged on the time contour composed of two segments with positive and negative time directions. For this path, Eq. (13) can be transformed to a form suitable for numerical calculations:

$$\begin{aligned}
I &= \exp \left\{ -\frac{1}{\hbar} \sum_{k=0}^N \sum_{n=0}^N \frac{1}{2} \eta_{kn} s_k^+ s_n^+ + \frac{1}{2} \eta_{kn}^* s_k^- s_n^- - \mu_{kn} s_k^+ s_n^- \right\}, \\
\eta_{kn} &= \frac{4}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} \sin^2 \frac{\omega \Delta t}{2} e^{-i\omega \Delta t |k-n|}, \quad 0 < k, n < N, \quad k \neq n, \\
\eta_{nn} &= \frac{2}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} (1 - e^{-i\omega \Delta t}), \quad 0 < n < N, \\
\eta_{0N} = \eta_{N0} &= \frac{4}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} \sin^2 \frac{\omega \Delta t}{4} e^{-i\omega(t-\Delta t/2)}, \\
\eta_{00} = \eta_{NN} &= \frac{2}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} (1 - e^{-i\omega \Delta t/2}), \\
\eta_{0n} = \eta_{n0} &= \frac{4}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} \sin \frac{\omega \Delta t}{4} \sin \frac{\omega \Delta t}{2} e^{-i\omega(n\Delta t - \Delta t/4)}, \quad 0 < n < N, \\
\eta_{Nn} = \eta_{nN} &= \frac{4}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} \sin \frac{\omega \Delta t}{4} \sin \frac{\omega \Delta t}{2} e^{-i\omega(t-n\Delta t - \Delta t/4)}, \quad 0 < n < N, \\
\mu_{kn} &= \frac{4}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} \sin^2 \frac{\omega \Delta t}{2} e^{-i\omega \Delta t (k-n)}, \quad 0 < k, n < N, \\
\mu_{NN} = \mu_{00} &= \frac{4}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} \sin^2 \frac{\omega \Delta t}{4}, \\
\mu_{N0} = \mu_{0N}^* &= \frac{4}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} \sin^2 \frac{\omega \Delta t}{4} e^{-i\omega(t-\Delta t/2)}, \\
\mu_{n0} = \mu_{0n}^* &= \frac{4}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} \sin \frac{\omega \Delta t}{4} \sin \frac{\omega \Delta t}{2} e^{-i\omega(n\Delta t - \Delta t/4)}, \quad 0 < n < N, \\
\mu_{Nn} = \mu_{nN}^* &= \frac{4}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} \sin \frac{\omega \Delta t}{4} \sin \frac{\omega \Delta t}{2} e^{-i\omega(t-n\Delta t - \Delta t/4)}, \quad 0 < n < N.
\end{aligned} \tag{15}$$

Finally, the system propagators appearing in Eq. (12) are computed by diagonalizing numerically the one-dimensional Hamiltonian H_0

$$\langle s' \sigma' | e^{-iH_0 \Delta t / \hbar} | s \sigma \rangle = \sum_n e^{-iE_n \Delta t / \hbar} \Phi_n(s', \sigma') \Phi_n(s, \sigma), \tag{16}$$

where E_n are the eigenvalues of H_0 and $\Phi_n(s, \sigma) \equiv \langle s \sigma | n \rangle$ the corresponding eigenfunctions. The sum in Eq. (16) does not converge with n , and inclusion of an infinite number of terms appears necessary. Indeed, terms corresponding to large quantum numbers are responsible for the standard highly oscillatory behavior of the real-time propagator. However, it is easily seen that if the propagator is to be used to calculate the evolution of a wave function which does not overlap with Φ_n for large n , the contribution of highly excited states will be small in the final result, and therefore such terms can be omitted from Eq. (16). Thus, an effective propagator can be constructed by including a finite number of states in Eq. (16), which will lead to accurate time evolution. Apart from replacing an infinite sum by a finite one, this procedure has the additional advantage of filtering out rapidly oscillatory high-energy contributions, leading to a smooth and well-behaved propagator.

Equations (12), (15), and (16) constitute our prescription for calculating $P(s, \sigma; t)$. The advantage of the

present scheme, as compared to direct discretization of Feynman's path integral for the probability density [30] is that, because Eq. (16) is exact for any time Δt , the system part of the propagator is treated exactly for any (however small) number of time slices whether the process is electronically adiabatic, nonadiabatic, or intermediate; as argued in [55], the result will converge very rapidly to the exact one as the number of time slices is increased.

III. SYSTEM-SPECIFIC DISCRETE-VARIABLE REPRESENTATION

The integrand of Eq. (12) is an oscillatory function. As argued in the Introduction, Monte Carlo methods are not suitable for evaluating such integrals, and we resort to quadrature methods.

In practice, performing the integrations in Eq. (12) requires $2N$ integrations on an s grid and $2N$ summations over the spin index. [Since with the present simple Hamiltonian the influence functional does not depend on spin indices, the summations over spin variables could actually be performed separately. However, even after eliminating the spin summation from Eq. (12) the integration on an ordinary s grid remains impractical for large enough N . Moreover, such a simplification would not be possible with a more general Hamiltonian (for example, if the system-bath coupling is different for the two diabatic surfaces) where the influence functional would depend on

spin paths as well.] For a typical grid with 30–50 points along the continuous s coordinate such a procedure is practically feasible if N does not exceed 2–3, which is by far not adequate if one is interested in the long-time behavior of $P(s, \sigma; t)$. On the other hand, it is clear that if the path integral, Eq. (10), had been discretized using some energy-eigenstate basis (rather than position states), a fairly small number of such basis states would have been sufficient; for example, a two-state basis leads to a qualitatively correct picture of tunneling in a symmetric double well. For this reason it is tempting to use the basis of system eigenstates Φ_n to discretize the propagator, as this will require fewer summations. However, because the system-bath coupling is a function of the system coordinate s , which is nonlocal in the energy basis, one would lose the advantage of using the influence functional (13).

To circumvent this difficulty, we transform the truncated energy basis to a new discrete “coordinate” basis, in which the position operator becomes diagonal [57]. The idea of using such “discrete variable representations” (DVR), in which the coordinate operator is diagonal, was proposed almost 30 years ago (see, e.g., [58]) for computing potential matrix elements and developed into a powerful numerical scheme for vibrational eigenvalue problems during the past decade [59]. The procedure we use here is closest to the potential-optimized system specific DVR [60]. Specifically, we diagonalize the position operator in the system eigenstate basis to obtain a new basis of functions $u_k(s, \sigma)$ such that

$$\hat{s}u_k(s, \sigma) = \tilde{s}_k u_k(s, \sigma). \quad (17)$$

The propagator in the new basis takes the form

$$\langle u_k | e^{-iH_0 \Delta t / \hbar} | u_k \rangle = \sum_n e^{-iE_n \Delta t / \hbar} T_{nk} T_{nk}^*, \quad (18)$$

where T_{nk} is the orthogonal transformation matrix

$$u_k(s, \sigma) = \sum_n T_{nk} \Phi_n(s, \sigma). \quad (19)$$

The wave functions $u_k(s, \sigma)$ are shown in Fig. 2 for the case when the surfaces V_1 and V_2 are shifted parabolas. Note that mixing between surfaces is small when only the two lowest-energy levels are taken into account [Fig. 2(a)]; that is, when \tilde{s}_k is positive (and approximately corresponds to the minimum of the right surface), the component of the wave function $u_k(s, 1)$ corresponding to the left surface is much smaller than $u_k(s, 2)$. This situation is typical of tunneling from lowest-energy levels, when the probability to be say on the right of the crossing point is practically the same as the probability to stay on surface 2. Including higher-energy levels increases mixing between the surfaces, especially for the states with \tilde{s}_k closest to the crossing point [Fig. 2(b)].

One can repeat the reasoning of the previous section in the DVR representation. Because the position operator is now diagonal, the influence functional is of the same form as in Eq. (15) except coordinates s_k are now replaced by discrete grid points \tilde{s}_k . Using a small grid, one cannot reproduce exactly the probability density $P(s, \sigma; t)$ (although a discrete analog of this quantity may be introduced), but is able to calculate various expectation values that are obtained by averaging any function of the coordinate s with this probability density. For example, the average position reads as

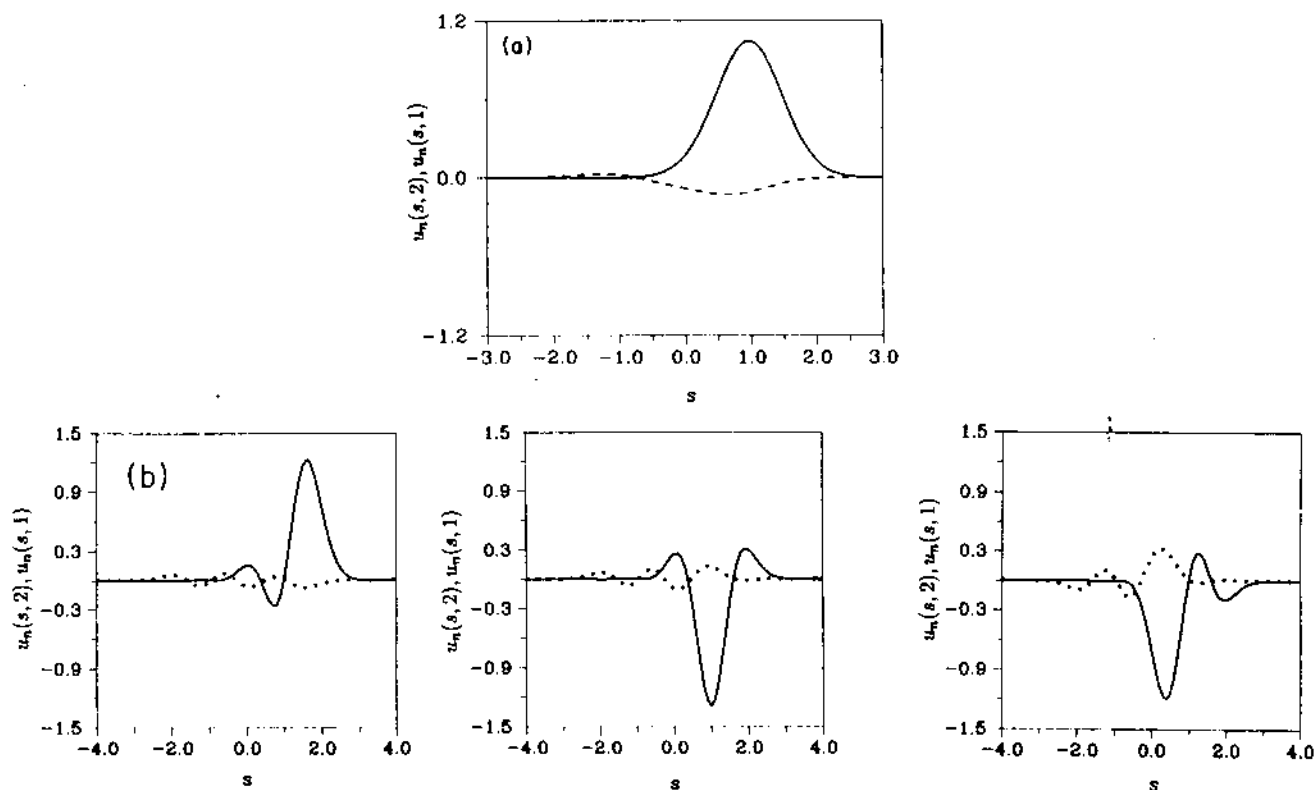


FIG. 2. Components $u_n(s, 2)$ (solid line) and $u_n(s, 1)$ (dashed line) of the DVR wave function corresponding to positive eigenvalues of the position operator in the case of (a) two and (b) six DVR points.

$$\begin{aligned}
\langle s(t) \rangle &= \sum_{\sigma=1}^2 \int ds s P(s, \sigma; t) \\
&= \sum_{k_0^{\pm}} \cdots \sum_{k_{N-1}^{\pm}} \sum_{k_N} \xi_{k_N} \langle u_{k_N} | e^{-iH_0 \Delta t / \hbar} | u_{k_{N-1}} \rangle \cdots \langle u_{k_1} | e^{-iH_0 \Delta t / \hbar} | u_{k_0} \rangle \\
&\quad \times \xi_{k_0} \xi_{k_0} \langle u_{k_0} | e^{iH_0 \Delta t / \hbar} | u_{k_1} \rangle \cdots \langle u_{k_{N-1}} | e^{iH_0 \Delta t / \hbar} | u_{k_N} \rangle \\
&\quad \times I(\xi_{k_0}^+, \xi_{k_1}^+, \dots, \xi_{k_{N-1}}^+, \xi_{k_0}^-, \xi_{k_1}^-, \dots, \xi_{k_{N-1}}^-, \xi_{k_N}; \Delta t), \tag{20}
\end{aligned}$$

where $\xi_k = \langle u_k | \phi \rangle$ is the amplitude of the initial system state in the DVR basis. Expressing the probability to be on one of the surfaces

$$P_{\sigma}(t) = \int ds P(s, \sigma; t) \tag{21}$$

in terms of the DVR representation requires projecting the final DVR state onto a state with definite value of σ ,

$$\begin{aligned}
P_{\sigma}(t) &= \int ds \sum_{k_0^{\pm}} \cdots \sum_{k_N} u_{k_N}^{\sigma}(s, \sigma) u_{k_N}^{-\sigma}(s, \sigma) \langle u_{k_N}^{\sigma} | e^{-iH_0 \Delta t / \hbar} | u_{k_{N-1}} \rangle \cdots \langle u_{k_1} | e^{-iH_0 \Delta t / \hbar} | u_{k_0} \rangle \\
&\quad \times \xi_{k_0} \xi_{k_0} \langle u_{k_0} | e^{iH_0 \Delta t / \hbar} | u_{k_1} \rangle \cdots \langle u_{k_{N-1}} | e^{iH_0 \Delta t / \hbar} | u_{k_N} \rangle \\
&\quad \times I(\xi_{k_0}^+, \xi_{k_1}^+, \dots, \xi_{k_{N-1}}^+, \xi_{k_0}^-, \xi_{k_1}^-, \dots, \xi_{k_{N-1}}^-, s; \Delta t) \\
&= \sum_{k_0^{\pm}} \cdots \sum_{k_N} \sum_{k_m} \lambda_{k_N}^{\sigma} \lambda_{k_m}^{\sigma} \langle u_{k_N}^{\sigma} | e^{-iH_0 \Delta t / \hbar} | u_{k_{N-1}} \rangle \cdots \langle u_{k_1} | e^{-iH_0 \Delta t / \hbar} | u_{k_0} \rangle \xi_{k_0} \xi_{k_0} \langle u_{k_0} | e^{iH_0 \Delta t / \hbar} | u_{k_1} \rangle \cdots \\
&\quad \times \langle u_{k_{N-1}} | e^{iH_0 \Delta t / \hbar} | u_{k_N} \rangle I(\xi_{k_0}^+, \xi_{k_1}^+, \dots, \xi_{k_{N-1}}^+, \xi_{k_0}^-, \xi_{k_1}^-, \dots, \xi_{k_{N-1}}^-, \xi_{k_m}; \Delta t), \tag{22}
\end{aligned}$$

where

$$\lambda_{k_n}^{\sigma} = \int ds u_k(s, \sigma) u_n(s, \sigma). \tag{23}$$

Equations (20) and (22) contain the most interesting information about the dynamics of the two-surface problem (4). These quantities will be calculated for a number of examples in the next section.

When only two energy levels are included in Eq. (16), the path samples two DVR points in the coordinate space, which is nothing but the spin-boson approximation [20]. Transformation to the DVR basis enables one to include as many energy levels as needed and to go smoothly from the spin-boson limit to the continuous coordinate case.

IV. NUMERICAL EXAMPLES

In the examples described below we assume a bath spectral density of the form

$$J(\omega) = m\gamma\omega \exp(-\omega/\omega_c), \tag{24}$$

where ω_c is a cutoff frequency. For simplicity, the diabatic coupling V_d is taken constant, although the approach described in this paper applies equally easily to surfaces and coupling function $V_d(s)$ of arbitrary form. The initial state of the system is chosen to be an eigenstate of one of the diabatic surfaces. As described in the previous section, if the system starts out from the ground state of one of the surfaces the simplest approximation one can make is to truncate the set of energy levels to the

lowest tunneling doublet so that there are only two DVR points, which approximately (but not exactly) coincide with the potential minima. Provided that (i) the asymmetry of the potential ϵ is much smaller than the vibration quantum $\hbar\omega_0$, (ii) the barrier height V^b is greater than the vibration quantum, and (iii) the friction coefficient γ is not too large so that intermultiplet dynamics are negligible, this spin-boson approximation is expected to work well.

In the first example, both diabatic surfaces are harmonic functions of frequency ω_0 . Figure 3 presents a plot of the average position $\langle s(t) \rangle$ against time for zero asymmetry for different friction coefficients, showing that the coherent oscillations are suppressed as the friction increases; these results were obtained using two DVR points. The number of time slices needed to obtain converged results ranged from 4 (for small friction) to 10 (for the strongest friction).

The friction strength for a two-level system is usually characterized by the Kondo parameter [20]

$$\alpha = 2m\gamma s_0^2 / \pi \hbar, \tag{25}$$

where $\pm s_0$ are the coordinates of the two points sampled by the path. This parameter ranges from zero to 0.90 for the data of Fig. 3. The coherent-incoherent transition occurs at α slightly above 0.5; this small discrepancy with the prediction of [20] that transition should occur exactly at $\alpha=0.5$ is due to the finite value of the cutoff frequency, which was assumed to be much greater than the tun-

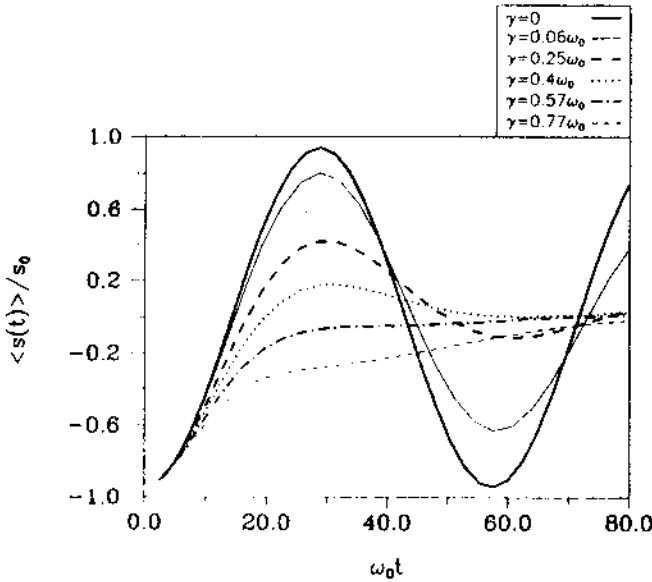


FIG. 3. Average position in units of s_0 as a function of dimensionless time in the spin-boson approximation for two parabolic surfaces $V_{1,2} = V_0(1 \pm s/s_0)^2/2$. The diabatic coupling between the surfaces is $V_d = 0.4\hbar\omega_0$, $V_0 = 2\hbar\omega_0$, the cutoff frequency is $\omega_c = 0.2\omega_0$, and the friction coefficient ranges from 0 to $0.77\omega_0$, as indicated. The tunneling splitting equals $0.11\hbar\omega_0$.

neling splitting in [20]. We note in passing that the present results demonstrate that direct summation over "spin flips" turns out a very efficient yet simple way to obtain the dynamics of the spin-boson model at times longer than the tunneling period (see also Ref. [40]).

Next, we proceed to study the effect of asymmetry on the behavior of $\langle s(t) \rangle$. When the asymmetry ϵ is comparable to the vibrational quantum of a surface, $\hbar\omega_0$, more energy levels are involved in the tunneling dynamics and a larger DVR basis is needed. If the friction were zero, the behavior of the system would strongly depend on whether or not the energy levels of the left and right surfaces are at resonance. At resonance, having started on the left surface, the particle will be found on the right with probability close to 1 after some time, whereas if the states are away from resonance, only a small part of the initial probability will leak to the other surface. Friction effectively broadens each energy level leading to incoherent rate dynamics and eventually eliminating the difference between resonant and nonresonant situations. This is demonstrated in Fig. 4 for two different values of asymmetry. The converged results were obtained with six DVR states and five time slices. Figure 4(a) shows a plot of $\langle s(t) \rangle$ for two parabolic surfaces with asymmetry $\epsilon = 0.6\hbar\omega_0$. At zero friction, the particle that started from the ground state of the left surface continues to stay mostly on the left. Coupling to a bath with low cutoff frequency affects only slightly the dynamics because of the lack of phonons with frequencies high enough to induce (through low orders in perturbation theory) transitions between various energy levels. When the system is coupled to a bath with cutoff frequency comparable to the energy-level spacing, $\langle s(t) \rangle$ behaves in a purely incoherent fashion relaxing towards equilibrium. In Fig.

4(b) another situation is depicted, where the asymmetry $\epsilon = 0.9\hbar\omega_0$ is such that the lowest-energy level of the left surface is close to the first excited level of the right one. In the absence of dissipation the system oscillates with a large amplitude between the two surfaces; dissipation suppresses these oscillations again leading to rate dynamics. Comparison of Figs. 4(a) and 4(b) shows that depending on the asymmetry, dissipation can either enhance or quench tunneling, always shifting the system towards relaxation to equilibrium.

As mentioned in the Introduction, a feature specific of nonadiabatic transitions is a nonmonotonic dependence of the transition probability on energy [11], which may be thought of as appearing because of interference between the two surfaces. For bound surfaces this implies that the splitting of energy levels induced by the diabatic coupling changes nonmonotonically with quantum number. In particular, splittings of higher levels may be smaller than the ground-state tunneling splitting and may even be equal to zero at certain parameters of the potential, such that the initially excited system may be trapped on one of

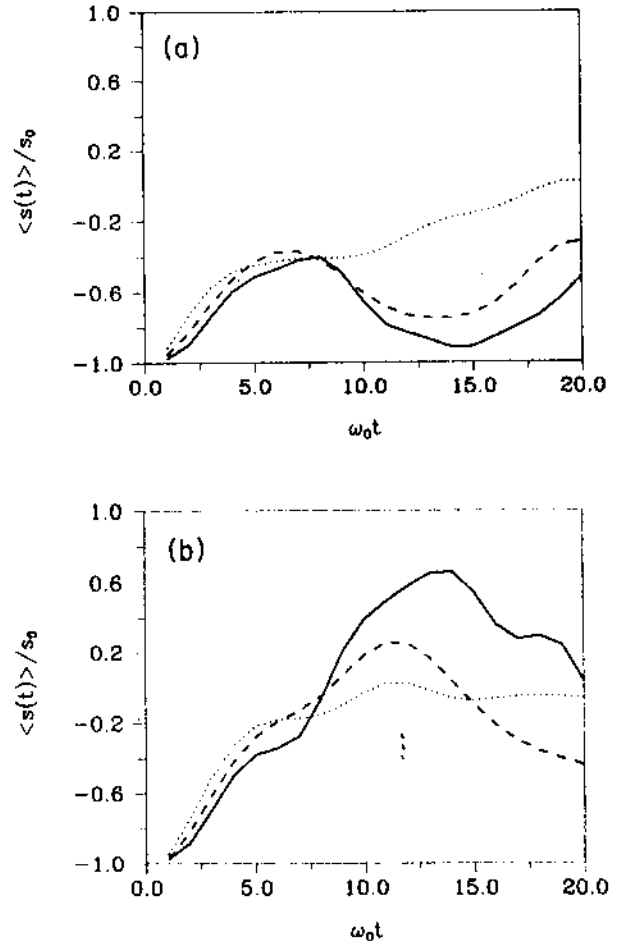


FIG. 4. Average position in units of s_0 as a function of dimensionless time for two parabolic surfaces $V_{1,2} = V_0(1 \pm s/s_0)^2/2 \pm \epsilon/2$, $V_0 = 2\hbar\omega_0$. The diabatic coupling is $V_d = 0.4\hbar\omega_0$, the friction coefficient is $\gamma = 0.4\omega_0$; the asymmetry is (a) $\epsilon = 0.6\hbar\omega_0$ and (b) $\epsilon = 0.9\hbar\omega_0$. Dashed line: $\omega_c = 0.2\omega_0$. Dotted line: $\omega_c = 0.6\omega_0$. The solid line corresponds to zero friction.

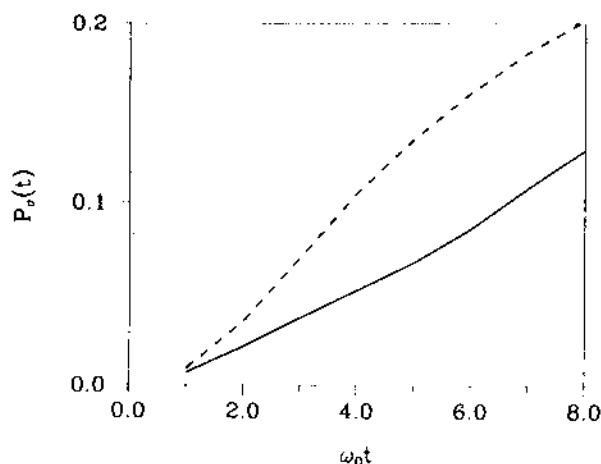


FIG. 5. The probability to be on the right surface having started in the first excited state (solid line) and in the ground state (dashed line) of the left surface. See text for the parameters of the surfaces.

the surfaces because of small probability of transition to the other surface. Dissipation leads to transitions between various energy levels within a single surface thereby facilitating transitions between the surfaces.

As an example, we studied the surfaces $V_{1(2)} = V_0 \ln[1 + (s \pm s_0)^2 / 2s_0^2]$, $V_0 / \hbar \omega_0 = 0.9$, $V_d = 0.12 V_0$. At these parameters the lowest state is split, while the first excited doublet, which has energy above the crossing point, is almost degenerate. The evolution of the probability to be on the right surface, when starting in the first excited state of the left surface, is shown in Fig. 5 for $\gamma = \omega_0$, where ω_0 is the harmonic frequency at the potential minimum; in the absence of dissipation this probability remains zero. For comparison, the same function is plotted for the case when the system starts in the ground state of the left surface (dashed line). The two curves are roughly parallel, but the first of them shows a "delay time" due to vibrational relaxation that must take place in order to allow transitions between the surfaces.

V. CONCLUDING REMARKS

This paper was inspired in large part by both experimental [12,61] and theoretical [32] evidences of nuclear tunneling in electron-transfer chemical reactions. Recent studies in ultrafast photoinduced electron transfer [62] have demonstrated that it may occur on a picosecond or subpicosecond time scale, that is, with a rate comparable with the rate of vibrational relaxation. Under such conditions, one may expect to observe dynamics much more complicated than simple exponential decay, which involves inherently quantum-mechanical long-time coherent effects. The techniques formulated here are well suited for simulating this kind of phenomena. On the other hand, solution of the dissipative curve crossing problem is of fundamental importance for quantum chemical reaction rate theory, since it provides an adequate description of electronically nonadiabatic processes. The numerical-propagator-discrete-variable representation of path integrals has been applied recently to compute flux-flux autocorrelation functions with the aim to obtain quantum-mechanical rate constants in multiple minimum potentials [56(b),57]. The ideas developed in those papers and here allow to view both adiabatic and nonadiabatic condensed phase reactions from a unique perspective.

In this paper we considered only a bath which is "cold," in Feynman's terminology. The generalization to finite temperatures is straightforward and is achieved by simply replacing the zero-temperature bath response function by that at finite $k_B T = \beta^{-1}$,

$$\alpha(t) = \sum_j \frac{C_j^2}{4\omega_j \sinh(\beta \hbar \omega_j / 2)} \times (e^{\beta \hbar \omega_j / 2} e^{-i\omega_j t} + e^{-\beta \hbar \omega_j / 2} e^{i\omega_j t}). \quad (26)$$

Increasing the temperature suppresses the phase coherence in a way similar to the effect of friction.

- [1] L. D. Landau, Phys. Z. Sowjetunion 2, 46 (1932).
- [2] C. Zener, Proc. R. Soc. London, Ser. A 137, 696 (1932).
- [3] E. C. G. Stueckelberg, Helv. Phys. Acta 5, 369 (1932).
- [4] P. Pechukas, Phys. Rev. 181, 174 (1969).
- [5] W. H. Miller and T. F. George, J. Chem. Phys. 56, 5637 (1972).
- [6] J. C. Tully and R. K. Preston, J. Chem. Phys. 55, 562 (1971).
- [7] F. A. Webster, P. J. Rossky, and R. A. Friesner, Comput. Phys. Commun. 63, 494 (1991).
- [8] M. Ya. Ovchinnikova, Dokl. Phys. Chem. 161, 259 (1965).
- [9] T. Holstein, Philos. Mag. 37, 49 (1978).
- [10] P. V. Coveney, M. S. Child, and A. Barany, J. Phys. B 18, 4557 (1985).
- [11] H. Nakamura, J. Chem. Phys. 87, 4031 (1987); H. Nakamura, Int. Rev. Phys. Chem. 10, 123 (1991); C. Zhu and H. Nakamura, J. Chem. Phys. 97, 8497 (1992).
- [12] R. A. Marcus and N. Sutin, Biochim. Biophys. Acta 811, 265 (1985).
- [13] J. S. Bader and D. Chandler, Chem. Phys. Lett. 157, 501 (1989).
- [14] A. O. Caldeira and A. J. Leggett, Phys. Rev. Lett. 46, 211 (1981); A. O. Caldeira and A. J. Leggett, Ann. Phys. (N.Y.) 149, 374 (1983); D. Waxman and A. J. Leggett, Phys. Rev. B 32, 4450 (1985).
- [15] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. 62, 251 (1990).
- [16] H. Grabert, U. Weiss, and P. Hänggi, Phys. Rev. Lett. 52, 2193 (1984); H. Grabert and U. Weiss, *ibid.* 53, 1787 (1984); H. Grabert, P. Olschowski, and U. Weiss, Phys. Rev. B 36, 1931 (1987).
- [17] A. I. Larkin and Yu. N. Ovchinnikov, Zh. Eksp. Teor. Fiz. [Sov. Phys. JETP] 59, 420 (1984).
- [18] E. Pollak, Phys. Rev. A 33, 4244 (1986); W. Hontscha, P.

- Hanggi, and E. Pollak, *Phys. Rev. B* **41**, 2210 (1990).
- [19] A. J. Bray and M. A. Moore, *Phys. Rev. Lett.* **49**, 1546 (1982).
- [20] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and M. Zwierger, *Rev. Mod. Phys.* **59**, 1 (1987).
- [21] R. Silbey and R. H. Harris, *J. Chem. Phys.* **80**, 2615 (1984); R. H. Harris and R. Silbey, *ibid.* **83**, 1069 (1985); R. Silbey and R. H. Harris, *ibid.* **93**, 7062 (1989).
- [22] P. E. Parris and R. Silbey, *J. Chem. Phys.* **83**, 5619 (1985).
- [23] C. Aslangul, N. Pottier, and D. Saint-James, *Phys. Lett.* **110A**, 249 (1895).
- [24] H. Dekker, *Phys. Rev. A* **35**, 1436 (1987).
- [25] H. Dekker, *Phys. Rev. A* **44**, 2314 (1991); *Physica A* **175**, 485 (1991).
- [26] L. D. Zusman, *Chem. Phys.* **49**, 295 (1980).
- [27] H. Frauenfelder and P. G. Wolynes, *Science* **229**, 337 (1985).
- [28] A. Garg, J. Onuchic, and V. Ambegaokar, *J. Chem. Phys.* **83**, 4491 (1985).
- [29] P. G. Wolynes, *J. Chem. Phys.* **86**, 1957 (1987).
- [30] R. P. Feynman and F. L. Vernon, *Ann. Phys. (N.Y.)* **24**, 118 (1963); R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
- [31] P. G. Wolynes, *J. Chem. Phys.* **87**, 6559 (1987).
- [32] J. S. Bader, R. A. Kuharski, and D. Chandler, *J. Chem. Phys.* **93**, 230 (1990).
- [33] J. N. Gehlen, D. Chandler, H. J. Kim, and J. T. Hynes, *J. Phys. Chem.* **96**, 1748 (1992).
- [34] J. N. Gehlen and D. Chandler, *J. Chem. Phys.* **97**, 4958 (1992).
- [35] C. H. Mak and J. N. Gehlen, *Chem. Phys. Lett.* **206**, 130 (1993).
- [36] V. A. Benderskii, V. I. Goldanskii, and D. E. Makarov, *Phys. Rep.* (to be published).
- [37] S. Mukamel and Yi. J. Yan, *Acc. Chem. Res.* **22**, 301 (1989).
- [38] J. M. Jean, R. A. Friesner, and G. R. Fleming, *J. Chem. Phys.* **96**, 5827 (1992).
- [39] Y. Tanimura and S. Mukamel, *Phys. Rev. E* **47**, 118 (1993).
- [40] R. Coalson, *J. Chem. Phys.* **94**, 1108 (1991).
- [41] D. Thirumalai and B. J. Berne, *Chem. Phys. Lett.* **116**, 471 (1985); D. Thirumalai and B. J. Berne, *Annu. Rev. Phys. Chem.* **37**, 401 (1986).
- [42] E. C. Behrman, G. A. Jongeward, and P. G. Wolynes, *J. Chem. Phys.* **79**, 6277 (1983); E. C. Behrman and P. G. Wolynes, *ibid.* **83**, 5863 (1985); R. E. Cline, Jr. and P. G. Wolynes, *ibid.* **88**, 4334 (1988); B. A. Mason, K. Hess, R. E. Cline, and P. G. Wolynes, *Superlattices Microstruct.* **3**, 421 (1987).
- [43] J. D. Doll, *J. Chem. Phys.* **81**, 3536 (1984); J. D. Doll and D. L. Freeman, *Science* **234**, 1356 (1986); J. D. Doll, R. D. Coalson, and D. L. Freeman, *J. Chem. Phys.* **87**, 1641 (1987).
- [44] J. Chang and W. H. Miller, *J. Chem. Phys.* **87**, 1648 (1987).
- [45] N. Makri, *Chem. Phys. Lett.* **159**, 489 (1989).
- [46] O. A. Sharafeddin, D. J. Kouri, N. Nayar, and D. K. Hoffman, *J. Chem. Phys.* **95**, 3224 (1991); D. K. Hoffman, N. Nayar, O. A. Sharafeddin, and D. J. Kouri, *ibid.* **95**, 8299 (1991); D. K. Hoffman and D. J. Kouri, *ibid.* **96**, 1179 (1992).
- [47] N. Makri, *J. Phys. Chem.* **97**, 2417 (1993).
- [48] V. S. Filinov, *Nucl. Phys.* **271**, 717 (1986).
- [49] N. Makri and W. H. Miller, *Chem. Phys. Lett.* **139**, 10 (1987); N. Makri and W. H. Miller, *J. Chem. Phys.* **89**, 2170 (1988).
- [50] J. D. Doll and D. L. Freeman, *Adv. Chem. Phys.* **73**, 120 (1988); J. D. Doll, D. L. Freeman, and M. J. Gillan, *Chem. Phys. Lett.* **143**, 277 (1988); J. D. Doll, T. L. Beck, and D. L. Freeman, *J. Chem. Phys.* **89**, 5753 (1988); T. L. Beck, J. D. Doll, and D. L. Freeman, *ibid.* **90**, 3181 (1989); J. D. Doll, D. L. Freeman, and T. L. Beck, *Adv. Chem. Phys.* **78**, 61 (1990).
- [51] C. Mak and D. Chandler, *Phys. Rev. A* **41**, 5709 (1990); **44**, 2352 (1991).
- [52] A. M. Amini and M. F. Herman, *J. Chem. Phys.* **96**, 5999 (1992).
- [53] N. Makri, *Comput. Phys. Commun.* **63**, 389 (1991).
- [54] C. H. Mak, *Phys. Rev. Lett.* **68**, 899 (1992).
- [55] N. Makri, *Chem. Phys. Lett.* **193**, 435; (1992); N. Makri, in *Time-Dependent Quantum Molecular Dynamics*, edited by J. Broeckhove and L. Lathouwers (Plenum, New York, 1992), p. 209.
- [56] (a) M. Topaler and N. Makri, *J. Chem. Phys.* **97**, 9001 (1992); (b) M. Topaler and N. Makri, *Chem. Phys. Lett.* **210**, 285 (1993).
- [57] M. Topaler and N. Makri, *Chem. Phys. Lett.* **210**, 448 (1993).
- [58] D. O. Harris, G. G. Engerholm, and W. D. Gwinn, *J. Chem. Phys.* **43**, 1515 (1965); A. S. Dickinson and P. R. Certain, *ibid.* **49**, 4209 (1968).
- [59] J. V. Lill, G. A. Parker, and J. C. Light, *Chem. Phys. Lett.* **89**, 483 (1982); J. C. Light, I. P. Hamilton, and J. V. Lill, *J. Chem. Phys.* **82**, 1400 (1985); J. V. Lill, G. A. Parker, and J. C. Light, *ibid.* **85**, 900 (1986); S. E. Choi and J. C. Light, *ibid.* **92**, 2129 (1990); Z. Bacic and J. C. Light, *ibid.* **85**, 4594 (1986); **86**, 3065 (1987); *Annu. Rev. Phys. Chem.* **40**, 469 (1989).
- [60] J. Echave and D. C. Clary, *Chem. Phys. Lett.* **190**, 225 (1992).
- [61] D. DeVault and B. Chance, *Biophys. J.* **6**, 825 (1966); D. DeVault, *Quantum-Mechanical Tunneling in Biological Systems* (Cambridge Univ. Press, Cambridge, 1984).
- [62] G. R. Fleming, J. L. Martin, and J. Breton, *Nature (London)* **333**, 190 (1988).