A unified framework for quantum activated rate processes. II. The nonadiabatic limit

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A recently proposed unified theoretical framework for quantum activated rate constants is further developed and explored. The case of electronically nonadiabatic rate processes is considered, and the weak coupling limit explicitly investigated by an expansion of the rate constant expression. By virtue of this approach, a semiclassical Golden Rule expression is derived after a series of steepest descent approximations. The semiclassical analysis in turn reveals a closed form path integral expression for the quantum activated rate constant in the nonadiabatic (Golden Rule) limit which is free of harmonic and/or classical approximations for the many-dimensional nuclear (vibronic) modes. The latter expression is amenable to direct calculation in realistic systems through computer simulation. © *1997 American Institute of Physics.* [S0021-9606(97)52505-0]

I. INTRODUCTION

The subject of electron transfer (ET) rates and their calculation has been the target of many analytical and numerical studies.[1,2] Recent computational approaches for computing ET rate constants range from those based on Fermi's Golden Rule (see, e.g., Ref. 3) to explicit quantum dynamical calculations on simplified models of ET processes (see, e.g., Refs. 4–9). In addition, approaches derived from path integral quantum transition state theory (PI-QTST) (Refs. 10–13) have been developed to calculate the ET rate based on the centroid density of the electronic state variable.[14–16] Despite the many theoretical and computational studies of ET reactions, a unified computational approach has not yet been developed which is capable of determining ET rate constants for arbitrary values of the electronic coupling in systems characterized by general nonlinear potentials and a significant degree of nuclear mode tunneling. Even in the nonadiabatic or weak-coupling limit, the calculation of the ET rate constant for arbitrary potentials is a challenge. (However, encouraging progress in the latter arena has been been reported by Wolynes,[17] and we will make contact with and extend this intriguing point of view from a different perspective.)

In a recent paper, it was shown that significant progress toward the calculation of ET rate constants for general systems can be achieved by exploring the structure of instanton theory in systems influenced by nonadiabatic transitions.[18] To briefly review this perspective, the approach[18] is based on the instanton expression for quantum rate constants[19–23] combined with a nonadiabatic dynamics formalism[24,25] adapted to treat the imaginary time instanton trajectory undergoing nonadiabatic transitions. As will be discussed later, this mathematical formalism is also contained within the umbrella of a unified theoretical framework for quantum activated rate constants, as was developed in Ref. 26. The resulting ''nonadiabatic instanton'' formulation is general and capable of treating nonquadratic diabatic potential energy surfaces and multiple electronic states. More importantly, it also provides a computational method for bridging the adiabatic and nonadiabatic limits of electron transfer processes. The theory was tested for the well-known spin-boson model as applied to ET reactions[3,17,27,28] with a single (Marcus-type) harmonic bath mode, obtaining excellent agreement with the analytical predictions in both the adiabatic and nonadiabatic (Golden Rule) limits. In addition, it was shown that nonlinearity in the diabatic potentials can readily be included in the calculations and may have a large effect on the rate constant. What was not contained in the previous work, however, was an analytical proof that the nonadiabatic instanton solution can be reduced to the usual Golden Rule expression in the weak coupling limit, nor was a numerical scheme presented to calculate the rates for the case of a continuum of bath modes. It is therefore a goal of this paper to analyze the weak coupling limit of the nonadiabatic instanton theory, both analytically and numerically.

It is also a goal of the present paper to explore the consequences of the general statement that the quantum rate constant is related to the imaginary part of the barrier partition function,[26] which is defined asymptotically for an appropriate unstable mode associated with the rate process. This mathematical formulation unifies classical activated rate theory, its quantum corrections at high temperature, and the instanton theory at low temperatures where the dynamics are strongly influenced by tunneling. It also provides an *a priori* rationale for the introduction of the Feynman path centroid variable into the quantum rate constant expression. As such, the theory can be used both to further justify the PI-QTST formula,[10–13] and to derive an improved quantum rate constant expression.[26] Importantly, quantum activated rate processes involving two or more diabatic electronic surfaces may be treated within the formalism.[18] As stated earlier, such systems are important in, e.g., electron transfer (ET) pro-

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cesses which are of broad interest to the chemistry community.

The nonadiabatic (weak coupling) limit of the two-state quantum activated rate formula will be explored in the present paper within the context of the framework presented in Ref. 26. The focus will be on the weak coupling (Golden Rule) limit, so that the partition function can be expanded in terms of the nonadiabatic coupling constant. A sequence of steepest descent approximations[29] will be carried out to derive a semiclassical formula of the Golden Rule rate constant and to reveal the origin of the imaginary part of the barrier partition function in the weak coupling regime. The result, when applied to the spin-boson model, is shown to recover the familiar rate formula for the spin-boson model, but the semiclassical expression also holds for more general nonlinear diabatic potential surfaces. The imaginary part of the barrier partition function is again shown to be the key concept in the latter approach. This term, which naturally arises from a steepest descent evaluation of the appropriate integral, is then shown to lead to a formula for the nonadiabatic (Golden Rule) rate constant which does not rely on assumptions for the vibronic modes (e.g., harmonic and/or classical). In addition, the final expression can be readily evaluated in computer simulations of realistic systems using imaginary time Feynman path integrals. The exponential (Arrhenius-type) term in the formula is the same as one proposed by Wolynes,[17] so in the end it will have been derived from two complementary perspectives. Importantly, however, the present approach also provides an expression for the pre-exponential factor so that actual nonadiabatic ET *rate constants*, not only activation free energies, can now be calculated in realistic path integral simulations, again being free of any assumptions about the vibronic mode character.

The present paper is organized as follows: The overall theoretical framework for quantum activated rate constants is presented in Sec. II, with the general concepts outlined in Sec. II A and the nonadiabatic instanton solution reviewed in Sec. II B. The nonadiabatic (weak coupling) limit of the theory is then derived semiclassically in Sec. II C and applied to the spin-boson model in Sec. II D. The implications of the analysis for the broader context of the rate constant calculation from a path integral formalism is next presented in Sec. III, while a numerical example is given in Sec. IV. Concluding remarks are found in Sec. V.

II. THEORY

A. Unified framework for quantum activated rate constants

The theory of quantum rate constants developed in Ref. 26 is centered around the concept of a ''barrier partition function,'' and in particular its imaginary part. This quantity arises from an asymptotic treatment of the partition function in the barrier region, the exact nature of which depends on the temperature of the system. Generally speaking, the quantum reactive flux can then be expressed as[26]

$$F \simeq \nu \ \mathrm{Im}\ Z_b , \tag{2.1}$$

where ν is a simple prefactor, given by $1/\hbar\beta$ in the instanton limit,[26] and $\mathrm{Im}\ Z_b$ is the imaginary part of the barrier partition function. In the following discussion of two-state systems, the latter function will first be analyzed in the instanton limit, and then in the nonadiabatic (Golden Rule) limit. The central theme in both cases is the identification of a steepest descent integration mode that yields the imaginary part of the partition function. This mode is the *unstable* or *reactive* mode. It has a clear interpretation in the classical, or nearly-classical, limit as the reaction coordinate mode at the free energy saddle point (i.e., transition state), but in the various quantum regimes it becomes more abstractly defined.[26] Nevertheless, the perspective of an unstable saddle point mode giving the imaginary part of the barrier partition function unifies many different results in quantum activated dynamics. More importantly, it helps to justify[26] new formulations such as PI-QTST and the path integral Golden Rule rate expression developed in Sec. III.

B. Nonadiabatic instanton formalism

Within the context of Eq. (2.1), we first consider the full nonadiabatic instanton solution,[18] which is applicable to systems having arbitrarily large off-diagonal couplings between the diabatic states. The general electron transferlike Hamiltonian for a many-body, multilevel system is given by

$$H = K(\dot{\mathbf{q}}) + V_d(\mathbf{q}), \tag{2.2}$$

where $K(\dot{\mathbf{q}})$ is the kinetic energy term for the the collection of N nuclear degrees of freedom for the system of interest, and $V_d(\mathbf{q})$ is the potential defined on an electronic diabatic basis set, i.e.,[18,30]

$$V_d(\mathbf{q}) = \sum_{\mu} |\mu\rangle V_\mu(\mathbf{q}) \langle\mu| + \sum_{\mu} \sum_{\nu>\mu} V_{\mu\nu}(\mathbf{q}) \times (|\mu\rangle\langle\nu| + |\nu\rangle\langle\mu|). \tag{2.3}$$

The terms $V_\nu(\mathbf{q})$ here are the diabatic potentials, and the function $V_{\mu\nu}(\mathbf{q})$ is the coupling matrix element between the μth and νth diabatic surfaces. The latter function is assumed to be real.

In two earlier papers,[18,26] we have argued that the the desired quantum activated rate constant k can be written in terms of imaginary time quantities as

$$k \simeq \frac{1}{\hbar\beta Z_\mu} \mathrm{Im}\ Z_{\mu\nu}, \tag{2.4}$$

where Z_μ is the partition function of the reactant state and $Z_{\mu\nu}$ is the transitional, or ''barrier,'' contribution to the partition function [cf. Eq. (2.1)], given by[18]

$$Z_{\mu\nu} = \int d\mathbf{q} \int d\mathbf{q}' \langle \mu, \mathbf{q} | \exp(-\beta H/2) | \nu, \mathbf{q}' \rangle \times \langle \nu, \mathbf{q}' | \exp(-\beta H/2) | \mu, \mathbf{q} \rangle. \tag{2.5}$$

Here, $\mathbf{q}$ and $\mathbf{q}'$ are understood to be confined to the region of the wells of diabatic surfaces $|\mu\rangle$ and $|\nu\rangle$, respectively.

Provided the effective barrier height is significantly larger than the thermal energy in the diabatic wells, the

steepest descent method can be applied to evaluate the imaginary part of $Z_{\mu\nu}$, which leads to the nonadiabatic instanton approximation for Eq. (2.4). The details of the instanton solution in the adiabatic limit have been elaborated by others.[19–23,31–33] In Ref. 18, however, a computational methodology was proposed to evaluate the instanton rate constant in the most general case which *bridges* the adiabatic and nonadiabatic limits. It should also be noted that the expression in Eq. (2.5) is not actually required within the larger context of Eq. (2.1), but it helps us in simplifying the nonadiabatic instanton formalism and in finding the instanton solution. [Stated differently, to evaluate Eq. (2.1) one can always find the instanton solution to evaluate Im Z_b, including the nonadiabatic transitions. Equation (2.5) is simply written so as to help isolate that solution.]

To proceed with the instanton solution of the rate constant, the imaginary time propagator in Eq. (2.5) is separated into the wave function propagation of the diabatic levels and the propagation arising from the kinetic energy term K, giving rise to the path integral

$$Z_{\mu\nu}=\int \mathscr{D}\mathbf{q}(\tau)\exp\left[-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\,\frac{1}{2}\,\dot{\mathbf{q}}(\tau)\cdot\mathbf{m}\cdot\dot{\mathbf{q}}(\tau)\right] \times T_{\mu\nu}[\hbar\beta,\hbar\beta/2,\mathbf{q}(\tau)]T_{\nu\mu}[\hbar\beta/2,0,\mathbf{q}(\tau)], \quad (2.6)$$

where $\mathbf{m}$ is the mass matrix. The quantity $T_{\nu\mu}$ is the overlap between the initial diabatic state $|\mu\rangle$ and the final diabatic state $|\nu\rangle$. The Bloch equation can be introduced to describe the evolution of the imaginary time electronic state propagator, i.e.,

$$-\frac{\partial u(\tau,\tau')}{\partial\tau}=V_d[\mathbf{q}(\tau)]u(\tau,\tau'), \quad (2.7)$$

so that

$$T_{\nu\mu}[\tau,\tau',\mathbf{q}(\tau)]=\langle\nu|u(\tau,\tau')|\mu\rangle, \quad (2.8)$$

which is a functional of the system nuclear path $\mathbf{q}(\tau)$. The imaginary time interval in Eq. (2.6) satisfies $0\leqslant\tau\leqslant\hbar\beta$.[34]

The stationary path of the Hamiltonian in Eq. (2.2) consists of the nuclear instanton trajectory and the self-consistent electronic wave function propagation in imaginary time arising from the coupling of the two subsystems. Following Pechukas,[24,25] who was the first to provide a stationary phase prescription for a self-consistent classical-like trajectory and time-dependent wave function based on Feynman's path integral formulation of quantum dynamics, we have developed a similar theory for the nonadiabatic quantum instanton solution so as to provide a means for calculating the electron transfer rate constant under general conditions.[18] Along these lines, an application of the steepest descent approximation to Eq. (2.6) leads to the equation of motion for the nuclear instanton coordinates[18]

$$\mathbf{m}\cdot\frac{d^2\mathbf{q}(\tau)}{d\tau^2}=\left\langle\frac{\partial H_d[\mathbf{q}(\tau)]}{\partial\mathbf{q}(\tau)}\right\rangle_d, \quad (2.9)$$

which is to be solved together with Eq. (2.7) to obtain the nonadiabatic instanton trajectory. Here, the quantum average $\langle\cdots\rangle_d$ is defined in Appendix A and is a functional of the nuclear path $\mathbf{q}(\tau)$. Because of the time reversal property of the amplitudes $T_{\nu\mu}$ and $T_{\mu\nu}$, the instanton trajectory is symmetric with respect to the imaginary time $\hbar\beta/2$. The same property holds true for the wave function.

To complete the instanton analysis, the second order functional derivative must be evaluated along the instanton trajectory.[25,29] The infinite set of eigenvalues of this functional derivative matrix contains a zero eigenvalue corresponding to the translationally invariant mode and a negative eigenvalue corresponding to the unstable mode.[21,26,35] In Appendix A, the appropriate treatment is summarized. One then arrives at the nonadiabatic instanton solution for the quantum activated rate constant, i.e.,[18]

$$k\simeq\frac{1}{Z_\mu\hbar\beta}\left(\frac{W}{2\pi\hbar D}\right)^{1/2}\exp(-S_{\rm inst}/\hbar), \quad (2.10)$$

where W and $S_{\rm inst}$ are the work and the action, respectively, along the instanton trajectory, and D is a properly normalized determinant of the second order derivative matrix, excluding the zero eigenvalue (cf. Appendix A). In Ref. 18, the notation ''Im'' is understood to be contained in the definition of $Z_{\mu\nu}$, and the reader should note the misprint in Eq. (2.21) of that paper in which the prefactor $(\hbar\beta Z_\mu)^{-1}$ is missing from the rate constant expression.

C. The weak coupling limit

In the limit of weakly coupled diabatic surfaces, the full nonadiabatic instanton solution is not necessary. In fact, the imaginary barrier partition function concept embodied in Eq. (2.1) leads to more straightforward approach. The strategy is to analyze the barrier partition function in the weak coupling limit through the steepest descent approximation. Here, we specialize to the two-state case with a coordinate-independent off-diagonal coupling, but the analysis can be readily generalized.

In the limit of small $V_{\mu\nu}$, the partition function can in general be expanded in terms of this parameter, resulting in the expression

$$Z=\mathrm{Tr}\left\{e^{-\beta\hat{h}_0}\hat{T}\,\exp\left[-\frac{1}{\hbar}\int_0^{\hbar\beta}d\tau(e^{\hat{h}_0\tau/\hbar}\hat{\Delta}_{\mu\nu}e^{-\hat{h}_0\tau/\hbar})\right]\right\} =\sum_\mu Z_\mu+\frac{1}{\hbar^2}\sum_\mu\sum_{\nu\neq\mu}V_{\mu\nu}^2\int_0^{\hbar\beta}d\tau_1\int_0^{\tau_1}d\tau_2 \times\mathrm{Tr}_c[e^{-h_\mu(\hbar\beta-\tau_1)/\hbar}e^{-h_\nu(\tau_1-\tau_2)/\hbar}e^{-h_\mu\tau_2/\hbar}]+\cdots, \quad (2.11)$$

where $\hat{\Delta}_{\mu\nu}=V_{\mu\nu}(|\mu\rangle\langle\nu|+|\nu\rangle\langle\mu|)$, $\hat{h}_0=\Sigma_\mu|\mu\rangle h_\mu\langle\mu|$ with $h_\mu=K(\dot{\mathbf{q}})+V_\mu(\mathbf{q})$. Also, $Z_\mu=\mathrm{Tr}_c\,e^{-\beta h_\mu}$ is the partition function of the μth diabatic surface, ''Tr_c'' denotes the coordinate-space trace, and $\hat{T}$ is the imaginary time-ordering operator. Clearly, one of the first summation terms of Eq. (2.11) can be identified as the reactant partition function, Z_μ. On the other hand, the second term of Eq. (2.11), which will be denoted by Z_2, must somehow contain the contribution to the imaginary time transition element in the weak coupling

limit if the theory outlined in Sec. II A is to hold together. More specifically, the imaginary part of Z_2, if it exists, must be associated with the imaginary part of the ''barrier partition function,'' Z_b, in Eq. (2.1). Recall that by definition the imaginary part of the barrier partition function is defined to arise from the steepest descent treatment of some key integration variable or ''saddle point mode,''[26] whether it be the classical reactive mode at high temperature, the instanton fluctuation mode at low temperature, or the path centroid mode in PI-QTST. Our purpose here is to discover the origin of the quantum saddle point mode in the weak coupling limit. To be consistent then, a steepest descent treatment will be carried out for all possible integrations to see what this perspective reveals.

Due to the periodicity of the trace implied in Eq. (2.11), the integrand of Z_2 is invariant with respect to one of the integral variables, τ_1 or τ_2, i.e., it depends only on $\tau=\tau_1-\tau_2$. Therefore, Z_2 can be rewritten as

$$Z_{2,\mu\nu}=\beta V_{\mu\nu}^2\,\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\ \mathrm{Tr}_c(e^{-h_\mu\tau'/\hbar}e^{-h_\nu\tau/\hbar}), \tag{2.12}$$

where $\tau'=\hbar\beta-\tau$ and the subscript $\mu\nu$ has been added to $Z_{2,\mu\nu}$ to denote the contribution from the coupling between the μth and νth diabatic surfaces.

A steepest descent (i.e., semiclassical) approximation can now be applied for the imaginary time path integrals involving the nuclear coordinates $\mathbf{q}$, giving

$$\begin{aligned}&\mathrm{Tr}_c(e^{-h_\mu\tau'/\hbar}e^{-h_\nu\tau/\hbar})\\&=\int d\mathbf{q}_1\int d\mathbf{q}_2\langle\mathbf{q}_1|e^{-h_\mu\tau'/\hbar}|\mathbf{q}_2\rangle\langle\mathbf{q}_2|e^{-h_\nu\tau/\hbar}|\mathbf{q}_1\rangle\\&\simeq\frac{1}{2\pi\hbar}\int d\mathbf{q}_1\int d\mathbf{q}_2\sqrt{(\partial_{12}^2S_\mu)(\partial_{12}^2S_\nu)}\\&\quad\times\exp\{-[S_\mu(\tau')+S_\nu(\tau)]/\hbar\},\end{aligned} \tag{2.13}$$

where $\partial_{12}^2S=\det(\partial^2S/\partial\mathbf{q}_1/\partial\mathbf{q}_2)$. Here, $S_\mu(\tau')[=S_\mu(\mathbf{q}_1,\mathbf{q}_2,\tau')]$ is the classical action on the inverted potential surface of $V_\mu(\mathbf{q})$ for a trajectory to go from $\mathbf{q}=\mathbf{q}_2$ to $\mathbf{q}=\mathbf{q}_1$ in the time interval τ', and $S_\nu(\tau)[=S_\nu(\mathbf{q}_2,\mathbf{q}_1,\tau)]$ is the classical action on the inverted potential surface of $V_\nu(\mathbf{q})$ for a trajectory to go from $\mathbf{q}=\mathbf{q}_1$ to $\mathbf{q}=\mathbf{q}_2$ in the time interval τ. Next, the steepest descent approximation is again employed to evaluate the integrals over the path endpoint variables $\mathbf{q}_1$ and $\mathbf{q}_2$, giving

$$\mathrm{Tr}_c(e^{-h_\mu\tau'/\hbar}e^{-h_\nu\tau/\hbar})\simeq P\ \exp[-S_{\mu\nu}(\tau)/\hbar], \tag{2.14}$$

where $S_{\mu\nu}(\tau)=S_\mu(\tau')+S_\nu(\tau)$ and the prefactor P is given by

$$P=\sqrt{\frac{\partial_{12}^2S_\mu\partial_{12}^2S_\nu}{\partial_{11}^2S_{\mu\nu}\partial_{22}^2S_{\mu\nu}-\partial_{12}^2S_{\mu\nu}\partial_{21}^2S_{\mu\nu}}} \tag{2.15}$$

with $\partial_{11}^2S=\det(\partial^2S/\partial\mathbf{q}_1\partial\mathbf{q}_1)$ and similar definitions apply for the other determinants. Here, the actions S_μ, S_ν, and $S_{\mu\nu}$ are evaluated at the stationary values of $\mathbf{q}_1$ and $\mathbf{q}_2$ which satisfy

$$\frac{\partial S_\mu(\tau')}{\partial\mathbf{q}_1}+\frac{\partial S_\nu(\tau)}{\partial\mathbf{q}_1}=0 \tag{2.16}$$

and

$$\frac{\partial S_\mu(\tau')}{\partial\mathbf{q}_2}+\frac{\partial S_\nu(\tau)}{\partial\mathbf{q}_2}=0, \tag{2.17}$$

i.e., the momentum is continuous at the surface switching times. The above equation implies a closed path in the phase space of $(\mathbf{q},\mathbf{p})$ but a discontinuous path on the potential surface because at positions $\mathbf{q}_1$ and $\mathbf{q}_2$ the stationary classical trajectory jumps from the μth surface to the νth surface, or vice versa.

Interestingly enough, the above steepest descent analysis of the coordinate integrations has not yet defined an imaginary part for the term $Z_{2,\mu\nu}$ in Eq. (2.12). Therefore, we now explore the final integration variable—over the imaginary time τ—from the steepest descent perspective. Ignoring the τ-dependence of the prefactor in Eq. (2.14), one finds the stationary condition for the imaginary time integration to be given by

$$\frac{\partial S_\mu(\hbar\beta-\tau_{\mathrm{st}})}{\partial\tau_{\mathrm{st}}}+\frac{\partial S_\nu(\tau_{\mathrm{st}})}{\partial\tau_{\mathrm{st}}}=0 \tag{2.18}$$

which in turn implies

$$E_\mu(\tau_{\mathrm{st}}')=E_\nu(\tau_{\mathrm{st}}), \tag{2.19}$$

where $\tau_{\mathrm{st}}'=\hbar\beta-\tau_{\mathrm{st}}$. This condition insures that the trajectory segments have a continuous energy.

After imposing the above equality on the stationary conditions Eqs. (2.16) and (2.17), one finds

$$V_\mu(\mathbf{q}_1)=V_\nu(\mathbf{q}_1), \tag{2.20}$$

and

$$V_\mu(\mathbf{q}_2)=V_\nu(\mathbf{q}_2), \tag{2.21}$$

which describes a closed classical path in the upside down potential surface of duration τ_{st} on potential V_ν and $\hbar\beta-\tau_{\mathrm{st}}$ on potential V_μ. In the weak coupling limit, the instanton trajectory is therefore recovered with a unique choice of τ_{st}. Since the nonadiabatic instanton trajectory is now reduced to an adiabatic instanton trajectory on the cusped potential connecting the two diabatic surfaces at their intersection, the self-consistency of the nuclear trajectory and the electronic wave function is explicitly solved.

The stationary-phase evaluation of Eq. (2.12) can now be completed to yield

$$Z_{2,\mu\nu}\simeq iPV_{\mu\nu}^2\,\frac{\beta}{\hbar}\left(\frac{2\pi\hbar}{|d^2S/d\tau^2|_{\mathrm{st}}}\right)^{1/2}\exp(-S/\hbar), \tag{2.22}$$

where $S=S_{\mu\nu}(\tau_{\mathrm{st}})$. The purely imaginary character of this quantity results from the fact that stationary variable τ_{st} corresponds to the saddle point of the imaginary time integration and, as such, gives rise to the imaginary part of the partition function to lowest nonzero order in the nonadiabatic coupling. This is the key insight which leads us to the more computationally useful path integral formulation of Golden Rate rate constants presented in the next section.

To be consistent with the semiclassical treatment of the barrier partition function, the reactant partition function can

also be evaluated in a similar fashion. Assuming a single minimum in the reactant diabatic surface, the steepest descent approximation yields a solution

$$Z_\mu \simeq P_0 \exp(-\beta V_0), \tag{2.23}$$

where V_0 is the potential minimum $[=V(\mathbf{q}_0)]$ and the prefactor P_0 is defined as

$$P_0 = \frac{1}{\det[2\sinh(\hbar\beta\sqrt{\mathbf{K}}/2)]}. \tag{2.24}$$

Here, $\mathbf{K}=\partial^2 V(\overline{\mathbf{q}_0})/\partial\overline{\mathbf{q}}\partial\overline{\mathbf{q}}$ is the mass-scaled force constant matrix, expanded around the reactant minimum $\mathbf{q}_0$. The above expression is exact in the harmonic limit and reasonably accurate in the anharmonic limit.

The substitution of Eqs. (2.22)–(2.23) into the definition of the quantum activated rate in Eq. (2.1) leads to the semiclassical expression

$$k \simeq \left(\frac{V_{\mu\nu}}{\hbar}\right)^2 \left(\frac{2\pi\hbar}{|d^2S/d\tau^2|_{\rm st}}\right)^{1/2} \exp[-S(\tau_{\rm st})/\hbar + \beta V_0], \tag{2.25}$$

where it has been assumed that the prefactors P and P_0 are weakly dependent on coordinates so in the region of interest the two are approximately the same, i.e., $P \simeq P_0$. This form of the quantum nonadiabatic rate constant results from a sequence of steepest descent approximations to the formula in Eq. (2.1). It is therefore a semiclassical Golden Rule rate constant expression. Yet, the derivation is quite general, obtained without invoking the linear response (i.e., harmonic) or classical bath approximations. Most importantly, in this derivation, suitable for the weak coupling nonadiabatic limit, the critical unstable saddle point mode is in the *imaginary time integration*. This point will be revisited in Sec. III, however, a few comments on the semiclassical Golden Rule expression [Eq. (2.25)] are first in order.

It is well-known that nonadiabatic electron transfer rates for a classical nuclear system can be cast in terms of a Landau–Zener-type frequency factor and an Arrhenius exponential factor, i.e.,

$$k_{\rm cl} = f e^{-\beta\Delta F}, \tag{2.26}$$

where ΔF is the free energy difference between the reactant minimum and the barrier top [i.e., at the cusp where $V(\mathbf{q})\equiv V_b$]. Clearly, in the rate expression in Eq. (2.25) the instanton action modifies the exponent, and all the nonexponential factors correspond to the frequency factor f. Since $S(\tau_{\rm st})/\hbar < \beta V_b$, it can be concluded that the quantum rate in Eq. (2.25) will be enhanced by quantum tunneling effects, as expected.

The form of Eq. (2.25) also suggests a numerical semiclassical scheme to calculate the quantum nonadiabatic rate constant. First, one would construct the cusped adiabatic potential by locating the intersection of the diabatic surfaces; next, one would find the instanton trajectory with the corresponding $\tau_{\rm st}$ and $S(\tau_{\rm st})$, then one would calculate a closed trajectory on the discontinuous cusped potential for $S(\tau_{\rm st}+\delta)$ and $S(\tau_{\rm st}-\delta)$, respectively; and finally, with $|d^2S/d\tau^2|_{\rm st} = [S(\tau_{\rm st}+\delta)+S(\tau_{\rm st}-\delta)-2S(\tau_{\rm st})]/\delta^2$, one would evaluate the rate constant from Eq. (2.25). As it turns out, a direct path integral approach seems more promising than the semiclassical calculation just outlined, and this will be described in the next section. Before doing that, however, a consideration of the well-known spin-boson model is in order to insure that the standard expression for the nonadiabatic rate constant in that case is recovered using the present theoretical formalism.

D. Analysis of the spin-boson model

The spin-boson model serves as the primary model for investigating nonadiabatic transitions because it is thought to capture the main features of, e.g., electron transfer reactions, while retaining a relative degree of simplicity. It is described by the Hamiltonian

$$H = \Delta\sigma_x + \sum_{i=1}^{N} \frac{1}{2} m_i \dot{q}_i^2 + \sum_{i=1}^{N} \frac{1}{2} m_i \omega_i^2 \left(q_i - \sigma_z \frac{c_i}{m_i\omega_i^2}\right)^2, \tag{2.27}$$

where σ is the Pauli spin matrix, $\Delta(=V_{\mu\nu})$ is one-half the tunnel splitting. Here, the set of coordinates $\{q_i\}$ constitutes the nuclear coordinates, i.e., the boson modes, with frequencies $\{\omega_i\}$, masses $\{m_i\}$, and coupling constants $\{c_i\}$. It can be shown that the influence of the nuclear coordinates on the electronic dynamics (the two-state spin variable) can be described by the spectral density, given in discrete form by[23]

$$J(\omega) = \frac{\pi}{2} \sum_{j=1}^{N} \frac{c_j^2}{\omega_j} \delta(\omega - \omega_j), \tag{2.28}$$

which in the classical limit is related to an appropriate friction kernel.

Substitution of the above Hamiltonian into the expression in Eq. (2.12) yields

$$Z_2 = \Delta^2 \frac{\beta}{\hbar} \int_0^{\hbar\beta} d\tau e^{-\Phi(\tau)/\hbar}, \tag{2.29}$$

where the imaginary time action factor reads

$$\Phi(\tau) = \frac{4}{\pi} \int d\omega \frac{J(\omega)}{\omega^2} [\coth(b/2) - \coth(b/2 - \omega\tau)] \tag{2.30}$$

with $b=\hbar\beta\omega$. For the spin-boson model the steps leading to Eqs. (2.29) and (2.30) involve no approximations since the steepest descent analysis and the cancellation of the prefactor P in Eq. (2.14) with P_0 in Eq. (2.23) are exact in this case.

Because of the spatial symmetry of the Hamiltonian [Eq. (2.27)], the stationary phase point $\tau_{\rm st}$ is simply the middle point of the thermal path, i.e., $\tau_{\rm st}=\hbar\beta/2$. Then, the application of the rate formula in Eq. (2.25), or equivalently in this case Eq. (2.1), leads to

$$k = \frac{\Delta^2}{\hbar} \left[\frac{2}{\hbar\pi^2} \int d\omega \frac{J(\omega)}{\sinh(\hbar\beta\omega/2)}\right]^{-1/2} \times \exp\left[-\beta \int_0^\infty d\omega \frac{J(\omega)}{\pi\omega} \frac{\tanh(\hbar\beta\omega/4)}{(\hbar\beta\omega/4)}\right], \tag{2.31}$$

which has been derived many times before and has been widely applied in theoretical and numerical studies of electron transfer processes (see, e.g., Ref. 3).

It should be noted that the imaginary time action $\Phi(\tau)$ can also be obtained by integrating out the harmonic coordinates and coupling the spin variables at two different time slices with the influence functional. However, the semiclassical evaluation of the imaginary time action outlined in the previous section and applied here holds for more general cases, regardless of the linearity of the nuclear system. It should also be noted that in Ref. 31 the *adiabatic* instanton solution was solved for the spin-boson model on the cusped potential constructed in a similar way as in Eq. (2.25) (see also Appendix B of Ref. 18). Though the imaginary time action thus obtained is correct, the prefactor in the adiabatic solution does not reflect the nonadiabaticity of the rate process and hence leads to a very different result from the semiclassical prediction based on Eq. (2.25).

III. PATH INTEGRAL EVALUATION OF THE GOLDEN RULE RATES

As was demonstrated in the previous section and earlier publications,[18,26] the imaginary part of the partition function directly gives rise to the rate constant if the dynamics can be properly described as an activated rate process. Simply using this fact, the semiclassical nonadiabatic rate expression in Eq. (2.25) can be derived in closed form based on Eq. (2.1), the expansion of the partition function in Eq. (2.11), and a sequence of semiclassical approximations. Interestingly, it becomes clear from that analysis that the imaginary time integration in Eq. (2.12) gives the leading imaginary part of the barrier partition function in the weak-coupling limit and, in turn, determines the nonadiabatic instanton trajectory. That is, it is the steepest descent evaluation of the integral over imaginary time τ in Eq. (2.12) which results in the imaginary part of the partition function. In the weak coupling limit, the imaginary time τ can thus be identified as the unstable quantum ''reactive mode'' variable just as the classical reaction coordinate and the quantum instanton are the reactive modes in the adiabatic high and low temperature limits, respectively.

Since the imaginary time τ in the Golden Rule limit of nonadiabatic electron transfer processes becomes the unstable reactive mode variable giving rise to the imaginary part of the barrier partition function, it then follows that Golden Rule rate constants can be computed directly from Eqs. (2.1) and (2.12) without semiclassical approximations for the nuclear mode path integrals. Equation (2.12), as it stands, represents a general form for the barrier partition function in the weak-coupling limit and thereby can serve as the starting point for a direct path integral evaluation of Golden Rule rate constants in general (i.e., nonquadratic) systems. To this end, a τ-dependent partition function is now defined as

$$Z(\tau) \equiv \mathrm{Tr}_c[e^{-(\hbar\beta-\tau)h_\mu/\hbar} e^{-h_\nu \tau/\hbar}], \tag{3.1}$$

which becomes Z_μ if $\tau=0$ and Z_ν if $\tau=\beta\hbar$. Also, a free energy $F(\tau)$ can be introduced as a function of the imaginary time τ according to

$$Z(\tau) \equiv \exp[-\beta F(\tau)]. \tag{3.2}$$

The free energy is then expanded around its stationary point τ_{st}, giving

$$F(\tau) = F(\tau_{\mathrm{st}}) + \frac{1}{2}\frac{d^2F(\tau_{\mathrm{st}})}{d\tau^2}(\tau-\tau_{\mathrm{st}})^2 + \cdots, \tag{3.3}$$

where the first derivative $dF(\tau_{\mathrm{st}})/d\tau$ vanishes because of the stationarity condition. Then, the steepest descent approximation for the imaginary time integration in $Z_{2,\mu\nu}$ in Eq. (2.12) gives

$$Z_{2,\mu\nu} \simeq i V_{\mu\nu}^2 \frac{\beta}{\hbar}\left(\frac{2\pi}{\beta|d^2F/d\tau^2|_{\mathrm{st}}}\right)^{1/2} \exp[-\beta F(\tau_{\mathrm{st}})]. \tag{3.4}$$

Here, the second derivative of the free energy is always negative, which will be more obvious once its explicit expression is derived in the next paragraph. Consequently, Eq. (3.4) can now be used in the universal rate expression in Eq. (2.1) to give

$$k \simeq \frac{V_{\mu\nu}^2}{\hbar^2 Z_\mu}\left(\frac{2\pi}{\beta|d^2F/d\tau^2|_{\mathrm{st}}}\right)^{1/2} \exp[-\beta F(\tau_{\mathrm{st}})], \tag{3.5}$$

which can be viewed as a general, closed-form Golden Rule rate formula. It should be noted that the application of Eq. (3.5) to the spin-boson Hamiltonian in Eq. (2.27) recovers the exact Golden Rule rate formula for that model in Eq. (2.31).

The rate expression in Eq. (3.5) is clearly applicable to realistic computer simulations. To make this more explicit, the partition function $Z(\tau)$ can be expressed in the framework of imaginary time Feynman path integrals as

$$Z(\tau) = \int \cdots \int \mathscr{D}\mathbf{q}(s) \exp\left\{-S_\mu[\mathbf{q}(s)]/\hbar + \int_0^\tau ds \Delta V[\mathbf{q}(s)]/\hbar\right\}, \tag{3.6}$$

where $\Delta V = h_\mu - h_\nu$ is the difference of the two diabatic energy surfaces and is assumed to be a function of coordinates only. Then, the first and second derivatives of the free energy in Eq. (3.3) can be explicitly evaluated, giving

$$\frac{dF}{d\tau} = -\frac{1}{\hbar\beta}\langle \Delta V(\mathbf{q})\rangle_\tau, \tag{3.7}$$

and

$$\frac{d^2F}{d\tau^2} = -\frac{1}{\hbar^2\beta}[\langle \Delta V(\mathbf{q})^2\rangle_\tau - \langle \Delta V(\mathbf{q})\rangle_\tau^2], \tag{3.8}$$

where $\langle f(\mathbf{q})\rangle_\tau$ denotes a τ-dependent thermal average or, explicitly,

$$\langle f(\mathbf{q})\rangle_\tau = \frac{\int\cdots\int \mathscr{D}\mathbf{q}(s) f[\mathbf{q}(\tau)] \exp\{-S_\mu[\mathbf{q}(s)]/\hbar + \int_0^\tau V[\mathbf{q}(s)]ds/\hbar\}}{\int\cdots\int \mathscr{D}\mathbf{q}(s) \exp\{-S_\mu[\mathbf{q}(s)]/\hbar + \int_0^\tau V[\mathbf{q}(s)]ds/\hbar\}}. \tag{3.9}$$

Since the second derivative is always negative as indicated in Eq. (3.8), the stationary point τ_{st} always corresponds to a maximum on the free energy curve $F(\tau)$, or equivalently, a minimum of the τ-dependent partition function.

With the explicit expressions in Eqs. (3.5)–(3.9) in hand, a numerical procedure to evaluate Golden Rule rate constants becomes possible. A path integral Monte Carlo simulation is employed to map out the τ-dependent free energy surface $F(\tau)$, the maximum is identified, the second derivative is computed, and the rate is thus determined in closed-form, including both the exponential and pre-exponential factors. The simplicity of this numerical prescription makes it applicable to a wide range of realistic processes (e.g., electron transfer) without assumptions for the functional form of the diabatic potentials or the classical vs quantum nature of the nuclear modes. In particular, the commonly employed practice of mapping the electron transfer system onto the spin-boson (harmonic bath) model is not necessary.

The complementary perspective of Wolynes[17] on this subject must certainly be noted. By writing the Golden Rule rate constant as $k \propto \int_{-\infty}^{\infty} dt' e^{i\phi(t')}$ he argued that the integral would be dominated by a saddle point in purely imaginary time, giving rise to an expression for the quantum Arrhenius-type exponential factor which is the same as the one derived above. This observation, he further suggested, could be exploited numerically with path integral Monte Carlo methods to calculate the quantum activation free energy in nonadiabatic systems. Wolynes' intuitive picture has now reappeared in the framework of the present paper and the unified rate expression in Eq. (2.1) evaluated in the weak-coupling limit. The present work goes one step further, however, in that a closed-form expression for the rate constant [Eq. (3.5)] has been derived. Furthermore, the weak coupling result is but a limiting case of the more general nonadiabatic instanton solution in Eq. (2.4).[18]

It should also be noted that the centroid density of the electronic state path variable $\sigma(\tau)$ was first shown to give the correct activation energy for electron transfer by Gehlen and Chandler[15] and was later investigated more extensively by Song and Stuchebrukhov[16] within the context of the spin-boson model. In their work, the concept of the electronic centroid variable was introduced as a natural extension of PI-QTST (Refs. 10–13) for electron transfer without full justification. By deducing the weak coupling expression from Eq. (2.1), it becomes apparent that the prefactor $1/\hbar\beta$ should be adopted regardless of temperature in the weak coupling limit, and that the use of electronic centroid variable is most appropriate for cases of small nonadiabatic coupling constants.

IV. A NUMERICAL EXAMPLE

In this section, numerical nonadiabatic instanton calculations are presented for the spin-boson model to illustrate the theory developed in the present and previous papers. It has already been shown that the theory is exact in the weak-coupling limit, so what remains is to explore the nonadiabatic instanton solution over the full range of coupling strengths.

To overcome the numerical difficulties associated with the infinite dimensionality implicit in the spin-boson model, a transformation can first be introduced from the spin-boson Hamiltonian to the two-level Brownian Hamiltonian. This derivation is found in Appendixes B and C. The transformation to the two-level Brownian oscillator Hamiltonian reduces the multidimensional spin-boson model to an essentially one-dimensional dissipative nonadiabatic instanton calculation, thus reducing the computational effort dramatically. However, it should be noted that there is no fundamental problem associated with the nonadiabatic instanton solution in multidimensional space.[18] The Brownian oscillator transformation is simply designed to facilitate numerical efficiency by making use of the Gaussian nature of the spin-boson bath modes.

The essential details of the numerical procedure for the nonadiabatic instanton method and its convergence properties have been discussed in the previous paper.[18] The algorithm consists of the following steps:

(1) The transformation based on relations Eqs. (B6)–(B8) is carried out for a given bath spectral density $J(\omega)$.
(2) An approximate instanton trajectory is used as an input. An educated guess is the instanton solution for the adiabatic surface in the strong coupling region or the instanton solution for the cusped barrier[31] in the weak coupling region.
(3) The Bloch equation in Eq. (2.7) is solved numerically for the given nuclear instanton path. At each time step $\epsilon = \hbar\beta/P$, the electronic (diabatic) states at that imaginary time is propagated for one time step. The initial state $|\mu\rangle$ and the final state $|\nu\rangle$ are taken to be the right and the left diabatic surfaces, respectively.
(4) The equation of motion in Eq. (2.9) is iterated to a converged instanton trajectory for the given electronic wave function. The rate of convergence depends on the discretization number and the initial input. Generally, it has been found that 10^2–10^3 iterations will yield convergence.
(5) Steps (3) and (4) are repeated as a loop until self-consistency is reached.
(6) Once the instanton solution is found, the fluctuation matrix in Eq. (A1) is computed and diagonalized. A vanishingly small eigenvalue assures a satisfactory stationarity

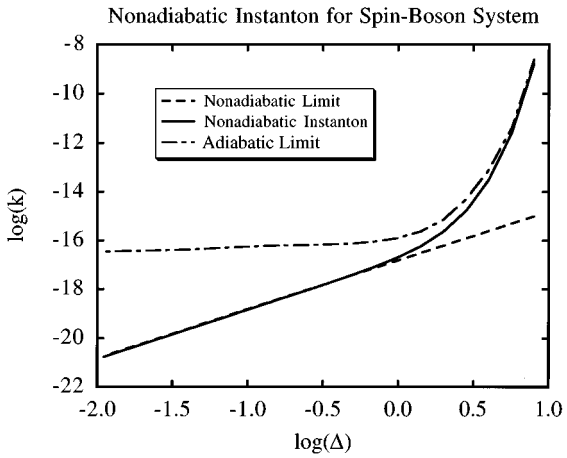

FIG. 1. A logarithmic plot of the rate constant k vs the nonadiabatic coupling constant Δ for the spin-boson Hamiltonian given in Eq. (2.27). For comparison, the Golden Rule prediction from Eq. (2.31) is plotted as a dashed line, and the adiabatic instanton rate constant is plotted as a dot–dashed line.

condition [Eq. (2.9)] and a negative eigenvalue indicates the metastability of the particular solution (i.e., the ''barrier'' partition function). The prefactor D in Eq. (2.10) can thus be calculated, and the action S and work W computed, hence yielding the instanton rate constant in Eq. (2.10).

The spin-boson Hamiltonian is defined by Eq. (2.27), and the spectral density in the present study was taken to be Ohmic with an exponential cutoff ω_c, giving

$$J(\omega)=\frac{\pi\hbar K}{2}\,\omega e^{-\omega/\omega_c}, \tag{4.1}$$

where K is the Kondo constant. The parameters were chosen in the present case to be $\hbar=1.0$, $\beta=3.0$, $\omega_c=0.707$, $K=0.25$. The Ohmic spectral density can be substituted into Eqs. (B6)–(B8) to yield $\omega_0^2=2\omega_c^2$, $\lambda^2=2\hbar K\omega_c^3$, and

$$\Omega\,\hat{\eta}(\Omega)=\frac{\int d\omega\,\omega^2 e^{-\omega/\omega_c}}{\int d\omega\,\omega^2 e^{-\omega/\omega_c}/(\omega^2+\Omega^2)}-2\omega_c^2-\Omega^2 \tag{4.2}$$

which was evaluated numerically. A discretization parameter of $P=200$ was used in the calculations, and the convergence of the wavefunction and the nonadiabatic instanton trajectory was always achieved in less than 100 iterations.

In Fig. 1, the spin-boson rate constant is plotted as a function of the coupling constant Δ on a logarithmic scale. In the strong coupling region, the nonadiabatic instanton rate approaches the adiabatic rate (dot–dashed line) because the coupling is strong enough that the quantum transition takes place on the lower adiabatic surface. The rate in this region has an exponential dependence on the coupling constant, namely, $k\propto\exp(\beta\Delta)$. In the weak coupling region, the nonadiabatic rate obviously becomes proportional to Δ^2, as predicted by the Golden Rule (dashed line). The rate in this region can be described by the linearized semiclassical rate expression Eq. (2.31). Overall, the nonadiabatic instanton solution bridges these two limits and is thus capable of treating systems described by an arbitrary nonadiabatic coupling strength. It should also be noted that numerically exact methods have been developed for studying the quantum dynamics of the spin-boson model for most values of the relevant parameters.[4–9] The nonadiabatic instanton approach, however, does not rely on a harmonic bath assumption which is key to the quantum dynamical methods.

V. CONCLUDING REMARKS

In the present paper, the weak-coupling nonadiabatic limit of a newly proposed[26] unified expression for the quantum activated rate constant has been explored. The latter expression is based on the imaginary part of the barrier partition function which, in turn, arises from a steepest descent integration over a generalized reactive mode in quantum systems. This mode is seen to change its character depending on the temperature and the system at hand. Indeed, in the nonadiabatic limit the saddle point mode appears in an imaginary time integration. This perspective leads to a semiclassical Golden Rule rate constant expression which is general and independent of any approximations for the character of the nuclear modes. Even more importantly, the steepest descent treatment of the nuclear modes can be avoided altogether, thus retaining only the steepest descent evaluation of the imaginary time integral. This approach gives rise to a closed-form expression for the Golden Rule rate constant which is also general and can be readily evaluated for realistic systems using imaginary time path integrals. By also using the imaginary part of the barrier partition function concept, the nonadiabatic instanton approach[18] was shown to go beyond the weak coupling expression through a study of the multidimensional spin-boson problem. The application of these ideas to realistic condensed phase systems is a priority for future research.

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APPENDIX A: EVALUATION OF THE NONADIABATIC INSTANTON PREFACTOR

In this appendix, the prefactor D in Eq. (2.10) is explicitly expressed as a normalized determinant of the second-order functional derivative matrix along the instanton trajectory.[29,35] This procedure is numerically best implemented for a discretized path, i.e.,

$$\frac{\delta^2 S}{\delta\mathbf{q}_i\delta\mathbf{q}_j}=\frac{\mathbf{m}}{\epsilon^2}\,(2\delta_{i,j}-\delta_{i,j+1}-\delta_{i,j-1})+\delta_{i,j}\left\langle\frac{\partial^2 H_d[\mathbf{q}(\tau)]}{\partial\mathbf{q}_i\partial\mathbf{q}_i}\right\rangle_d+\epsilon\mathbf{C}_{d,ij}, \tag{A1}$$

where the indices i and j denote two different discretized imaginary time slices, $\mathbf{q}_i$ and $\mathbf{q}_j$ are the corresponding nuclear coordinates along the instanton path, and $\epsilon=\hbar\beta/P$, with P being the number of discretizations. Here, the quantum fluctuation correlation matrix is given by

$$\mathbf{C}_{d,ij}=\left\langle \frac{\partial H_d[\mathbf{q}(\tau)]}{\partial \mathbf{q}_i}\, u(\tau_i,\tau_j)\, \frac{\partial H_d[\mathbf{q}(\tau)]}{\partial \mathbf{q}_j}\right\rangle_d - \left\langle \frac{\partial H_d[\mathbf{q}(\tau)]}{\partial \mathbf{q}_i}\right\rangle_d \left\langle \frac{\partial H_d[\mathbf{q}(\tau)]}{\partial \mathbf{q}_j}\right\rangle_d . \tag{A2}$$

The quantum average over the diabatic basis for $\tau\leqslant\hbar\beta/2$ is introduced here as

$$\langle f(\tau)\rangle_d=\frac{\langle \nu|u(\hbar\beta/2,\tau)f(\tau)u(\tau,0)|\mu\rangle}{\langle \nu|u(\hbar\beta/2,\tau)u(\tau,0)|\mu\rangle}, \tag{A3}$$

or, if $\tau\geqslant\hbar\beta/2$, then

$$\langle f(\tau)\rangle_d=\frac{\langle \nu|u(\hbar\beta,\tau)f(\tau)u(\tau,\hbar\beta/2)|\mu\rangle}{\langle \nu|u(\hbar\beta,\tau)u(\tau,\hbar\beta/2)|\mu\rangle}. \tag{A4}$$

In Eqs. (A3) and (A4), the denominators are independent of the variable τ. The quantum averages are carried out by assuming a particular nuclear path $\mathbf{q}(\tau)$ and are thus functionals of the nuclear paths.

The dimensionality implicit in the above equations is such that $\delta^2 S/\delta\mathbf{q}_i\delta\mathbf{q}_j$ is a matrix of dimension $N\times P$, where N is the number of physical degrees of freedom of the system. When diagonalizing this matrix, there will be a negative eigenvalue giving rise to the imaginary part of the partition function, and a zero eigenvalue corresponding to the translationally invariant mode.[21] The existence of a zero eigenvalue is an indication of a true instanton solution. The removal of the zero eigenvalue requires the proper normalization.

For a free particle, the matrix describing the quantum path fluctuations is given by

$$\frac{\delta^2 S}{\delta\mathbf{q}_i\delta\mathbf{q}_j}=\frac{\mathbf{m}}{\epsilon^2}\,(2\delta_{i,j}-\delta_{i,j+1}-\delta_{i,j-1}). \tag{A5}$$

A normal-mode transformation leads to the eigensolutions of the matrix in Eq. (A5), i.e.,[36]

$$\lambda_l=2(m/\epsilon^2)[1-\cos(2\pi l/P)], \tag{A6}$$

where the index l ranges from $-(P-1)/2$ to $(P-1)/2$ for odd values of P, and it ranges from $-(P-2)/2$ to $P/2$ for even values of P. The case of $l=0$ gives a zero eigenvalue which corresponds to the translational invariance in the free particle space. Removal of this zero eigenvalue leads to the condition[36]

$$\prod_{l\neq 0}\lambda_l=(m/\epsilon^2)^{P-1}P^2, \tag{A7}$$

which recovers the correct free particle density.

Therefore, the instanton matrix in Eq. (A1) is normalized to the free particle prefactor, giving

$$D=\lim_{P\to\infty}\frac{1}{P^2}\,\det{}'\left(\epsilon^2\mathbf{m}^{-1}\,\frac{\delta^2 S}{\delta\mathbf{q}_i\delta\mathbf{q}_j}\right), \tag{A8}$$

where ''det′'' stands for the value of the determinant with the zero eigenvalue removed. The above equation is used in the prefactor in Eq. (2.10).

APPENDIX B: THE TWO-LEVEL BROWNIAN OSCILLATOR MODEL

The two-level Brownian oscillator model has been popularized as an analytically solvable model to describe electronic absorption line shapes and various nonlinear optical processes in condensed phases.[37,38] In this model, the system and the bath are explicitly separated as $H=H_s+H_b$, where the system Hamiltonian is given by

$$H_s=\Delta\sigma_x+\frac{1}{2}\,m\dot{q}^2+\frac{1}{2}\,m\omega_0^2\left(q-\frac{\lambda}{m\omega_0^2}\,\sigma_z\right)^2 \tag{B1}$$

and the bath Hamiltonian is given by

$$H_b=\sum_{j=1}^{N-1}\left[\frac{1}{2}\,\overline{m}_j\dot{x}_j^2+\frac{1}{2}\,\overline{m}_j\overline{\omega}_j^2\left(x_j+\frac{\overline{c}_n}{\overline{m}_j\overline{\omega}_j^2}\,q\right)^2\right]. \tag{B2}$$

Here, q is the Brownian oscillator coordinate, with its bare frequency ω_0 and bare coupling constant λ, and the set of coordinates $\{x_j\}$ constitutes the bath modes, with frequencies $\{\overline{\omega}_j\}$, masses $\{\overline{m}_i\}$, and coupling constants $\{\overline{c}_l\}$. To distinguish from the similar parameters in the spin-boson Hamiltonian in Eq. (2.27), the bath parameters here are denoted with an overbar.

In the context of imaginary time path integrals, the bath Hamiltonian can be explicitly integrated out, resulting in the system path integral[28]

$$S_s/\hbar=\frac{1}{\hbar}\int_0^{\hbar\beta}d\tau H_s[q(\tau)]+\beta m\sum_{n>0}\Omega_n\hat{\eta}(\Omega_n)|\tilde{q}_n|^2, \tag{B3}$$

where the last term is the influence functional. Here, $\tilde{q}_n$ is the Fourier transform of the path $q(\tau)$, defined as

$$\tilde{q}_n=\frac{1}{\hbar\beta}\int_0^{\hbar\beta}d\tau q(\tau)e^{-i\Omega_n\tau}, \tag{B4}$$

with $\Omega_n=2\pi n/\hbar\beta$, and $\hat{\eta}(\Omega_n)$ is the Laplace transformation of the mass-scaled friction kernel, defined by

$$\hat{\eta}(\Omega_n)=\sum_{j=1}^{N}\frac{\overline{c}_j^2}{m\overline{m}_J\overline{\omega}_j^2}\,\frac{\Omega_n}{\Omega_n^2+\overline{\omega}_j^2}. \tag{B5}$$

Since the two models are equivalent, there exists a unique transformation between the spin-boson and the Brownian oscillator Hamiltonians. The derivation of this transformation is presented in Appendix C. With the definition of the spectral density in Eq. (2.28), we can rewrite the relations given by Eqs. (C2), (C8), and (C10) as

$$\omega_0^2=\frac{\int d\omega\omega J(\omega)}{\int d\omega J(\omega)/\omega}, \tag{B6}$$

$$\lambda^2=\frac{2m}{\pi}\int d\omega\omega J(\omega), \tag{B7}$$

and

$$\Omega_n \hat{\eta}(\Omega_n) = \frac{\int d\omega \omega J(\omega)}{\int d\omega \omega J(\omega)/(\omega^2+\Omega_n^2)} - \omega_0^2 - \Omega_n^2. \tag{B8}$$

Thereby, all the parameters of the Brownian oscillator can be determined from the spectral density of the spin-boson model $J(\omega)$.

An important consequence of this transformation can be easily noted. Without the inclusion of the influence functional, the system Hamiltonian in Eq. (B1) gives an activation energy

$$E_a = \frac{\lambda^2}{2m\omega_0^2} = \frac{1}{\pi} \int d\omega \, \frac{J(\omega)}{\omega}, \tag{B9}$$

which recovers exactly the classical activation energy of the spin-boson Hamiltonian. When substituting into the single-mode rate expression, one obtains

$$k \simeq \frac{\Delta^2}{\hbar} \sqrt{\frac{\pi \sinh(b/2)}{2E_a \hbar \omega_0}} \exp\left[-\beta E_a \frac{\tanh(b/4)}{(b/4)} \right], \tag{B10}$$

with $b = \hbar\beta\omega_0$. This expression approximates the Golden Rule rate constant and recovers the exact classical limit. In view of Eq. (B10), it might be reasonable to use ω_0 as a characteristic frequency of the nuclear system and to include the friction kernel only when both dissipation *and* quantum effects are significant. It should also be noted that the friction kernel Eq. (B8) is determined by the functional form of the spectral density but is independent of its strength.

APPENDIX C: TRANSFORMATION BETWEEN THE SPIN-BOSON AND BROWNIAN OSCILLATOR HAMILTONIANS

In this appendix, we will derive the transformation from the spin-boson Hamiltonian to the two-level Brownian oscillator Hamiltonian (see also Refs. 31 and 39). First, we rewrite the relevant potential terms of the spin-boson Hamiltonian given in Eq. (2.27) as

$$\sum_{i=1}^{N} \sigma_z c_i q_i = \sigma_z \lambda q, \tag{C1}$$

where $q = \Sigma_{i=1}^N g_i q_i$, $g_i = c_i/\lambda$, and

$$\lambda^2 = \sum_{i=1}^{N} c_i^2. \tag{C2}$$

For simplicity, a unit mass is assumed in this appendix. Obviously, the new variable q is the collective coordinate which couples directly to the spin variable. Our goal is to find an effective potential for the term $\Sigma_{i=1}^N \omega_i^2 q_i^2/2$ such that it consists of a set of harmonic oscillator coordinates $\{x_j\}$ linearly coupled to q, that is

$$\sum_{i=1}^{N} \frac{1}{2} \omega_i^2 q_i^2 = \frac{1}{2} \omega_0^2 q^2 + \sum_{j=1}^{N-1} \frac{1}{2} \overline{\omega_j^2} \left(x_j + \frac{\overline{c_j}}{\overline{\omega_j^2}} q \right)^2 \equiv V_{\text{eff}}. \tag{C3}$$

In another words, we want to find a linear transformation from the coordinate set $\{q_i\}$ to the collective coordinate q_0 and its orthogonal set $\{x_j\}$.

A general coordinate transformation can be carried out by making use of the identity

$$\prod_{i=1}^{N} \int dq_i \delta\left(q - \sum_{i=1}^{N} g_i q_i \right) \exp\left[-\beta \sum_{i=1}^{N} \frac{1}{2} (\omega_i^2 q_i^2 + \Omega^2 q_i^2) \right]$$
$$= \prod_{j=1}^{N-1} \int dx_j \exp\left[-\beta \left(V_{\text{eff}} + \frac{1}{2} \Omega^2 q^2 + \sum_{j=1}^{N-1} \frac{1}{2} \Omega^2 x_j^2 \right) \right], \tag{C4}$$

where Ω is a real variable to be specified and V_{eff} is the effective potential given in the right-hand side of Eq. (C3). Completing the Gaussian integration, we have[40–42]

$$W(\Omega) = \omega_0^2 + \Omega^2 - \sum_{j=1}^{N-1} \frac{\overline{c_j^2}}{\overline{\omega_j^2} + \Omega^2} + \sum_{j=1}^{N-1} \frac{\overline{c_j^2}}{\overline{\omega_j^2}} \tag{C5}$$

and

$$\prod_{i=1}^{N} (\omega_i^2 + \Omega^2) = W(\Omega) \prod_{j=1}^{N-1} (\overline{\omega_j^2} + \Omega^2), \tag{C6}$$

where W is an auxiliary function defined as

$$\frac{1}{W(\Omega)} = \sum_{i=1}^{N} \frac{g_i^2}{\omega_i^2 + \Omega^2}. \tag{C7}$$

The identity Eq. (C6) has been derived before and has been widely used in the Hamiltonian formulation of transition state theory.[43]

With these identities in hand, the frequency of the collective mode q is found to be

$$\omega_0^2 = W(0) = \left(\sum_{i=1}^{N} \frac{g_i^2}{\omega_i^2} \right)^{-1}, \tag{C8}$$

which can be interpreted as the average collective frequency of the nuclear system.

Now with the expression for ω_0 and λ explicitly given by Eqs. (C2) and (C8), the system Hamiltonian (B1) is well-defined, but the bath Hamiltonian Eq. (B2) is yet to be determined. However, the full parameterization is not necessary because the effect of the bath is to introduce dissipation into the system. This effect is fully captured in the path integral framework by the friction kernel, given as

$$\Omega_n \hat{\eta}(\Omega_n) = \sum_{j=1}^{N-1} \left[\frac{\overline{c_j^2}}{\overline{\omega_j^2}} - \frac{\overline{c_j^2}}{(\overline{\omega_j^2} + \Omega_n^2)} \right]. \tag{C9}$$

An application of the identity in Eq. (C5) leads to

$$\Omega_n \hat{\eta}(\Omega_n) = W(\Omega_n) - W(0) - \Omega_n^2$$
$$= \frac{1}{\Sigma_{i=1}^N g_i^2/(\omega_i^2 + \Omega_n^2)} - \frac{1}{\Sigma_{i=1}^N g_i^2/\omega_i^2} - \Omega_n^2, \tag{C10}$$

which defines the dissipation on the system Hamiltonian. The three relations Eqs. (C2), (C8), and (C10) can be recast in a continuous form as given in Eqs. (B6)–(B8).

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