A unified framework for quantum activated rate processes. I. General theory

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It is shown that several existing quantum reaction rate theories can be unified around a single mathematical framework. These theories include the high temperature parabolic barrier approximation, the instanton approach, and the path integral quantum transition state theory. In particular, it is shown that the quantum reactive flux can be approximated as a product of a simple frequency factor times the imaginary part of the barrier partition function. The latter term arises from the steepest descent solution to the partition function in the barrier region, while the prefactor can be interpreted as the frequency of the stationary barrier trajectory. Importantly, the analysis introduces the imaginary time Feynman path centroid variable into the expression for the quantum activated rate constant in an *a priori* way. The present theoretical framework also allows for an analytical treatment of the quantum activated rate problem in the vicinity of the crossover temperature, and for a generalization of the saddle point analysis in an extended-dimensional quantum mechanical space of the Fourier path modes. © *1996 American Institute of Physics.* [S0021-9606(96)51640-5]

I. INTRODUCTION

From both the analytical and numerical point of view, quantum reaction rate theory has been one of the most active and challenging areas of theoretical chemistry during the past sixty years (for a review, see, e.g., Ref. 1). At high temperatures, chemical reactions are dominated by thermally activated barrier crossings described by classical transition state theory (TST) and its high temperature quantum mechanical corrections.[2] At low temperatures, tunneling effects can significantly enhance the reaction rate, and the WKB or instanton theory gives a good estimate of quantum rate constant.[3–7] Thus the quantum reaction rate in these two temperature regimes is dominated by very different mechanisms, so it is typically calculated using different theories. The goal of this paper is to formally unify the theories in these two regimes within a single mathematical framework.

At high temperatures, modifications of classical TST theory are often introduced to account for quantum effects by virtue of the parabolic barrier approximation and linear response theory. For example, Wolynes[2] derived the exact quantum rate for the parabolic barrier coupled to a multidimensional Gaussian bath by a direct calculation of the reactive flux correlation correlation function in the path integral formulation. The resulting quantum rate formula consists of the classical Kramers–Grote–Hynes prefactor,[8,9] a quantum harmonic correction, and the classical Arrhenius exponential factor. For a one-dimensional parabolic barrier, the analogous expression can be obtained by evaluating the classical TST rate expression with the Boltzmann distribution function replaced with the Wigner distribution function at the transition state.[3] This result can be interpreted as the quantum transition state theory (QTST) rate constant for parabolic barriers. Along these lines, Pollak showed[10] that a normal mode analysis of the Hamiltonian for a parabolic barrier coupled to a Gaussian bath, in conjunction with the parabolic quantum transition state theory (QTST), leads to the exact quantum mechanical reaction rate expression as derived by Wolynes. Accordingly, for a real anharmonic barrier coupled to a real condensed phase ''bath,'' a parabolic fit according to the curvature at the barrier, along with the application of the linear response approximation to describe the dissipation from the bath, is often employed to yield the ''high temperature'' approximation to the quantum rate constant. The difficulty associated with this approximation is its divergence below a certain temperature, called the ''crossover'' temperature. This divergence is also often used as the criterion for the temperature at which quantum tunneling effects become dominant. In these instances (and perhaps in others), a simple harmonic QTST is inadequate for describing the quantum activated rate process.

On the other hand, the low temperatures deep tunneling regime can be described by the periodic orbit,[3] or instanton,[5] approach which results from a sequence of stationary-phase approximations to a semiclassical rate expression. In this theory, the quantum reactive flux at low temperatures is related to the so-called ''bounce'' trajectory on the inverted potential energy surface. Various versions and derivations of the instanton solution can be found in literature.[3–6,11–17] By extending the instanton analysis to the dissipative quantum regime, Caldeira and Leggett[6,14] demonstrated an exponential decrease of the rate with increasing friction strength at zero temperature. Grabert, Weiss, Hänggi, and others[15–17] generalized the theory for dissipative quantum tunneling to finite temperatures and have shown that the rate exhibits an exponential power law enhancement with temperature over the zero temperature limit. Recently, the instanton analysis has been extended by the present authors[18] to self-consistently include nonadiabatic transitions to other poten-

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tial surfaces in order to properly describe electron transfer and similar multistate processes over the full range of coupling strengths.

Over time, a clear theoretical challenge has been to smoothly join the high temperature parabolic barrier approximation to the low temperature instanton solution in the crossover region without *ad hoc* connection formulae. Along these lines, a general theory of metastability was constructed by Affleck[12] for temperatures below and above the crossover within a narrow transition region. Grabert and Weiss[19] also derived a dissipative crossover formula by means of a functional integral analysis, while, through the use of Miller's semiclassical transition state theory,[3,20] Hänggi and Hontscha[21] obtained a correction to the parabolic TST rate valid below crossover. The semiclassical TST approach has also recently been revisited in a compelling way.[22,23] All of these rate expressions give the same result, or nearly the same result, at the crossover temperature, but they begin to deviate from each other away from crossover. A more unified approach is therefore desirable, particularly one which is suited for numerical implementation in complex many-dimensional systems.

An important step in the direction of a unified theory of quantum activated dynamics is path integral quantum transition state theory (PI-QTST).[24–27] In this theory, one introduces the imaginary time Feynman path centroid constraint into a formally exact quantum rate expression and then factorizes that expression into the Feynman centroid density and a velocity factor. After invoking an approximation for the latter term, the quantum centroid density occupies a role in the PI-QTST formula directly analogous to the classical Boltzmann density in the classical TST expression.[24–26] The PI-QTST expression recovers the exact parabolic QTST result at high temperatures while remaining accurate and nondivergent at and below the crossover temperature. At very low temperatures, however, the PI-QTST formula gives a slightly different and somewhat less accurate result than the instanton expression.[24,26] Nevertheless, the intuitive concept of the path centroid variable leads to a QTST which behaves surprisingly well even at low temperatures and, most importantly, can be readily applied in simulations of very complex systems (see, e.g., Refs. 28–30) A recent numerical study[31] of quantum dissipative barrier crossing problems has found very good agreement between PI-QTST rates and exact quantum time correlation function results[32] over a wide range of parameters. The PI-QTST approach has also been successfully applied to electron transfer processes for which the centroid constraint is imposed on the discrete electronic state variable.[33–37] Moreover, improved variational implementations[25,38–41] of PI-QTST have been developed to treat general multidimensional systems, though a rigorous bound on the PI-QTST rate constant does not exist as in the classical theory.

A recent extensive theoretical study[42–46] has revealed that path centroid quantities are the quantum mechanical analog to many classical quantities, both statistically and dynamically (for a review, see Ref. 47). Yet, the theoretical reason for the central role of the the path centroid variable in quantum activated rate theory is not immediately obvious. Indeed, all previous derivations of the PI-QTST formula[24–26,38] have introduced the centroid constraint without much justification except the prior knowledge that the PI-QTST formula recovers the well-known results in different limits, and it bridges these limits, as mentioned previously. On the other hand, it has been shown[24,48] that the centroid variable naturally arises if one wishes to evaluate the instanton rate constant. In the present paper, we significantly expand on this point of view by also considering the high temperature limit. This analysis provides an *a priori* justification for the introduction of the centroid variable in quantum activated dynamics, while also identifying a mathematical framework which unifies previous quantum activated rate expressions on a common footing.

The present paper is organized as follows: In Sec. II, the unified mathematical framework for the quantum reactive flux is presented. The relationship of this approach to PI-QTST is next developed in Sec. III which explains the central role of the path centroid variable in quantum activated dynamics. Some analysis of the theory is then given in Sec. IV along with some speculations for future research. Finally, some numerical studies are presented in Sec. V and concluding remarks are given in Sec. VI.

II. MATHEMATICAL FRAMEWORK

In this section, we seek to develop a unified mathematical framework for quantum activated dynamics. To be specific, we will identify a single expression from which the primary, but more specialized, descriptions of quantum activated dynamics in different temperature and analytical limits can be derived. In order to accomplish this goal, the parabolic barrier model is analyzed in detail, while the low temperature instanton theory is also visited to provide a key supporting perspective. In the end, a ''universal'' expression will be suggested, but one should always bear in mind that truly exact results for *general* systems are rare, if not impossible, and the present case is no exception. Accordingly, for general problems the following theoretical analysis is not exact, but in the end it does appear to be a reasonable candidate for a unified mathematical perspective in the field of quantum activated dynamics.

It is well-known that real time quantum correlation functions can be related to their imaginary (Euclidean) time counterparts through an analytical continuation, $\tau\rightarrow\tau+it$, also known as the Wick rotation.[49] Since barrier crossing is essentially a real time dynamical process, any quantum rate theory which seeks to determine the rate from the equilibrium distribution relies at some (perhaps unknown) level on an analytic continuation. One such prescription is the reactive flux correlation function, given in terms of the present discussion by[50]

$$F=\lim_{t\rightarrow\infty} F(\tau+it), \tag{2.1}$$

where the correlation function $F(\tau+it)$ is defined as

$$F(\tau+it)=\mathrm{Im}\,\frac{\partial}{\partial\tau}\,\mathrm{Tr}[e^{-\beta H}h_P(\tau+it)h_P(0)]. \tag{2.2}$$

Here, $h_P(\tau)$ is the imaginary time reactant state population operator $h_P(\tau)=\theta[q(\tau)-q_b]$, where θ is the step-function and q_b is the position of the dividing surface along the reaction coordinate q, usually taken to be at or near the top of the barrier.

At this point, the reactive flux can be formally factorized as

$$F=\mathrm{Im}\lim_{t\to\infty}\frac{\partial}{\partial\tau}\,\langle h_P(\tau+it)h_P(0)\rangle_b Z_b\equiv\mathrm{Im}(fZ_b), \tag{2.3}$$

where $\langle\cdots\rangle_b$ stands for an thermal average in the barrier region, and Z_b is the partition function in the barrier region which will be discussed later. By decomposing the prefactor f and barrier partition function Z_b into their real and imaginary parts, the reactive flux can be rewritten as

$$F=(\mathrm{Re}\,f\,)(\mathrm{Im}\,Z_b)+(\mathrm{Im}\,f\,)(\mathrm{Re}\,Z_b). \tag{2.4}$$

The prefactor f in the above equation cannot be evaluated exactly for general systems. However, in the thermally activated regime (i.e., above crossover, as defined by $\hbar\beta\omega_b<2\pi$, where ω_b is the magnitude of the unstable barrier frequency), the barrier region can be approximated by a parabolic potential

$$V(q)\approx V_0-\tfrac{1}{2}m\omega_b^2(q-q_b)^2 \tag{2.5}$$

with $V_0=V(q_b)$, $V^{(1)}(q_b)=0$, and $V^{(2)}(q_b)=-m\omega_b^2$. The prefactor in Eq. (2.3) can be evaluated exactly as outlined in Appendix A to give

$$f=\lim_{t\to\infty}\frac{\partial}{\partial\tau}\,\langle h_P(\tau+it)h_P(0)\rangle_b=\frac{\omega_b}{2\pi}. \tag{2.6}$$

Interestingly, it is found in the parabolic barrier limit that the prefactor f *has no imaginary part*. Below the crossover temperature, it may not be possible to rigorously prove this, but the instanton theory (as described later), as well as physical considerations for the $t\to\infty$ limit of the imaginary part of the time correlation function, suggest it is so. If $\mathrm{Im}\,f=0$, the above considerations suggest that for quantum activated rate processes the reactive flux is related to the imaginary part of the barrier partition function, appropriately defined for the temperature of the system, giving

$$F\propto\mathrm{Im}\,Z_b. \tag{2.7}$$

In the case of the parabolic barrier (i.e., above crossover), the proportionality constant is given by $\omega_b/2\pi$. As will be shown later, below crossover this constant is $1/\hbar\beta$.

These arguments strongly suggest that the quantum reactive flux depends on the imaginary part of the barrier partition function. But what exactly is this quantity in the most general sense for a given temperature? The barrier partition function Z_b can be formally given in terms of a Feynman path integral[51–53] by the expression

$$Z_b=\int\cdots\int_b\mathscr{D}q(\tau)\exp\{-S[q(\tau)]/\hbar\}, \tag{2.8}$$

where a single dimension is considered here for notational simplicity and $S[q(\tau)]$ is the usual Euclidean time action functional, given by

$$S[q(\tau)]=\int_0^{\hbar\beta}d\tau\{\tfrac{1}{2}m\dot{q}(\tau)^2+V[q(\tau)]\}. \tag{2.9}$$

Note that the subscript ''b'' on the path integration in Eq. (2.8) implies a special treatment for the barrier region which we now elaborate. For the case of a parabolic barrier, the barrier partition function, Z_{pb}, is given by

$$Z_{\mathrm{pb}}=\left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2}\frac{(\hbar\beta\omega_b/2)}{\sin(\hbar\beta\omega_b/2)}\exp(-\beta V_0)\times\int dq\,\exp[\beta m\omega_b^2(q-q_b)^2/2], \tag{2.10}$$

The above integral is divergent for an integration along the real axis, but the coordinate rotation $q\to iq$ yields a well-defined value for the imaginary part of Z_{pb}.[11] We then obtain from Eqs. (2.7) and (2.10) the well-known result for the parabolic barrier reactive flux[4]

$$F_{\mathrm{pb}}=\frac{k_BT}{h}\frac{(\hbar\beta\omega_b/2)}{\sin(\hbar\beta\omega_b/2)}\exp(-\beta V_0). \tag{2.11}$$

It is of particular interest to relate the above derivation and discussion to the path centroid-based PI-QTST, which will be done in later sections.

Below the crossover temperature, the analysis of the barrier partition function becomes more difficult, or at least different, because the nonlinearity of the potential in the barrier region becomes important and there is extensive quantum tunneling. In the low temperature regime, the instanton theory[3,5] proves to be most useful for this analysis. Consider a general many-dimensional system described by a single barrier region and asymptotic reactant and product states. The barrier partition function for a multidimensional system is described by

$$Z_b=\int\cdots\int_b\mathscr{D}\mathbf{q}(\tau)\exp\{-S[\mathbf{q}(\tau)]/\hbar\}. \tag{2.12}$$

Application of the steepest descent approximation to Eq. (2.12) leads to the Euler–Lagrangian equations of motion for the coordinates on the inverted potential, i.e.,[3,5]

$$\mathbf{m}\cdot\frac{d^2\mathbf{q}(\tau)}{d\tau^2}=\frac{\partial V[\mathbf{q}(\tau)]}{\partial q(\tau)}, \tag{2.13}$$

where $\mathbf{m}$ is the diagonal mass matrix and the periodic condition on the instanton or ''bounce'' trajectory is $\mathbf{q}(\hbar\beta)=\mathbf{q}(0)$. For a regular barrier, satisfying $V^{(2)}(q_b)=-m\omega_b^2<0$ and $V^{(4)}(q_b)\geqslant 0$ along the barrier coordinate, Eq. (2.13) has a trivial (single point) solution at the transition state for $\hbar\beta\omega_b<2\pi$ and a bounce solution for $\hbar\beta\omega_b>2\pi$. This criterion then defines the crossover temperature ($T_0=1/k_B\beta_0$), i.e.,[54]

$$\hbar\beta_0\omega_b=2\pi \tag{2.14}$$

at which the bounce trajectory coalesces to the transition state. For a divergent barrier, satisfying $V^{(2)}(q_b)=m\omega_b^2<0$ and $V^{(4)}(q_b)<0$, there is always a bounce solution. Unless specified otherwise, the present discussion will be for a regular barrier which is always bounded from below.

To proceed, the action is expanded around the bounce trajectory, giving

$$S[q(\tau)]=S_{\text{inst}}+\int d\tau\int d\tau'\,\frac{\delta^2 S}{\delta\tilde{q}(\tau)\,\delta\tilde{q}(\tau')}\,\tilde{q}(\tau)\tilde{q}(\tau'), \tag{2.15}$$

where $\tilde{q}(\tau)=q(\tau)-q_{\text{inst}}(\tau)$ represents the quantum fluctuation away from the instanton path. Then, the steepest descent approximation formally leads to

$$Z_b=\mathcal{N}\,\frac{1}{\sqrt{\det[\delta^2 S/\delta\tilde{q}(\tau)\,\delta\tilde{q}(\tau')]}}\,\exp(-S_{\text{inst}}/\hbar), \tag{2.16}$$

where $\mathcal{N}$ is a normalization factor to be specified and the determinant is understood as the product of eigenvalues of the linear operator in functional space. Though similar to the Van Vleck prefactor, the prefactor in Eq. (2.16) is intrinsically divergent because the spectrum of the second order functional derivative consists of an isolated negative eigenvalue and a zero eigenvalue.[5] The zero eigenvalue can be removed by explicitly integrating out the corresponding eigenmode, whereas the negative mode is integrated by an analytical continuation leading to the purely imaginary barrier partition function $Z_b=iZ_{\text{inst}}$. Thus the simple coordinate rotation $q\rightarrow iq$ performed on the above crossover reactive mode has now been extended to the quantum fluctuation mode corresponding to the negative eigenvalue (and it will also be related to the path centroid mode in the next section[48]).

In order to complete the instanton analysis, a second order functional derivative must be evaluated along the instanton trajectory. This procedure is numerically best implemented for a discretized path, i.e.,

$$\frac{\delta^2 S}{\delta\mathbf{q}_i\,\delta\mathbf{q}_j}=\frac{\mathbf{m}}{\epsilon^2}\,(2\delta_{i,j}-\delta_{i,j+1}-\delta_{i,j-1})+\delta_{i,j}\,\frac{\partial^2 V[\mathbf{q}(\tau)]}{\partial\mathbf{q}_i\partial\mathbf{q}_j}, \tag{2.17}$$

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. 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 $N\times P$. When diagonalizing this matrix, there will be a negative eigenvalue giving rise to the imaginary part of the barrier partition function, and a zero eigenvalue corresponding to the translationally invariant mode.[5] The existence of a zero eigenvalue is an indication of a true instanton solution. The removal of the zero eigenvalue requires the proper normalization, which is explained in Appendix A of Ref. 18. After the removal of the zero eigenvalue, the rest of the normalized determinant is given by

$$D=\lim_{P\rightarrow\infty}\frac{1}{P^2}\,\det{}'\left(\epsilon^2\mathbf{m}^{-1}\,\frac{\delta^2 S}{\delta\mathbf{q}_i\,\delta\mathbf{q}_j}\right), \tag{2.18}$$

where det$'$ stands for the value of the determinant with the zero eigenvalue removed. The translationally invariant mode is then integrated along the bounce trajectory, resulting in a prefactor of $\sqrt{W/2\pi\hbar}$.

Putting all of the factors together from the above analysis, we obtain the instanton approximation Z_{inst} for the imaginary part of the barrier partition function, i.e.,

$$\text{Im}\,Z_b\simeq Z_{\text{inst}}=\sqrt{\frac{W}{2\pi\hbar D}}\,\exp(-S_{\text{inst}}/\hbar), \tag{2.19}$$

where W and S_{inst} are the work and action of the bounce trajectory, respectively, and D is a properly normalized determinant as defined above. The quantum instanton reactive flux is given by

$$F\simeq\frac{1}{\hbar\beta}\,\text{Im}\,Z_b. \tag{2.20}$$

More discussions of the instanton solution can be found in Appendix B. By comparison with Eq. (2.4), the prefactor at low temperature is clearly given by

$$\begin{aligned} f=\text{Re}\,f&=\lim_{t\rightarrow\infty}\text{Re}\,\frac{\partial}{\partial\tau}\,\langle h_P(\tau+it)h_P(0)\rangle_b\\ &\simeq\frac{1}{\hbar\beta}. \end{aligned} \tag{2.21}$$

The ''barrier partition function'' perspective in semiclassical activated dynamics has been further elaborated in Refs. 22 and 23.

It is also important to mention the case of a metastable potential well. Langer and others[11,38] have shown that for such systems the barrier partition function is twice the imaginary part of the well free energy. The imaginary part of the well free energy can in turn be related to a thermal average over the imaginary part of the well eigenvalues, i.e., the lifetimes of the metastable states. Thus the imaginary part of the well free energy can be related to the thermal decay rate, and this is often taken as a ''formal'' basis for instanton theory. Interestingly, the barrier partition function contains the same information, and it can be understood from the perspective of the asymptotic treatment of the overall partition function in the barrier region. To quadratic order, this treatment is equivalent to the steepest descent approximation with an analytic continuation $q\rightarrow iq$ of the appropriate integration variable for the temperature at hand.[11] In fact, the barrier partition function Z_b can only be comprehended in the asymptotic sense. For example, there does not exist a well-defined global partition function for a metastable potential well or an unbounded barrier crossing problem such as an Eckart barrier. Also, for a closed system such as a double-well, the global system partition function is a positive-definite real quantity. In this case, the barrier partition function is literally *defined* to be some asymptotic approximation to the partition function around a saddle-point mode, i.e., a steepest descent approximation in the barrier region. The imaginary part of the barrier partition function arises from the mathematical rotation of the relevant integration variable for the unstable mode to the imaginary axis.[11] (The exact nature of that integration variable is of considerable significance, as we shall see in the next section.[48]) In effect, the imaginary part of the barrier partition function results from the thermal fluctuations of the unstable mode in imaginary space and the thermal fluctuations of the stable modes in real space. It seems fairly remarkable that the result of an apparent mathematical trick to evaluate a divergent integral could be intimately related to the rate of a quantum activated process, but it does indeed seem to be so.

Combining the results from the preceding analysis, we find that the quantum reactive flux for a one-dimensional system can be written in the following unified form:

$$F \simeq \nu \, \mathrm{Im} \, Z_b , \tag{2.22}$$

where ν is a simple piecewise continuous frequency factor, given by

$$\begin{aligned} \nu &= \frac{\omega_b}{2\pi}; \quad \hbar\beta\omega_b < 2\pi, \\ &= \frac{1}{\hbar\beta}; \quad \hbar\beta\omega_b \geqslant 2\pi, \end{aligned} \tag{2.23}$$

and it is understood that the barrier partition function Z_b is treated in an appropriate asymptotic fashion, depending on the temperature. The reactive flux expression in Eq. (2.22) is valid at all temperatures and in the classical limit. The important result embodied in Eq. (2.22) might also have been inferred by piecing together several known analytical results, but the derivation in Appendix A, leading to Eq. (2.6), provides a key formal link between the high and low temperature limits.

For many-dimensional systems, the above equations should be modified to include the effects of the coupling to a thermal bath. The basic form of the expression in Eq. (2.22) is the same, but the barrier partition function is now defined for the complete many-dimensional system and, by invoking the linear response approximation,[7] the expression for the frequency factor is given by

$$\begin{aligned} \nu &= \frac{\lambda_0^{\ddagger}}{2\pi}; \quad \hbar\beta_0^{\ddagger} < 2\pi, \\ &= \frac{1}{\hbar\beta}; \quad \hbar\beta\lambda_0^{\ddagger} \geqslant 2\pi, \end{aligned} \tag{2.24}$$

where $\lambda_0^{\ddagger}$ is the Grote–Hynes frequency,[9] given by

$$\lambda_0^{\ddagger} = \frac{\omega_b^2}{\lambda_0^{\ddagger} + \hat{\eta}(\lambda_0^{\ddagger})/m} . \tag{2.25}$$

Here, m is the effective mass of the reaction coordinate and $\hat{\eta}(z)$ is the Laplace transform of the classical friction kernel at the top of the barrier[9] (i.e., the frequency-dependent friction). The crossover temperature in the many-dimensional case is now defined by $\hbar\beta_0\lambda_0^{\ddagger} = 2\pi$ (see, e.g., Ref. 1 for a discussion).

Before proceeding to the next section, it should be noted that the present formulation of quantum activated dynamics is not limited to adiabatic reactions. Indeed, in the case of nonadiabatic transitions, Eq. (2.22) can be generalized to read[18]

$$F \simeq \nu \, \mathrm{Im} \, Z_{\mu,\nu} , \tag{2.26}$$

where

$$Z_{\mu,\nu} = \int d\mathbf{q} \int d\mathbf{q}' |\langle \mu, \mathbf{q} | \exp(-\beta H/2) | \nu, \mathbf{q}' \rangle|^2 \tag{2.27}$$

and $\mathbf{q}$ and $\mathbf{q}'$ are understood to be in the region of the wells of the diabatic reactant and product states, respectively. Note that the notation ''Im'' was absorbed into the definition of $Z_{\mu,\nu}$ in Ref. 18. The choice of the prefactor ν in the nonadiabatic case is less clear, but using Eq. (2.24) with a barrier frequency determined from the lowest *adiabatic* potential energy surface will give a result consistent with the known analytical limits.

III. PATH INTEGRAL QUANTUM TRANSITION STATE THEORY

The expression for the quantum reactive flux in Eq. (2.22) allows us to rationalize, even provide an *a priori* argument for, the central role of the imaginary time path centroid variable in quantum activated dynamics.[24–27,47] Elements of this argument have already appeared elsewhere,[24,38,48,55] but the final outcome in this section is somewhat different and more general.

As described many times in the literature, the definition of the imaginary time path centroid density is given by[52,56,57]

$$\rho_c(q_c) = \int \cdots \int \mathscr{D}q(\tau) \delta(q_c - \tilde{q}_0) \exp\{-S[q(\tau)]/\hbar\}, \tag{3.1}$$

where a one-dimensional notation is again employed for simplicity, and the centroid variable $\tilde{q}_0$ is defined as the zero frequency Fourier mode of the path $q(\tau)$, i.e.,

$$\tilde{q}_0 = \frac{1}{\hbar\beta} \int_0^{\hbar\beta} d\tau q(\tau). \tag{3.2}$$

The exact quantum partition function can be formally expressed as the centroid trace[52,56,57]

$$Z = \int dq_c \exp[-\beta V_c(q_c)], \tag{3.3}$$

where the effective centroid potential is given by

$$V_c(q_c) = -k_B T \ln[\rho_c(q_c)]. \tag{3.4}$$

At this point, the effective centroid potential can be used to evaluate the barrier partition function within the steepest descent approximation.[48] To do so, the centroid potential is expanded at its maximum q^* in the barrier region, giving

$$V_c(q_c) \simeq V_c(q^*) + \tfrac{1}{2} V_c^{(2)}(q^*)(q_c - q^*)^2. \tag{3.5}$$

Here, the maximum of the centroid potential q^* is determined by

$$\langle V^{(1)}(q^*)\rangle_c=0, \tag{3.6}$$

and the curvature of the centroid potential is determined by

$$V_c^{(2)}(q^*)=\langle V^{(2)}(q^*)\rangle_c-\beta[\langle \overline{V^{(1)}}(q^*)\overline{V^{(1)}}(q^*)\rangle_c - \langle V^{(1)}(q^*)\rangle_c^2], \tag{3.7}$$

where $\langle f(q^*)\rangle_c$ denotes a centroid-constrained average at the transition state or, explicitly,

$$\langle f(q^*)\rangle_c = \frac{\int\cdots\int \mathscr{D}q(\tau) f[q(0)]\delta(q^*-\tilde{q}_0)\exp\{-S[q(\tau)]/\hbar\}}{\int\cdots\int \mathscr{D}q(\tau)\delta(q^*-\tilde{q}_0)\exp\{-S[q(\tau)]/\hbar\}}. \tag{3.8}$$

and $\overline{V}=\int_0^{\hbar\beta}d\tau V[q(\tau)]/\hbar\beta$.

Now comes a crucial point. If the curvature of the centroid potential is negative, then the centroid variable is the ideal variable by which to evaluate the barrier partition function via a steepest descent approximation to Eq. (3.3) along the imaginary axis (i.e., $q_c\rightarrow iq_c$). That is,

$$Z_b\simeq i\rho_c(q^*)\int_{-\infty}^{\infty}dq_c \exp[-\beta|V_c^{(2)}(q^*)|(q_c-q^*)^2/2] = i\left(\frac{2\pi}{\beta|V_c^{(2)}(q^*)|}\right)^{1/2}\rho_c(q^*). \tag{3.9}$$

After the steepest descent evaluation of the barrier partition function using Eq. (3.9), the expression for the quantum reactive flux [Eq. (2.22)] is then given by

$$F\simeq\nu\left(\frac{2\pi}{\beta|V_c^{(2)}(q^*)|}\right)^{1/2}\rho_c(q^*), \tag{3.10}$$

where $|V_c^{(2)}(q^*)|$ is the absolute value of the curvature of the effective centroid potential at its maximum. It should be noted that the centroid-based expression given above for the quantum activated rate constant is somewhat different from the PI-QTST expression[24–26] and from the low temperature formula derived in Ref. 48. Simplifying further, the expression for the quantum rate constant is given by

$$k\simeq\nu\frac{(2\pi/\beta|V_c^{(2)}(q^*)|)^{1/2}}{\int_{-\infty}^{q^*}dq_c\, e^{-\beta V_c(q)}}e^{-\beta V_c(q^*)}. \tag{3.11}$$

This formula, as with the PI-QTST formula, is readily evaluated by numerical path integral techniques, and a simple prescription has been given here for the prefactor ν as well [i.e., Eq. (2.24)].

For higher temperatures, particularly above crossover, the frequency factor is given by $\nu=\lambda_0^\ddagger/2\pi$ and $|V_c^{(2)}(q^*)|$ can be approximated by $m\omega_b^2$. In this case, Eq. (3.11) reduces to the well-known PI-QTST formula[25] for many-dimensional systems

$$k_{\text{PI-QTST}}=\frac{\lambda_0^\ddagger}{\omega_b}\frac{(2\pi m\beta)^{-1/2}}{\int_{-\infty}^{q^*}dq_c\, e^{-\beta V_c(q)}}e^{-\beta V_c(q^*)}. \tag{3.12}$$

The PI-QTST result has thus been recovered from the point of view of the present analysis. Note, however, that Eq. (3.11) is likely to be more accurate then the PI-QTST result in Eq. (3.12) over the entire temperature range. Also, for low temperatures, the prefactor ν in Eq. (3.11) is given by $1/\hbar\beta$ and the equation becomes an approximation[24,27,48] to the instanton result [Eq. (2.20)].

In light of the general expression for the quantum activated rate constant in Eq. (2.22), the above steepest descent approach provides a rationale as to why the centroid variable and its equilibrium density at the transition state are so important in determining the value of the quantum thermal rate constant. The centroid constraint arises *naturally* in this analysis without being artificially introduced.[24,38] Indeed, the quantum reaction coordinate q is clearly defined to be the coordinate which possesses the unstable centroid mode, and the quantum transition state along the coordinate is specified by the value of $q=q^*$ which gives a maximum in the effective centroid potential in the barrier region[24] (and this *may not* be the same as the classical transition state[24,39]).

While the above expressions have been given for a one-dimensional reactive system, they are readily generalized to many-dimensional systems in a transparent fashion. In the latter scenario, the effective centroid potential in Eq. (3.4) is replaced by the *centroid potential of mean force* (CPMF) along the reaction coordinate q, also to be denoted here by $V_c(q_c)$. This quantity is defined as in Eqs. (3.3) and (3.4), but it now depends on the reduced centroid density[26]

$$\rho_c(q_c)=\int\cdots\int \mathscr{D}\mathbf{q}(\tau)\delta(q_c-\tilde{q}_0)\exp\{-S[\mathbf{q}(\tau)]/\hbar\}. \tag{3.13}$$

As a convention, in the equations above and below the bold fonts stand for vectors and matrices (in the present case, for the coordinates of the many-dimensional system). With the concept of the CPMF in hand, Eqs. (3.7)–(3.12) are thus applicable to many-dimensional systems.

It is also possible to generalize the centroid density treatment of the barrier partition function to a rotated saddle point in multidimensional space if the discussion is restricted to linear transformations of the system coordinates. In particular, if the saddle point is defined in terms of the rotated coordinate

$$z=\sum_{i=1}^{N}U_i q_i, \tag{3.14}$$

with $|\mathbf{U}_i|=1$ being a unit vector and z the reactive barrier coordinate (i.e., the local reaction path), then one can write the reduced centroid density along this coordinate as[25,26]

$$\rho_c(z_c)=\int\cdots\int \mathscr{D}\mathbf{q}(\tau)\delta(z_c-\tilde{z}_0)\exp\{-S[\mathbf{q}(\tau)]/\hbar\}, \tag{3.15}$$

where $\tilde{z}_0$ is the centroid of the reactive coordinate. The partition function can be similarly defined as

$$Z=\int dz_c \exp[-\beta V_c(z_c)], \tag{3.16}$$

where the centroid potential of mean force along z is given by

$$V_c(z_c) = -k_B T \ln[\rho_c(z_c)]. \tag{3.17}$$

In a manner similar to that outlined before, the CPMF along z can be used to evaluate the barrier partition function within the steepest descent approximation by first expanding it about the maximum as defined at $z^\ddagger$, giving

$$V_c(z_c) \simeq V_c(z^\ddagger) + V_c^{(1)}(z^\ddagger)(z_c - z^\ddagger) + \tfrac{1}{2} V_c^{(2)}(z^\ddagger)(z_c - z^\ddagger)^2. \tag{3.18}$$

Note that the second term on the right-hand side of this equation is zero by definition. The derivatives above are given by the rotated version of Eqs. (3.6) and (3.7), i.e.,

$$\langle \wp V(z^\ddagger) \rangle_c = 0, \tag{3.19}$$

and

$$\begin{aligned} V_c^{(2)}(z^\ddagger) = \langle \wp^2 V(z^\ddagger) \rangle_c - \beta[\langle \wp \overline{V}(z^\ddagger) \wp \overline{V}(z^\ddagger) \rangle_c \\ - \langle \wp V(z^\ddagger) \rangle_c^2], \end{aligned} \tag{3.20}$$

where the symbol $\wp$ denotes the derivative along the reaction path: $\wp = \Sigma_{i=1}^N U_i \boldsymbol{\partial}_i$. The rotated dividing surface is to be chosen normal to the direction of the negative eigenvalue of centroid-constrained force constant matrix, and the transition state $z^\ddagger$ is defined to be the position of the centroid-constrained free energy maximum along the rotated reactive barrier coordinate. In Eqs. (3.19) and (3.20), the general centroid-constrained averages are given by expressions similar to Eq. (3.8), i.e.,

$$\langle f(z^\ddagger) \rangle_c = \frac{\int \cdots \int \mathscr{D}\mathbf{q}(\tau) f[\mathbf{q}(0)] \delta(z^\ddagger - \tilde{z}_0) \exp\{-S[\mathbf{q}(\tau)]/\hbar\}}{\int \cdots \int \mathscr{D}\mathbf{q}(\tau) \delta(z^\ddagger - \tilde{z}_0) \exp\{-S[\mathbf{q}(\tau)]/\hbar\}}. \tag{3.21}$$

With the rotated saddle point in hand, the centroid density in terms of the rotated coordinate ρ can be approximated by the saddle point expression

$$\rho_c(z_c) \simeq \rho_c(z^\ddagger) \exp[-\beta V_c^{(2)}(z^\ddagger)(z_c - z^\ddagger)^2]. \tag{3.22}$$

If $V_c^{(2)}(z^\ddagger) < 0$, then the imaginary part of the barrier partition function can be evaluated using the steepest descent approach as before, yielding the reactive flux from Eq. (2.22) as

$$F \simeq \nu \left(\frac{2\pi}{\beta |V_c^{(2)}(z^\ddagger)|} \right)^{1/2} \rho_c(z^\ddagger). \tag{3.23}$$

The above prescription to determine the dividing surface also applies to classical transition state theory where the variational principle requires the transition state flux through the dividing surface to be minimized.[58–61] For a coordinate-dependent dividing surface, the flux through the surface is proportional to the constrained partition function integrated on the dividing surface weighted by a Jacobian factor. Therefore, in the case of a planar dividing surface, minimizing the flux is equivalent to finding the planar dividing surface according to the criterion in Eq. (3.20), at least to quadratic order.[26,39,40] Following this argument, a self-consistent centroid TST theory of quantum dissipative barrier crossing has been formulated.[62] On the other hand, a general variational principle in PI-QTST will be difficult to rigorously justify since, as shown in the present work, PI-QTST is based on a steepest descent approximation to the barrier partition function and a high temperature approximation for the frequency factor.

In this section, the main result of PI-QTST [Eq. (3.12)] has been related to Eq. (2.22) through the centroid-based analysis of the barrier partition function [cf. Eq. (3.9)]. In the process, a new expression for the quantum rate constant, Eq. (3.11), was derived which, in principle, is more accurate than the PI-QTST expression over a broader temperature range. These considerations also lead to some interesting analytical and conceptual perspectives, which are described in the next section. One of these perspectives pertains to the analytical treatment of the crossover problem, while the other concerns the form of the optimal low temperature analysis[48] of the basic rate constant expression, Eq. (2.22), thereby generalizing upon the usual centroid activated rate perspective.[24–26]

IV. ANALYSIS

The central quantity in the expression for the quantum rate constant [Eq. (2.22)] is the imaginary part of the barrier partition function Z_b. As such, this situation compels us to consider the implications of the steepest descent perspective for this quantity. Indeed, one can imagine expressing the barrier partition function in terms of an integration over a *finite* number of Fourier path modes $\tilde{q}_n$, given from the Fourier decomposition of the paths by

$$q(\tau) = \sum_{n=-\infty}^{\infty} \tilde{q}_n e^{i\Omega_n \tau}, \tag{4.1}$$

where $\Omega_n = 2\pi n/\hbar\beta$. One is then free to express the barrier partition function as an integration over an effective extended-dimensional Fourier mode density, $\rho(q_c, \ldots, q_m)$,[63] where

$$\begin{aligned} \rho(q_c, \ldots, q_m) = \int \cdots \int \mathscr{D}q(\tau) \delta(q_c - \tilde{q}_0) \prod_{n=1}^{m} \delta(q_n - \tilde{q}_n) \\ \times \exp\{-S[q(\tau)]/\hbar]\} \end{aligned} \tag{4.2}$$

and

$$\begin{aligned} Z_b &= \int dq_c \cdots \int dq_m \rho(q_c, \ldots, q_m) \\ &\equiv \int dq_c \cdots \int dq_m \exp[-\beta V_{\text{eff}}(q_c, \ldots, q_m)]. \end{aligned} \tag{4.3}$$

Here, the integrations in the above equation are understood to be in the barrier region, as required, and $V_{\text{eff}}(q_c, \ldots, q_m)$ is an effective ''potential of mean force'' for the subset of Fourier path modes $(\tilde{q}_c, \ldots, \tilde{q}_m)$, as defined above.[63] For simplicity, the m-dimensional expression in Eq. (4.2) has been developed for a problem having one physical dimension. For multidimensional systems, the effective potential for the subset of Fourier path modes is a potential-like function in an extended $m\times N$-dimensional space, which is larger than the physical dimension of the system N. This formulation of the barrier partition function within the context of the quantum rate constant expression [Eq. (2.22)] leads to two interesting perspectives which are now described.

A. Crossover

The expression in Eq. (2.11) for the reactive flux of the parabolic barrier diverges at the crossover temperature. On the other hand, the instanton expression in Eq. (2.20) is inappropriate above the crossover temperature since the bounce solution to the barrier partition function shrinks to a trivial solution. The path centroid-based expressions in Eqs. (3.11) and (3.12) are uniformly valid through the crossover temperature, but they are essentially numerical in spirit (i.e., the key quantities are usually determined from numerical path integral simulations for realistic systems). In terms of analytic theory, it is generally regarded as being unsatisfactory to have two distinctive solutions which do not match smoothly in the crossover regime. While a number of authors have proposed solutions to this problem (for a review, see Ref. 1), it shall be examined here within the context of the present theory [i.e., Eq. (2.22)] based on the steepest descent solution to the barrier partition function. We will also draw upon the Fourier path mode perspective introduced in Eqs. (4.1)–(4.3). The outcome of the derivation in this subsection resembles the perturbative analysis of the transition between thermal hopping and quantum tunneling of Grabert and Weiss.[19] However, since the emphasis is placed on an asymptotic Fourier mode analysis of the imaginary part of the barrier partition function, we obtain a somewhat different result.

Given the parabolic potential in Eq. (2.5), the imaginary time action functional in Eq. (2.9) takes a simple quadratic form. With the aid of a Fourier expansion of the paths, rewritten in this instance as

$$q(\tau)-q_b=\sum_{n=-\infty}^{\infty}\tilde{q}_n\,\exp(i\Omega_n\tau), \tag{4.4}$$

the action functional for the potential in Eq. (2.5) is diagonalized as

$$S[q(\tau)]/\hbar=\tfrac{1}{2}m\beta\sum_{n=-\infty}^{\infty}\overline{\Omega}_n^2|\tilde{q}_n|^2, \tag{4.5}$$

where the eigenvalue $\overline{\Omega}_n$ is given by

$$\overline{\Omega}_n^2=\Omega_n^2-\omega_b^2 \tag{4.6}$$

with $\Omega_n=2\pi n/\beta\hbar$. The zeroth mode $\tilde{q}_0$, i.e., the centroid, has a negative eigenvalue which gives rise to the imaginary part of the barrier partition function in the steepest descent integration along the imaginary axis. The divergence of the parabolic barrier reactive flux expression in Eq. (2.11) at the crossover is due to the disappearance of the first eigenvalue $\overline{\Omega}_1$. However, this divergence for real barriers can be avoided by including higher-order nonquadratic corrections in the $\tilde{q}_1$ integration within the context of the rate expression Eq. (2.22) and the extended Fourier mode space representation of the barrier partition function, as formulated in Eq. (4.3) (in this case for $m=1$). This analysis illustrates the utility of the barrier partition function perspective in dealing with the crossover problem, as well as the extended-space Fourier mode picture.

For simplicity, the crossover analysis will be presented for a one-dimensional barrier crossing problem and then extended to dissipative systems at the end. The barrier potential is first expanded beyond quadratic order, giving

$$V(q)=V_0-\frac{1}{2!}m\omega_b^2(q-q_b)^2+\frac{1}{3!}c(q-q_b)^3+\frac{1}{4!}g(q-q_b)^4, \tag{4.7}$$

where $V(q_b)=V_0$, $V^{(1)}(q_b)=0$, $V^{(2)}(q_b)=-m\omega_b^2$, $V^{(3)}(q_b)=c$, and $V^{(4)}(q_b)=g$. The sign of g is assumed positive as otherwise the instanton solution exists at all temperatures. The higher moments of the potential are then expressed in terms of the Fourier path modes as

$$\frac{1}{\hbar\beta}\int_0^{\hbar\beta}d\tau[q(\tau)-q_b]^3=\tilde{q}_0^3+6\tilde{q}_0|\tilde{q}_1|^2+3(\tilde{q}_1^2\tilde{q}_2^*+\tilde{q}_1^{*2}\tilde{q}_2)+\cdots \tag{4.8}$$

and

$$\frac{1}{\hbar\beta}\int_0^{\hbar\beta}d\tau[q(\tau)-q_b]^4=\tilde{q}_0^4+12\tilde{q}_0^2|\tilde{q}_1|^2+12\tilde{q}_0(\tilde{q}_1^2\tilde{q}_2^*+\tilde{q}_1^{2*}\tilde{q}_2)+6|\tilde{q}_1|^4+\cdots \tag{4.9}$$

where $\tilde{q}_n^*$ is the complex conjugate of $\tilde{q}_n$. It can become a formidable task to deal with all of the lengthy expansions. Fortunately, as in the WKB approximation to the real-time Green function where an asymptotic analysis has been devised to treat the divergence at the caustics,[53] a similar procedure applies here. By considering the Taylor expansion Eqs. (4.7)–(4.9) at the barrier top as an asymptotic expansion of the imaginary time action, to lowest order it can be reduced to

$$S/\hbar=-\tfrac{1}{2}m\beta\omega_b^2\left(\tilde{q}_0-\frac{c}{\omega_b^2}|\tilde{q}_1|^2\right)^2+m\beta\overline{\Omega}_2^2\left|\left(\tilde{q}_2+\frac{c}{\overline{\Omega}_2^2}\tilde{q}_1^2\right)\right|^2+m\beta\overline{\Omega}_1^2|\tilde{q}_1|^2+\beta\frac{A}{2}|\tilde{q}_1|^4+\sum_{n>2}m\beta\overline{\Omega}_n^2|\tilde{q}_n|^2, \tag{4.10}$$

where

$$A=\frac{g}{2}+\frac{c^2}{m\omega_b^2}-\frac{c^2}{2m\overline{\Omega}_2^2}. \tag{4.11}$$

The reduction of the Fourier mode expansion of the potential into Eq. (4.10) is approximate, but simplifies considerably the subsequent analysis. For example, it can be shown from Eq. (4.10) that as the temperature approaches the crossover from above the effective potential for the $|\tilde{q}_1|$ mode changes from a simple harmonic well to a symmetric double well. This symmetry breaking indicates a transition from a trivial stationary point to an instanton solution.

At this point, all the higher-order Fourier mode integrations except for $|\tilde{q}_1|^2$ can be performed exactly as in the case of the parabolic approximation. Similarly, the steepest descent integration over the centroid variable can be performed. The result of these operations is given by

$$Z_b = \int dq_c \int dq_1 \, \exp[-\beta V_{\mathrm{eff}}(q_c, q_1)] = Z_{\mathrm{pb}} \, \mathrm{Corr}(\Delta), \tag{4.12}$$

where the correction term Corr(Δ) arises from the integration over $y = |q_1|^2$ and is given by

$$\begin{aligned} \mathrm{Corr}(\Delta) &= \frac{\int_0^\infty dy \, \exp(-\beta m \overline{\Omega_1^2} y - \beta A y^2/2)}{\int_0^\infty dy \, \exp(-\beta \overline{\Omega_1^2} y)} \\ &= \Delta \sqrt{2\pi} \, \mathrm{erf}(-\Delta) e^{\Delta^2/2}. \end{aligned} \tag{4.13}$$

This result has the same structure as the earlier result obtained by Grabert and Weiss,[19] except for the definition of Δ. Here, it is defined as

$$\Delta = m(\Omega_1^2 - \omega_b^2)\sqrt{\beta/A}, \tag{4.14}$$

where ‘‘erf’’ is the error function

$$\mathrm{erf}(\Delta) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\Delta} dx \, e^{-x^2/2}. \tag{4.15}$$

By virtue of the above result, Eq. (4.12), as well as Eq. (2.22), the asymptotic expression for reactive flux around the crossover temperature has the structure

$$F \simeq \mathrm{Corr}(\Delta) F_{\mathrm{pb}}, \tag{4.16}$$

where the parabolic barrier reactive flux is given by Eq. (2.11). The above ‘‘high temperature’’ asymptotic expression matches smoothly onto the parabolic expression Eq. (2.11) and extends continuously below the crossover temperature. It remains valid until $\overline{\Omega_2^2}$ becomes zero which then makes it necessary to include the Fourier mode $\tilde{q}_2$ in the expression for the generalized Fourier mode barrier partition function [Eq. (4.3)] to generalize the analysis. Alternatively, the instanton solution can be asymptotically treated in the crossover region from below and smoothly bridged with the high temperature asymptotic expression [Eq. (4.16)]. This approach is outlined in Appendix B.

The high temperature asymptotic approach can also be readily generalized to quantum barrier crossings in dissipative systems, at least for a reaction coordinate linearly coupled a Gaussian bath.[64] As usual, in such cases the total Hamiltonian for the system is given by

$$H = \frac{p_q^2}{2m} + V(q) + \sum_{i=1}^{N} \left[\frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 \left(x_i - \frac{c_i}{m_i \omega_i^2} q \right)^2 \right], \tag{4.17}$$

where $\{x_i, p_i\}$ are the canonically conjugate bath variables and $\{m_i, \omega_i, c_i\}$ are the corresponding masses, frequencies, and coupling constants, respectively. Despite its apparent simplicity, the above Hamiltonian provides a model for many quantum processes in the dissipative condensed phase environment so long as the linear response approximation is valid. The path integration over the bath variables from the above Hamiltonian leads to a path integral action functional of the form

$$\begin{aligned} S[q(\tau)] = \int_0^{\hbar\beta} d\tau \{ \tfrac{1}{2} m \dot{q}(\tau)^2 + V[q(\tau)] \} \\ + \hbar\beta \sum_{n=1}^{\infty} \Omega_n \hat{\eta}(\Omega_n) |\tilde{q}_n|^2 / m, \end{aligned} \tag{4.18}$$

where $\hat{\eta}(s)$ is the Laplace transform of the friction kernel, defined in the discrete limit by

$$\hat{\eta}(s) = \sum_{i=1}^{N} \frac{c_i^2}{m_i \omega_i^2} \frac{s}{s^2 + \omega_i^2}. \tag{4.19}$$

With the aid of the above expression, all of the results in this section remain the same if the definition in Eq. (4.6) is modified to be

$$\overline{\Omega_n^2} = \Omega_n^2 - \omega_b^2 + \Omega_n \hat{\eta}(\Omega_n)/m. \tag{4.20}$$

Accordingly, the crossover temperature is defined where the eigenvalue of $\tilde{q}_1$ vanishes,[54] namely,

$$\Omega_1^2 - \omega_b^2 + \Omega_1 \hat{\eta}(\Omega_1)/m = 0, \tag{4.21}$$

where $\Omega_1 = 2\pi/\hbar\beta$.

B. Low temperature generalization of the saddle point analysis

The second perspective of this section—and perhaps the most compelling one for future investigation—is concerned with the steepest descent evaluation of the barrier partition function through Eq. (4.3) in the low temperature limit.[48] Under *normal* circumstances (i.e., not too low temperatures and not too asymmetric barriers), the centroid variable $\tilde{q}_0$ is the natural variable about which to perform the steepest descent integration along the imaginary axis as outlined in the previous section and in Ref. 48. However, in some instances at low enough temperatures the curvature of the centroid potential $V_c(q_c)$ in Eq. (3.4), as specified by Eq. (3.7), may be positive *everywhere* in the barrier region. Furthermore, for highly asymmetric metastable barriers, there may also be pathological low temperature behavior in the centroid-based approach.[48] In these cases, an intriguing point of view emerges. Instead of a saddle point integration using just the centroid variable as in Eq. (3.9), the saddle point analysis and the steepest descent integration can be generalized in terms of a combination of the subset of path Fourier modes $\{\tilde{q}_m\}$ in Eq. (4.3). In these pathological cases, it is actually *necessary* to pursue such a generalization in order to have a sensible evaluation of the imaginary part of the barrier partition function.[48] Thus in such cases the saddle point may not involve the centroid mode alone, but instead the problem maps onto a kind of classical-like transition state calculation in the extended space of the effective Fourier mode potential $V_{\text{eff}}(q_c,\ldots,q_m)$.

To explore this idea in more detail, the path integral action functional can be Fourier decomposed in the following general way:

$$S[q(\tau)]=m\hbar\beta\sum_{n=1}^{\infty}\Omega_n|\tilde{q}_n|^2+\int_0^{\hbar\beta}d\tau V[q(\tau)]. \tag{4.22}$$

The higher the value of n, the higher the positive ''frequency'' of that mode in the saddle point region of the effective Fourier mode potential $V_{\text{eff}}(q_c,\ldots,q_m)$ as defined in Eq. (4.3). As a consequence of this result, it is expected that the $m=1$ mode should be the highest Fourier mode necessary to include in Eq. (4.3) for most systems. To carry out the generalized saddle point procedure, one must then find the saddle point for the effective Fourier mode potential $V_{\text{eff}}(q_c,q_1)$, determine the linear combination (or ''normal mode'') of the centroid mode q_c and the first Fourier mode q_1 along the direction of steepest descent at the saddle point, and then perform the integration over that mode in the complex plane. At the same time, an integral is performed along the real axis for the stable normal mode orthogonal to the steepest descent mode (cf. Ref. 48). This perspective for a generalized quantum TST saddle point in the extended-dimensional space of the Fourier modes is presently under investigation in this group and elsewhere.[65]

V. NUMERICAL EXAMPLES

In this section, the theory described in the previous sections is illustrated by a study of a one-dimensional Eckart barrier and an Eckart barrier coupled to a Gaussian bath. The emphasis here is on the crossover behavior from the high temperature thermally activated barrier crossing to low temperature quantum tunneling.

The Eckart barrier potential is given by[66]

$$V(q)=V_0\ \text{sech}^2(q/a) \tag{5.1}$$

with the parameter value of $2\pi V_0/\hbar\omega_b=12$ in the present calculations. The transition state is located at $q_b=0$ with $V(q_b)=V_0$, and the barrier frequency is given by

$$m\omega_b^2=2V_0/a^2. \tag{5.2}$$

Two dimensionless parameters can be introduced, given by $b=\hbar\beta\omega_b$ (or $\mu=b/2\pi$) and $\zeta=\beta V_0$, such that all relevant quantities are expressed in terms of these two parameters.

A quantum correction factor Γ can be defined as the ratio of the quantum to classical reactive flux, which is written as

$$\Gamma=F_{\text{qm}}/F_{\text{cl}}. \tag{5.3}$$

In one-dimension, a simple estimate of this quantum correction is the high temperature parabolic correction, given by

$$\Gamma_{\text{pb}}=\frac{(b/2)}{\sin(b/2)}, \tag{5.4}$$

which, as stated before, is invalid below the crossover temperature, i.e., for $\beta>\beta_0=2\pi/\hbar\omega_b$. We thus consider the higher-order correction derived in Sec. IV, where the Taylor expansion of the potential in Eq. (4.7) has coefficients $c=0$ and $g=16V_0/a^4$ in the Eckart barrier case, and the parameter defined in Eq. (4.11) assumes the value of $A=8V_0/a^4$. Substituting these expressions into Eqs. (4.13)–(4.16), one obtains the expression

$$\Gamma_{\text{HT}}=\Gamma_{\text{pb}}\Delta\sqrt{2\pi}\ \text{erf}(-\Delta)\exp(\Delta^2/2) \tag{5.5}$$

with the variable Δ given explicitly as

$$\Delta=(\mu^{-2}-1)\sqrt{\zeta/2}. \tag{5.6}$$

Below crossover, an analytic instanton solution can be explicitly found for the Eckart barrier, giving

$$\Gamma_{\text{inst}}=\frac{\sqrt{4\pi\zeta}}{\mu}\exp[\zeta(1-1/\mu)^2], \tag{5.7}$$

which holds for $\beta>\beta_0$. The uniform asymptotic instanton solution Eq. (B3) reads

$$\Gamma_{\text{LT}}=\text{erf}(-\Delta_{\text{LT}})\Gamma_{\text{inst}} \tag{5.8}$$

with the parameter

$$\Delta_{\text{LT}}=(\mu-1/\mu)\sqrt{\zeta/2}. \tag{5.9}$$

Finally, Affleck's crossover formula can be written as

$$\Gamma_{\text{AF}}=\sqrt{\frac{4\pi\zeta}{\mu}}\ \text{erf}(\Delta_{\text{AF}})\exp(\Delta_{\text{AF}}^2/2) \tag{5.10}$$

with the parameter

$$\Delta_{\text{AF}}=(1-\mu)\sqrt{\frac{2\nu}{\mu}}. \tag{5.11}$$

The derivation of the above expressions can be found in Appendix B.

For comparison, a quantum correction was also calculated from Eq. (3.10), given by

$$\Gamma_Q=2\pi\nu\left(\frac{m}{|V_c^{(2)}(q^*)|}\right)^{1/2}\frac{\rho_c(q^*)}{\rho_{\text{cl}}(q^*)}, \tag{5.12}$$

where ν is given by Eq. (2.23). The usual PI-QTST correction,[24,26] given by

$$\Gamma_{\text{PI-QTST}}=\rho_c(q^*)/\rho_{\text{cl}}(q^*), \tag{5.13}$$

was also calculated. In both cases, the quantum centroid density was numerically computed by a path integral Monte Carlo calculation.

All of the values of the quantum correction factor Γ calculated from the above expressions are tabulated in Table I for the set of temperatures from $b=3$ to 12 along with the exact data obtained from Ref. 67. Clearly, the parabolic approximation Eq. (5.5) diverges for $\beta>\beta_0$. The uniform asymptotic formulae, Eqs. (5.5) and (5.8), approaching the crossover from above and below, respectively, agree with the

TABLE I. Quantum correction factors[a] for the symmetric Eckart barrier.

b	Γ_{exact}	Γ_{pb}	Γ_{HT}	Γ_{AF}	Γ_{LT}	Γ_Q	$\Gamma_{\text{PI-QTST}}$
3	1.5	1.50	1.46	1.70		1.62	1.42
4	2.1	2.20	2.00	2.25		2.24	1.87
5	3.1	4.18	3.04	3.21	4.05	3.46	2.72
6	5.2	21.3	5.17	5.19	5.32	5.85	4.31
8	22.0		21.0	27.4	20.0	22.3	17.0
10	162.0		136.2	816.7	135.2	142.0	103.5
12	1970.0		2687.4		1613.2	1695.2	1242.7

[a] The various quantum correction factors are defined as follows: Γ_{exact} is the exact data for the Eckart barrier obtained from Ref. 67; Γ_{pb} is the parabolic approximation from Eq. (5.4); Γ_{HT} is the high temperature asymptotic expression from Eq. (5.5); Γ_{AF} is the Affleck crossover expression from Eq. (5.10); Γ_{LT} is the low temperature asymptotic expression from Eq. (5.9); Γ_Q is the path integral result from Eq. (5.12); and $\Gamma_{\text{PI-QTST}}$ is the PI-QTST result from Eq. (5.13).

exact results quite well beyond the crossover point. By contrast, the Affleck crossover expression Eq. (5.10) behaves reasonably well around crossover, but it starts to deviate in both the low and high temperature limits. As pointed out earlier, the PI-QTST correction Eq. (5.13) is a stable approximation to the more accurate quantum rate formula [Eq. (2.22)], so it is no surprise that is incorporates the dominant quantum tunneling effects even at low temperatures, which of course has been discussed many times previously (see, e.g., Ref. 24, 26, and 68) The new formula, Eq. (5.12), is seen to be even more accurate than the PI-QTST result over the temperature range studied.

As an application to a multidimensional barrier crossing, the Eckart barrier coupled to a Gaussian bath, as described by Eq. (4.17), was studied. The bath degrees of freedom were integrated out to yield an influence functional of the form in Eq. (4.18) with the friction kernel given in the present case by

$$\hat{\eta}(s)=\frac{f}{s+\omega_c}, \tag{5.14}$$

where the friction strength $f=1.0$ and the correlation time $1/\omega_c=1.0$, both in dimensionless units scaled by β, ω_b, and V_0. The crossover temperature is determined from Eq. (4.20) to be $\beta_0=1.325(2\pi/\hbar\omega_b)$. It is clear from the one-dimensional analysis that a good analytical estimation of the reactive flux is the asymptotic form Eq. (4.16). The multidimensional generalization is rather straightforward and is described in the previous section. The PI-QTST quantum estimate of the reactive flux is given in the dissipative case from Eq. (3.12), where the centroid density was evaluated at the barrier top including the dissipative influence functional.

The results of calculations with and without dissipation are shown in Fig. 1 in the form of $\log(F/Z_{\text{bath}})$ versus b, where Z_{bath} is the quantum partition function for the pure Gaussian bath. The curves depict the asymptotic analytical data [i.e., Eq. (4.16) with (4.20) above crossover and Eq. (5.8) with the computational procedure outlined in Appendix B below crossover] and the PI-QTST data [Eq. (5.13)]. It is seen that the dissipationless flux decreases, but tends to level off at low temperatures because of the quantum tunneling effect, whereas the dissipative flux decreases more significantly at lower temperature because the friction reduces the quantum tunneling. This tendency has been well investigated in the study of metastable wells.[1] It is also interesting to note the agreement of the PI-QTST result with the asymptotic analytical results, especially for the dissipative barrier crossing.

VI. CONCLUDING REMARKS

The primary motivation of the present paper has been to provide a general unified framework for quantum activated dynamics. The outcome of this effort is Eq. (2.22), a factorization of the quantum reactive flux expression into the imaginary part of the barrier partition function, defined in the steepest descent limit of the imaginary time Feynman path integral, and a well-defined simple prefactor which can be interpreted as the frequency of the corresponding saddle-point solution. Depending on the analytic character of the steepest descent solution, the imaginary part of the barrier partition function can be shown to be related to the high temperature parabolic approximation or the low temperature instanton solution, and thus it naturally introduces the crossover temperature which distinguishes the two regimes. While the instanton result was already known, the high temperature

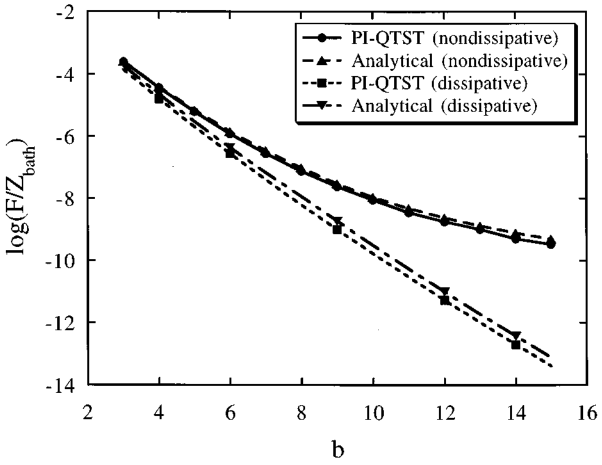

FIG. 1. A logarithmic plot of the reactive flux (actually F/Z_{bath}) vs $b(=\hbar\beta\omega)$ for the one-dimensional Eckart barrier (the upper curves) and for the Eckart barrier coupled to a dissipative bath (the lower curves). The analytical curves are calculated from Eq. (4.16) above crossover and from Eq. (B3) below crossover. For comparison, the PI-QTST estimate of the rate is also shown in both cases.

analysis is new, hence providing the missing element required for a unified mathematical framework.

Importantly, the perspective based on the imaginary part of the barrier partition function naturally introduces the Feynman path centroid variable into the topic of quantum activated dynamics.[24–27,48] A saddle-point approximation to the main formula [Eq. (2.22)] leads to a simplified formula for the quantum activated rate constant [cf. Eq. (3.11)]. Upon further analysis, this argument also provides a derivation of the well-known PI-QTST rate constant expression[24–26] given in Eq. (3.12). This perspective reveals the underlying reasons for both the advantages and limitations[48] of the PI-QTST approach, both as an analytical formalism and as a numerical technique, especially for quantum reactions in the condensed phase where other approaches may become impractical.

Two interesting analytical perspectives also emerge from the present theory which are based on a representation of the barrier partition function in terms of an integration over a limited set of Fourier path modes. In the first perspective, an asymptotic expression is derived to smoothly extend the parabolic barrier result for the quantum rate constant below the crossover temperature. In the second perspective, the saddle point analysis is generalized[48] to include higher-order Fourier path modes beyond the zero frequency mode (i.e., the centroid), thus generalizing the PI-QTST result.

In Sec. V, a study of a nondissipative and a dissipative Eckart barrier was presented to illustrate the various aspects of the theoretical developments presented in the previous sections. Emphasis was placed on the accuracy of the different reactive flux expressions. The numerical evidence clearly demonstrates the accuracy of the asymptotic analytical approach. It also shows that the centroid-based formula in Eq. (3.11) is accurate over a wide temperature range. The consistently good results of this theory, as well as the older PI-QTST expression, support the assertion that the path centroid variable occupies a central role in the computation of quantum activated rate constants under most circumstances.

Finally, several extensions and applications are likely to follow directly from the theoretical development in this paper. First, the multidimensional steepest descent analysis based on the centroid theory can help to rationalize various flavors of variational theories,[25,38–41] perhaps resulting in a systematic approach for computing the rate constant in complex condensed phase systems beyond the usual PI-QTST strategy. Second, a formulation based on the imaginary part of the barrier partition function is likely to lead to improved and efficient approaches for solving the multidimensional instanton problem, especially for nonseparable, even nonadiabatic, potentials.[18] Success in the latter arena will rest on our ability to find an efficient numerical procedure to compute the imaginary part of the barrier partition function directly and accurately. These and other issues will be explored in future research.

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APPENDIX A: EVALUATION OF THE PARABOLIC BARRIER PREFACTOR

In Sec. II, the quantum reactive flux in Eq. (2.22) was formulated as the product of the prefactor ν and the barrier partition function Z_b. Above crossover, the expression for the prefactor [cf. Eq. (2.3)] can be evaluated in the parabolic barrier limit, Eq. (2.5), and thus be determined in closed form. However, this derivation is not completely straightforward because of the divergent nature of certain integrals. To begin, the imaginary time population correlation function is written as

$$\langle h_P(\tau)h_P(0)\rangle_b = \frac{\int_0^\infty\int_0^\infty dx_1\, dx_2\; G(x_1,x_2,T-\tau)G(x_2,x_2,\tau)}{\int_{-\infty}^\infty\int_{-\infty}^\infty dx_1\, dx_2\; G(x_1,x_2,T-\tau)G(x_2,x_2,\tau)}, \tag{A1}$$

where $T=\hbar\beta$ and the imaginary time propagator for the parabolic barrier is given by

$$G(x_1,x_2,\tau)=\sqrt{\frac{m\omega_b}{2\pi\hbar\,\sin(\omega_b\tau)}}\exp\left\{-\frac{m\omega_b}{2\hbar\,\sin(\omega_b\tau)}\times[(x_1^2+x_2^2)\cos(\omega_b\tau)-2x_1x_2]\right\} \tag{A2}$$

with $x=q-q_b$. Both the numerator and denominator of Eq. (A1) diverge as a result of the integration. Nevertheless, the ratio of the two yields a finite analytical expression, i.e.,

$$\langle h_P(\tau)h_P(0)\rangle_b = \frac{1}{2\pi}\arctan\frac{2\sin(\omega_b T)}{\sqrt{\sin(b_1)/\sin(b_2)}+\sqrt{\sin(b_2)/\sin(b_1)}}, \tag{A3}$$

with $b_1=\omega_b(T-\tau)$ and $b_2=\omega_b\tau$. We then take the derivative with respect to τ, make the replacement $\tau=\tau+it$, and take the limit $t\to\infty$. For brevity, the lengthy derivation is omitted here. Finally, making use of the identity

$$\lim_{t\to\infty}\frac{\sin[\omega_b(T-\tau-it)]}{\sin[\omega_b(\tau+it)]}=\exp(i\pi+i\omega_b T), \tag{A4}$$

we arrive at

$$\lim_{t\to\infty}\frac{\partial}{\partial t}\langle h_P(\tau+it)h_P(0)\rangle_b=\frac{\omega_b}{2\pi}, \tag{A5}$$

which is the prefactor given in Eq. (2.6).

APPENDIX B: UNIFORM ASYMPTOTIC CROSSOVER ANALYSIS OF THE INSTANTON SOLUTION

As was demonstrated in Sec. II, an instanton solution in the quantum tunneling regime is essentially a nontrivial bounce stationary solution to the imaginary part of partition function and exists only below the crossover temperature. In the crossover regime, as the periodic trajectory shrinks, the integration of the quantum fluctuations in the barrier partition function cannot be extended to infinity and the determinant Eq. (2.16) from the functional integration is to be modified by an error function. Though in principle the asymptotic analysis can be carried out in the context of functional integration of the barrier partition function, it is much more straightforward to present a derivation based on an expansion about the instanton energy. One begins with the WKB transmission coefficient[69] valid for tunneling energies E below the barrier potential maximum V_0, giving[3]

$$F=\frac{1}{2\pi\hbar}\int_{\infty}^{V_0} dE\; e^{-\beta E} e^{-W(E)/\hbar}, \tag{B1}$$

where $1/2\pi\hbar$ is the free particle flux density and $W(E)$ is the action integral along the tunneling trajectory, i.e.,

$$\begin{aligned} W(E)&=\oint dx\sqrt{2m[V(x)-E]}\\ &=W(E_{\text{inst}})+W'(E_{\text{inst}})(E-E_{\text{inst}})\\ &\quad+\tfrac{1}{2}W''(E_{\text{inst}})(E-E_{\text{inst}})^2+\cdots . \end{aligned} \tag{B2}$$

In the second line above, the action integral has been expanded about the instanton energy. A steepest descent approximation on the energy variable in the integration Eq. (B1) immediately leads to a low temperature asymptotic flux expression, or a asymptotic instanton solution,

$$\begin{aligned} F_{\text{LT}}&=\frac{1}{\hbar\beta\sqrt{2W_{\text{inst}}\pi\hbar D}}\,\text{erf}\left[\beta(V_0-E_{\text{inst}})\sqrt{\frac{D\hbar}{W_{\text{inst}}}}\right]\\ &\quad\times\exp(-S_{\text{inst}}/\hbar), \end{aligned} \tag{B3}$$

where ‘‘erf’’ is the error function defined in Eq. (4.15). Here, S_{inst} and E_{inst} are the action and energy of the bounce trajectory, respectively, and the corresponding work function is $W_{\text{inst}}=W(E_{\text{inst}})$. Also, a simple identity can be applied[13]

$$W|T'|=T^2D, \tag{B4}$$

where $T=\hbar\beta$ in the case of the instanton.[3,5] The above expression also implies a numerical procedure to evaluate $|T'(E)|$ when an analytical form for $T(E)$ is not available as is the case for a dissipative system described by an influence functional.

At temperatures significantly lower than the crossover temperature, the error function reduces to unity and one recovers the conventional instanton solution in Eq. (2.20), or in the equivalent form

$$F_{\text{inst}}=\frac{1}{\sqrt{2\pi\hbar|T'(E_{\text{inst}})|}}\exp(-S_{\text{inst}}/\hbar). \tag{B5}$$

The appearance of the error function in the low temperature expression Eq. (B3) and in the high temperature expression Eq. (4.13) is not a coincidence as the two share a common origin. When the temperature approaches the crossover from below, the bounce trajectory shrinks and thus the full quantum fluctuation is not allowed because of the confinement of the volume enclosed by the bounce trajectory. As a result, the Gaussian functional integral cannot be extended to infinity and a truncation in the integral limit introduces the error function. In fact, a comparison with the asymptotic expression in Eqs. (4.13)–(4.16) suggests

$$\Delta_{\text{LT}}=\beta(E_{\text{inst}}-V_0)\sqrt{\frac{D\hbar}{W_{\text{inst}}}} \tag{B6}$$

which can be shown to be the same as the definition of Eq. (4.14) at the crossover temperature.

Though the existence of a bounce trajectory on the inverted potential surface imposes the requirement $T=\hbar\beta>2\pi/\omega_b$, Eq. (B3) is by no means limited to this condition because S_{inst} and E_{inst} can be extrapolated above the crossover if the analytical form of these quantities are known. In other words, the flux above the crossover temperature is the analytic continuation of the low temperature instanton solution as the bounce trajectory evolves into the complex coordinate space. This argument can be further clarified by Taylor expanding S_{inst} and E_{inst} around the crossover temperature β_0, giving

$$\begin{aligned} F_{\text{AF}}&=\frac{1}{\sqrt{|2\pi\hbar T_0'|}}\,\text{erf}\left[(\beta-\beta_0)\sqrt{\frac{\hbar}{|T_0'|}}\right]\\ &\quad\times\exp\left[-\beta V_0+\tfrac{1}{2}(\beta-\beta_0)^2\frac{\hbar}{|T_0'|}\right] \end{aligned} \tag{B7}$$

which is a well-known result derived by Affleck.[12] Clearly, the asymptotic instanton expression Eq. (B3) bridges the crossover expression Eq. (B7) smoothly to the instanton expression Eq. (B5).

Again, the similarity of the two crossover expressions, i.e., Eq. (B7) and Eq. (4.17) leads to the conviction that the two are essentially equivalent in the crossover regime. In fact, we can prove that the variables of the error function in the two formulae are the same. Following the asymptotic analysis leading to Eq. (4.10), we can write the work function of the instanton trajectory as

$$W=-\frac{2}{A}Tm^2\Omega_1^2\overline{\Omega}_1^2 \tag{B8}$$

which in turn yields

$$T'=-\frac{T}{dW/dE}=-\frac{TA}{4m^2\omega_b^4} \tag{B9}$$

with $T=\hbar\beta$. Substituting this expression into the variable of the error function in Eq. (B7) gives

$$\Delta_{\text{AF}}=(\beta_0-\beta)\sqrt{\frac{\hbar}{|T_0'|}}=(\beta_0-\beta)\frac{2\omega_b^2 m}{\sqrt{\beta A}} \tag{B10}$$

which, in the limit of $T \rightarrow 2\pi/\omega_b$, becomes exactly the same as the definition of Eq. (4.13). Therefore, all three flux expressions above agree at the crossover temperature.

Since $W(E)$ in Eq. (B2) is expanded about the instanton energy E_{inst} instead of the barrier top V_0, the asymptotic expression obtained as in Eq. (B3) smoothly bridges the low temperature solution to the thermally activated regime. Thus, Eq. (4.16) and Eq. (B3) represent two uniform asymptotic reactive flux expressions, one from the thermally activated regime and one from the quantum tunneling regime, and the two match exactly at the crossover temperature. Without the uniform asymptotic expressions, the reactive flux is evaluated in the three temperature regimes separately, with a rather arbitrary procedure to match the three solutions. Furthermore, the error functions in both Eq. (4.16) and Eq. (B3) arise because of the modification in the integration space of the barrier partition function at the crossover temperature.

Finally, we will address the multidimensional formulation of the instanton solution. An obvious choice is to solve for the bounce trajectory in the full multidimensional hyperspace, which is a formidable numerical task as the dimensionality increases. An alternative is to integrate out the bath degrees of freedom, giving an influence functional, and to then solve for the effective instanton trajectory in the reduced action space. For a general discussion, interested readers are referred to a previous paper[18] where we developed a methodology to incorporate dissipative effects as well as nonadiabaticity into instanton calculations. As described in the main text, the most standard approach to include dissipative effects is the Gaussian bath model of Eq. (4.17) All of the formulae in this section will be valid if the bounce trajectory is solved with the influence functional.

Consider a barrier potential linearly coupled to a harmonic bath as in Eq. (4.17) (note that care must be taken to account for the counter term in that Hamiltonian). The path integration over the bath modes introduces an influence functional such that the imaginary time action reads

$$S[q(\tau)] = \int_0^{\hbar\beta} d\tau \{ \tfrac{1}{2} m \dot{q}(\tau)^2 + V[q(\tau)] \} - \frac{1}{2\hbar} \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau \, d\tau' \, q(\tau) c(|\tau-\tau'|) q(\tau') \tag{B11}$$

where the influence functional kernel $c(|\tau-\tau'|)$ is related to the spectral density $J(\omega)$ implicit in Eq. (4.19) by

$$c(|\tau-\tau'|) = \frac{\hbar}{\pi} \int_0^{\infty} d\omega \, J(\omega) \, \frac{\cosh(\hbar\beta\omega/2 - \omega|\tau-\tau'|)}{\sinh(\hbar\beta\omega/2)} \tag{B12}$$

and

$$J(\omega) = \frac{\pi}{2} \sum_{i=1}^{N} \frac{c_i^2}{m_i \omega_i} \, \delta(\omega - \omega_i). \tag{B13}$$

The stationary instanton trajectory obeys the appropriate Euler–Lagrangian equation

$$m \frac{d^2 q(\tau)}{d\tau^2} = \frac{dV[q(\tau)]}{dq} - \frac{1}{\hbar} \int_0^{\hbar\beta} d\tau' \; c(|\tau-\tau'|) q(\tau') \tag{B14}$$

with the periodicity condition $q(\hbar\beta) = q(0)$. Next, the steepest descent approximation is applied to the barrier partition function is in Eq. (2.15), and the second-order functional derivative is explicitly given in the discretized limit of the instanton trajectory as

$$\frac{\delta^2 S}{\delta q_i \delta q_j} = \frac{m}{\epsilon^2} (2\delta_{i,j} - \delta_{i,j+1} - \delta_{i,j-1}) + \delta_{i,j} \frac{\partial^2 V(q_i)}{\partial q_i^2} - \epsilon c_{ij}, \tag{B15}$$

where the discretized influence functional kernel is defined by

$$c_{ij} = c(|\tau_i - \tau_j|) \tag{B16}$$

with $\epsilon = \hbar\beta/P$, P being the discretization number. With Eq. (B14) in place of Eq. (2.13) and Eq. (B16) in place of Eq. (2.17), the evaluation of the instanton barrier partition function is the same as for a one-dimensional barrier, with the final result given by Eq. (2.19).

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