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A theory for the quantum activated rate constant in dissipative systems

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Abstract

An analytical theory is developed for the quantum activated rate constant in general systems. The theory relies on a variationally determined effective quadratic potential and is valid at all temperatures. The formalism extends previously developed theoretical approaches based on the parabolic barrier/linear response approximation.

1. Introduction

In an upcoming publication [1], it will be shown that most existing quantum theories for activated rate processes can be unified within a single mathematical framework (see Ref. [2] for a review of activated dynamics). These theories include the high-temperature parabolic barrier approximation [3], the instanton solution [4–6], and the path integral quantum transition state theory [7–10] (PI-QTST). Within this unified framework, the quantum reactive flux can be expressed as

$$F = \nu \ \mathrm{Im}\ Z_{\mathrm{b}}, \tag{1}$$

where Im Z_{b} is the imaginary part of the barrier partition function, itself corresponding to the steepest descent solution of the partition function in the barrier region in various limits [1], and ν is a simple prefactor which can be interpreted as the frequency of the stationary trajectory [1]. In the case of a parabolic barrier reaction coordinate coupled to a multidimensional Gaussian (dissipative) bath, the expression for the prefactor is known to be given by [1,3]

$$\nu = \frac{\lambda_0^{\ddagger}}{2\pi}, \tag{2}$$

where $\lambda_0^{\ddagger}$ is the classical Grote–Hynes frequency [11], given by

$$\lambda_0^{\ddagger} = \frac{\omega_{\mathrm{b}}^2}{\lambda_0^{\ddagger} + \hat{\eta}(\lambda_0^{\ddagger})/m}. \tag{3}$$

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 [11] (i.e. the frequency-dependent friction). The crossover temperature is the point at which the parabolic barrier solution breaks down if the barrier frequency is

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taken as the classical value. Crossover is defined by $\hbar\beta_0\lambda_0^\ddagger = 2\pi$ (see, e.g., Ref. [2] for a discussion). The expressions above provide the required framework for the theory developed in the following pages.

One of the most important features of the framework outlined in Ref. [1] is that the imaginary time Feynman path centroid mode was shown to arise naturally within the steepest descent picture for the imaginary part of the barrier partition function (see also Ref. [12]). In the present Letter, this perspective is used in conjunction with the optimal quadratic approximation (OQA) of Ref. [13] to derive a general closed-form variational expression for the quantum activated rate constant which encompasses, and extends, the quantum variational PI-QTST theory of Voth [8] and, in the classical limit, the Kramers–Grote–Hynes theory [11,14].

Before proceeding to the present theoretical formulation, it should be noted that other variational approximations have been developed based on PI-QTST in order to treat activated rate processes in general multidimensional systems [8,15–19]. In these cases, the term 'variational' refers to a rotation of the centroid dividing surface, as first described in Ref. [8], to minimize the reduced Feynman centroid density [9] defined for that hypersurface in the transition state region. Since it gives the exact Wolynes expression [3] for the activated rate in the case of a parabolic barrier coupled to a Gaussian bath, such a variational procedure can be rigorously justified in that limit [8]. However, for general (non-quadratic) systems a variational rotation of the centroid dividing surface cannot be completely justified because of the lack of a rigorous bound on the PI-QTST rate constant versus the exact one, in contrast to the classical TST limit. Nonetheless, such variational PI-QTST approaches have exhibited remarkably good quantitative behavior [17,18], so there remains considerable motivation to find their underlying fundamental justification. In the present work, however, the phrase 'variational' refers primarily to a variational mapping of a real non-quadratic barrier system onto a completely quadratic one so that, in turn, the rotation of the centroid dividing surface is fully justified (actually the identification of the steepest descent path [1]). In doing so, a new closed-form expression for the quantum activated rate constant in non-linear dissipative systems is derived.

2. Theory

To begin, we briefly review the multidimensional saddle point approximation for the path centroid mode from our earlier paper [1]. The key idea is to evaluate the imaginary part of the barrier partition function in Eq. (1) by a steepest descent approximation to the integral over the centroid mode $\tilde{z}_0$ of a rotated coordinate z, the former being defined as

$$\tilde{z}_0 = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} \mathrm{d}\tau\ z(\tau), \tag{4}$$

where the latter variable is the rotated coordinate

$$z = \sum_{i=1}^{N} U_i q_i. \tag{5}$$

Here, $|\vec{U}_i| = 1$ is a unit vector and the coordinates $\{q_i\}$ are the original system coordinates. Using the above definitions, one can write the reduced centroid density along the z coordinate as the Feynman path integral [1,8,9]

$$\rho_c(z_c) = \int \cdots \int \mathcal{D}q(\tau)\,\delta(z_c - \tilde{z}_0) \times \exp\{-S[q(\tau)]/\hbar\}, \tag{6}$$

where $S[q(\tau)]$ is the imaginary time action functional for all system coordinates q. The system partition function can then be defined as [1]

$$Z = \int \mathrm{d}z_c\ \exp[-\beta V_c(z_c)], \tag{7}$$

where the centroid potential of mean force (CPMF) along z is given by [1]

$$V_c(z_c) = -k_B T\ \ln[\rho_c(z_c)]. \tag{8}$$

As outlined in Ref. [1], 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 denoted by $z^\ddagger$, giving

$$V_c(z_c) \approx V_c(z^\ddagger) + V_c^{(1)}(z^\ddagger)(z_c - z^\ddagger) + \tfrac{1}{2}V_c^{(2)}(z^\ddagger)(z_c - z^\ddagger)^2. \tag{9}$$

Note that the second term on the right-hand-side of this equation is zero by definition of the maximum. The derivatives above are given by

$$V_c^{(1)}(z^\ddagger) = \langle \wp V(z^\ddagger)\rangle_c = 0, \tag{10}$$

and

$$V_c^{(2)}(z^\ddagger) = \langle \wp^2 V(z^\ddagger)\rangle_c - \beta\Big[\langle \wp\bar{V}(z^\ddagger)\wp\bar{V}(z^\ddagger)\rangle_c - \langle \wp V(z^\ddagger)\rangle_c^2\Big], \tag{11}$$

where the symbol $\wp$ denotes the derivative along the reaction path, i.e. $\wp = \Sigma_{i=1}^N U_i\vec{\partial}_i$, and $\bar{V} \equiv \int_0^{\hbar\beta} \mathrm{d}\tau\, V[\boldsymbol{q}(\tau)]/\hbar\beta$. Also, in Eqs. (10) and (11) the general centroid-constrained averages are given by [1]

$$\langle f(z^\ddagger)\rangle_c = \left[\int\cdots\int \mathscr{D}\boldsymbol{q}(\tau) f[\boldsymbol{q}(0)]\,\delta(z^\ddagger - \tilde{z}_0) \times \exp\{-S[\boldsymbol{q}(\tau)]/\hbar\}\right] \times \left[\int\cdots\int \mathscr{D}\boldsymbol{q}(\tau)\,\delta(z^\ddagger - \tilde{z}_0) \times \exp\{-S[\boldsymbol{q}(\tau)]/\hbar\}\right]^{-1}. \tag{12}$$

From the above equations, the transition state $z^\ddagger$ is defined to be the position of the centroid-constrained free energy maximum along the rotated reactive barrier coordinate, while the rotated dividing surface is chosen to be normal to the direction of the eigenvector corresponding to the negative eigenvalue of the centroid-constrained force constant matrix. This procedure insures that the absolute value of the curvature $V_c^{(2)}(z^\ddagger)$ is maximized. Also, from Eq. (8) in terms of the rotated coordinates the centroid density can be evaluated using the saddle point expression

$$\rho_c(z_c) \approx \rho_c(z^\ddagger)\,\exp\Big[-\beta V_c^{(2)}(z^\ddagger)(z_c - z^\ddagger)^2\Big]. \tag{13}$$

If $V_c^{(2)}(z^\ddagger) < 0$, as it is under normal circumstances, then the imaginary part of the barrier partition function can be evaluated from Eqs. (7) and (13) using the steepest descent approach and the analytical continuation $z_c \to \mathrm{i}z_c$, thus yielding the reactive flux from Eq. (1) as

$$F \approx \nu\left(\frac{2\pi}{\beta\,|V_c^{(2)}(z^\ddagger)|}\right)^{1/2} \rho_c(z^\ddagger). \tag{14}$$

The general procedure for determining the dividing surface outlined in the previous paragraphs is difficult to implement for realistic non-linear many-body systems. This situation is partly because the evaluation of the centroid-constrained multidimensional path integral in Eq. (6) has to be iterated until the optimized dividing surface is found from the conditions on Eqs. (10) and Eq. (11). An alternative to the brute force numerical approach is the effective quadratic approximation [13] which replaces the real potential surface by a variationally optimized quadratic potential surface so that the centroid-constrained averages of Eqs. (10) and (11) reduce to multidimensional Gaussian averages. (A related, but somewhat different approach to this problem was taken in Ref. [8] which we will return to later.) For brevity, only the key results of this derivation will be given here without the explicit mathematical steps. Interested readers can find more details in previous papers [1,13,20].

To start, only reactive systems which are coupled to Gaussian (linearly responding) dissipative baths will be considered. The effective Hamiltonian for such a system can be written as [21]

$$H = \frac{p_q^2}{2m} + V(q) + \sum_{i=1}^{N}\left[\frac{p_i^2}{2m_i} + \tfrac{1}{2}m_i\omega_i^2\left(x_i - \frac{c_i}{m_i\omega_i^2}q\right)^2\right], \tag{15}$$

where $\{x_i, p_i\}$ are the effective bath variables and $\{m_i, \omega_i, c_i\}$ are the corresponding masses, frequencies, and coupling constants, respectively. Despite its simplicity, this Hamiltonian is capable of providing a physical description of many dynamical processes in the condensed-phase environment. The above Hamiltonian gives rise to a friction kernel for the motion along the coordinate q, the Laplace transform of which is given by

$$\hat{\eta}(s) = \sum_{i=1}^{N}\frac{c_i^2}{m_i\omega_i^2}\frac{s}{s^2+\omega_i^2}. \tag{16}$$

Within the context of Eq. (16), the goal is to map the activated barrier crossing problem onto an effective multidimensional quadratic system so that a closed-form expression for the rate constant can be obtained from Eq. (14). In this context, the Gaussian bath, the unstable mode, and the linear couplings can be solved from the extended optimal quadratic approximation (OQA) equations [13]:

$$\langle \nabla V(\bar{q}+\tilde{q})\rangle_{\mathrm{C}} = 0, \tag{17}$$

$$\langle \nabla : \nabla V(\bar{q}+\tilde{q})\rangle_{\mathrm{C}} = \mathbf{K}, \tag{18}$$

$$\langle \nabla_i \wp V(\bar{q}+\tilde{q})\rangle_{\mathrm{C}} = c_i, \tag{19}$$

where $\mathbf{K}$ is the optimized effective force constant matrix, ∇ is the partial derivative vector $\nabla_i = \partial/\partial q_i$, and $\wp$ is the derivative along the reaction path as defined in Eq. (11). Here, vectors and matrices are denoted by bold fonts, and optimized quantities are denoted by bars. The notation $\langle \cdots \rangle_{\mathrm{C}}$ above denotes a multidimensional Gaussian average centered at $\bar{q}$ with a centroid constraint on the reactive coordinate z. For example,

$$\begin{aligned}\langle V(\bar{q}+\tilde{q})\rangle_{\mathrm{C}} = &\left(\int \mathscr{D}\tilde{q}(\tau) V(\bar{q}+\tilde{q}(\tau))\,\delta\left(z^{\ddagger}-\tilde{z}_0\right)\right.\\ &\left.\times\exp\left(-\sum_n \tilde{q}_n\cdot\mathbf{C}_n^{-1}\cdot\tilde{q}_n/2\right)\right)\\ &\times\left(\int \mathscr{D}\tilde{q}(\tau)\,\delta\left(z^{\ddagger}-\tilde{z}_0\right)\right.\\ &\left.\times\exp\left(-\sum_n \tilde{q}_n\cdot\mathbf{C}_n^{-1}\cdot\tilde{q}_n/2\right)\right)^{-1}\end{aligned} \tag{20}$$

where $\tilde{q}_n$ is a Fourier mode of $\tilde{q}(\tau)$, defined as

$$\tilde{q}(\tau) = \sum_n \tilde{q}_n \exp(\mathrm{i}\Omega_n\tau) \tag{21}$$

and $\Omega_n = 2\pi n/\hbar\beta$. The Gaussian width factor matrix $\mathbf{C}$ in this case, can be formally expressed as

$$\mathbf{C}_n^{-1} = \beta m\Omega_n^2\mathbf{I} + \beta\mathbf{K}, \tag{22}$$

where $\mathbf{I}$ is the N-dimensional identity matrix. The centroid-constrained form of the OQA equations in Eqs. (17)–(22) are quite similar to the variational effective quadratic equations developed in Refs. [22–24] for other purposes, the key difference being that the centroid dividing surface is simultaneously optimized along with the variational parameters as described below.

A unitary matrix $\mathbf{U}$ can be found to diagonalize the mass-scaled force constant matrix $\bar{\mathbf{K}}$, giving the eigenfrequencies and the corresponding thermal Gaussian widths. According to the criterion implied from the rate theory of the previous paper [1], i.e. Eqs. (10) and (11), the planar dividing surface of Eq. (5) is determined by the direction of the unstable eigenvalue, which in this case is the eigenvector corresponding to the negative eigenvalue of the force constant matrix $\bar{\mathbf{K}}$. Thus, the optimized average positions $\{\bar{q}\}$, the optimized force constant matrix $\mathbf{K}$ and the unitary matrix $\mathbf{U}$ are variationally obtained as the self-consistent solution to the transcendental matrix equations Eqs. (17)–(22) in N-dimensional space. Subsequently, the reactive flux can be approximately obtained for the optimized quadratic reference frame of an unstable parabolic barrier coupled to a set of linear harmonic oscillators.

More explicitly, when the self-consistent quadratic approximation is applied to the Gaussian bath model described by Eq. (15), a direct substitution into Eqs. (17–22) leads to the following expressions:

$$\langle V'(q_{\mathrm{b}}+\tilde{q})\rangle_{\alpha} + c_0 q_{\mathrm{b}} = 0 \tag{23}$$

and

$$\mathbf{K} = \begin{pmatrix} -m\bar{\omega}_{\mathrm{b}}^2 + c_0 & c_1 & \cdots & c_N \\ c_1 & m_1\omega_1^2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ c_N & 0 & \cdots & m_N\omega_N^2 \end{pmatrix}, \tag{24}$$

where the renormalized barrier frequency $\bar{\omega}_{\mathrm{b}}$ is given by

$$\langle V''(q_{\mathrm{b}}+\tilde{q})\rangle_{\alpha} = -m\bar{\omega}_{\mathrm{b}}^2, \tag{25}$$

and the bath-induced coefficient c_0 is given by

$$c_0 = \sum_{i=1}^{N} \frac{c_i^2}{m_i\omega_i^2}. \tag{26}$$

In Eq. (25), the notation $\langle \ldots \rangle_{\alpha}$ stands for the constrained one-dimensional Gaussian average defined below in Eq. (33). Eq. (23) defines the effective barrier top, while Eq. (24) leads to the effective friction kernel.

The unitary transformation which diagonalizes the mass-scaled force constant matrix $\bar{\mathbf{K}}$ yields

$$\mathbf{U}\bar{\mathbf{K}}\mathbf{U}^{\dagger} = [\mathbf{I}\lambda^2], \tag{27}$$

with a negative eigenvalue λ_0^2 identified with the reactive barrier frequency, i.e. $-\lambda_0^2 = \lambda_{\mathrm{r}}^2$. Thus, the rotated coordinates can be related to the mass-scaled version of the old ones by the transformation

$$\{z, y_1, \cdots, y_N\} = U\{\tilde{q}, \tilde{x}_1, \cdots, \tilde{x}_N\}, \tag{28}$$

where the eigenvector corresponding to the negative eigenvalue λ_0, z, is identified as the reactive barrier coordinate, and the eigenvectors corresponding to the positive eigenvalues, $\{y_1, \cdots, y_N\}$, are identified as the stable-mode coordinates perpendicular to the reactive barrier coordinate. Therefore, the projection of the centroid-constrained Gaussian average in Eq. (20) onto the original barrier coordinate q defines a set of Gaussian widths for the Fourier path modes in the quadratic reference system, i.e. [13]

$$\alpha_{n \neq 0} = \frac{1}{\beta m \Omega_n^2 + \mathbf{K}_{00}} = \frac{1}{m\beta\left(\Omega_n^2 - \overline{\omega}_b^2 + \Omega_n \hat{\eta}(\Omega_n)/m\right)} \tag{29}$$

and

$$\alpha_0 = \frac{1}{m\beta}\left(\frac{U_{00}^2}{\lambda_r^2} - \frac{1}{\overline{\omega}_b^2}\right) = \frac{1}{\beta\overline{\omega}_b^2}(\chi - 1). \tag{30}$$

The zero-component of the Gaussian width α_0 in Eq. (30) results from the classical thermal fluctuations coming from the degrees-of-freedom other than the reactive barrier. The parameter χ in that equation is explicitly given by [25–27]

$$\chi - 1 = \frac{(\hat{\eta}(\lambda_r)/\lambda_r - \mathrm{d}\hat{\eta}(\lambda_r)/\mathrm{d}\lambda_r)/2m}{1 + (\hat{\eta}(\lambda_r)/\lambda_r + \mathrm{d}\hat{\eta}(\lambda_r)/\mathrm{d}\lambda_r)/2m} \tag{31}$$

and λ_r is related to $\overline{\omega}_b$ by the Grote–Hynes relation [11], but now for the effective parameters, i.e.

$$\lambda_r = \frac{\hat{\omega}_b^2}{\lambda_r + \hat{\eta}(\lambda_r)/m}. \tag{32}$$

With these definitions in hand, it is straightforward to explicitly express the averages appearing in Eqs. (23) and (25) as

$$\langle V(q_b + \tilde{q})\rangle_\alpha = \frac{1}{\sqrt{2\pi\alpha}} \int \mathrm{d}\tilde{q}\, V(q_b + \tilde{q}) \times \exp(-\tilde{q}^2/2\alpha), \tag{33}$$

where the Gaussian width α is given here by

$$\alpha = \sum_{n=-\infty}^{\infty} \alpha_n. \tag{34}$$

After solving the transcendental equations in Eqs. (23)–(25) self-consistently, and substituting the result into Eq. (14) with the prefactor ν also determined from the effective quadratic parameters, one arrives at the final expression for the quantum reactive flux

$$F = \frac{1}{h\beta}\frac{\lambda_r}{\omega_b}\prod_{n=1}^{\infty}\left[\frac{1}{1 - \overline{\omega}_b^2/\Omega_n^2 + \hat{\eta}(\Omega_n)/m\Omega_n}\right] \times Z_{\mathrm{bath}} G(\overline{\omega}_b, \alpha)\exp(-\beta V_0), \tag{35}$$

where $G(\overline{\omega}_b, \alpha)$ is the non-linearity correction, given by

$$G(\overline{\omega}_b, \alpha) = \exp\left[-\beta\langle \Delta V(q_b + \tilde{q}) - \tfrac{1}{2} m\omega_b \tilde{q}^2\rangle_\alpha\right], \tag{36}$$

and Z_{bath} is the bath partition function, given by

$$Z_{\mathrm{bath}} = \prod_{i=1}^{N} \frac{1}{2\sinh(\hbar\beta\omega_i/2)}. \tag{37}$$

In the above equations, the effective Kramers–Grote–Hynes factor λ_r/ω_b represents the modification of the reactive barrier frequency due to the coupling to the Gaussian bath, the quantum effects, and the non-linearity of the potential barrier, while the term in the square bracket represents an effective multi-dimensional quadratic quantum correction [3]. The term V_0 in Eq. (35) is the value of the potential at the classical barrier top, while ΔV in Eq. (36) equals $V(q) - V_0$.

3. Discussion

The equation derived in Eq. (35) has several appealing characteristics, four of which we will now describe. First, the result is valid for all temperatures, both above and below crossover, as long as the second derivative $V_c^{(2)}(z^\ddagger)$ in Eq. (11) is negative [1]. This property arises from the variational principle implicit in the OQA equations [13] which, in turn, insures that the variational parameters will adjust themselves to yield a finite result for the rate. Second, in the highly quantum mechanical limit of Eq. (35), the classical contribution α_0 of Eq. (30) can be ignored compared to the purely quantum contributions α_n. Thus, $\alpha \approx \sum_{n \neq 0} \alpha_n$ in Eqs. (23), (25), (33) and (35), and, as a result, the variational PI-QTST theory of Voth [8] is recovered. Third, in the classical limit, $\alpha = \alpha_0$ and Eq. (35) becomes an effective Kramers–Grote–Hynes equation which includes the influence of the barrier non-linearity. The fourth characteristic, and perhaps the most appealing, is the fact that Eq. (35) has a relatively simple form, keeping in the spirit of both the classical Kramers–Grote–Hynes [11,14] and quantum Wolynes [3] results for a parabolic barrier coupled to a Gaussian bath, while at the same time extending those theories to include the effects of barrier non-linearity and tunneling.

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