Unified approach to the quantum-Kramers reaction rate

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Reactive processes hindered by one or a series of intervening potential barriers play an ubiquitous role in chemical and physical sciences.[1] Over the last few years there has been a flurry of activity in order to incorporate quantum effects (at all temperatures) into the rate theory.[1(a),2] In absence of quantum tunneling one deals with generalized Kramers theory.[1,3] In this context, it should be emphasized that (position)-diffusion controlled Kramers theory is equivalent[1(a),4] to classical many-body transition state theory.[5] The inclusion of quantum tunneling into the Kramers theory is more sophisticated. In the high temperature regime, quantum effects of a reacting system coupled to an environment (i.e., dissipation) have been studied first by Wolynes[6]; his result has since been rederived via other high temperature methods by several authors.[7] In particular, Pollak[7(c)] has rederived the result of Wolynes by use of standard many-body quantum transition state theory (QTST) in which classical partition functions are simply substituted by their quantum counterparts and the classical transmission of "one" above the barrier threshold $E = E_b$ is substituted by a temperature averaged parabolic transmission coefficient $\kappa = \frac{1}{2}\hbar\beta\mu/\sin(1/2\hbar\beta\mu)$ (i.e., the Wigner correction[8]) wherein μ denotes the relaxation (angular) frequency along the reaction path at the saddle point. All of these high temperature quantum rate theories, however, exhibit a divergence at the crossover temperature $T_0 = \hbar\mu/(2\pi k)$,[9] above which activated events dominate over tunneling transitions. A quantum rate theory covering all temperatures has been put forward in terms of the "bounce" formalism for dissipative metastable systems.[1(a),2] In doing so, one uses path integral methods for the reduced dynamics and expresses the rate in terms of an imaginary part for the free energy F (i.e., Im F). Within this method, the many-body quantum rate Γ is given by the two expressions[1(a),2,10,11]

$$\Gamma = -\frac{2}{\hbar}\,\mathrm{Im}\,F\begin{cases}1; & T \leqslant T_0 \quad (1a)\\ \dfrac{T_0}{T}; & T > T_0 \quad (1b)\end{cases}$$

which match smoothly at $T = T_0$.[11] It is rather unfortunate, however, that expression (1b) cannot be uniquely derived from the theory for temperatures $T \leqslant T_0$. The presence of the additional factor (T_0/T) has thus triggered some criticism within the scientific community which in some cases went so far as to question[12] the validity of the results. It is, therefore, highly desirable to have a *unique* approach covering both high temperatures and low temperatures on the same basis. Such an approach indeed can be given. Our starting point will be based on the nonseparable many-body QTST put forward by Miller in 1975.[13] By use of the semiclassical approximation the quantum reactive flux yields for the rate Γ the expression[13] $[E_T = E - \Sigma_{i=2}^{N}(n_i + 1/2)\hbar\omega_i(E_T)]$

$$\Gamma = Z_0^{-1}\frac{1}{2\pi\hbar}\int_0^\infty dE\exp(-\beta E) \times \sum_{(n_2,\ldots,n_N)=0}^{\infty}\{1+\exp[B(E_T)/\hbar]\}^{-1}. \quad (2)$$

Z_0 is the partition function of the metastable state and the sum in Eq. (2) is a cumulative reaction probability. $B(E_T)$ denotes the action along an unstable periodic orbit $q_1(\tau)$, $\tau = it$, with period $T(E_T)$ at energy E_T available for the reactive mode on the upside-down potential surface of N coupled degrees of freedom. The set $\{\omega_i(E_T)\}$ are dynamical stability frequencies.[13] We assume that the one-dimensional reaction coordinate $q_1 = q$ moves in a metastable potential $V(q)$ and obeys the classical, dissipative equation of motion:

$$\ddot{q} + \int_0^t ds\,\gamma(t-s)\dot{q}(s) + \frac{1}{M}\frac{\partial V}{\partial q} = 0. \quad (3)$$

These dynamics can be derived from the underlying total Hamiltonian of reactive system coupled bilinearly to a bath of harmonic oscillators [e.g., see Eq. (8) in Ref. 4]. The whole crux within the approach in Eq. (2) consists, of course, in the evaluation of the action $B(E_T)$, period $T(E_T)$, and stability frequencies $\omega_i(E_T)$. Guided by some results of recent work[14-16] we can now evaluate Eq. (2) further: For temperatures $T > T_0$ the integral in Eq. (2) is dominated by energies near the barrier top, $E_T \geqslant E_b$. In that regime we can use a harmonic, local adiabatic approximation:

$$\omega_i(E_T) \cong \lambda_i^*, \quad T(E_T) \cong 2\pi/\mu. \quad (4a)$$

Here the set $\{\lambda_i^*\}$ are the normal mode (angular) frequencies of the transverse coordinates at the saddle point $q_1 = q_b$ and μ is given by the positive solution of $\mu = [\frac{1}{4}\hat{\gamma}^2(\mu) + \omega_b^2]^{1/2} - \frac{1}{2}\hat{\gamma}(\mu)$, with $\omega_b^2 = 1/M\,|V''(q = q_b)|$, and $\hat{\gamma}(\omega)$ denotes the Laplace transform of $\gamma(t)$ [see Refs. 3(b) and 3(c)]. The action in full phase space will be approximated by the dissipation-modified action for a parabolic barrier,[17] i.e.,

$$B(E_T) \cong \left[E_b + \sum_{i=2}^{N}(n_i + 1/2)\hbar\lambda_i^* - E\right]2\pi/\mu. \quad (4b)$$

Note that $\{\lambda_i^*\}$ as well as μ change as a function of the coupling strength $\hat{\gamma}(\mu)$. Inserting Eqs. (4a) and (4b) into Eq. (2), and interchanging the integration in Eq. (2) with the sums then yields the known quantum rate result,[6,7] i.e., for $T > T_0$,

$$\Gamma = \left\{\frac{\mu}{\omega_b}\frac{\omega_0}{2\pi}\exp(-\beta E_b)\right\} \times \prod_{n=1}^{\infty}\frac{\omega_0^2 + n^2\nu^2 + n\nu\hat{\gamma}(n\nu)}{-\omega_b^2 + n^2\nu^2 + n\nu\hat{\gamma}(n\nu)}, \quad (5)$$

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where $\nu = 2\pi/\hbar\beta$ and $\omega_0^2 = (1/M)V''(q = q_0)$ is the frequency in the well bottom. Equation (5) agrees with Eq. (1b).[2,11] For the last part in Eq. (5) we made use of an identity, derived originally by Pollak [see Eqs. (20) and (25) in Ref. 7(c)], that involves the partition function $Z_0^{-1} = \prod_{i=1}^{N} [2\sinh(\frac{1}{2}\hbar\beta\lambda_i^0)]$ at the well bottom.

At temperatures $T \sim T_0$, the integral in Eq. (2) becomes dominated by energies $E_T < E_b$, where $B(E_T) > 0$. Expanding the action near $E_T = E_b$ we set more accurately for $E_T < E_b$ with $T' = -B''(E_b)$:

$$B(E_T) \cong (E_b - E_T)\frac{2\pi}{\mu} + \frac{1}{2}(E_b - E_T)^2|T'|. \quad (6)$$

By use of Eqs. (4a) and (6) we now evaluate the integral in Eq. (2) to arrive, at the explicit result[18] [$\mathrm{Erfc}(x) = 2\pi^{-1/2}\int_{-\infty}^{x} dy \exp -y^2$]

$$\Gamma = \frac{\sinh[(1/2)\hbar\beta\lambda_1^0]}{(2\pi\hbar|T'|)^{1/2}} \prod_{i=2}^{N} \frac{\{2\sinh[(1/2)\hbar\beta\lambda_i^0]\}}{\{2\sinh[(1/2)\hbar\beta\lambda_i^*]\}}$$
$$\times \mathrm{Erfc}\left\{\left(\frac{\hbar}{2|T'|}\right)^{1/2}(\beta - \beta_0)\right\}$$
$$\times \exp\left[-\beta E_b + \frac{\hbar}{2|T'|}(\beta_0 - \beta)^2\right], \quad T \sim T_0. \quad (7)$$

This rate is shown to *precisely equal* the result of the bounce-crossover theory[11] using Eq. (1a). Near $T \gtrsim T_0$ the expression in Eq. (7) matches the expression in Eq. (5). At lower temperatures, $T \ll T_0$, the action must be evaluated by taking the *full* nonlinearity into account.[16] In that regime, however, the integral in Eq. (2) can be evaluated by a steepest descent approximation.[16]

In conclusion, many-body QTST in Eq. (2) complemented by the set of equations (4) and (6) provides a *unified* approach to the quantum Kramers rate[1(a),2] that works at all temperatures.

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[16]P. Hänggi, Z. Phys. B **68**, 181 (1987); in particular see Eq. (4.9) where T' should read $|T'|$. For very weak dissipation, the error for the many-body QTST result in Eq. (2), induced by deviations from the Boltzmann distribution, becomes exponentially smaller with decreasing temperature.

[17]We address the WKB limit [i.e., $(\hbar\mu/E_b) \ll 1$] and weak noise $kT/E_b \ll 1$. Thus, corrections to the harmonic approximation for $\omega_i(E_T)$ and $B(E_T)$ yield for $T > T_0$ only small corrections of the order $kT_0/E_b \ll 1$ to the leading prefactor in Eq. (5).

[18]In doing the integration we neglect small WKB corrections [$\propto \sqrt{(\hbar\mu/2\pi E_b)}\exp -(2\pi E_b/\hbar\mu)$]. Anharmonic corrections for $\omega_i(E_T)$ again lead to negligible prefactor corrections of order kT_0/E_b. Note that near $T \sim T_0$, the prefactor is proportional to the inverse WKB parameter, i.e., $(2\pi\hbar|T'|)^{-1/2}/\mu \propto (E_b/\hbar\mu)^{1/2} \gg kT_0/E_b$.