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Quantum Theory of Activated Events in Condensed Phases

Peter G. Wolynes
School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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The quantum analog of Kramers's classical theory of the rate of activated events is presented. By means of a path-integral approach, the correlation function expression for the rate of barrier crossing by a quantum mechanical particle coupled to a heat bath is evaluated for finite temperatures. Tunneling effects are dramatically diminished by the frictional influence of the heat bath.

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The dynamics of activated events in which a free-energy barrier must be surmounted plays a central role in many areas of physical science, most notably chemical kinetics. In this paper we turn our attention to the quantum mechanical description of activated events in condensed phases. This problem also has several aspects which are relevant to other problems in the dynamics of quantum mechanical systems with dissipation.

Since Kramers,[1] a popular model of an activated event has been a particle moving classically in a double-well potential while coupled to a heat bath. Recent studies[2-4] have clarified several points about the influence of the heat bath on an activated event. First, it can modify the effective potential on which the dynamics takes place. Second, it provides a dissipative mechanism which alters the course of an activated event materially. When the interaction with the heat bath is weak, the rate, classically, is limited by the rate at which energy can be supplied to the reactive degree of freedom. When the interaction is strong the rate is limited by the Brownian diffusion of the reaction coordinate. Because of these effects the traditional transition-state theory[5] of the rates of activated events is often not quantitatively accurate. Although the classical description is doubtless adequate for many situations, significant quantum effects appear when light particles are being transferred or when the temperature is low. Examples include proton transfer reactions[6] in which large isotope effects are observed,[7] tunneling in low-temperature solids,[8] and, more speculatively, quantum nucleation in various field theories with unstable vacuums.[9]

The model that we consider is the quantum analog of Kramers's model, a quantum mechanical particle in a double well coupled to a Gaussian heat bath providing dissipation and fluctuating forces. The analysis starts with an expression for the rate constant originally derived by Yamamoto using linear response theory.[10] This correlation function expression can be evaluated with use of a path-integral representation of the thermal density matrix and the time evolution operator.[11] The path-integral approach is convenient because it allows the inclusion of the effect of the heat bath as an influence functional in much the same way as in Feynman's theories of the polaron[12] and quantum noise phenomena[13] and because it facilitates a semiclassical approximation, making the comparison with classical theories easy. Following Kramers, it is assumed that the time correlation function can be evaluated with use of a potential accurate only near the barrier top—an inverted parabola. While this is a rather accurate approximation for moderate to high damping, in the classical regime, its validity is more limited in the quantum regime. Nevertheless, with this approximation the analysis can be carried out exactly. In the classical limit the result reduces to that given by the Grote-Hynes generalization of Kramers's theory to frequency-dependent friction.[4] In the limit of zero damping the theory reduces to the simple forms of quantum transition-state theory used for many years to interpret kinetic isotope effects.[14] It is also shown that quantum tunneling effects are diminished by the damping from the heat bath. A similar conclusion has been reached for the zero-temperature case independently in a heuristic development due to Caldeira and Leggett.[15] The present finite-temperature theory, in contrast, is most accurate at high temperatures. Ishioka[16] has also come to this conclusion for high temperatures on the basis of a Wigner-Kirkwood expansion of a quasiphenomenological master equation. His analysis appears to be flawed, however. In his derivation of the Wigner-Kirkwood expansion he incorrectly assumes that the equilibrium reduced density matrix is unchanged by the coupling to the heat bath and he solves his resulting master equations with an expansion valid only at high damping.

The rate constant can be represented as the limit of the Kubo-transformed reactive-flux correlation function[10]:

$$k=\lim_{t\to\infty}k_K(T)$$

$$=\frac{1}{\beta\hbar}\lim_{t\to\infty}\int_0^{\beta\hbar}\frac{d\eta\langle\xi(0)\dot{\xi}(t+i\eta)\rangle}{\langle\delta\xi(0)\rangle^2}, \tag{1}$$

where ξ is a unit Heaviside function measuring the occupancy of one side of the double well, β is the inverse temperature, and the denominator is the mean square fluctuation in the occupancy. We mean by the limit that there is a plateau value[2] which is well defined when there is a clear separation of time scales between the chemical reaction rate and the inherent molecular time scale. As noted by Pechukas,[17] this expression already illustrates a difference from the classical case. In classical mechanics the initial value of the flux correlation function equals the rate constant given by transition-state theory. The quantum reactive flux vanishes initially because of the cyclic invariance of the trace, and rises on the thermal time scale βh. Physically, this difference arises because the linear response preparation of the initial nonequilibrium state classically leads to a sharp discontinuity in the density at the barrier top, which is smeared out wave mechanically by diffraction effects. If the thermal time scale and the dynamical time scales are comparable quantum transition-state theory becomes somewhat ambiguous.

In order to carry out the averaging over the bath degrees of freedom, the thermal density matrix and the evolution operators are represented by a functional integration over the trajectories of the entire system. Because of the trace, only paths periodic on the interval 0 to $i\beta h$ are included. The reactive-flux correlation function can be conveniently written in terms of $G(x_1,t_1;x_2,t_2)$, the restricted sum over paths passing through x_1 at time t_1, and x_2 at time t_2; x labels the reaction coordinate. When G is written as a path integral, the integration over the bath degrees of freedom can be explicitly carried out in two cases: if the bath is made up of harmonic oscillators, or if each of the many individual degrees of freedom of the heat bath is weakly coupled to the reaction coordinate. G can then be expressed as a path integral in which the path probability amplitude is modified by a Gaussian influence functional[13]:

$$G=\int\mathfrak{D}x(t)\exp[(iS_0/\hbar)(x)+(i/\hbar)\iint dt\,ds\,\gamma(t,s)x(t)x(s)]. \tag{2}$$

Here $S_0(x)$ is the Lagrangian for the bare double-well system; the additional influence phase contains information about the dissipation arising from the coupling to the heat bath. It is important to note a difference between our way of using the influence functional and the way it is used by Feynman and Vernon. They assume that initially the system can be considered to be in a state in which the system and bath are independent so that the density matrix factorizes. The exact equilibrium density matrix does not factorize so that in evaluating time correlation functions the influence phase couples dynamics for both real and imaginary time. An amusing but familiar feature of quantum mechanics is that dissipation and thermodynamic effects are intimately connected, unlike the classical situation where damping and structural, thermodynamic effects of the heat bath can be clearly separated.

A semiclassical approximation to G can be found by the usual steepest-descent method applied to the path integral.[18] Rather than carry out this analysis for a general potential, we now make an approximation motivated by Kramers's classical theory. When the damping is moderately strong, the correlation function $\langle\xi(0)\dot{\xi}(t)\rangle$ classically reaches its plateau value in such a short time that the particle does not leave the vicinity of the barrier top. We therefore use the inverted harmonic oscillator potential with a frequency fitting the actual potential at the barrier top to evaluate the quantum mechanical correlation function. For an inverted oscillator potential the semiclassical analysis is exact and leads to a Gaussian form for G. Because of the Gaussian nature of G, it is possible to express the result in terms of the response function satisfying the classical equation

$$d^2g/dt^2-\omega^{\dagger 2}g+\int\gamma(t,s)g(s)\,ds=\delta(t-t') \tag{3}$$

over the time interval 0 to $i\beta\hbar$ subject to periodic boundary conditions. $i\omega^\dagger$ is the pure imaginary, undamped frequency of the inverted oscillator. Because of the periodicity this response function can by expanded in a Fourier series:

$$g(t)=\sum_{N=0}^{\infty}\frac{\cos\omega_N t}{-\omega_N^2-\omega^{\dagger 2}+i\zeta(\omega_N)\omega_N}, \tag{4}$$

where $\omega_N = 2\pi N/i\beta\hbar$ and $\zeta(\omega)$ is the frequency-dependent drag coefficient which is related to γ through a finite Fourier transform. With $g(t)$ in hand, the reactive flux (before the Kubo transform is performed) can be written as

$$k(t) = -\frac{1}{2\pi}\left(\frac{g_+}{g_-}\right)^{1/2}\frac{1}{g_+}\frac{dg_+}{dt}\left[\prod_{N=-\infty}^{\infty}\left(\frac{-\omega^{\dagger 2}-\omega_N^{\,2}+i\zeta(\omega_N)\omega_N}{\omega_0^{\,2}-\omega_N^{\,2}+i\zeta(\omega_N)\omega_N}\right)\right]^{-1/2}\exp(-\beta E^\dagger), \tag{5}$$

where $g_\pm = g(0) \pm g(t)$, $E^\dagger$ being the barrier height, ω_0 the frequency associated with the reactant well. The thermodynamic prefactor in the rate expression is a product over the Fourier modes.

Most often $\zeta(\omega)$ can be adequately represented as a rational function, in the upper half complex-ω plane. Then both the infinite products for the traces and the infinite series for the response function can be analytically computed. If the poles of the frequency-dependent susceptibility are at $\omega^{(j)}$ with residues A_j, the response function is given as a finite sum of hypergeometric functions[19]:

$$g(t) = \sum_j \frac{A_j}{2\omega^{(j)}}\left[{}_2F_1\left(1, \frac{-i\omega^{(j)}\beta\hbar}{2\pi}, 1-\frac{i\omega^{(j)}\beta\hbar}{2\pi}; e^{2\pi t/\beta\hbar}\right) + {}_2F_1\left(1, \frac{-i\omega^{(j)}\beta\hbar}{2\pi}, 1-\frac{i\omega^{(j)}\beta\hbar}{2\pi}; e^{-2\pi t/\beta\hbar}\right)\right] \tag{6}$$

and the infinite products can be represented as gamma functions.

The large-time asymptotic properties of the hypergeometric functions determine the overall rate constant. For each of the poles of the susceptibility lying in the upper half-plane both hypergeometric functions vanish asymptotically. There is one unstable mode of motion at the barrier top, however. This gives a pole in the lower half-plane at $-i\omega_u$ which leads to an exponentially growing contribution to $g_\pm$. Using the gamma function representation of the infinite products, it follows that

$$k = -\frac{\omega_u\omega^\dagger}{2\pi\omega_0}\exp(-\beta E^\dagger)\frac{\prod_j \Gamma(-i\omega^{\dagger(j)}\beta\hbar/2\pi)}{\prod_j \Gamma(-i\omega_0^{(j)}\beta\hbar/2\pi)}. \tag{7}$$

The $\omega^{\dagger(j)}$'s are the poles of the susceptibility for motion near the barrier top. This is the main result of the paper.

In the classical limit this tunneling factor approaches unity leading to the result found by Grote and Hynes.[4] In the zero-damping limit the poles in the susceptibility occur in pairs, giving the traditional quantum transition-state result,

$$k = \frac{\omega_0}{2\pi}\exp(-\beta E^\dagger)\frac{(\beta\hbar\omega^\dagger/2)/\sinh(\beta\hbar\omega^\dagger/2)}{(\beta\hbar\omega_0/2)/\sinh(\beta\hbar\omega_0/2)}.$$

This result diverges for $\beta\hbar\omega^\dagger = 2\pi$. Traditional derivations based on one-dimensional scattering theory[14] indicate that this arises from the fact that below this temperature the tunneling probability for an inverted harmonic oscillator potential does not decrease as rapidly as the Boltzmann factor increases, as the energy of an incoming wave decreases. Despite the singularity, derivations of the undamped result via scattering theory show that this result is accurate to within a few percent[20] at $\beta h\omega^\dagger = \pi$. It is reasonable to expect similar accuracy for the damped results for temperatures as low as $\beta = \pi/h\omega_u$. By expanding the gamma functions in powers of their argument it is easy to see that according to the present approximation the tunneling correction to order $\hbar^2$ is unchanged by the damping.

In Fig. 1 representative results for the rate constant as a function of temperature for various values of the drag coefficient are plotted. Damping profoundly decreases the tunneling effects, and should therefore be taken into account in the interpretation of kinetic isotope effects in condensed phases. The results in Fig. 1 involve the assumption that the drag is independent of frequency. If a Lorentzian frequency dependence of the friction is assumed, one finds that the tun-

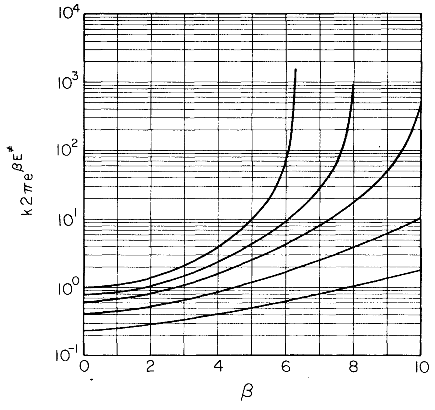

FIG. 1. The Arrhenius prefactor of the rate constant $[2\pi k\exp(\beta E^\dagger)]$ is plotted as a function of the dimensionless inverse temperature β for several values of the drag coefficient. The magnitudes of both the well and barrier frequencies are taken to be unity. The curves from top to bottom correspond with $\zeta = 0.01$, 0.5, 1, 2, and 4 in the same units.

neling is increased as the characteristic time scale of the friction is increased, at fixed zero-frequency friction. For finite friction these results exhibit divergences at sufficiently low temperature just as in the frictionless case. Further studies that take into account the potential away from the barrier-top region are then warranted. Outside the low-temperature regime we also expect deviations from the present result for sufficiently low damping because the classically rate-limiting energy-dissipation processes are not adequately described by motion near the top of the barrier.

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