# Study of the Coupling Dependence of Relaxation Rates in a Model of Low-Temperature Tunneling Dynamics

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A model of low-temperature tunneling dynamics in a double-well system is studied. The various relaxation rates in the problem are computed as a function of the system—bath coupling strengths. An interpretation of frictional effects is made that permits comparison between the quantum tunneling system and classical and semiclassical barrier hopping models of excitation transfer in double-well systems.

#### Introduction

The dynamics of a tunneling system interacting with a heat bath of harmonic oscillators has been extensively studied in a model that considers the lowest two levels of a symmetric double-well system, with the coupling taken to be linear in both the system and bath coordinates.<sup>1-4</sup> Parris and Silbey<sup>5</sup> treated the more general case of a tunneling system composed of two coupled sets of vibrational levels, thus allowing for excited state dynamics in the double-well problem. Here we study in detail a specific case of the problem treated by Parris and Silbey, namely the symmetric double-well system composed of four levels, with tunneling between the upper vibrational levels only (see Figure 1). In particular, we examine in detail the dependence of the various rates in the problem as a function of the coupling parameters that mediate the system–bath interactions.

We wish to study this simple model for a variety of reasons. First, by providing solutions to the dynamics of the tunneling particle, complete with explicit expressions for the various rates in the problem, we can hope to make contact with experiments probing both the temperature and coupling strength dependence of low-temperature systems that contain an interplay between tunneling and vibrational relaxation.<sup>6</sup>

Our study may also stand on its own as an example of a simple quantum system with relaxation properties that depend on both tunneling and vibrational dynamics. In this light, our system may be viewed as a quantum tunneling analog of the double-well extensions of Kramers problem.<sup>7,8</sup> The classical Kramers problem treats the transport of a Brownian particle over a barrier due to interactions with a heat bath. The problem has approximate analytical solutions in two limiting situations. When the frictional coupling between the particle and the bath is small, thermal equilibration within the well is very slow relative to the dynamics of the particle near the barrier top. When the damping is large, the well is assumed to be in thermal equilibrium, and the rate-limiting step in the escape process is the flux near the barrier top. Thus, analytical solutions can be found when there is a clear separation of time scales between thermal well equilibration and escape dynamics near the barrier peak.

Our model contains quantum analogs to classical well equilibration and barrier flux. In our model, intrawell vibrational relaxation mirrors the classical equilibration of the particle in the well, while tunneling between excited vibrational states is analogous to classical barrier flux. Frictional effects are introduced by coupling the particle to a bath of harmonic oscillators. We wish to show the similarities and differences



**Figure 1.** Energy level diagram of the tunneling part of the Hamiltonian (eq 1). *j* indicates the tunneling matrix element in the upper (n = 1) vibrational manifold. 2j indicates the tunnel splitting of the upper vibrational manifold.  $\Omega$  is the energy difference of the two manifolds.  $1/\tau$  and  $1/\tau'$  are the intramanifold relaxation rates caused by interaction with the phonon bath.  $F_{01}$  and  $F_{10}$  are the intermanifold relaxation rates caused by the interaction with the phonon bath.

between this simple quantum model and the classical Kramers problem.

Recently, studies have integrated low-temperature quantum effects and classical barrier hopping.<sup>4,6,8,9</sup> These "quantum Kramers" problems include tunneling corrections to the classical rate of escape and show explicitly the crossover between the classical and quantum regimes. In contrast, we focus purely on the quantum dynamics, so that comparisons may be made with the analogous classical problem.

### The Hamiltonian

Our Hamiltonian may be written as  $(\hbar = 1)$ 

$$H = \sum_{q} \omega_{q} a_{q}^{+} a_{q} + \Omega I_{1} + J \sigma_{1x} + V_{0} \sigma_{0z} + V_{1} \sigma_{1z} + V_{R}$$
(1)

where

$$I_1 = |\mathbf{R}_1\rangle\langle\mathbf{R}_1| + |\mathbf{L}_1\rangle\langle\mathbf{L}_1| \tag{2}$$

$$\sigma_{1x} = |\mathbf{R}_1\rangle\langle \mathbf{L}_1| + |\mathbf{L}_1\rangle\langle \mathbf{R}_1| \tag{3}$$

$$\sigma_{nz} = |\mathbf{L}_n\rangle\langle\mathbf{L}_n| - |\mathbf{R}_n\rangle\langle\mathbf{R}_n|; \quad (n = 0, 1)$$
(4)

$$V_n = \sum_q g_{qn}(a_q + a_q^+); \quad (n = 0, 1)$$
 (5)

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 $V_{\rm R}$  is the, as yet, unspecified vibrational relaxation term. Such a Hamiltonian is a four-level extension of the spin-boson Hamiltonian<sup>1</sup> that includes vibrational relaxation.<sup>4</sup> Our Hamiltonian models a double-well system consisting of left and right sites. Each site contains two separate vibrational manifolds. The manifolds are linearly coupled to the displacement of the modes of a bath of harmonic oscillators, with a coupling strength  $g_{qn}$ , where q lables the mode of the bath and n lables the state of the vibrational manifold (n = 0, 1). The energy separation of the manifolds is given by  $\Omega$ , which is assumed to be larger than any other energy in the problem, with the exception of the cutoff frequency ( $\omega_c$ ) of the bath. Tunneling occurs only between excited vibrational levels. Vibrational relaxation is assumed to occur in the vibrational manifolds of a given site only (i.e. the left and right sites are not vibrationally coupled). Figure 1 shows an energy level diagram of our system.

In order to facilitate the calculation of relaxation rates in the problem, we perform a variational polaron transformation<sup>2</sup> on the Hamiltonian (eq 1). The unitary operator

$$U = \prod_{n} U_{n}; \quad (n = 0, 1)$$
(6)

$$U_n = \exp\left[-\sigma_{nz} \sum_{q}^{f_{qn}} (a_q - a_q^+)\right]$$
(7)

effects the transformation. We will be concerned with calculating the mean position of the tunneling particle,

$$\langle Q(t) \rangle = \langle \sigma_{0z}(t) + \sigma_{1z}(t) \rangle \tag{8}$$

Since  $\sigma_{0z}$  and  $\sigma_{1z}$  commute with U, we note

$$\langle Q(t) \rangle = Tr[(\sigma_{0z} + \sigma_{1z})Q(t)] = Tr[(\sigma_{0z} + \sigma_{1z})(UQ(t)U^{+})]$$
 (9)

We may thus define a reduced density matrix

$$\sigma(t) = Tr_b[U\varrho(t)U^+] \tag{10}$$

from which the dynamics of the tunneling particle are calculated. The transformation thus defines an appropriate zeroth-order Hamiltonian from which perturbation theory can be used.

The variational constants  $f_{qn}$  are chosen to minimize the free energy. In the absence of tunneling and the vibrational relaxation term, the Hamiltonian is diagonalized by the choice  $f_{qn} = g_{qn}$  (since there is no tunneling in the lower vibrational manifold,  $f_{0n} = g_{0n}$ ). When the coupling of the tunneling system to the bath vanishes,  $f_{qn} = 0$ . In the general case we expect  $f_{qn}$ to fall between these two limiting values, while providing an upper bound on the free energy.

After switching to a basis

$$|1\rangle = \frac{1}{\sqrt{2}} (|\mathbf{L}_0\rangle + |\mathbf{R}_0\rangle) \tag{11}$$

$$2\rangle = \frac{1}{\sqrt{2}} (|\mathbf{L}_0\rangle - |\mathbf{R}_0\rangle) \tag{12}$$

$$|3\rangle = \frac{1}{\sqrt{2}}(|\mathbf{L}_1\rangle + |\mathbf{R}_1\rangle) \tag{13}$$

$$4\rangle = \frac{1}{\sqrt{2}} (|\mathbf{L}_1\rangle - |\mathbf{R}_1\rangle) \tag{14}$$

the transformed Hamiltonian may be written

$$\tilde{H} = \tilde{H}_0 + \tilde{V} + \tilde{V}_R \tag{15}$$

$$\tilde{H}_0 = (\Omega + j)|3\rangle\langle 3| + (\Omega - j)|4\rangle\langle 4| + \sum_n \omega_n a_n^+ a_n$$
(16)

$$\tilde{V} = \Psi(|3\rangle\langle 3| - |4\rangle\langle 4|) + \Phi|4\rangle\langle 3| + \Phi^+|3\rangle\langle 4| \quad (17)$$

$$\tilde{V}_{\rm R} = \gamma [b^+|1\rangle\langle 3| + b|3\rangle\langle 1| + b^+|2\rangle\langle 4| + b|4\rangle\langle 2|]$$
(18)

where

$$\Psi = \frac{1}{2}(\psi_1 + \psi_1^+) \tag{19}$$

$$\Phi = \left[\varphi_1 + \frac{1}{2}(\varphi_1 - \varphi_1^+)\right]$$
(20)

$$\psi_1 = J \exp\left[-2\sum_n \frac{f_{1n}}{\omega_n} (a_n - a_n^+)\right] - j$$
 (21)

$$j = J \exp\left[-2\sum_{n} \left(\frac{f_{1n}}{\omega_n}\right)^2 \coth\left(\frac{\beta\omega_n}{2}\right)\right]$$
(22)

$$\varphi_1 = \sum_n (g_{1n} - f_{1n})(a_n^+ + a_n) \tag{23}$$

$$f_{1n} = \frac{g_{1n}}{\left(1 + \frac{2j}{\omega_n} \coth\left(\frac{\beta\omega_n}{2}\right) \tanh(\beta j)\right)}$$
(24)

and b ( $b^+$ ) is an annihilation (creation) operator for the mode of the bath responsible for vibrational relaxation (e.g. an optical mode of the lattice). For our choice of the vibrational relaxation term,  $\tilde{V}_{\rm R}$ , we keep only the energy-conserving terms and assume that there is a single mode in resonance with the transition energy  $\Omega$ .<sup>10</sup> To keep the discussion as simple as possible, only one-phonon terms are retained. In a more realistic treatment, multiphonon processes would be included.<sup>10</sup> Note that  $\gamma$  is a coupling strength with units of energy.

The vibrational (one-phonon) part of the Hamiltonian is postulated in a specific form *after* the unitary transformation is made on the Hamiltonian. Since the thermal average of  $\tilde{V}_R$  is zero, no modification of the  $f_{qn}$  is necessary.<sup>2</sup> Our form for  $\tilde{V}_R$ will clearly be accurate only in the weak-coupling limit for vibrational relaxation. In the strong-coupling limit, we must view our form of  $\tilde{V}_R$  as merely suggestive of the physics we are trying to model. Furthermore, the vibrational scattering rates are limited by the vibrational energy splitting  $\Omega$ . Since these rates must be smaller than  $\Omega$  (or else distinct vibrational states could not be resolved), we need not worry about incorrect use of weak coupling equations (Redfield equations) for all physically acceptable values of  $\gamma$ .

The variational polaron transformation defines a partitioning of the Hamiltonian into "new" unperturbed  $(\tilde{H}_0)$  and interaction  $(\tilde{V} + \tilde{V}_R)$  parts. Note, however, that a large part of the original interaction may be contained in  $\tilde{H}_0$ . This partitioning of the Hamiltonian makes the use of low-order perturbation theory on the "new" interaction part possible even in the strong-coupling limit, since much of the "old" interaction is placed into  $\tilde{H}_0$ . In our transformed picture, we note that the tunneling matrix

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element (eq 22) is "renormalized" by a Franck-Condon factor,<sup>2</sup> which reduces the tunneling rate between sites.

### **Dynamics**

Standard Redfield theory<sup>11</sup> is used to find equations of motion for the population difference between states of the left and right wells:

$$\langle Q(t) \rangle = s_{0x}(t) + s_{1x}(t) \tag{25}$$

$$s_{0x}(t) = \langle 1|\sigma(t)|2\rangle + \langle 2|\sigma(t)|1\rangle$$
(26)

$$s_{1x}(t) = \langle 3|\sigma(t)|4\rangle + \langle 4|\sigma(t)|3\rangle \tag{27}$$

where  $\sigma(t)$  is the time-dependent reduced density operator of the system. Defining

$$s_{0y} = i(\langle 1|\sigma(t)|2\rangle - \langle 2|\sigma(t)|1\rangle)$$
(28)

$$s_{1v} = i(\langle 3|\sigma(t)|4\rangle - \langle 4|\sigma(t)|3\rangle)$$
(29)

we find, after invoking the usual Redfield-like approximations<sup>5,12</sup> (neglecting terms connecting states  $|1\rangle$ ,  $|2\rangle$  to states  $|3\rangle$ ,  $|4\rangle$  due to the rapid oscillation in the phase of such terms, and decoupling the population and the coherence variables), the equations of motion

$$\dot{s}_{0x} = -F_{01}s_{0x} - F_{10}s_{1x} \tag{30}$$

$$\dot{s}_{1x} = -2js_{1y} - \left(\frac{1}{\tau}\right)s_{1x} - F_{01}s_{0x} - F_{10}s_{1x}$$
(31)

$$\dot{s}_{0y} = -F_{01}s_{0y} - F_{10}s_{1y} \tag{32}$$

$$\dot{s}_{1y} = 2js_{1x} - \left(\frac{1}{\tau'}\right)s_{1y} - F_{01}s_{0y} - F_{10}s_{1y}$$
(33)

The expressions for the rates<sup>4</sup> are given by

$$\frac{1}{\tau} = \Gamma_{pd} + \frac{1}{2} [1 + e^{-2\beta j}] [\Gamma - \Gamma']$$
(34)

$$\frac{1}{\tau'} = \Gamma_{pd} + \frac{1}{2} [1 + e^{-2\beta j}] [\Gamma + \Gamma']$$
(35)

$$\Gamma_{pd} = 2 \int_{-\infty}^{\infty} dt \, \langle \Psi(t) \Psi(0) \rangle \tag{36}$$

$$\Gamma = \int_{-\infty}^{\infty} dt \, e^{2ijt} \langle \Phi^+(t)\Phi(0) \rangle \tag{37}$$

$$\Gamma' = \int_{-\infty}^{\infty} dt \ e^{2ijt} \langle \Phi(t)\Phi^+(0)\rangle \tag{38}$$

$$F_{01} = e^{-\beta[\Omega+j]}\Lambda^+ + e^{-\beta[\Omega-j]}\Lambda^-$$
(39)

$$F_{10} = \Lambda^+ + \Lambda^- \tag{40}$$

$$\Lambda^{+} = \frac{\gamma^{2}}{2} \int_{-\infty}^{\infty} dt \, \langle b(t)b^{+} \rangle \, \mathrm{e}^{i[\Omega+j]t} \tag{41}$$

$$\Lambda^{-} = \frac{\gamma^{2}}{2} \int_{-\infty}^{\infty} \mathrm{d}t \left\langle b(t)b^{+}\right\rangle \mathrm{e}^{i[\Omega-j]t} \tag{42}$$

Expressions for the vibrational relaxation rates are readily evaluated,

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$$F_{01} = \chi^2 \omega_c \left[ \frac{1}{(e^{\beta(\Omega+j)} - 1)} + \frac{1}{(e^{\beta(\Omega-j)} - 1)} \right]$$
(43)

$$F_{10} = \chi^2 \omega_{\rm e} \left[ \frac{1}{(1 - {\rm e}^{-\beta(\Omega + j)})} + \frac{1}{(1 - {\rm e}^{-\beta(\Omega - j)})} \right] \quad (44)$$

 $\chi$  is a unitless vibrational coupling strength defined through the relationship

$$\frac{\gamma^2 \varrho(\Omega)}{2} = \chi^2 \omega_c \tag{45}$$

where  $\rho(\Omega)$  is the density of states of the bath at frequency  $\Omega$ . Note that we have approximated  $\rho(\Omega + j)$  as  $\rho(\Omega)$  since  $\Omega \gg j$ .

To proceed further in the determination of the coupling dependence of the various rates, we choose a spectral density of the form

$$\tilde{J}(\omega) = \frac{\Delta \omega^3}{\omega_c^2} e^{-\omega/\omega_c}$$
(46)

where  $\Delta$  is a dimensionless coupling strength. This definition of the spectral density corresponds to that of a three-dimensional harmonic solid in the deformation potential approximation.<sup>1,2</sup>

The effective tunneling matrix element, j, can be expressed

$$j = J \exp\left[-\frac{2}{\pi} \int_0^\infty \frac{\tilde{J}(\omega) \coth(\beta \omega/2) \, d\omega}{(\omega + 2j \coth(\beta \omega/2) \tanh(\beta j))^2}\right]$$
(47)

where J is the value of the tunneling matrix element in the absence of the bath. For this choice of the spectral density, the behavior of j is very simple. For small values of  $\Delta$ ,  $j \approx J$ . When  $\Delta$  is large, j decreases to zero exponentially with increasing  $\Delta$ .

With the previous definitions, the pure dephasing rate can be expressed as

$$\Gamma_{\rm pd} = 2j^2 [\int_{-\infty}^{\infty} dt \left(\cosh(\xi(t)) - 1\right)]$$
(48)

where

$$\xi(t) = \frac{4}{\pi} \int_{-\infty}^{\infty} d\omega \ \tilde{J}(\omega) \frac{(\cos(\omega t) \coth(\beta \omega/2) - i \sin(\omega t))}{(\omega + 2j \coth(\beta \omega/2) \tanh(\beta j))^2}$$
(49)

For small  $\Delta$ 

$$\Gamma_{\rm pd} \approx \frac{8J^2 \Delta^2}{\pi^2 \omega_{\rm c}^4} \int_0^\infty \frac{d\omega \, \omega^6 \, {\rm csch}^2(\beta \omega/2) ({\rm e}^{-2\omega/\omega_{\rm c}} + 1)}{(\omega + 2J \, {\rm coth}(\beta \omega/2) \, {\rm tanh}(\beta J))^4} \tag{50}$$

For large  $\Delta$ , we evaluate eq 45 by expanding about the saddle point  $z = t + i(\beta/2) = 0$  in the  $(\beta, t)$  plane. Under this approximation, the pure dephasing rate takes the form

$$\Gamma_{\rm pd} \approx \frac{A e^{-B\Delta}}{\sqrt{\Delta}}$$
 (51)

where

$$A = \frac{\omega_c \pi J^2}{\left[2 \int_0^\infty d\omega \, \omega^3 \operatorname{csch}(\beta \omega/2)\right]^{1/2}}$$
(52)

ì

$$B = \frac{4}{\pi \omega_c^2} \int_0^\infty d\omega \,\,\omega e^{-\omega/\omega_c} \left( \coth\left(\frac{\beta\omega}{2}\right) - \operatorname{csch}\left(\frac{\beta\omega}{2}\right) \right) \quad (53)$$

Note that this rate has a familiar form identical to the hopping rate in the theory of the small polaron.<sup>13</sup> It can easily be shown that, in the high-temperature limit for the bath ( $\beta \omega_c \ll 1$ ), the pure dephasing rate has the activated form

$$\Gamma_{\rm pd} = A {\rm e}^{-\epsilon/k_b T} \tag{54}$$

where  $A = (J^2 \pi / [2(2\omega_c k_b T)^{1/2}]$  and  $\epsilon = 2\omega_c \Delta / \pi$ .

We now compute the  $\Delta$  dependence of the rates  $1/\tau$  and  $1/\tau'$ . Using the properties of thermal averaging of boson operators over an equilibrium phonon distribution,<sup>14</sup> we find

$$\Gamma = \frac{3\Delta j^3}{\omega_c^2 \pi} e^{-2j/\omega_c} (\coth(\beta j) + 1) + j^2 \int_{-\infty}^{\infty} dt \ e^{2ijt} \sinh(\xi(t))$$
(55)

A similar calculation holds for  $\Gamma'$ . In the small  $\Delta$  limit,

$$\frac{1}{\tau} = \frac{21}{3\tau'} \approx \frac{2J^3 \Delta}{\omega_c^2 \pi} e^{-2J/\omega_c} (1 + e^{-2\beta J}) (\coth(\beta J) + 1) \quad (56)$$

to lowest order in  $\Delta$ . For large  $\Delta$ ,

$$\frac{1}{\tau} = \frac{11}{2\tau'} \approx \frac{Ae^{-B\Delta}}{\sqrt{\Delta}}$$
(57)

showing the same behavior in this limit as the pure dephasing rate (to lowest order in  $\Delta$ ). We see that, in both the small and large  $\Delta$  limit,  $1/\tau \approx 1/\tau'$ . This allows for great simplification in the solution to eqs 26–29 in these two limits.

First we consider  $F \gg j$ ,  $1/\tau$ , i.e. the limit of fast vibrational relaxation. Here we find (assuming  $s_{0x}(0) = 1$  and all other initial values are zero)

$$\langle Q(t) \rangle \approx \tanh\left(\frac{\beta\Omega}{2}\right) \exp\left(-\frac{1}{\tau(e^{\beta\Omega}+1)}\right) \cos\left(\frac{2jt}{e^{\beta\Omega}+1}\right)$$
 (58)

where we have let the fast transients that establish thermal equilibrium to the left well damp out.

In the limit J,  $1 / \tau \gg F$  (i.e. slow vibrational relaxation) we find

$$\langle Q(t) \rangle \approx \exp(-F_{01}t) \cos\left(\frac{2JF_{01}F_{10}t}{(1/\tau)^2 + 4J^2}\right)$$
 (59)

#### Discussion

The two limits considered above provide fertile ground for simple physical interpretation. First we must determine what constitutes the rate of population transfer in each case.

In the limit  $F \gg j$ ,  $1/\tau$ , i.e. vibrational relaxation is fast compared to interwell dynamics, our solution exhibits two competing processes. The first is dephasing described by the damping rate  $(1/\tau)(e^{\beta\Omega} + 1)^{-1}$ . The second is coherent tunneling with a rate  $2j(e^{\beta\Omega} + 1)^{-1}$ . In most low-temperature situations for which  $F \gg j$ ,  $1/\tau$  (with a spectral density  $\tilde{J}(\omega) \sim \omega^3$ , realistic values for the critical frequency,  $\omega_c$ , and  $\Delta \sim \mathcal{O}(1)$ ),  $j \gg 1/\tau$ . Thus we can consider the population transfer to be coherent and governed solely by  $j(\Delta)$ . This agrees with our intuition; when  $F \gg j$ ,  $1/\tau$ , the system essentially starts out with an equilibrium Boltzmann distribution of population in the left well, and the rate-limiting step is the tunneling to the right well. In the limit of fast interwell dynamics compared to vibrational relaxation,  $(j, 1 / \tau \gg F)$ , we again find competition between coherent and incoherent population transfer. In this case, however, dephasing is faster, and the rate is essentially given by F, the vibrational scattering rate. This is again indicative of the rate-limiting step, which, in this regime, corresponds to vibrational scattering between the ground and excited states by phonons.

The physical processes in two limits discussed above resemble the processes that govern the high and low damping limits in the classical Kramers problem.8 The similarities, however, are quite vague, due to the fact that there seems to be no simple analog to classical friction in this simple model. In the case of a two-level system coupled to a harmonic bath, it is wellknown<sup>1,15</sup> that a macroscopic (Markovian) friction parameter may be related to the coupling strength only when the bath has an ohmic spectral density  $(\tilde{J}(\omega) \sim \omega \text{ for small } \omega)$ . In this case,  $\eta$ , the macroscopic coefficient of friction, is proportional to  $\Delta$ . In our model, the spectral density is "superohmic", and thus the classical equations of motion for our particle would contain a memory term corresponding to a frequency-dependent friction. Furthermore, the introduction of vibrational relaxation (and thus an additional coupling parameter) further hinders the comparison to the classical Kramers problem.

As a simple example, we can construct a model that shows some interesting similarities with the classical treatment. We will interpret the escape rate  $R_{\rm esc}$  as the rate of population transfer, as previously discussed. We assume that the bath has an ohmic spectral representation. Further, we assume that the relationship between the macroscopic friction parameter  $\eta$  and the coupling strength  $\Delta$  is valid even when vibrational relaxation is possible. Lastly, as a simple and crude approximation, we assume that the coupling strength to the optical modes is equal to the average coupling strength to the acoustic modes. Thus,  $\chi^2 \approx \Delta$ .

In this highly idealized model we find, for small friction ( $\Delta \propto \eta \ll 1$ ), an escape rate arising from the vibrational relaxation rate (see eq 43),

$$R_{\rm esc} = \Delta \omega_{\rm c} \left[ \frac{1}{(\exp \left[ (\Omega + j)/(k_{\rm b}T) \right] - 1)} + \frac{1}{(\exp \left[ (\Omega - j)/(k_{\rm b}T) \right] - 1)} \right] (60)$$

For larger values of  $\Delta$  ( $\Delta > \pi/4$ ) the tunneling matrix element *j* vanishes. The escape rate becomes  $(1/\tau)(e^{\beta\Omega} + 1)^{-1}$ . Care must be taken in the calculation of  $1/\tau$  due to an infrared divergence in the integral. The result, valid for  $\beta\omega_c \gg 1$ , is<sup>16</sup>

$$R_{\rm esc} \approx \frac{J^2 \sqrt{\pi}}{2\omega_{\rm c} ({\rm e}^{\left[\Omega/(k_{\rm b}T)\right]} + 1)} \left(\frac{\pi k_{\rm b}T}{\omega_{\rm c}}\right)^{(4\Delta/\pi)-1} \frac{\Gamma(2\Delta/\pi)}{\Gamma((2\Delta/\pi) + 1/2)}$$
(61)

Note that in both cases the rate shows a complex activation and that the rate increases for small friction and then turns over and goes to zero for large values of friction. In the limit  $\Omega/(k_bT) \gg 1$ , the escape rate in both the small and large  $\Delta$  limits show approximate Arrhenius behavior with an activation energy  $\Omega$ . This vibrational energy gap is analogous to the barrier height in the classical case. The rate increases linearly with friction for small friction and goes to zero in a fairly complicated way for large friction. In the low-friction, low-temperature limit, our result is identical to the "quasiclassical behavior"  $\sim$  $\exp(-\beta\Omega)\Delta$ . For larger values of friction and low temperatures,



**Figure 2.** Behavior of  $R_{\rm esc}$  for values of  $\Delta > \pi/4$ . Solid lines represent  $R_{\rm esc}$ , and dotted lines represent "quasiclassical" rate  $\sim \exp(-\beta\Omega)(1/\Delta)$  normalized to the same starting value. The upper group is for  $\beta\Omega$  = 5 while the lower group is for  $\beta\Omega = 6$ . J is taken to be 1 cm<sup>-1</sup>,  $\omega = 100$  cm<sup>-1</sup>, and  $\Omega = 50$  cm<sup>-1</sup>.

the rate vanishes more quickly than the "quasiclassical"  $\sim \exp(-\beta\Omega)(1/\Delta)$ , although the behavior is qualitatively similar (see Figure 2). This can be compared to the classical case,<sup>8</sup> where the temperature dependence shows Arrhenius behavior (with a barrier height activation energy) and the rate is proportional to  $\eta$  for small  $\eta$  and to  $1/\eta$  for large  $\eta$ . Thus, in this case the ohmic bath quantum model shows behavior similar to that of the classical model, for a superohmic bath, the quantum model shows distinct behavior.

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## **References and Notes**

(1) Leggett, A. J.; Chakravarty, S.; Dorsey, A. T.; Fisher, M. P. A.; Garg, A.; Zwerger, W. Rev. Mod. Phys. **1987**, 59, 1. Silbey, R.; Harris, R. A. J. Phys. Chem. 1989, 93, 7062. Aslangul, C.; Pottier, N.; Saint-James,
 D. J. Phys. (Paris) 1986, 47, 1657. Caldeira, A. O.; Leggett, A. Ann. Phys. (N.Y.) 1983, 149, 374 and 1984, 153, 445(E).

(2) Silbey, R.; Harris, R. A. J. Chem. Phys. 1984, 80, 2615. Harris, R. A.; Silbey, R. J. Chem. Phys. 1985, 83, 1069. Zwerger, W. Z. Phys. B 1983, 53, 87. Aslangul, C.; Pottier, N.; Saint-James, D. J. Phys. (Paris) 1985, 46, 2031.

(3) Carmeli, B.; Chandler, D. J. Chem. Phys. 1985, 90, 3400.

(4) Weiss, U. Quantum Dissipative Systems; World Scientific: Singapore, 1993.

(5) Parris, P. E.; Silbey, R. J. Chem. Phys. 1985, 83, 5619.

(6) Benderskii, V.; Makarov, D.; Wight, C. In Advances in Chemical Physics; Prigogine, I., Rice, S., Eds.; John Wiley & Sons: New York, 1994; Vol. LXXXVIII.

(7) Kramers, H. A. Physica **1940**, 7, 284. Carmeli, B.; Nitzan, A. J. Chem. Phys. **1986**, 85, 146. Van Kampen, N. G. Stochastic Processes in Physics and Chemistry; North Holland: Amsterdam, The Netherlands, 1992.

(8) Hanggi, P.; Talkner, P.; Borkovec, M. Rev. Mod. Phys. 1990, 62, 251. Fleming, G. R., Hanggi, P., Eds. Activated Barrier Crossing; World Scientific: Singapore, 1993.

(9) Wolynes, P. G. Phys. Rev. Lett. 1981, 47, 968.

(10) Nitzan, A.; Jortner, J. Mol. Phys. 1973, 25, 713.

(11) Redfield, A. Adv. Magn. Reson. 1965, 1. Wertheimer, R.; Silbey, R. Chem. Phys. Lett. 1980, 75, 243. Blum, K. Density Matrix Theory and Applications; Plenum: New York, 1981. Dattagupta, S. Relaxation Phenomena in Condensed Matter Physics; Academic Press: New York, 1987.

(12) Silbey, R. In *Relaxation Processes in Molecular Excited States*; Funfschilling, J., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989.

(13) Mahan, G. D. Many-Particle Physics; Plenum: New York, 1983.
(14) Grover, M. K.; Silbey, R. J. Chem. Phys. 1969, 52, 2099. Messiah,

A. Quantum Mechanics; Wiley: New York, 1976; Vol. 1.

(15) Zwanzig, R. J. Stat. Phys. **1973**, *9*, 215. Chandler, D. Introduction to Modern Statistical Mechanics; Oxford University Press: Oxford, U.K., 1987.

(16) Weiss, U.; Grabert, H.; Hanggi, P.; Riseborough, P. Phys. Rev. **1987**, 35B, 9535. The earlier derivations of this type of rate resulted in a form  $R_{\rm esc} = \{2J^2\pi/[\omega_c(e(\Omega/(k_bT)) + 1)]\}[\cos(2\Delta)/2\Delta][2\pi k_bT/\omega_c]^{(4\Delta/\pi)-1}$ . While this reproduces the temperature dependence properly, it gives the wrong coupling dependence. In fact, with this result,  $R_{\rm esc}$  can become negative! This is due to the method of approximation involved in the integral. See: Chakravarty, S.; Kivelson, S. Phys. Rev. Lett. **1983**, 50, 1811. Duke, C. B.; Mahan, G. D. Phys. Rev. **1965**, 139A, 1965.

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