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# Low temperature tunneling dynamics in condensed media

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There has been considerable interest recently in the low temperature dynamics of condensed phase tunneling phenomena. In this paper we consider the interplay between quasiparticle transport and vibrational relaxation; the former taking place via tunneling in a double well potential, and the latter occurring due to interactions of the tunneling system with a harmonic bath. Taking the system-bath interactions to be linear in the bath coordinates, and explicitly allowing for a vibrationally excited well, we present a unified treatment of the weak and strong coupling regimes and obtain reduced equations of motion for the tunneling particle position operator. Solutions are obtained for several important limiting cases. In particular, we find that at sufficiently low temperatures, the dynamical behavior strongly resembles that of multisite spin jump model.

## I. INTRODUCTION

There have been a number of papers written recently addressing the dynamics of a simple tunneling system coupled to a heat bath of harmonic oscillators.<sup>1-5</sup> Typically in these investigations the two lowest levels of a symmetric double-well potential are considered and the coupling between the tunneling system and the heat bath is taken to be linear in both the bath and the system coordinates. This simple model, while providing insight into the general effects of dissipation on quantum mechanical systems, has been shown to possess some particularly interesting features, which arise from the tendency towards localization associated with the system-bath interaction, and the tendency towards delocalization brought about by the tunneling matrix element connecting the states associated with the two potential minima. Indeed, it has been shown that the competition between these two effects give rise to a renormalization of the tunneling matrix element, and a concomitant reduction in the coherent (or oscillatory) component of transport between the two wells. Among the more interesting features associated with this renormalization is the strict localization that can occur at zero temperature when the coupling between the system and the bath is of the form characterizing Ohmic dissipation.<sup>2,4,5</sup>

In this letter we present calculations intended to address those circumstances when it is not possible to exclude from consideration energetically higher levels of the tunneling system. The need to consider states higher in energy than the two lowest might arise, e.g., because of conditions involved in the preparation of the system, or because of bath temperatures which are high enough to allow a nonnegligible population of excited tunneling states. In this paper, therefore, we consider a tunneling system comprised of two coupled sets of vibrational levels, each set being associated with one of two spatially separated, but otherwise identical, "sites" (which we shall distinguish by the terms "right" and "left"). We denote by  $\Omega$  the spacing between levels at each site, and bare tunneling matrix elements connect those states of the same energy which are located on different sites. It is transport between the sites which is our primary interest. Thus, we

consider the details of those processes which lead to vibrational relaxation of the tunneling system only insofar as they affect the dynamics of site-to-site transfer.<sup>6</sup>

The two tunneling states of lowest energy, the bath, and the interaction between the bath and the two lowest states form the tunneling system of earlier investigations. The inclusion of higher states allows us to consider additional effects not possible in the two-state model, including, e.g., the possibility of thermal promotion to the generally more mobile upper states, activated transfer, vibrational relaxation, etc. The paper is laid out as follows: In the next section we introduce the starting Hamiltonian, which we immediately transform using a variational procedure employed by Silbey and Harris<sup>5</sup> in their analysis of the two-state tunneling problem. The variational approach paves the way for an evaluation of the (reduced) density matrix of the tunneling system, obtained in a standard way via elimination of the bath variables. From this we obtain equations for the (time-dependent) expectation value of the tunneling-system position operator for an initial condition describing localization on one side of the potential. General features of the solutions to these equations are discussed and, in order to illustrate these features more clearly, the special case in which there are two levels per site is studied in some detail.

## II. THE HAMILTONIAN

We write, as our starting Hamiltonian, a sum of terms representing a ladder of separate two-state tunneling systems, each coupled linearly to the same bath of harmonic oscillators. The systems are separated in energy by an amount  $\Omega$ , which is assumed to be larger than any other energy in the problem with the possible exception of the upper cutoff frequency  $\omega_c$  of the bath. Bare (bath independent) tunneling matrix elements connect states on the right to states on the left. These matrix elements are assumed to be different for each manifold. We denote by  $J_n$  the matrix element connecting the two states in the  $n$ th level. In addition we include a bath-independent interaction  $V_R$  connecting the vibrational states at each site, the major effect of which will be to cause relaxation of the vibrational energy levels.

Denoting the state in the  $n$ th vibrational level on the right-hand side of the well by  $|R_n\rangle$  and that on the left by  $|L_n\rangle$ , we write the total Hamiltonian  $H$  as follows:

$$\begin{aligned} H &= H_B + \sum_n H_n + V_R, \\ H_B &= \sum_q \omega_q a_q^+ a_q, \\ H_n &= n\Omega \{ |R_n\rangle \langle R_n| + |L_n\rangle \langle L_n| \} \\ &\quad + J_n \{ |R_n\rangle \langle L_n| + |L_n\rangle \langle R_n| \} \\ &\quad + V_n \{ |L_n\rangle \langle L_n| - |R_n\rangle \langle R_n| \}, \end{aligned} \quad (1)$$

where

$$V_n \equiv \sum_q g_{qn} (a_q + a_q^+). \quad (2)$$

In Eqs. (1) and (2),  $a_q$  and  $a_q^+$  are the annihilation and creation operators for the bath mode of frequency  $\omega_q$ , and the  $g_{qn}$  are coupling constants governing the interaction between the  $n$ th vibrational level of the tunneling system and the  $q$ th bath mode. We leave the form of the relaxation term  $V_R$  unspecified for the moment. In Fig. 1, we display an energy level diagram for the tunneling system described by this Hamiltonian.

The number of levels in Eq. (1) which we need to include explicitly will depend upon the temperature of the bath and the initial conditions. Since we generally expect the tunneling matrix elements  $J_n$  to increase with  $n$ , it may happen that at some level,  $n_0$  say, the tunnel splitting  $2J_{n_0}$  will become

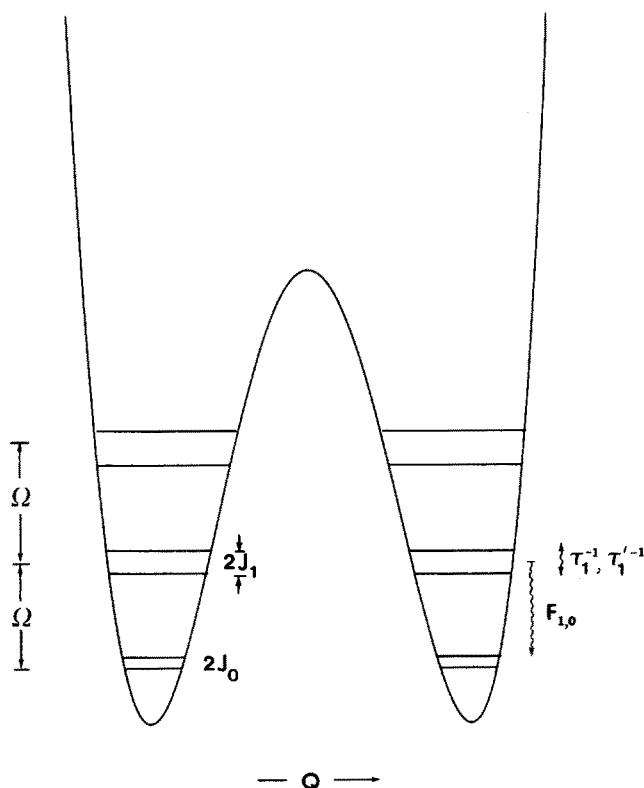


FIG. 1. Energy level diagram indicating the tunneling part of the Hamiltonian (1), with energy levels  $n\Omega$  and tunnel splittings  $2J_n$ . Also indicated are relaxation rates which arise due to interactions with the bath. The rates  $F_{n,m}$  bring about relaxation between different vibrational levels while the rates  $1/\tau_n$ ,  $1/\tau_n'$  relate to relaxation of the two states within a given vibrational level.

greater than the vibrational energy spacing  $\Omega$ . We make the stipulation in what follows, therefore, that the initial conditions and temperature are such that we need to include only levels  $n$  such that  $n \ll n_0$ . This ensures that the levels retain their identity, but puts an upper limit on the temperatures which we may consider, viz. we require that  $n_0\Omega \gg k_B T$ . On the other hand,  $k_B T$  may be large with respect to  $\Omega$  itself, provided that  $n_0 \gg 1$ . Note that we neglect bare tunneling matrix elements from, e.g., state  $n$  on the left to state  $m$  ( $\neq n$ ) on the right.

For later purposes it will be convenient to introduce an alternate representation, viz. the basis which diagonalizes the tunneling (i.e., bath independent) part of the Hamiltonian. We define the following linear combinations:

$$|\pm_n\rangle \equiv (1/2)^{1/2} \{ |L_n\rangle \pm |R_n\rangle \}. \quad (3)$$

In this basis the Hamiltonian for the  $n$ th level may be written

$$\begin{aligned} H_n &= n\Omega (|+_n\rangle \langle +_n| + |-_n\rangle \langle -_n|) \\ &\quad + J_n (|+_n\rangle \langle +_n| - |-_n\rangle \langle -_n|) \\ &\quad + V_n (|+_n\rangle \langle -_n| + |-_n\rangle \langle +_n|). \end{aligned}$$

We now perform a transformation on the Hamiltonian to obtain a basis more appropriate for perturbation theory. We define the unitary operator  $U = \prod_n U_n$ , where

$$\begin{aligned} U_n &= \exp \{ -(|L_n\rangle \langle L_n| - |R_n\rangle \langle R_n|) \\ &\quad \times \sum_q (f_{qn}/\omega_q) (a_q - a_q^+) \}. \end{aligned} \quad (4)$$

The variational constants  $f_{qn}$ , for the moment unspecified, are to be chosen later to minimize the free energy. For  $J_n = V_R = 0$ ,  $g_{qn} = f_{qn}$  diagonalizes  $H$ , while in the absence of bath-system interactions the choice  $f_{qn} = 0$  leaves the Hamiltonian diagonal in the basis (3). In the general case, however, we must write the transformed Hamiltonian

$$\mathcal{H} = U H U^+ = \mathcal{H}^0 + \mathcal{V}, \quad (5a)$$

$$\mathcal{H}^0 = H_B + \sum_n \mathcal{H}_n, \quad (5b)$$

$$\begin{aligned} \mathcal{H}_n &= \Omega_n (|R_n\rangle \langle R_n| + |L_n\rangle \langle L_n|) \\ &\quad + \mathcal{J}_n (|R_n\rangle \langle L_n| + |L_n\rangle \langle R_n|), \end{aligned} \quad (5c)$$

$$\mathcal{V} = \sum_n \mathcal{V}_n + \mathcal{V}_R, \quad (5d)$$

$$\begin{aligned} \mathcal{V}_n &= \varphi_n (|L_n\rangle \langle L_n| - |R_n\rangle \langle R_n|) \\ &\quad + \psi_n |L_n\rangle \langle R_n| + \psi_n^+ |R_n\rangle \langle L_n|. \end{aligned} \quad (5e)$$

The energy of the  $n$ th level is now  $\Omega_n = n\Omega + \sum_q \{ f_{qn} f_{qn} - 2g_{qn} \}$ , the renormalized tunneling matrix elements are given by

$$\mathcal{J}_n = J_n \exp \{ -2 \sum_q (f_{qn}/\omega_q)^2 \coth(\beta\omega_q/2) \}, \quad (6)$$

and the perturbation terms appearing in Eqs. (5d) and (5e) are defined as follows:

$$\varphi_n = \sum_q (g_{qn} - f_{qn}) (a_q + a_q^+),$$

$$\psi_n = J_n \exp \{ -2 \sum_q (g_{qn}/\omega_q) (a_q - a_q^+) \} - \mathcal{J}_n,$$

$$\mathcal{V}_R = U V_R U^+. \quad (7)$$

The perturbation terms can be thought of as fluctuations in the tunneling matrix elements around their best average values ( $\psi_n$ ) and residual fluctuations in the localized energies ( $\varphi_n$ ). The former terms will allow transport from  $|R\rangle$  to  $|L\rangle$ , but only in an "incoherent" way, while the latter terms will impede transport by instantaneous breaking of the degeneracies.

We now consider the form of the relaxation term  $\mathcal{V}_R$ . For the sake of tractability, we assume: (1) that  $\mathcal{V}_R$  only connects vibrational states located at the same site; (2) that only tunneling states differing by one quantum of vibrational excitation are connected; and (3) the matrix elements of  $\mathcal{V}_R$  connecting states on the right are the same as those on the left. We write

$$\mathcal{V}_R = \sum_n \xi_n \{ |L_n\rangle\langle L_{n+1}| + |L_{n+1}\rangle\langle L_n| + |R_n\rangle\langle R_{n+1}| + |R_{n+1}\rangle\langle R_n| \}, \quad (8)$$

where the  $\xi_n$  are bath operators. Finally, we also impose the additional requirement that the thermal average of  $\xi_n$  over an equilibrium distribution of bath states is identically zero. Obviously, the conditions we have imposed on  $\mathcal{V}_R$  are suggestive of linear coupling between the bath and the two separated vibrational ladders. Thus, while it is certainly a reasonable choice in the weak coupling limit in which  $\mathcal{V}_R$  is very close to  $V_R$  (i.e.,  $U \approx 1$ ), it must, in the strong coupling regime, be considered only as a useful approximation which contains the essential physics we wish to examine. As we will see, moreover, the exact form of  $\mathcal{V}_R$  will not play an important role in the analysis to be presented.

The next step is to determine the variational constants  $f_{qn}$ , as in Ref. 5, by minimizing the Bogoliubov–Peierls<sup>7</sup> bound on the free energy  $A = -\beta^{-1} \ln[\text{Tr} \exp(-\beta\mathcal{H})]$ . With the assumptions made above about  $\mathcal{V}_R$ , the thermal average of  $\mathcal{V}$  is zero and the bound is given by

$$A_B - A_{\text{phon}} = -\beta^{-1} \ln \{ \sum_n \exp(-\beta\Omega_n) 2 \cosh(\beta \mathcal{J}_n) \}. \quad (9)$$

Minimizing Eq. (9) with respect to the variational constants then gives the following expression for  $f_{qn}$ :

$$f_{qn} = g_{qn} \{ 1 + (2\mathcal{J}_n/\omega_q) \coth(\beta\omega_q/2) \tanh(\beta\mathcal{J}_n) \}^{-1}, \quad (10)$$

which are (perhaps not surprisingly) just the results that arise<sup>5</sup> when the individual tunneling systems are uncoupled. It is worth mentioning, however, that if we had not assumed the thermal average of  $\mathcal{V}_B$  equal to zero, then the result (10) would have to be modified by adding a term of order  $\langle \xi_n \rangle / \Omega$  to the argument of the hyperbolic tangent.

As in Ref. 5, Eqs. (10) and (6) give an implicit equation for the purely coherent tunneling matrix elements  $\mathcal{J}_n$ . The solutions to these equations, it has been shown, depend critically on the nature of the bath interaction through the functions  $J^n(\omega) \equiv \pi \sum_q (g_{qn})^2 \delta(\omega - \omega_q)$ . In particular if, as  $\omega \rightarrow 0$ , these functions do not go to zero faster than  $\omega$ , then the tunneling matrix elements for the "fully clothed" representation, which has  $f_{qn} = g_{qn}$  for all  $q$ , will be identically zero due to a divergence in the sums appearing in Eq. (6). If this choice of the variational constants represents a true mini-

mum for the free energy, then the subsequent dynamics will depend entirely on the (incoherent) Golden Rule rate as determined by the fluctuations of  $\mathcal{V}$ . Also, at zero temperature the incoherent contribution to the dynamics can disappear as well, yielding stable left- or right-localized states. This is, in fact, what happens for certain ranges of the system parameters in the case of Ohmic dissipation, where  $J^n(\omega) = \eta_n \omega$  for  $\omega \ll \omega_c$ , the cutoff frequency of the bath. The various parameter regimes for the two-level system coupled to an Ohmic bath have been discussed by Silbey and Harris<sup>5</sup>: We will make use of some of their results in what follows.

In the case of a two-level system interacting with a *monochromatic* bath, a system for which exact results are available, it has been pointed out that the Silbey–Harris<sup>5</sup> variational procedure produces results which are less accurate than the effective adiabatic method of Carmeli and Chandler.<sup>3</sup> In this case, the Silbey–Harris result is only seriously inaccurate if  $g_0^2$  and  $J_0$  are both large compared to the bath frequency  $\omega_0$ . In spite of this, the Silbey–Harris result is quite good (agreeing with the results in Refs. 1–3) for the Ohmic bath. This may seem surprising since the feature of the Ohmic bath which drives the effective tunneling matrix element to zero is the small  $\omega$  behavior of the coupling. We believe the resolution rests on two points: (1) in the bath of many frequencies the *total free energy* is largely determined by the high frequency modes ( $\omega > J_0$ ), and (2) when one considers the effect of the low frequency modes (which may possibly yield inaccurate results as mentioned above), one must use a  $J_0$  in which the effect of the high frequency modes has already been included; this reduces  $J_0$  considerably. Thus the effective Hamiltonian for the low frequency modes has a small  $J_0$  and (possibly) a large  $g_0^2$ ; in this case the Silbey–Harris theory should be accurate. Although we have no proof for these assertions, we believe they do indicate why the theory works as well as it does. We emphasize, moreover, that in both Ref. 5 and the present paper, the variational procedure only provides a route to  $\mathcal{H}_0$  and  $\mathcal{V}$ ; the main concern is with a description of the relaxation.

### III. EQUATIONS OF MOTION

We are now in a position to consider the equations of motion for the reduced density matrix  $\sigma(t)$ , from which the time dependence of relevant observables may be calculated. We assume that  $\mathcal{H}^0$ , found by the variational procedure outlined above, gives a good description of the average dynamics of the system, so good, in fact, that we may treat the remaining terms effectively using second order perturbation theory. Reduced equations of this sort have been derived previously by a number of workers.<sup>8,9</sup> To second order in  $\mathcal{V}$ ,

$$\partial \sigma_{nm}(t) / \partial t = -i\omega_{nm} \sigma_{nm}(t) - \sum_{pq} R_{nmpq} \sigma_{pq}(t), \quad (11)$$

where  $n$  labels the eigenstates (3) of  $\mathcal{H}^0$  and the relaxation matrix is given by

$$R_{nmpq} = - \int_0^\infty d\tau \left[ \langle \mathcal{V}_{qm}(\tau) \mathcal{V}_{np} \rangle \exp(-\omega_{qm}\tau) + \langle \mathcal{V}_{qm} \mathcal{V}_{np}(\tau) \rangle \exp(-\omega_{np}\tau) - \delta_{qm} \sum_s \langle \mathcal{V}_{ns}(\tau) \mathcal{V}_{sp} \rangle \exp(-i\omega_{sp}\tau) - \delta_{pn} \sum_s \langle \mathcal{V}_{qs} \mathcal{V}_{sm}(\tau) \rangle \exp(-i\omega_{qs}\tau) \right]. \quad (12)$$

In Eqs. (11) and (12), the angled brackets indicate a trace of the enclosed bath operators over an equilibrium distribution of bath states, and the frequencies  $\omega_{nm} = E_n - E_m$  come from the eigenvalues of  $\mathcal{H}^0$ . For example, in the basis (3) we may write

$$\mathcal{H}_n = (\Omega_n + \mathcal{J}_n) | +_n \rangle \langle +_n | + (\Omega_n - \mathcal{J}_n) | -_n \rangle \langle -_n |, \quad (13)$$

so that  $\Omega_n \pm \mathcal{J}_n$  are the aforementioned eigenvalues; while the interaction terms of the Hamiltonian take the form

$$\mathcal{V}_n = (1/2)(\psi_n + \psi_n^+) \{ | +_n \rangle \langle +_n | - | -_n \rangle \langle -_n | \} + [\varphi_n + (\psi_n - \psi_n^+)/2] | -_n \rangle \langle +_n | + [\varphi_n - (\psi_n - \psi_n^+)/2] | +_n \rangle \langle -_n |, \quad (14)$$

$$\mathcal{V}_R = \sum_n \mathcal{L}_n [ | +_n \rangle \langle +_{n+1} | + | +_{n+1} \rangle \langle +_n | + | -_n \rangle \langle -_{n+1} | + | -_{n+1} \rangle \langle -_n | ]. \quad (15)$$

We are interested specifically in the time development of the position of the tunneling particle. We therefore define a dimensionless position operator  $Q$  whose value is 1 if the particle is on the left-hand side of the potential barrier and  $-1$  if it is on the right, i.e.,

$$Q = \sum_n (|L_n\rangle \langle L_n| - |R_n\rangle \langle R_n|) = \sum_n (|+_n\rangle \langle -_n| + |-_n\rangle \langle +_n|). \quad (16)$$

In obtaining the equation of motion for  $Q$  it is also useful, as is done, e.g., in spin systems, to introduce the quantities

$$s_{nx} = \langle +_n | \sigma(t) | -_n \rangle + \langle -_n | \sigma(t) | +_n \rangle, \\ s_{ny} = i(\langle +_n | \sigma(t) | -_n \rangle - \langle -_n | \sigma(t) | +_n \rangle). \quad (17)$$

Clearly,  $s_{nx}$  is related to the position expectation value for the  $n$ th level, since  $\langle Q(t) \rangle = \sum_n s_{nx}(t)$ . In fact,  $s_{nx}(t)$  represents the population difference, at energy level  $n$ , between the left- and right-hand sides of the potential barrier.

It should go without saying, that the equations of motion for the full reduced density matrix are rather complicated. Frequently, however, there is a decoupling that occurs which separates the density matrix into smaller subsets of coupled variables. For example, elements of the density matrix connecting states in different manifolds (such as  $\langle +_n | \sigma | -_m \rangle$  with  $m \neq n$ ) will be oscillating at a very large frequency [ $\sim (n - m)\Omega$ ] with respect to elements connecting states in the same manifold. Their effects on these elements will quickly average out, therefore, and the coupling may be neglected. For similar reasons, as well as others discussed elsewhere,<sup>9</sup> a decoupling can occur between the *population* variables, which are represented by the diagonal elements of  $\sigma$ , and the *transition* variables, represented by the off-diagonal elements. In what follows we assume this to be the case and therefore, in view of the form taken by the position operator  $Q(t)$ , concentrate on the vectors  $s_x$  and  $s_y$ , whose components,  $s_{nx}$  and  $s_{ny}$ , respectively, are defined in Eq. (17). Thus, using the assumptions stated above we write, based on Eqs. (11) and (12), the following equations of motion:

$$\partial s_x / \partial t = -2\mathbf{J}s_y - \mathbf{A}s_x - \Lambda s_x, \quad (18a)$$

$$\partial s_y / \partial t = 2\mathbf{J}s_x - \mathbf{B}s_y - \Lambda s_y, \quad (18b)$$

where the matrices  $\mathbf{J}$ ,  $\mathbf{A}$ ,  $\mathbf{B}$ , and  $\Lambda$  appearing in Eqs. (18) have the form

$$\mathbf{J}_{n,m} = \mathcal{J}_n \delta_{n,m}, \quad (19a)$$

$$\mathbf{A}_{n,m} = (1/\tau_n) \delta_{n,m}, \quad (19b)$$

$$\mathbf{B}_{n,m} = (1/\tau'_n) \delta_{n,m}, \quad (19c)$$

and

$$\Lambda_{n,m} = \{F_{n,n+1} + F_{n,n-1}\} \delta_{n,m} + F_{n+1,n} \delta_{m,n+1} + F_{n-1,n} \delta_{m,n-1}. \quad (19d)$$

The relaxation terms  $F_{n,m}$ ,  $\tau_n$ , and  $\tau'_n$  appearing in Eq. (19) are given explicitly in terms of bath operator correlation functions in Appendix A.

In this form the equations resemble those for a multisite spin jump model in which the  $n$ th energy doublet is represented as one of the sites available to a fictitious spin 1/2 particle. With this interpretation, the tunnel splitting plays the role of the local field, the terms with  $\tau_n$ ,  $\tau'_n$  represent relaxation within the  $n$ th doublet, the  $F_{n,n\pm 1}$  terms represent scattering between doublets, and the instantaneous dynamics is determined by the "local" environment, i.e., vibrational level, in which the "spin" finds itself. Of course, the scattering here is really the vibrational relaxation that is taking place, and the "environmental parameters" associated with the nearest neighbors to which the particle jumps are highly correlated and nontranslationally invariant. Nonetheless, this analogy provides a useful framework with which to discuss qualitative features of the tunneling dynamics. Let us consider some limiting cases. We will be interested in an initial condition for which the particle is localized on one side of the well with some probability distribution governing the initial vibrational population, i.e., we set  $s_{ny}(0) = 0$  and  $s_{nx}(0) = a_n$ , the latter being the initial population of the  $n$ th level. (In spin terms, we assume that the spin is initially "up" in the eigenbasis of  $s_x$ , and distributed according to the  $a_n$  over the various levels.) In the limit of no vibrational relaxation ( $\Lambda = 0$ ), the two-state systems at each level decouple from one another and evolve independently, i.e.,

$$s_{nx}(t) = a_n \{ \lambda_n^+ - \lambda_n^- \}^{-1} \{ [\lambda_n^+ - (1/\tau'_n)] \exp(-\lambda_n^+ t) - [\lambda_n^- - (1/\tau'_n)] \exp(-\lambda_n^- t) \}, \quad (20)$$

where

$$\lambda_n^\pm = (1/\tau_n + 1/\tau'_n)/2 \pm \{ (1/\tau_n - 1/\tau'_n)^2/4 - (2\mathcal{J}_n)^2 \}^{1/2}. \quad (21)$$

Thus each level evolves like a damped harmonic oscillator, with the frequency of the  $n$ th level given by the imaginary part of Eq. (21) and the decaying amplitude determined by the real part. If there are many levels initially occupied then the oscillations of the  $s_{nx}(t)$  can, due to the distribution of frequencies, quickly dephase and make the net position  $\langle Q(t) \rangle$  decay to zero long before any of the individual levels. Thus, even in the limit in which the transport is quite coherent in all levels (i.e.,  $|\mathcal{J}_n| \gg 1/\tau_n, 1/\tau'_n$ ), the observed transport properties could appear to be incoherent due to this type

of dephasing. (Which is similar to that due to inhomogeneous broadening in the spin case.) This would continue to hold in the presence of relaxation provided that relaxation times (as determined by  $\Lambda$ ) were considerably longer than the time associated with this type of dephasing. On the other hand, this effect is, clearly, very strongly dependent upon the initial distribution of the vibrational levels: thus, if only one level were initially populated the subsequent dynamics would reflect only the frequencies and damping rates associated with that level, and the subsequent effects of vibrational repopulation would be more apparent.

In the opposite situation in which the relaxation between vibrational levels is the fastest process occurring, one would expect something analogous to motional narrowing to take place. To see this let us assume that the solution to the problem of pure relaxation is known, i.e., let us denote by  $G_{n,m}(t)$  the solution to Eq. (18) for  $s_{nx}(t)$  with  $\mathbf{J}$ ,  $\mathbf{A}$ , and  $\mathbf{B}$  all equal to zero and with  $G_{n,m}(0) = \delta_{n,m}$ . Introducing Laplace transforms  $f(\epsilon) = \int_0^\infty dt f(t) \exp(-\epsilon t)$ , with  $\epsilon$  the Laplace variable conjugate to time, we may write a formal solution to the full Eq. (18) in the form

$$\begin{aligned} s_{nx}(\epsilon) &= \sum_r \{a_r - 2\mathcal{J}_r s_{ry}(\epsilon) - (1/\tau_r) s_{rx}(\epsilon)\} G_{n,r}(\epsilon), \\ s_{ny}(\epsilon) &= \sum_r \{2\mathcal{J}_r s_{rx}(\epsilon) - (1/\tau'_r) s_{ry}(\epsilon)\} G_{n,r}(\epsilon). \end{aligned} \quad (22)$$

Since the matrix  $\Lambda$  is of the master equation type, we know that at sufficiently long times  $G_{n,m}(t)$  will go to an equilibrium value  $h_n$  which is independent of  $m$ . [An examination of the form of the matrix elements of  $\Lambda$  reveals that since, by assumption, the vibrational energy separation is much larger than the tunnel splitting, we may, in fact, to good approximation set  $h_n$  equal to  $\exp(-\beta\Omega_n)/Z$ , where  $Z = \sum_n \exp(-\beta\Omega_n)$ .] Thus the Laplace transform  $G_{n,m}(\epsilon)$  may be expressed in the form

$$G_{n,m}(\epsilon) = h_n/\epsilon + \sum_\mu C_\mu^{m,n} (\epsilon + \Lambda_\mu)^{-1},$$

where the  $\Lambda_\mu$  are the nonzero eigenvalues of the matrix  $\Lambda$ , and the  $C_\mu^{m,n}$  are constants. Now when relaxation occurs on a time scale which is much shorter than that associated with transport, we may approximate the Green's functions  $G_{n,m}(\epsilon)$  by  $h_n/\epsilon$ , which is the form it takes for  $\epsilon \ll \Lambda_\mu$ , and thereby solve Eq. (22) to obtain

$$\begin{aligned} s_{nx}(\epsilon) &= h_n \{ \epsilon + \mathcal{W}(\epsilon) \}^{-1}, \\ \mathcal{W}(\epsilon) &= \langle 2\mathcal{J}^2 \{ \epsilon + \langle 1/\tau' \rangle \}^{-1} + \langle 1/\tau \rangle, \end{aligned} \quad (23)$$

which gives for the operator  $Q$ :

$$\begin{aligned} \langle Q(t) \rangle &= \sum_n s_{nx}(t) \\ &= \{ \lambda^+ - \lambda^- \}^{-1} [ \lambda^+ - \langle 1/\tau' \rangle ] \exp(-\lambda^+ t) \\ &\quad - [ \lambda^- - \langle 1/\tau' \rangle ] \exp(-\lambda^- t), \end{aligned} \quad (24)$$

where

$$\begin{aligned} \lambda^\pm &= (\langle 1/\tau \rangle + \langle 1/\tau' \rangle) / 2 \pm \{ (\langle 1/\tau \rangle \\ &\quad - \langle 1/\tau' \rangle)^2 / 4 - \langle 2\mathcal{J}^2 \rangle \}^{1/2}. \end{aligned} \quad (25)$$

The quantity  $\langle 1/\tau \rangle \equiv \sum_n h_n (1/\tau_n)$  appearing in Eqs. (23)–(25) is the average of the relaxation parameter  $1/\tau_n$  over the equi-

librium distribution of vibrational levels. (Not to be confused with our earlier usage of the angled bracket.) Similar definitions hold for  $\langle 1/\tau' \rangle$  and  $\langle \mathcal{J}^2 \rangle$ . Comparison with Eq. (20) shows that in the limit of very fast vibrational relaxation the dynamics of the multilevel tunneling system mimic that of a particle in a *single* two-state tunneling system whose parameters are just those of the average "environment" in which the particle finds itself: of course in this case the average is a thermal one. The solutions are independent of the initial level populations provided one looks at times greater than the vibrational relaxation time: in addition, the dephasing which arose earlier due to a distribution of frequencies has disappeared. It is in this sense that a "motional narrowing" has taken place.

In between these two limits we expect there generally to be a certain amount of dephasing due to vibrational relaxation as well as to the existence of many frequencies and rates. The resulting behavior can exhibit wide variation depending upon the functional dependence of the tunneling frequencies  $\mathcal{J}_n$  and dephasing times  $\tau_n$  on the level index. For example, in the case of an Ohmic bath it has already been mentioned that the tunneling frequencies can disappear for certain critical ranges of the coupling parameters. Since the coupling is in general level dependent, and since in any case we expect  $|\mathcal{J}_{n+1}/\mathcal{J}_n| > 1$ , it might arise that the lower levels would be overdamped and thus incapable of significant site-to-site transfer, so that the only viable channel would be that of thermal promotion to more mobile excited states. Such a process would clearly be strongly activated with temperature.

To examine some of these possibilities in a more quantitative way let us consider the case of one-quantum vibrational excitation of the well, *in which we consider only the two lowest states at each site (four states in all)*. Equation (18) then reduces to four equations in four unknowns, and the solution for  $\langle Q(t) \rangle$  takes the form of a linear combination of four (generally complex) exponentials. Let us consider first the zero temperature limit.

(a)  $T = 0$ . At zero temperature we expect the relaxation rate  $F_{0,1}$  governing upward transitions to vanish so that the tunneling in the lower doublet is unaffected by the presence of the upper doublet. In addition, it will be noticed from Appendix A that the relaxation parameters  $\tau_n$  and  $\tau'_n$  depend upon two terms: a pure dephasing term ( $\Gamma_{npd}$ ) and a term (containing  $\Gamma_n$  and  $\Gamma'_n$ ) which deals with relaxation within a doublet. We expect, in general, that at zero temperature the pure dephasing term will be zero with the *downward* population relaxation rate between doublets large compared to the downward rate *within* a doublet (this argument is based on a comparison of the density of states at the relevant energies). Depending on the nature of the bath interaction, several of the other rates in the problem can disappear as well. For example, in the case of Ohmic dissipation if  $\eta_1$ ,  $\eta_0 > \pi/2$  and  $J_n/\omega_c < 1$ , then all rates and tunneling frequencies are zero<sup>5</sup> with the exception of the downward relaxation rate  $F_{1,0}$ . Hence a particle initially located on side of the barrier will remain so for all time. If, on the other hand, the friction coefficient for the lower well leads to localization while the upper level retains a finite tunneling rate (i.e.,

$\eta_0 > \pi/2 > \eta_1$ ) then  $\mathcal{J}_0 = 1/\tau_0 = 1/\tau'_0 = 0$  and the dynamical matrices simplify so as to yield the eigenvalues  $\lambda = 0$  (doubly degenerate), and

$$\lambda = -\{F_{1,0} + \Gamma_1 \pm [(\Gamma'_1/2)^2 - (2\mathcal{J}_1)^2]^{1/2}\}.$$

The dynamics in the upper doublet will then be identical to that of a single two-level system possessing a finite lifetime  $1/F_{1,0}$ . (Similar, e.g., to an electronically excited dimer.)

When  $\eta_1$  and  $\eta_0$  are both less than  $\pi/2$  in the Ohmic case, and always in the case of a more general bath, zero temperature transport will be possible in both manifolds. Due to population transfer downward, however, the upper doublet will act as a source term for the lower doublet. The general solution to Eq. (18) for zero temperature, which includes the above mentioned limiting cases, can be written as follows:

$$\begin{aligned} \langle Q(t) \rangle &= s_{1x}(t) + s_{0x}(t), \\ s_{1x}(t) &= a\varphi_{xx}^1(t), \\ s_{0x}(t) &= (1-a)\varphi_{xx}^0(t) \\ &+ aF \int_0^t dt' \{\varphi_{xx}^0(t-t')\varphi_{xx}^1(t') \\ &+ \varphi_{xy}^0(t-t')\varphi_{xy}^1(t')\}, \end{aligned} \quad (26)$$

where

$$\begin{aligned} \varphi_{xx}^i(t) &= (C_+^i - C_-^i)^{-1} \{C_+^i \exp(-\lambda_+^i t) \\ &- C_-^i \exp(-\lambda_-^i t)\}, \\ \varphi_x^i(t) &= 2\mathcal{J}_i (C_+^i - C_-^i)^{-1} \{\exp(-\lambda_+^i t) \\ &- \exp(-\lambda_-^i t)\}, \end{aligned} \quad (27)$$

with the exponents given by

$$\begin{aligned} \lambda_{\pm}^0 &= \Gamma_0/2 \pm \{(\Gamma'_0/2)^2 - 4\mathcal{J}_0^2\}^{1/2}, \\ \lambda_{\pm}^1 &= F + \Gamma_1/2 \pm \{(\Gamma'_1/2)^2 - 4\mathcal{J}_1^2\}^{1/2}, \end{aligned} \quad (28)$$

and the prefactors by  $C_{\pm}^i = \pm 2[\lambda_+^i - \lambda_-^i] - (\Gamma'_i/2)$ . For simplicity of notation we have written  $F = F_{1,0}$  and  $a = a_1$  in the above equations. Notice that, by our previous arguments,  $\lambda_{\pm}^1$  will have a large damping term ( $F$ ) and a small, possibly oscillatory part while  $\lambda_{\pm}^0$  will be more delicately balanced between under and overdamping because all the terms in it will be small.

We have written the formula (26) for  $\langle Q(t) \rangle$  so as to make explicitly apparent the terms involving uncoupled dynamics in the lower doublet,  $(1-a)\varphi_{xx}^0(t)$ , the terms involving uncoupled dynamics in the upper doublet,  $a\varphi_{xx}^1(t)$ , and the coupling terms which depend upon the downward populating rate  $F$  and the initial population in the upper doublet  $a$ . Thus, the only possible effect on tunneling in the lower doublet is due to the initial population in the upper two levels. In the physically plausible limit that  $F$  is the fastest rate in the problem (or  $1/F$  the shortest time scale), we can write  $\varphi_{xx}^1(t) \approx \exp(-Ft)$  and  $\varphi_{xy}^1(t) \approx 0$  so that

$$\begin{aligned} \langle Q(t) \rangle &\approx a \exp(-Ft) + (1-a)\varphi_{xx}^0(t) \\ &+ aF \int_0^t dt' \exp[-F(t-t')]\varphi_{xx}^0(t') \\ &\approx a \exp(-Ft) + [1-a \exp(-Ft)]\varphi_{xx}^0(t). \end{aligned} \quad (29)$$

(b)  $T > 0$ . To understand qualitatively the  $T > 0$  case it is worthwhile to invoke the spin analogy mentioned earlier. We may think of the lower doublet as one spin site with splitting  $\mathcal{J}_0$ ; the upper doublet as a second site, of the higher energy and splitting  $\mathcal{J}_1$ ;  $F_{0,1}$  as the jump rate from the lower site to the upper one and  $F_{1,0}$  as the jump rate in the other direction. [ $F_{0,1} = \exp(-\beta\Omega)F_{1,0}$  by detailed balance.] To complete this description, we associate rates (or inverse widths) to both doublets which are related to  $\tau_1$  and  $\tau_0$ . The problem then looks like a spin exchange model.<sup>10</sup> We expect to see "narrowing" (i.e., slow relaxation) in the fast exchange limit (where  $F_{0,1}$  and  $F_{1,0}$  are large compared to energy differences) and two distinct rates in the slow jump regime, etc. In fact, since  $\Omega$  must be large compared to  $\mathcal{J}_0, \mathcal{J}_1$  in order for this model to represent tunneling, only certain of these limits will apply.

When the coupling to the bath is very strong, the tunneling frequencies  $\mathcal{J}_n$  may be zero (as in the Ohmic case with  $\eta_n > \pi/2$ ) or at least very small compared to the damping times  $\tau_n, \tau'_n$ . When this is the case we may neglect the matrix  $\mathbf{J}$  in Eqs. (18) and the equations for  $\mathbf{s}_x$  and  $\mathbf{s}_y$  decouple.

In this limit we find

$$\begin{aligned} \langle Q(t) \rangle &= \{\lambda_+ - \lambda_-\}^{-1} \{(\lambda_+ - \gamma)\exp(-\lambda_+ t) \\ &- (\lambda_- - \gamma)\exp(-\lambda_- t)\}, \end{aligned}$$

$$\begin{aligned} \lambda_{\pm} &= \{(1/\tau_1) + (1/\tau_0) + F_{1,0} + F_{0,1}\}/2 \\ &\pm \{[(1/\tau_1) - (1/\tau_0) + F_{1,0} - F_{0,1}]^2/4 \\ &+ F_{1,0}F_{0,1}\}^{1/2}, \end{aligned}$$

$$\gamma = F_{1,0} + F_{0,1} + a/\tau_0 + (1-a)/\tau_1. \quad (30)$$

In the general case, however, both doublets will possess nonnegligible splittings and widths. If we make the assumption that a single parameter governs relaxation within a given doublet, i.e., set  $\tau_n = \tau'_n$ , then the matrices  $\mathbf{A}$  and  $\mathbf{B}$  are equivalent and the four eigenvalues of the system of Eqs. (18) may be obtained straightforwardly by diagonalization. Thus, for this situation, the most general form taken by  $\langle Q(t) \rangle$  will be the sum of four exponentials of the type  $\exp(-\lambda t)$  with constants  $\lambda = \lambda_+, \lambda_+^*, \lambda_-,$  and  $\lambda_-^*$  given by

$$\begin{aligned} \lambda_{\pm} &\equiv \{(1/\tau_1) + (1/\tau_0) + i(2\mathcal{J}_1 \\ &+ 2\mathcal{J}_0) + F_{1,0} + F_{0,1}\}/2 \\ &\pm \{[(1/\tau_1) - (1/\tau_0) + i(2\mathcal{J}_1 - 2\mathcal{J}_0) \\ &+ F_{1,0} - F_{0,1}]^2/4 + F_{1,0}F_{0,1}\}^{1/2}. \end{aligned} \quad (31)$$

From Eq. (31) the dynamical behavior associated with the previously discussed limits of fast and slow vibrational relaxation are easily inferred. When transport is very fast with respect to relaxation we find a linear increase in the damping rate and a tunneling frequency shifted relative to that of the zero relaxation limit (20), in which the eigenvalues are just those of the two uncoupled levels. For  $F \ll 1/\tau_n, \mathcal{J}_n$  we obtain from Eq. (31),

$$\begin{aligned} \lambda_+ &\sim 1/\tau_1 + F_{1,0} + i[2\mathcal{J}_1 - \Delta], \\ \lambda_- &\sim 1/\tau_0 + F_{0,1} + i[2\mathcal{J}_0 + \Delta], \\ \Delta &= 2F_{0,1}F_{1,0}(\mathcal{J}_1 - \mathcal{J}_0)\{[(1/\tau_1) \\ &- (1/\tau_0)]^2 + 4(\mathcal{J}_1 - \mathcal{J}_0)^2\}^{-1/2}. \end{aligned} \quad (32)$$

(In writing the above expression for  $\Delta$  we have also assumed  $F_{1,0}F_{0,1}$  small compared to the denominator in that expression.)

In the fast exchange limit (large  $F$ ) the exponentials again separate into two sets; one set, which is associated with a rapid decay and exponent

$$\lambda_- \approx \frac{[(1/\tau_1) + i2\mathcal{J}_1]F_{0,1} + [(1/\tau_0) + i2\mathcal{J}_0]F_{1,0}}{F_{0,1} + F_{1,0}} \approx \frac{(1/\tau_1)\exp(-\beta\Omega) + (1/\tau_0) + i[2\mathcal{J}_1 \exp(-\beta\Omega) + 2\mathcal{J}_0]}{1 + \exp(-\beta\Omega)} \tag{33}$$

which, by our previous notation may be expressed as  $\lambda_- = \langle 1/\tau \rangle + i2\langle \mathcal{J} \rangle$ .

As a final interesting case consider the possibility that transport in the lower doublet is extremely inhibited ( $1/\tau_0, \mathcal{J}_0 \approx 0$ ) and that population relaxation between doublets is slow compared to transport processes in the upper doublet. For simplicity we take  $F_{0,1} = F_{1,0} = F \ll \mathcal{J}_1, 1/\tau_1$ . We then obtain from Eq. (31) a component corresponding to motion in the upper doublet, additionally damped by  $F$ , i.e.,  $\lambda_+ \approx (1/\tau_1) + F + i2\mathcal{J}_1$ ; along with another much longer lived component which decays at the rate  $\lambda_- \approx F$ . Thus, as one would expect, in this situation the "rate limiting step" is that associated with thermal promotion to the more mobile excited state.

#### IV. SUMMARY

In the present paper we have described tunneling in a symmetric double well potential at temperatures low compared to the barrier height but large enough to allow for excitation of the vibrational levels associated with small oscillations about the potential minima. We have obtained, using the variational method introduced by Silbey and Harris for this problem, equations of motion to describe transport across the barrier, including relaxation effects brought about due to coupling of the tunneling system to a heat bath. The equations we have obtained are found to resemble those describing a spin 1/2 particle migrating over a set of energetically nonequivalent sites; an analogy which we have found worthwhile to pursue in light of known effects which arise in the theory of such systems. In particular concepts such as inhomogeneous broadening and motional narrowing, which are common in spin problems, are found to be useful in understanding the dynamics of the tunneling problem in appropriate limits.

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#### APPENDIX A

The constants appearing in Eq. (19) are defined as follows. The quantities  $\tau_n$  and  $\tau'_n$  are related to relaxation and dephasing *within* a given sublevel and are given by

$$(1/\tau_n) = \Gamma_{npd} + (1/2)[1 + A(2\mathcal{J}_n)] [\Gamma_n - \Gamma'_n], \tag{A1}$$

$\lambda_+ \sim F_{1,0} + F_{0,1}$ , corresponds to the approach to thermal equilibrium of the initial level distribution; the other set, which is more directly related to transport gives a frequency and damping rate that are thermal averages of those associated with each level, i.e., we obtain from Eq. (31) when  $F \gg 1/\tau_n, \mathcal{J}_n$ ,

$$(1/\tau'_n) = \Gamma_{npd} + (1/2)[1 + A(2\mathcal{J}_n)] [\Gamma_n + \Gamma'_n], \tag{A2}$$

where  $A(\omega) \equiv \exp(-\hbar\omega/k_B T)$ , and

$$\Gamma_{npd} = (1/2) \int_{-\infty}^{\infty} dt \langle [\psi_n(t) + \psi_n^+(t)] [\psi_n(0) + \psi_n^+(0)] \rangle, \tag{A3}$$

$$\Gamma_n = \int_{-\infty}^{\infty} dt \exp(i2\mathcal{J}_1 t) \langle \{ \varphi_n(t) - (1/2)[\psi_n(t) - \psi_n^+(t)] \} \times \{ \varphi_n(0) + (1/2)[\psi_n(0) - \psi_n^+(0)] \} \rangle, \tag{A4}$$

$$\Gamma'_n = \int_{-\infty}^{\infty} dt \exp(i2\mathcal{J}_1 t) \langle \{ \varphi_n(t) + (1/2)[\psi_n(t) - \psi_n^+(t)] \} \times \{ \varphi_n(0) + (1/2)[\psi_n(0) - \psi_n^+(0)] \} \rangle. \tag{A5}$$

The constants  $F_{n,m}$  characterize processes in which the particle goes from one sublevel to another and, in fact, are responsible for relaxation of the vibrational levels. They are given by the following expressions:

$$F_{n,n+1} = \{ A(\Delta_n^+) \Lambda_n^+ + A(\Delta_n^-) \Lambda_n^- \}, \tag{A6}$$

$$F_{n+1,n} = - \{ \Lambda_n^+ + \Lambda_n^- \}, \tag{A7}$$

where

$$\Delta_n^\pm \equiv \{ \Omega_{n+1} - \Omega_n \} \pm \{ \mathcal{J}_{n+1} - \mathcal{J}_n \},$$

and

$$\Lambda_n^\pm = (1/2) \int_{-\infty}^{\infty} dt \langle \zeta_n(t) \zeta_n(0) \rangle \exp(i\Delta_n^\pm t). \tag{A8}$$

In obtaining Eqs. (A1)–(A8) from the defining Eq. (12) we have assumed that the elements of  $R$  are real (i.e., we have neglected any frequency shifts), and used the fact that correlation functions of the sort appearing in Eq. (12) obey detailed balance relations of the usual type, which manifest themselves in the Boltzmann factors  $A(\omega)$  appearing above and insure the correct equilibrium distribution.

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