

## Brief Reports

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### Ohmic dissipation in a dimerized molecular chain

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We analyze a simple model of quantum tunneling in a dimerized lattice characteristic of those in which solid-state excimers have been observed. The model we pose proves to be exactly diagonalizable, allowing the time dependence of tunneling within a molecular pair to be determined to quadrature. The complete time and temperature dependence of exact results are studied numerically, and approximate solutions are tested against these numerical results. Oscillatory decay of a localized initial distribution toward a delocalized final distribution is found at both finite and zero temperature. The decay envelope at finite temperatures is eventually exponential, while that found at zero temperature is eventually power law.

The present work complements a previous study<sup>1</sup> which addressed the problem of excimer fluorescence spectra in dimerized molecular crystals.<sup>2-5</sup> Dimerization of the crystal is such that each unit cell presents a two-state tunneling problem. Here, a Hamiltonian whose eigenstates provided a natural description of observed excimer states is diagonalized exactly, and is found to represent an Ohmic system in one space dimension.

The so-called "theory of quantum tunneling" has been studied in great depth by many authors employing an impressive arsenal of theoretical techniques.<sup>6</sup> Without digressing on the minutiae which distinguish elementary models,<sup>7</sup> we note that our model does not reduce to the conventional spin-boson problem, which can be viewed as a two-state truncation of the well-known polaron problem of solid-state physics.<sup>6,9</sup> Ours is, in fact, a much simpler model which admits exact diagonalization by conventional transformation techniques drawn from polaron theory.<sup>10,11</sup> While our model is very similar to a "rotated" version of the conventional spin-boson problem, it is not equivalent to the "rotating wave" Hamiltonian of quantum optics.<sup>6</sup> More closely related are models of excitation transport such as those considered by Sewell,<sup>2</sup> Duke and Mahan,<sup>13</sup> Rackovsky and Silbey,<sup>14</sup> and Munn and Silbey.<sup>11</sup>

We refer the reader to Ref. 1 for a detailed discussion of the physical origins of the model. Here, we directly pose the Hamiltonian describing the motion of an excitation in the excited cell,

$$H = H_{\text{ex}} + H_{\text{ph}} + H_{\text{mod}} + H_{\text{trans}}, \quad (1a)$$

$$H_{\text{ex}} = E(a_1^\dagger a_1 + a_2^\dagger a_2) + J(a_1^\dagger a_2 + a_2^\dagger a_1), \quad (1b)$$

$$H_{\text{ph}} = \sum_{q\alpha} \hbar\omega_{q\alpha} b_{q\alpha}^\dagger b_{q\alpha}, \quad (1c)$$

$$H_{\text{mod}} = \sum_{q\alpha} \hbar\omega_{q\alpha} (b_{q\alpha}^\dagger + b_{-q\alpha}) \left[ \frac{1}{2}(\chi_{11}^{q\alpha} + \chi_{22}^{q\alpha})(a_1^\dagger a_1 + a_2^\dagger a_2) + \chi_{12}^{q\alpha}(a_1^\dagger a_2 + a_2^\dagger a_1) \right], \quad (1d)$$

$$H_{\text{trans}} = \sum_{q\alpha} \hbar\omega_{q\alpha} (b_{q\alpha}^\dagger + b_{-q\alpha}) \times \left[ \frac{1}{2}(\chi_{11}^{q\alpha} - \chi_{22}^{q\alpha})(a_1^\dagger a_1 - a_2^\dagger a_2) \right]. \quad (1e)$$

An excitation of monomer  $i$  of the dimer at the origin is created by  $a_i^\dagger$  and a phonon of mode  $q$  of branch  $\alpha$  is created by  $b_{q\alpha}^\dagger$ ;  $\chi_{ii}^{q\alpha}$  and  $\chi_{12}^{q\alpha}$  are the "local" and "nonlocal" excitation-phonon coupling coefficients, respectively. The coupling coefficients and phonon frequencies for this model have been given in Ref. 1. The zeroth-order Hamiltonian  $H_0 = H_{\text{ex}} + H_{\text{ph}} + H_{\text{mod}}$  corresponds to the case of symmetric local coupling ( $\chi_{11}^{q\alpha} = \chi_{22}^{q\alpha}$ ); antisymmetric local coupling contributions are contained in  $H_{\text{trans}}$ .  $H_0$  can be exactly diagonalized to polaronlike states between which  $H_{\text{trans}}$  induces transitions. Since we are interested in systems such as those studied in Ref. 1 where antisymmetric perturbations can be considered to be small, we address ourselves to the quantum problem posed by  $H_0$  and neglect  $H_{\text{trans}}$  from our analysis. (Note: were  $H_{\text{trans}}$

retained and nonlocal coupling terms neglected instead,  $H$  would describe the usual spin-boson problem.)

The reduced density matrix of a single particle can be expressed as<sup>15,16</sup>

$$\rho_{\mu\nu}(t) = \text{Tr}[\sigma(0)a_\nu^\dagger(t)a_\mu(t)], \quad (2)$$

where  $\mu, \nu$  label the states of the bare excitation and  $\sigma(0)$  is the full density matrix of the excitation-phonon system at the initial time. (We assume that at  $t=0_-$  the phonon bath is in thermal equilibrium and the excitation is prepared by optical absorption at  $t=0$ .) To study dynamics we need consider only the difference of the two diagonal elements and the difference of the two off-diagonal elements, which we denote by  $p(t)$  and  $v(t)$ , respectively,

$$p(t) = \rho_{11}(t) - \rho_{22}(t), \quad (3a)$$

$$v(t) = i[\rho_{12}(t) - \rho_{21}(t)], \quad (3b)$$

for which we find the exact solutions

$$p(t) = e^{-\Phi(t,T)} \{p(0)\cos[\Theta(t)] + v(0)\sin[\Theta(t)]\}, \quad (4a)$$

$$v(t) = e^{-\Phi(t,T)} \{v(0)\cos[\Theta(t)] - p(0)\sin[\Theta(t)]\}. \quad (4b)$$

These results resemble those of the damped harmonic oscillator. The resemblance, however, depends on the emergence of secular growths in the oscillator phase  $\Theta(t)$  and the envelope function exponent  $\Phi(t,T)$ , which may be written as

$$\Phi(t,T) = c \int_0^\infty d\omega J_\Phi(\omega) \frac{[1 - \cos(\omega t)]}{\omega^2} \coth\left(\frac{\hbar\omega}{2k_B T}\right), \quad (5)$$

$$\Theta(t) = \frac{\Delta\tilde{E}}{\hbar} t - \int_0^\infty d\omega J_\Theta(\omega) \frac{\sin(\omega t)}{\omega^2}, \quad (6)$$

where

$$\Delta\tilde{E} = 2J - 2 \sum_{q\alpha} \hbar\omega_{q\alpha} \chi_{12}^{-q\alpha} (\chi_{11}^{q\alpha} + \chi_{22}^{q\alpha}), \quad (7)$$

$$cJ_\Phi(\omega) = \sum_{q\alpha} \omega_{q\alpha}^2 |2\chi_{12}^{q\alpha}|^2 \delta(\omega - \omega_{q\alpha}), \quad (8)$$

$$J_\Theta(\omega) = \sum_{q\alpha} \omega_{q\alpha}^2 \chi_{12}^{-q\alpha} (\chi_{11}^{q\alpha} + \chi_{22}^{q\alpha}) \delta(\omega - \omega_{q\alpha}). \quad (9)$$

For the one-dimensional model in Ref. 1, the sums in (8) and (9) can be evaluated to yield

$$J_\Phi(\omega) = \omega \text{Re} \left\{ \frac{1 - (\omega/\omega_a)^2}{[1 - (\omega/\omega_1)^2][1 - (\omega/\omega_2)^2]} \right\}^{1/2}, \quad (10)$$

$$J_\Theta(\omega) = cJ_\Phi(\omega) \left[ \frac{F_0}{G} + \frac{4F_1}{G} \frac{\omega_1^2}{\omega_a^2} \left| 1 - \frac{\omega^2}{\omega_1^2} \right| \left| 1 - \frac{\omega^2}{\omega_2^2} \right| \right], \quad (11)$$

where  $\text{Re}\{z\}$  means the real part of  $z$ . The detailed definitions of the new quantities appearing in the above expressions are given in Ref. 1; here we only note that

$$c = 4G^2\omega_a / \pi\hbar k_2\omega_1\omega_2 \quad (12)$$

is a constant measuring the strength of the nonlocal coupling,  $\omega_a$  is the acoustic-phonon bandwidth, and  $\omega_1$  ( $\omega_2$ ) is the highest (lowest) optical phonon frequency.

At low frequencies,  $J_\Phi(\omega)$  vanishes as the first power of  $\omega$ ; this linear dependence of  $J_\Phi(\omega)$  on  $\omega$  places our dimerized chain in the class of Ohmic systems.

We note that while  $\Theta(t)$  contains contributions from  $J$  and both local and nonlocal couplings,  $\Phi(t,T)$  depends only on nonlocal coupling and the phonon structure. In this respect the envelope function here is closely related to quantities developed in the context of the degenerate Rabi problem.<sup>17-22</sup>

Since the model we study in this paper can be exactly diagonalized, all our results thus far are exact. Unfortunately, closed expressions for  $\Phi(t,T)$  and  $\Theta(t)$  are unavailable; thus, we turn to their approximate determination.

The time development of the average phase as given by  $\Theta(t)$  holds few surprises;

$$\Theta(t) \approx (2J/\hbar)t, \quad t \ll \omega_a^{-1} \quad (13a)$$

$$\approx (\Delta\tilde{E}/\hbar)t, \quad t \gg \omega_a^{-1}. \quad (13b)$$

The ‘‘phonon-assisted’’ nature of the tunneling process shows up clearly at this point. The vibrational relaxation of the excited state causes shifts in molecular equilibria, inducing changes in the overlap integrals giving rise to tunneling; thus, the tunneling frequency changes on the time scale of the vibrational relaxation. The average tunneling frequency may be either increased or decreased as a result of phonon assistance.

The more interesting result is to be found in the envelope function which modulates this average oscillation. The contribution of the optical modes to  $\Phi(t,T)$  is much weaker than the contribution of the acoustic modes, and in fact makes no significant contribution to the long-time decay. Thus, we focus on that part of the envelope function derived from acoustic phonons.

At an arbitrary temperature,  $\Phi^{(a)}(t,T)$  will generally contain contributions from both the thermal and zero-point motions of the lattice. It is advantageous to divide  $\Phi^{(a)}(t,T)$  into two parts,  $\Phi^{(a)}(t,0)$  and  $\Delta\Phi^{(a)}(t,T) \equiv \Phi^{(a)}(t,T) - \Phi^{(a)}(t,0)$ , representing the zero-point and thermal contributions, respectively.

The precise asymptotic behavior of  $\Phi^{(a)}(t,T)$  in the short- and long-time limits has been determined in Ref. 16 for all temperatures. Here, we identify interpolation functions which have the same asymptotic behaviors as the exact functions, and test these interpolation functions by comparing them with the exact functions evaluated numerically, adjusting the interpolation functions to the extent possible in order to obtain the best agreement.

At short times, we find at any temperature

$$\Phi^{(a)}(t,T) \approx \frac{1}{2}ca(T)t^2, \quad t \ll \tau_a, \quad (14)$$

where

$$a(T) = \int_0^{\omega_a} d\omega J_\Phi(\omega) \coth(\hbar\omega/2k_B T). \quad (15)$$

and  $\tau_a = O\{\omega_a^{-1}\}$  is a time scale to be specified below.

Making use of the special properties of Ohmic systems, the long-time asymptote of  $\Phi^{(a)}(t,0)$  can be written as

$$\Phi^{(a)}(t,0) \approx c \ln(\eta\omega_a t), \quad t \gg \tau_a, \quad (16)$$

where  $\eta$  is a numerical constant given by

$$\ln \eta = \gamma + \int_0^{\omega_a} d\omega \{ [J_\Phi(\omega) - \omega] / \omega^2 \}, \quad (17)$$

in which  $\gamma = 0.5772 \dots$  is Euler's constant.

In order to interpolate between the temporal limits of  $\Phi^{(a)}(t, 0)$ , we define a "stretched" Kubo function  $\exp[-K_\nu(x)]$ , where

$$K_\nu(x) = \mu [\exp^{-(x/\mu)^\nu} - 1 + (x/\mu)^\nu]^{1/\nu}, \quad (18a)$$

$$\mu = 2^{(1-1/\nu)}, \quad (18b)$$

in terms of which the usual Kubo function exponent is  $K_1(x)$ . The advantage of the stretched Kubo function is that its short- and long-time limits are independent of the value taken by  $\nu$ ,

$$K_\nu(x) \approx \frac{1}{2}x^2, \quad x \ll 2^{(1-1/\nu)} \quad (19a)$$

$$\approx x, \quad x \gg 2^{(1-1/\nu)}. \quad (19b)$$

However, the crossover time scale can be adjusted somewhat by tuning the value of  $\nu$ ; in our case,  $\nu = 2$  provides a satisfactory fit. Thus,

$$\Phi^{(a)}(t, 0) \approx c \ln[1 + a(0)\tau_a^2 K_2(t/\tau_a)]. \quad (20)$$

The time scale  $\tau_a$  is now determined to be

$$\tau_a = \eta\omega_a / a(0). \quad (21)$$

In Fig. 1, we compare (20) with the exact  $\Phi^{(a)}(t, 0)$  obtained numerically. The oscillations in the exact  $\Phi^{(a)}(t, 0)$  which do not appear in our approximate function are due to the finite value of the acoustic-phonon bandwidth. They could be incorporated by using a more complex interpolation function; however, this would not add significantly to our understanding of the processes involved.

It has been shown in Ref. 16 that

$$\lim_{t \rightarrow \infty} \Delta\Phi^{(a)}(t, T) / t = c / \tau_b, \quad (22)$$

where

$$\tau_b = \hbar / \pi k_B T. \quad (23)$$

This long-time result depends only on the Ohmic nature of the system, and so is identical to the finding of Chakravarty and Leggett<sup>23</sup> in the context of the spin-boson problem.

For interpolating between the temporal limits of  $\Delta\Phi^{(a)}(t, T)$ , one approach is to generalize Chakravarty and Leggett's formula for the pure Ohmic case, corresponding here to the limit of an infinite acoustic-phonon bandwidth. Chakravarty and Leggett<sup>23</sup> found for such systems,

$$\Delta\Phi^{(a)}(t, T) = c \ln[(\tau_b/t) \sinh(t/\tau_b)]. \quad (24)$$

Since we have a finite acoustic-phonon bandwidth, this function does not hold precisely in our case. We should expect this form to hold at low temperatures, where the decay should be insensitive to the existence of a finite acoustic-phonon bandwidth. At higher temperatures, we should still expect this form to offer a good approximation since low frequencies dominate the long-time

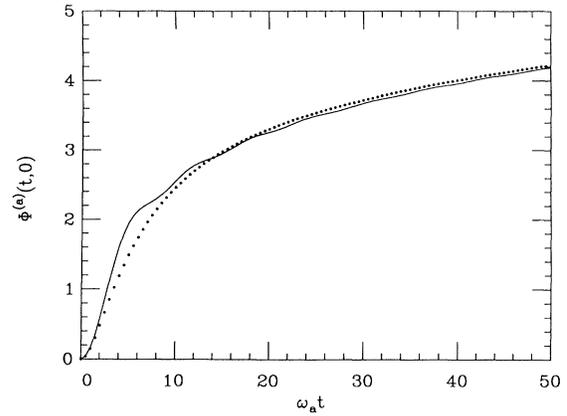


FIG. 1. Solid lines denote the exact zero-point contribution to the acoustic decay exponent obtained numerically. Dotted lines denote the interpolation function (20). The constant  $c$  has the value 1.0.

behavior; however, when  $k_B T > \hbar\omega_a$ , we should at least expect some differences to appear in the temperature dependences of the coefficients appearing in (24). Thus we use (24) as a temporal template whose coefficients must be determined to be consistent with the known exact short- and long-time limits. This being done, we find

$$\Delta\Phi^{(a)}(t, T) \approx c(\tau_c/\tau_b) \ln[(\tau_c/t) \sinh(t/\tau_c)]. \quad (25)$$

One can easily see that  $\tau_c$  does not influence the rate of exponential decay at long times [cf. (22)] so the long-time limit provides no information regarding the value of  $\tau_c$ . We obtain this information instead from the short-time limit which allows only one choice of  $\tau_c$  which will yield the correct short time behavior:

$$\tau_c^{-1} = 3\tau_b [a(T) - a(0)]. \quad (26)$$

This temperature dependence is in agreement with intuitive arguments identifying  $\tau_c^{-1}$  with the effective bandwidth of the thermally excited phonons. From the method used in its construction, we should expect this interpolation function to be accurate at both short and long times for all temperatures, and at low temperatures for all times. In Fig. 2, we compare this interpolation function with the exact function evaluated numerically and find the agreement to be excellent.

At an arbitrary temperature, both thermal motion and zero-point motion contribute simultaneously. Recombining these two contributions, our approximate envelope function is found to be

$$e^{-\Phi^{(a)}(t, T)} \approx \{ [1 + a(0)\tau_a^2 K_2(t/\tau_a)] \times [(\tau_c/t) \sinh(t/\tau_c)]^{\tau_c/\tau_b} \}^{-c}. \quad (27)$$

Figure 3 shows the exact decays to be very well approximated by the interpolation function (27).

This simple model of quantum tunneling has arisen from studies of solid-state exciters. It is distinct from the spin-boson model in that the latter focuses on the modulation of monomer energies  $E_1\{Q\}$ ,  $E_2\{Q\}$  only, while here the crucial element is the modulation of the

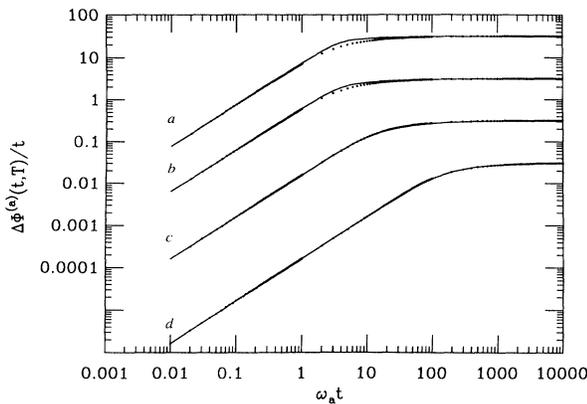


FIG. 2. Solid lines denote the exact thermal contribution to the acoustic decay exponent obtained numerically. Dotted lines denote the interpolation function (25). In all curves, the constant  $c$  has the value 1.0; (a)  $k_B T = 0.01 \hbar \omega_a$ , (b)  $k_B T = 0.1 \hbar \omega_a$ , (c)  $k_B T = 1.0 \hbar \omega_a$ , and (d)  $k_B T = 10.0 \hbar \omega_a$ .

resonance integral  $J\{Q\}$ . In fact, since we have focused on the symmetric-coupling case ( $E_1\{Q\} = E_2\{Q\}$ ) of the general problem considered in Ref. 1, the crucial element of the usual spin-boson problem (the energy difference  $E_1\{Q\} - E_2\{Q\}$ ) is absent from our present analysis. Having in mind dimerized, excimer-forming molecular crystals, we have simplified our analysis by studying exciton transfer within a single unit cell of a dimerized harmonic chain. The simplicity thereby gained proves in this case to be enough to allow a simple and exact diagonalization. Diagonalization remains possible in the face of a number of generalizations, including consideration of

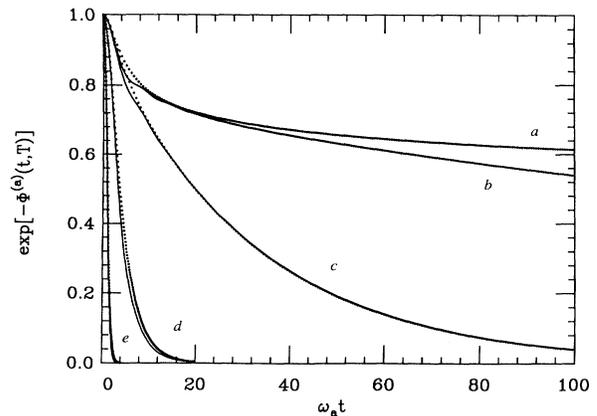


FIG. 3. Dotted lines denote the exact acoustic envelope function obtained by evaluating (5) numerically. Solid lines denote the interpolation function (27) evaluated for the same temperatures and parameter values. In all curves, the constant  $c$  has the value 0.1; (a)  $k_B T = 0 \hbar \omega_a$ , (b)  $k_B T = 0.01 \hbar \omega_a$ , (c)  $k_B T = 0.1 \hbar \omega_a$ , (d)  $k_B T = 1.0 \hbar \omega_a$ , and (e)  $k_B T = 10.0 \hbar \omega_a$ .

higher dimensions and more realistic phonon spectra. While the formal structure of our result can be expected to persist in these more general cases, the Ohmic property is not robust, depending as it does on the detailed interplay of coupling geometry, lattice structure, and lattice dimensionality.

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