Time evolution of the nonadiabatic nonlinear quantum dimer

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We analyze the set of coupled equations which describe the strong interactions between a moving quasiparticle in a solid and vibrations of the solid responsible for self-trapping and other polaronic and solitonic phenomena. The goal of the investigation is the examination of novel effects, if any, of relaxing the traditional (adiabaticity) assumption of disparate time scales for the quasiparticle motion and the vibrations. The study uncovers several striking phenomena including an approach to the self-trapped stationary states of the adiabatic dimer and the coexistence of a static and a dynamic transition in the behavior of the quasiparticle motion.

I. INTRODUCTION

A fundamental problem of condensed matter physics concerns the description of the influence of strong interactions of the lattice on quasiparticles such as electrons or excitons moving in solids. Recent approaches to this problem have been based on discrete nonlinear quantum evolution equations.[1-11] In this paper we present new results regarding the coupled evolution of such quasiparticles and of the lattice oscillators with which they interact, obtained without making the usual "adiabatic" approximation.

The essential feature of the systems of interest to the present investigation is a strong interaction between a quasiparticle which moves on a lattice in keeping with a quantum evolution equation, and oscillators whose displacements modulate the quasiparticle parameters such as the site energy. Several different sets of coupled equations for the moving quasiparticle and the lattice vibrations have been arrived at from microscopic analysis or postulated.[1-5] We focus here on the prototypical set used by Scott[2,3] and his collaborators.[4,5] Of their two coupled equations, one for the moving quasiparticle and the other for the (optical) vibration which interacts with the quasiparticle, we simplify the second and write

$$idc_m/dt = V(c_{m+1}+c_{m-1})+Ex_m c_m , \qquad (1.1)$$

$$d^2x_m/dt^2+\alpha(dx_m/dt)+\omega^2 x_m = -(\text{const})|c_m|^2 . \qquad (1.2)$$

Equation (1.1) describes the evolution of the quasiparticle: its amplitude for occupation of the site m is $c_m(t)$ and its (nearest-neighbor) intersite transfer matrix element is V. Equation (1.2) describes the evolution of the lattice vibrations with which the quasiparticle interacts: the oscillator at site m has displacement $x_m(t)$ and frequency ω, and is damped at a rate α. The strong interaction between the quasiparticle and the lattice oscillators is represented by the last terms in each of (1.1) and (1.2): the site energy of the quasiparticle is proportional to the displacement of the oscillator at site m; and the equilibrium

position of the oscillator is shifted by the presence of the quasiparticle at site m by an amount proportional to the probability of site occupation. In writing (1.2) above, the simplification we have made relative to the equations of Scott and co-workers[2-5] is to replace the dispersion of the lattice vibrations by a damping term. Our damped dispersionless (Einstein) oscillators do describe the essential physics of the removal of energy at a given site but do not incorporate intersite motion of the x vibrations.

It has been known[12] for a long time that the remarkable physics of the systems described by the above equations stems from the respective last terms in (1.1) and (1.2) through a feedback phenomenon and gives rise to polaronic and solitonic behavior. Much past work in this area has been based on a time scale disparity argument: the vibrations described by the x's are assumed to reach their equilibrium positions rapidly (typically within picoseconds) relative to the evolution of the quasiparticle. The time derivatives of the x's in (1.2) are then neglected and the resulting discrete nonlinear Schrödinger equation

$$idc_m/dt = V(c_{m+1}+c_{m-1})-\chi|c_m|^2 c_m \qquad (1.3)$$

is taken as a point of departure for the analysis of the evolution of the quasiparticle. Although (1.3) had been obtained as early as 1959 by Holstein[12] (albeit in its stationary form) and although much physics has been extracted from (1.3) through numerical analysis,[4,5] exact solutions of (1.3) are not known in general. However, it has been found recently[7,8] that considerable insight can be gained into the essential physics of the system through exact analytical solutions of (1.3) when the system has only two sites ($m = 1, 2$). Results available in the literature pertinent to this dimer version are exact time evolution in terms of Jacobian elliptic functions for arbitrary initial conditions,[7(a),8(a),8(b)] explicit demonstration of self-trapping transitions and other rich behavior in the time evolution,[7,8] evaluation of the stationary self-trapped states of the dimer,[4,7(b),8(a)] application of the analysis to specific experimentally realizable dimer systems,[8(a),8(c)] and evaluation of nonlinear memory functions.[10,11] Encouraged by the success of the dimer

analysis, we decided to address, in the dimer context, the question of whether relaxing the disparate time scale argument in the coupled equations results in novel physical behavior. The striking results we found form the content of this paper.

In Sec. II we set out the dimer evolution equations which constitute our point of departure, and derive from them two coupled equations of motion for the quasiparticle site occupation probability and the oscillator displacements. In Sec. III we analyze these equations, report several novel results, and describe them graphically. In Sec. IV we give an approximate analysis which clarifies the connection between the nonadiabatic dimer studied here and its adiabatic version studied earlier. Concluding comments are presented in Sec. V.

II. COUPLED EVOLUTION EQUATIONS FOR THE DIMER

In order to arrive as rapidly as possible at the essential physics of our problem, it is advisable (although by no means essential) to consider a simplification of the oscillator equation (1.2). We will assume that the damping coefficient α is large enough to justify the neglect of the second derivative of the oscillator displacements. More formally, we take the limit $\omega \rightarrow \infty$, $\alpha \rightarrow \infty$, $\omega^2/\alpha = \Gamma$. The evolution of the oscillator displacements x towards their equilibrium positions now possesses a single characteristic "vibrational relaxation" time, viz., $\alpha/\omega^2 \equiv 1/\Gamma$, and (1.2) reduces to

$$dx_m/dt + \Gamma x_m = -(\chi\Gamma/E)|c_m|^2 . \qquad (2.1)$$

The constant factor in (1.2) has been expressed in (2.1) as $\chi\Gamma/E^2$ in terms of the vibrational relaxation rate Γ and of E and χ. The quantity E which appears in (1.1) is the rate of change of the quasiparticle site energy with the oscillator displacement, and is of little importance to the present analysis except as a proportionality constant. The new quantity χ, which we will call the nonlinearity parameter, occurs naturally in the study of the adiabatic dimer[7,8] and represents the lowering of the site energy of the quasiparticle that occurs as a result of the feedback phenomenon. Equation (2.1) describes the oscillator being driven by relaxation processes at rate Γ to its dynamic equilibrium position which is the product of $-(\chi/E)$ and the probability that the oscillator site is occupied by the quasiparticle. Although the relaxation processes could actually be quite complex and involve vibrational dispersion and interactions with other degrees of freedom, we have assumed here that they may all be described through the single rate Γ.

The dimer (two-site) case of (1.1) and of (2.1) forms the point of departure for our present analysis:

$$idc_1/dt = Vc_2 + Ex_1c_1 , \qquad (2.2)$$

$$idc_2/dt = Vc_1 + Ex_2c_2 , \qquad (2.3)$$

$$dx_1/dt + \Gamma x_1 = -(\chi\Gamma/E)|c_1|^2 , \qquad (2.4)$$

$$dx_2/dt + \Gamma x_2 = -(\chi\Gamma/E)|c_2|^2 . \qquad (2.5)$$

In this paper, we will focus attention on the simplest

initial condition: the two oscillators are in their equilibrium positions in the absence of the quasiparticle, i.e., $x_1(0)=x_2(0)=0$, and the quasiparticle is placed suddenly on one of the sites: $|c_1(0)|^2=1$, $|c_2(0)|^2=0$. A physical example of such sudden placement is the injection of a photoinduced carrier in a molecular crystal, or the creation of an electronic excitation through absorption of radiation.[13] Density-matrix equations can then be derived and used to deduce the following coupled pair describing the interaction of $p(t) \equiv |c_1|^2 - |c_2|^2$, the difference in the probabilities of occupation of the two sites, and of $y(t) \equiv (-E/\chi)[x_1(t)-x_2(t)]$, the difference between the displacements of the two oscillators normalized in the manner shown:

$$d^2p(t)/dt^2 = Ap(t) - Bp^3(t) + C(t) , \qquad (2.6)$$

$$dy(t)/dt + \Gamma y(t) = \Gamma p(t) . \qquad (2.7)$$

The details of the passage from (2.2)–(2.5) to (2.6) and (2.7) are similar to those provided for the adiabatic analysis in the Appendix to Ref. 8(a). The constants A and B in (2.6) are given, as in the adiabatic case[7] for initial occupation of one site, by

$$A = (\chi^2/2) - 4V^2; \quad B = \chi^2/2 , \qquad (2.8)$$

and $C(t)$, the correction term which marks the difference between the present analysis and the usual "adiabatic procedure" involving the replacement of $y(t)$ by $p(t)$, is given by

$$C(t) = -\chi^2 \left[y(t) \int_0^t ds\, y(s)[dp(s)/ds] + \tfrac{1}{2}[p(t)-p^3(t)] \right] .$$
$$(2.9)$$

Equations (2.6) and (2.7) constitute our point of departure for the subsequent analysis.

III. RESULTS

We have not yet been able to obtain exact analytical solutions to the coupled equations (2.6) and (2.7). However, our numerical investigations of those equations, equivalently of (2.2)–(2.5), have resulted in the following remarkable findings.

(a) The probabilities of the two-site states settle at long times into constant values. Inspection establishes these values for this *nonadiabatic* dimer to be essentially the *stationary-state* probabilities of the *adiabatic* dimer found first by Eilbeck *et al.*[4] For $\chi \leq 2V$ these values equal $\tfrac{1}{2}$. For $\chi \geq 2V$ they are given by $\tfrac{1}{2}\{1\pm[1-(2V/\chi)^2]^{1/2}\}$. Earlier studies of damping[9] were based on the procedure of appending stochastic Liouville equation terms to the dimer evolution and resulted in an approach to equal probability distribution on the two sites. It is well known that the unphysical behavior stems from the infinite-temperature nature of the stochastic Liouville equation used. It is indeed satisfying that the present analysis forces the probabilities into the correct stationary values.

(b) For values of the damping rate Γ which are large enough (with respect to other rates such as V in the system), the evolution of the probabilities *first follows the Jacobian elliptic function* dynamics of the adiabatic dimer

deduced analytically by Kenkre and Campbell,[7] and then *settles* into the stationary-state values given by Eilbeck *et al.*[4] The short-time evolution is approximately described by $cn(2Vt|\chi/4V)$ for $\chi<4V$ and by $dn(\frac{1}{2}\chi t|4V/\chi)$ for $\chi>4V$.

(c) A consequence of the conjunction of (a) and (b) is that, for appropriately large values of Γ, the variation of the nonlinearity parameter χ shows the *coexistence* of two transitions: the static transition at $\chi=2V$ and the dynamic transition at $\chi=4V$. The former is reflected in the long-time behavior in that the asymptotic value of the probabilities is $\frac{1}{2}$ for $\chi<2V$ but different from $\frac{1}{2}$ for $\chi>2V$. The latter is seen in the short-time behavior in that the probabilities are characteristic of the cn function and oscillate on both sides of $\frac{1}{2}$ for $\chi<4V$ but are characteristic of the dn function and oscillate only on one side of $\frac{1}{2}$ for $\chi>4V$.

(d) The probabilities exhibit a potentially *misleading evolution* for $2V<\chi<4V$: at first their oscillations are damped to the value $\frac{1}{2}$. After apparently settling into the value $\frac{1}{2}$, they swing away into the stationary-state values which are other than $\frac{1}{2}$ and given in (a) above. If numerical analysis were not carried out far enough, one could conclude erroneously that the dimer equilibrates to an equal-probability state on the two sites. Practical relevance to experiments is that long-time measurements with different characteristic times could lead to sharply different interpretations of the stationary behavior of this system.

(e) For $\chi>2V$, whether the long-time limit of the probability of occupation of a given site is $\frac{1}{2}\{1+[1-(2V/\chi)^2]^{1/2}\}$ or $\frac{1}{2}\{1-[1-(2V/\chi)^2]^{1/2}\}$, is a
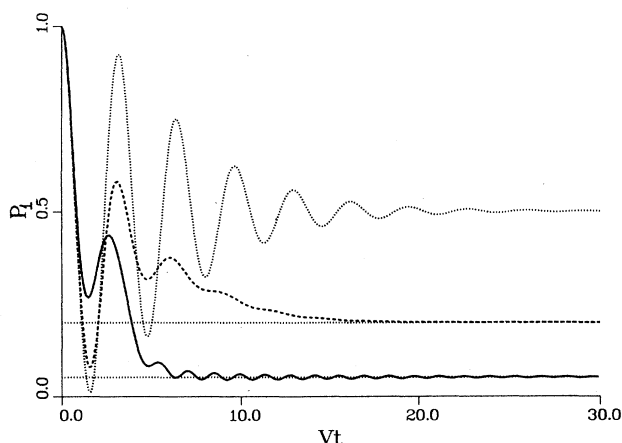
function of the value of the damping rate Γ. Thus, a variation in Γ causes the equilibrium value to switch back and forth between the two options.

We present these results graphically in Figs. 1–5. While detailed comments will be found in the respective figure captions, a brief explanation follows. The quantity plotted in Figs. 1–5 is the probability of the initially occupied site in the nonadiabatic dimer as a function of the dimensionless time Vt. In Fig. 1 we consider three different values of the nonlinearity parameter χ/V and
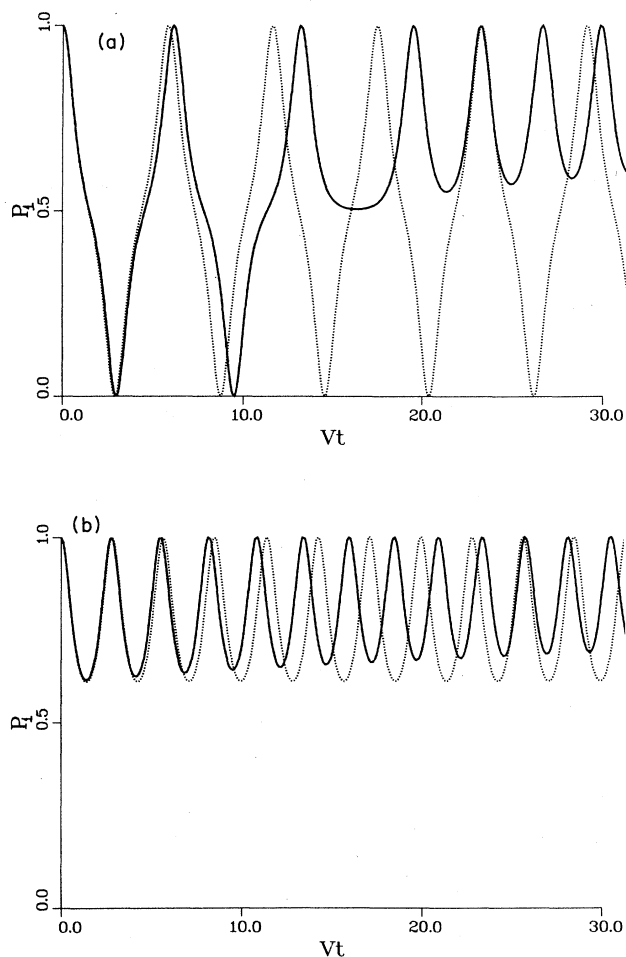

FIG. 2. The probability of the initially occupied site in the nonadiabatic dimer plotted as a function of the dimensionless time Vt in the case of rapid vibrational relaxation ($V/\Gamma=2\times10^{-3}$) showing the recovery of the adiabatic evolution at short times. The nonlinearity parameter χ/V is 3.9 (i.e., below the "dynamic transition" value 4) in (a) and 4.1 (i.e., above the "dynamic transition" value) in (b). Solid lines denote the nonadiabatic dimer. The dotted lines represent the adiabatic dimer and are a plot of $cn(2Vt|\chi/4V)$ in (a) and of $dn(\frac{1}{2}\chi t|4V/\chi)$ in (b). The nonadiabatic dimer probability coincides with the adiabatic counterpart at short times but decreases in amplitude as it tends to the stationary-state value at long times, while the adiabatic probability oscillates with constant amplitude.

FIG. 1. The probability of the initially occupied site in the nonadiabatic dimer plotted as a function of the dimensionless time Vt for three values of the nonlinearity parameter χ/V, showing the evolution to the stationary states of the adiabatic dimer. The value of the vibrational relaxation time $1/\Gamma$ (in units of $1/V$) is 1. In the case of $\chi/V=1$ (dotted oscillating line) the limiting value is seen to be 0.5 whereas, for $\chi/V=2.5$ (dashed line) and 4.5 (solid line), it is different from 0.5. The stationary-state values for the *adiabatic* dimer for the last two cases are given by $\frac{1}{2}\{1-[1-(2V/\chi)^2]^{1/2}\}$ and are 0.2 and 0.052, respectively, and are shown by dotted straight lines.
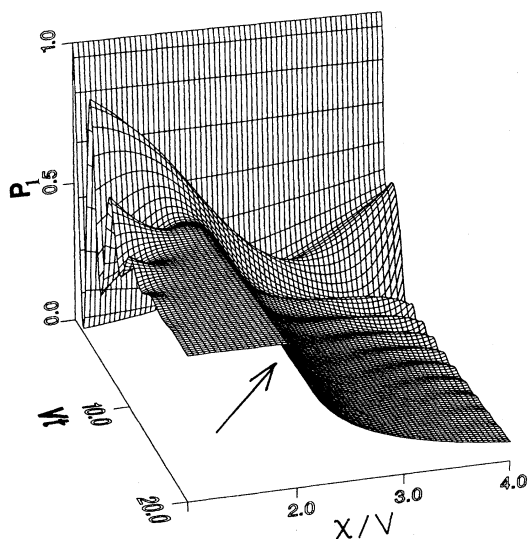
FIG. 3. The static transition at $\chi=2V$ reflected in the asymptotic limit of the probability. The probability of the initially occupied site is plotted along the vertical axis. The time (in units of $1/V$) and the nonlinearity ratio χ/V are plotted along the horizontal axes. The asymptotic (large-time) limit of the probability is the constant 0.5 for $\chi<2V$ but clearly undergoes a transition at $\chi=2V$ and begins to decrease as χ increases beyond $2V$. The transition is marked by an arrow. The value of Γ/V is taken to be 2.

FIG. 5. The switching of the limiting values of the probability of the initially occupied site between the two stationary-state values as the vibrational relaxation time $(1/\Gamma)$ is varied. The probability is plotted on the vertical axis and time t and Γ (in units of $1/V$ and of V, respectively) are plotted on the two horizontal axes. Three occurrences of the switching are seen clearly as the Γ/V axis is traversed. The value of χ/V is taken to be 2.5.

see that the nonadiabatic dimer evolves at long times to the stationary states of the *adiabatic* dimer. For $\chi<2V$, which is the case represented by the dotted line in Fig. 1, the limiting value is $\frac{1}{2}$. For $\chi>2V$, represented by the dashed and the solid lines, the limiting values are those of the self-trapped states of the adiabatic dimer: 0.2 and
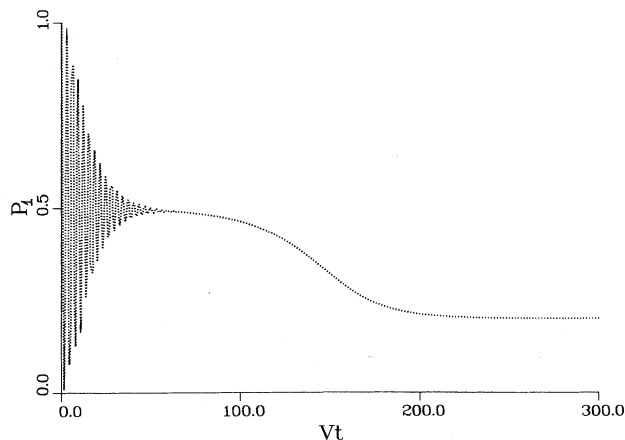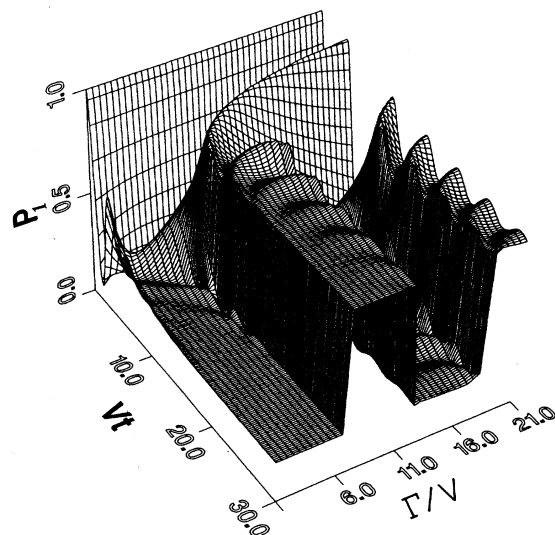

FIG. 4. The "misleading" evolution of the probability of the initially occupied site as it oscillates and damps *first* to the value 0.5 and then swings away to settle eventually into the stationary value corresponding to the self-trapped state. Measurements with probe times of the order of $100/V$ or smaller would tend to lead to the interpretation that the dimer equilibrates equally between the two sites whereas experiments with longer probe times would show that equilibration occurs at the self-trapped state value 0.2. The value of Γ/V is taken to be 0.15.

0.052, respectively. Figure 1 thus explains observation (a) above.

Observation (b) is described by Figs. 2(a) and 2(b). For rapid vibrational relaxation $(V/\Gamma=2\times10^{-3})$, Figs. 2 shows the similarity of the evolution of the nonadiabatic dimer at short times to that of the adiabatic dimer. The "dynamically free" case $(\chi<4V)$ is shown in Fig. 2(a) and the "dynamically self-trapped" case $(\chi>4V)$ in Fig. 2(b). For short times, the solid line, which describes the nonadiabatic dimer, follows closely the dotted line, which is a plot of $\text{cn}(2Vt|\chi/4V)$ in Fig. 2(a) and of $\text{dn}(\frac{1}{2}\chi t|4V/\chi)$ in Fig. 2(b).

The coexistence of the static and the dynamic transitions commented on in (c) above is difficult to appreciate from a single plot. The dynamic transition is described clearly by Figs. 2(a) and 2(b), which represent the two sides of the transition. Figure 3 shows the static transition. The horizontal axes are Vt and χ/V. Traversing the latter axis, one can see the transition (marked by arrow in Fig. 3) in the long-time limit of the probability as χ crosses $2V$.

The "misleading" evolution of the probability discussed in (d) is the subject of Fig. 4. The probability appears to damp to the value $\frac{1}{2}$ but swings away to settle for long times into the stationary value corresponding to the self-trapped state which, in the case of Fig. 4, is 0.2.

Figure 5 displays the switching of the limiting values of the probability of the initially occupied site between the two stationary state values as the vibrational relaxation time $(1/\Gamma)$ is varied. This phenomenon would be particularly important in the case of an extended system since an excitation could find itself self-trapped on arbitrary
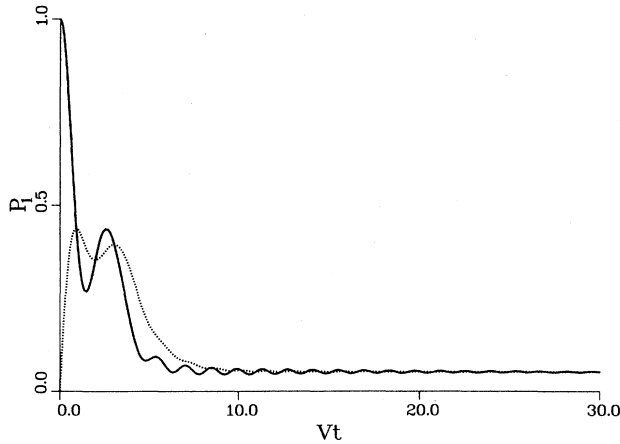
FIG. 6. The time evolution of the displacement of the oscillator at the initially occupied site shown along with that of the probability of occupation by the quasiparticle to emphasize the absence of the adiabaticity assumption in the present investigation. Parameter values correspond to the solid line of Fig. 1: $\chi/V = 4.5$ and $\Gamma/V = 1$. The dashed line represents the oscillator displacement normalized by the factor χ/E. The adiabatic analysis assumes this normalized displacement to rise to (and follow) the probability instantaneously.

sites in the lattice depending on an interplay of the initial condition and of the relaxation rate.

The standard adiabatic analysis eliminates consideration of the x's, i.e., the displacement of the oscillators, by assuming that they follow the probabilities instantaneously. The present analysis allows one to examine this process which in reality takes a finite time. We present Fig. 6 for this purpose. The solid line represents the probability of the initially occupied site with the same parameters as those for the solid line in Fig. 1. For those parameters, the dashed line in Fig. 6 describes the rise of the oscillator displacement (normalized through the factor $-\chi/E$) from its initial zero value to the value of the probability.

IV. ANALYTICAL ARGUMENTS IN THE CASE OF FAST RELAXATION

In this section we present analytical arguments which assist one in understanding the results of the numerical investigation reported above, particularly for the highly physical case of fast vibrational relaxation. We also derive a closed equation for the probability difference $p(t)$ in that limit.

In order to understand the relation between the nonadiabatic dimer and the adiabatic dimer, we examine the "correction term" $C(t)$ defined in (2.9). Consider a quantity $z(t)$ which obeys the equation

$$dz(t)/dt + \Gamma z(t) = \Gamma f(t) . \tag{4.1}$$

If $f(t)$ were to vary sinusoidally, in particular as $\cos \omega t$, the exact solution of (4.1) could be written trivially in the form

$$z(t) = [z(0) - \cos^2 \phi] e^{-\Gamma t} + (\cos \phi) f(t - \text{const}) , \tag{4.2}$$

where ϕ is given by $\tan^{-1}(\omega/\Gamma)$ and the delay constant in f equals ϕ/ω. If $1/\Gamma$ is small with respect to the characteristic time for $f(t)$, viz. $1/\omega$, one can write

$$z(t) \approx f[t - (1/\Gamma)] \approx f(t) - (1/\Gamma) df(t)/dt \tag{4.3}$$

if one's interest lies only in $t \gg 1/\Gamma$. If we now assume[14] that (4.3) will hold approximately for driving functions $f(t)$ more general than sinusoidal, take z to be the displacement difference $y(t)$ in (2.7) and $f(t)$ to be $p(t)$ as in (2.8), we can evaluate the correction term $C(t)$ of (2.9) to first order in $1/\Gamma$ as

$$C(t) = (\chi^2/\Gamma) \left[p(t) \int_0^t ds [dp(s)/ds]^2 \right.$$

$$\left. - \tfrac{1}{2}(1 - p^2)(dp/dt) \right] . \tag{4.4}$$

A closed equation for $p(t)$ then follows:

$$d^2p/dt^2 + (\chi^2/2\Gamma)(1 - p^2)(dp/dt) = A'p - Bp^3 . \tag{4.5}$$

By contrast, in the adiabatic case, p obeys

$$d^2p/dt^2 = Ap - Bp^3 , \tag{4.6}$$

(4.6) being simply (2.6) without the $C(t)$ term. Comparison of (4.5) and (4.6) shows two differences. The nonadiabatic equation (4.5) has a "friction" term proportional to dp/dt which drives the p to its stationary-state value, and the term proportional to p on its right-hand side is not the constant A of the adiabatic case but is time dependent:

$$A' = (\chi^2/2) - \left[4V^2 - (\chi^2/\Gamma) \int_0^t ds [dp(s)/ds]^2 \right] . \tag{4.7}$$

Equation (4.5) can be looked upon as describing a fictitious classical oscillator whose displacement is represented by the quantity p. The correction to A provided by the new term in A' clearly represents a dissociative antirestoring force acting on the fictitious oscillator since the factor $(\chi^2/\Gamma) \int_0^t ds [dp(s)/ds]^2$ multiplying $p(t)$ in (4.7) is always positive. As $t \to \infty$, the value of dp/dt must either vanish, or oscillate, or tend to a nonzero constant, or grow without limit. The last three possibilities would cause dp/dt to have a positive nonvanishing value. The antirestoring force would then grow without bound and dissociate the fictitious oscillator. It is guaranteed, however, that this cannot happen since p, being the probability difference between the two dimer sites, is constrained to lie between -1 and 1. It follows that dp/dt vanishes as $t \to \infty$.

We have thus concluded that the long-time evolution of the probabilities governed by (4.5) is to stationary values. These values are given by putting the derivatives of p equal to zero in (4.5). Ignoring the trivial solution $[p(\infty) = 0]$, we obtain, for the stationary probability difference,

$$p(\infty) = \left[1 - \left[(8V^2/\chi^2) \right. \right.$$

$$\left. \left. - (2/\Gamma) \int_0^\infty ds [dp(s)/ds]^2 \right] \right]^{1/2} . \tag{4.8}$$

The difference $A' - A$ has a strong effect on the station-

ary states given by (4.8). Neglect of that difference would lead one to the erroneous conclusion that $p(\infty) = [1-(8V^2/\chi^2)]^{1/2}$. The latter value corresponds not to the stationary states but to the average values around which the initially localized adiabatic dimer oscillates.[7] The correct adiabatic result for the stationary states is[4,7(b),8(a)]

$$p(\infty) = [1-(4V^2/\chi^2)]^{1/2} . \qquad (4.9)$$

The integral $\int ds\,[dp(s)/ds]^2$ thus builds up from its initial zero value to $2\Gamma V^2/\chi^2$ as $t \to \infty$. Given that dp/dt vanishes as $t \to \infty$ [as we have shown from (4.5) above], it is straightforward to return to the original equations of motion (2.2)–(2.5), set the x derivatives equal to zero, substitute the x values thus obtained in (2.2) and (2.3), and obtain the stationary-state values of the probabilities by taking c_1 and c_2 to be proportional to $\exp(i\varepsilon t)$ where ε is the energy of the stationary state. The result is indeed as given by Eilbeck et al.[4] We have thus explained why the probabilities in the nonadiabatic dimer are driven to the stationary values of the adiabatic dimer.

Equation (4.5) also shows that the adiabatic time evolution is recovered for short times provided the relaxation rate Γ is large enough. For short times, p^2 differs little from its initial value 1, and the friction term, which is proportional to $1-p^2$, is negligible. The term which describes the difference between A' and A is also negligible at short times since it is proportional to the integral of a nonsingular function from 0 to t. The correction $C(t)$ to the adiabatic evolution may be ignored, (4.5) does not differ from (4.6) for short times, and the characteristic Jacobian elliptic function evolution[7] is thus observed. Equation (4.5) also shows that a representative time for the probability evolution is Γ/χ^2.

It is no doubt also possible to derive a different closed equation in p by substituting the solution

$$y(t) = y(0) + \int_0^t du\, \Gamma e^{-\Gamma(t-u)} p(u) \qquad (4.10)$$

from (2.6) in (2.7). However, the resulting equation for p is highly nonlocal in time and much less useful than (4.5) above.

V. CONCLUDING REMARKS

The primary results of our analysis are the observations (a)–(e) made in Sec. III and described through Figs. 1–5, and Eqs. (4.5), (4.7), and (4.8). For the case of rapid vibrational relaxation, these equations describe, respectively, the evolution of the dimer probabilities, the nonadiabatic correction to the "restoring" term A, and the stationary-state probabilities of the nonadiabatic dimer. We hope to report further analytical work on the basis of those equations in the near future. The main physics to emerge from the present investigation is the recovery of the adiabatic evolution at short times and the approach towards the adiabatic stationary states at long times. The former occurs only if vibrational relaxation is fast on the scale of the other time constants of the system such as V, while the latter occurs for slow as well as fast relaxation. It is important to realize that the adiabatic evolution

(treated, for instance, in Refs. 4, 5, and 7–12) does *not* show approach to the adiabatic stationary states. The discrete nonlinear Schrödinger equation (1.3) (which provides the adiabatic description) can be used either (i) to extract its stationary states as in Refs. 4, 7(b), and 8(a) or (ii) to solve the initial value problem as in Refs. 7(a) and 8. The results of (ii) do not show evolution towards the results of (i) because no damping agents appear in the discrete nonlinear Schrödinger equation. Nor does the approach towards the stationary states occur if such damping is put in externally as in Ref. 9. It is remarkable that it does occur naturally in the present investigation. Our manner of introducing damping in this study is in the vibrational relaxation process and therefore appropriate from the physics of the system. We mention in passing that our results have a bearing on some questions that have often been asked in the context of energy transfer in molecular crystals and photosynthetic systems.[13,15,16] One of these questions addresses the issue of whether it is ever possible for electronic excitations produced by the absorption of light in such systems to find themselves localized in various places in a manner that has been described as being like "raisins in a pudding."[15] Our study shows explicitly that strong excitation-phonon interactions can indeed lead to this picturesque state of affairs.

The starting point of our analysis is (2.2)–(2.5) and contains the replacement of the oscillator equation (1.2) by (2.1) which describes a tendency to exponential nonoscillatory evolution. This replacement requires no apology since it is quite physical in many systems and its simplicity allows us to characterize the vibrational relaxation by a single rate. We have, however, also studied the dimer evolution in the absence of such replacement and present Fig. 7 as an example of the results. We see that the analysis of (2.1) involving the limit $\omega^2 \to \infty$, $\alpha \to \infty$,
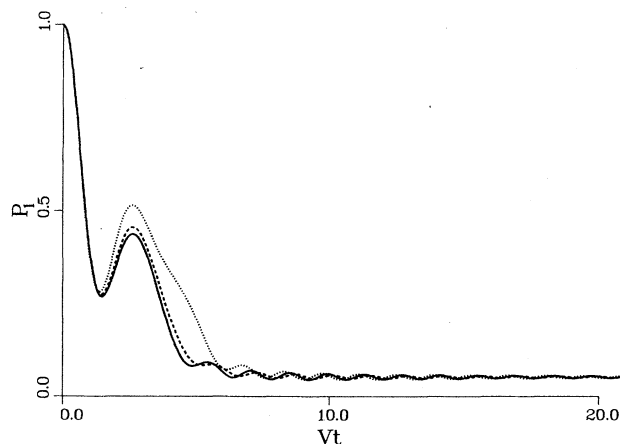

FIG. 7. The probability of the initial occupied site plotted to examine the validity of the replacement of (1.2) by (2.1) which involves the approximation of a single vibrational relaxation time, i.e., the limit $\omega^2 \to \infty$, $\alpha \to \infty$, $\omega^2/\alpha = \Gamma$. The solid line is the result of the approximation (2.1). The actual evolution resulting from (1.2) is described by the dotted line for $\omega^2 = 10$, by the dashed line for $\omega^2 = 50$, and is indistinguishable from the solid line for $\omega^2 = 200$. The description provided by (2.1) is thus seen to provide an excellent approximation to (1.2).

$\omega^2/\alpha = \Gamma$ (solid line), provides an excellent approximation to the actual evolution via (1.2) with $\omega^2 = 10$ (dotted line) and $\omega^2 = 50$ (dashed line). For $\omega^2 = 200$, the description given by (2.1) is indistinguishable from the actual evolution. Surely, the case of low ω^2 (e.g., $\omega^2 = 1$)—not represented in Fig. 7—does show oscillations not described by the solid line (ω here is in units of V). Real systems with such low damping in the vibrational evolution are rare. It is, furthermore, straightforward to generalize our analysis to such systems.

The use of the damped dispersionless oscillator equation (1.2) in place of the undamped equation with dispersion used by Scott and co-workers[2-5] requires comment. An equation with dispersion and no damping is unphysical for the *dimer* which we have undertaken to study, although it is certainly appropriate for long chains or crystals. In the absence of damping, the vibrational energy would not be depleted in the dimer. Physical dimers[11] are coupled to a reservoir (consisting, for instance, of other vibrational degrees of freedom) with which they exchange energy, and must therefore be treated either by stating explicitly the dynamics of the reservoir degrees of freedom or through damping terms as we have done in (1.2).

Finally, a remark concerning terminology might be appropriate. There has been some discussion as to whether the traditional assumption of neglecting the time derivatives of the vibrations x to obtain closed nonlinear equations for the quasiparticle amplitudes should in fact be called an "adiabatic" assumption. We have used the term only to follow what appears to be standard usage and stress that the physics under which that assumption is valid is *rapid* vibrational evolution.

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