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Self-localized energy transfer in a dissipative environment

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The influence of dephasing processes on the motion of self-localized quasiparticles in molecular chains is studied within a density-matrix description. Applying the so-called self-trapping approximation, the strong coupling to vibrational degrees of freedom can be taken into account by a quadratic nonlinearity in the density-matrix equations. If dephasing is neglected, the results agree well with those of the so-called D_2 ansatz in the theory of Davydov solitons. The delicate dependence of the soliton formation on the employed particle-vibration coupling is demonstrated. Using the standard model for the exciton motion in α-helical structures of polypeptides, it is shown that the soliton motion over more than ten molecules in the chain requires a dephasing time below some hundred femtoseconds. Thus the soliton mechanism of energy transport in biological systems at physiological temperatures seems very improbable.

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I. INTRODUCTION

No experiment has been carried out to clarify whether the concept of the so-called Davydov solitons [1] in α-helical structures of polypeptides is right or wrong, but a large amount of theoretical investigations have been published over the last decade on this subject (see, e.g., [2–15]). The assumption of the coupling of high-frequency CO stretching vibrations of the amino group inside the polypeptide backbone (amide-I vibrations) to longitudinal deformations of the whole α-helix has been of central importance. The motion of the first type of vibrational excitations along the chain originates from a weak resonance interaction. The second type forms longitudinal chain phonons due to a coupling of adjacent peptide groups via the hydrogen bridges. Within a certain parameter range of the coupling strength between both excitations, they can move together as a soliton which combines the localized CO stretching vibration and a local deformation of the α helix.

Beside molecular-dynamics calculations [11] which fully neglect the quantum nature of all incorporated vibrations, more sophisticated descriptions based on the solution of the time-dependent Schrödinger equation have been published [4–10,12–15]. Following Davydov [1,3] these approaches describe the local CO vibration as a Frenkel exciton and incorporate the quantum nature of the longitudinal α-helix vibrations. Usually one deals with polymeric chains of some ten segments so that it is impossible to construct the correct solution of the time-dependent Schrödinger equation. Instead, different types of an ansatz for the time-dependent wave function have been proposed.

Beside the dynamics of the closed quantum system of excitons and longitudinal chain phonons, the coupling to a dissipative environment and finite-temperature effects are of considerable physical interest. One treatment for the soliton motion at finite temperatures has been presented by Davydov [3] (see also [10]). Instead of considering the motion of the soliton on a chain with zero phonons, an ansatz is introduced for the time-dependent wave function which contains an incoherent superposition of states with phonons excited according to a thermal distribution. A stochastic description has been proposed in another approach [6] where the vibrational part of the equations of motion is generalized to a Langevin-like equation. A density-matrix theory has also been formulated [8,9] to study finite-temperature effects. But explicit numerical results have not yet been presented for the soliton motion in a dissipative environment allowing phase and energy relaxation.

It is the aim of the present paper to apply such a density-matrix description to study the motion of self-localized excitation energy along a chain coupled to a dissipative environment. Emphasis is placed on the dephasing processes of the soliton wave function. The coupling to the environment is taken into account in second-order perturbation theory. Beside this weak coupling to environmental degrees of freedom one has a strong coupling of the molecular excitation to the longitudinal chain phonons which is essential for the soliton formation. Different approaches are known to consider this strong coupling. They are based, e.g., on an expansion in appropriately chosen vibrational wave functions [16]. Within a density-matrix description this approach is tedious for systems with a large number of vibrational modes [17].

Therefore we consider the coupling to the vibrational degrees of freedom here only within the so-called self-trapping approximation. This approach has already been used to study the effect of nonlinearity and dissipation for a molecular dimer [18,19]. It results in a nonlinear equation of motion for the density matrix. Although the self-trapping approximation is based on a classical description of the vibrational modes, it is sufficient to study the influence of dephasing processes on the soliton motion.

In particular, our approach allows a comparison with the results of earlier calculations (see, e.g., [15]).

Additionally, our approach extends previously published calculations discussing effects of static disorder along the chain on the mobility of the solitons. In [15] a random distribution of the site energies as well as of the intersite coupling strength has been used. Then the soliton formation could be studied by solving the corresponding equations of motion which follow from a particular ansatz for the time-dependent wave function. We will study dynamic disorder using the density-matrix approach which yields the dynamics of the quasiparticle phonon system of the chain averaged with respect to a thermal ensemble of environmental states.

The paper is organized as follows. In the next section we introduce a general model for the quasiparticle motion in a molecular system. By dividing the whole set of vibrational degrees of freedom into a class coupling strongly to the quasiparticle and in a remaining set one naturally introduces the concept of a thermal environment (or heat bath). The corresponding contributions to the density-matrix equations are discussed. Section III deals with the application of the general approach to the single-chain standard model of soliton motion in α-helical polypeptide structures. Numerical results will be presented in the fourth section.

II. DENSITY-MATRIX EQUATIONS

A. General model

The motion of a single quasiparticle (e.g., Frenkel exciton) can be described by the following general expression of the Hamiltonian for the vibronic states of the quasiparticle in the site representation:

$$H=\sum_{m,n} h_{mn}(\{P_j,X_j\})A_m^\dagger A_n\ . \tag{1}$$

Here, the quantities $A_m^\dagger$ and A_n define the creation and annihilation operators of the quasiparticles at molecular sites m and n, respectively. Their definite statistics depend on the actual type of the considered quasiparticle. The matrix elements h_{mn} of the Hamiltonian are functions of all vibrational momenta P_j and vibrational coordinates X_j. They read in detail

$$h_{mn}(\{P_j,X_j\})=\delta_{mn}T(\{P_j\})+W_{mn}(\{X_j\})\ . \tag{2}$$

T is the kinetic-energy operator of the vibrational coordinates. The diagonal parts of the potential W_{mn} comprise the various potential-energy surfaces U_m in the diabatic representation of the particle-vibration system (neglecting any dynamic coupling). The interaction potentials between different sites of the molecular system are contained in the off-diagonal parts, i.e.,

$$W_{mn}(\{X_j\})=\delta_{mn}U_m(\{X_j\})+(1-\delta_{mn})V_{mn}(\{X_j\})\ . \tag{3}$$

In order to describe the quasiparticle motion the reduced one-particle density matrix (RDM)

$$\rho_{mn}(t)=\mathrm{tr}(\hat{w}(t)A_m^\dagger A_n) \tag{4}$$

is of interest. It contains the time-dependent statistical operator $\hat{w}(t)$ of the considered system. The time-dependent occupation probabilities $P_m(t)$ for the local quasiparticle states are given by the diagonal elements of the RDM. One easily verifies the following equations of motion for the RDM:

$$i\hbar\frac{\partial}{\partial t}\rho_{mn}(t)=\sum_k[\mathrm{tr}(\hat{w}(t)W_{nk}(\{X_j\})A_m^\dagger A_k) -\mathrm{tr}(\hat{w}(t)W_{km}(\{X_j\})A_k^\dagger A_n)]\ . \tag{5}$$

The right-hand side comprises higher-order mixed particle-vibration density matrices. The restriction to a single quasiparticle ($\sum_n A_n^\dagger A_n=1$) avoids the appearance of the vibrational kinetic energy.

The further treatment of the density-matrix equations essentially depends on the strength of the coupling of the quasiparticle to the various vibrational modes. Therefore, we provide a separation of the modes into two different classes corresponding to strong and weak coupling strength, respectively. The first class comprises the modes $\{Q_j\}$ and the second class the modes $\{q_\xi\}$.

To give a precise definition of what is a strong and a weak coupling we compare the so-called reorganization energies for a transition of the quasiparticle from site m to site n. Generally, these quantities are defined as the energetic value of the diabatic potential surface U_n at the position of the minimum of the potential surface U_m. Therefore, our classification requires the validity of the following inequality:

$$U_n(\{Q_j^{(m)}\},\{q_\xi^{(n)}\})>>U_n(\{Q_j^{(n)}\},\{q_\xi^{(m)}\})\ , \tag{6}$$

where $Q_j^{(m)}$ and $q_\xi^{(m)}$ ($Q_j^{(n)}$ and $q_\xi^{(n)}$) are the minimum coordinates of the diabatic potential surface U_m (U_n) with respect to the modes Q_j and q_ξ.

B. Self-trapping approximation

This approximation aims at an effective description for the strong interaction between a large number of vibrational degrees of freedom and the quasiparticle motion. First of all it provides the neglection of quantum fluctuations in decoupling the higher-order functions in Eq. (5) with respect to the vibrational part and the quasiparticle contribution, i.e.,

$$i\hbar\frac{\partial}{\partial t}\rho_{mn}(t)=\sum_k[W_{nk}(\{X_j\})\rho_{mk}(t) - W_{km}(\{X_j\})\rho_{kn}(t)]\ . \tag{7}$$

Furthermore it assumes that the characteristic velocity of the vibrational modes is much larger than the corresponding velocity of the quasiparticle motion. Then the vibrational modes can react instantaneously on the particle motion and we can drop corresponding time derivatives. The actual values of the vibrational coordinates are determined by the following algebraic equations:

$$\sum_{m,n}\frac{\partial W_{mn}}{\partial X_j}\rho_{mn}(t)=0\ . \tag{8}$$

If these equations allow a definite solution with respect to the vibrational coordinates, namely, $X_j = X_j(\rho_{mn})$, we can insert these solutions into Eqs. (7) to obtain a closed set of nonlinear RDM equations. The corresponding nonlinearities describe the self-trapping process as the gain of quasiparticle energy due to the localization of the wave function in the molecular system.

Although the combination of the assumption of high frequencies for the vibrational modes together with its classical description is questionable, the used approach provides an effective description of the mutual particle-vibration coupling for large molecular systems.

We note in passing that the assumed relation between the vibrational motion and the particle motion is typical for nonadiabatic transfer phenomena. However, in the standard treatment of nonadiabatic transfer the single transfer event occurs from a totally thermalized initial state.

Let us finally relate the above approach to a somewhat more general density-matrix description (see, e.g., [18]). If one tries by standard methods to formulate a perturbation expansion of the exciton-vibration coupling within the equations of motion for the density matrix one ends up with correlation functions for the vibrational coordinates Q_j of any order. By restricting these to $\langle Q_j(t)\rangle$, solving the corresponding equation of motion, and inserting the result into the equation of the density matrix, one obtains the non-Markovian version of the self-trapping approximation. The next order correlation function $\langle Q_j(t)Q_{j'}(t')\rangle - \langle Q_j(t)\rangle\langle Q_{j'}(t')\rangle$ describes by definition fluctuations around the expectation value of Q_j. Therefore it has been argued [8,9] that the restriction to density-matrix equations with both of these correlation functions is appropriate to incorporate finite temperature effects. But as illustrated by the considerations in this section, such an approach leads to a classical description of the vibrational motion and is equivalent to the self-trapping approximation. For the full quantum-mechanical description of the vibrational motion at finite temperatures all types of correlation functions have to summed. A corresponding density-matrix approach has been recently published for the case of a molecular dimer [17].

C. Dephasing mechanism

Let us continue by considering the vibrational modes $\{q_\xi\}$ showing a small reorganization energy. In this section we only discuss the general structure of the corresponding contributions to the density-matrix equations. It is not our intention to present here an environmental model adequate to, e.g., the exciton motion in polypeptides.

Because of the weak coupling of the vibrational modes $\{q_\xi\}$ to the quasiparticle motion we assume thermal equilibrium for these modes considering them as a heat bath with a given temperature. Supposing additionally parabolic potential surfaces of the same curvature for all molecular sites m, the corresponding contribution to the potential W_{mn} reads

$$W_{mn}(\{q_\xi\}) = \sum_\xi [\delta_{mn}\tfrac{1}{2}\mu_\xi\omega_\xi^2 q_\xi^2 + g_\xi(m,n)q_\xi] \; . \qquad (9)$$

The off-diagonal contributions in the coupling function $g_\xi(m,n)$ stem from an expansion of the intersite potential V_{mn} with respect to the vibrational coordinates q_ξ. (The generalized coordinates q_ξ have been introduced for the molecular system in its ground state, and thus the expansion starts with a linear contribution in q_ξ.)

The consideration of this coupling up to second order is standard and has already been discussed for the coordinates Q_j in the previous section. The details of the derivation of the corresponding terms in the density-matrix equations have been described at length in the literature (see, e.g., [18]). Here we only quote the result. The contributions to the equations of motion for the density matrix have the following general form:

$$\left[\frac{\partial}{\partial t}\rho_{mn}(t)\right]_{\text{particle-bath}} = -\sum_{k,l}[\gamma_{nkkl}\rho_{ml}(t) + \gamma_{lkkm}\rho_{ln}(t) - 2\gamma_{nklm}\rho_{lk}(t)] \; . \qquad (10)$$

The generalized damping functions γ are defined by the second-order correlation functions of the environmental coordinates q_ξ. (The assumption of weak coupling and thermal equilibrium prevents the separate consideration of the expectation values of q_ξ.)

Since no particular model for the coupling to dissipative modes in α-helices is known, it is sufficient to restrict the right-hand side of Eq. (10) to the dephasing contributions

$$\left[\frac{\partial}{\partial t}\rho_{mn}(t)\right]_{\text{particle-bath}} = -(1-\delta_{mn})\frac{1}{\tau_{mn}}\rho_{mn}(t) \; . \qquad (11)$$

τ_{mn} defines the characteristic time for the dephasing process of the quasiparticle wave function with respect to the sites m and n. One can imagine that the dephasing times are caused by environmental modes modulating the site energies as well as the intercenter coupling.

Furthermore, the description used allows to interpret the dephasing times also as due to the second-order correlation functions of the first class of vibrational coordinates Q_j within the improved self-trapping approximation mentioned at the end of the previous section.

III. SOLITON MOTION IN A MOLECULAR CHAIN

To enable a comparison with the various calculations of the motion of Davydov solitons in α-helical polypeptide structures we specify our general equations according to the widely used standard model for these systems (see, e.g., [15]). This standard model reduces the three spines of hydrogen-bonded chains in the α helix to a single one. The localized high-frequency CO stretching vibrations (amide-I vibration, $\hbar\omega \approx 0.5$ eV) define the single quasiparticles of Frenkel-exciton type whereas the vibrations along the hydrogen-bonded chain constitute the set $\{Q_j\}$ of longitudinal vibrational modes. All remaining vibrational degrees of freedom of the polymer form the dissipative environment.

Starting from our general Hamiltonian (1) for the case of a chain of N identical sites (amino groups in the hydrogen-bonded chain) with parabolic potential-energy surfaces we end up with the standard model introduced above for the description of Davydov solitons

$$U_m(\{Q_q\}) = E_0 + \sum_q \frac{\hbar\omega_q}{4} |Q_q + 2g_q^*(m)|^2 \; . \tag{12}$$

E_0 defines the identical site energies and q counts the longitudinal normal modes of the molecular chain. To remain sufficiently simple they can be defined by assuming periodic boundary conditions ($q = -\pi/a + 2\pi L/aN$, $L = 1, \ldots, N$, a is the lattice constant). The dimensionless normal-mode coordinates of the longitudinal chain phonons are related to the usual annihilation and creation operators c_q and $c_q^\dagger$ according to $Q_q = c_q + c_{-q}^\dagger$. The dimensionless exciton-vibration coupling reads

$$g_q(m) = \frac{\kappa\Delta}{(2N\hbar\mu\omega_q^3)^{1/2}} (1 - e^{-iaq}) e^{iaqm} \; . \tag{13}$$

It stems from the dependence $E_0 + \Delta(u_m - u_{m-1})$ of the amide-I vibration on the hydrogen bond length where u_m are the local distortions. The dispersion law has the standard form

$$\omega_q^2 = 4\frac{\kappa}{\mu}\sin^2(qa/2) \; , \tag{14}$$

where κ is the spring constant of the chain defined by the hydrogen bridges between the different peptide groups.

One usually neglects the possible dependence of the potential V_{mn} on the vibrational degrees of freedom. It is simply given by the resonance interaction J_{mn} between adjacent sites in the chain. In the present case the resonance interaction can be reduced to a nearest-neighbor coupling

$$J_{mn} = (\delta_{m+1,n} + \delta_{m-1,n}) J \; . \tag{15}$$

The approximate form of the equations of motion for the normal-mode coordinates reads

$$Q_q = -2 \sum_{m=1}^{N} g_q^*(m) \rho_{mm} \tag{16}$$

and in final form the RDM equations are obtained as

$$\frac{\partial}{\partial t}\rho_{mn}(t) = -(1-\delta_{mn})\frac{1}{\tau_{mn}}\rho_{mn}(t) - i\Delta\omega_{mn}\rho_{mn}(t) - \frac{i}{\hbar}\sum_k [J_{nk}\rho_{mk}(t) - J_{km}\rho_{kn}(t)] \; . \tag{17}$$

The self-trapping contribution results in a shift of the transition frequencies which depends on the site occupation probability ρ_{kk} according to

$$\Delta\omega_{mn} = \sum_k \left[2\sum_q \omega_q \,\mathrm{Re}([g_q(m) - g_q(n)] g_q^*(k)) \rho_{kk}(t) \right] \; . \tag{18}$$

The shift of the transition frequencies can be further simplified using the explicit form of the exciton-vibration coupling (13). We obtain a local expression with respect to the site occupation probabilities

$$\Delta\omega_{mn} = \frac{\kappa\Delta^2}{\hbar}[\rho_{mm}(t) - \rho_{nn}(t)] \; . \tag{19}$$

The local character of this expression depends essentially on the difference $u_m - u_{m-1}$ in the exciton-vibration coupling. For example, if one considers a model with the symmetric expression $u_{m+1} - u_{m-1}$ the nonlinear self-trapping contribution remains nonlocal with respect to the site occupation probabilities.

IV. NUMERICAL RESULTS

To have clear evidence for the effect of the dephasing of the wave function we consider a homopolymeric chain [regular chain with identical site energies, exciton-vibration coupling (13) and resonance interaction (15)]. Providing also a homogeneous environment all dephasing times τ_{mn} reduce to a single value τ_d. For the numerical solution of the density-matrix equations it is useful to rescale all energies with respect to the resonance interaction J and all time arguments with respect to $\hbar/J$. The rescaled dephasing time reads $\theta_d = \tau_d J/\hbar$ and the dimensionless self-trapping constant follows as $\chi = \kappa\Delta^2/J$. The dynamics in the regular chain are controlled by these two parameters.

As the initial condition for all calculations we take the excitation of an exciton at the first site, i.e., $\rho_{mm}(0) = \delta_{mn}\delta_{m1}$. The RDM equations are solved for a chain of 20 molecules as well as a chain of 50 molecules. Such a chain length is sufficient to determine the velocity of the motion of the excitation energy and to reduce the influence of boundary effects of the chain. To visualize certain details of the soliton motion the case of a chain of 20 molecules is especially useful.

First of all let us consider for reference the motion of a self-localized exciton on a chain of 20 molecules for the case of a relative large self-trapping constant $\chi = 3$ so that the energy gain by the exciton localization amounts to three times the magnitude of the resonance interaction. Figure 1(a) shows the soliton motion for infinite dephasing time, whereas Fig. 1(b) corresponds to the case of finite dephasing time $\theta_d = 10$. The large value of χ produces complex patterns after reflection of the soliton at the end of the chain which are absent for smaller values of χ (see below). These patterns together with localization of the excitation energy vanish already for the moderate dephasing time assumed in Fig. 1(b). A homogeneously distributed occupation probability over the whole chain is reached for a rescaled time of approximately $2\theta_d$.

The influence of the dephasing mechanism on soliton formation and soliton pinning is studied more systematically in Fig. 2. It shows the occupation probability P_1 of the first chain element (of a chain of 20 sites) for various values of χ. In Fig. 2(a) the dephasing effect is neglected ($\theta_d = \infty$). We observe how the time dependence of P_1 changes if χ is increased. The localized structure for $\chi = 0$ at the rescaled time of about 20 indicates the recurrence of the still localized occupation probability. Even without the mechanism of self-localization the initially prepared exciton wave packet remains rather localized. This is demonstrated once again by the localized structure at the rescaled time of about 42. At this time the wave packet has already been reflected 3 times at the chain ends.

The shift of the localized structure in the P_1 curves to larger times for increasing χ indicates the well-known effect of decreasing soliton velocity with increasing nonlinearity. The localized structure does not reappear for $\chi = 3$ in accordance with Fig. 1(a). The oscillations of P_1 in the eighth and ninth curves of Fig. 2(a) indicate the transition to an immobile soliton. For $\chi = 3.5$ it remains confined to a few sites at the beginning of the chain with a complex oscillating motion (compare Fig. 3). For $\chi = 4.5$ and 5 the occupation probability remains pinned nearly completely at the first site of the chain. This result coincides with the estimation that soliton pinning should occur if the localization energy $\kappa\Delta^2$ of an exciton in a molecular chain overcomes the delocalization energy $2|J|$.

The results of Fig. 2(a) drastically change if we take a value of $\theta_d = 10$. Figure 2(b) displays the central result of our paper. The recurrence behavior of the occupation probability for smaller values of χ is nearly totally removed and the pinned state of the soliton has been destroyed in a time comparable to θ_d. There is no stabiliza-

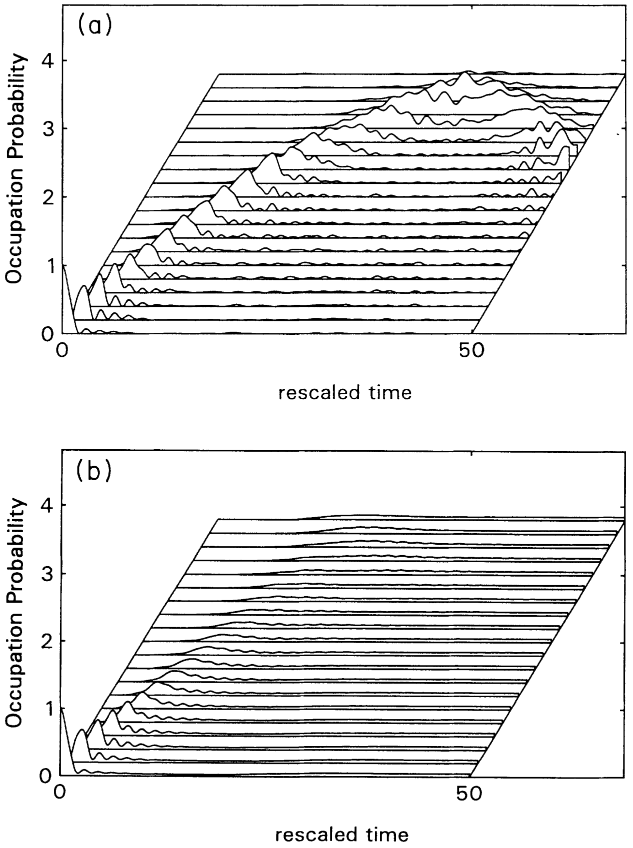

FIG. 1. Occupation probability P_m of the mth site of a chain of 20 molecules vs rescaled time (sites are counted from the front panel backwards) for a rescaled self-trapping constant $\chi = 3$ and (a) infinite dephasing time ($\theta_d = \infty$), (b) $\theta_d = 10$.

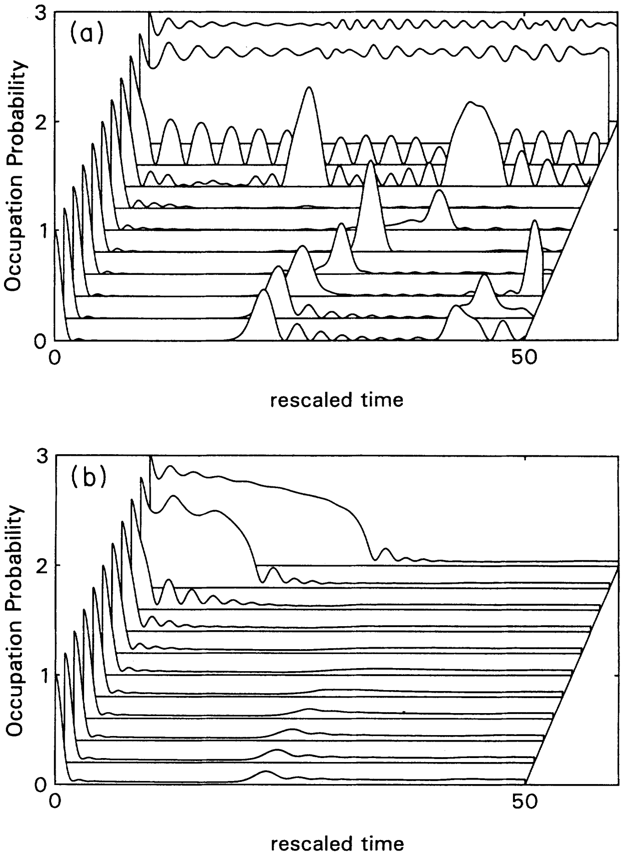

FIG. 2. Occupation probability P_1 of the first site of a chain of 20 molecules vs rescaled time; the rescaled self-trapping constant χ is increased from 0 to 5 in steps of 0.5 (from the front panel backwards). (a) Infinite dephasing time ($\theta_d = \infty$); (b) $\theta_d = 10$.

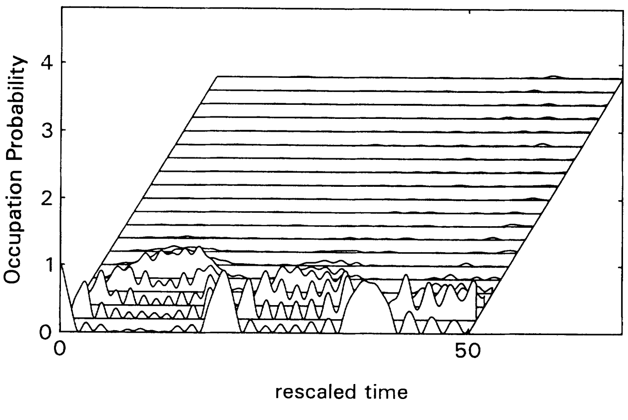

FIG. 3. Same as Fig. 1(a) ($\theta_d = \infty$) but for $\chi = 3.5$.

tion of the soliton achievable by increasing the nonlinearity. In all cases the dephasing distributes the initially localized occupation probability over the whole chain although this process takes somewhat longer for large values of χ. From our calculations of the transfer dynamics in a molecular dimer [17] we estimate that the time at which the pinned soliton has been destroyed is proportional to $\theta_d e^{\chi}$. More details will be published in a forthcoming paper.

Now let us specify the calculations for the parameters typical for the standard model of α-helical polypeptides. Using the elasticity constant of the hydrogen bridges $\kappa = 13$ N/m, the coupling constant of the high-frequency excitation with the longitudinal chain deformation $\Delta = 62$ pN, and the resonance interaction $J = 0.967$ meV, we obtain the self-trapping constant $\chi = 1.91$. The upper limit of the chain phonons lies near 10 meV. Hence, the static solution of the equations of motion for the chain vibrations is justified, and we expect that it coincides with the results of the D_2 ansatz.

The results of the corresponding numerical calculations are displayed in Fig. 4. The range of the rescaled time shown corresponds to 34 ps. A comparison of the results of Fig. 4(a) with those of, e.g., [15] shows satisfactory coincidence. However, the soliton pictured in Fig. 4(a) does not survive the decrease of the dephasing time from infinity to the finite value $\theta_d = 10$. Figure 4(b) shows the quickly attained equipartition of the originally self-localized occupation probability. If the dephasing time becomes comparable to the time which the exciton needs to move through the chain we cannot expect the arrival of a strongly localized wave packet. $\theta_d = 10$ corresponds to a dephasing time of slightly less than 2 ps and is therefore in the upper range of typical values for molecular systems. Thus the concept of self-localized energy transport in polypeptides appears very questionable.

On the other hand, studying the exciton motion without the soliton mechanism ($\chi = 0$) one obtains curves with overall features which deviate only slightly from those of Fig. 4(a). In particular, the excitation moves once through the chain without any effect of dispersion. Of course, this coincidence is destroyed if one introduces disorder into the chain (compare [15]).

As discussed in Sec. II, dephasing results from the coupling to the environment and from finite-temperature fluctuations of the longitudinal chain modes. If the temperature is increased the dephasing time decreases. At the same time the soliton wave function of the exciton-vibration system and thus the phase coherence of the exciton over different sites of the chain is destroyed. The resulting tendency towards equipartition of the occupation probability strongly diminishes the self-localization.

It should be noted that our result for the destruction of solitons by the dephasing mechanism is different to the finite temperature results within the so-called D_1 ansatz for the time-dependent wave function. In that case the self-localization of the excitation energy is supported by the decreasing of the resonance interaction and thus a decreasing of the exciton mobility by a Huang-Rhys-type factor. However, this result seems questionable although it is correct in the D_1 approach. Investigating the exciton transfer in a simple dimer model one obtains a contrasting picture. If temperature and the nuclear tunneling rate are sufficiently small, the excitation energy which shall be initially localized, say at the first monomer, remains localized at the minimum of this diabatic poten-

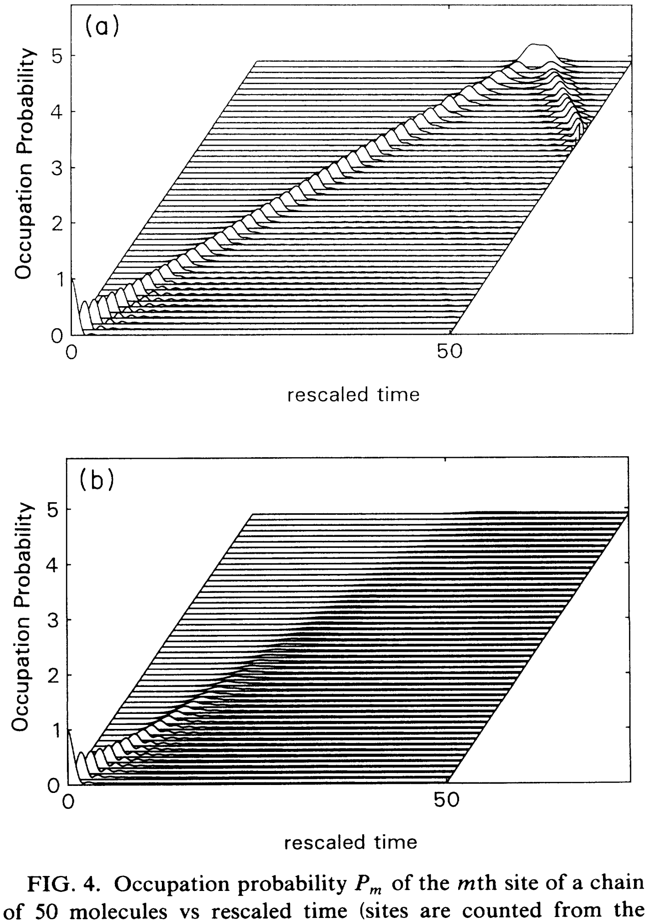

FIG. 4. Occupation probability P_m of the mth site of a chain of 50 molecules vs rescaled time (sites are counted from the front panel backwards) for a rescaled self-trapping constant $\chi = 1.901$ according to the standard model of an α-helical polypeptide chain and for (a) infinite dephasing time ($\theta_d = \infty$), (b) $\theta_d = 10$.

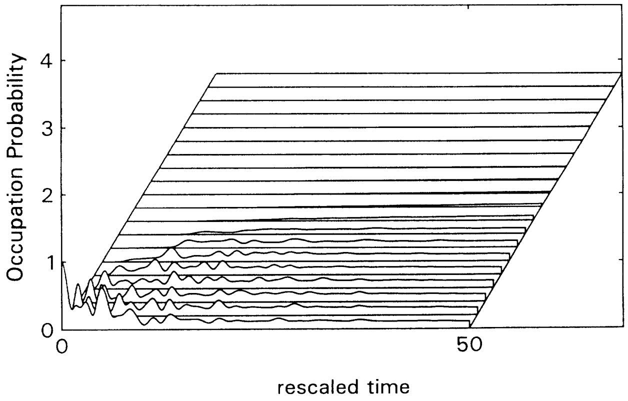

FIG. 5. Same as Fig. 4(a) ($\theta_d = \infty$, $\chi = 1.901$), but for 20 molecules and a self-trapping contribution according to the symmetric exciton-vibration coupling $u_{m+1} - u_{m-1}$.

tial surface. However, if the temperature is increased higher vibrational states are occupied and the transfer to the other monomer becomes easier. This phenomenon is known as the change from the nuclear tunneling region to the activated transfer. As discussed in [17] this result holds true also for transfer scenarios beyond the incoherent (hoppinglike) region.

If the self-trapping contribution, Eq. (18), does not include the occupation probabilities in a nonlocal manner as introduced in the general form in this equation, then soliton formation does not appear. Figure 5 demonstrates the result of a corresponding calculation taking the local exciton-vibration coupling proportional to $u_{m+1}-u_{m-1}$ instead of $u_m - u_{m-1}$.

V. CONCLUSIONS

The density-matrix theory has been utilized to study the influence of dephasing effects on the time-dependent wave function of self-localized exciton-vibration states in a molecular chain. The self-localization mechanism has been incorporated in the density-matrix description in a manner equivalent to the so-called D_2 ansatz in the theory of Davydov solitons. The physical background of this approach corresponds to a classical description of the vibrational modes together with the assumption of their instantaneous reaction to the exciton motion. This last assumption is equivalent to the high-frequency limit of the vibrational modes compared with the exciton velocity. For the standard model of α-helical polypeptides the corresponding ratio of a mean vibrational frequency and the resonance interaction $\hbar\omega/J$ amounts to a value much larger than unity. The comparison of our numerical results (for the case of infinite dephasing time) with those obtained by a direct use of the D_2 ansatz justifies this reasoning.

However, the self-trapped motion is drastically influenced by finite dephasing times as one has to expect from general physical arguments. In the discussed model there does not occur any long-time stabilization against dephasing of the soliton wave packet by the nonlinear coupling mechanism. Hence, our approach produces a strong argument against soliton formation and self-localized energy transport by the α-helical parts of proteins at physiological temperatures.

Although the coupling to a dissipative environment has been included into the density-matrix equations only by dephasing rates we believe that a complete description does not alter the present results. Corresponding calculations are in progress.

Finally it is necessary to mention that, in view of the specific aim of the present calculations, the basic conceptual problem of the correct description of the motion of self-localized excitation energy has not been touched here. But to indicate a possible way to solve this problem we refer to our density-matrix theory of electron transfer dynamics [17]. In that approach we used the density-matrix theory for the (diabatic) representation of the coupled electron-vibration states of the single monomers of a molecular dimer embedded in a dissipative environment. Taking into account all vibrational states this representation gives an exact description of the electron-vibration states of the corresponding monomer. With respect to a numerical solution of the density-matrix equations for the case of a single vibrational mode one reaches a (numerically) correct description by considering a sufficiently large number of excited vibrational states. The coupling of the monomers in the dimer via the transfer integral does not introduce any further complication for the numerical solution.

In the present case of the coupled states of localized excitons and longitudinal vibrations of a molecular chain the density matrix in the representation of coupled exciton-vibration states reads $\rho(m,\{M_q\};n,\{N_q\})$ where m and n are the site indices and M_q and N_q the vibrational quantum numbers of the mode q. Clearly, the problem is too complex for any numerical solution. The large number of density-matrix elements expands the dimension of the corresponding dynamic system too rapidly. But one can try to reduce the number of longitudinal vibrational modes to one or two effective modes. Then the problem becomes tractable and one can hope to reach some new insight into the exciton-vibrational dynamics in molecular chains. Corresponding systems are presently being studied.

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