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# Excitation oscillations in conformationally disordered chains with random traps

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In this work the short-time dynamics of quenched Frenkel excitons in binary, coiled chains is investigated by numerical calculations. Quenching is modeled by means of a non-Hermitian damping Hamiltonian accounting for interstitional traps. The dependence of donor and acceptor response functions to δ-pulse excitation is examined as a function of diagonal disorder, off diagonal disorder induced by random non-nearest-neighbor contacts (degree of coiling), coupling strength, and two types of initial conditions (localized and nonlocalized). The results clearly demonstrate that the relaxation behavior shows significant oscillations even after averaging over a representative ensemble of chain configurations and over all possible initial localized conditions over a wide range of model parameters.

## I. INTRODUCTION

Transport of electronic excitation among aromatic sites fixed to a polymer chain is usually considered to be an incoherent process, the dynamics of which being governed by a Pauli master equation. This concept has been applied both in analytical theory[1] and in computer simulations.[2,3] The hopping exciton model has its justification in the limit of large phonon coupling and strong chain vibrations which destroy the phase relations of migrating excitations. The other limiting case is coherent excitation motion which arises from strong, short-ranged site-to-site interaction at very low phonon temperatures where the nuclear motional degrees of freedom are frozen in. The coherent approach of optical dynamics has so far obtained little attention in polymers, if any at all. However, in the light of the spectacular progress in femtosecond spectroscopy, oscillatory excitation phenomena should give rise to more and more interest, both experimentally and theoretically.

In the absence of a heat bath, a widely accepted model for coherent exciton motion is Schrödingers' equation for Frenkel excitons,[4] which, applied to any finite system of chromophores, predicts an oscillating time dependence of the individual site-occupation probabilities of the chromophores. A great deal of work has been devoted to the study of Frenkel excitons in condensed systems with some kind of disorder, i.e., lattice defects, randomly placed traps or impurities, and inhomogeneous broadening. These investigations were concerned with both stationary quantities such as the absorption line shapes or the density of states[5–7] and transient response functions subsequent to δ-pulse excitation.[8–10] Huber and coworkers used analytical theories and numerical methods to compute absorption line shapes for a Frenkel Hamiltonian with inhomogeneously broadened transition frequencies.[5] This group also investigated the asymptotic δ-pulse response behavior of trapped systems on the basis of the coherent potential approximation, the *t*-matrix method, and numerical simulation.[9] The problem of random trapping was also addressed by Parris who resorted to eigenvector analysis of the Frenkel Hamiltonian and also suggested an approximate, effective Schrödinger equation with a continuous Hamiltonian, the solutions of which are in good agreement to the asymptotic decay profile.[10]

All these transient studies[9,10] have in common that they were directed toward trapping in periodic arrays of chromophores for which disorder was introduced either by the position of the traps or by imposing certain distribution functions on the parameters of the Hamiltonian, thus leaving its general structure, that is, tridiagonal in the case of the one-dimensional (1D) tight-binding model, unaffected. In coiled 2D and 3D chains, however, the conformational multitude shows up in a special type of site disorder which creates a fluctuation of non-nearest-neighbor couplings and thus novel aspects in Frenkel exciton dynamics. The effects of this disorder caused by the polymer conformation and by the randomness of donor acceptor sequences on the absorption line shapes of coiled chains were investigated by us in a very recent publication.[11] In the present work we extend our objectives to the computation of transient response functions of trapped molecular chains. The basic idea of modeling the above-mentioned conformational disorder is to generate chain configurations via the Pivot–Monte Carlo algorithm[12] and assign one of two different species of chromophores—referred to as donors and acceptors—randomly to the segments. Acceptors are assumed to be coupled to an interstitional trap, which is modeled by a purely imaginary trapping Hamiltonian.[8] The next step is then to calculate the specific Hamiltonian for this configuration and compute the interesting excitation survival probabilities by expansion of the state vector in stationary solutions of the Schrödinger equation. Averaging over the configuration space of the chains finally yields the statistical average of the excitation survival functions. In this procedure we are dealing with a particular form of *off-diagonal* disorder which exhibits the most typical features of coiled polymers, namely, nonbond, non-nearest-neighbor contacts.

The aim of this study is to elucidate transient features of coherent excitation transport in a binary site ensemble of donors and acceptors attached to a 2D polymer chain.

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Special emphasis is devoted to the circumstances under which the population relaxation of trapped chains shows oscillatory or overdamped behavior. Important questions which will be addressed in this context deal with the effects of disorder, energetic intrachain parameter $\phi$, and strength of electronic coupling as well as the influence of statistical mechanical averaging on the oscillatory behavior of the survival probability for both donors and acceptors.

The format of the paper is as follows. In Sec. II we describe the system under investigation and formulate our approach to the computation of occupation and survival probabilities of interest. Section III defines a particular system of binary 2D chain conformations and gives the results of various simulation runs. In Sec. IV we summarize the most important findings.

## II. PHYSICAL MODEL AND APPLIED METHODS

For the present purpose the polymer chain shall be given by the $N$ steps of a self-avoiding random walk on a square lattice with nearest-neighbor distance $a$. Neglecting the phonon bath, such a system of chromophores can be described by the Frenkel Hamiltonian

$$\hat{\mathbf{H}}=\sum_{k=1}^{N}\varepsilon_k\hat{\mathbf{a}}_k^\dagger\hat{\mathbf{a}}_k+\sum_{k,l=1}^{N}J_{k,l}\hat{\mathbf{a}}_k^\dagger\hat{\mathbf{a}}_l-i\sum_{k=1}^{N}\gamma_k\hat{\mathbf{a}}_k^\dagger\hat{\mathbf{a}}_k\ , \tag{1}$$

which does not account for thermal degrees of freedom and the electronic structure of the chromophores. This model assumes that only one molecular state interacts with other molecules. In the first two terms, which form the unquenched Frenkel Hamiltonian $\hat{\mathbf{H}}^h$, the operators $\hat{\mathbf{a}}^\dagger$ and $\hat{\mathbf{a}}$ denote creation and annihilation operators for an exciton at the $k$th chromophore and $\varepsilon_k$ is the unperturbed energy level of the corresponding state. The last term containing the damping constant $\gamma_k$ accounts for the irreversible removal of the exciton from the system due to interstitional trapping and emission of a photon.

The coupling strength $J_{k,l}$ between site $k$ and $l$ is assumed to be of dipolar origin and is written in the form

$$J_{k,l}=\begin{cases}\dfrac{Ja^3}{|\mathbf{r}_k-\mathbf{r}_l|^3}, & |\mathbf{r}_k-\mathbf{r}_l|\le r_c,\\ 0, & |\mathbf{r}_k-\mathbf{r}_l|>r_c,\end{cases} \tag{2}$$

where $\mathbf{r}_k$ specifies the spatial coordinates of site $k$, $r_c$ is a cutoff radius, and $a$ is the distance between two adjacent chromophores. $J$ then denotes the coupling strength at nearest-neighbor distance.

The polymer is imbedded in a random potential of a disordered matrix (at low temperatures), so that the $\varepsilon_k$ are subject to a diagonal disorder (inhomogeneous broadening) for which a Gaussian distribution is a sound theoretical result.[13] Therefore the $\varepsilon_k$ are drawn from the distribution

$$P(\varepsilon_k,\bar{\varepsilon},\sigma)=\frac{1}{\sigma\sqrt{2\pi}}e^{-(\varepsilon_k-\bar{\varepsilon})^2/2\sigma^2}\ , \tag{3}$$

with average $\bar{\varepsilon}$ and width $\sigma$.

In this work we consider only one-exciton states and write them with the help of the excitonic vacuum state $|0\rangle$ in the form

$$|\psi(t)\rangle=\sum_k\psi_k(t)\hat{\mathbf{a}}_k^\dagger|0\rangle\ . \tag{4}$$

Schrödingers' equation for one-particle states is then given by

$$i\hbar\frac{d\psi_k(t)}{dt}=\sum_l H_{k,l}\psi_l(t)\ , \tag{5}$$

with matrix elements of the Hamiltonian [Eq. (1)]

$$H_{k,l}=\delta_{k,l}(\varepsilon_k-i\gamma_k)+(1-\delta_{k,l})J_{k,l}\ . \tag{6}$$

The state vector can be expanded in the one-exciton eigenbasis of the Hamiltonian according to

$$\psi_r(t)=\sum_l c_l u_{l,r}e^{-iE_lt/\hbar}\ , \tag{7}$$

so that the occupation probabilities $p_r(t)$ take the form

$$p_r(t)=\psi_r(t)\psi_r^*(t)=\sum_k\sum_l c_kc_l^*u_{k,r}u_{l,r}^*e^{-i(E_k-E_l)t/\hbar} \tag{8}$$

Using the abbreviations

$$\begin{aligned}&c_k=a_k+ib_k,\quad d_1^{ij}=a_ia_j+b_ib_j\ ,\\&\mathbf{u}^{(r)}=\mathbf{v}^{(r)}+i\mathbf{w}^{(r)},\quad d_2^{ij}=b_ia_j-a_ib_j\ ,\\&E_k=\hbar(\omega_k-i\kappa_k),\quad d_3^{ijr}=v_i^{(r)}v_j^{(r)}+w_i^{(r)}w_j^{(r)}\ ,\\&\omega_{ij}=\omega_i-\omega_j,\quad d_4^{ijr}=w_i^{(r)}v_j^{(r)}-v_i^{(r)}w_j^{(r)}\ ,\\&\kappa_{ij}=\kappa_i+\kappa_j\ ,\end{aligned} \tag{9}$$

Eq. (8) can be rewritten as

$$\begin{aligned}p_r(t)&=\sum_{i,j}\{(d_1^{ij}d_3^{ijr}-d_2^{ij}d_4^{ijr})\cos\omega_{ij}t+(d_2^{ij}d_3^{ijr}+d_1^{ij}d_4^{ijr})\sin\omega_{ij}t\}e^{-\kappa_{ij}t}\\&=\sum_i d_1^{ii}d_3^{iir}e^{-2\kappa_it}+2\left\{\sum_{i>j}(d_1^{ij}d_3^{ijr}-d_2^{ij}d_4^{ijr})\cos\omega_{ij}t+\sum_{i>j}(d_2^{ij}d_3^{ijr}+d_1^{ij}d_4^{ijr})\sin\omega_{ij}t\right\}e^{-\kappa_{ij}t}\ .\end{aligned} \tag{10}$$

Since the Hamiltonian is not Hermitian, the eigenenergies $E_j$ are in general not real and the occupation probabilities $p_r(t)$ are exponentially damped oscillations.

This approach to the occupation probabilities, and hence to the donor and acceptor response functions, requires the explicit computation of all eigenvalues and eigenvectors. Furthermore, the initial value problem $\psi(t=0)=\psi^0$ has to be solved in order to determine the coefficients $c_l$ from Eq. (7). For chains not too long ($<50-100$), both tasks can be successfully solved by using NAG-LIB routines from the computer library.

For the primary excitation process, we will consider two types of initial conditions, referred to as localized and delocalized, respectively. In the first case the excitation is initially localized to *one* donor chromophore. This situation can be the result of an incoherent excitation mechanism due to a transition from a higher-energy level of the chromophore, electronic level crossing, etc. In order to minimize the structural information of the system under investigation, we assume that all donor molecules are equally likely excited at $t=0$ so that the experimentally observed quantities are averages over all equivalent initial excitation conditions. However, this only affects the coefficients $c_r$, and hence $d_1^{ij}$, $d_2^{ij}$ and the averaged occupation probabilities have the same form as Eq. (10), with $d_1^{ij}, d_2^{ij}$ replaced by the averaged quantities $\langle d_1^{ij}\rangle_{\text{IC}}, \langle d_2^{ij}\rangle_{\text{IC}}$. This procedure is, of course, equivalent to solving the Van Neumann–Liouville equation with the Hamiltonian [Eq. (1)] for the density matrix $\rho_{nm}(t)$ under the corresponding initial condition $\rho_{nm}(0)=\rho_{nm}^0$ ($=\delta_{n,n}/N_D$ if $n$ denotes a donor and 0 otherwise), but the latter requires the diagonalization of an $N^2$-dimensional matrix, whereas with our approach the dimension of the eigenvalue problem scales linear with the chain length. In terms of computation time, this ratio is $N^6/N^3$. When applying this model to a concrete experimental situation, this average might be simplified if, e.g., only very few donors, or even only one donor, can be initially excited.

The other extreme of the delocalized initial condition corresponds to initial excitation due to direct absorption of a photon into the one-exciton absorption band as computed in Ref. 11. In this case the exciton-photon interaction Hamiltonian determines the (normalized) initial exciton state and predicts $\psi_k(t=0)=1/\sqrt{N}$ for sample sizes much smaller than the optical wavelengths, which correspond to the $\mathbf{k}=0$ exciton in a periodic aggregate.[9]

So far, we have described the computation of the occupation probabilities of sites on a single chain, but the macroscopic observables in experiments with diluted polymer blends are averages over all possible realizations of chain conformations, so that a configurational average has to be carried out.

In order to generate a manifold of chain conformations, we use an implementation of the Pivot algorithm[12] on a square lattice, as outlined in a previous publication.[11] This is a dynamic method which generates a chain geometry from a given one by a suitable Markhov process, so that a detailed balance relation is satisfied. The spatial extension of the polymer is controlled by an energy parameter $\phi$, which characterizes the interaction of the polymer with its surroundings and is chosen such that $\phi \rightarrow \infty$ corresponds to a contact-free chain. As also pointed out in Ref. 11, the randomness of the chain conformations entails a randomness of off-diagonal matrix elements and hence a structural randomness of the Hamiltonian.

All together the averaged occupation probabilities $\bar{p}_r(t)$ are given by

$$\bar{p}_r(t)=\Bigg\langle \sum_i \langle d_1^{ii}\rangle_{\text{IC}} d_3^{irr} e^{-2\kappa_i t}+2\left\{\sum_{i>j}(\langle d_1^{ij}\rangle_{\text{IC}} d_3^{ijr}-\langle d_2^{ij}\rangle_{\text{IC}} d_4^{ijr})\cos\omega_{ij}t \right. \\ \left. +\sum_{i>j}(\langle d_2^{ij}\rangle_{\text{IC}} d_3^{ijr}+\langle d_1^{ij}\rangle_{\text{IC}} d_4^{ijr})\sin\omega_{ij}t\right\} e^{-\kappa_{ij}t}\Bigg\rangle_{\text{conf}}, \tag{11}$$

where the symbol $\langle \cdots \rangle_{\text{IC}}$ denotes averaging over all equivalent localized initial conditions and $\langle \cdots \rangle_{\text{conf}}$ represents the average over a representative ensemble of chain configurations, generated by the Pivot algorithm. In case of delocalized initial conditions, the average $\langle \cdots \rangle_{\text{IC}}$ degenerates into the corresponding quantity itself.

## III. RESULTS

In the following numerical simulations with coiled chains, special emphasis is given to the *short-time* behavior. The $N$ segments of a generated chain are randomly occupied by one of two species of chromophores, referred to as donors ($D$) and acceptors ($A$). The latter are assumed to be optically inactive and thus are not involved in the primary excitation process. Without loss of generality we choose a basis in which $i=1,\ldots,N_D$ refers to donors and $i=N_D+1,\ldots,N_D+N_A=N$ to acceptors. Both species may be diagonally disordered according to the Gaussian distribution [Eq. (3)] with parameters $\bar{\varepsilon}_D,\sigma_D$ for donors and $\bar{\varepsilon}_A,\sigma_A$ for acceptors. Furthermore, the damping constants $\gamma_i$ have the values $\gamma_D$ for donors ($i=1,\ldots,N_D$) and $\gamma_A$ for acceptors ($i=N_D+1,\ldots,N_D+N_A$). Finally, the nearest-neighbor coupling constant $J$ from Eq. (2) now depends on the specific transfer process (donor-donor, acceptor-acceptor, donor-acceptor) and can have the values $J_{DD}$, $J_{AA}$, or $J_{DA}$.

For this situation donor (acceptor) survival probability $P_D(t)$ [$P_A(t)$] is defined as the probability of finding the exciton at one of the donor [acceptor] sites at time $t$:

$$P_D(t)=\sum_{i=1}^{N_D} p_i(t), \quad P_A(t)=\sum_{i=N_D+1}^{N_D+N_A} p_i(t) . \tag{12}$$

In order to obtain the averaged quantities $\bar{P}_D(t),\bar{P}_A(t)$, the averages in Eq. (11) have to be carried out.

Prior to presenting our results, we demonstrate that the initial slope of the occupation probabilities of donors and acceptors is 0 for both types of initial conditions.

Starting from Schrödingers' equation (5), one concludes $dp_i/dt|_{t=0}=0$, because

$$\begin{aligned}\frac{dp_k}{dt}&=\frac{d}{dt}(\psi_k^*\psi_k)\\&=\frac{d\psi_k^*}{dt}\psi_k+\psi_k^*\frac{d\psi_k}{dt}\\&=\frac{i}{\hbar}\sum_{l=1}^{N_D+N_A}(H_{k,l}^*\psi_l^*\psi_k-H_{k,l}\psi_k^*\psi_l)\ ,\\\frac{dp_k(t)}{dt}&=\frac{2}{\hbar}\mathrm{Im}\left[\psi_k^*(t)\sum_{l=1}^{N_D+N_A}H_{k,l}^h\psi_l(t)\right]+2\gamma_k p_k(t)\ .\end{aligned}\tag{13}$$

In the case of a real Hamiltonian $\mathbf{H}^h$ [Eq. (1)] and under the assumption of real initial conditions, the derivatives of the occupation probabilities at $t=0$ take the values

$$\frac{dP_D(0)}{dt}=2\sum_{k=1}^{N_D}\gamma_k p_k(0)\ ,\tag{14}$$

$$\frac{dP_A(0)}{dt}=0\ .\tag{15}$$

This also holds for complex initial conditions, as long as acceptors are not excited at $t=0$. If $\gamma_k$ is nonzero only for acceptor chromophores, then $dP_D(t)/dt|_{t=0}=0$ because we assumed that only donors get initially excited (localized or delocalized).

Unless stated differently we will present results for chains of length 20 ($N_D=N_A=10$), restrict ourselves to nearest-neighbor interaction ($r_c/a=1$), and assume donors to be unquenched ($\gamma_D/J=10^{-6}$ and $\gamma_A/J=0.1$). The fluorescence of the donors is not taken into account here, since it only produces an exponential factor in $P_D,P_A$. Since fluorescence lifetimes are usually by several orders of magnitude larger than characteristic times of excitation energy transport, this does not affect the results presented below, but therefore $\gamma_A$ actually corresponds to the difference of donor and acceptor damping constants. Except for the first figure, the response functions are averaged over all 10 equivalent initial conditions and over 1000 configurations. Energies are given in units of $J$, and we use a scaled time $tJ/\hbar$.

### A. Localized initial conditions

Below, we present results for initial conditions such that the excitation is initially localized on a single donor and the average over the positions of the initially excited donor has been carried out. As will be shown below, this is the worst case situation for observing excitation oscillations in the decay profiles, wherefore all relevant parameter variations are described here.

As a first result, we show the partial suppression of oscillations in the survival probabilities $P_D(t),P_A(t)$ because of conformationally averaging for equal coupling strengths $J_{DD}=J_{AA}=J_{DA}=J$ and isoenergetic donors and acceptors ($\varepsilon_i=\varepsilon_D=\bar{\varepsilon}_D=10J$, $i=1,\ldots,N_D$, $\varepsilon_i=\varepsilon_A=\bar{\varepsilon}_A=5J$, $i=N_D+1$, $N_D+N_A$, and $\sigma_D=\sigma_A=0$). In Fig. 1 the response function of a single configuration for one randomly chosen localized initial condition (thick solid line) is compared to the average over all 10 initial conditions for the same configuration (dashed line). The effect of the configurational manifold can be seen in the dotted line, where 1000 chains were used for averaging. As with most other situations, the decay profiles are characterized by a pronounced initial oscillation followed by a multiexponential decay with superimposed, damped oscillations. This initial oscillation in $\bar{P}_D(t),\bar{P}_A(t)$ compares very well to the response functions for a donor-acceptor dimer with otherwise the same parameters. For the thin solid line, delocalized initial conditions were used (see Sec. III B). This figure clearly

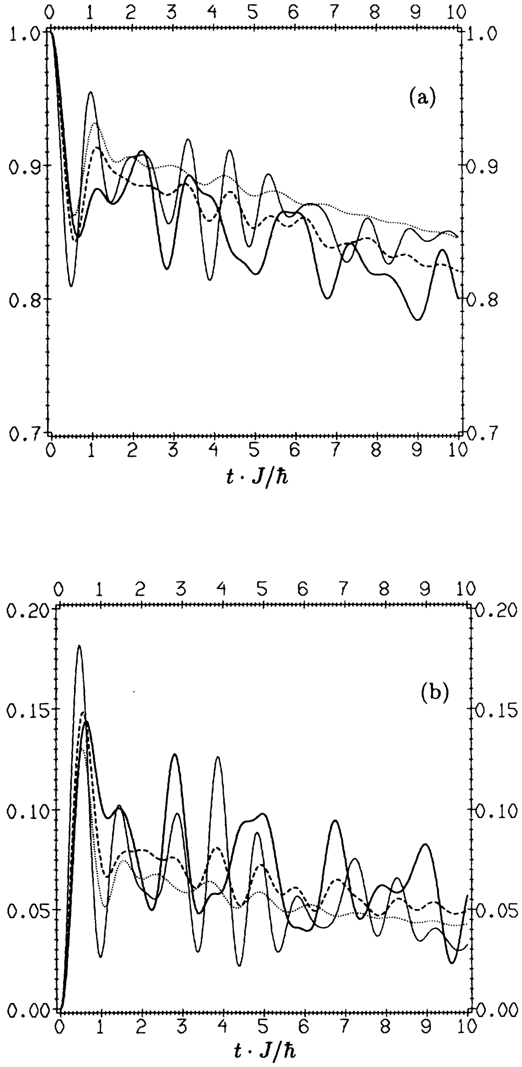

FIG. 1. Effect of averaging on the survival probabilities for (a) donors and (b) acceptors. The thick solid lines show $\bar{P}_D(t),\bar{P}_A(t)$ for one random configuration and one randomly chosen localized initial condition. Using the delocalized initial condition for the same chain with otherwise identical parameters yields the thin solid graphs (see Sec. III B). The dashed lines were obtained after averaging over all possible localized initial conditions on the same chain. Finally, the dotted lines show the survival probabilities averaged over all localized initial conditions and 1000 configurations.

shows that averaging over initial conditions has a more severe effect on the destruction of oscillations than configurational averaging.

Figure 2 shows the effect of different acceptor energies on the survival probabilities, the other parameters being the same as before. In the case that acceptor energies are equal to donor energies, the excitation transport from donors to acceptors is most efficient. The donor population decays rapidly, which accounts for the pronounced population of the acceptors on the chain, and both response signals decay, showing slight oscillatory contributions only. With decreasing acceptor energy, i.e., increasing difference $|\varepsilon_D - \varepsilon_A|$, the transport to the acceptors becomes more and more inefficient, as the donor decay slows down and acceptors get less and less populated. The explanation for this behavior is obviously the reflection of the exciton—initially residing on a donor—at the boundaries of connecting donor subunits of the chain because of inhomogeneities, i.e., different acceptor energies.

In the remainder of this section, the acceptor energy has been set again to the lower value $\varepsilon_A/J = 5$. The consequences of chain coiling—characterized by $\phi$—on $P_D(t)$ and $P_A(t)$, respectively, are shown in Fig. 3 for values $\phi = \infty, 0.4, 0, -0.4$, the remaining parameters being the same as in Fig. 1. The limit $\phi = \infty$ corresponds to an ensemble of contact-free chains, and so the top graph in Fig. 3(a) and the bottom graph in Fig. 3(b) are averages over all possible donor-acceptor configurations on a linear chain because $r_c/a = 1$. With decreasing $\phi$ the number of non-nearest-neighbor contacts increases and the transport efficiency of the exciton from donors to acceptors becomes better [as $P_D(t)$ is shifted to smaller and $P_A(t)$ to larger amplitudes]. This is the same behavior as one expects from an incoherent transport mechanism. Note that the oscillations in $\bar{P}_D(t)$ and $\bar{P}_A(t)$ decrease in amplitude with increasing number of non-nearest-neighbor contacts.

Another possibility to increase the efficiency of trap-

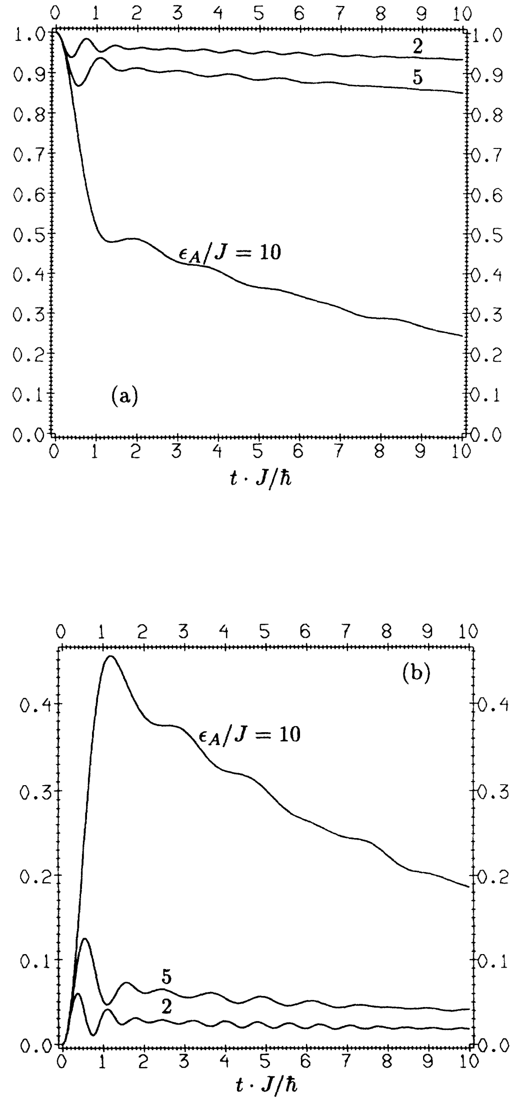

FIG. 2. Averaged survival probabilities for (a) donors and (b) acceptors as a function of acceptor energy $\varepsilon_A$.

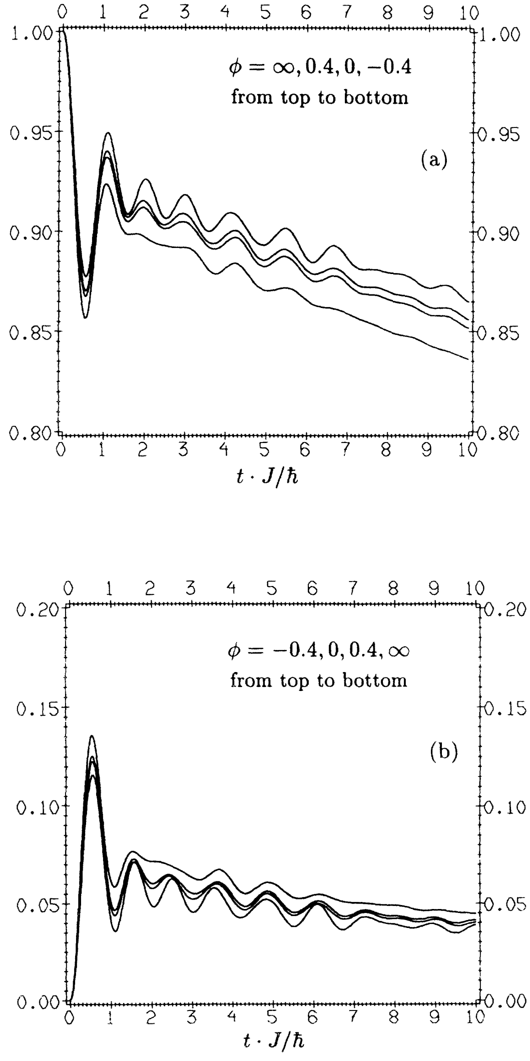

FIG. 3. Dependence of the averaged survival probabilities for (a) donors and (b) acceptors on chain coiling, i.e., $\phi$.

ping is the inclusion of diagonal disorder. In Fig. 4, $\phi$ is set again to 0 and the other parameters have the same values as in Fig. 1, while the width of the distribution of self-energies for donors and acceptors is simultaneously varied ($\sigma_D = \sigma_A = \sigma$). With increasing $\sigma$ oscillations in $P_D(t)$ and $P_A(t)$ get suppressed and the transport of the exciton to the acceptors increases. This happens in a more pronounced fashion than in Fig. 3 already in the first oscillation. We also compared $\bar{P}_D(t), \bar{P}_A(t)$ of isoenergetic sites to isoenergetic donors and distributed acceptors as well as to distributed donors and isoenergetic acceptors. The behavior is in agreement with the previous situation, as an increase in diagonal disorder increases the efficiency of the transport into acceptors and damps oscillatory admixtures. In general, diagonally disordered acceptors increase the transport efficiency more than diagonally disordered donors.

Figure 5 shows the effect of different coupling strengths $J_{DA}$ between donors and acceptors. The parameters are $\varepsilon_D/J = \varepsilon_A/J = 10$, $\sigma_D = \sigma_A = 0$, and $J = J_{DD} = J_{AA}$. In the case of weak donor acceptor coupling, the exciton remains on the donor subunits of the chains and acceptors get hardly populated, so that $P_D(t)$ decays slowly. When increasing the coupling strength beyond $J_{DA}/J = 1$, marked oscillations show up and their amplitude and frequency increases with $J_{DA}$. The dotted graphs correspond to $J_{DA}/J = 2$ and the dashed graphs to $J_{DA}/J = 5$. Furthermore, the amplitude of the first oscillation and the accompanying steep initial slope increase with $J_{DA}$ as well, but the decays are not accelerated. The fastest decay occurs at $J_{DA} = J$ because $J_{DA} \neq J$ represents also inhomogeneities which hinder the donor acceptor transport due to reflections.

The response functions for chain lengths 20 and 100 at an identical donor-acceptor ratio $N_D/N_A = 9$ are com-

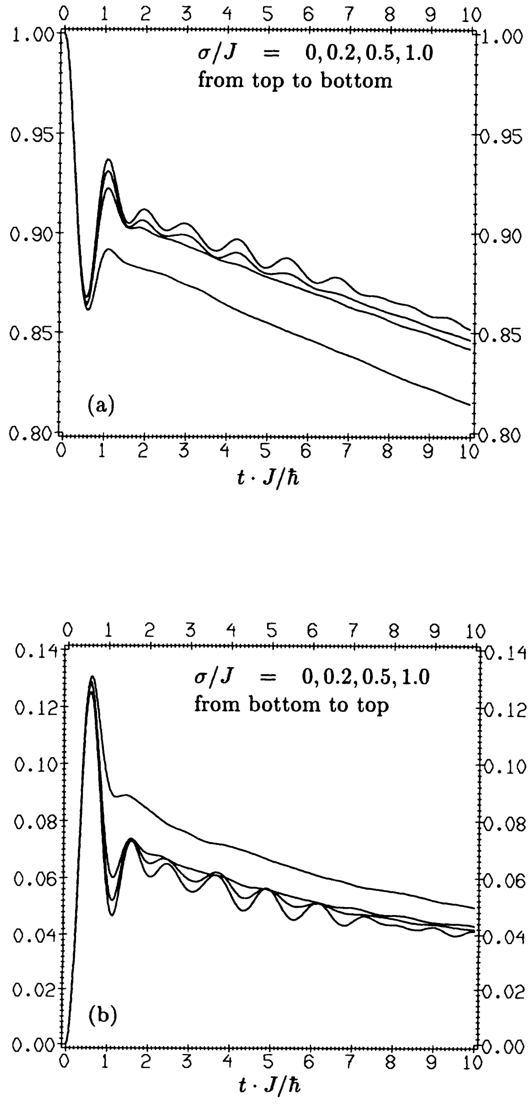

FIG. 4. Averaged survival probabilities for (a) donors and (b) acceptors as a function of diagonal disorder $\sigma = \sigma_D = \sigma_A$.

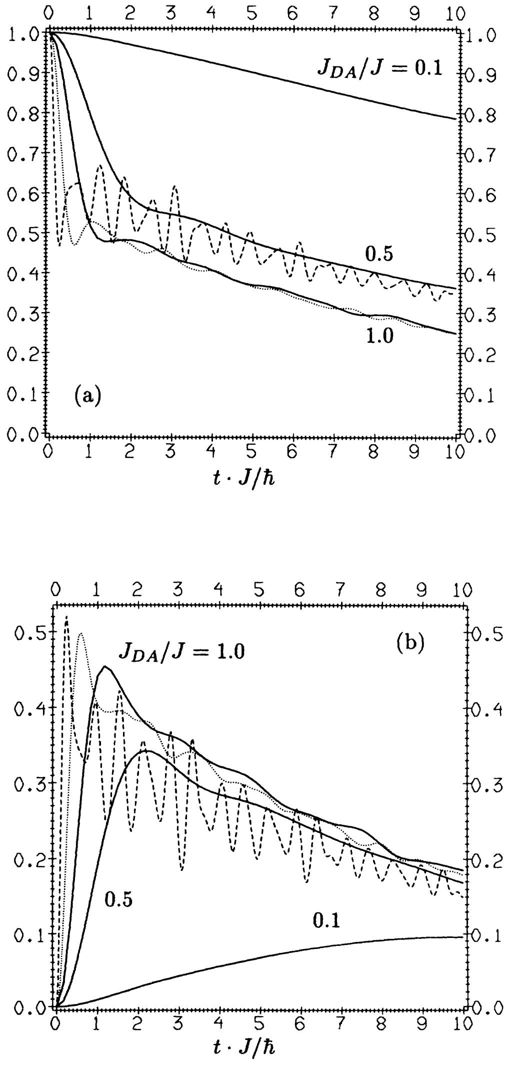

FIG. 5. Dependence of averaged survival probabilities for (a) donors and (b) acceptors on donor-acceptor coupling strength $J_{DA}$. The dashed line corresponds to $J_{DA}/J = 2$ and the dotted one to $J_{DA}/J = 5$.

pared to each other in Fig. 6, the other parameters are taken again from Fig. 1. Obviously, the short-time dynamics is not affected at all by the chain length, although this has nothing to do with the convergence of certain observables with increasing chain length, as observed in Ref. 11. It is rather a consequence of the short-time scale on which we observe the response functions. The initially created exciton is just under the influence of the immediate surroundings, i.e., its next neighbors, because of its finite group velocity.

### B. Delocalized initial conditions

The preceding section showed the major tendencies of the transient donor and acceptor response functions under worst case conditions with respect to oscillatory dynamics. Here we repeat some of these computations for the delocalized initial condition relevant for direct absorption of a photon into the one-exciton absorption band:

$$\psi_k^0 := \begin{cases} 1/\sqrt{N_D}, & k=1,\ldots,N_D, \\ 0, & k=N_D+1,\ldots,N_D+N_A. \end{cases} \tag{16}$$

For the sake of comparison, the variation of $\phi$ with parameters taken from Fig. 3 is depicted in Fig. 7. The basic tendencies remain unchanged, but the amplitudes have changed. In contrast to localized initial conditions, the response functions are not averaged over the initial position of the excitation, which results in larger amplitudes of the superimposed oscillations for the donor as well as for the acceptor response. This can also be seen in Fig. 1: At one randomly chosen chain conformation, the response functions are shown for one randomly chosen localized initial condition (thick solid line), the average over all localized initial conditions (dashed line), and for the delocalized initial condition (thin solid line). On the short-time scale investigated in this study, the decay is

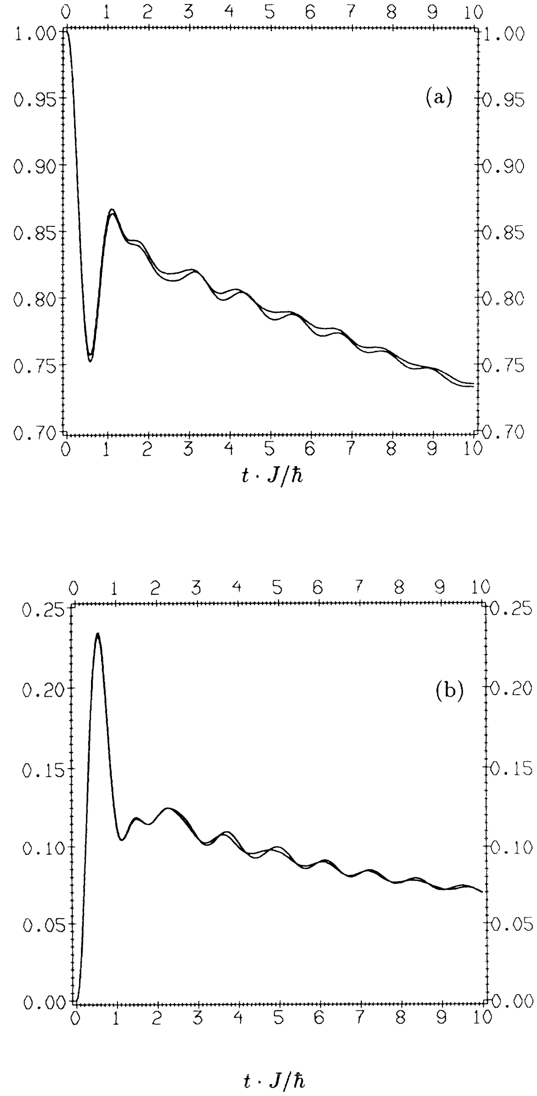

FIG. 6. Averaged survival probabilities for (a) donors and (b) acceptors for chains of length $N=20$ and 100 with a donor-acceptor ratio of $N_D/N_A=\frac{1}{9}$.

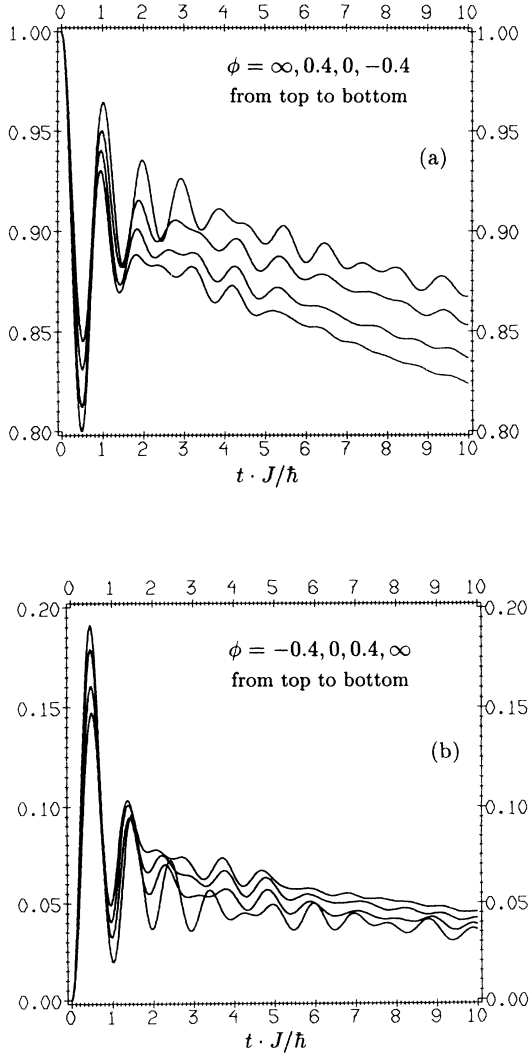

FIG. 7. Dependence of the averaged survival probabilities for (a) donors and (b) acceptors on chain coiling, i.e., $\phi$ for delocalized initial conditions.

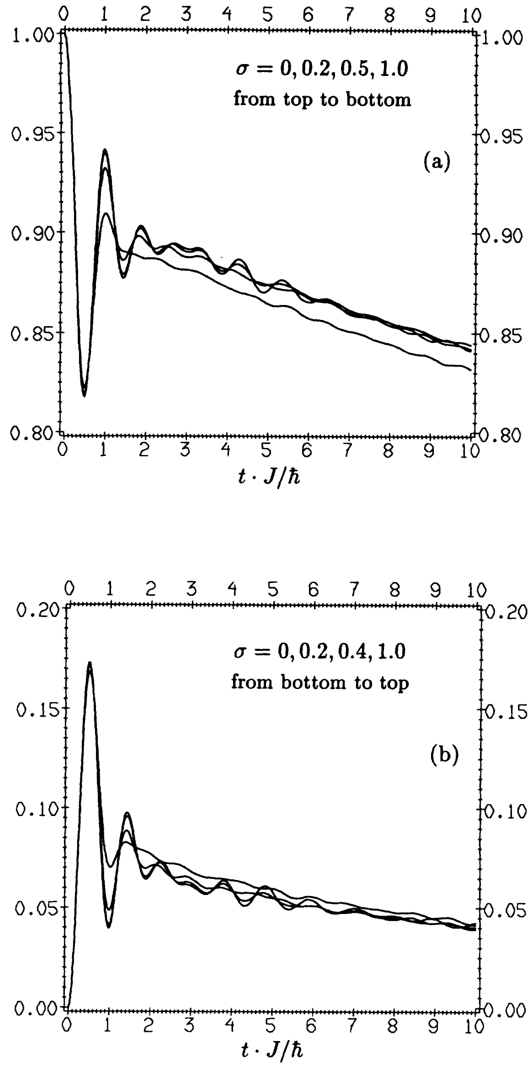

FIG. 8. Dependence of the averaged survival probabilities for (a) donors and (b) acceptors on $\sigma$ for delocalized initial conditions.

equally fast for both types of initial conditions. The same holds for Fig. 8, where the width of inhomogeneous broadening $\sigma$ is varied in analogy to Fig. 4. Comparison with the corresponding localized initial conditions Figs. 7 and 4 shows that a differentiation with respect to the excitation mechanism is not possible.

## IV. SUMMARY

In the present work the short-time dynamics of excitation energy transport in configurationally disordered chains was investigated by numerical techniques applied to Schrödinger's equation for quenched Frenkel excitons in the absence of a heat bath. Donor [acceptor] response functions $P_D(t)$ $[P_A(t)]$ to $\delta$-pulse excitation were computed as the probability of finding the exciton at any arbitrary donor [acceptor] site at time $t$. We used two types of initial conditions in order to describe different excitation mechanisms of the chromophoric system. In the case of *localized initial conditions,* one arbitrary donor is initially excited because of an incoherent transition from a higher state or electronic level crossing. This situation is interesting because it uses a minimum of information about the system and involves an additional average over the location of the initially localized exciton. In the case of direct absorption of a photon into the one-exciton absorption band, delocalized initial conditions [Eq. (16)] are appropriate. In order to compute macroscopically observable quantities, the so-obtained donor and acceptor response functions were averaged over the manifold of possible chain conformations, realizations of diagonal disorder, and location of the initially created exciton in the case of localized initial conditions.

The central concern of this paper was the dependence of these averaged donor and acceptor response functions on various model parameters as well as the question of whether or not oscillatory behavior can still be observed even after averaging over the addressed types of disorder.

The presented results clearly show for both types of initial conditions that the efficiency of the exciton transport from donor to acceptor subunits is best under homogeneous conditions (isoenergetic self energies $\varepsilon_D, \varepsilon_A$, identical coupling strengths $J_{DD} = J_{DA} = J_{AA} = J$). It furthermore increases with increasing degree of coiling ($\phi$) and diagonal disorder ($\sigma_D, \sigma_A$). Another striking finding is that the twofold averaging over the configuration space of the chains and the location of the initial excitation still leave a significant amount of oscillations in the decay profiles. The choice of initial conditions only affects the amplitudes of superimposed oscillations in the response functions, which are larger in the delocalized case because no average over different initial conditions is carried out.

These findings suggest that oscillatory phenomena could be observed by ultrafast detection techniques in future experiments, thus opening the possibility to verify a coherent transport mechanism. For systems with a higher degree of order (known excitation center, well-defined donor-acceptor sequence, etc.), these effects become much more pronounced and the presented model is general enough to be adapted to a variety of such experimentally interesting situations.

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