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Donor-acceptor electron transport mediated by solitons

L. S. Brizhik[*]
Bogolyubov Institute for Theoretical Physics, 03680 Kyiv, Ukraine

B. M. A. G. Piette[†] and W. J. Zakrzewski[‡]
Department of Mathematical Sciences, University of Durham, Durham DH1 3LE, United Kingdom

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We study the long-range electron and energy transfer mediated by solitons in a quasi-one-dimensional molecular chain (conjugated polymer, alpha-helical macromolecule, etc.) weakly bound to a donor and an acceptor. We show that for certain sets of parameter values in such systems an electron, initially located at the donor molecule, can tunnel to the molecular chain, where it becomes self-trapped in a soliton state, and propagates to the opposite end of the chain practically without energy dissipation. Upon reaching the end, the electron can either bounce back and move in the opposite direction or, for suitable parameter values of the system, tunnel to the acceptor. We estimate the energy efficiency of the donor-acceptor electron transport depending on the parameter values. Our calculations show that the soliton mechanism works for the parameter values of polypeptide macromolecules and conjugated polymers. We also investigate the donor-acceptor electron transport in thermalized molecular chains.

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I. INTRODUCTION

There is a large class of biological [1–5] systems and synthetic molecular systems [6–9], in which charges or excitons (molecular excitations) migrate from site to site through multiple sites embedded in a complex system. In many cases an electron transport takes place from a donor to an acceptor through some intermediate molecules or systems such as macromolecules or molecular bridges. An example of such an electron transport in biological systems is the so-called electron-transport chain in redox processes in respiration [10]. Such a chain represents a series of macromolecules onto which electrons can be transferred via redox reactions, so that each compound plays the role of a donor for the "preceding" molecule and acceptor for the "succeeding" molecule. The electron transport in chains also takes place in photosynthesis [10], where the energy is extracted from sunlight via a redox reaction, such as oxidation of sugars and cellular respiration. The location of the electron-transport chain varies for different systems: it is located in the inner mitochondrial membrane in eukaryotes, where oxidative phosphorylation with ATP synthase takes place, or in the thylakoid membrane of the chloroplast in photosynthetic organisms, or in the cell membrane in bacteria [10].

It is known that some molecules in the electron-transport chain, such as NADH-ubiquinone oxidoreductase, flavoproteids, cytochrome *c*-oxidase *cyt*-aa_3, and cytochrome *cyt*-bc_1 complexes are proteins with large molecular weight and thus they are practically fixed in the corresponding membrane. A significant fraction of these proteins is in the alpha-helical conformation, which can support the transport of electrons in the form of electrosolitons [11,12]. Some other molecules in the electron-transport chains, like quinone or cytochrome *cyt-c*, possess much smaller molecular weight. They are highly soluble and can move relatively easily outside the mitochondrial membrane, carrying electron from a heavy donor to a heavy acceptor.

Recently, many conjugated donor-acceptor copolymer semiconductors, which show intramolecular charge transfer on large distances, have been synthesized. Among them are donor-acceptor pairs mediated by salt bridges [13], thienopyrazine-based copolymers [14], *n*-type conjugated polymers based on electron-deficient tetraazabenzodifluoranthene diimide [15–18], etc. Such conjugated polymer semiconductors with electron donor-acceptor transfer have become of growing interest for organic electronic applications [19–22], such as photovoltaic cells [23–25], light emitting diodes (LEDs) [26–29], and field-effect transistors [30–33]. During the past decade more evidence for the electron transport in DNA [34–38] (see review [39]) has also been reported.

In theoretical studies such electron-transport systems are modeled as complexes which include a donor molecule weakly bound to a bridge molecule, which, in turn, is weakly bound to an acceptor molecule. The bridge itself can be modeled as a potential barrier through which the electron tunneling takes place (see, e.g., [40] and references therein.) In some other studies the bridge is modeled as a molecule with superexchange electron interactions [41,42]. Such models have been studied in various approximations in [40–43], etc., and it has also been shown that the rate of electron transfer or of the electron tunneling time from a donor to an acceptor varies with the length of the intermediate bridge. For short bridges, of up to 5–7 units, it increases with the number of units, while for longer bridges [41,42] it remains constant. Indeed, it has been shown that an electron transfer in bis-porphyrin donor-acceptor compounds with polyphenylene spacers shows a weak distance dependence [44]. In some other approaches the electron transport in donor-acceptor systems is modeled as arising from the coupling of the system to a thermal bath and is described by the so-called quantum master equations (QME) or polaronic QME [45].

The importance of bridging molecular structures for the long-range electron transfer has been anticipated a long time

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[*] brizhik@bitp.kiev.ua

[†] B.M.A.G.Piette@durham.ac.uk

[‡] W.J.Zakrzewski@durham.ac.uk

ago. In many cases the bridge induces long-range effective charge transport in donor-acceptor systems or transport between two electrodes even at low temperatures. This indicates that in such systems the mechanism of the electron transport is different from the mechanisms based on thermal excitations or superexchange interaction.

Another type of processes in macromolecules, close to the systems considered above in its mathematical description, is the transfer of energy released in the hydrolysis of ATP into ADP molecules, through macromolecules. This energy is stored in the form of AMID-I vibration of the nearest peptide group. This quantum of energy can be self-trapped in a soliton state and propagate to the opposite end of the macromolecule almost without energy dissipation [11,12]. It is known that biological macromolecules are not symmetric: on both ends of the proteins they have some prosthetic groups that are nonamino acid inorganic, or organic, portions of the protein, which are required for the biological activity of the protein. These prosthetic groups can be different on different sides of the protein. A prosthetic group at the end of a protein close to the hydrolysis of ATP into ADP can affect the time evolution of the initial excitation and can either facilitate or prevent the formation of a soliton in a macromolecule. On the other hand, a prosthetic group on the other end of a protein determines what happens when a soliton arrives there: it can either be reflected back or be absorbed by the prosthetic group in which case its energy can be utilized for the metabolic needs of the cell.

It is well known that in polymers and in macromolecules the electron-lattice interaction is significant, and that this can result in the formation of large solitons which are bound states of an electron and a molecular excitation. In particular, in quasi-one-dimensional systems which satisfy the adiabatic approximation (and polymers and macromolecules do satisfy these conditions [12]), electrons can be self-trapped in solitonlike states, which are bound states of an electron and a self-induced local distortion of the molecular chain. In such soliton states the electron and the lattice distortion can propagate together at some velocity [11,12]. Indeed, both analytical and numerical studies (see review [12]) confirmed the existence of stable soliton states, whose energy is lower than the energy of a free electron, due to the electron-lattice interaction. In numerical studies, chains of finite length, which are formed by identical lattice units, have been considered and it was shown that an initial excitation at one end of the chain evolves into a soliton, which propagates to the opposite end, reflects back, and then keeps bouncing back and forth between them (see, e.g., [12]).

The role of the prosthetic groups in the formation of a soliton and its behavior at the farther end of a macromolecule have so far neither been studied for molecular solitons nor for electrosolitons. Also the problem of an electron transport from a donor molecule to an acceptor molecule, mediated by a soliton in a macromolecule, has not been studied in much detail. Therefore, in the present paper we study the role of the prosthetic groups in the time evolution of initial excitations in quasi-one-dimensional molecular chains, and investigate the possibility of electron transport in a donor-acceptor system, mediated by a molecular chain when the electron-lattice interaction is taken into account. In this paper we model a macromolecule as an isolated polypeptide chain. A more realistic structure of a macromolecule in a soliton mediated donor-acceptor electron transport system will be reported elsewhere.

In the first section of the paper, we describe our model of soliton interaction with a donor and an acceptor. In the third section, using known physical values, we derive some range of relevant values for the dimensionless parameters of our model. In the following section, we study our model numerically, showing the range of parameter values for which a soliton can be spontaneously created on the chain and then be absorbed by the acceptor. Finally, in the last section, we study the thermal stability of our model and we end the paper with some conclusions.

II. HAMILTONIAN OF THE SYSTEM AND DYNAMIC EQUATIONS

Let us consider a molecular chain made out of N sites with a donor molecule or a prosthetic group on the left and an acceptor molecule or another prosthetic group on the right. For convenience in both cases we use the terms "donor" and "acceptor," respectively, and we use the term "electron" for a proper electron and a molecular excitation. We label the molecules in the principal chain with the indices $1,2,\dots,N-1,N$, while the donor molecule corresponds to $n=0$, and the acceptor molecule to $n=N+1$.

The Hamiltonian function of such a system can be written in the form of the sum of three terms, accounting for the Hamiltonians of an electron, lattice, and electron-lattice interaction:

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_{\text{ph}} + \mathcal{H}_{e\text{-ph}}. \tag{1}$$

Here

$$\begin{aligned}\mathcal{H}_e = {}& \overline{\mathcal{E}}_d|\Psi_0|^2 + \overline{\mathcal{E}}_a|\Psi_{N+1}|^2 \\ & + \sum_{n=1}^{N}[\overline{\mathcal{E}}_0|\Psi_n|^2 - (1-\delta_{n,N})(\overline{J}\Psi_n^*\Psi_{n+1} + \text{c.c.})] \\ & - (\overline{J}_d\Psi_0^*\Psi_1 + \text{c.c.}) - (\overline{J}_a\Psi_N^*\Psi_{N+1} + \text{c.c.}),\end{aligned} \tag{2}$$

$$\begin{aligned}\mathcal{H}_{\text{ph}} = {}& \frac{1}{2}\left[\frac{P_d^2}{M_d} + w_d(U_0 - U_1)^2\right] \\ & + \frac{1}{2}\left[\frac{P_a^2}{M_a} + w_a(U_N - U_{N+1})^2\right] \\ & + \sum_{n=1}^{N}\frac{1}{2}\left[\frac{P_n^2}{M} + w(1-\delta_{n,N})(U_n - U_{n+1})^2\right],\end{aligned} \tag{3}$$

$$\begin{aligned}\mathcal{H}_{e\text{-ph}} = {}& \chi_d|\Psi_0|^2(U_1 - U_0) + |\Psi_1|^2 \\ & \times[\chi_d(U_1 - U_0) + \chi(U_2 - U_1)] \\ & + \chi_a|\Psi_{N+1}|^2(U_{N+1} - U_N) \\ & + \sum_{n=2}^{N-1}\chi[|\Psi_n|^2(U_{n+1} - U_{n-1})] \\ & + |\Psi_N|^2[\chi(U_1 - U_0) + \chi(U_2 - U_1)].\end{aligned} \tag{4}$$

Our notation is as follows: $\overline{\mathcal{E}}_0$ is the on-site electron energy, $\overline{J}$ is the resonance integral, M is the mass of a unit cell, χ is the electron-lattice coupling constant, and w is the elasticity of the bond in the principal chain. The indexes d and a refer to the donor and acceptor molecules, respectively. Furthermore, in our notation, Ψ_n is the electron wave function on site n, U_n is the displacement of the nth molecule from its equilibrium position, and P_n is its canonically conjugate momentum. Moreover, the electron wave function satisfies the normalization condition

$$\sum_{n=0}^{N+1} |\Psi_n|^2 = 1. \tag{5}$$

In its general form the Hamiltonian (1) has been introduced by Fröehlich and is known as the Fröhlich Hamiltonian. The explicit form of the various terms in it depends on the specific model. Here we study the model which consists of a long chain $n = 1,2,\ldots,N$ of identical sites ("atoms") with a donor and an acceptor "molecules" attached to the chain on the left $n = 0$ and the right $n = N + 1$ terminals, respectively. We describe the principal chain in the nearest-neighbor approximation and consider the case when the chain can be sufficiently well approximated by one electron band and one acoustical phonon mode which describes the longitudinal displacements of the unit cells from their positions of equilibrium. The electron-lattice interaction Hamiltonian induces a dependence of the electron Hamiltonian on the lattice distortions. Here we assume that the dependence of the on-site electron energy on the lattice distortion is much weaker than that of the intersite electron interaction energy. If the parameters of the principal chain satisfy the conditions of the adiabatic approximation the Hamiltonian leads to a system of Davydov equations [11,12], which in the continuum approximation possess a solution in the form of the so-called Davydov's soliton. Such a soliton describes a self-trapped quasiparticle (molecular excitation, electron, hole), bound to the self-created localized lattice distortion. The electron wave function in this case is given by a solution of the nonlinear Schrödinger equation with the self-induced deformation potential, proportional to the probability of the electron presence at the given site. Such a soliton, which is in fact a special form of a one-dimensional large polaron, propagates along the chain with constant velocity, determined by the initial conditions of its excitation (in the absence of the external field). Within the harmonic description of the lattice, which we consider here, the velocity of the soliton is bound from above by the sound velocity in the chain. It is worth mentioning that in the opposite case, i.e., when only the dependence of the on-site electron energy on the lattice distortion is taken into account, the resulting Hamiltonian describes the Su-Schrieffer-Heeger model, which admits kink solutions and is applicable to such polymers, as polyacetylene [46]. It has also been shown that in the adiabatic approximation, in the continuum limit, the dependence of the on-site electron energy on the lattice distortion leads to the rescaling of the electron-lattice coupling constant coming from the dependence of the intersite electron interaction energy on the lattice distortion [47]. Therefore, to avoid extra parameters, we restrict our model to the one described above.

This model had, in fact, been used first to explain high efficiency of the energy storage and energy transfer in alpha-helical proteins. Later on it has been extended to explain the long-range charge transport in macromolecules and conducting polymers, such as polydiacetylene, etc. (see [11,12] and references therein). The results of these analytical studies have also been confirmed by numerous computer simulations of discrete systems [12]. Some indirect experimental evidence of soliton's (large polaron's) existence in quasi-one-dimensional systems have been reported in [48–56].

So far as we know, the problem of the electron transport from a donor molecule to an acceptor via a intermediate long molecular chain, in which we take into account the electron-lattice interaction, has not yet been studied. Therefore, in the present paper we generalize the Davydov model, described above, to study the long-range donor-acceptor charge transport mediated by a molecular chain. Mathematically, this model, as it was mentioned in the Introduction, can describe also donor-bridge-acceptor systems, with bridge chains that are large enough and for appropriate values of the parameters of the system.

Substituting the above Hamiltonian function into the Hamilton equations for the generalized "coordinates" of the electron Ψ_n and lattice U_n and their canonically conjugate momenta $i\hbar\Psi_n^*$ and P_n, respectively, we obtain

$$\begin{aligned}
M_d\frac{d^2U_0}{dt^2} &= w_d(U_1 - U_0) + \chi_d(|\Psi_0|^2 + |\Psi_1|^2),\\
M\frac{d^2U_1}{dt^2} &= w_d(U_0 - U_1) + w(U_2 - U_1) - \chi_d(|\Psi_0|^2 + |\Psi_1|^2) + \chi(|\Psi_1|^2 + |\Psi_2|^2),\\
M\frac{d^2U_n}{dt^2} &= w(U_{n+1} - 2U_n + U_{n-1}) + \chi(|\Psi_{n+1}|^2 - |\Psi_{n-1}|^2), \quad n = 2,\ldots,N-1,\\
M\frac{d^2U_N}{dt^2} &= w(U_{N-1} - U_N) + w_a(U_{N+1} - U_N) - \chi(|\Psi_N|^2 + |\Psi_{N-1}|^2) + \chi_a(|\Psi_N|^2 + |\Psi_{N+1}|^2),\\
M_a\frac{d^2U_{N+1}}{dt^2} &= w_a(U_N - U_{N+1}) - \chi_a(|\Psi_N|^2 + |\Psi_{N+1}|^2).
\end{aligned} \tag{6}$$

The equations for the electron wave function are

$$\begin{aligned}
i\hbar\frac{d\Psi_0}{dt} &= \overline{\mathcal{E}}_d\Psi_0 - \overline{J}_d\Psi_1 + \chi_d(U_1-U_0)\Psi_0,\\
i\hbar\frac{d\Psi_1}{dt} &= \overline{\mathcal{E}}_0\Psi_1 - \overline{J}_d^*\Psi_0 - \overline{J}\Psi_2 + [\chi_d(U_1-U_0)+\chi(U_2-U_1)]\Psi_1,\\
i\hbar\frac{d\Psi_n}{dt} &= \overline{\mathcal{E}}_0\Psi_n - \overline{J}(\Psi_{n+1}+\Psi_{n-1}) + \chi(U_{n+1}-U_{n-1})\Psi_n, \quad n=2,\dots,N-1,\\
i\hbar\frac{d\Psi_N}{dt} &= \overline{\mathcal{E}}_0\Psi_N - \overline{J}\Psi_{N-1} - \overline{J}_a\Psi_{N+1} + [\chi(U_N-U_{N-1})+\chi_a(U_{N+1}-U_N)]\Psi_N,\\
i\hbar\frac{d\Psi_{N+1}}{dt} &= \overline{\mathcal{E}}_a\Psi_{N+1} - \overline{J}_a^*\Psi_N + \chi_a(U_{N+1}-U_N)\Psi_{N+1}.
\end{aligned} \tag{7}$$

To allow the electron to transfer from the chain to the acceptor, we must add an extra interaction that will favor such a transition. The first coupling that comes to mind is to make the electron energy on the acceptor complex, $\overline{\mathcal{E}}_a = \overline{J}(D_a + i\gamma_a)$, where γ_a would correspond to an electron transfer. Unfortunately, this does not preserve the electron probability (5). Indeed, if we consider the last two equations in system (7) neglecting in them all terms which do not contain γ,

$$\frac{d\Psi_N}{d\tau} = -\gamma_a\Psi_N, \quad \frac{d\Psi_{N+1}}{d\tau} = \gamma_a\Psi_{N+1}, \tag{8}$$

where the rescaled time τ is defined below by Eq. (12), the solution of this equation is

$$\Psi_N(\tau) = \Psi_N(0)e^{-\gamma_a\tau}, \quad \Psi_{N+1}(\tau) = \Psi_{N+1}(0)e^{\gamma_a\tau}, \tag{9}$$

which describes the exponential decrease of the electron probability amplitude on the terminal site of the chain and exponential increase on the acceptor, i.e., a sink at the acceptor. It follows from Eqs. (8) and (9) that the total electron probability is not conserved if the parameter γ_a is a constant.

We can address this problem by using instead a nonlinear coupling of the form $\gamma_a = A_a|\Psi_{N+1}|^2$ for the first equation and $-iA_a|\Psi_N|^2\Psi_{N+1}$ for the second one so that (8) becomes

$$\frac{d\Psi_N}{d\tau} = -A_a|\Psi_{N+1}|^2\Psi_N, \quad \frac{d\Psi_{N+1}}{d\tau} = A_a|\Psi_{N+1}|^2\Psi_{N+1}. \tag{10}$$

To see that the electron probability is conserved, we multiply each equation in (10) by the corresponding complex-conjugate function Ψ_m^*, then multiply the equations which are complex conjugates to Eqs. (10), by the corresponding function Ψ_m and extract the results. This gives

$$\sum_m \Psi_m^*\frac{d\Psi_m}{d\tau} + \Psi_m\frac{d\Psi_m^*}{d\tau} = \frac{d\sum_m|\Psi_m|^2}{d\tau} = 0. \tag{11}$$

Note also that, for completeness, we also add a dissipation term, proportional to Γ, to our lattice equations.

Before we write down the full set of equations, it is convenient to introduce the dimensionless time τ and unit length l, given respectively by

$$\tau = \frac{\overline{J}}{\hbar}t, \quad l = \frac{\hbar}{\sqrt{M\overline{J}}}. \tag{12}$$

Then defining the dimensionless parameters

$$C = \frac{\hbar^2 w}{M\overline{J}^2}, \quad C_{d,a} = \frac{\hbar^2 w_{d,a}}{M_{d,a}\overline{J}^2}, \quad G = \frac{\chi l}{\overline{J}}, \quad G_{d,a} = \frac{\hbar^2\chi_{d,a}}{M_{d,a}\overline{J}^2 l}, \tag{13}$$

as well as

$$\begin{aligned}
C_{d,a} &= \frac{M}{M_{d,a}}\frac{w_{d,a}}{w}C, \quad G_{d,a} = \frac{M}{M_{d,a}}\frac{\chi_{d,a}}{\chi}G,\\
J_d &= \frac{\overline{J}_d}{\overline{J}}, \quad J_a = \frac{\overline{J}_a}{\overline{J}},
\end{aligned} \tag{14}$$

and

$$m_{d,a} = \frac{M_{d,a}}{M}, \quad v_{d,a} = \frac{w_{d,a}}{w}, \quad x_{d,a} = \frac{\chi_{d,a}}{\chi}, \tag{15}$$

the equations (6) and (7) become

$$\begin{aligned}
i\frac{d\Psi_0}{d\tau} &= (E_0+D_d)\Psi_0 - J_d\Psi_1 + x_dG(u_1-u_0)\Psi_0,\\
\frac{d^2u_0}{d\tau^2} &= \frac{v_d}{m_d}C(u_1-u_0) + \frac{x_d}{m_d}G(|\Psi_0|^2+|\Psi_1|^2) - \Gamma\frac{du_0}{d\tau},\\
i\frac{d\Psi_1}{d\tau} &= E_0\Psi_1 - J_d\Psi_0 - \Psi_2 + [x_dG(u_1-u_0)+G(u_2-u_1)]\Psi_1,\\
\frac{d^2u_1}{d\tau^2} &= v_dC(u_0-u_1) + C(u_2-u_1) - x_dG(|\Psi_0|^2+|\Psi_1|^2) + G(|\Psi_1|^2+|\Psi_2|^2) - \Gamma\frac{du_1}{d\tau},
\end{aligned}$$

$$
\begin{aligned}
i\frac{d\Psi_n}{d\tau} &= E_0\Psi_n - (\Psi_{n+1}+\Psi_{n-1}) + G(u_{n+1}-u_{n-1})\Psi_n, \quad n = 2,\ldots,N-1,\\
\frac{d^2u_n}{d\tau^2} &= C(u_{n+1}-2u_n+u_{n-1}) + G(|\Psi_{n+1}|^2-|\Psi_{n-1}|^2) - \Gamma\frac{du_n}{d\tau}, \quad n = 2,\ldots,N-1,\\
i\frac{d\Psi_N}{d\tau} &= E_0\Psi_N - \Psi_{N-1} - J_a\Psi_{N+1} + [G(u_N-u_{N-1}) + x_aG(u_{N+1}-u_N)]\Psi_N - iA_a|\Psi_{N+1}|^2\Psi_N,\\
\frac{d^2u_N}{d\tau^2} &= C(u_{N-1}-u_N) + v_aC(u_{N+1}-u_N) - G(|\Psi_N|^2+|\Psi_{N-1}|^2) + x_aG(|\Psi_N|^2+|\Psi_{N+1}|^2) - \Gamma\frac{du_N}{d\tau},\\
i\frac{d\Psi_{N+1}}{d\tau} &= (E_0+D_a)\Psi_{N+1} - J_a\Psi_N + x_aG(u_{N+1}-u_N)\Psi_{N+1} + iA_a|\Psi_N|^2\Psi_{N+1},\\
\frac{d^2u_{N+1}}{d\tau^2} &= \frac{v_a}{m_a}C(u_N-u_{N+1}) - \frac{x_a}{m_a}G(|\Psi_N|^2+|\Psi_{N+1}|^2) - \Gamma\frac{du_{N+1}}{d\tau}.
\end{aligned}
\tag{16}
$$

III. PARAMETER VALUES

In this section we analyze the experimental data to determine the range of parameter values for the real donor-acceptor systems which we will use in our numerical modeling of the system of equations derived above.

The parameter values for the polypeptide macromolecules are as follows: $\overline{J}_{\text{AMID-1}} = 1.55 \times 10^{-22}\ \text{J} \approx 10^{-3}$ eV; $\overline{J}_e \approx 0.1$–$0.01$ eV $\approx 10^{-21}$–10^{-20} J; $\chi = (35$–$62)$ pN; $w = 39$–58 N/m, $V_{\text{ac}} = (3.6$–$4.5) \times 10^3$ m/s [12]. The molecular masses of large macromolecules, which participate in the electron-transport chain in redox processes are as follows: NADH-ubiquinone oxidoreductase—980 kDa; cytochrome bc_1 complex—480 kDa; cytochrome c-aa_3 oxidase—420 kDa. Mass of Cyt-c is 12 kDa, in which the hem-A group has a molecular mass 852 Da, and hem-B group has 616 Da, which are 3–5 times bigger than the molecular mass 100–200/Da of amino acids, that form macromolecules. The study of the mitochondrial electron-transport chain shows that the electrochemical potential for the transfer of the electrons is $E_{e\text{-}c} = +1.135$ V [4,5].

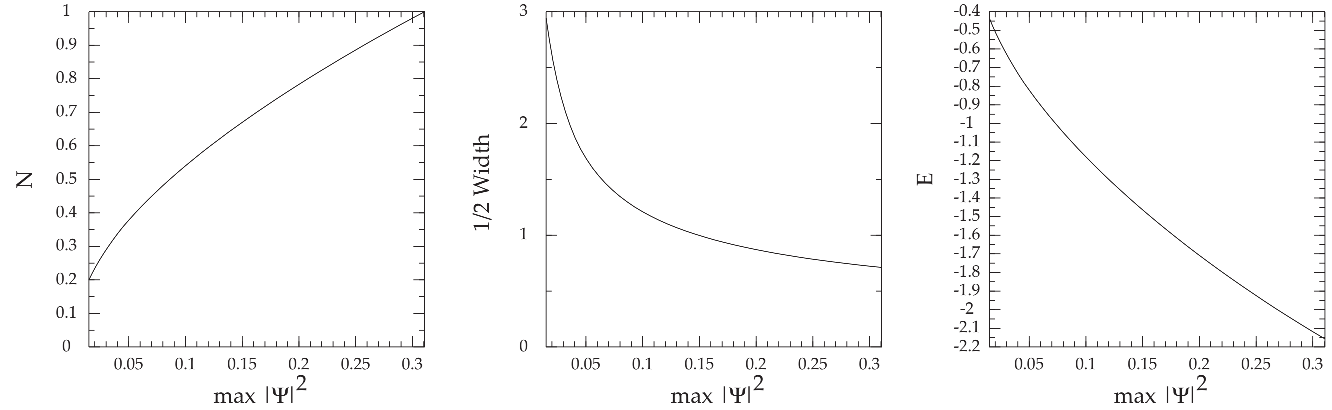
The molecular mass of many conjugated polymer semiconductors varies in the interval (10–176) kDa, and the hole mobility lies typically in the range (4×10^{-4})–$(1.6 \times 10^{-3})\ \text{cm}^2/(\text{V s})$. The ionization potential and electron affinity potential for some donor-acceptor copolymer semiconductor molecules are in the ranges (2.5–4.5) eV and (1.5–3.1) eV, respectively [2]. The electrochemical band gap $E_g^{(\text{el})} = E_{\text{IP}} - E_{\text{EA}}$ is 1.5 eV for BTTP, 1.84 eV for BTTP-P, and 2.24 eV for BTTP-F, which are 0.4–0.6 eV larger than the optically determined ones $E_g^{(\text{opt})} = 1.1$–1.6 eV. This difference can be explained by the exciton binding energy of conjugated polymers which is thought to be in the range of $E_{\text{ex}} \approx 0.4$–$1.0$/eV [3]. Thieno pyrazine-based donor-acceptor copolymers, such as BTTP, BTTP-T, BTTP-F, BTTP-P, have moderate to high molecular masses, broad optical absorption bands that extend into the near-infrared region with absorption maxima at 667–810 nm, and small optical band gaps (1.1–1.6 eV). They show ambipolar redox properties with low ionization potentials (HOMO levels) of (4.6–5.04) eV. The field-effect mobility of holes varies from $4.2 \times 10^{-4}\ \text{cm}^2/(\text{V s})$ in BTTP-T to $1.6 \times 10^{-3}\ \text{cm}^2/(\text{V s})$ in BTTP-F (see [14]). The reduction potentials of BTTP, BTTP-P, and BTTP-F are -1.4, -1.73, and -1.9 V (vs SCE), respectively. The oxidation potentials of the copolymers are in the range 0.29–0.71 V (vs SCE). The onset oxidation potential and onset reduction potential of the parent copolymer BTTP are 0.2 and -1.3 V, respectively, which give an estimate for the ionization potential (IP, HOMO level) of 4.6 eV ($E_{\text{IP}} = E_{\text{ox}}^{\text{onset}} + 4.4$) and an electron affinity (EA, LUMO level) of 3.1 eV ($E_{\text{EA}} = E_{\text{red}}^{\text{onset}} + 4.4$). The 4.6 eV E_{IP} value of BTTP is 0.3 eV less than that of poly(3-hexylthiophene) (4.9 eV), whereas its E_{EA} value (3.1/eV) is 0.6 eV higher than that reported for the poly(2,3-dioctylthieno[3,4-b]pyrazine) homopolymer (≈2.5 eV). An E_{IP} value of 4.64 eV and E_{EA} value of 2.8 eV were found in the case of BTTP-P [14].

Below, in our paper we investigate a set of model parameters close to those encountered in polypeptide macromolecules or bridge-mediated donor-acceptor systems, summarized above. In particular, we study the case when the elasticity constants, electron resonant constants, electron-lattice couplings, and the energy differences between donor, acceptor, and macromolecule are comparable. From the summary of the experimental data given above we estimate the dimensionless parameters introduced above as $|D_{d,a}| \approx 0$–10, $m_{d,a} \approx 3$–10, and $v_{d,a} \approx x_{d,a} \approx 0.1$–$0.3$. Here we have taken into account the fact that binding of donor and acceptor molecules to the molecular chain is weaker than binding between the units in the chain, as the binding by the van der Waals forces or by chemical binding is weaker than the binding in the chain. We also assume that the distance between the donor (acceptor) molecule and the chain is larger than the lattice constant in the molecular chain, and so the corresponding electron-lattice coupling is significantly weaker.

Moreover, for the chain itself, we have taken exactly the same parameters as in [57], i.e., $C = 0.88$ and $G = 0.8$, which correspond to the physical values of polypeptides and conducting polymers. For most of our simulations, we have used the value $\Gamma = 0.2$. The dependence on that parameter will be studied in the last section.

IV. RESULTS OF NUMERICAL MODELING

Before we analyze numerically the propagation of the soliton along the chain it is useful to study some properties of the soliton on the lattice. The reason is that when a soliton is generated on the chain by the donor some radiation is



(a) (b) (c)

FIG. 1. Properties of the stationary soliton as a function of its maximum density $\max_n |\Psi_n|^2$. (a) Norm $N = \sum_n |\Psi_n|^2$; (b) soliton width; (c) soliton energy.

emitted as well and the soliton only carries a fraction of the total electron probability density. Thus it is very difficult to determine exactly the properties of the soliton like its size or its energy from the numerical data. On the other hand, the average value of the maximum probability density, $\max_n |\Psi_n|^2$, of the soliton is very easy to determine, even if the soliton oscillates. To determine the properties of the soliton, we have thus computed the energy, half width, and the total norm of static solitons as a function of their maximum density. The results are presented in Fig. 1.

To analyze the transfer of the soliton from the donor to the acceptor via the chain we have performed numerical simulations where we have put the electron on the donor as an initial condition. We have then integrated the equations (16) numerically until the electron was located on the acceptor or spread out over the chain. We have used mostly chains of 50 nodes, which for realistic systems is relatively long, but we have also studied how the electron transport was affected as the length of the chain was varied. Using the set of parameters given above, we have performed many simulations varying the parameters for the donor and acceptor sites, i.e., J_d, D_d and J_a, D_a, A_a, respectively, determining the range of parameter values for which a soliton was generated by the donor and those for which the electron was absorbed by the acceptor. We have also identified the parameter values for which the tunneling was optimal.

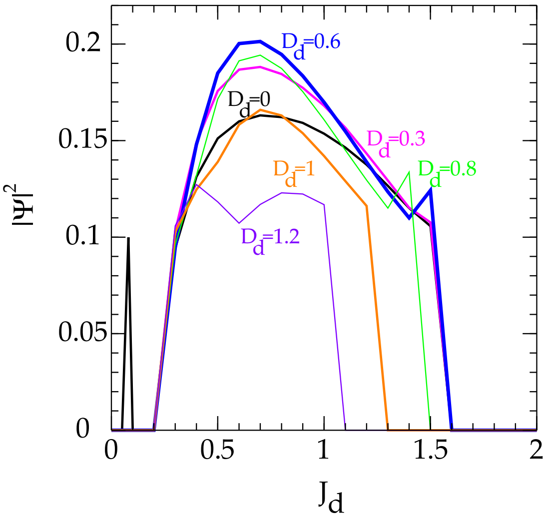


FIG. 2. (Color online) Maximum of $|\Psi|^2$ as a function of D_d and J_d for $x_d = v_d = 0.1$.

In these simulations, when the coupling parameters were suitable, the electron quickly moved onto the chain where it created a local deformation of the chain in which it then was self-trapped in a localized solitonlike state. Then the soliton moved along the chain at a constant speed until it reached the acceptor. As is shown later in this paper, the soliton is not perfect, as the system of equations (16) is not completely integrable, but in the best cases most of the electron density forms a soliton, while the rest forms small waves that diffuse along the chain.

We then scanned the parameters D_d and J_d and, as one can see from Fig. 2, for the case $x_d = v_d = 0.3$, a soliton is formed for a wide range of values, roughly for $D_D \in [0,1.2]$ and $J_d \in [0.3,1.5]$. The optimal values of D_d and J_d for the formation of a soliton as well as the properties of the corresponding soliton are given in Table I. As the soliton oscillates after its creation the values of $|\Psi|^2$ were obtained by averaging their values when the soliton was in the chain interval $n \in [7,18]$. We note from Table I that the values for which a soliton is generated do not depend much on x_d, but that, on the other hand, the soliton amplitude increases with x_d.

We have also investigated the dependence of the rigidity of the coupling between the donor and acceptor to the chain and have varied both v_d and v_a by two orders of magnitude and we found that the size of the soliton generated on the chain

TABLE I. Optimal parameter values for the formation of a soliton and the absorption of a soliton by the acceptor for the chain with $v_d = v_a = 0.1$, $C = 0.88$, $G = 0.8$, and $M_d = M_a = 3$.

x_d	x_a	D_d	J_d	Sol max $\|\Psi\|^2$	N	D_a	J_a	A_a	$\|\Psi_a\|^2_{t=50}$
0.1	0.1	0.6	0.7	0.183	0.75	0.2	0.13	4	0.64
0.3	0.3	0.6	0.7	0.201	0.81	0.3	0.12	4	0.69
0.6	0.6	0.8	0.7	0.219	0.82	0.7	0.11	3.4	0.76
1	1	2.2	0.9	0.251	0.89	1.1	0.14	2.9	0.702

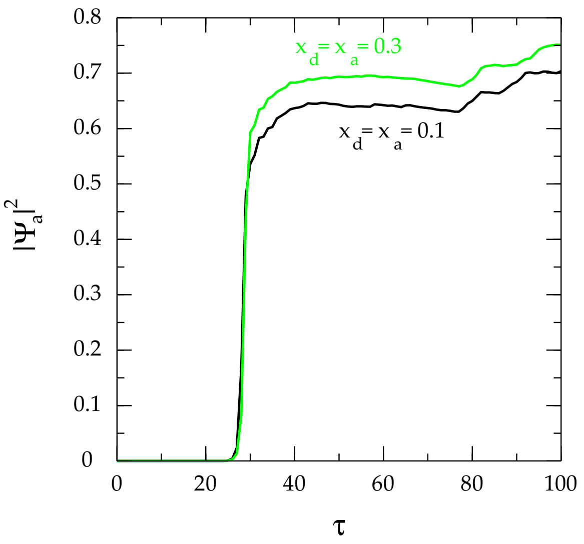
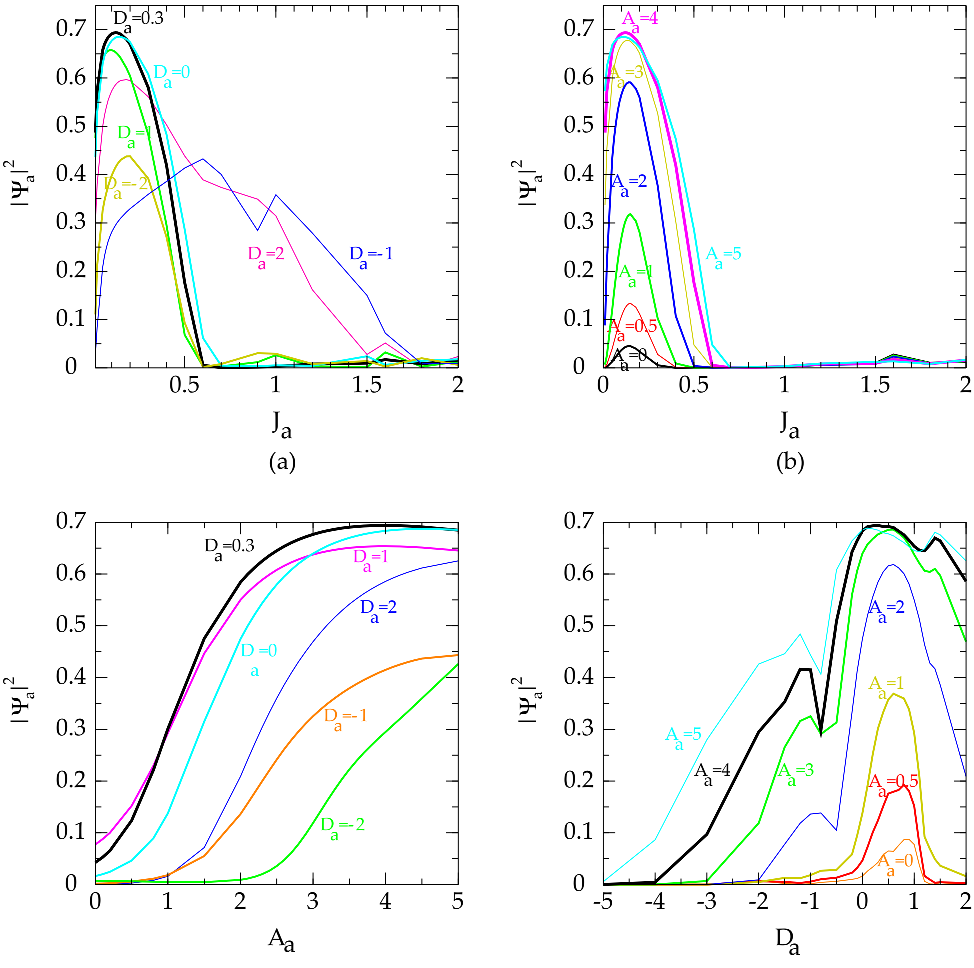


FIG. 3. (Color online) Electron probability $|\Psi|^2$ on the acceptor as a function of time (in adimensional units) for the parameter values listed in Table I for $x_d = x_a = 0.1$ and $x_d = x_a = 0.3$. $N = 50$.

or the amount of absorption of the electron probability by the acceptor only changed by a few percent. For this reason we have performed all our studies, to be discussed below, using the values $v_d = v_a = 0.1$.

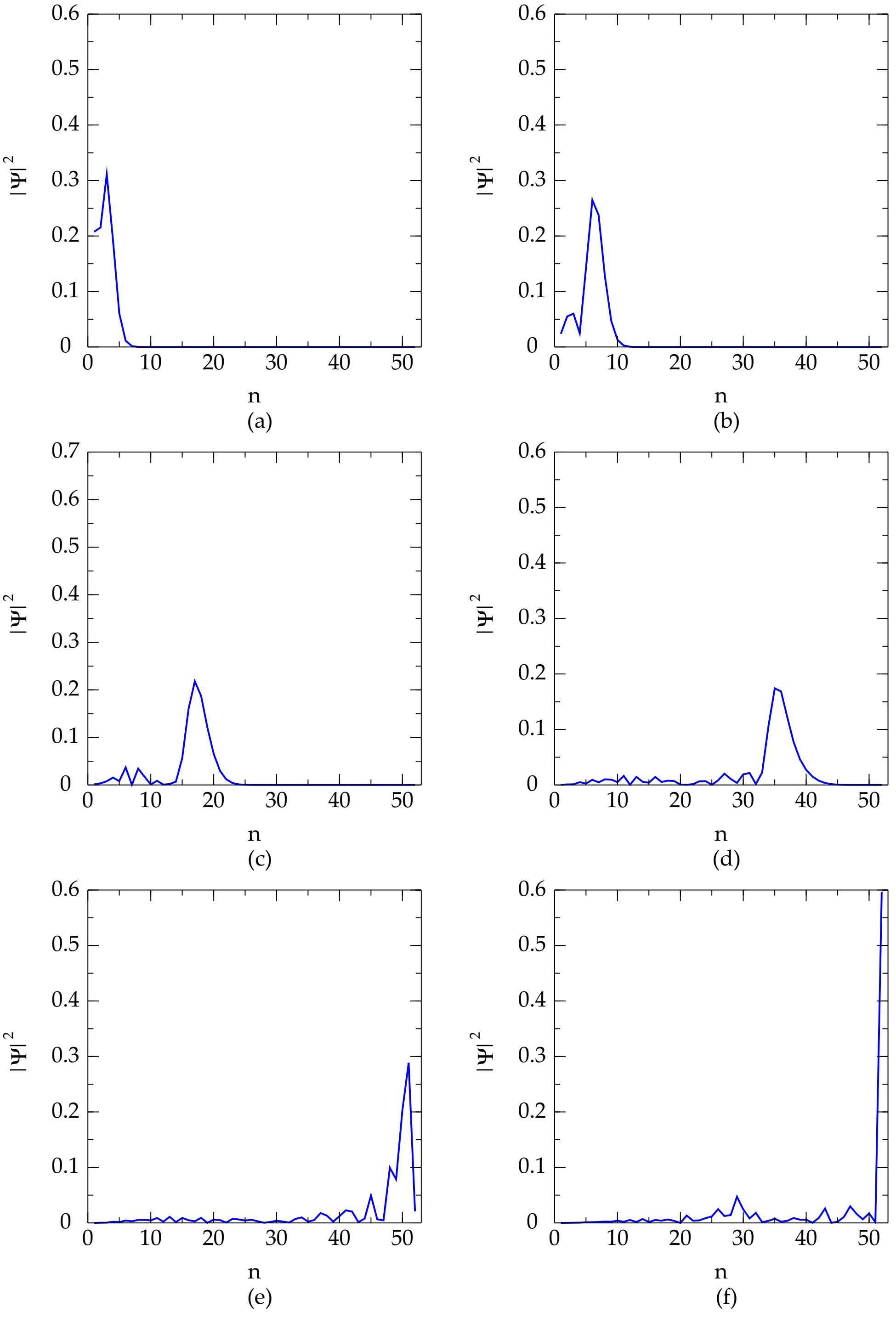
When the soliton arrives at the end of the chain, it can be absorbed by the acceptor when the coupling between the chain and the acceptor is appropriate. When the absorption is present, the soliton is absorbed very quickly and $|\Psi_a|^2$, the electron density on the acceptor site, rises very rapidly from zero to a constant value as seen in Fig. 3. The electron density fluctuates a little because the waves on the chain are also progressively absorbed by the acceptor site, but those waves have to bounce several times between the two ends of the chain before being slowly absorbed.

To evaluate the efficiency of absorption, we have taken the value of $|\Psi_a|^2$ at $t = 50$ for a chain of 50 nodes, which is the value just after the plateau has been reached (see Fig. 3). For the four values of x_d, we have taken the values of D_d and J_d from Table I, for which the largest soliton was generated and we have scanned the values of D_a and J_a, taking $x_a = x_d$ and $v_a = v_d$, to determine when the soliton was absorbed by the acceptor site. The parameter values for which the



(a)
(b)
(c)
(d)

FIG. 4. (Color online) Absorption of soliton by the acceptor: $|\Psi|^2$ at $\tau = 50$. $M_d = M_a = 3$, $C = 0.88$, $v_d = v_a = 0.1$, $G = 0.8$, $x_d = x_a = 0.3$, $D_a = 0.6$, and $J_d = 0.7$; (a) as a function of J_a for different D_a and $A_a = 4$; (b) as a function of J_a for different A_a and $D_a = 0.3$; (c) as a function of A_a for different D_a and $J_a = 0.12$; (d) as a function of D_a for different A_a and $J_a = 0.12$.



(a) (b)

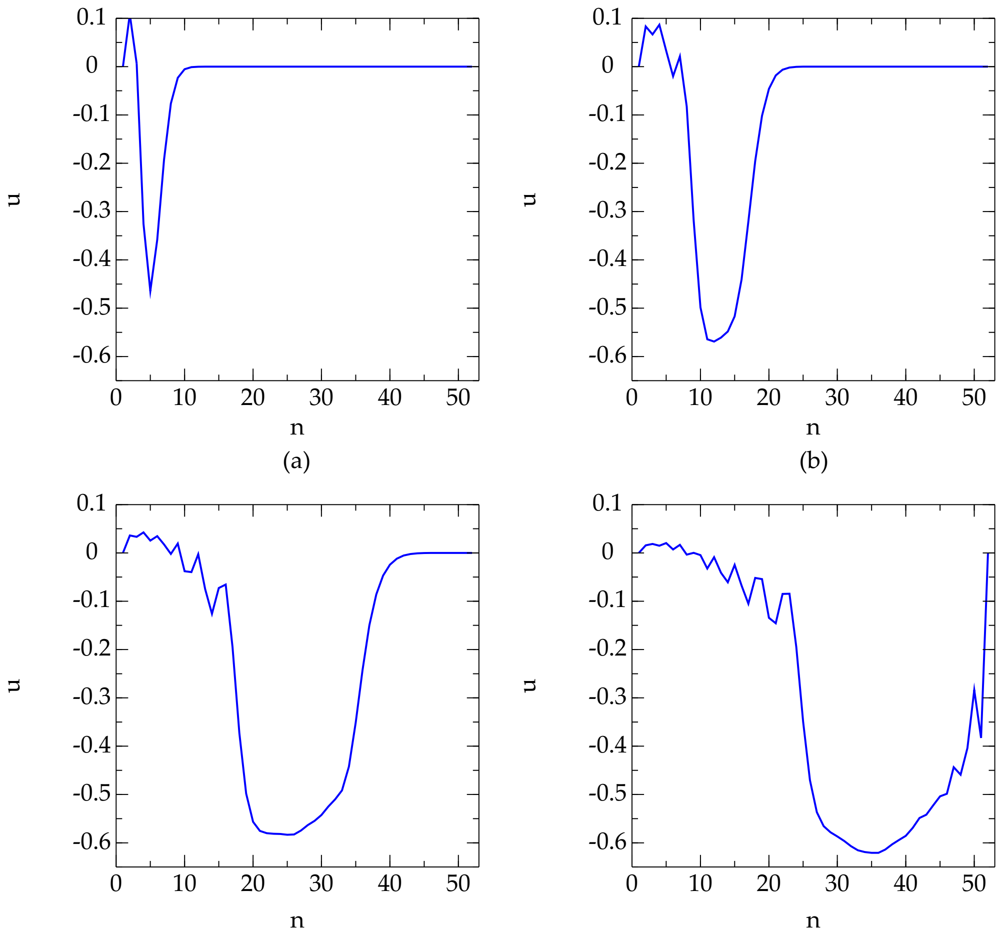
(c) (d)

(e) (f)

FIG. 5. (Color online) Profile $|\Psi|^2$ of the soliton on a chain with 50 nodes. At $\tau = 0$, not shown, the soliton is exclusively on the donor ($|\Psi_d|^2 = 1$). $M_d = M_a = 3$, $C = 0.88$, $v_d = v_a = 0.1$, $G = 0.8$, $x_d = x_a = 0.3$, $D_d = 0.6$, $J_d = 0.7$, $D_a = 0.3$, $J_a = 0.12$, and $A_a = 4$. (a) $\tau = 2$, (b) $\tau = 4$, (c) $\tau = 10$, (d) $\tau = 20$, (e) $\tau = 28$, and (f) $\tau = 40$.

absorption is the largest are presented in Table I. Most of our simulations were performed up to $\tau = 2000$ and in all cases $|\Psi_a|^2$ stayed constant or very slowly increased after the soliton was absorbed. The slow increase of $|\Psi_a|^2$ was caused by the slow absorption of remaining wave on the lattice by the acceptor.

The parameter region in which the absorption takes place is relatively large. In Fig. 4 we present the electron probability density just after the absorption ($t = 50$) for different values of the parameters J_a, D_a, and A_a for the case $x_d = x_a = 0.3$, $D_d = 0.6$, and $J_d = 0.7$. One can clearly see that when $A_a > 2$ the absorption does not vary much. The electron coupling, J_a, on the other hand, must lie approximately in the range 0.1 to 0.4. To have a good absorption the energy level of the acceptor, D_a, must lie approximately in the range -0.5 to 2. So overall the electron absorption takes place for a relatively large domain



(a) (b) (c) (d)

FIG. 6. (Color online) Displacement u of unit cells on a chain with 50 nodes. $M_d = M_a = 3$, $C = 0.88$, $v_d = v_a = 0.1$, $G = 0.8$, $x_d = x_a = 0.3$, $D_d = 0.6$, $J_d = 0.7$, $D_a = 0.3$, $J_a = 0.12$, and $A_a = 4$. (a) $\tau = 4$, (b) $\tau = 10$, (c) $\tau = 20$, and (d) $\tau = 28$.

of the parameters. We have performed a similar analysis for other values of x_a and x_d and we have found very similar results. We have also varied m_a and m_d and found that the variation of these parameters has virtually made no difference.

In Fig. 5, we present the time dependence of the electron density across the chain for the case $x_d = x_a = 0.1$, $D_d = 0.6$, $J_d = 0.7$, $D_a = 0.2$, $J_a = 0.13$, and $A_a = 4$. At $t = 0$ the electron is exclusively on the donor and it is rapidly transferred to the chain. A soliton is then formed and its maximum probability (charge density) is approximately $|\Psi|^2 = 0.18$ which, from Fig. 1(a), corresponds to an approximate norm of 0.64. We can thus conclude that, in this case, two-thirds of the electron probability density is located in the soliton, while the rest forms some ripples that propagate along the chain. Once the electron reaches the other end of the chain it is rapidly absorbed by the acceptor.

In Fig. 6 we present the displacement fields for four of the profiles shown in Fig. 5. It shows clearly that the front edge of the soliton corresponds to a negative displacement followed by a tail that widens as time increases. Looking at Fig. 5 we can also see that the soliton position matches the middle of the front drop of the displacement field u. So relative to the position of the center of the soliton, the displacement field exhibits an S shape curve as expected. We also notice that the tail of the displacement field corresponds to a slow relaxation of the lattice vibration which does not travel as fast as the soliton itself.

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V. THERMAL STABILITY

In the previous section, we have shown that an electron can spontaneously be transferred from a donor to a chain on which it is self-trapped in a soliton state and propagates to the opposite end of the chain where it can be absorbed by the acceptor. As this was all performed at zero temperature, we must now study how these results are modified when thermal effects are added to our system and, in particular, study the thermal stability of the electron transport on the chain. To perform the analysis numerically, we have proceeded by thermalizing the donor-chain-acceptor system to a given temperature in the absence of an extra electron. After the system had reached a stable thermal state, we have put the electron on the donor and we have looked at how it generated a soliton and how that soliton was then absorbed by the acceptor. The thermalization was performed by adding the following Langevin term

$$L_n = F_n(t) - \Gamma \frac{dU_n}{d\tau} \tag{17}$$

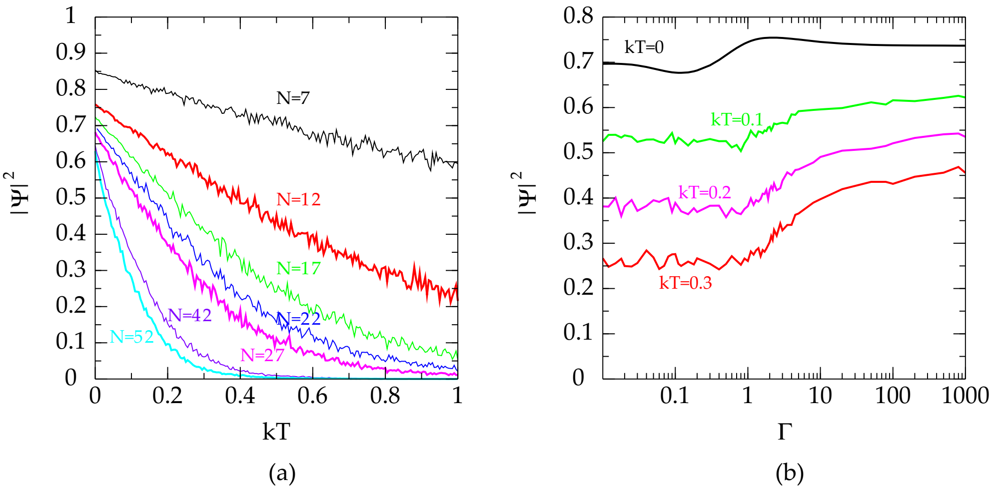

FIG. 7. (Color online) $|\Psi|^2$ on the acceptor for $x_d = x_a = 0.3$, $D_d = 0.6$, $J_d = 0.7$, $D_a = 0.3$, $J_a = 0.12$, and $A_a = 4$: (a) as a function of the temperature for chain of different length; (b) as a function of Γ for various temperatures.

to Eqs. (16) for each U_n fields. Γ in (17) is an absorption parameter and the thermal noise $F_n(\tau)$ is a Gaussian white noise of zero mean value and variance given by

$$\langle F_n(\tau_1)F_m(\tau_2)\rangle = 2\Gamma kT\delta(\tau_1-\tau_2)\delta_{n,m}, \tag{18}$$

i.e., we describe it by a random function with a normal distribution satisfying the constraint (18). In our numerical simulations $F(\tau)$ has been kept constant during the time step interval $d\tau$ and we used $\delta(\tau_2-\tau_1)=1/d\tau$.

As the process is randomized, we have performed 100 simulations on a chain with 50 nodes for each set of parameters at each temperature and then we averaged the values obtained for the amount of absorption by the acceptor. For $kT = 0$ there was no need to do this so we only performed one simulation. The simulations were performed using the parameter values given in Table I and the temperature was increased up to the value for which the soliton was not stable enough to transfer the electron across the lattice. The results are presented in Fig. 7 for the case $x_a = x_d = 0.3$. The other three cases considered in Table I gave nearly identical results.

From our results we see that the electron can easily propagate through the lattice even at relatively high temperature. In our units, kT is measured in units of $\overline{J}$ which for α helices is of the order of 0.1 eV. So at physiological temperature, $kT \approx 0.025$ eV, about a third of the electron probability can be transferred through the chain as a soliton.

All the simulations so far have been performed using the energy dissipation coefficient $\Gamma = 0.2$ and we decided to investigate how the results described above depend on the value of Γ. The results of these investigations are presented in Fig. 7(b) from which we see that the amount of absorption, even for $kT = 0$, modifies the effectiveness of the system of transferring the electron from the donor to the acceptor by about 10%. The optimal absorption occurs for $\Gamma \approx 2.2$. This optimal value is determined by the balance between the energy loss due to radiation by the soliton of sound waves and energy gain due to electron binding with the self-created lattice deformation. We would like to reiterate that the system (16) is not an integrable system even in the continuum limit and so the soliton can generate phonon-electron waves during its time evolution, although the waves can be very small, as in the present studies for the given parameter values. As Γ increases we have observed that the soliton size decreases faster as it propagates along the chain and so one would expect the absorption to decrease as well, but what Fig. 7(b) suggests is that the transfer between the chain and the acceptor is somehow enhanced by a larger absorption. At bigger values of Γ thermal oscillations of the lattice cites and radiation of linear waves are weaker, and this enhances the electron transfer of the electron from a soliton state in the end of the chain into the acceptor.

VI. CONCLUSIONS

In this paper, we have studied the transfer of a quasiparticle (an electron, molecular excitation, exciton, etc.) from a donor to an acceptor mediated by a molecular chain through which the electron is transferred in a soliton state. We have presented a model in which a donor and an acceptor molecules are connected to both ends of the chain with a coupling between these two molecules and the chain itself. We have then solved the discrete nonlinear equations describing this system numerically and we have found that, for a broad range of coupling parameters, the electron spontaneously tunnels to the nearest end of the chain, where it is self-trapped in a soliton state and then propagates to the opposite end of the chain coherently with constant velocity and weak energy dissipation. At this end of the chain the electron is transferred to the acceptor when the coupling parameters belong to a suitable range of values.

For the considered parameters of the principal chain the adiabatic approximation is expected to be valid. As shown in Ref. [11], in the continuum approximation, the electron ground state in such a chain is described by a soliton, which is a bound state of an electron self-trapped in the localized lattice deformation. This analytical result has been confirmed by numerical simulations (see Ref. [12]). Such a two-component (electron + lattice deformation) soliton in a molecular chain has been called "Davydov soliton" [12].

In the present paper we have found the range of parameters of a donor molecule, at which the evolution of an electron probability provides sufficient conditions for the generation of a soliton in the principal chain. Strictly speaking, in a discrete chain this soliton is a solitonlike localized electron state, stable enough to propagate to the opposite end of the chain with very little energy dissipation. The analytical study of this problem is in progress.

We have investigated numerically the broad range of parameters for which such a transfer is possible. We have shown that the long-range electron transfer is possible, and effective, if the energy level of the electron on the donor, D_d, is in the range [0,1.2] in units of $\overline{J}$, while the electron coupling between the donor and the chain, J_d, must be in the range [0.3,1.5]. We have also found that the effective electron transfer from the soliton state in the chain to the acceptor molecule takes place when the parameters of the acceptor are $D_a \in [-0.5,2]$, $J_a \in [0.1,0.4]$, and $A_a > 2$.

We then investigated how the electron transfer depends on the length of the chain and have found, not surprisingly, that when the chain is longer, it takes longer for the soliton to travel across the chain. Moreover, the amplitude of the soliton decreases slowly as the soliton travels along the chain and so the effectiveness of the electron transport also decreases slowly as the chain becomes longer.

We also studied the thermal stability of the soliton transport and have found that the effectiveness of the electron transport on the chain decreases as the temperature increases but that, for chains that are not excessively long, the transfer can still take place even at temperature of the order of $kT = 0.5$ in units of $\overline{J}$. This implies that for polypeptide chains the electron transport can occur via a solitonic state not only at low but also at physiological temperatures.

We also studied the dependence of the soliton transport for various values of the damping coefficient Γ and found that the electron absorption depends only very weakly on the value of this parameter.

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