Electron Transfer in Donor-Acceptor Systems: Many-Particle Effects and Influence of Electronic Correlations

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We investigate electron transfer processes in donor-acceptor systems with a coupling of the electronic degrees of freedom to a common bosonic bath. The model allows to study many-particle effects and the influence of the local Coulomb interaction $U$ between electrons on donor and acceptor sites. Using the non-perturbative numerical renormalization group approach we find distinct differences between the electron transfer characteristics in the single- and two-particle subspaces. We calculate the critical electron-boson coupling $\alpha_c$ as a function of $U$ and show results for density-density correlation functions in the whole parameter space. The possibility of many-particle (bipolaronic) and Coulomb-assisted transfer is discussed.

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Introduction - Electron transfer (ET) is a fundamental process in chemistry, biology and physics, for example in corrosion of metals, charge transfer in semiconductors, enzymatic activities, cell metabolism, and photosynthesis [1, 2]. The characterization of ET processes in bio-molecules is an important step towards an understanding of the biological function of many proteins and towards the possible construction of bio-molecular electronic devices or biosensors. Theoretical investigations of ET processes typically start from a two-site model for the electronic degrees of freedom at the donor and acceptor sites which are coupled via a tunneling matrix element $t$.

The correlated dynamics of electrons and vibronic modes (phonons) is essential for the ET characteristics. If the phonons are treated classically, one arrives at the Marcus theory [3]. A quantum mechanical treatment of the phononic degrees of freedom results in models related to the spin-boson model, in which the phonons are modeled by an infinite set of harmonic oscillators with a continuous spectral density $J(\omega)$ [4, 5].

The following two limiting cases of ET processes are well understood. If the tunneling (or hopping) matrix element $t$ is small we are in the limit of nonadiabatic ET. In the opposite limit, where $t$ is large, the ET is adiabatic and the Born-Oppenheimer theorem holds. (The time of the electron moving from the donor to the acceptor is too short for the vibronic modes to change their configuration.). Both limits are realized in ET processes in proteins but of particular interest are those parameters which lie in the crossover regime. In this case, non-perturbative methods have to be applied (see, for example, Ref. 7).

If the electronic part is treated in a one-particle picture it reduces to two localized quantum states and can be modeled by a two-level system or spin, leading to a description in terms of the spin-boson model. In many cases this may not be the adequate picture — many-particle effects and electron-electron interactions have to be taken into account, for example if a more realistic modeling of the electronic degrees of freedom is required [8, 9], if more than one electron is transferred simultaneously [10], or for a proper description of exciton transfer [11].

In this paper we propose a two-site electron-boson model to investigate many-particle effects and the role of electron-electron interactions. As sketched in Fig. 1 the model contains both a local Coulomb interaction $U$ and the coupling to a common bosonic bath. Our approach goes beyond earlier work in which only the electronic degrees of freedom involved in the ET transfer were considered (see Refs. 8, 9, 11) or the coupling to the bosonic bath was treated within the spin-boson model [7] without considering many-particle effects and electronic correlations.

We discuss competition or cooperation of vibronic and electronic effects (electron correlations) during the ET...
process by using the bosonic numerical renormalization group (NRG) method \[12, 13\] which is non-perturbative and can be used in the whole parameter regime between the adiabatic and nonadiabatic limits. We indeed find a significant difference between the ET characteristics in the single-particle subspace (which can be mapped onto the spin-boson model) and the two-particle subspace in which many-particle effects have to be considered. The coupling to the bosonic bath turns out to favor the formation of bipolarons, whereas a local Coulomb repulsion tends to delocalize the electrons.

Model and Method - The two-site electron-boson model is given by the following Hamiltonian:

\[
H_{\text{eb}} = \sum_{\sigma, i = \text{D, A}} \varepsilon_i c_{i\sigma}^\dagger c_{i\sigma} - t \sum_{\sigma} \left( c_{\text{D}\sigma}^\dagger c_{\text{A}\sigma} + c_{\text{A}\sigma}^\dagger c_{\text{D}\sigma} \right) + U \sum_{i = \text{A, D}} c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{i\uparrow} c_{i\downarrow} + \sum_n \omega_n b_n^\dagger b_n + (g_{\text{NA}} A + g_{\text{ND}} D) \sum_n \lambda_n \left( \frac{b_n^\dagger + b_n}{2} \right). \tag{1}
\]

The operators \(c_{i\sigma}^\dagger\) denote annihilation (creation) operators for fermions with spin \(\sigma\) on the donor (\(i = \text{D}\)) and acceptor (\(i = \text{A}\)) sites; \(n_{\text{A/D}}\) is defined as \(n_i = \sum_{\sigma} c_{i\sigma}^\dagger c_{i\sigma}\). The first three terms of the Hamiltonian eq. 1 correspond to the two-site Hubbard model investigated in Ref. \[2\] with \(\varepsilon_i\) the on-site energies, \(t\) the hopping matrix element, and \(U\) the local Coulomb interaction for two electrons on either donor or acceptor sites. This part of the model can be easily extended to include non-local Coulomb correlations between electrons on donor and acceptor sites; for simplicity, we restrict the discussion here to local Coulomb terms only. The last two terms in eq. 1 describe the free bosonic bath and the coupling between electrons and bosons, respectively. In the following we set \(g_{\text{A}} = 1\) and \(g_{\text{D}} = -1\), assuming a symmetric shift of the phonon displacements due to the electronic occupancy at donor and acceptor sites.\[2, 3, 4\]

In analogy to the spin-boson model \[8\], the coupling of the electrons to the bath degrees of freedom is completely specified by the bath spectral function

\[
J(\omega) = \pi \sum_n \lambda_n^2 \delta(\omega - \omega_n). \tag{2}
\]

Here we assume an Ohmic bath, corresponding to the situation in many proteins \[14\], with \(J(\omega) = 2\pi n_0\omega, 0 < \omega < \omega_c\), with \(\alpha\) the dimensionless coupling strength and \(\omega_c\) a cut-off which sets the energy scale in the following (\(\omega_c = 1\)).

The Hamiltonian eq. 1 conserves both particle number \(n_{\text{el}}\) and total spin of the electrons. The Hilbert space of the full model can therefore be divided into subspaces labeled by \((Q, S_z)\), with \(Q = n_{\text{el}} - 2\) (so that \(Q = 0\) corresponds to half-filling) and \(S_z\) the 3-component of the total spin.

Here we only consider the subspaces \((Q, S_z) = (-1, 1/2)\) and \((Q, S_z) = (0, 0)\). In the subspace \((-1, 1/2)\), which we term the single-electron subspace, the model eq. 1 is equivalent to the spin-boson model:

\[
H_{\text{sb}} = -\frac{\Delta}{2} \sigma_x + \frac{\varepsilon}{2} \sigma_z + \sum_n \omega_n a_n^\dagger a_n + \frac{\sigma_z}{2} \sum_n \lambda_n (a_n + a_n^\dagger), \tag{3}
\]

with \(t = \Delta/2, \varepsilon_D = \varepsilon/2, \varepsilon_F = -\varepsilon/2\). The two-electron subspace \((Q, S_z) = (0, 0)\) is the main focus of the calculations presented in this paper: The electronic degrees of freedom in this subspace can be represented by the four-dimensional basis

\[
|i\rangle = \{ |\uparrow\downarrow, 0\rangle, |\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle, |0, \uparrow\downarrow\rangle \}, \tag{4}
\]

with the notation \(|a, d\rangle\) describing the occupation at the donor \((d)\) and acceptor \((a)\) sites. Consider now the 4 × 4-matrix \(M_{\text{sb}}^{Q=0} = \langle i|H_{\text{sb}}|j\rangle\) \((i, j = 1, \ldots, 4)\) with the matrix elements taken only with respect to the electronic degrees of freedom. Introducing the notation

\[
\hat{Y} = \sum_n \omega_n b_n^\dagger b_n, \quad \hat{X} = \sum_n \lambda_n \left( \frac{b_n^\dagger + b_n}{2} \right), \tag{5}
\]

we arrive at the matrix

\[
M_{\text{sb}}^{Q=0} = \begin{pmatrix}
\epsilon + U + 2\hat{X} + \hat{Y} & -t & t & 0 \\
-t & \hat{Y} & 0 & -t \\
t & 0 & \hat{Y} & t \\
0 & -t & t & -\epsilon + U - 2\hat{X} + \hat{Y}
\end{pmatrix}. \tag{6}
\]

The matrix \(M_{\text{sb}}^{Q=0}\) defines the starting point for our numerical calculations.

The technique we are using here, the bosonic NRG, has been described in detail in Refs. \[12, 13\] in the context of the spin-boson model. The basic features of the bosonic NRG are as follows: (i) the logarithmic discretization of the bath spectral function \(J(\omega)\) in intervals \([\Lambda^{-n+1}, \Lambda^{-n}]\), with \(n = 0, 1, \ldots, \infty\) and \(\Lambda > 1\) the NRG discretization parameter (all the results shown in this paper have been calculated using \(\Lambda = 2\)); within each of these intervals only one bosonic degree of freedom is retained as a representative of the continuous set of degrees of freedom. (ii) The mapping of the resulting Hamiltonian onto a semi-infinite chain. (iii) The iterative diagonalization of the chain-Hamiltonian via successively adding one site to the chain.

The bosonic NRG has been shown to give very accurate results for the spin-boson model \[12, 13\]. One of its strengths is the flexibility to handle a variety of models involving the coupling of a small subsystem (here the electronic degrees of freedom at donor and acceptor sites) to a bosonic bath. The application to the two-electron subspace of the two-site electron-boson model is therefore straightforward.
Results - Let us first consider the zero-bias case \( \epsilon = 0 \); for temperature \( T = 0 \) [15]. In the single-electron subspace, this gives \( \epsilon = 0 \) for the corresponding spin-boson model which allows the observation of a quantum phase transition between a localized phase and a delocalized phase at a critical \( \alpha_c(\Delta) \geq 1 \) [3, 6]. For the value of \( t = 0.1 \) we find \( \alpha_c(\Delta) \approx 1.2, \) naturally independent of \( U \) for the single-electron subspace (dashed line in Fig. 2b). Note that \( \alpha_c(\Delta) \) deviates from the exact value \( \alpha_c(\Delta, t = 0) \) due to the finite \( t \) and the value of \( \Delta \) as discussed in detail in Ref. [13].

In the two-electron subspace we also observe a transition between a localized and a delocalized phase (solid line in Fig. 2b). However, the dynamics of the two electrons is now correlated which leads to a \( U \)-dependent \( \alpha_c(U) \). Note that even for \( U = 0 \) we find \( \alpha_c(U = 0) \neq \alpha_c(U = -1) \). This is because the coupling to the common bosonic bath generates an effective interaction between the two electrons [the energy of the total system is lower when both electrons occupy the same lattice site (D or A) as compared to the case of equal occupancy on D and A which does not result in a displacement of the oscillators]. In other words, many-particle effects are present in the system even if the Coulomb interaction is assumed to be very small which is in close analogy to the physics of the Holstein model [10]. In our model, the situation is more complicated; due to the coupling to a continuous bath, the effective interaction is always frequency dependent (there is no limit in which it could be reduced to a static one). Nevertheless, the net sign of the effective interaction is clearly negative, in agreement with the behavior of the double occupancy shown in Fig. 3 which increases with increasing coupling to the bosonic bath.

This also explains, to some degree, the shape and the asymmetry of the phase boundary \( \alpha_c(U) \): a repulsive \( U > 0 \) partly cancels the attractive interaction from the coupling to the bosonic bath so that increasing \( U \) favors delocalization of the electrons (for a similar feature in the Hubbard-Holstein model, see Ref. [17]).

An interesting consequence of this increase is that the lines \( \alpha_c(U = 1) \) and \( \alpha_c(U = 0) \) cross at some value of \( U \) \( \approx 2.4 \); for \( U > U^* \) there exists a region in the phase diagram with \( \alpha_c(U = 1) < \alpha < \alpha_c(U = 0) \) where the system is localized in the single-electron subspace but delocalized in the two-electron subspace. This can lead to interesting effects of the electron transfer dynamics: the addition of a second electron to the donor site drives the system from the localized to the delocalized phase so that either one of the electrons is enabled to hop to the acceptor site (such a process could be termed Coulomb-assisted transfer) or both electrons hop in a single event (bipolaronic transfer).

The dependence of the critical \( \alpha_c \) on \( t \) in the two-electron subspace is shown in Fig. 2a) for various values of \( U \). As expected, increasing \( t \) tends to delocalize the electrons, similar to the behavior in the single-electron subspace (see, for example, Fig. 8 in Ref. [13]).

To study the dynamics of the electron transfer process in the two-electron subspace we calculate the density-density correlation function \( C(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} C(t) dt \) with

\[
C(t) = \frac{1}{2} \left\langle [n_D(t) - n_A(t), n_D(0) - n_A(0)]_+ \right\rangle .
\]

In the single-electron subspace, the quantity corresponds to the well-studied spin-spin correlation function [1, 2].

Figure 3 shows the NRG results for \( C(\omega) \) for various values of \( \alpha \) and \( U \) with the temperature set to
The bosonic NRG is a very flexible tool and we are planning to investigate a number of extensions of the present model in the future. A generalization of the level structure allows, for example, the modeling of excitation transfer (see Ref. [1] and the models proposed in Ref. [18]). Furthermore, the extension to three or more sites allows the investigation of multistep transfer processes and the influence of dissipation in the transport through (short) one-dimensional chains (see, for example, Ref. [14]).

In general, the method presented here is a starting point for a more realistic description of electron and excitation transfer in those molecular systems where many-particle effects have to be considered.

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