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Model exact many-body studies of charge transfer through bridged systems

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Abstract

A new dynamical method is employed to study charge transfer probabilities between a donor and an acceptor coupled via a long π-conjugated bridge, within a correlated many-body picture. The initial state of the composite system (donor + bridge + acceptor) is taken to be the direct product of the ground state of the bridge Hamiltonian with specified occupancies in the donor and the acceptor orbitals. This $t = 0$ state is evolved using the many-body model Hamiltonian of the composite system. We find that for the interacting model, the rate of electron transfer depends strongly on the initial occupancy of the acceptor orbital. The electron transfer rate is quite different from the spin exchange rate and emphasizes the spin-charge separation in one-dimensional Hubbard models.

Electron transfer reactions are extremely important in chemical as well as biological processes [1–7]. These involve the transfer of an electron from a donor state to an acceptor state. In general the donor (D) and the acceptor (A) are spatially well separated. The underlying system is a donor–bridge–acceptor (DBA) complex, wherein D and A sites are coupled to a bridge (B), which is usually a macromolecule. The primary technological goal in this field has been to construct molecular switches and wires with conjugated organic molecules and polymers acting as the bridge material [8]. The same DBA model also provides the mechanism of charge transfer between localized sites in biologically significant processes such as photosynthesis and respiration [9].

Most of the theoretical studies assume that the bridge provides virtual orbitals that create an effective electronic coupling between the D and the A sites [1, 2, 5, 6, 10]. This mechanism often reduces the problem to an effective two-state Hamiltonian consisting only of D and A states, with the off-diagonal Hamiltonian matrix element providing the coupling between D and A. The nonadiabatic electron-transfer rate can then be deduced from the Fermi golden rule.

However, the most important question is: how do the energetics and structure of the bridge affect the electron transfer rate? The bridge energetics can influence the strength of the D–A coupling, if the bridge eigenstates can strongly mix with D and A states, thereby making the partitioning technique unrealistic. An alternative approach for charge-transfer involves considering a Hückel or an extended Hückel Hamiltonian for the bridge, and studying the electron transfer problem within a Green function approach [11]. In these models, explicit electron correlations are completely ignored, although it is known that correlations often lead to qualitatively different, yet correct, descriptions.

In this paper, we employ a correlated model Hamiltonian within the DBA description of the system for all the constituents. We consider the bridge to be a linear π-conjugated chain, known to be a highly correlated system [12]. Furthermore, in many DBA systems, the D and A sites are transition metal ions, (e.g., Fe^{II}, Cu^{II}, etc) and it is well known that the d-electrons have strong on-site Coulomb interactions. Our model thus provides a more physical realization of the DBA system. In the presence of interactions, the probability of electron transfer to an empty site is larger than it is to a partially occupied site. The probability of the relevant site being empty, partially occupied or doubly occupied also depends very strongly on the electron correlation strength. Thus, incorporating electron–electron interactions is crucial to the study of electron-transfer processes [13].

We model the DBA system as a nondegenerate Hubbard chain of $(N + 2)$ sites consisting of a D site, an A site, and a linear bridge of N sites. The total Hamiltonian for the DBA system has two parts.

$$H = H_0 + H_{\text{int}} \tag{1}$$

$$\begin{aligned} H_0 &= \beta' c_{\text{D}}^{\dagger} c_1 + \sum_{i=2}^{N+1} \beta[1 + (-1)^i \delta] c_i^{\dagger} c_{i+1} + \beta' c_{\text{A}}^{\dagger} c_{N+1} + \text{h.c.} \\ H_{\text{int}} &= U' n_{\text{D}\uparrow} n_{\text{D}\downarrow} + \sum_{i=2}^{N+1} U n_{i\uparrow} n_{i\downarrow} + U' n_{\text{A}\uparrow} n_{\text{A}\downarrow} \end{aligned} \tag{2}$$

where H_0 and H_{int} are the noninteracting and interacting parts of the full Hamiltonian H. The bridge has N atoms (atoms 2 to $N + 1$), U is the on-site repulsion parameter for the bridge atoms and U' that for D and A sites. β is the intra-bridge hopping integral and β' that between the D/A and the terminal bridge site. The bridge bonds have a bond-alternation δ.

The initial wavepacket for the real time dynamics is obtained as the direct product of the ground state of the bridge with D and A orbitals having specified occupancies. The ground state of the bridge Hamiltonian can be expressed as

$$|\psi_{\text{B}}\rangle = \sum_k a_k |\chi_k\rangle \tag{3}$$

where the χ_k are the Slater determinants constructed from the bridge orbitals with N electrons. The two specific initial states we have considered correspond to [1] single electron on the D site with the A site being empty, and [2] the D site has one electron and the A site also has one electron, but with opposite spin. The corresponding initial wavefunctions for the full DBA system, $\psi_{\text{DBA}}^{(i)}$, $i = 1, 2$, in the augmented basis are

$$\begin{aligned} \psi_{\text{DBA}}^{(1)} &= |\psi_{\text{B}}\rangle \otimes c_{\sigma,\text{D}}^{+} |0\rangle \\ \psi_{\text{DBA}}^{(2)} &= |\psi_{\text{B}}\rangle \otimes c_{\sigma,\text{D}}^{+} c_{-\sigma,\text{A}}^{+} |0\rangle \end{aligned} \tag{4}$$

where σ corresponds to spin orientation and vacuum refers to the D and A orbitals. $\psi_{\text{DBA}}^{(i)}$ can be expanded in the eigenvectors $\{\phi_k^{\text{DBA}}\}$ of $\hat{H}$ as

$$\psi_{\text{DBA}}^{(i)} = \sum_k d_k^{(i)} \phi_k^{\text{DBA}}. \tag{5}$$

Given the eigenvalues $\{E_k\}$ of $\hat{H}$, the time evolution of $\psi^{(i)}_{\mathrm{DBA}}$ is trivially given by

$$\psi^{(i)}_{\mathrm{DBA}}(t) = \sum_k d^{(i)}_k \phi^{\mathrm{DBA}}_k \mathrm{e}^{-\mathrm{i}E_k t/\hbar}. \tag{6}$$

Clearly, this explicitly needs all the eigenvalues and eigenstates of the DBA system which is computationally prohibitive for $N \geqslant 6$; the Hilbert space dimensionality increases exponentially with N. One way around this is to evolve in small discrete time steps, Δt, using only the linear term in the expansion of $\exp(-\mathrm{i}\hat{H}t/\hbar)$. Unitarity of the transformation is preserved by equating the backward and forward time evolved states, evolved by $\Delta t/2$, starting respectively with $\psi(t + \Delta t)$ and $\psi(t)$ [14],

$$\left(1 + \frac{\mathrm{i}\hat{H}\Delta t}{2\hbar}\right)\psi(t + \Delta t) = \left(1 - \frac{\mathrm{i}\hat{H}\Delta t}{2\hbar}\right)\psi(t). \tag{7}$$

Equation (7) can be cast into a set of inhomogeneous linear algebraic equations by using a Slater determinantal basis. One can then solve the set of linear algebraic equations by an iterative method [15], and can calculate a number of properties at each time step. Given an initial state, and the parameters of the Hamiltonian, we have calculated the time dependent probabilities of finding an electron at the D site ($P^{(i)}_{\mathrm{D^1BA^0}}(t)$), at the A site ($P^{(i)}_{\mathrm{D^0BA^1}}(t)$), and at both the D and the A sites ($P^{(1)}_{\mathrm{D^1BA^1}}(t)$)

$$\begin{aligned}
P^{(i)}_{\mathrm{D^1BA^0}}(t) &= \sum_k |\langle c^+_{\mathrm{D}}\chi_k|\psi^{(i)}_{\mathrm{DBA}}(t)\rangle|^2 \\
P^{(i)}_{\mathrm{D^0BA^1}}(t) &= \sum_k |\langle c^+_{\mathrm{A}}\chi_k|\psi^{(i)}_{\mathrm{DBA}}(t)\rangle|^2 \\
P^{(1)}_{\mathrm{D^1B^+A^1}}(t) &= \sum_k |\langle c^+_{\mathrm{D}}c^+_{\mathrm{A}}\chi_k|\psi^{(1)}_{\mathrm{DBA}}(t)\rangle|^2
\end{aligned} \tag{8}$$

for the two cases $i = 1, 2$. The superscript on D and A specifies the number of electrons at that site; B and B^+ represent the neutral and singly ionized bridge, respectively.

In the case of spin exchange in case 2, the probability, $P^{(2)}_{\sigma,\tau}(t)$, can be obtained as

$$P^{(2)}_{\sigma,\tau}(t) = \sum_k |\langle c^+_{\sigma,\mathrm{D}}c^+_{\tau,\mathrm{A}}\chi_k|\psi^{(2)}_{\mathrm{DBA}}(t)\rangle|^2 \tag{9}$$

where σ and τ are the spin states. The total probability of electron transfer or spin exchange, in our study, includes all possible final states of the bridge molecule. We choose $\beta' = 1$ in all cases; this sets the energy scale. The Hubbard U and U' parameters are also taken to be equal.

Before we include the electron correlations, we present some results on the noninteracting DBA system. In this limit, the infinite system is metallic for $\delta = 0$. However, for nonzero δ, a gap opens in the excitation spectrum of the infinite system. For a finite system, energy levels, $E_n = \pm\sqrt{2(\beta^2 + \delta^2) + 2(\beta^2 - \delta^2)\cos(4\pi n/N)}$, with $n = 0, \pm1, \pm2, \ldots, \pm(N-2)/4$, are discrete. The energy levels consist of two sets of states which fall into two bands, with an energy gap separating them. As we consider D and A site energies to be zero, the D and A levels will lie in the middle of the band gap. The total width of the energy bands is 4β. In this picture, we can compare results for weak and strong link between D/A sites and the bridge. The weak link case, $\beta/\beta' \gg 1$, is characterized by widely spaced bridge energy levels while the strong link case, $\beta/\beta' \ll 1$, is characterized by narrowly spaced energy levels, for finite N. These have been realized by setting: (a) $\beta = 10$ and (b) $\beta = 0.5$. Note that, in (b), the bridge orbitals are almost localized, resembling σ-type orbitals [16], while (a) resembles a completely delocalized π-system [17]. Thus, these two cases can be used to compare conjugated and nonconjugated bridge systems.

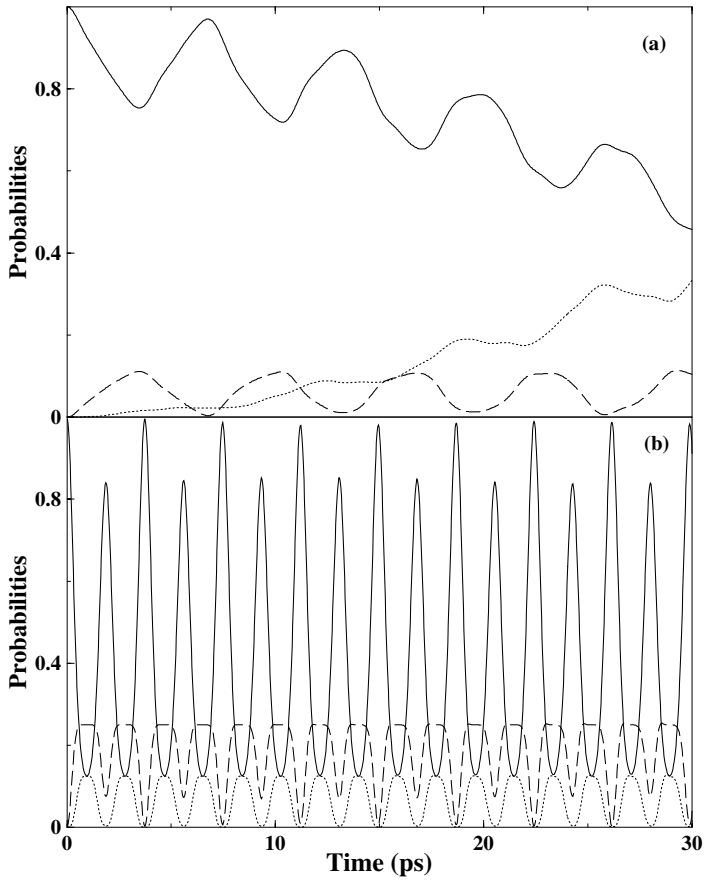

Figure 1. Probabilities, $P^{(1)}_{D^1BA^0}$ (solid), $P^{(1)}_{D^0BA^1}$ (dotted), and $P^{(1)}_{D^1B^+A^1}$ (dashed), as a function of time for (a) weak link and (b) strong link situations discussed in the text.

In figure 1 we plot the probabilities of D and A occupancies ($P^{(1)}_{D^1BA^0}(t)$ and $P^{(1)}_{D^0BA^1}(t)$, respectively) as a function of time for the two values of β for a bridge length of 10 sites. In the weak link situation (a), the electron transfer can be effectively described by a two-state model, and the probabilities oscillate with time with the mean probability decreasing (increasing) with time for $P^{(1)}_{D^1BA^0}(t)$ ($P^{(1)}_{D^0BA^1}(t)$). The probability of finding an electron on both D and A with the bridge in a positively charged state, $P^{(1)}_{D^1B^+A^1}(t)$, varies sinusoidally with time. This indicates that the electron hop between the bridge and the A site behaves like a two-level system. We also note that the oscillation of the probability $P^{(1)}_{D^1B^+A^1}(t)$ is out of phase with that in $P^{(1)}_{D^1BA^0}(t)$. In this situation, we could describe the system as essentially a D–A system with the bridge playing almost no role.

For the strong link situation (b), the probabilities are characterized by sharply peaked structures. Interestingly, at a peak in $P^{(1)}_{D^1BA^0}(t)$ one observes a dip in $P^{(1)}_{D^0BA^1}(t)$ as well as a dip in $P^{(1)}_{D^1B^+A^1}(t)$ and vice versa. We also note that $P^{(1)}_{D^1B^+A^1}(t)$ shows a sinusoidal behaviour with twice the periodicity of $P^{(1)}_{D^1BA^0}(t)$ or $P^{(1)}_{D^0BA^1}(t)$. At every alternate period, the initial state is regained with almost unit probability. The probability of electron transfer from D to A with the bridge remaining neutral is oscillatory with an amplitude of about 0.1, quite unlike in the weak link case, where this probability showed a gradual increase with time. We also find that when

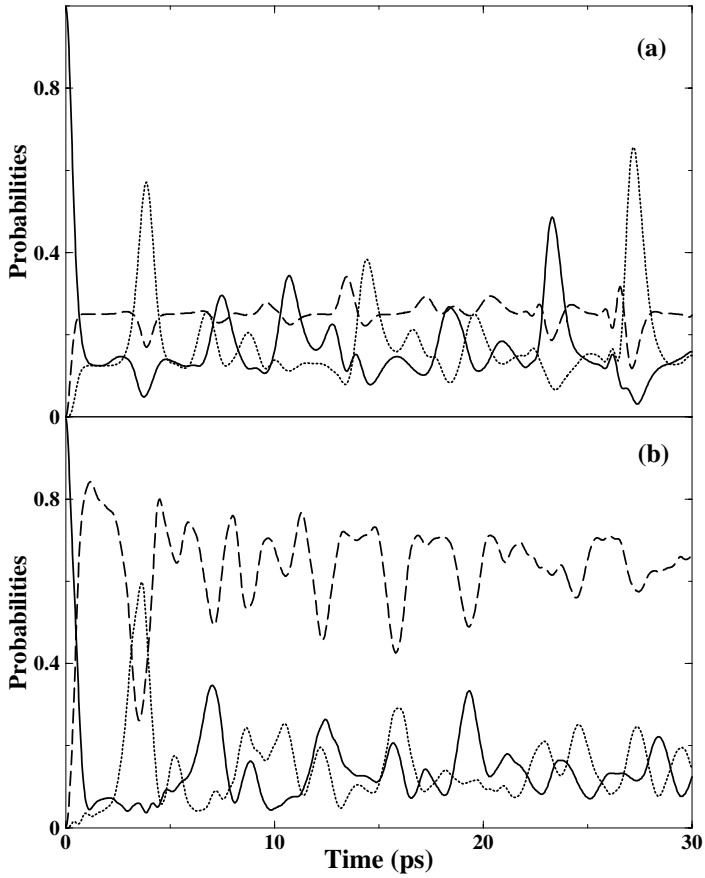

Figure 2. The same probabilities as in figure 1, for (a) a $\beta = 1$ Hückel chain and (b) a Hubbard chain with $U/\beta = 5$, for case (1).

the initial state has lowest probability, the probability that the bridge has an excess electron is quite high. Thus the two-state model is inadequate for the strong link situation where the states involved are not just the D and A states, rather the D–B–A composite states [11].

The Hubbard model is a good approximation for systems where the valence electrons are strongly shielded, and the bands are narrow. The extended Hubbard model has been widely successful in describing the charge and spin excitations in conjugated polymers [12]. We compare the results of the Hückel and Hubbard models in case (1) mentioned above, for the processes $D^1BA^0 \longrightarrow D^1B^+A^1$ and $D^1BA^0 \longrightarrow D^0BA^1$ and in case (2) for the processes $D^1BA^1 \longrightarrow D^1B^+A^2$ and $D^1BA^1 \longrightarrow D^0BA^2$. In figure 2, we plot these occupation probabilities for the Hückel (with $\beta = 1$) as well as for the Hubbard bridge (with $U/\beta = 5$) of ten sites for case (1). For the Hubbard model, the probability $P^{(1)}_{D^1B^+A^1}(t)$ is quite large at all times. This is because the positively charged bridge has a lower probability for doubly occupied sites and the state is easily attained via a single hop from the bridge to the acceptor. The probabilities of $P^{(1)}_{D^1BA^0}(t)$ and $P^{(1)}_{D^0BA^1}(t)$ are much smaller than the probability of $P^{(1)}_{D^1B^+A^1}(t)$. Indeed, the decay in the probability of the initial state, $P^{(1)}_{D^1BA^0}(t)$, is very rapid and so is the rise in the probability of the state $P^{(1)}_{D^1B^+A^1}(t)$. It is also worth noting that the Hückel model, for the same transfer parameters, yields a lower probability for the state $D^1B^+A^1$.

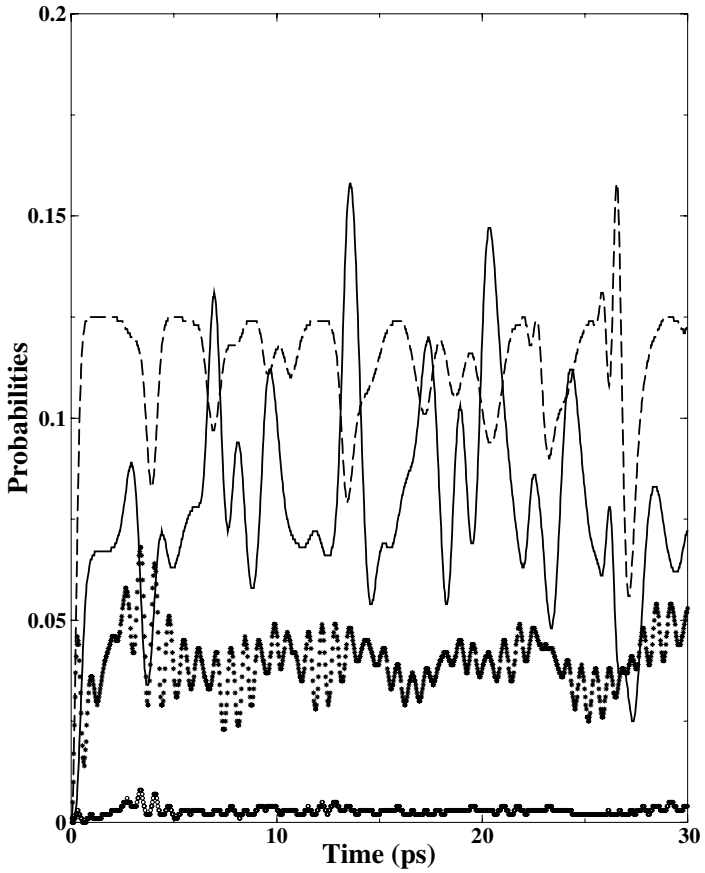

Figure 3. Charge transfer probabilities as a function of time for case (2). $P^{(1)}_{D^0BA^2}$ (solid curves for the Hückel model and circles for the Hubbard model) and $P^{(1)}_{D^1B^+A^2}$ (dashed curves for the Hückel model and stars for the Hubbard model).

For case (2) we have plotted the occupation probabilities, $P^{(2)}_{D^1B^+A^2}(t)$ and $P^{(2)}_{D^0BA^2}(t)$, as a function of time both for the Hückel model and the Hubbard model, in figure 3. Note that the state $D^1B^+A^2$ can be generated by a single electron hop from the bridge to the A site, while the generation of state D^0BA^2 requires either one hop from the state $D^1B^+A^2$ or two sequential hops from the initial state, D^1BA^1. In the Hückel model, both the processes occur with almost similar average integrated probabilities $\sim$0.12. However, for the Hubbard model, the first process has almost zero probability while the second process has finite but half the corresponding Hückel probability values. This is because, for the Hubbard model, the first process costs a Hubbard repulsion of $U' = 5\beta$, since the A site is doubly occupied. On the other hand, in the second process, this energy cost is somewhat compensated by lower electron–electron repulsion energy for the bridge, as in the final configuration the bridge remains in a singly ionized state. Note that, for the Hückel model, no such energy cost is required for the double occupancy of either the D or the A site, while the gain in bridge stabilization energy is finite for the ionized Hückel bridge.

One of the important results of the Hubbard model in one dimension is that the spin and charge degrees of freedom of an electron are decoupled (the spin and charge velocities are different). Such a decoupling is realized only in one dimension and in the large U limit.

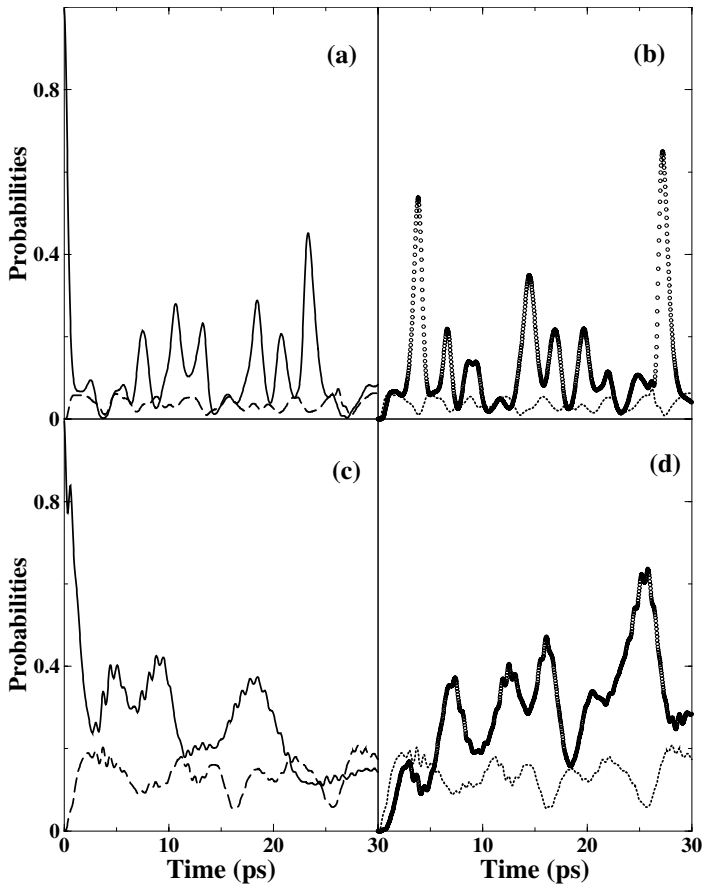

Figure 4. Time dependent spin-exchanged probabilities, $P^{(2)}_{D^{\uparrow}BA^{\downarrow}}$ (solid), $P^{(2)}_{D^{\uparrow}B^{*}A^{\uparrow}}$ (dashed), $P^{(2)}_{D^{\downarrow}BA^{\uparrow}}$ (circle) and $P^{(2)}_{D^{\downarrow}B^{*}A^{\downarrow}}$ (dotted) for the Hückel model ((a) and (b)) and the Hubbard model ((c) and (d)) for case (2) discussed in the text.

Because of this decoupling, the spectrum of charge excitations remain separated from those of spin excitations, and the low-energy excitations of the system are gapless spin excitations (spin waves) of the uniform antiferromagnetic spin-1/2 chain [18]. Therefore, the mechanism in which the bridge is in a virtual spin excited state is preferred. In contrast, the spin and charge excited states are one and the same for the Hückel model.

We study the spin exchange rate processes by following the time evolution of the probability $P^{(2)}_{\sigma,\tau}(t)$, starting with the initial state $\psi^{(2)}_{DBA}(0)$ for both Hückel and Hubbard models. There are four possible spin states for the donor–acceptor pair: $D^{\uparrow}A^{\uparrow}$, $D^{\downarrow}A^{\downarrow}$, $D^{\uparrow}A^{\downarrow}$, and $D^{\downarrow}A^{\uparrow}$. The initial state corresponds to $D^{\uparrow}A^{\downarrow}$ with the bridge in the neutral ground state.

In the Hückel model, the $D^{\uparrow}A^{\uparrow}$ or the $D^{\downarrow}A^{\downarrow}$ states (states with spin-flip at one end) can be reached from the initial state as follows: $D^{\uparrow}BA^{\downarrow} \longrightarrow D^{\uparrow\downarrow}B^{+}A^{\downarrow} \longrightarrow D^{\downarrow}B^{*}A^{\downarrow}$, where B^{*} is the excited state of the neutral bridge. The spin-exchanged state $D^{\downarrow}A^{\uparrow}$ can however be reached as follows: $D^{\uparrow}BA^{\downarrow} \longrightarrow D^{\uparrow\downarrow}B^{2+}A^{\uparrow\downarrow} \longrightarrow D^{\downarrow}BA^{\uparrow}$, where B^{2+} is the doubly ionized state of the bridge. The intermediate state in this process will have comparatively lower energy. Thus, in the Hückel model, the spin-exchange process will have a higher probability than the spin-flip process at either the D end or the A end. This is reflected in the probability for these processes shown in figures 4(a) and (b), where the spin-flip process has almost negligible

probability. In the Hubbard model the probabilities of spin-flip at a single end is comparable to the probability of the spin exchange process (figures 4(c) and (d)) and all these probabilities are significant. The origin of this difference between the Hückel and Hubbard models lies in electron correlations. The intermediate state for spin-flip at a single end as well as spin exchange goes through a doubly occupied end site. The energy of this virtual state is U' above the ground state for the Hubbard model. For the spin-flip process, with the configurations $D^{\uparrow}A^{\uparrow}$ and $D^{\downarrow}A^{\downarrow}$, the final state of the bridge is a low-energy spin excited state, while for the spin-exchange process, the final state of the bridge could be the ground state. Therefore, we find that the spin exchange process has a slightly higher probability than the process involving spin-flip at one end, in a correlated model.

To conclude, mechanisms of charge and spin transfer have been studied for interacting and noninteracting DBA systems using a new dynamical method. The electron transfer is shown to occur mainly through nearest-neighbour hopping and the probabilities have strong dependence on interaction parameters. We also find that the charge transfer process in the Hubbard model depends critically on the initial occupancies of the donor and acceptor orbitals. If the acceptor orbital is initially empty, electron transfer to the acceptor is favoured. On the other hand, if the acceptor orbital is initially singly occupied, spin exchange between D and A is preferred over electron transfer to the acceptor site.

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