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Spin-flip processes of polarons by magnetic impurities in conjugated polymers

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By employing an adaptive time-dependent density-matrix-renormalization-group method, the spin-flip process of polarons is investigated in a polymer chain with magnetic impurities. Being driven by an external electric field, a polaron carrying both spin $1/2$ and charge $\pm e$ moves at a constant speed in the polymer chain. When the polaron passes through a specific site, which couples to a magnetic impurity via spin-exchange interaction, a spin-flip process is observed if its spin is antiparallel to the impurity spin. Our results show that the spin-flip probability is enhanced by the on-site Coulomb interaction and increases with increase in the spin-exchange integral. Additionally, some possible applications of the spin-state swap between the polaron and the impurity are discussed. © 2009 American Institute of Physics. [doi:10.1063/1.3247189]

I. INTRODUCTION

Recently, extensive studies have been focused on physical phenomena that involve the spin degree of freedom¹⁻³ of mobile charge carriers. Controlling and understanding the dynamics and transport of spins are an experimental and theoretical challenge aiming at the development of mesoscopic systems for spintronics applications. Semiconductor spintronic devices have attracted considerable attention, since the discovery of long spin lifetimes in semiconductor structures.⁴ Compared with inorganic materials, organic molecules and polymers have much longer spin lifetimes due to the weak spin-orbit interaction and hyperfine interaction, suggesting that organic materials have significant potential for novel spintronic devices. Furthermore, organic electronics is a burgeoning field, providing low-cost alternatives to electronic and photonic devices such as light emitting diodes, field effect transistors, and photovoltaic cells that are presently the domain of conventional inorganic semiconductors. Therefore, the prospect of applying spintronic principles to organic electronics is alluring.

On the other hand, the investigation of a quantum-impurity or quantum dot in a correlated system is an interesting topic both for fundamental and for technological reasons, such as charging effects,⁵ Coulomb blockade (CB),⁶⁻⁸ spin blockade,⁹ voltage-controlled spin polarization,¹⁰ tunneling magnetoresistance,¹¹ quantum tunneling of magnetization,¹² and Kondo effects.¹³ The study of real-time dynamics in quantum-impurity systems (QISs) is of fundamental importance for understanding this fascinating phenomena. In this paper, we will discuss the spin-flip effect of polarons induced by magnetic impurities in conjugated poly-

mers. From the theoretical point of view, we consider a side radical which connects with the carbon atom in the organic polymer chain. The QIS used in this work is schematically depicted in Fig. 1. The main zigzag chain consists of carbon atoms with π itinerant electrons, and R is a type of side radicals containing an unpaired electron (acting as a single-site magnetic impurity). It is assumed that there are antiferromagnetic interactions between the π -electron spins along the main chain and the residual spin of the radical.¹⁴

It has been well-known that in organic polymers, due to the strong electron-lattice interactions, additional electrons or holes will induce self-localized excitations, such as solitons,^{15,16} polarons,¹⁷ and bipolarons.¹⁸ As a result, it has been generally accepted that the charge carriers in conjugated polymers are these excitations including both charge and lattice distortion.¹⁵ A polaron bears spin $1/2$ and electric charge $\pm e$. There have been extensive researches about the polaron dynamics in organic polymers.¹⁹⁻²⁸ However, these studies did not take into account the spin degree of freedom of polarons. In an earlier paper, the spin-flip process of polarons in a polymer chain with a single-site classical magnetic impurity was discussed by one of the authors and his co-workers.²⁹ In this paper, we will go further to perform a full quantum treatment of this impurity to investigate the correlation effects in the inelastic scattering process. Our simulations show that the polaron spin does flip due to the presence of this magnetic impurity. Moreover, some possible applications of the spin-state swap between the polaron and the impurity are discussed.

The paper is organized as follows. In the following section, we present Su-Schrieffer-Heeger (SSH) model modified to include electron-electron and spin-exchange interactions for a polymer chain under the influence of an external electric field, and describe the dynamical evolution method used

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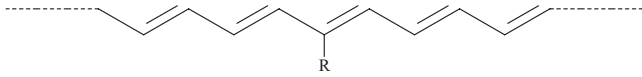


FIG. 1. Schematic diagram of the QIS.

in this work. In Sec. III the spin-flip processes of polarons by magnetic impurities will be discussed. A summary is given in the last section.

II. MODEL AND METHOD

We use the well-known SSH model¹⁵ with an additional part to include the magnetic impurity. The model is thus described by the Hamiltonian

$$H = H_{\text{el}} + H_{\text{latt}} + H_E. \quad (1)$$

The first part is to describe the electron energy, which contains the electron-lattice coupling and the spin correlation between π electrons and the residual spin of the radical, modeled by Hubbard extension of a SSH-type Hamiltonian^{30–32} and a spin-exchange term

$$H_{\text{el}} = - \sum_{n,\sigma} t_n [c_{n,\sigma}^\dagger c_{n+1,\sigma} + H.c.] + U \sum_n c_{n\uparrow}^\dagger c_{n\uparrow} c_{n\downarrow}^\dagger c_{n\downarrow} + J \mathbf{S}_{n_i} \cdot \mathbf{S}_i, \quad (2)$$

where $t_n [\equiv t_0 - \alpha(u_{n+1} - u_n)]$ is the hopping integral between site n and $n+1$ with α being electron-lattice coupling constant and u_n being the monomer displacement of site n from its undimerized equilibrium position; U is the on-site Coulomb interaction; $c_{n,\sigma}^\dagger (c_{n,\sigma})$ is the creation (annihilation) operator of an electron with spin σ at site n ; J is the spin-exchange integral at the impurity site n_i ; \mathbf{S}_{n_i} is the itinerant electron spin at site n_i , and \mathbf{S}_i is the spin of the magnetic impurity. The second part in Eq. (1) is to describe lattice elastic potential energy and kinetic energy, respectively,

$$H_{\text{latt}} = \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 + \frac{M}{2} \sum_n \dot{u}_n^2, \quad (3)$$

where K represents the force constant originating from the σ -bond between carbon atoms and M the mass of a site, such as that of a CH-unit for *trans*-polyacetylene. In this work, we consider finite chains with fixed ends. The electric field $E(t)$ is constant over the entire system. It is included in the Hamiltonian as a scalar potential. This gives the following contribution to the Hamiltonian:

$$H_E = \sum_{n,\sigma} V_n(t) \left(c_{n,\sigma}^\dagger c_{n,\sigma} - \frac{1}{2} \right), \quad (4)$$

$V_n(t) = E(t)|e|(na + u_n)$ being site energies due to the applied external electric field. The model parameters we use in this work are those generally chosen for *trans*-polyacetylene:¹⁵ $t_0 = 2.5$ eV, $K = 21.0$ eV/Å², $\alpha = 4.1$ eV/Å, $a = 1.22$ Å, and $M = 1349.14$ eV fs²/Å², and a bare optical phonon energy $\hbar\omega_0 = \hbar\sqrt{4K/M} = 0.16$ eV.

The initial configurations of the polaron are obtained by minimizing the total energy of the chain. Then the lattice configurations at time $t(>0)$ can be obtained by the equation of motion for the atomic

$$M\ddot{u}_n(t) = -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + \alpha \sum_\sigma [\langle \psi(t) | c_{n,\sigma}^\dagger c_{n+1,\sigma} - c_{n-1,\sigma}^\dagger c_{n,\sigma} + h.c. | \psi(t) \rangle] + |e|E(t) \sum_\sigma \left[\langle \psi(t) | c_{n,\sigma}^\dagger c_{n,\sigma} | \psi(t) \rangle - \frac{1}{2} \right], \quad (5)$$

where $|\psi(t)\rangle$ are the time-evolved states at time t . In principle, the time evolution can be done by operating on $|\psi(t)\rangle$ with the time evolution operator:

$$|\psi(t+dt)\rangle = e^{-iH(t)dt/\hbar} |\psi(t)\rangle = e^{-i\tau H(t)} |\psi(t)\rangle. \quad (6)$$

The time development of the lattice distortions and the electronic wave functions are obtained by solving the coupled equation of motion Eq. (5) and the time-dependent Schrödinger equation Eq. (6). Then the expectation value of the polaron spin at every time step is given by

$$S_p^z(t) = \frac{1}{2} \sum_n \langle \psi(t) | c_{n\uparrow}^\dagger c_{n\uparrow} - c_{n\downarrow}^\dagger c_{n\downarrow} | \psi(t) \rangle. \quad (7)$$

The real-time dynamics of such a many-body system including both electron-phonon and electron-electron interactions is highly nontrivial. A recently developed numerical method, the adaptive time-dependent DMRG (Ref. 33) which is an efficient implementation of Vidal's time-evolving block-decimation algorithm³⁴ in the DMRG framework,³⁵ enables us to perform this task. The key idea of time-dependent DMRG (t-DMRG) is to incorporate the second order Suzuki–Trotter (ST) decomposition of the time evolution operator Eq. (6) into the DMRG finite-system algorithm. The second order ST decomposition of the one-dimensional Hamiltonian as employed in Eq. (1) can be written as

$$e^{-i\tau H} \approx e^{-i\tau H_1/2} e^{-i\tau H_2/2} \dots e^{-i\tau H_N/2} \times e^{-i\tau H_N/2} \dots e^{-i\tau H_2/2} e^{-i\tau H_1/2} + O(\tau^3), \quad (8)$$

where H_i is the Hamiltonian of the bond i . The DMRG representation of the wave function at a particular step i during the finite-system sweep is

$$|\psi\rangle = \sum_{|\alpha_i, \alpha_{i+1}\rangle} \psi_{|\alpha_i, \alpha_{i+1}\rangle} |l\rangle |\alpha_i\rangle |\alpha_{i+1}\rangle |r\rangle, \quad (9)$$

where $|l\rangle$ and $|r\rangle$ represent the states of the left and right blocks (in a truncated basis, optimally selected as eigenvectors of a density matrix), and $|\alpha_i\rangle$ and $|\alpha_{i+1}\rangle$ represent the states of the two central sites. An operator acting on sites i and $i+1$ (only involving nearest neighbors) can be applied to $|\psi\rangle$ exactly, and re-expressed in the same optimal basis as

$$[A\psi]_{|\alpha_i, \alpha_{i+1}\rangle} = \sum_{\alpha'_i, \alpha'_{i+1}} A_{\alpha_i, \alpha_{i+1}; \alpha'_i, \alpha'_{i+1}} \psi_{|\alpha'_i, \alpha'_{i+1}\rangle}. \quad (10)$$

Thus, the time evolution operator of the bond i can be applied exactly on the DMRG step i . As a consequence, the

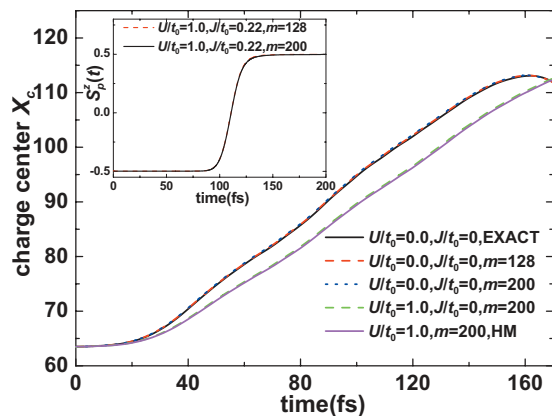


FIG. 2. The time evolution of the charge center X_c of the polaron for different numbers of states m kept in DMRG, here the “HM” stands for a pure Hubbard model (see Ref. 25). The inset shows the time evolution of S_p^z for $U/t_0=1.0$ and $J/t_0=0.22$ (see text).

time evolution is done by applying $e^{-i\tau H_i/2}$ at DMRG step i . Then basis transformations to the left or right are performed, until the next part of Eq. (8) can be applied. We thus apply the full operator of Eq. (8) by sweeping the site i through the system. The price to be paid is that a truncation error is introduced at each iteration step of the sweep as is known from the static DMRG. A full sweep evolves the system one time step τ . The error introduced by the second order decomposition is order τ^3 in each time step. Thus, upon evolving the system one time unit ($1/\tau$ steps), an order τ^2 error is introduced. However, the errors mentioned can be well controlled by increasing m (the states remained per block) or decreasing τ . Previous works on the dynamics of solitons/polarons/bipolarons in conjugated polymers show that the t-DMRG method is an efficient approach to perform a real-time dynamics of many-body systems including both electron-electron and electron-phonon interactions.^{25–28} In this paper, we present quasioxact numerical results of the real-time dynamics of the Hamiltonian Eq. (1) for realistic sizes of up to $N=128$ sites.

III. RESULTS AND DISCUSSIONS

In our simulation, a polymer chain with total sites $N=128$ is considered. The magnetic impurity is bonded at the 88th site, and the polaron is located at the center of the chain initially. When the electric field is turned on, the polaron is accelerated first, and then moves toward the magnetic impurity with a constant velocity as one entity consisting of both charge and lattice defect. The stability for the polaron velocity occurs because the moving polaron shall emit localized phonons—multibreather excitations, which bear the increased energy of the system due to the external electric field.²³ In order to reduce the lattice vibration in the accelerated process of the polaron, the electric field is turned on smoothly, that is, the field strength changes as $E(t)=E_0 \exp[-(t-t_c)^2/t_w^2]$ for $0 < t < t_c$, $E(t)=E_0$ for $t > t_c$ with t_c being a smooth turn-on period, t_w the width. Here, we take $t_w=40$ fs, $t_c=20$ fs. The time evolution of the charge center X_c of the polaron under a moderate electric field, $E_0=2.0$ mV/Å, is shown in Fig. 2. In order to confirm the

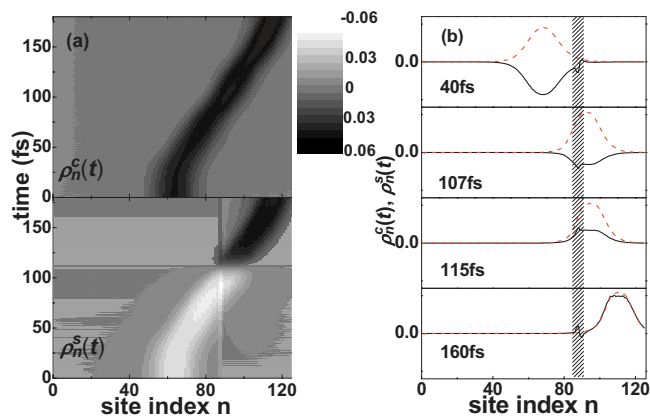


FIG. 3. (a) Charge density $\rho_n^c(t)$ and spin density $\rho_n^s(t)$ at different times for the QIS, calculated with parameters $U/t_0=1.0$, $J/t_0=0.22$, and $E_0=2.0$ mV/Å. (b) Spin density (solid line) and charge density (dashed line) of the polaron around the time when the spin-flip takes place, the shadow region correspond to the location of the impurity.

validity of our results, we compare the t-DMRG calculations with the exact numerical results for a noninteracting ($U=0$, $J=0$) chain of the same set of parameters described above. The excellent agreement was found in both the charge center X_c and the staggered bond parameters (not shown in the figure) up to time $t \sim 180$ fs even when keeping $m=128$ states per block. In the following we always keep $m=200$ states and use a time step $\tau=0.05$ (in unit of \hbar/t_0).

Now we turn on the interactions and investigate the role of correlation effects in the inelastic scattering process. When the polaron comes sufficiently close to the magnetic impurity, the spin-exchange interaction will be active, and the polaron spin undergoes a spin-flip process if it is antiparallel to the impurity spin. Thus, we consider an incident polaron representing an electron with spin $|\downarrow\rangle$ traveling toward the magnetic impurity containing an unpaired electron with spin $|\uparrow\rangle$, i.e., the z -component of total spin $S^z=0$. By adjusting the parameters of spin-exchange energy and the strength of the electric field, the system can be designed to produce a complete spin-exchange process between the polaron and the impurity while the polaron crosses the region of the impurity. This effect is illustrated in Fig. 3. As can be seen in Fig. 3(a), displaying the time dependence of the smoothed excessive electron charge density $\rho_n^c(t)=1/4[\rho_{n-1}^c+2\rho_n^c+\rho_{n+1}^c]-1$ and spin density $\rho_n^s(t)=1/4[\rho_{n-1}^s+2\rho_n^s+\rho_{n+1}^s]$, the spin of the polaron flips while the charge just moves along the chain. At about $U/t_0=1.0$ and $J/t_0=0.22$, the spin flips nearly completely, i.e., S_p^z changes from $-1/2$ to $1/2$ [see Fig. 3(b)]. The impurity spin, not shown in the picture, should be $-S_p^z(t)$ because of the conservation of z -component of total spin. If the polaron spin parallel to the impurity spin, the spin states almost do not change when the polaron passes through the impurity because of the spin-exchange only occurring between two opposite spins, i.e., $S_{n_i}^+ S_i^+ |\uparrow\rangle=0$ and $S_{n_i}^- S_i^- |\downarrow\rangle=0$.

Clearly, the spin-flip rate [defined by $S_p^z(t)-S_p^z(0)$] is a function of spin-exchange integral J and the propagation time along the coupling region. Figure 4 shows the time evolution of S_p^z for different spin-exchange integrals, J . From this figure, it can be observed that the spin-flip rate increases

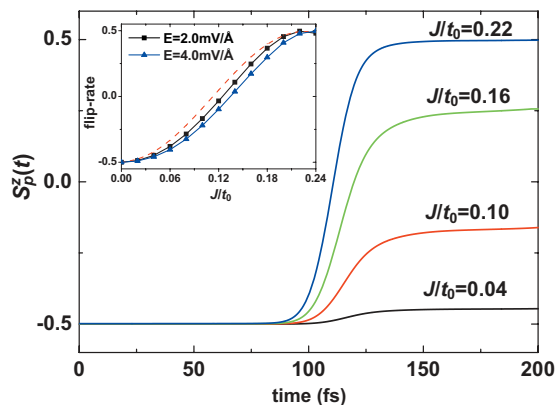


FIG. 4. Time evolution of S_p^z for different values of J with $U/t_0=1.0$ and $E_0=2.0$ mV/Å. The inset shows J dependence of the spin-flip rate, the dashed line is a cosine function fitting.

with the increasing of J . This can be understood easily, since the magnetic impurity acts as a spin-flip term, the stronger is the interaction J , the more easily the spin can be flipped. In addition, the propagation time is determined by the external electric field. For a smaller electric field, the polaron has a smaller velocity and takes more time to pass through the impurity, and a higher spin-flip rate is expected. If the polaron is still under the influence of the impurity and its spin has been flipped to $S_p^z=1/2$, the spin of the polaron will be flipped again. As a result, we will see an oscillation of $S_p^z(t)$ for a sufficiently large J , and its period depends primarily on the spin-exchange integral J . This behavior is similar to a simple two-spin system. Given an initial state $|\psi(0)\rangle=|\uparrow\downarrow\rangle$, just similar to the encounter of the polaron and the impurity, two spins coupled by an exchange constant J will evolve into $|\psi(t)\rangle=\cos(Jt/2\hbar)e^{iJt/4\hbar}|\uparrow\downarrow\rangle-i\sin(Jt/2\hbar)e^{iJt/4\hbar}|\downarrow\uparrow\rangle$, then the time evolution of z -component spin is given by $S^z(t)=(1/2)\cos(Jt/\hbar)$. Therefore, the oscillation is nothing but the analog of the Rabi oscillation.^{36,37} For this impurity system, due to the many-particle effect, the J -dependent of spin-flip rate cannot be expressed as a cosine function any more (see the insert in Fig. 4). Moreover, the presence of the magnetic impurity allows to manipulate the spin of polarons by an external spin-exchange. The spin of a polaron can be or cannot be flipped by the impurity molecule, which shows that the magnetic impurity molecule can work as a filter to the passage of spin, i.e., it can control spin transport.

Next, we vary the Coulomb interaction strength U and discuss its effect on the spin-flip process. Figure 5 illustrates the time evolution of S_p^z for different U , as an example, we choose $J/t_0=0.22$ for an antiferromagnetic impurity and $J/t_0=-0.22$ for the ferromagnetic case. From this figure, the following issues should be addressed: (1) the velocity of the polaron is suppressed by the on-site electron-electron interaction, as discussed above, a smaller velocity favors the rate of spin-flip. (2) Compared with the ferromagnetic impurity, an antiferromagnetic impurity flips the spin more easily. (3) The Coulomb repulsion U enhances the spin-flip for this two type impurities. This can be understood as that the Hubbard U increases the probability of singly occupied states, which will favor the spin exchange between the polaron and the impurity.

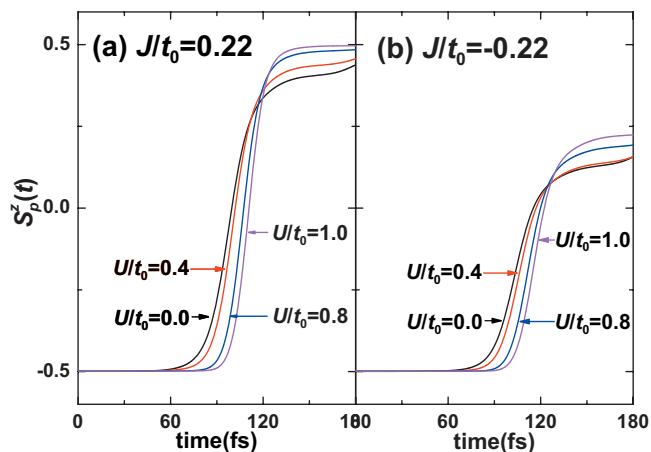


FIG. 5. U dependence of the $S_p^z(t)$ for (a) antiferromagnetic impurity with $J/t_0=0.22$, and for (b) ferromagnetic impurity with $J/t_0=-0.22$.

Finally, the field of quantum computing is attracting considerable experimental and theoretical attention.³⁸ The minimal requirements for a quantum computer architecture are the existence of fundamental quantum bits (qubit) and the ability to carry out single- and two-qubit operations such as swap and controlled-NOT (CNOT). Actually, electron spin states, e.g., electrons or nucleus, have been regarded to be the most promising candidates for qubits, and quantum-information processing can be performed via changes in the electron spin states. If we define the spin-up state $|\uparrow\rangle$ as logic 0, and the spin-down one $|\downarrow\rangle$ as logic 1, as shown above, the spin states of the polaron and the impurity are exchanged after scattering, resulting in a swap for the two spins, i.e., $|0,1\rangle\leftrightarrow|1,0\rangle$. Furthermore, if we consider two impurities, after twice acting of this swap operation, the information of the first impurity is transported to the second one by the polaron. Such results indicate that the qubit-qubit interaction can be mediated by the propagation of polarons, which implies that the polaron in polymers might be a good candidate to be an information carrier in molecular scale. Clearly, many techniques should be implemented before the physical realization, such as how to control the creation of single polaron with a given spin, how to initialize the impurity spin, how does one read out the states of spins, what is the coherence time of the spins, and so on.

IV. SUMMARY

In summary, we have investigated the spin-flip process of polarons induced by a magnetic impurity in a polymer chain by using an adaptive t-DMRG method for this many-body evolution problem. It has been shown that the probability of the spin-flip increases with increasing the spin-exchange integral J . Moreover, if we keep the spin-exchange energy J fixed, we find that the on-site Coulomb interaction U favors the spin-flip. Additionally, the spin-exchange between the polaron and the impurity allows the implementation of the swap operation in this quantum-impurity system. Finally, the spin-exchange strengths J used in this paper might be much larger than that of realistic materials, how-

ever, the spin-flip rate can be increased effectively by reducing the external electric field or increasing the Coulomb repulsion.

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