

## Spin-Flip Process of Polarons in Conjugated Polymers with Magnetic Impurities \*

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Being driven by an external electric field, a polaron carrying both spin 1/2 and charge  $\pm e$  moves at a constant speed in a polymer chain. When the polaron passes through a specific site, which couples to a magnetic impurity via spin-exchange interactions, its spin undergoes a spin-flip process if it is antiparallel to the impurity spin. Our numerical simulation shows that (a) a swap-like operation is performed between the polaron and impurity during the scattering process (b) polarons might be good candidates to be information carriers in the molecular scale.

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Recently, extensive studies have been focused on physical phenomena that involve the spin degree of freedom<sup>[1–3]</sup> of charge carriers. Controlling and understanding the dynamics and transport of spins is an experimental and theoretical challenge aimed at the development of mesoscopic systems for spintronic applications. Semiconductor spintronic devices have attracted considerable attention, since the discovery of long spin lifetimes in semiconductor structures.<sup>[4]</sup> Compared with inorganic materials, organic molecules and polymers have much longer spin lifetimes due to the weak spin-orbit interaction and hyperfine interaction, which suggests 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 field of quantum computing is attracting considerable experimental and theoretical attention.<sup>[5]</sup> 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). Electron spin states, e.g., electrons or nuclei, have been regarded to be the most promising candidates for qubits<sup>[6–12]</sup> because of their well-defined Hilbert spaces and their relatively long decoherence times compared to the orbital degrees of freedom.<sup>[13]</sup> For most of the spin-based schemes, swap

action  $U_{sw}$ , in which two spins exchange their states, is one of the most basic operations. A spin-flip can result from precession in the external static magnetic field<sup>[14]</sup> or irradiation of the electron system by an electromagnetic wave with frequency adjusted to the Zeeman splitting.<sup>[15]</sup> The spin swap can be caused by an exchange interaction between the two electrons.<sup>[7]</sup> In this Letter, we propose a possible swap scheme based on the spin-exchange between polarons and magnetic impurities in a quantum impurity system (QIS). The QIS used in this work is schematically depicted in Fig. 1. From the theoretical point of view, we consider a side radical that connects with the carbon atom in the organic polymer chain. The main zigzag chain consists of carbon atoms with  $\pi$  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  $\pi$ -electron spins along the main chain and the residual spin of the radical.<sup>[16]</sup>

It is 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, polarons, and bipolarons. As a result, it has been generally accepted that the charge carriers in conjugated polymers are those excitations including both charge and lattice distortions.<sup>[17]</sup> A polaron bears spin 1/2 and charge  $\pm e$ . There have been extensive studies on polaron dynamics in organic polymers.<sup>[18–25]</sup> However, these studies did not take into account the spin degree of freedom of polarons. In this study, we focus on the spin dynamics of polarons due to the presence of magnetic impurities. When

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the polaron moves through the site which couples to the magnetic impurity, the localized spin undergoes a spin-flip process if it is antiparallel to the spin of the impurity, or not if they are parallel. The qubit-like characteristics are studied by means of a numerical solution of the time-dependent Schrödinger equation for a number of physical cases of interest.

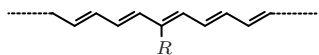


Fig. 1. Schematic diagram of the QIS.

We use the well-known Su–Schrieffer–Heeger (SSH) model<sup>[17]</sup> with an additional part to include the magnetic impurity. The model is thus described by the Hamiltonian

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

The first part is to describe the electron energy

$$H_e = - \sum_{n,\sigma} t_n [e^{i\gamma A(t)} c_{n,\sigma}^\dagger c_{n+1,\sigma} + \text{h.c.}] + J \mathbf{S}_{n_i} \cdot \mathbf{S}_i, \quad (2)$$

where  $t_n \equiv t_0 - \alpha(u_{n+1} - u_n)$  is the hopping integral between sites  $n$  and  $n + 1$ , and  $t_0$  is used as the unit of energy,  $\alpha$  is the electron-lattice coupling constant and  $u_n$  the monomer displacement of site  $n$  from its undimerized equilibrium position;  $c_{n,\sigma}^\dagger (c_{n,\sigma})$  is the creation (annihilation) operator of an electron with spin  $\sigma$  at site  $n$ ;  $J$  is the spin-exchange integral at the impurity site  $n_i$ ;  $\mathbf{S}_{n_i} = \frac{1}{2} \sum_{\alpha\beta} c_{n_i,\alpha}^\dagger (\boldsymbol{\sigma})_{\alpha\beta} c_{n_i,\beta}$  is the itinerant electron spin at site  $n_i$ , and  $\mathbf{S}_i$  is the spin of the magnetic impurity. The spin-exchange can be written as  $J \mathbf{S}_{n_i} \cdot \mathbf{S}_i = J [\frac{1}{2} (S_{n_i}^+ S_i^- + S_{n_i}^- S_i^+) + S_{n_i}^z S_i^z]$ . The vector potential  $A(t)$  is introduced to describe a uniform external electric field along the chain under the periodic boundary condition, the relation between the potential  $A(t)$  and the uniform electric field  $E(t)$  is given by  $E(t) = -(1/c) \partial A(t) / \partial t$ , where  $\gamma \equiv ea/\hbar c$  is a constant quantity,  $c$  the light speed,  $e$  the absolute value of the electronic charge, and  $a$  the lattice constant. 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  $K$  denotes the force constant originating from the  $\sigma$ -bond between carbon atoms and  $M$  the mass of a unit-cell. The model parameters we use in this work are those generally chosen for trans-polyacetylene<sup>[17]</sup>  $t_0 = 2.5$  eV,  $K = 21.0$  eV/Å<sup>2</sup>,  $\alpha = 4.1$  eV/Å,  $a = 1.22$  Å, and  $M = 1349.14$  eVfs<sup>2</sup>/Å<sup>2</sup>.

We consider an acoustic polaron passing through the magnetic impurity as a first step to understand the spin-flip scattering process, and the optical polaron case will be discussed elsewhere. An acoustic polaron

is created as the initial state when there is only one electron in the conduction band, which can be treated exactly because the Hilbert space is small enough to perform a complete diagonalization procedure. The initial configurations of the acoustic 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 displacements:

$$M \ddot{u}_n(t) = -K [2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + \alpha [e^{i\gamma A(t)} \langle \psi(t) | c_n^\dagger c_{n+1} - c_{n-1}^\dagger c_n | \psi(t) \rangle + \text{c.c.}], \quad (4)$$

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

$$|\psi(t + \Delta t)\rangle = e^{-iH(t)\Delta t/\hbar} |\psi(t)\rangle. \quad (5)$$

The time step  $\Delta t$  is chosen so that the changes of  $u_n(t)$  and  $A(t)$  are always very small in the electronic scale during this interval. Hence, the time development of the lattice distortions and the electronic wave functions are obtained by solving the coupled equation of motion Eq. (4) and the time-dependent Schrödinger equation Eq. (5). Then the expectation value of the polaron spin at every time step is given by

$$S_z^p(t) = \frac{1}{2} \sum_n \langle \psi(t) | c_{n\uparrow}^\dagger c_{n\uparrow} - c_{n\downarrow}^\dagger c_{n\downarrow} | \psi(t) \rangle. \quad (6)$$

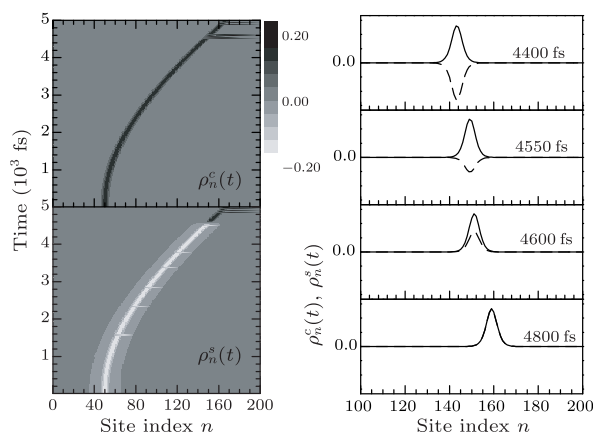
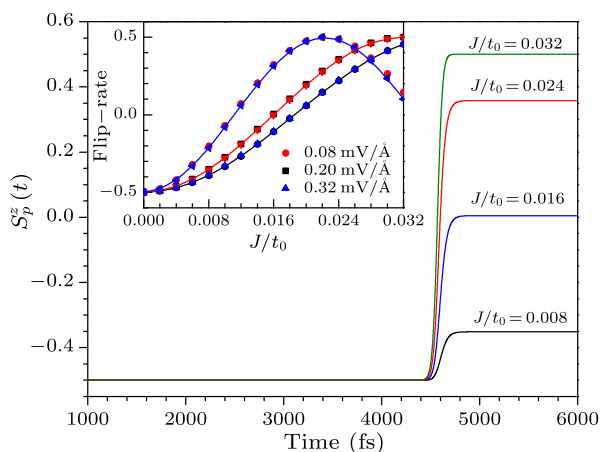


Fig. 2. (a) Charge density  $\rho_n^c(t)$  and spin density  $\rho_n^s(t)$  of the acoustic polaron at different times for the QIS, calculated with parameters  $J/t_0 = 0.032$  and  $E_0 = 0.2$  mV/Å. (b) Charge density (solid line) and spin density (dashed line) of the polaron around the time when the spin-flip takes place.

In our simulation, a polymer chain with total sites  $N = 200$  is considered. The magnetic impurity is bonded at the 150th site, while the polaron is centered at the 50th site initially. When the electric field is turned on, the polaron is accelerated firstly, then it moves toward the magnetic impurity with a constant velocity, see Fig. 2(a). In order to reduce the lattice

vibration in the accelerated process of the acoustic polaron, the electric field is turn 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  $t_c < t$  with  $t_c$  being a smooth turn-on period,  $t_w$  the width. Here, we take  $E_0 = 0.2 \text{ mV/\AA}$ ,  $t_w = 50 \text{ fs}$ , and  $t_c = 200 \text{ fs}$ .



**Fig. 3.** (Color online) Time evolutions of  $S_p^z$  for different values of  $J$ . The inset shows  $J$  dependence of the spin-flip rate, the solid lines are cosine functions fitting.

When the polaron comes sufficiently close to the magnetic impurity, the spin-exchange interaction will be active. Within the picture of a two-spin system, swapping is achieved by switching the coefficients of the unpolarized  $|\uparrow\downarrow\rangle$  and  $|\downarrow\uparrow\rangle$  states, or equivalently, changing the coefficient of the singlet component by a  $\pi$  phase shift relative to the triplet states.<sup>[26]</sup> The phase shift can be obtained by the Heisenberg exchange term  $H = J\mathbf{S}_{n_i} \cdot \mathbf{S}_i$ . Hence, 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. 2. As can be seen in Fig. 2(a), displaying the time dependence of the charge density  $\rho_n^c(t) = \langle\psi(t)|c_{n\uparrow}^\dagger c_{n\uparrow} + c_{n\downarrow}^\dagger c_{n\downarrow}|\psi(t)\rangle$  and spin density  $\rho_n^s(t) = \langle\psi(t)|c_{n\uparrow}^\dagger c_{n\uparrow} - c_{n\downarrow}^\dagger c_{n\downarrow}|\psi(t)\rangle$ , the spin of the polaron flips while the charge just moves along the chain. At about  $J/t_0 = 0.032$ , the polaron spin flips nearly completely, i.e.,  $S_p^z$  changes from  $-\frac{1}{2}$  to  $\frac{1}{2}$  (see Fig. 2(b)). The impurity spin, not shown in the figure, should be  $-S_p^z(t)$  because of the conservation of the  $z$ -component of total spin. 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.,  $|\uparrow\downarrow\rangle \Leftrightarrow |\downarrow\uparrow\rangle$ . Furthermore, if we consider two impurities, after twice acting out this swap operation, the information of the first

impurity is transported to the second one by the polaron. For the case of the polaron spin parallel to the impurity spin, the spin states almost do not change when the polaron passes through the impurity due to the spin-exchange only occurring between two opposite spins, i.e.,  $S_{n_i}^+ S_i^- |\uparrow\uparrow\rangle = 0$  and  $S_{n_i}^+ S_i^- |\downarrow\downarrow\rangle = 0$ . Clearly, many techniques should be implemented before the physical realization, such as how to control the creation of single polarons with a given spin, how to initialize the impurity spin, how one reads out the states of spins, what the coherence time of the spins is, and so on.

Obviously, 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. Fig. 3 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 with increasing  $J$ . This can be understood easily, since the magnetic impurity acts as a spin-flip term, and the stronger 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. For this impurity system, the  $J$ -dependent of spin-flip rate can be expressed as a cosine function (see the inset in Fig. 3), which indicates that the spins of the polaron and impurity can be described by an effective two-spin system (given a initial state  $|\psi(0)\rangle = |\uparrow\downarrow\rangle$ ), two spins coupled by an exchange constant  $J$  will evolve into  $|\psi(t)\rangle = \cos(\frac{Jt}{2\hbar})e^{iJt/4\hbar}|\uparrow\downarrow\rangle - i\sin(\frac{Jt}{2\hbar})e^{iJt/4\hbar}|\downarrow\uparrow\rangle$ , then the time evolution of  $z$ -component spin is given by  $S^z(t) = \frac{1}{2}\cos(\frac{Jt}{\hbar})$ . An effective spin Hamiltonian quite faithfully describes the QIS:

$$H_{\text{eff}} = J_{\text{eff}}\mathbf{S}_p \cdot \mathbf{S}_i, \quad (7)$$

in which  $J_{\text{eff}} = \pi\hbar J/T_0 J_0$  gives the effective strength of exchange coupling, where  $T_0$  is the propagation time along the coupling region, and  $J_0$  is the spin-exchange integral energy that causes a complete spin-flip process (which is about  $0.032t_0$  within current parameters). Obviously,  $J_{\text{eff}}$  is a function of external electric field and the type of radicals attached, which provides a controlled interaction between the spins. For a specific duration  $\tau_s$  of the effective spin-spin coupling such that  $\int_0^{\tau_s} J_{\text{eff}} dt/\hbar = \pi \pmod{2\pi}$ , the time evolution  $U_s(t) = T \exp(-i \int_0^t H_{\text{eff}} dt/\hbar)$  corresponds to the swap operator  $U_{\text{sw}}$ . In addition, the  $U_{\text{sw}}$  allows the manipulation of the spin of polarons by an external spin-exchange. The spin of a polaron can be flipped by the impurity molecule or dose not change, which shows that the magnetic impurity molecule can work as a filter to the passage of spin, i.e., it can control spin transport.

In summary, we have investigated the spin-flip process of an acoustic polaron induced by a magnetic impurity in a polymer chain. Our results show that, with suitable design, the spin-exchange between the polaron and the impurity allows the implementation of the swap operation in this quantum impurity system. Furthermore, 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 the molecular scale. The spin-exchange strengths  $J$  used in this paper might be much larger than those of realistic materials; however, the spin-flip rate can be increased effectively by reducing the external electric field.

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