Simulations of polaron spin inversion in an organic semiconductor: Comparison of two mechanisms

Hui Wang [a], Xiang-Ru Kong [a], Bin Cui [a], Dong-Mei Li [a], Kun Gao [a], Yuan Li [a,*], De-Sheng Liu [a,b,*]

[a] School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China
[b] Department of Physics, Jining University, Qufu 273155, People's Republic of China

ABSTRACT

We present a model study of the effects of two mechanisms, the Rashba spin–orbit coupling and the spin-flip term, on the polaron spin inversion in an organic semiconductor. We find that, while both mechanisms can impact the polaron spin by changing the polaron level from a spin eigenstate to a spin superposition state, substantial difference can be observed in the static and dynamical properties of the polaron. Given the values of model parameters relevant to conjugated polymers, the magnitude of the polaron spin inversion caused by the spin–orbit coupling is much smaller than that by the spin-flip term. When the dynamical properties of the polaron are considered, spin oscillations induced by both mechanisms are observed when the polaron moves along the polymer chain driven by external electric field. Interestingly, the length of the polaron motion during one spin oscillation period remains constant in the case of spin–orbit coupling, while it is enhanced with increasing the driven electric field in the case of spin-flip term, in which larger spin diffusion length and longer spin relaxation time can be expected.

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1. Introduction

Organic spintronics, starting from the first discoveries of spin-polarized injection into organic semiconductor [1] and giant magnetoresistance in organic spin valves [2], has developed rapidly in recent years due to its important potential application in next generation functional devices. Organic semiconductors are expected to be excellent material candidates for spintronic applications because of their advantages in many aspects. On one hand, the spin diffusion length in organic semiconductors is extremely long as compared with that in their inorganic counterparts because of the weak spin–orbit coupling (SOC) and hyperfine interactions (HFI) in these materials. On the other hand, organic semiconductors are low cost and can be easily processed through large-area techniques in experiment and industry. As such, organic semiconductors have been widely employed in the fabrication of organic functional devices, such as organic spin valves, field-effect transistors, light-emitting diodes, and photovoltaic cells [2–5].

The understanding of spin relaxation mechanisms in organic semiconductors is very important for improving the performance of organic spintronic devices. In experiment, it was demonstrated that the spin diffusion length in the organic layer of organic spin valves is directly correlated with the magnetoresistance of the devices [2,6], and the spin relaxation process is mainly caused by the HFI in many organic systems [7–10]. Furthermore, the SOC is also excepted to be a significant source of spin relaxation in organic semiconductors such as Xq_3 (X = Al, Ga, In, Bi) and the triethylsilylethynyl series [11,12]. However, the spin relaxation mechanisms of organic semiconductors are actually very complicated and expected to be material dependent. For instance, temperature-dependent probes of the spin diffusion length in two structures of poly (3-hexyl thiophenes) revealed that distinct spin relaxation mechanisms can be observed under different charge transport mechanisms of these materials [13]. On the theoretical side, by Monte Carlo simulations of the HFI in organic semiconductors, Bobbert et al. revealed that the spin diffusion length in these materials weakly depend on temperature but is sensitive to the magnetic field [14]. Yu explored the impact of SOC on the spin properties of hopping charge transport in organic semiconductors and demonstrated that the temperature dependence of the spin diffusion length in Alq3 can be accounted for by a theory based on the SOC in these systems [15,16]. Harmon and Flatté proposed a spin-flip-based mechanism in structural disordered organic solids by using the percolation theory and demonstrated that faster spin-flip transitions are very important for producing magnetoresistance in these systems [17]. More recently, Wu et al. showed that the quenching of quantum correlation between the carrier's

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* Corresponding authors at: School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China (D.-S. Liu).

E-mail addresses: liyuan_sdu@mail.sdu.edu.cn (Y. Li), liuds@sdu.edu.cn (D.-S. Liu).

spin and the HFI-induced local spin environment also represents an important factor responsible for the magnetoresistance in organic semiconductors [18]. The results of these investigations indicate that the spin interactions such as HFI and SOC play important roles in impacting the spin relaxation processes in organic semiconductors.

While significant progresses have been made, the spin relaxation mechanism in organic semiconductors, in particular how the relevant spin interactions operate in the spin relaxation process, still remains controversial [19,20]. In real materials, in addition to the SOC and HFI as mentioned above, more factors such as the thermal effect [21] and the scattering of magnetic impurities [22] can also contribute to spin flip in the systems, making the modeling of spin relaxation in organic semiconductors more complicated. Moreover, while spin-dependent polaron hopping in disordered organic semiconductors has been extensively studied, spin relaxation based on polaron drift in organic semiconductors was much less investigated in the literature. In particular, the dynamical properties of polaron spin under different spin interactions still remain unclear. Recently, a mechanism based on spin-flip term that is very similar in form to the Rashba SOC [23,24] was proposed to interpret the spin relaxation in one-dimensional organic systems [25]. The spin-flip term was introduced to model the factors responsible for spin flip other than the Rashba SOC. As revealed by Xie et al. [25], the Rashba SOC and the spin-flip term are expected to play different roles in impacting the spin-dependent properties of polarons in organic semiconductors. In this paper, we aim to perform a detailed study on the Rashba SOC and the spin-flip term in a model Hamiltonian and compare the impacts of these two mechanisms on the polaron static and dynamical properties in conjugated polymer.

2. Model and method

In our simulations, without loss of generality, we consider a one-dimensional polymer chain of trans-polyacetylene. The Hamiltonian of the system can be described with the well-known Su–Schrieffer–Heeger (SSH) model by expanding to incorporate the spin interactions of our interest [26,27]:

$$H = H_e + H_L + H_{so} + H_{sf}. \tag{1}$$

The first term represents the electronic part of the Hamiltonian:

$$H_e = -\sum_{n,s}[t_0 - \alpha(u_{n+1} - u_n)](c_{n,s}^+ c_{n+1,s} + c_{n+1,s}^+ c_{n,s}), \tag{2}$$

where t_0 denotes the average electronic transfer integral, α the electron–lattice coupling parameter, and u_n the lattice displacement at the nth site. $c_{n,s}^+$ and $c_{n,s}$ respectively describe the creation and annihilation operator of π electrons at the nth site with spin s. The second term in Eq. (1) denotes the lattice part of the Hamiltonian for acoustic vibrations:

$$H_L = \sum_n \left[\frac{K}{2}(u_{n+1} - u_n)^2 + \frac{1}{2}M\dot{u}_n^2 \right], \tag{3}$$

where K denotes the elastic constant and M the mass of a CH group.

The last two terms in Eq. (1) represent the Hamiltonians of the spin interactions that will be focused in this work. One is the Hamiltonian of the Rashba SOC (simply referred to as SOC hereafter) that, for the one-dimensional polymer chain we consider, can read [23,24]:

$$H_{so} = -t_{so}\sum_n \left(c_{n+1,\uparrow}^+ c_{n,\downarrow} - c_{n+1,\downarrow}^+ c_{n,\uparrow} + h.c. \right), \tag{4}$$

where t_{so} denotes the SOC parameter $t_{so} = \beta/2a$ with β the strength parameter and a a lattice constant. The other one, H_{sf}, is the spin-

flip term that describes the factors responsible for spin flip other than the SOC mechanism and can be formulated as:

$$H_{sf} = -t_{sf}\sum_n \left(c_{n+1,\uparrow}^+ c_{n,\downarrow} + c_{n+1,\downarrow}^+ c_{n,\uparrow} + h.c. \right). \tag{5}$$

It is noted that the spin-flip term of Eq. (5) is very similar in form to that of the SOC of Eq. (4).

The static polaron properties of the system can be obtained by diagonalizing the Hamiltonian of Eq. (1) at the equilibrium geometry of the lattice. In the presence of SOC or spin-flip term, the electronic wave function can be expanded on the spin-dependent Wannier basis $\left| \psi_\mu \right\rangle = \sum_{n,s} Z_{\mu,n,s} |n,s\rangle$, where μ describes the μth energy level and $Z_{\mu,n,s}$ the probability amplitude of the state $\left| \psi_\mu \right\rangle$ at the nth site with spin s. The energy level, wave function, and equilibrium lattice geometry can be obtained by solving the combined eigen equation of electron:

$$-[t_0 - \alpha(u_{n+1} - u_n)]Z_{\mu,n+1,s} - [t_0 - \alpha(u_n - u_{n-1})]Z_{\mu,n-1,s}$$
$$\mp t_{so}(Z_{\mu,n-1,-s} - Z_{\mu,n+1,-s}) - t_{sf}(Z_{\mu,n-1,-s} + Z_{\mu,n+1,-s}) = \varepsilon_\mu Z_{\mu,n,s} \tag{6}$$

and the balance equation of lattice

$$u_{n+1} - u_n = \frac{\alpha}{K}\sum_s \left(\frac{1}{N-1}\sum_{n=1}^N \rho_{n,n+1,s} - \rho_{n,n+1,s} \right), \tag{7}$$

where $\rho_{n,n',s} = \sum_{\mu=1}^{occ} Z_{\mu,n,s}^* Z_{\mu,n',s}$ denotes the charge density matrix.

To simulate the transport of polaron, we apply along the polymer chain an external electric field with the form of $E_0 = -\partial A(t)/\partial t$, where A denotes the time-dependent vector potential. The electronic Hamiltonian including the effect of electric field in the periodic boundary condition can accordingly be written as [28,29]:

$$H_e = -\sum_{n,s} t_{n,n+1}(e^{-i\gamma A}c_{n,s}^+ c_{n+1,s} + h.c.), \tag{8}$$

where the coefficient γ is defined as $\gamma = ea/\hbar$, with a the lattice constant and e the electron charge. The evolution of the electronic states can be obtained by solving the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}Z_{\mu,n,s}(t) = -t_{n,n+1}e^{i\gamma A}Z_{\mu,n+1,s}(t) - t_{n,n-1}e^{-i\gamma A}Z_{\mu,n-1,s}(t)$$
$$- s \cdot t_{so}(e^{-i\gamma A}Z_{\mu,n-1,-s}(t) - e^{i\gamma A}Z_{\mu,n+1,-s}(t))$$
$$- t_{sf}(e^{-i\gamma A}Z_{\mu,n-1,-s}(t) + e^{i\gamma A}Z_{\mu,n+1,-s}(t)) \tag{9}$$

while the evolution of the lattice coordinates can be described by the Newtonian equation of motion:

$$M\ddot{u}(t) = K(u_{n+1}(t) + u_{n-1}(t) - 2u_n(t))$$
$$+ \alpha\left\{ e^{i\gamma A}\left[\rho_{n,n+1}^c(t) - \rho_{n-1,n}^c(t) \right] + c.c \right\}. \tag{10}$$

The charge and spin distributions of polaron on the nth site at time t can be calculated by:

$$\rho_n^c(t) = \sum_{\mu=1}^{occ}\left(|Z_{\mu,n,\uparrow}(t)|^2 + |Z_{\mu,n,\downarrow}(t)|^2 \right) - 1 \tag{11}$$

and

$$\rho_n^s(t) = \sum_{\mu=1}^{occ}\left(|Z_{\mu,n,\uparrow}(t)|^2 - |Z_{\mu,n,\downarrow}(t)|^2 \right), \tag{12}$$

respectively. The total spin of the system can be obtained by summing over all the lattice sites as $s^t(t) = \sum_n \rho_n^s(t)$. To track the movement of polaron, we calculate the center of the polaron state p_c that, in the periodic boundary condition, is defined as: