Spontaneous spin polarization in organic thiophene oligomers

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ABSTRACT

We studied the spin polarization phenomenon of injected charges in organic thiophene oligomer by using extended Su–Schrieffer–Heeger (SSH) model including electron–electron interaction, spin–orbit coupling as well as spin–flip effect. Our simulation shows that a charged carrier is spontaneously spin polarized, which has a lower energy than the non-polarized one. This polarization is related with the amount of injected charges and the polymerization of the molecule.

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1. Introduction

The spin properties of injected charge carriers are vital to organic spintronic devices [1–4]. Comparing to inorganic semiconductors, organic semiconductors (OSCs) have strong intramolecular carbon–carbon covalent bonds and weak intermolecular Van der Waals forces, which makes OSCs soft and the devices easily to be manufactured industrially. Because of the strong electron–phonon (e–ph) coupling, it is indicated that one extra electron (or hole) in OSCs will form a self-trapped state called a polaron, and two extra electrons (or holes) will form a bipolaron [5]. Both of these carriers are usually considered localized in space [6], although the localization may be strong or weak depending on different materials [7]. The formation, dissociation, collision and transformation of these self-trapped states could induce plenty of phenomena in organic spintronic devices. All these features make OSCs promising materials for the application of spintronics.

The first organic spin valve device LSMO ($La_xSr_{1-x}MnO_3$)/sexithienyl (T6)/LSMO has been designed by Dediu et al. [8]. They measured the I–V curve with electrodes spin polarized random and parallel by applying a magnetic field, and found a significant magnetoresistance (MR), which implies that the injected charges are spin polarized in the organic layer. In 2003, Xie et al. proposed a model and studied spin polarized injection in $Re_{1-x}Ak_xMnO_3$/polymer interfaces [5]. They found that there exists a spin density polarization in the polymer near the interface. The spin density oscillates and decays into the polymer. Then Fu et al. investigated the dynamic process of charge injection within the framework of a nonadiabatic approach [9,10]. It was found that, for a nonmagnetic metal contact, the injected charges form wave packets due to the strong e–ph coupling in the conjugated polymer. A wave packet may contain up to two electronic units, which depends upon the injection condition. As the system is spin degenerate within their model, the wave packet has no spin.

Recently, Tarafder et al. studied spin polarization in a Alq_3 molecule by using first-principle simulation method [11]. They found that the injected charges have a lower energy in a spin polarized state than a non-polarized one. The polarization or magnetic moment increases nearly linearly with the injected charge quantity. They analyzed that, when the asymmetric Alq_3 molecule is doped with electrons, the three Al–N bonds will change their lengths which causes spin splitting and finally magnetic moment induced by ferromagnetic coupling appears in the molecule. But Alq_3 contains a metal atom which

make it difficult to elucidate the reason for the charge induced magnetism. Very recently, Hou et al. studied spin polarization of a pure organic material. They calculated a charged thiophene oligomer by using density functional theory method [12]. They also found that the charged oligomer is spin polarized. However the polarization characteristic in the polymerized oligomer is different from that in small molecule Alq$_3$. The emergence and variation of the net magnetic moment is related to both the amount of charge injected and the polymerization of the oligomer. In combination with model analysis, they concluded that the strong electron–electron (e–e) interaction and e–ph coupling in organic materials are responsible for the spin polarization.

In this paper, we try to present a model study on the spin polarization of injected charges in thiophene from its oligomer to polymer form. Compared to the first-principle calculation, we can simulate a much large molecule system. The model and formula are given in Section 2. Calculations are presented and results are analyzed in Section 3. Finally, in Section 4 a conclusion is made.

2. Model

We set a tight-binding model for a oligothiophene molecule, which is a typical OSC material and widely used in organic spintronic devices [8]. The monomer of thiophene oligomers is a flat five-membered heterocyclic ring, as shown in the inset of Fig. 2. There are two conductive channels in the thiophene oligomer, the carbon–carbon (C–C) back bone and the carbon–sulfur (C–S) bond. By using a non-degenerate version of the one-dimensional extended SSH (Su–Schrieffer–Heeger) model [6,13,14], The Hamiltonian of a thiophene oligomer is,

$$H = H_{el} + H_{ee} + H_{so} + H_{sf} + H_{latt} \quad (1)$$

The first term of the Hamiltonian means electron transfer with spin conservation among CH unit sites, which is site position dependent [14],

$$H_{el} = -\sum_{n,s} t_{n,n+1}\left(C_{n+1,s}^{\dagger}C_{n,s} + h.c.\right)$$
$$- \sum_{n,s} t'\left(C_{4n-3,s}^{\dagger}C_{4n,s} + h.c.\right)$$
$$- \sum_{n,s} t''\left(C_{4n,s}^{\dagger}C_{4n,s} + C_{4n-3,s}^{\dagger}C_{4n-3,s}\right) \quad (2)$$

where $t_{n,n+1}$ means the electron transfer integral along C–C back bone, it can be written as,

$$t_{n,n+1} = t_0 - \alpha(u_{n+1} - u_n) - t_1 \cos(\pi/2) \quad (3)$$

where t_0 is the electron transfer integral in a uniform lattice. α is the e–ph coupling constant which leads to the distortion of the lattice. u_n is the deviation from the uniform configuration. t_1 is the nondegenerate parameter. $C_{n,s}^{\dagger}(C_{n,s})$ denotes the electron creation (annihilation) operator at site n with spin s. t' and t'' respectively represent the additional electron transfer integral along C–S bonds and the on-site energy of the sulfur atom.

The second term of Hamiltonian (1) denotes e–e interaction, a Hubbard form is adopted,

$$H_{ee} = \frac{1}{2}\sum_{n,s} U C_{n,s}^{\dagger}C_{n,s}C_{n,-s}^{\dagger}C_{n,-s} \quad (4)$$

where U represents the strength of on-site Coulomb interaction.

The third term of Hamiltonian (1) denotes the spin–orbit coupling. Although it is usually considered that, in OSC materials, the spin–orbit coupling is relatively weaker than that in inorganic semiconductors [3], we still want to know the effect of spin–orbit coupling on the spin polarization. In tight-binding approach, the spin–orbit coupling can be written as [15–17],

$$H_{so} = -\frac{1}{2}\sum_{n,s} t_{so}\left(C_{n+1,s}^{\dagger}C_{n,-s} - C_{n+1,-s}^{\dagger}C_{n,s} + h.c.\right)$$
$$- \frac{1}{2}\sum_{n,s} t'_{so}\left(C_{4n,s}^{\dagger}C_{4n-3,-s} - C_{4n,-s}^{\dagger}C_{4n-3,s} + h.c.\right) \quad (5)$$

where t_{so} and t'_{so} respectively donate spin–orbit coupling strength in the C–C back bone and the C–S bonds.

Besides the spin–orbit coupling, there also exist many other factors that are responsible to the spin-flip mechanisms [18], such as the hyperfine interaction from the hydrogen nuclei [19], the thermal effect [8] as well as the spin-related scattering. In the fourth term of Hamiltonian (1), we summarized these effects by introducing a spin-flip term,

$$H_{sf} = -\sum_{n,s} t_{sf}\left(C_{n+1,s}^{\dagger}C_{n,-s} + h.c.\right)$$
$$- \sum_{n,s} t'_{sf}\left(C_{4n,s}^{\dagger}C_{4n-3,-s} + h.c.\right) \quad (6)$$

similarly, t_{sf} and t'_{sf} respectively donate spin-flip strength in the C–C back bone and the C–S bonds.

The last term of Hamiltonian (1) represents the lattice distortion energy, which is treated classically by,

$$H_{latt} = \frac{1}{2}\sum_n K(u_{n+1} - u_n)^2 + \sum_n K'(u_{n+1} - u_n) \quad (7)$$

where K denotes the lattice elastic constant. The second term in Eq. (7) is a necessary mathematical treatment to avoid the collapse of the oligomer chain, and $K' = -1.25\alpha$ [20].

Because spin related interactions are included in our model, the spin is no longer a good quantum number. The electronic wave function is spin hybrid and is written in superposition state $\psi_\mu = \sum_{n,s} Z_{\mu,n,s}|n,s\rangle$, where $Z_{\mu,n,s}$ means the probability amplitude of state ψ_μ at site n with spin s, which is determined by the following eigenvalue equation,

$$-t_{n-1,n}Z_{\mu,n-1,s} - t_{n,n+1}Z_{\mu,n+1,s} - (t'Z_{\mu,n+3,s} + t''Z_{\mu,n,s})\Delta\left(\frac{n+3}{4}, \text{int}\right)$$
$$- (t'Z_{\mu,n-3,s} + t''Z_{\mu,n,s})\Delta\left(\frac{n}{4}, \text{int}\right) + U\bar{n}_{n,-s}Z_{\mu,n,s}$$
$$\mp t_{so}(Z_{\mu,n-1,-s} - Z_{\mu,n+1,-s}) - t_{sf}(Z_{\mu,n-1,-s} + Z_{\mu,n+1,-s})$$
$$\mp t'_{so}\left[Z_{\mu,n-3,-s}\Delta\left(\frac{n}{4}, \text{int}\right) - Z_{\mu,n+3,-s}\Delta\left(\frac{n+3}{4}, \text{int}\right)\right]$$
$$- t'_{sf}\left[Z_{\mu,n-3,-s}\Delta\left(\frac{n}{4}, \text{int}\right) + Z_{\mu,n+3,-s}\Delta\left(\frac{n+3}{4}, \text{int}\right)\right] = \varepsilon_\mu Z_{\mu,n,s} \quad (8)$$