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Polarons and bipolarons in polythiophene in the presence of magnetic field

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Abstract

Spin degeneracy in conjugated polymers will be destroyed in the presence of magnetic field because of the existence of Zeeman splitting. The characteristic of carriers in polythiophene is studied in the framework of a tight binding model. It is found that spin polarons can be created preferentially in energy when electrons are doped under a reasonable magnetic field considering the influence of electron–electron interactions and electron–phonon coupling, which is favorable for spin polarized transport in organic semiconductors and is of great importance in the field of organic spintronics.

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1. Introduction

Polarons and bipolarons are supposed to be charge carriers generated upon doping or photo-excitation in organic semiconductors especially in high conjugated conducting polymers. A polaron has spin $\frac{1}{2}$ and electronic charge $\pm$e, whereas a bipolaron is spinless with charge $\pm$2e. Wei et al. [1,2] studied the hysteretic conductance switching as a result of the formation of polaron and negative differential resistance (NDR) effect in organic spin-valve systems. In 2006, Xie et al. [3] established the picture of wave packets as the charges are injected into organic polymers from a metal electrode.

Which is the favorable carrier, a polaron or a bipolaron? It is a very controversial subject [4–7]. With the rapid development of spintronics in organic field [8] the stability of polarons over bipolarons becomes important as only polarons carry spins and realize spin transport. Experimentally, Dediu et al. [9] reported the magnetoresistance (MR) in a sandwich of $Re_{1-x}Sr_xMnO_3$/sexithienyl/$Re_{1-x}Sr_xMnO_3$, which means spin injection from $Re_{1-x}Sr_xMnO_3$ into sexithienyl (T_6). More recently, Xiong et al. [10] designed a spin valve of $La_{0.67}Sr_{0.33}MnO_3$/Alq_3/Co and observed low-temperature giant MR effects as large as 40%, which indicates that π-conjugated organic polymers may offer a promising alternative approach to semiconductor spintronics, by virtue of their relatively strong electron–phonon coupling and large spin coherence. Both of them seem to show that the carriers in organic layers are spin polarons.

Present theoretical investigation based on the physical models, such as the Brazovskii–Kirova (BK) model [11] and the well-known SSH model [12] indicates that the doped electrons will form so-called self-trapping states, i.e., spin polarons or spinless bipolarons due to the strong electron–phonon coupling. However, it was found that a double charged bipolaron is energetically favorable to two single charged polarons. The inclusion of electron–electron interactions may block the forming of bipolarons, but present investigation did not give a satisfying conclusion due to the difficulty in treating the electron–electron interaction [13].

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The case will be different if the magnetic field is applied in a conjugated polymer chain. As spin degeneracy of the energy levels is destroyed because of the existence of Zeeman splitting, a bipolaron with two opposite spin electrons bounded up will have a higher energy than a pair of polarons and become energetically nonequivalent, which means that a bipolaron cannot form easily in the conjugated polymer when the magnetic field attaches a critical value. This picture is favorable for spin injection into an organic semiconductor as a bipolaron cannot carry spins.

In the present work, we investigated the characteristics of doped electrons in sexithieny1-like organic polymers (polythiophene) under the existence of magnetic field. Effects of electron–phonon coupling and electron–electron interactions on the stability of polarons have been carefully studied. The model Hamiltonian is described and the formulae are derived in the next section. Section 3 presents the results and Section 4 gives a summary.

2. Model

Sexithieny1 is a small molecular oligomer. It can be polymerized to form polymer polythiophene (T_n), which has a nondegenerate ground state. The Hamiltonian for this kind of polymer or oligomer can be written as

$$H = H_e + H_{latt}, \tag{1}$$

The electronic part including electron–lattice coupling is

$$H_e = H_0 + H' + H_B, \tag{2}$$

$$\begin{aligned} H_0 = & -\sum_{i,\sigma} t_{i,i+1,\sigma}(a^+_{i+1,\sigma}a_{i,\sigma} + a^+_{i,\sigma}a_{i+1,\sigma}) \\ & -\sum_{i,\sigma} t_2(a^+_{4i-3,\sigma}a_{4i,\sigma} + a^+_{4i,\sigma}a_{4i-3,\sigma}) \\ & -\sum_{i,\sigma} t_3(a^+_{4i-3,\sigma}a_{4i-3,\sigma} + a^+_{4i,\sigma}a_{4i,\sigma}), \end{aligned} \tag{3}$$

$$H' = U\sum_{i,\sigma} n_{i,\sigma}n_{i,-\sigma} + V\sum_{i,\sigma,\sigma'} n_{i,\sigma}n_{i+1,\sigma'}, \tag{4}$$

$$H_B = \sum_{i,\sigma} g.\vec{\mu}_\sigma \cdot \vec{B}a^+_{i,\sigma}a_{i,\sigma}, \tag{5}$$

where H_0 describes the interactions between the electrons and bond lattice [14,15]. $a^+_{i,\sigma}(a_{i,\sigma})$ is the electron creation (annihilation) operator at lattice site i with spin $\sigma(\sigma = \uparrow, \downarrow)$. The electron transfer integral is $t_{i,i+1} = t_0 - \alpha(u_{i+1} - u_i) - t_1\cos(i\pi/2)$ with t_0 the transfer integral in a uniform (undimerized) lattice and u_i the displacement of the ith carbon atom. α is the electron–phonon coupling constant and t_1 is confinement constant which guarantees the nondegenerate characteristics of the ground state. t_2 and t_3 express the effect of sulfur atoms on π-electrons. It depends in general upon the coupling strength between sulfur atom and its two neighboring carbon atoms. There are two sources of contributions. The electron hopping between lattice points *4i*-3 and *4i* via sulfur atom is given by t_2, and t_3 is the effective confinement of π electrons due to the sulfur atom. Taking the carbon atom binding energy to be zero, the renormalized couplings are approximately represented by parameters t_2 and t_3. In the actual calculation, we assume $t_2 = t_3$. The motion of the sulfur atoms is entirely ignored because of its much bigger mass than that of carbon atoms. H' the electron–electron interaction can be treated in the Hartree–Fock approximation with $n_{i,\sigma} = a^+_{i,\sigma}a_{i,\sigma}$, U and V the on-site and nearest-neighbor Coulomb repulsion strengths, respectively [16]. H_B corresponds to Zeeman splitting due to the external magnetic field. The magnitude of magnetic moment $\vec{\mu}_\sigma$ is described by $\mu_\sigma = \sqrt{3}\mu_B$ with μ_B the Bohr magneton. Here, we take the effective g factor is 1. For simplicity, the electronic orbital magnetic moment is not included.

The lattice part is described by

$$H_{latt} = \tfrac{1}{2}\sum_i K(u_{i+1} - u_i)^2, \tag{6}$$

where K denotes the corresponding elastic constant.

The electronic eigenstate $|\psi_{\mu,\sigma}\rangle = \sum_i Z_{i,\mu,\sigma}a^+_{i,\sigma}|0\rangle$ and the eigenvalue $\varepsilon_{\mu,\sigma}$ can be solved from the Schrödinger equation of the electronic Hamiltonian in Eq. (1),

$$\begin{aligned} & \vec{\mu}_\sigma \cdot \vec{B}Z_{m,\mu,\sigma} - t_{m-1,m}Z_{m-1,\mu,\sigma} - t_{m,m+1}Z_{m+1,\mu,\sigma} \\ & \quad - (t_2Z_{m-3,\mu,\sigma} + t_3Z_{m,\mu,\sigma})\Delta\left(\frac{m}{4}, \text{int}\right) \\ & \quad - (t_2Z_{m+3,\mu,\sigma} + t_3Z_{m,\mu,\sigma})\Delta\left(\frac{m+3}{4}, \text{int}\right) \\ & \quad + UX_{m,-\sigma}Z_{m,\mu,\sigma} + V[(X_{m+1,\sigma} + X_{m+1,-\sigma}) \\ & \quad + (X_{m-1,\sigma} + X_{m-1,-\sigma})]Z_{m,\mu,\sigma} \\ & \quad = \varepsilon_{\mu,\sigma}Z_{m,\mu,\sigma}. \end{aligned} \tag{7}$$

The notations in Eq. (7) are described as follows:

$$\Delta(x, \text{int}) = \begin{cases} 1, & x = \text{integer}, \\ 0, & \text{otherwise}. \end{cases} \tag{8}$$

$X_{n,\sigma}$ represents the charge distribution with spin σ,

$$X_{n,\sigma} = \sum_\mu{}' |Z_{n,\mu,\sigma}|^2, \tag{9}$$

where the prime means sum over the occupied states.

The total energy is obtained by the expectation value of Hamiltonian (1) at the ground state $|\psi_{\mu,\sigma}\rangle$,

$$E_t = \langle\psi_{\mu,\sigma}|H_e|\psi_{\mu,\sigma}\rangle + \tfrac{1}{2}\sum_i K(u_{i+1} - u_i)^2. \tag{10}$$

The static lattice configurations of the system are determined by the minimization of the total energy in the above expression:

$$\begin{aligned} u_m = \tfrac{1}{2}\Bigg[& u_{m-1} + u_{m+1} + \frac{2\alpha}{K}\sum_{\mu,\sigma}{}'(Z_{m+1,\mu,\sigma}Z_{m,\mu,\sigma} \\ & - Z_{m,\mu,\sigma}Z_{m-1,\mu,\sigma})\Bigg] \end{aligned} \tag{11}$$

where the prime means sum over the occupied states.