



## Polarons in organic ferromagnets

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### ABSTRACT

With an Anderson-like model including the electron-lattice interaction, the polaron formation in quasi-one-dimensional organic ferromagnets with spin radicals is investigated theoretically. In the presence of an additional electron, distortions of spin and charge densities are observed both in the main chain and radicals. A polaron-like lattice distortion confined with fractional charges and spins may be formed in the main chain, where the amplitude is tuned by the electron hopping between the main chain and radicals and the electron-electron interaction. The confined spins and charges are inconsistent in position, which is caused by the asymmetric modification of charges and spins from the low-energy electrons triggered by the polaron lattice distortion. A phase diagram of the polaron formation is given with different electron hopping and electron-electron strengths. The case of a nonzero on-site energy difference between the radicals and the main chain is also discussed. A background charge density wave is found in the main chain due to the charge transfer between the main chain and spin radicals, which hampers the formation of the polaron.

### 1. Introduction

Organic spintronics, which manipulates the freedom of electronic spin based on organic materials, has attracted more and more attention in recent years [1–3]. Organic materials are promising in the development of flexible and low-costing electronic devices. Especially, the spin-orbit and hyperfine interactions in organic materials are weak, which is advantaged for the spin transport and storage. Another characteristic of organic materials is the strong electron-lattice (e-l) interaction. In the presence of an extra electron, it is known that nonlinear excitations such as polarons, bipolarons or solitons may be formed in polymers [4,5], where the excess charges are surrounded by the lattice distortion and can move along the polymer under an electric field. Polarons are particularly important as a polaron contains one unit charge and spin, which may serve as efficient spin and charge carriers simultaneously in most organic conjugated materials. The formation, injection, and transport of polarons in polymers have been investigated extensively in past decades [6–9].

Organic ferromagnets (OFs) are especially fascinating in organic spintronics, since they combine both the organic and ferromagnetic properties. OFs are usually fabricated artificially by introducing various paramagnetic centers with unpaired electrons, such as transition metal ions or organic spin radicals. The latter is a valid way to obtain pure OFs, such as *poly*-(1,4-bis(2,2,6,6-tetramethyl-4-piperidyl-1-oxyl)-butadiene (*poly*-BIPO). *poly*-BIPO is synthesized from polyacetylene, where

the hydrogen atoms are replaced alternately by spin radicals containing unpaired electrons. At ground state, the radical spins will form a ferromagnetic order due to the spin coupling between the radical spins and the spins of  $\pi$  electrons in the main chain [10,11]. Recently, the design of organic devices with the utilization of OFs has triggered lots of interests. For example, Yoo et al. [12] has measured the spin dependent electron transport characteristics of  $V[\text{TCNE}]_x$  by connecting the molecule to Au electrodes, which obtained a 2.5% magnetoresistance. Li et al. [13] has studied the magnetoresistance of this material by using magnetic and nonmagnetic electrodes, where even a room temperature magnetoresistance effect was observed when an  $\text{AlQ}_3$  layer was inserted between the magnetic molecule and the electrode. Several theoretical designs of devices were also proposed involving spin filtering and spin diode effects in the frame of quantum transport [14–17].

Prior to the transport study of the OF, the understanding of the charge and spin properties of the carriers is crucial. Due to the spin correlation with radicals, the existence of the above nonlinear excitations as well as their spin-charge properties in OFs is obscure. The picture of soliton has been investigated by Xiong et al. in the organic ferromagnetic polymer *m*-polydiphenylcarbene (*m*-PDPC) [18]. The polarons in the *poly*-BIPO were also discussed recently, where a distinct property of spin-charge disparity of the polaron is obtained [19]. However, in the previous work, an extended Su-Schrieffer-Heeger (SSH) model [20] combined with a Kondo term was used, where the unpaired electron on each radical is looked as a local spin without charge and

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spin transfer with the main chain. This is incomplete to understand the polarons in real OFs because of the possible spin and charge exchange between the main chain and radicals. In this paper, an improved model, Anderson-like model, is used to study the polarons in the OF, where not only the electron hopping between the main chain and the radicals is included, but also the difference of their on-site energies is considered. The focus is that when an electron is doped into the OF, whether a polaron can be formed and how about the spin and charge relation in the case of the nonlocal spin model for the radicals.

The paper is organized as follows. In Section 2, we introduced the model Hamiltonian for the OFs and the details of the theoretical method. The results of the numerical calculations are presented and analyzed in Section 3, where a simple case without on-site energy difference between the main chain and radicals is first discussed including the effects of electron hopping term and electron-electron (e-e) interaction, and then a non-zero on-site energy difference is considered. In Section 4, a brief summary is given.

## 2. Model and method

Here we considered the quasi-one-dimensional OF *poly*-BIPO. As shown in Fig. 1, the molecule is composed of a  $\pi$ -conjugated carbon chain and spin radicals attached to the odd sites of the main chain. Each radical has an unpaired electron. An Anderson-like model is used to describe the OF while the e-l interaction in the main chain is included. The Hamiltonian of the whole system is written as

$$H = H_0 + H_1. \quad (1)$$

Here  $H_0$  is the Hamiltonian of the main chain in the form of an extended SSH model [20],

$$H_0 = -\sum_{i,\sigma} [t_0 - \alpha y_i] (c_{i+1,\sigma}^\dagger c_{i,\sigma} + c_{i,\sigma}^\dagger c_{i+1,\sigma}) + \frac{K}{2} \sum_i y_i^2 + U_0 \sum_i c_{i,\uparrow}^\dagger c_{i,\uparrow} c_{i,\downarrow}^\dagger c_{i,\downarrow} \quad (2)$$

The first term describes the hopping of  $\pi$  electrons along the main carbon chain with  $N_1$  sites.  $t_0$  is the hopping integral of the  $\pi$  electrons along a uniform chain, and  $\alpha$  denotes the e-l coupling constant.  $y_i$  is the lattice distortion with  $y_i \equiv u_{i+1} - u_i$ , where  $u_i$  is the lattice displacement of the carbon atom at the  $i$ th site.  $c_{i,\sigma}^\dagger (c_{i,\sigma})$  denotes the creation (annihilation) operator of an electron at the  $i$ th site with spin  $\sigma$ . The spin index  $\sigma$  assumes the numerical values  $\uparrow \equiv 1$  and  $\downarrow \equiv -1$ . The second term is the elastic energy of the lattice with elastic coefficient  $K$  due to the lattice distortion. The last term is the on-site e-e interaction between  $\pi$  electrons described with Hubbard model.  $U_0$  is the interaction strength.

$H_1$  describes the Hamiltonian of the side radicals and the electron hopping between the radicals and the main chain.

$$H_1 = \sum_{i,\sigma} \varepsilon_1 \delta_{i,o} c_{iR,\sigma}^\dagger c_{iR,\sigma} - t_{mR} \sum_{i,\sigma} \delta_{i,o} (c_{i,\sigma}^\dagger c_{iR,\sigma} + c_{iR,\sigma}^\dagger c_{i,\sigma}) + U_1 \sum_i \delta_{i,o} c_{iR,\uparrow}^\dagger c_{iR,\uparrow} c_{iR,\downarrow}^\dagger c_{iR,\downarrow}. \quad (3)$$

$\varepsilon_1$  is the on-site energy of electrons at the radicals relative to the carbon atoms in the main chain.  $\delta_{i,o}$  means that the radicals only hang on the odd sites of the main chain with  $\delta_{i,o} = 1$  ( $\delta_{i,o} = 0$ ) for odd (even) atoms.  $t_{mR}$  is the electron hopping integral between the main chain and the side radicals  $R$ .  $c_{iR,\sigma}^\dagger (c_{iR,\sigma})$  denotes the creation (annihilation) operator of electron at the dangling site  $iR$ .  $U_1$  describes the on-site Hubbard repulsion strength at the dangling site.

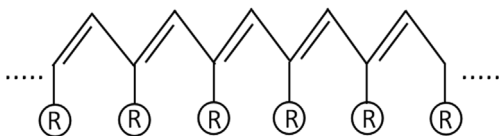


Fig. 1. Simplified structure of quasi-one-dimensional organic ferromagnet.

With Hartree-Fork approximation to treat the e-e interaction, the electronic states of the OF can be obtained by solving the eigenequations of the system with an initial lattice configuration:

$$\varepsilon_{\mu,\sigma} Z_{\mu,i,\sigma} = -(t_0 - \alpha y_i) Z_{\mu,i+1,\sigma} - (t_0 - \alpha y_{i-1}) Z_{\mu,i-1,\sigma} + U_0 \bar{n}_{i,-\sigma} Z_{\mu,i,\sigma} - t_{mR} \delta_{i,o} Z_{\mu,iR,\sigma} \quad (4)$$

$$\varepsilon_{\mu,\sigma} Z_{\mu,iR,\sigma} = \varepsilon_1 Z_{\mu,iR,\sigma} - t_{mR} \delta_{i,o} Z_{\mu,i,\sigma} + U_1 \bar{n}_{iR,-\sigma} Z_{\mu,iR,\sigma}. \quad (5)$$

Here  $\varepsilon_{\mu,\sigma}$  is the eigenenergy and  $Z_{\mu,i,\sigma}$  is eigen function in the Wannier space.  $\bar{n}_{i,\sigma}$  is the average electron number on the  $i$ th site with spin  $\sigma$ ,

$$\bar{n}_{i,\sigma} = \sum_{\mu,occ} Z_{\mu,i,\sigma} Z_{\mu,i,\sigma}, \quad \bar{n}_{iR,\sigma} = \sum_{\mu,occ} Z_{\mu,iR,\sigma} Z_{\mu,iR,\sigma}. \quad (6)$$

occ. means the occupied states of electrons.

The eigenequations are solved with the initial lattice configuration  $y_i$  and electron density  $\bar{n}_{i(iR),\sigma}$ . After obtaining the eigen function  $Z_{\mu,i,\sigma}$ , the new lattice configuration is calculated with

$$y_i = -\frac{2\alpha}{K} \sum_{\mu,\sigma,occ} Z_{\mu,i,\sigma} Z_{\mu,i+1,\sigma} + \frac{2\alpha}{N_1 K} \sum_{i=1}^{N_1} \sum_{\mu,\sigma,occ} Z_{\mu,i,\sigma} Z_{\mu,i+1,\sigma}. \quad (7)$$

Here a periodic boundary condition is adopted. The electron number is also recalculated with Eq. (6). Eqs. (4)–(7) need to be solved self-consistently until a stable state is achieved. In each iteration, the energy levels are reordered and the electrons occupy the lowest levels. After the iteration, the charge density  $\rho_{c,i(iR)}$  and spin density  $\rho_{s,i(iR)}$  along the polymer can be obtained, which are defined as  $\rho_{c,i(iR)} = 1 - (\bar{n}_{i(iR),\uparrow} + \bar{n}_{i(iR),\downarrow})$  in unit of elementary charge  $e > 0$  and  $\rho_{s,i(iR)} = \frac{1}{2} (\bar{n}_{i(iR),\uparrow} - \bar{n}_{i(iR),\downarrow})$  in unit of  $\hbar$ .

During the numerical calculations, the parameters are adopted as those for *poly*-BIPO [10,11,14,21]:  $t_0 = 2.5$  eV,  $\alpha = 4.5$  eV/Å and  $K = 21.0$  eV/Å<sup>2</sup>. For simplicity, we set  $U_0 = U_1 = U$ , and introduce dimensionless interaction parameters  $u = U/t_0$ ,  $t_1 = t_{mR}/t_0$ , and  $\varepsilon = \varepsilon_1/t_0$ .

## 3. Results and discussion

### 3.1. Neutral state at $\varepsilon = 0$

The system considered here contains 80 carbon atoms ( $N_1 = 80$ ) in the main chain and 40 radical sites. We start from a simple case by neglecting the on-site energy difference between the carbon atoms and the radical sites, that is,  $\varepsilon = 0$ . The neutral ground state is first calculated in the case of half filling. The e-e interaction  $u$  and the electron hopping term  $t_1$  between the main chain and radicals are taken as  $u = 0.6$  and  $t_1 = 0.3$ . The lattice configuration, energy band, charge density and spin density are investigated and plotted in Fig. 2. Here a smoothed lattice configuration is used defined as  $\tilde{y}_i = \frac{1}{4} (-1)^i (2y_i - y_{i+1} - y_{i-1})$ . It is found that the lattice is dimerized like most polymers. The energy bands consist of six bands with three spin-up bands and three spin-down ones. The two highest and the two lowest cosine-like bands are slight spin-split near the Fermi energy (zero point) with an energy gap of about 2.4 eV. The left two flat bands appear in the gap with a spin splitting of about 0.8 eV. Compared with the normal polymer polyacetylene, the appearance of the two bands in the gap comes from the radicals. It has been proved that the spin splitting of the two flat bands originates from the e-e interaction [18]. In the case of half filling, only the two lowest cosine-like bands and one spin-down flat band in the gap are occupied. Thus, the molecule is ferromagnetic with net up spins  $S = 1/2$  in one unit. The picture is consistent with others' calculations about magnetic property of various OFs using Anderson-like model [18,22–24]. The charge density and spin density at the ground state are given in Fig. 2(c) and (d). It is found that the charge density keeps zero, which is same to our previous work in the frame of local radical spin model [19]. The spin density demonstrates that the net up spins mainly distributes in the radicals with 0.47 spins per radical site. About 0.03 up

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