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Spin-charge disparity of polarons in organic ferromagnets

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ABSTRACT

Polaron formation in quasi-one-dimensional organic ferromagnets is studied based on an extended Su–Schrieffer–Heeger model combined with a Kondo term. The charge distribution of the polaron is found to be highly asymmetric under spatial reflection, due to the spin radicals. On the contrary, the spin density is nearly symmetric; the spin asymmetry introduced by the extra electron inducing the polaron formation is nearly compensated by the spin polarization of the lower-energy states. We discuss these results on the basis of real-space mean-field calculations and symmetry arguments.

1. Introduction

Organic spintronics, i.e., the manipulation of electronic spin degrees of freedom in organic molecules, has attracted increasing interest in recent years [1–3]. One of the characteristic properties of organic materials is the strong electron–lattice interaction. This makes the ground state of conjugated organic materials dimerized. For example, trans-polyacetylene, trans-$(CH)_x$, with uniform C–C bond lengths would be a one-dimensional metal with a half-filled band. However, the system can lower its energy by spontaneously forming a dimerized state with alternating short and long bonds [5,4]. This Peierls instability opens a dimerization gap in the electronic spectrum, which induces the conjugated organic materials as organic semiconductors. The strong electron–lattice interaction also leads to another important effect: Electrons or holes doped into a polymer typically self-trap and form nonlinear excitations such as polarons and bipolarons [4,6]. A polaron consists of an electron (hole) with specific spin together with a localized distortion of the polymer chain. The whole polaron can move under an electric field as a quasiparticle, which is crucial for organic light-emitting diodes and organic spin-valve devices [7,8].

Organic ferromagnets are particularly fascinating since they combine ferromagnetic and polaronic properties. Purely organic ferromagnets not containing transition-metal ions can be realized by using spin radicals [9–13], which are usually heterocycles containing an unpaired electron [14]. For example, the organic ferromagnet poly-(1,4-bis(2,2,6,6-tetramethyl-4-piperidyl-1-oxyl)-butadiin (poly-BIPO) can be obtained from polyacetylene by replacing every other H atom by a radical carrying an unpaired electron [9,10]. Since charge fluctuations in the radicals are weak, one can describe them by local spins in a Kondo-type model. There is an exchange coupling, thought to be antiferromagnetic, between the π electrons in the main carbon chain and the radical spins. It has been found that the energy of the molecule is minimized when all radical spins are ferromagnetically aligned [9,10,15,16]. This is easy to understand: Since the states of the π electrons are extended, they interact with many radical spins. The exchange interaction favors antiferromagnet alignment between each π electron and all the radical spins it interacts with, which leads to ferromagnetic alignment of the radical spins. poly-BIPO is an example for a

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non-Kekulé π-conjugated organic ferromagnet. The stability of ferromagnetism in such compounds has been studied in detail in theoretical chemistry [17–19]. Although the instability of the unsaturated radicals remains a challenge to the experimental synthesis, remarkable progress has been made by experimentalists in recent years and several classes of stable organic spin radicals have been obtained [9,10,14].

The growing field of organic spintronics offers the prospect of designing spintronics devices based on organic ferromagnets. For example, Yoo et al. [20] and Li et al. [21] have investigated the magnetoresistance of V[TCNE]$_x$-based devices (TCNE stands for tetracyanoethylene) by connecting the organic magnets to normal and magnetic electrodes. Theoretical studies also indicate that organic ferromagnets may be used to design spin filters [22,23] and spin diodes [24]. However, any understanding of transport in such materials requires us to first understand the properties of the carriers, for which the spin coupling with radicals and the electron–lattice interaction are crucial. The study of these properties is the objective of the present work.

In this paper, we study the effects of adding an extra electron to a ferromagnetic polymer such as poly-BIPO. It is found that the extra electron forms a polaron, which is dramatically different from a polaron in a nonmagnetic chain and indeed in any other material we are aware of. Specifically, its charge density is highly asymmetric, whereas its spin density, relative to the chain without polaron, is nearly symmetric. We show that this disparity is enhanced by the proximity of poly-BIPO to the transition to a periodic phase and discuss it in terms of the ease with which the charge and spin densities can adapt in order to lower the polaron energy.

The paper is organized as follows. In Section 2, the model Hamiltonian for the organic ferromagnets and the details of the theoretical approach are introduced. In Section 3, the results of the numerical calculations are presented and analyzed. To investigate the effect of spin radicals, we first consider the case without electron–electron interactions, where the neutral state and the polaron states are discussed consecutively. Finally, the electron–electron interaction is included. A brief summary is given in Section 4.

2. Model and method

We describe a quasi-one-dimensional organic ferromagnet such as poly-BIPO. The molecule consists of a π-conjugated carbon chain and spin radicals attached to the odd sites. Each radical contains an uncompensated spin $\mathbf{S}_i$. We assume an antiferromagnetic coupling between the spin of the π electrons and the radical spins $\mathbf{S}_i$. Such molecules can be well described by an extended Su–Schrieffer–Heeger (SSH) model [25] combined with a Kondo term. The Hamiltonian is written as [15,16]

$$H = -\sum_{i,\sigma}(t_0 - \alpha y_i)\left(c_{i+1,\sigma}^{\dagger}c_{i,\sigma} + \text{H.c.}\right) + \frac{K}{2}\sum_i y_i^2$$
$$+ U\sum_i c_{i,\uparrow}^{\dagger}c_{i,\uparrow}c_{i,\downarrow}^{\dagger}c_{i,\downarrow} + J\sum_i \delta_{i\text{ odd}}\mathbf{S}_i \cdot \mathbf{s}_i. \quad (1)$$

The first term describes the hopping of π electrons along the carbon chain. Here, $c_{i,\sigma}^{\dagger}$ ($c_{i,\sigma}$) denotes the creation (annihilation) operator of an electron at site i with spin σ. t_0 is the hopping integral between two neighboring sites of a uniform chain and α denotes the electron–lattice coupling constant. y_i is the lattice distortion $y_i \equiv u_{i+1} - u_i$, where u_i is the displacement of the carbon atom at site i. The second term is the elastic energy due to the lattice distortion with elastic coefficient K. The third term is the on-site electron–electron interaction of strength U. The last term denotes the antiferromagnetic coupling between the π-electron spins $\mathbf{s}_i = \sum_{\sigma\sigma'}c_{i,\sigma}^{\dagger}(\boldsymbol{\sigma}_{\sigma\sigma'}/2)c_{i,\sigma'}$ and the radical spins $\mathbf{S}_i$, with strength $J > 0$, and $\delta_{i\text{ odd}} = 1$ ($\delta_{i\text{ odd}} = 0$) for i odd (even). Periodic boundary conditions are assumed.

The ground state of the molecule is calculated using a mean-field approximation for the spin–spin and electron–electron interactions. We obtain the eigenenergies $\varepsilon_{\mu,\sigma}$ and the eigenstates $|\psi_{\mu,\sigma}\rangle$ with (real) eigenfunctions $\psi_{\mu,\sigma,i}$ in Wannier space by solving the Schrödinger equation

$$\varepsilon_{\mu,\sigma}\ \psi_{\mu,\sigma,i} = \sum_j H_{\sigma,ij}^{\text{MF}}\ \psi_{\mu,\sigma,j}$$
$$\equiv -(t_0 - \alpha y_i)\ \psi_{\mu,\sigma,i+1} - (t_0 - \alpha y_{i-1})\ \psi_{\mu,\sigma,i-1}$$
$$+ U\ \bar{n}_{i,-\sigma}\psi_{\mu,\sigma,i} + J\delta_{i\text{ odd}}\langle S_i^z\rangle\frac{\sigma}{2}\ \psi_{\mu,\sigma,i}, \quad (2)$$

where $\langle S_i^z\rangle$ is the average value of the radical spin, assumed to be in the z direction, and $H_{\sigma,ij}^{\text{MF}}$ is the matrix element of the mean-field Hamiltonian for the π electrons with spin σ. The spin quantum number σ assumes the numerical values $\uparrow \equiv 1$ and $\downarrow \equiv -1$. Throughout the paper, we enumerate the states such that $\varepsilon_{\mu',\sigma} > \varepsilon_{\mu,\sigma}$ for $\mu' > \mu$. The average occupation number of π electrons at site i with spin σ is $\bar{n}_{i,\sigma} = \sum_{\mu\text{ occ}}|\psi_{\mu,\sigma,i}|^2$. The sum is over all occupied states, i.e., all states with $\varepsilon_{\mu,\sigma}$ up to the Fermi energy. The lattice distortion $y_i = u_{i+1} - u_i$ in Eq. (2) is determined by minimizing the total energy

$$E(\{y_i\}) = \sum_{\mu,\sigma\text{ occ.}}\varepsilon_{\mu,\sigma}(\{y_i\}) + \frac{K}{2}\sum_i y_i^2 - U\sum_i \bar{n}_{i,\uparrow}\bar{n}_{i,\downarrow} \quad (3)$$

with respect to the distortions y_i. The sum $\sum_{\mu,\sigma\text{ occ.}}$ is over all occupied states. The constraint $\sum_i y_i = 0$ is implemented using a Lagrange multiplier. This leads to the equation (recall that $\psi_{\mu,\sigma,i}$ is real)

$$y_i = -\frac{2\alpha}{K}\sum_{\mu,\sigma\text{ occ.}}\psi_{\mu,\sigma,i}\psi_{\mu,\sigma,i+1}$$
$$+ \frac{2\alpha}{NK}\sum_k\sum_{\mu,\sigma\text{ occ.}}\psi_{\mu,\sigma,k}\psi_{\mu,\sigma,k+1}. \quad (4)$$

Eqs. (2) and (4) are solved self-consistently [15].

For the numerical calculations we use parameter values appropriate for poly-BIPO [15,26,22]: $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21.0$ eV/Å^2 and $\langle S_i^z\rangle = 1/2$. We introduce dimensionless interaction strengths $j = J/t_0$ and $u = U/t_0$. The net charge density $\rho_{c,i}$ in units of the elementary charge $e > 0$ and the spin density $\rho_{s,i}$ of π electrons in the main chain, in units of $\hbar$, are defined as $\rho_{c,i} \equiv -(\bar{n}_{i,\uparrow} + \bar{n}_{i,\downarrow} - 1)$ and $\rho_{s,i} \equiv (\bar{n}_{i,\uparrow} - \bar{n}_{i,\downarrow})/2$, respectively.