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Theoretical model and numerical calculations for a quasi-one-dimensional organic ferromagnet

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A theoretical model is proposed to describe the quasi-one-dimensional organic ferromagnet *poly*BIPO. Different from Ovchinnikov's model, we consider the itineracy of π electrons, the strong electron-phonon interaction, and electron-electron correlation in a one-dimensional system. Within the mean-field theory and Hartree approximation, allowing for full lattice relaxation, a set of self-consistent iterative equations is established to study the effects of π electrons on the ferromagnetic order in the organic materials. The results of our calculations show that the ground state of the system is a stable ferromagnetic state. In the ferromagnetic ground state, the energy levels of the π electrons will split off with respect to different spins. However, owing to the Peierls distortion of the lattice, all of the π electrons will form an antiferromagnetic spin-density-wave chain.

I. INTRODUCTION

Since the discovery of quasi-one-dimensional organic superconductors and conductors, low-dimensional conjugated polymer systems have attracted much interest. Aroused by the discovery of these materials, researchers have synthesized pure organic ferromagnets from organic molecules and hydrocarbons.[1] Several organic ferromagnets have been produced, such as *poly*-BIPO,[2,3] *m*-PDPC,[4] and pyro-PAN.[5] Organic polymer ferromagnets are different from common ferromagnets, since there are few transition-metal impurities which can bring about the usual magnetic properties from the strong correlation between the itinerant or localized *d* or *f* electrons and the itinerant *s* electrons.

Although many attempts at synthesizing new organic ferromagnets have been made in order to understand the origin of ferromagnetic properties, we know only very little about these materials. However, recent progress in the study of conjugated π-electron systems, such as polyacetylene,[6] has stimulated our research. The ferromagnetic spin correlation between unpaired electrons (residual spin) of a kind of particular side radical may be brought about by the antiferromagnetic correlation between π electrons along the main chain. This has been achieved by Ovchinnikov *et al.*[2] and Cao *et al.*[3] who synthesized an organic ferromagnetic called *poly*BIPO. They proposed a simplified structure of *poly*BIPO schematically shown in Fig. 1(a), which contained the main structural features of *poly*BIPO. The main zigzag chain consists of carbon atoms, and R is a kind of side radical containing an unpaired electron. In order to illustrate the magnetic properties of *poly*BIPO,[7] they treated the π electrons along the main carbon chain as an antiferromagnetic spin chain, and assumed that there are antiferromagnetic interactions between the π-electron spin and the residual spin of radical R. Then, all of the residual spins of the radical R will try to form a ferromagnetic spin chain as shown in Fig. 1(b). Here, π electrons along the main chain play an important role in the ferromagnetic order in this kind of material. But, this kind of treatment of a π electron is too simple, and some effects are neglected. First, the π electrons are itinerant along the main chain instead of localized. Second, there is a strong electron-phonon interaction and electron-electron interaction in a one-dimensional system, and the change of electronic properties will lead to a lattice relaxation. Considering these effects in detail will clarify the effect of π electrons on the origin of ferromagnetic order in organic materials.

In this paper, we will discuss the magnetic and electronic properties of the simplified structure of *poly*BIPO proposed by Ovchinnikov [see Fig. 1(a)]. Although, it is straightforward to include an additional modulation with the period of four atoms in *poly*BIPO, we use here the simpler system so that the model has as few parameters as possible and yet contains the essential physics. We will use a Hamiltonian including terms describing the antiferromagnetic spin correlations between the π electrons and the residual spin of unpaired electrons at radical R, terms describing the itinerant π electrons and the distortion of the lattice, and terms describing the electron-electron interactions between π electrons. Within mean-field theory, a set of self-consistent itinerant equations are established.

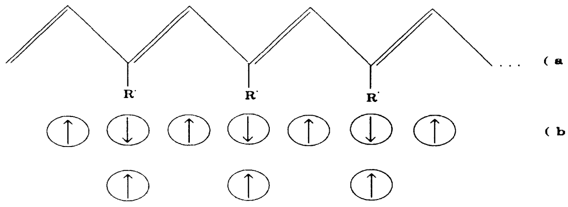

FIG. 1. The simplified structure of (a) *poly*BIPO and (b) the arrangement of spin.

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Using the equations, we numerically studied the system. In Sec. II, we will give the theoretical model and the numerical method. The results and discussions will be given in Sec. III.

II. THEORY MODEL AND NUMERICAL MODEL

The Hamiltonian employed for our study contains the following terms:

$$H = H_{\mathrm{SSH}} + H_{e\text{-}e} + H_{R\text{-}s} \ . \tag{1}$$

H_{SSH} is the Su-Schrieffer-Heeger Hamiltonian[8] including terms describing the π-electron hopping and the electron-phonon interactions:

$$H_{\mathrm{SSH}} = -\sum_{i,\sigma}[t_0 + \alpha(U_i - U_{i+1})](C^{\dagger}_{i+1,\sigma}C_{i,\sigma} + \mathrm{H.c.}) + \frac{K}{2}\sum_i (U_i - U_{i+1})^2 \ , \tag{2}$$

where U_i is the displacement of the ith lattice site, t_0 is the transfer or overlap integral when $U_i = 0$ for all n, α is the rate of change of the overlap integral with distance between nearest neighbors, $C^{\dagger}_{i,\sigma}$ and $C_{i,\sigma}$ are creation and annihilation operations for a π electron with spin σ on the ith site, respectively, where i labels the carbon atoms along the chain and $\sigma(=\alpha,\beta)$ labels the direction of spin where α denotes the up spin and β denotes the down spin, K is the effective spring constant between the adjacent units.

The second term $H_{e\text{-}e}$ describes the interactions between π electrons:

$$H_{e\text{-}e} = U\sum_i n_{i\alpha}n_{i\beta} \ . \tag{3}$$

U (>0) is the effective repulsive energy between two π electrons when they are on the same carbon atom, and $n_{i\sigma} = C^{\dagger}_{i\sigma}C_{i\sigma}$.

The third term, $H_{R\text{-}s}$, describes the antiferromagnetic correlations between the spin $\mathbf{S}_i$ of π electrons and the residual spin $\mathbf{S}_{iR}$ of R:

$$H_{R\text{-}s} = J_f\sum_i \delta_{i2}\mathbf{S}_{iR}\cdot\mathbf{S}_i \ . \tag{4}$$

Here we assume that every side radical has a noncompensated spin $\mathbf{S}_{iR}$. Since there is no purely one-dimensional ferromagnetic, we may conceive that there exists chain-radical interaction, and we assume the coupling $J_f > 0$ between the chain and side radical is isotropic. The radical R connects with the odd carbon atom, then

$$\delta_{i2} = \begin{cases} 1, & i \text{ is odd} \ , \\ 0, & i \text{ is even} \ . \end{cases} \tag{5}$$

It is convenient to use the following transformations:

$$\begin{aligned} h &= \frac{H}{t_0} \ , \\ u &= \frac{U}{t_0} \ , \\ j_f &= \frac{J_f}{t_0} \ , \\ \lambda &= \frac{2\alpha^2}{\pi t K} \ , \\ y_i &= (-1)^i\frac{\alpha}{t_0}(U_i - U_{i+1}) \ , \end{aligned} \tag{6}$$

then h becomes

$$h = -\sum_{i,\sigma}[1 + (-1)^i y_i](C^{\dagger}_{i+1,\sigma}C_{i,\sigma} + \mathrm{H.c.}) + \frac{1}{\lambda\pi}\sum_i y_i^2 + u\sum_i n_{i\alpha}n_{i\beta} + j_f\sum_i \delta_{i2}\mathbf{S}_{iR}\cdot\mathbf{S}_i \ . \tag{7}$$

At first we consider the term

$$\mathbf{S}_{iR}\cdot\mathbf{S}_i = [S^z_{iR}S^z_i + \tfrac{1}{2}(S^+_{iR}S^-_i + S^-_{iR}S^+_i)] \ , \tag{8}$$

using the mean-field approximation we divide S^z_{iR} as follows:

$$S^z_{iR} = \langle S^z_{iR}\rangle + \Delta S^z_{iR} \ . \tag{9}$$

Here $\langle \cdots \rangle = \langle G|\cdots|G\rangle$ is the average with respect to the ground state $|G\rangle$. Then Eq. (7) can be written as[9]

$$h = -\sum_{i,\sigma}[1 + (-1)^i y_i](C^{\dagger}_{i+1,\sigma}C_{i,\sigma} + \mathrm{H.c.}) + \frac{1}{\lambda\pi}\sum_i y_i^2 + u\sum_i n_{i\alpha}n_{i\beta} + j_f\sum_i \delta_{i2}\langle S^z_{iR}\rangle\left[\frac{n_{i\alpha} - n_{i\beta}}{2}\right] \ . \tag{10}$$

This is the Hamiltonian that we can numerically study using a self-consistent iterative method.[10] With the initial values of $\langle S^z_{iR}\rangle$, the lattice configurations, and the density matrix given, the eigenenergies ε_i and the expansion coefficients $Z_{\mu,i}$ of the molecular orbitals can be obtained from the Schrödinger equation:

$$h^{\sigma}\left[\sum_i C^{\dagger}_{i,\sigma}Z^{\sigma}_{\mu,i}\right] = \varepsilon^{\sigma}_{\mu}\left[\sum_i C^{\dagger}_{i,\sigma}Z^{\sigma}_{\mu,i}\right] \ , \quad \sigma = \alpha,\beta \ , \quad \mu = 1,2,\ldots,N^{\sigma}_e \ . \tag{11}$$

Here N^{σ}_e is the number of electrons of each spin. From Eqs. (10) and (11), treating the π-electron interaction terms $H_{e\text{-}e}$ with the Hartree approximation, we can get the eigenvalue equations of the system:

$$-[1+(-1)^i y_i]Z^{\alpha}_{\mu,i+1}-[1+(-1)^i y_i]Z^{\alpha}_{\mu,i-1}+\left[u\sum_{\substack{\mu'\\(\mathrm{occ})}} Z^{\beta *}_{\mu',i}Z^{\beta}_{\mu',i}+\frac{j_f\delta_{i2}\langle S_{iR}\rangle}{2}\right]Z^{\alpha}_{\mu,i}=\varepsilon^{\alpha}_{\mu}Z^{\alpha}_{\mu,i}, \tag{12}$$

$$-[1+(-1)^i y_i]Z^{\beta}_{\mu,i+1}-[1+(-1)^i y_i]Z^{\beta}_{\mu,i-1}+\left[u\sum_{\substack{\mu'\\(\mathrm{occ})}} Z^{\alpha *}_{\mu',i}Z^{\alpha}_{\mu',i}-\frac{j_f\delta_{i2}\langle S_{iR}\rangle}{2}\right]Z^{\beta}_{\mu,i}=\varepsilon^{\beta}_{\mu}Z^{\beta}_{\mu,i}\ . \tag{13}$$

The total energy of the system with the Hamiltonian [see Eq. (10)] is

$$E(y_i)=-\sum_{\substack{i,\sigma\\(\mathrm{occ})}}\left[[1+(-1)^i y_i]\sum_{\substack{\mu\\(\mathrm{occ})}}[Z^{\sigma *}_{\mu,i+1}Z^{\sigma}_{\mu,i}+Z^{\sigma *}_{\mu,i}Z^{\sigma}_{\mu,i+1}]\right]+\frac{1}{\lambda\pi}\sum_i y_i^2+u\sum_i\sum_{\substack{\mu\\(\mathrm{occ})}}\sum_{\substack{\mu'\\(\mathrm{occ})}}|Z^{\alpha}_{\mu,i}|^2|Z^{\beta}_{\mu',i}|^2+\sum_i\sum_{\substack{\mu\\(\mathrm{occ})}}\frac{j_f\delta_{i2}\langle S^z_{iR}\rangle}{2}[|Z^{\alpha}_{\mu,i}|^2-|Z^{\beta}_{\mu,i}|^2]\ . \tag{14}$$

New values of the dimerization order parameter y_i are calculated by minimizing the total energy of the system with respect to y_i:

$$y_i=2\pi\lambda(-1)^i\left[\sum_{\substack{\mu,\sigma\\(\mathrm{occ})}}Z^{\sigma}_{\mu,i}Z^{\sigma}_{\mu,i+1}-\frac{1}{N}\sum_i\sum_{\substack{\mu,\sigma\\(\mathrm{occ})}}Z^{\sigma}_{\mu,i}Z^{\sigma}_{\mu,i+1}\right]\ . \tag{15}$$

Here, we have used the periodic boundary conditions, and (occ) means those states occupied by electrons. Equations (12)–(15) let us get the optimized configuration and energy levels of the system self-consistently. We can also get the density of electron of each spin at every lattice site as

$$n^{\sigma}_i=\sum_{\substack{\mu\\(\mathrm{occ})}}Z^{\sigma *}_{\mu,i}Z^{\sigma}_{\mu,i}\ . \tag{16}$$

III. NUMERICAL RESULTS AND DISCUSSIONS

We now consider a single periodic chain. The chain length is $N=100$ and the number of π electrons is $N_e=100$. We assume that the radical R connects with the odd carbon atom (see Fig. 1). From Eqs. (12) and (13), we know that the eigenvalue equation is unsymmetrical about spin owing to the term $H_{R\text{-}s}$. So we must solve the given equations with different spins. In order to study the ground state, we always fill the π electrons in the possible lowest levels in every iterative step.

In our calculation, there are three parameters λ, u, and j_f. From Fig. 1 we can see that the main chain of this kind of simplified structure of *poly*BIPO is the same as that of polyacetylene. So we can estimate the parameters λ and u with parameters of polyacetylene as $\lambda=0.1$ and $u=2.0$.[6] j_f (>0) is the antiferromagnetic exchange integral between $\mathbf{S}_{iR}$ and $\mathbf{S}_i$, and we will perform a calculation with j_f varying from 0.0 to 1.0. Another important value is $\langle S^z_{iR}\rangle$, which describes the magnetic order of $\mathbf{S}_{iR}$. $\langle S^z_{iR}\rangle=0$ means that there is no spontaneous magnetization in the ground state, so there is no ferromagnetic order. But if $\langle S^z_{iR}\rangle\neq 0$, the ground state will show ferromagnetic order of $\mathbf{S}_{iR}$. With a given value of $\langle S^z_{iR}\rangle$, we can calculate the total energy of the system by Eq. (15). Figure 2 shows the total energy vs $\langle S^z_{iR}\rangle$. It is seen clearly that for $j_f\neq 0$, the total energy of the system is the lowest when $\langle S^z_{iR}\rangle=\pm\frac{1}{2}$. The total energy decreases with increasing of j_f. When $j_f=0$, we get a straight line, which means that the total energy does not relate to $\langle S^z_{iR}\rangle$. So if $j_f\neq 0$, the ground state of the system will be a ferromagnetic state, in which all the residual spins of side radical R point to the same direction. And the larger j_f is, the more stable the state is.

For $j_f=0.5$ and $\langle S^z_{iR}\rangle=\frac{1}{2}$, which means all the residual spins of radical R point up, we calculated the energy levels of the π electron shown in Fig. 3, where i indicates the ith energy level, and the energy level is t_0 dependent. We can see clearly that the energy levels belonging to different spins split off, which is different from the case for $j_f=0$ shown in Fig. 3 as a short-dashed line. Our calculation shows that the degree of splitting is proportional

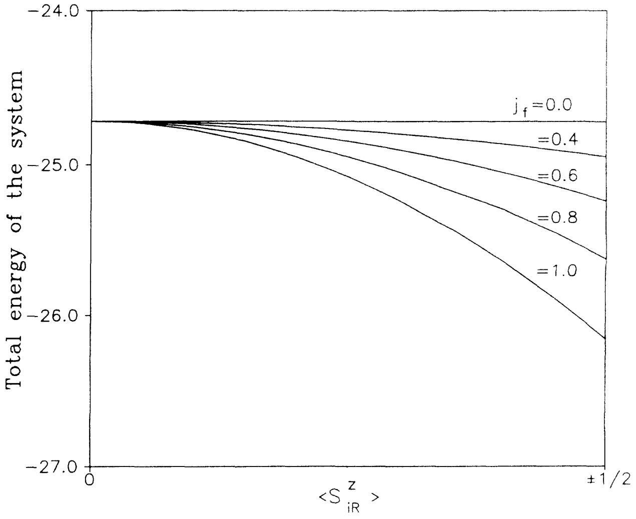

FIG. 2. The total energy vs $\langle S^z_{iR}\rangle$ with different j_f.

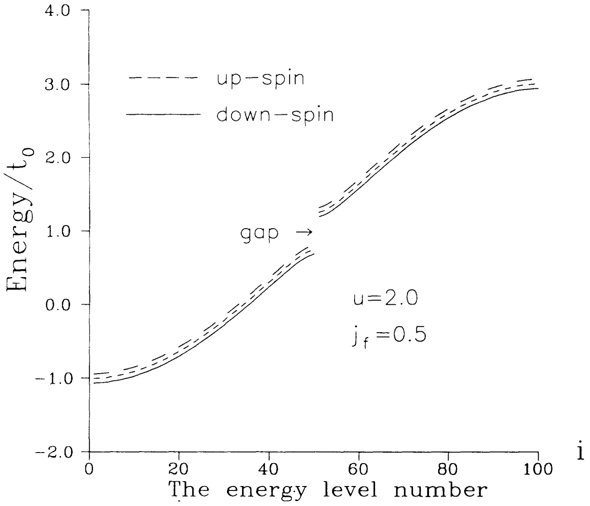

FIG. 3. The energy levels of the π electron for $u=2.0$ and$j_f=0.5$, and the short-dashed line shows the energy levels of the π electron for $j_f=0.0$.

to j_f. Figure 3 also tells us that the down-spin energy level is lower than up-spin energy level, so π electrons try to fill in the down-spin energy levels. But on the other hand, owing to Peierls distortion, an energy gap appears in the middle of the band, which is about $0.5t_0$. Our calculation shows that the splitting is smaller than the gap in a wide range of j_f. So in the ground state, half of the valence band is still occupied by up-spin electrons, and the other half is occupied by down-spin electrons.

At the same time, owing to the term $H_{R\text{-}s}$, the density of electrons with different spins at every site, n_i^α and n_i^β, will also become different. So, along the chain a distribution of density of spin will appear, which can be expressed as $\Delta n_i=(n_i^\alpha-n_i^\beta)/2$. At the odd sites, the spin density is negative, which means the spins of π electrons try to point down. At the even sites, the spin density is positive, which means the spins of π electrons try to point up. These are the results of the on-site repulsion u between π electrons. This kind of arrangement of spins is an antiferromagnetic spin-density wave (SDW), which is consistent with our above assumption that all the residual spins of radical R point up.

In conclusion, we have numerically investigated the electronic and magnetic properties of a theoretical model proposed for a quasi-one-dimensional organic polymer ferromagnet. The results presented in this paper show that the ground state of the system is a stable ferromagnetic state as a result of the electron-electron correlation between π electrons and the antiferromagnetic exchange correlation between the π electrons and the unpaired electrons of side radicals. In the ferromagnetic ground state, the energy levels of the π electron will split off with respect to different spins, however, owing to the Peierls distortion of the lattice, all of the π electrons will form a antiferromagnetic spin-density-wave chain. Throughout the calculations we are deeply convinced that, though the conjugated π electrons themselves show no ferromagnetic order, they play an important role in the origin of the ferromagnetic order in quasi-one-dimensional organic materials. Although, at the present stage of the synthesis, only a few products show ferromagnetic properties, we believe that this kind of conjugated π-electron system is a good candidate for organic polymer ferromagnet.

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[1] J. S. Miller, A. J. Epstein, and W. M. Reiff, Chem. Rev. **88**, 201 (1988).

[2] Y. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov, and V. N.Spector, Nature (London) **326**, 370 (1987).

[3] Y. Cao, P. Wang, Z. Hu, S. Z. Li, L. Y. Zhang, and J. G. Zhao, Synth. Met. **27**, B625 (1988).

[4] H. Iwamura, T. Sugawara, K. Itoh, and T. Takui, Mol. Cryst. Liq. Cryst. **125**, 379 (1985).

[5] Yu. A. Katulevskii, M. A. Magrupov, and A. A. Muminov, Phys. Status Solidi A **127**, 223 (1991).

[6] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, Rev. Mod. Phys. **60**, 781 (1988), and references therein.

[7] A. A. Ovchinnikov and V. N. Spector, Synth. Met. **27**, B615 (1988); in *Frontiers of Macromolecular Science*, edited by T. Saegusa, T. Higashimura, and A. Abe (Blackwell Science, Cambridge, MA, 1989), p. 455.

[8] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).

[9] K. Nasu, Phys. Rev. B **33**, 330 (1986).

[10] S. Stafstrom and K. A. Chao, Phys. Rev. B **30**, 2098 (1984).