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Theoretical model of an organic ferrimagnetic state for a bipartite lozenge chain

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A model for one-dimensional bipartite lozenge chain is proposed. By unrestricted Hartree-Fock approximation, we find that the system should exhibit ferrimagnetic ordering for a half filled band. In the ground state, the energy levels of electrons will split off with respect to different spins and the electrons along the chain will form an antiferromagnetic spin-density wave. The ground state of the system will be more stable with increasing of the on-site Hubbard term.

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I. INTRODUCTION

Low-dimensional materials have long been of interest to chemists and physicists because of their distinctive physical properties. Recently, quasi-one-dimensional organic ferromagnetic systems have attracted considerable attention since several kinds of organic ferromagnets,[1–5] such as *m*-PDPC (Ref. 1) and *p*-NPNN (Ref. 2), have been discovered. In organic polymer molecular ferromagnets, there are no ions of the type which are usually magnetic (e.g., iron, nickel, etc.) present. In order to obtain organic ferromagnets, McConnell[6] proposed intermolecular ferromagnetic interactions in the organic molecules. Then Mataga[7] reported another strategy to prepare organic ferromagnets based on intermolecular ferromagnetic interactions in very large molecules. The basic idea of this proposal is the synthesis of alternate hydrocarbon in the high-spin ground state.

The bipartite lozenge chain structures leading to highly degenerate one-particle states are depicted in Fig. 1(a). The model polymer of Fig. 1(a) is a well-known structure in inorganic chemistry,[8] where M and L represent a metal atom and a suitable ligand, respectively. This structure is experimentally similar to that studied in Ref. 4. In a series paper,[9–11] Yao *et al.* proposed a theoretical model for the quasi-one-dimensional organic ferromagnet. They studied the structure of *poly*-BIPO. In their model, the π electrons along the main carbon chain are considered to be itinerant while the unpaired electrons at the side radicals are regarded to have no freedom except their spins. The antiferromagnetic exchange interaction between these electrons was imposed. Consequently, the ground state of this model is a ferrimagnet. In other words, although the spin correlation of electrons in the ground state is antiferromagnetic, the system has also an unsaturated ferromagnetism. By means of the exact diagonalization of finite clusters and Monte Carlo simulation, Macêdo *et al*. studied the model shown in Fig. 1(a). At half filling, the ground state of this model exhibits also ferrimagnetic long-range ordering.[12] The theory of Macêdo *et al.* was further improved by Tian and Lin.[13]

In this paper, we focus our attention on the bipartite lozenge chain shown in Fig. 1(b), the unit cell contains two sublattices A and B, the site A being connected by hopping t_0 to four sites of B, whereas the sites of B have only two nearest-neighbor sites of A. An on-site Hubbard-Coulomb repulsion U is assumed on every site. Considering the electron-phonon interaction and the antiferromagnetic spin correlation between the itinerant electrons, we propose a theoretical model for the bipartite lozenge chain, which consists of the Su-Schrieffer-Heegger Hamiltonian describing the electron-phonon interaction on the chain and the Hubbard term describing the on-site electron-electron interactions. Within the mean-field theory and the Hartree-Fock approximation, a set of self-consistent equations are established. Using these equations, we numerically studied the system. In Sec. II, we will give the model and the method. Results and discussions will be given in Sec. III.

II. THEORETICAL MODEL AND NUMERICAL METHOD

The generalized Hamiltonian that has been employed for modeling the system is given by

$$H=-\sum_{\langle A,B\rangle,\sigma}[t_0+\gamma(U_A-U_B)](C^{+}_{A,\sigma}C_{B,\sigma}+\mathrm{H.c.})+\frac{K}{2}\sum_{\langle A,B\rangle}(U_A-U_B)^2+U\sum_{\langle A,B\rangle}(n_{A\alpha}-n_{B\beta}), \qquad (1)$$

where t_0 is the transfer or overlap integral, γ is the rate of change of the overlap integral with distance between nearest neighbors, K is the effective spring constant between the adjacent units, $C^{+}_{A,\sigma}(C_{A,\sigma})$ denotes the creation (annihilation) operator of an electron with spin σ on the sublattice A, and $U_A(U_B)$ is the displacement of the carbon atom on the

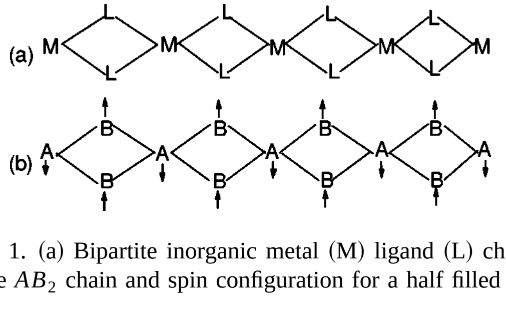

FIG. 1. (a) Bipartite inorganic metal (M) ligand (L) chain; (b) Bipartite AB_2 chain and spin configuration for a half filled band.

sublattice $A(B)$. U describes the Hubbard on-site electron-electron repulsion on the chain, and $n_{A\sigma}=C^{+}_{A,\sigma}C_{A,\sigma}$ ($\sigma=\alpha,\beta$), where α and β denote up spin and down spin, respectively.

It is convenient to cast all quantities into dimensionless forms as

$$h=\frac{H}{t_0},\quad u=\frac{U}{t_0},\quad \lambda=\frac{2\gamma^2}{\pi t_0 K},$$

$$y_{\langle A,B\rangle}=\frac{\gamma}{t_0}(U_A-U_B). \tag{2}$$

Then the Hamiltonian is transferred as follows:

$$h=-\sum_{\langle A,B\rangle,\sigma}[1+y_{\langle A,B\rangle}](C^{+}_{A,\sigma}C_{B,\sigma}+\text{H.c.})$$
$$+u\sum_{\langle A,B\rangle}(n_{A\alpha}n_{B\beta})+\frac{1}{\lambda\pi}\sum_{\langle A,B\rangle}y^2_{\langle A,B\rangle}. \tag{3}$$

By treating the electron-electron interaction in the Hartree-Fock approximation, we can obtain the eigenenergies $\varepsilon^{\sigma}_{\mu}$, the expansion coefficients $Z^{\sigma}_{\mu,\langle A,B\rangle}$ of the molecular orbital, and the optimized geometry $y_{\langle A,B\rangle}$ from the follow self-consistent iterative equation:

$$-[1+y_{\langle A,B\rangle}]Z^{\sigma}_{\mu,\langle A,B\rangle+1}-[1+y_{\langle A,B\rangle-1}]Z^{\sigma}_{\mu,\langle A,B\rangle-1}$$
$$+u\left(\sum_{\substack{\mu'\\(occ)}}Z^{\bar{\sigma}}_{\mu'\langle A,B\rangle}(Z^{\bar{\sigma}}_{\mu'\langle A,B\rangle}{}^{*})\right)Z^{\sigma}_{\mu,\langle A,B\rangle}=\varepsilon^{\sigma}_{\mu}Z^{\sigma}_{\mu,\langle A,B\rangle}, \tag{4}$$

$$y_{\langle A,B\rangle}=-\pi\lambda\left(\sum_{\substack{\mu\sigma\\(occ)}}Z^{\sigma}_{\mu,\langle A,B\rangle}Z^{\sigma}_{\mu,\langle A,B\rangle+1}\right.$$
$$\left.-\frac{1}{N}\sum_{\langle A',B'\rangle}\sum_{\substack{\mu\sigma\\(occ)}}Z^{\sigma}_{\mu,\langle A',B'\rangle}Z^{\sigma}_{\mu,\langle A',B'\rangle+1}\right). \tag{5}$$

Here the periodic boundary condition has been employed for the chain. N is the number of sites on the chain, and (occ) refers to those states occupied by electrons. The values of the dimerization order parameter are calculated by minimizing the total energy $E(y_{\langle A,B\rangle})$ of the system with respect to $y_{\langle A,B\rangle}$.

$$E(y_{\langle A,B\rangle})=-\sum_{\langle A,B\rangle\sigma}\left((1+y_{\langle A,B\rangle})\sum_{\substack{\mu\sigma\\(occ)}}[Z^{\sigma}_{\mu,\langle A,B\rangle}(Z^{\sigma}_{\mu,\langle A,B\rangle+1})^{*}\right.$$
$$\left.+Z^{\sigma}_{\mu,\langle A,B\rangle+1}(Z^{\sigma}_{\mu,\langle A,B\rangle})^{*}]\right)+\frac{1}{\pi\lambda}\sum_{\langle A,B\rangle}y^2_{\langle A,B\rangle}$$
$$+u\sum_{\langle A,B\rangle}\left(\sum_{\substack{\mu,\mu'\\(occ)}}|Z^{\alpha}_{\mu,\langle A,B\rangle}|^2|Z^{\beta}_{\mu'\langle A,B\rangle}|^2\right). \tag{6}$$

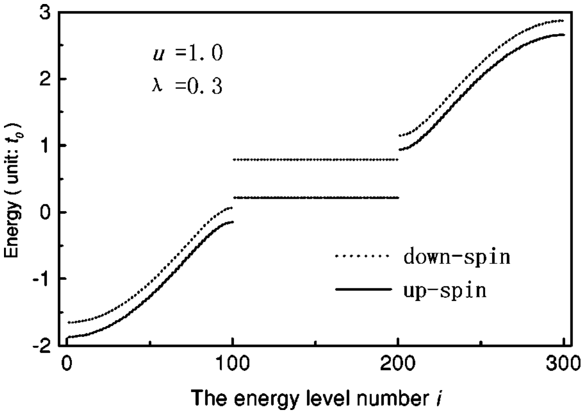

FIG. 2. The energy levels of the electrons for $u=1.0$ and $\lambda=0.3$. The dashed line and the solid line correspond to down spin and up spin, respectively.

From Eqs. (4)–(6), we can obtain the optimized configuration and energy levels of the system self-consistently. We can also obtain the spin density and the charge density of electrons at every site as

$$S_A=\frac{1}{2}[\langle n_{A\alpha}\rangle-\langle n_{A\beta}\rangle],\quad S_B=\frac{1}{2}[\langle n_{B\alpha}\rangle-\langle n_{B\beta}\rangle], \tag{7}$$

$$\langle n_{A\alpha}\rangle=\sum_{\substack{\mu,A\\(occ)}}Z^{\sigma}_{\mu,A}(Z^{\sigma}_{\mu,A})^{*},\quad \langle n_{B\alpha}\rangle=\sum_{\substack{\mu,B\\(occ)}}Z^{\sigma}_{\mu,B}(Z^{\sigma}_{\mu,B})^{*}. \tag{8}$$

The starting geometry in the iterative optimization process is usually the one with zero dimerization. A set of solutions are reached, independent of the starting configuration. The criterion for terminating the optimization is that between two successive iterations, the difference is less than 10^{-6} for the displacement order parameter and spin density.

III. NUMERICAL RESULTS AND DISCUSSIONS

We consider a system which consists of a periodic conjugated chain shown in Fig. 1(b). The chain contains 300 sites ($A=100$ and $B=200$) and 300 electrons, each on every site. From Eqs. (4), we know that the eigenvalue equation is unsymmetrical about spin owing to the on-site e-e interaction. 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 calculations, the energy and the on-site Hubbard repulsion u are measured in the unit of t_0. Since the chain of this system is the same as that of polyacetylene, we can choose commonly used parameters: $t_0=2.5$ eV for the hopping integral on the chain and $\lambda=0.1\sim0.5$ for the electron-phonon coupling. The on-site Hubbard repulsion u at every site varies from 0 to 4.

First, we discuss electron energy levels and the stability of ferromagnetic ground state of the system. Figure 2 shows the energy levels of the system when $\lambda=0.3$, and $u=1.0$, where ith indicates the level, and the energy level is t_0 dependent. We can see clearly that energy levels belonging to different

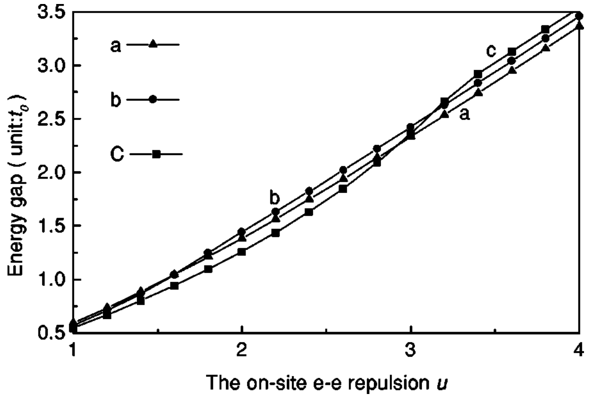

FIG. 3. The energy gap versus the *e-e* interaction. Curves a, b, and c correspond to $\lambda = 0.1$, $\lambda = 0.3$, and $\lambda = 0.5$, respectively. The gap increases with increasing of the Hubbard term *u*.

spins split off. The energy spectra contain three up-spin bands and three down-spin bands, each of which contains 100 energy levels. The up-spin bands have lower energy than the down-spin bands. The middle two bands are highly degenerate. The energy spectra are half filled since there is one electron on every site. So the ground state of the system is a high-spin ferromagnetic state. We must notice that the energy gap $\Delta = \varepsilon_{\downarrow} - \varepsilon_{\uparrow}$ between the middle localized up-spin and down-spin bands is a very important parameter. The larger the gap is, the more stable the high-spin state is. Our calculation shows that the degree of splitting is proportional to *u*. Figure 3 shows the gap varies with *u*. We can see that the gap increases continually with increasing of the Hubbard term *u*. This means that the ferromagnetic ground state of the system will be more stable with increasing of the *u*.

Now we turn to study the spin-density wave and the charge-density wave of the system. We find that the charge density at every site is equal to 1, but the spin density at site *A* is $S_A < 0$, and the spin density at site *B* is $S_B > 0$. This is owing to the charge density with up spin at site *A* has been transferred to site *B*, meanwhile the charge density with down spin at site *B* transferred onto the site *A* (e.g., $n_{A\alpha} = 0.32$, $n_{A\beta} = 0.68$, $n_{B\alpha} = 0.84$, and $n_{B\beta} = 0.16$, when $u = 2.0$ and $\lambda = 0.3$). As a consequence, the net spin density has been found at every site. It is shown that the electrons at site *A* and site *B* along the chain is antiferromagnetically correlated. A salient feature here is that the spin magnitudes on site *A* and *B* are unequal, indicating ferrimagnetic ordering.[12] Figures 4 and 5 show spin densities at different sites as a function of the on-site Hubbard term *u*. Curves a, b, and c correspond to $\lambda = 0.1$, $\lambda = 0.3$, and $\lambda = 0.5$, respectively. We find an average total spin per unit cell $S = |S_A| + 2S_B = \frac{1}{2}$, as required by Lieb's theorem.[14] We can see that with increasing of Hubbard constant *u*, the spin densities $|S_A|$ and $|S_B|$ increase continually. This means that the antiferromagnetic exchange interaction between electrons at site *A* and site *B* will be stronger with the increasing of *u*.

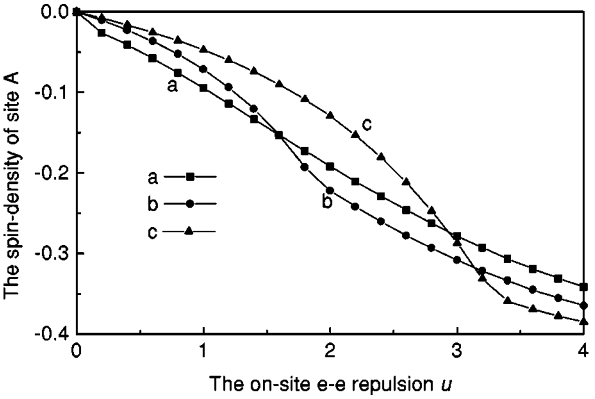

FIG. 4. The spin density of site *A* versus the *e-e* interaction. Curves a, b, and c correspond to $\lambda = 0.1$, $\lambda = 0.3$, and $\lambda = 0.5$, respectively.

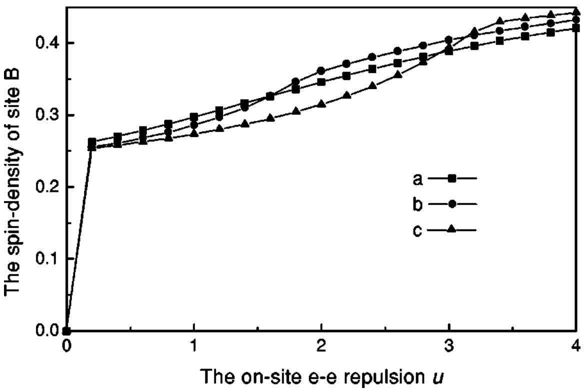

FIG. 5. The spin-density of site *B* versus the *e-e* interaction. Curves a, b, and c correspond to $\lambda = 0.1$, $\lambda = 0.3$, and $\lambda = 0.5$, respectively.

In the system, λ is the electron-phonon coupling parameter. The larger the λ, the stronger the electron-phonon coupling. At half filling, the density of states (DOS) is shown in Fig. 6 for $u = 2$. Figures 6(a), 6(b), and 6(c) correspond to $\lambda = 0$, $\lambda = 0.3$, and $\lambda = 0.5$, respectively. Here, Fig. 6(a) is the result studied in Ref. 12 when $\lambda = 0$. Owing to Peierls distortion, it is found that an energy gap appears between the top of the lower up-spin band (the upper localized down-spin band) and the lower localized up-spin band (the bottom of

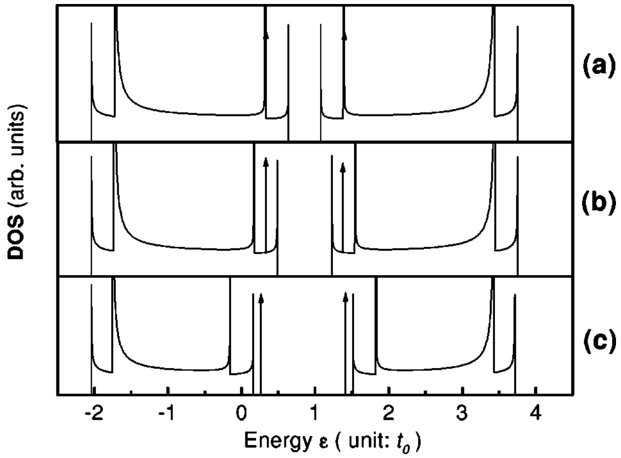

FIG. 6. Density of state (DOS) for AB_2 chain at half filling. (a) $u = 2$, $\lambda = 0$, (b) $u = 2$, $\lambda = 0.3$, and (c) $u = 2$, $\lambda = 0.5$. Vertical arrows indicate localized bands.

the upper down-spin band). We can see that the stronger the electron-phonon coupling, the larger the gap [see Figs. 6(b) and 6(c)]. But, the up-spin band is always lower than the down-spin band for the middle two localized levels. So, in the ground state, one-third of valence band is always occupied by down-spin electrons, and the two-thirds of valence is occupied by up-spin electrons. The ground state of the system is a high-spin ferromagnetic state.

In summary, we have numerically investigated the electronic and magnetic properties of quasi-one-dimensional bipartite lozenge organic polymer chain, whose topology produces flat bands in the electronic spectrum. It has been found that this system should exhibit ferrimagnetic ordering at half filling as a result of the on-site Hubbard interactions between electrons. In the ferromagnetic ground state, the energy levels of electrons will split off with respect to different spins and the electrons at site *A* and site *B* along the main chain will form an antiferromagnetic spin-density wave. The increasing of the on-site Hubbard term makes the ground state of the system more stable.

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