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Spin configurations of π electrons in quasi-one-dimensional organic ferromagnets

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Based on a theoretical model proposed for quasi-one-dimensional organic polymer ferromagnets, the spin configuration of π electrons in a π-conjugated carbon chain with a single and two side radicals, which contains unpaired electrons, is investigated. The strong electron-phonon interaction and electron-electron interaction in the one-dimensional system are taken into account self-consistently. It is found that around the unpaired electrons there appears a π-electron spin-polarization cloud with alternation of the sign and the amplitude of the spin density extending over a certain distance, which reduces rapidly with the increasing of electron-phonon coupling. In order to obtain ferromagnetic order in this kind of material, the number of carbon atoms, which is intermittent between two neighbor side radicals, should be odd. It is shown that the π-orbital alternation will result in a Peierls transition which stabilizes the magnetic order.

I. INTRODUCTION

In recent years, several research groups have successfully synthesized several organic ferromagnets, such as poly-BIPO [1,4-bis(2,2,6,6,-tetramethyl-4-piperidyl-1-oxyl)],[1] *m*-PDPC (polydiphenylcarbene),[2] and *p*-NPNN (nitrophenyl nitronyl nitroxide).[3] In organic polymer molecular ferromagnets there are no ions of the type which are usually magnetic (e.g., iron, nickel, etc.) present. What we really need for magnetic order is the existence of partially filled orbits. The search for the origin of ferromagnetism in organic ferromagnets has become a challenge that has attracted considerable attention.[4]

Currently there are two main avenues explored for obtaining organic ferromagnets. The first one is configurational admixing of a virtual triplet excited state with the ground state for a chain of alternating radical cation donors and radical anion accepters.[5,6] The second approach, suggested by Mataga[7] and Ovchinnikov,[8] is the synthesis of organic polymers in the high-spin ground state.

The synthesis[9,10] of poly-BIPO makes the second approach important and hopeful. Ovchinnikov and Spector[11] successfully attached a kind of free radicals, which contain unpaired electrons, as side groups to the carbon backbone, as schematically shown in Fig. 1. They found that the quasi-one-dimensional (quasi-1D) structure shows ferromagnetic properties at room temperature. However, for this kind of quasi-1D organic polymer ferromagnet, many things are still unclear, and at the present stage of the synthesis, only a small fraction shows ferromagnetic properties. Further studies are necessary.

In this kind of alternating hydrocarbon, one important problem is the strong electron-phonon interaction, which might change the magnetic properties of the system dramatically. Allowing for full lattice relaxation and considering the antiferromagnetic correlation between itinerant π electrons and the localized unpaired electrons at the side radicals, we have proposed a theoretical model for the quasi-one-dimensional organic ferromagnet poly-BIPO.[12] We found that the π electrons along the main chain play an important role for the ferromagnetic order. As a completion of above work, in this article we will concentrate on the spin configuration of π electrons in a π-conjugated carbon chain with one or two side radicals, based on the theoretical model proposed by us. Considering the strong electron-phonon interaction and electron-electron interaction in the one-dimensional system, we study the system self-consistently. We find that around the unpaired electrons appears a π-electron spin-polarization cloud. In order to obtain ferromagnetic order in this kind of material, the number of carbon atoms between two neighboring side radicals should be odd. It is shown that the π-orbital alternation will result in a Peierls transition which stabilizes the magnetic order. The theoretical model and the computational method will be given in Sec. II. We present the results and give the discussion in Sec. III.

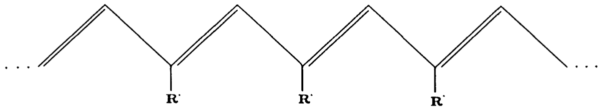

FIG. 1. Simplified structure of poly-BIPO. $R^{\cdot}$ means a kind of side free radical containing an unpaired electron.

II. THEORETICAL MODEL AND COMPUTATIONAL METHOD

We consider a π-conjugated carbon chain with side radicals, each of which contains an unpaired electron. We assume that every side radical has a noncompensated spin $\mathbf{S}_{iR}$. Since there is no purely one-dimensional ferromagnet, we may conceive that there exists a chain-radical interaction, and we assume the coupling $J_f > 0$ between the spin $\mathbf{S}_i$ of the π electrons and the residual spin $\mathbf{S}_{iR}$ of the R radical is isotropic. The Hamiltonian that has been employed for modeling the polymer is given by

$$H = -\sum_{i,\sigma}[t_0 + \alpha(V_i - V_{i+1})](C^\dagger_{i+1,\sigma}C_{i,\sigma} + \text{H.c.}) + \frac{K}{2}\sum_i (V_i - V_{i+1})^2 + U\sum_i n_{i\alpha}n_{i\beta} + J_f\sum_i \delta_i \mathbf{S}_{iR}\cdot\mathbf{S}_i \ , \tag{1}$$

where i labels the carbon atoms along the chain, σ $(=\alpha,\beta)$ labels the direction of spin where α denotes up and β denotes down spin, V_i is the displacement of the ith lattice site, t_0 is the transfer or overlap integral when $V_i = 0$ 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 operators, respectively, for a π electron with spin σ on the ith site, K is the effective spring constant between the adjacent units. U (>0) is the effective repulsive energy between two π electrons when they are on the same carbon atom and $n_{i\sigma} = C^\dagger_{i\sigma}C_{i\sigma}$.

Here δ_i defines the connection of the side radicals, and if the ith carbon atom connects with a side radical then $\delta_i = 1$; otherwise $\delta_i = 0$. In order to minimize the total energy in our self-consistent calculation, it is convenient to use the following transformations:

$$h = \frac{H}{t_0} \ , \quad u = \frac{U}{t_0} \ , \quad j_f = \frac{J_f}{t_0} \ , \quad \lambda = \frac{2\alpha^2}{\pi t_0 K} \ , \qquad y_i = (-1)^i \frac{\alpha}{t_0}(V_i - V_{i+1}) \ . \tag{2}$$

Using the mean-field approximation[12] to deal with the last term of Hamiltonian (1), h becomes

$$h = -\sum_{i,\sigma}[1 + (-1)^i y_i](C^\dagger_{i+1,\sigma}C_{i,\sigma} + \text{H.c.}) + \frac{1}{\lambda\pi}\sum_i y_i^2 + u\sum_i n_{i\alpha}n_{i\beta} + j_f\sum_i \delta_i \langle S^z_{iR}\rangle \left[\frac{n_{i\alpha} - n_{i\beta}}{2}\right] \ . \tag{3}$$

Here $\langle \cdots \rangle = \langle G | \cdots | G \rangle$ is the average with respect to the ground state $|G\rangle$. 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 $Z^\sigma_{\mu,i}$ of the molecular orbitals can be obtained from the Schrödinger equation

$$h^\sigma \left[\sum_i C^+_{i,\sigma} Z^\sigma_{\mu,i}\right] = \varepsilon^\sigma_\mu \left[\sum_i C^+_{i,\sigma} Z^\sigma_{\mu,i}\right] \ , \qquad \sigma = \alpha,\beta \ , \quad \mu = 1,2,\ldots,N^\sigma_e \ . \tag{4}$$

Here, N^σ_e is the number of electrons of each spin. From Eqs. (3) and (4), treating the π-electron interaction terms $H_{e\text{-}e}$ with the Hartree approximation, we can get the following self-consistent iterative equations:

$$-[1 + (-1)^i y_i]Z^\alpha_{\mu,i+1} - [1 + (-1)^i y_i]Z^\alpha_{\mu,i-1} + \left[u\sum_{\substack{\mu' \\ (\text{occ})}} Z^{\beta *}_{\mu',i}Z^\beta_{\mu',i} + \frac{j_f\delta_i\langle S^z_{iR}\rangle}{2}\right] Z^\alpha_{\mu,i} = \varepsilon^\alpha_\mu Z^\alpha_{\mu,i} \ , \tag{5}$$

$$-[1 + (-1)^i y_i]Z^\beta_{\mu,i+1} - [1 + (-1)^i y_i]Z^\beta_{\mu,i-1} + \left[u\sum_{\substack{\mu' \\ (\text{occ})}} Z^{\alpha *}_{\mu',i}Z^\alpha_{\mu',i} - \frac{j_f\delta_i\langle S^z_{iR}\rangle}{2}\right] Z^\beta_{\mu,i} = \varepsilon^\beta_\mu Z^\beta_{\mu,i} \ , \tag{6}$$

$$y_i = 2\pi\lambda(-1)^i \left[\sum_{\substack{\mu,\sigma \\ (\text{occ})}} Z^\sigma_{\mu,i}Z^\sigma_{\mu,i+1} - \frac{1}{N}\sum_i \sum_{\substack{\mu,\sigma \\ (\text{occ})}} Z^\sigma_{\mu,i}Z^\sigma_{\mu,i+1}\right] \ . \tag{7}$$

Here, periodic boundary conditions are used, and (occ) means those states occupied by electrons. New values of the dimerization order parameter y_i are calculated by minimizing the total energy $E(y_i)$ of the system with respect to y_i:

$$E(y_i) = -\sum_{\substack{i,\sigma \\ (\text{occ})}} \left\{[1 + (-1)^i y_i]\sum_{\substack{\mu \\ (\text{occ})}}[Z^{\sigma *}_{\mu,i+1}Z^\sigma_{\mu,i} + Z^{\sigma *}_{\mu,i}Z^\sigma_{\mu,i+1}]\right\} + \frac{1}{\lambda\pi}\sum_i y_i^2 + u\sum_i \sum_{\substack{\mu \\ (\text{occ})}} \sum_{\substack{\mu' \\ (\text{occ})}} |Z^\alpha_{\mu,i}|^2 |Z^\beta_{\mu',i}|^2 + \sum_i \sum_{\substack{\mu \\ (\text{occ})}} \frac{j_f\delta_i\langle S^z_{iR}\rangle}{2}[|Z^\alpha_{\mu,i}|^2 - |Z^\beta_{\mu,i}|^2] \ . \tag{8}$$

The distribution of spin density of π electrons along the main chain can be obtained self-consistently as

$$\delta n_i = (n^\alpha_i - n^\beta_i)/2 = \left[\sum_{\substack{\mu \\ (\text{occ})}} Z^{\alpha *}_{\mu,i}Z^\alpha_{\mu,i} - \sum_{\substack{\mu \\ (\text{occ})}} Z^{\beta *}_{\mu,i}Z^\beta_{\mu,i}\right] / 2 \ . \tag{9}$$

The starting geometry in the iterative optimization process is usually the one with zero dimerization. The stability of the optimized geometry is always tested by using another starting configuration and performing the optimization once again. For all systems included in this study, the same optimal ground state was reached, independent of the starting configuration. The criterion for terminating the optimization is that, between two successive iterations, the difference is less than 10^{-5} Å for the dimerization order parameter and less than 10^{-5} for the spin density.

III. RESULTS AND DISCUSSION

We consider a periodic chain of 80 carbon atoms and 80 π electrons. From Eqs. (5) and (6), we know that the eigenvalue equations are unsymmetrical about spin as a result of the electron-electron correlation and the antiferromagnetic correlation between π electrons and the unpaired electrons at the side radicals. So in the system, the spin degeneracy has been lifted, and we must solve the given equations with different spins. In order to study the ground state, we always fill the π electrons in the lowest possible levels in every iterative step.

First, we consider a chain with a single side radical. We assume that this side radical connects with the 40th carbon atom and the unpaired electron at this side radical has spin up. Figure 2 shows the distributions of spin density δn_i with different parameters. From all three figures, we can see that around the unpaired electron appears a π electron spin-polarization cloud with alternation of the sign and the amplitude of the spin density extending over a certain distance. Such a spin-polarization cloud is produced in order to decrease the electron-electron Coulomb repulsion. It is this alternation of the sign and the amplitude of spin density that provides an opportunity for the exchange interaction between the unpaired electrons of the side radicals. Here, the unsymmetrical distribution of the spin-polarization cloud is the result of the fact that the number of the carbon atoms is even in our calculation. Figures 2(a) and 2(b) show the changes of the distribution of spin density with increasing electron-phonon coupling λ. When $\lambda=0.05$ [shown in Fig. 2(a)], weak dimerization happens in the ground state, and we can see that the spin-polarization cloud can extend all over the main chain with weak decay. When $\lambda=0.1$ [shown in Fig. 2(b)], which is a typical value for a one-dimensional π-conjugated carbon atom chain, strong dimerization happens in the ground state, and we find that a localized distribution of spin density appears.

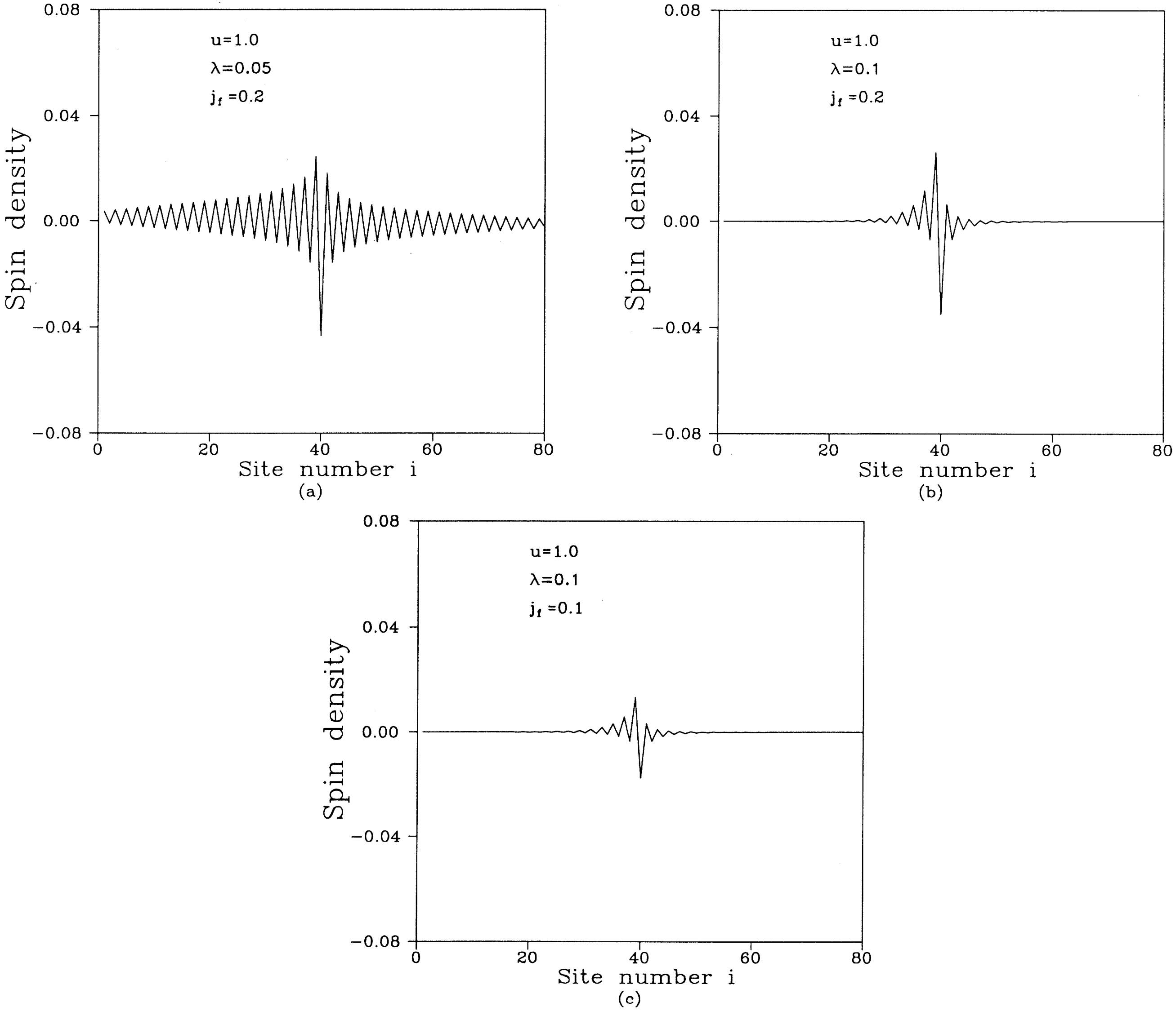

FIG. 2. Spin density δn_i of π electrons with different parameters. (a) $u=1.0$, $j_f=0.2$, and $\lambda=0.05$. (b) $u=1.0$, $j_f=0.2$, and $\lambda=0.1$. (c) $u=1.0$, $j_f=0.1$, and $\lambda=0.1$.

Therefore, for larger electron-phonon coupling λ, only two nearby unpaired electrons can interact, mediated by π electrons. Figure 2(c) shows the distribution of spin density when $u=1.0$, $\lambda=0.1$, and $j_f=0.1$. We find that, in spite of the lower amplitude of the spin density, it is almost the same as the case of $u=1.0$, $\lambda=0.1$, and $j_f=0.2$ [shown in Fig. 2(b)]. So the strength of the antiferromagnetic exchange integral between $\mathbf{S}_{iR}$ and $\mathbf{S}_i$ affects only the amplitude of the spin density.

Then, we consider a chain with two side radicals, one of which is fixed and the other can be shifted away from the fixed one. Figure 3 shows the total energy E of the system as a function of the number N of carbon atoms between the two carbon atoms with which two side radicals connect. Here, the dashed line shows the case when the two unpaired electrons of the two side radicals have antiparallel spin arrangement, the solid line shows the case when the two unpaired electrons have parallel spin arrangement, and we consider the total energy of the system when $N=0$ and the two unpaired electrons have a parallel spin arrangement as the zero-energy line. We can see that the total energy of the system vibrates with the change of N. When N is odd, the solid line has lower energy; this means two unpaired electrons try to have a parallel spin arrangement. On the other hand, when N is even, the two unpaired electrons try to have an antiparallel spin arrangement. In order to get organic ferromagnets, a parallel spin arrangement between the unpaired electrons is needed, so the number N of carbon atoms should be odd. From Fig. 3, we can also find that the vibrational amplitude is reduced with increasing N. This means that the exchange interaction between unpaired electrons is reduced with increasing N. This is due to the fact that there is less overlap between the two spin-polarization clouds for larger N.

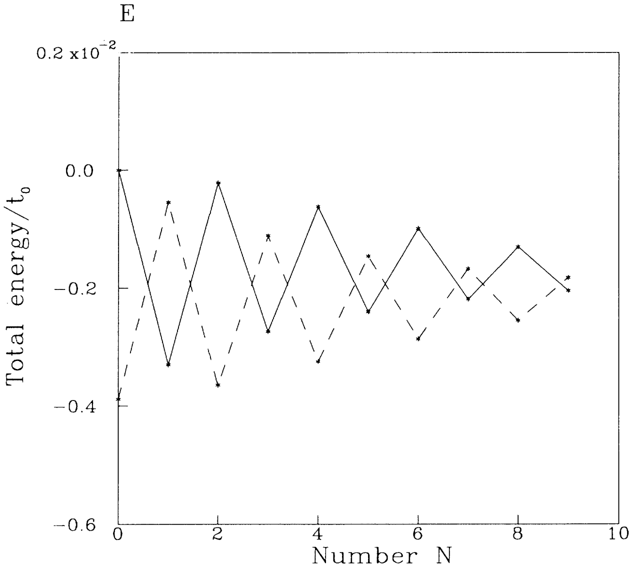

FIG. 3. Total energy of the system as a function of the number N of carbon atoms between two carbon atoms with which two side radicals connect, with $u=1.0$, $j_f=0.2$, and $\lambda=0.1$. Here, the dashed line shows the case that the two unpaired electrons at the side radicals have different spin directions, the solid line shows the case that the two unpaired electrons have the same spin direction, and we consider the total energy of the system when $N=0$ and two unpaired electrons have the same spin direction as the zero-energy line.

The organic ferromagnetic system is a very exciting field for materials scientists. The magnetic properties of this system can vary extensively with a change of structure. Studies on the structure of the main chain and the π electrons are important. In this article, based on the theoretical model proposed for quasi-one-dimensional organic polymer ferromagnets, the spin configuration of π electrons in a π-conjugated carbon chain with one or two side radicals, which contain unpaired electrons, are investigated in detail. As a consequence, we find that around the unpaired electrons appears a π-electron spin-polarization cloud with alternation of the sign and the amplitude of the spin density extending over a certain distance, which reduces rapidly with increasing electron-phonon coupling. Mediated by the π-electron spin-polarization cloud, a parallel spin arrangement of the unpaired electrons can be obtained. The calculations of the total energy show that, in order to obtain ferromagnetic order in this kind of material, the number of carbon atoms between two neighboring side radicals should be odd. It is also shown that the π-orbital alternation will result in a Peierls transition which stabilizes the magnetic order. Throughout this article, we are deeply convinced that, when a π-conjugated system is structured in a definite way, it can show ferromagnetic properties. Although, at the present stage of synthesis, only a few products show ferromagnetic properties, we believe that this kind of conjugated π-electron system will have practical importance in the future.

ACKNOWLEDGMENTS

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