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Density matrix renormalization group studies on one-dimensional π-conjugated organic ferromagnet with side radicals

K.L. Yao[1,2,a], G.Y. Sun[1], and W.Z. Wang[1]

[1] Department of Physics and the State key Lab. of Laser Technology, Huazhong University of Science and Technology, Wuhan, 430074, PR China
[2] The International Center of Materials Physics, The Chinese Academy of Science, Shengyang, 110015, PR China

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Abstract. By using the density matrix renormalization group (DMRG) and the self-consistent numerical method, we obtain a high spin ground state with localized spin density describing spin localization and the soliton describing the distortion of the lattice configurations along the main chain. Different electron-phonon interactions result in different configurations of solitons. When the electron-phonon coupling along the main chain is larger than a critical value λ_c, a transition from a single soliton-like distortion to a pair of soliton-like distortions along the main chain takes place. Such critical value λ_c depends mainly on the intersite Coulomb interactions. The spin density wave along the main chain is always localized around the center of soliton-like distortions.

PACS. 75.40.Mg Numerical simulation studies – 75.30.Ds Spin waves

1 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 and p-NPNN, have been discovered. In order to obtain organic ferromagnets, Mataga [6] reported a strategy to prepare organic ferromagnets based on intramolecular ferromagnetic interaction in very large molecules. The basic idea of this proposal is the synthesis of alternate hydrocarbon in the high-spin ground state. The main chain consists of carbon atoms each with one π-electron and R is a kind of side radicals containing an unpaired electron. Considering the itinerary of π-electrons, the Hubbard electron-electron correlation, electron-phonon coupling and the antiferromagnetic spin correlation between π-electrons and side radical electrons, Yao *et al.* [7] obtained a ferromagnetic ground state, in which a parallel spin arrangement of the unpaired electrons at side free-radical can be gained and there exists an antiferromagnetic spin density wave along the main chain. A simplified structure of quasi-one-dimensional organic polymer ferromagnets is shown in Figure 1a. The zigzag main chain consists of carbon atoms, each with a π-electron and R is a kind of side radicals containing an unpaired electron. In this paper, we consider the Hubbard electron-electron repulsion, the strong electron-phonon interaction and antiferromagnetic spin correlation between π-electron on the main chain and the unpaired electron at the side radical. We will use the periodic boundary conditions for the density-matrix renormalization-group (DMRG) method. The DMRG algorithm, introduced by White [8], has proven to be extremely successful for calculating the ground state properties of model Hamiltonians for very large system sizes in one dimension [9–13]. However, the DMRG has not been applied to organic ferromagnets, which were studied by mean-field theory [14], Monte Carlo method and random phase approximation [15] before. To our knowledge, this is the first time that the DMRG algorithm is applied to organic ferromagnets. Using the DMRG and the self-consistent numerical methods, we obtain a high spin ground state with the localized spin density describing the spin localization and the soliton describing the distortion of the lattice along the main chain. We found different electron-phonon interactions result in different configurations of solitons.

2 The model Hamiltonian and numerical method

Since the DMRG algorithm has been described in detail by White [8], we only give a brief summary of the scheme with reference to the present situation. Figure 1b shows the superblock configuration of one-side radical coupled to

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[a] e-mail: klyao@hust.edu.cn

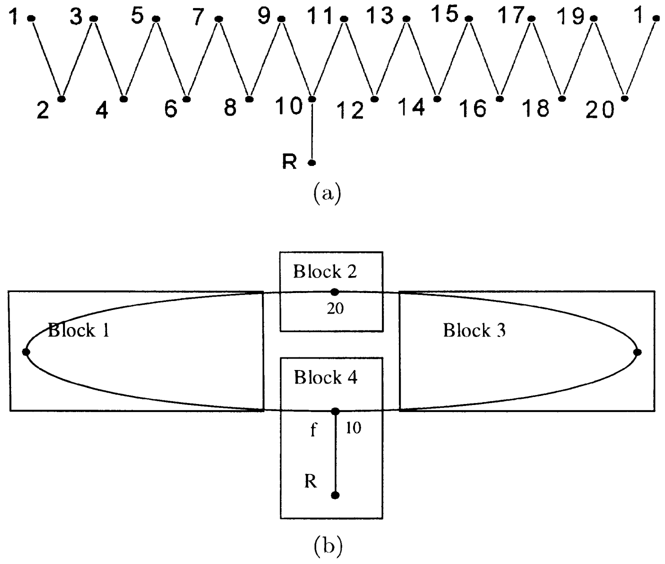


Fig. 1. (a) The structure of quasi-one-dimensional conjugated polymer with one radical. (b) The DMRG scheme for an impurity spin S_f coupled to a chain containing N spin sites. Block 2 contains one spin, while Block 4 contains the side radical and one nearest-neighbor spin. The truncation is carried out for Blocks 1 and 3.

the main chain with an even number of sites N. Block 2 contains one spin, namely the 20th spin. Block 4 contains the side radical R and its nearest neighbor spin $\mathbf{S}_\mathrm{f}$, namely the 10th spin. In each step of the enlargement, a single spin is added to Block 1 on the side with connection to Block 2, and Block 3 is formed by reflection of Block 1. After the number of sites included on the main chain reaches N, we increase in each step Block 1 by one spin and reduce Block 3 by one spin. Iteration stops when a satisfied convergence is gained.

In this paper we study the problem of spin-1/2 quasi-one dimensional organic ferromagnetic conjugated polymer with one side radical. The model in Figure 1a is described by the Hamiltonian:

$$H = H_\mathrm{m} + H_\mathrm{r} \tag{1}$$

where H_m is the Hamiltonian of the main chain and H_r described the Hamiltonian related to the side radical. H_m and H_r are given explicitly as follows:

$$\begin{aligned} H_\mathrm{m} = &-\sum_{l,\sigma}\left[t_\mathrm{m} - \gamma\left(\mu_{l+1} - u_l\right)\right]\left(C^+_{l,\sigma}C_{l,\sigma} + \mathrm{h.c.}\right) \\ &+\frac{k}{2}\sum_l \left(u_l - u_{l+1}\right)^2 + U_\mathrm{m}\sum_l n_{l,\alpha}n_{l,\beta} \end{aligned} \tag{2}$$

$$H_\mathrm{r} = J_\mathrm{f}\,\mathbf{S}_\mathrm{f}\cdot\mathbf{S}_\mathrm{R} \tag{3}$$

where t_m is the hopping integral of the π-electron along the main chain, γ is the electron-lattice coupling constant, and k is the elastic constant of the lattice. $C^+_{l,\sigma}$ $(C_{l,\sigma})$ $(\sigma = \alpha, \beta)$, α and β being up-spin and down-spin, respectively, denotes the creation(annihilation) operator of a π-electron with spin σ on the main chain and u_l is the displacement of the lth carbon atom along the main chain. U_m describes the Hubbard on-site electron-electron repulsion along the main chain, and $n_{l,\sigma} = C^+_{l,\sigma}C_{l,\sigma} \cdot J_\mathrm{f}$ $(J_\mathrm{f} > 0)$ is the antiferromagnetic coupling between the main chain and the side radical. R and f respectively label the side radical and the atom coupled to the side in the main chain, as shown in Figure 1b. The term $\mathbf{S}_\mathrm{f}\cdot\mathbf{S}_\mathrm{R}$ can be written as

$$\mathbf{S}_\mathrm{f}\cdot\mathbf{S}_\mathrm{R} = S^z_\mathrm{f}\,\mathbf{S}^z_\mathrm{R} + \frac{1}{2}\left[\mathbf{S}^+_\mathrm{f}\,\mathbf{S}^-_\mathrm{R} + \mathbf{S}^+_\mathrm{R}\,\mathbf{S}^-_\mathrm{f}\right]$$

where S^+_f and S^-_f denote the Pauli spin matrix:

$$S^z_\mathrm{f} = \frac{1}{2}\left(n_{\mathrm{f},\alpha} - n_{\mathrm{f},\beta}\right), S^+_\mathrm{f} = C^+_{\mathrm{f},\alpha}C_{\mathrm{f},\beta}, S^-_\mathrm{f} = C^+_{\mathrm{f},\beta}C_{\mathrm{f},\alpha}$$

In implementing the DMRG algorithm, we first cast the SSHH Hamiltonian into a dimensionless form. By defining:

$$\begin{gathered} h = H/t_\mathrm{m}, u = U_\mathrm{m}/t_\mathrm{m}, \lambda = 2\gamma^2/\left(\pi t_\mathrm{m} k\right) \\ \gamma_l = (-1)^l\left(\gamma/t_\mathrm{m}\right)\left(u_{l+1} - u_l\right), J = J_\mathrm{f}/t_\mathrm{m} \end{gathered}$$

we have

$$\begin{aligned} h = &-\sum_{l,\sigma}\left[1 - (-1)^l\gamma_l\right]\left(C^+_{l,\sigma}C_{l+1,\sigma} + \mathrm{h.c.}\right) \\ &+\frac{1}{\pi\lambda}\sum_l \gamma_l^2 + u\sum_l n_{l,\alpha}n_{l,\beta} + J\mathbf{S}_\mathrm{f}\cdot\mathbf{S}_\mathrm{R}. \end{aligned} \tag{4}$$

Using the Hellmann-Feynman theorem and applying the constraint:

$$\sum_l (-1)^l\gamma_l = 0$$

we have the self-consistency equation:

$$\gamma_l = -(-1)^l\pi\lambda\left(p_l - \frac{1}{N}\sum_m p_m\right)$$

with bond order:

$$p_l = \left\langle \frac{1}{2}\sum_\sigma\left(C^+_{l,\sigma}C_{l+1,\sigma} + \mathrm{h.c.}\right)\right\rangle$$

N being the total number of sites of the main chain. We use the periodic boundary condition $C^{(+)}_{l,\sigma} = C^{(+)}_{N+1,\sigma}$ and $u_{N+1} = u_1$.

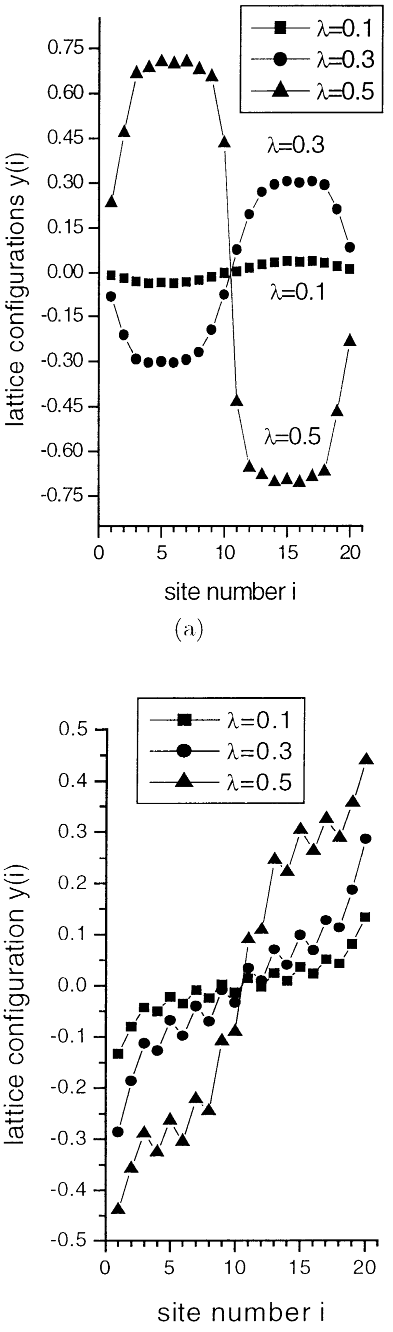
From the above equation, we see that given any lattice configuration, we can calculate the electronic states using DMRG algorithm, then, through the self-consistency equation, we obtain a new lattice configuration.

The main chain of the polymer studied contains $N = 20$ carbon atoms each with a π-electron. The side radical, containing one unpaired electron, connects with the f atom, shown in Figure 1b. The Hamiltonian in equation (1) conserves the total number of electrons and the total z-component of the spins. Equivalently we can use the number of up-spin electrons and the number of spin-down electrons as good quantum numbers. The states with different quantum numbers are decoupled from each other, so we set up the Hamiltonian within each subspace with fixed quantum numbers. By looping up-spin number from 0 to $N+1$, we find that the ground state is in the subspaces where $S^z = \pm 1/2$. For convenience, we work in the subspace where $S^z = -1/2$. The dimension is thus greatly reduced, but for longer chains, it is still not feasible for direct diagonalization. We resort to the Lanczos method [16] when solving for the low-lying target states.

We keep 120 states for Block 1 and sweep through lattice four to five times. The estimated truncation errors are typically of the order of 10^{-5}. About 10 to 50 iterations are usually needed to reach convergence in the lattice configuration. The stability of the optimized configuration is always tested by using another starting configuration and performing the optimization once again. The criterion for terminating the optimization is that between two successive iterations, the difference is less than 10^{-8} for the displacement order parameter. We checked our results against those by direct diagonalization [17] for the main chain up to 8 sites. A full agreement was reached.

3 The numerical results

First, in the absence of the side radical, *i.e.* $J = 0.0$, we calculate the lattice configurations and spin densities on the main chain. The configurations of lattice distortion along the main chain for $\lambda = 0.1$, 0.3, 0.5 are shown in Figure 2a. When the electron-phonon interaction $\lambda = 0.1$, there is no distortion on the main chain. For $\lambda = 0.3$, a domain wall soliton occurs in the middle of the main chain. But for $\lambda = 0.5$, the soliton and antisoliton appear along the main chain. Figure 3a shows the distribution of spin density. For $\lambda = 0.1$, there is no soliton. The spin density is uniformly 0.0 on the main chain. With the increasing of λ, soliton comes into existence. Spin density is localized around the soliton and the center of it.

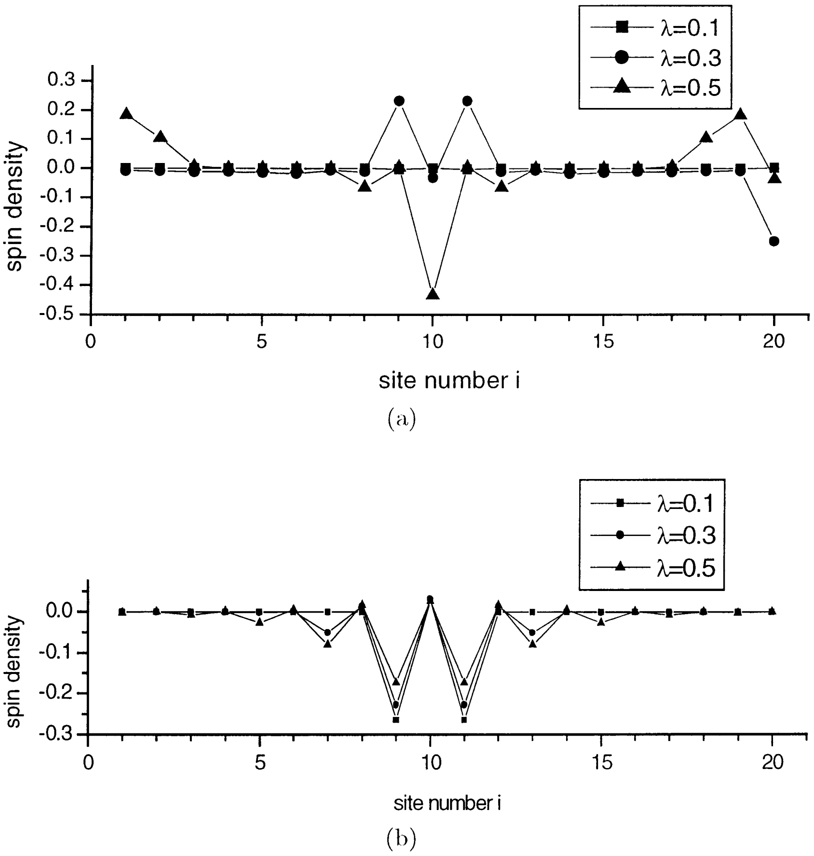


(a)

(b)

Fig. 2. (a) The configuration of lattice distortion along the main chain in the absence of the side radical for $u = 1.0$, $J = 0.0$ and $\lambda = 0.1$, 0.3, and 0.5 with $N = 20$ atoms. (b) The configuration of lattice distortion along the main chain for $u = 1.0$, $J = 5.0$ and $\lambda = 0.1$, 0.3, and 0.5 with $N = 20$ atoms.

Second, we discuss the distortion of lattice configurations along the main chain with the side radical. In one-dimensional conducting polymers such as polyacetylene, due to the electron-phonon interaction, there exist various domain solitons [18]. For the quasi-one dimensional organic ferromagnetic polymer, we could find that there exists a soliton at the two ends of the main chain. When the electron-phonon coupling along the main chain is larger than a critical value $\lambda_c = 0.1 \sim 0.2$, which depends mainly on the electron-electron interaction u, a transition along the main chain from a single soliton-like distortion to a pair of soliton-like distortions takes place. The configurations of lattice distortion along the main chain for $\lambda = 0.1$, 0.2 and 0.3 are plotted in Figure 2b. From the figure, we found that the side radical atom at the midpoint induces to generate a soliton along the main chain. Thus, there exist a pair of soliton-like behavior distortions ($\lambda > \lambda_c$) along the main chain. Such a pair of soliton-like behavior is different from that of the trans-polyacetylene. The important self-trapped single soliton or a pair of solitons (or a polaron) in trans-polyacetylene depends upon whether the number of carbon atoms in the main chain is odd or even. However, it is interesting that a pair of solitons appear in a π-conjugated main chain with an even number of carbon atoms. Furthermore, we did similar studies for the



(a)

(b)

Fig. 3. (a) The spin density on the main chain in the absence of the side radical for different electron-phonon interaction λ. (b) The spin density on the main chain with the side radical for different electron-phonon interaction λ.

case with 20 carbon atoms, and found that a soliton-like distortion also appears along the main chain.

Now, we turn to study of the spin density wave of the system. It is found that the charge density with up-spin at the side radical has been transferred to the main chain, while the charge density with down-spin of the main chain transferred onto the side radical. It is shown that the charge density with up-spin transferred from the side radical to the main chain equals the charge density with down-spin transferred from the main chain to the side radical irrespective of the values of parameters λ, u, and J. So the charge density is 1 on every carbon atom. Figure 3b shows the spin density of the main chain with $u = 1.0$ and $J = 5.0$. There are alternative spins at odd sites and even sites along the main chain. Our calculation also shows that the spin density wave along the main chain is always localized around the center of soliton-like distortions. With the increasing of λ, we find that the distribution of spin density is localized strongly. Owing to the antiferromagnetic coupling, we could expect that there is net spin on every side radical if the side radicals connect with odd sites along the main chain. It follows that the polymer studied in reference [7] will show ferromagnetism irrespective of the electron-phonon coupling λ.

4 Conclusions

By using the density matrix renormalization group method, the soliton-like distortions along a quasi-one dimensional π-conjugated organic polymer ferromagnet, consisting of N π-electrons and one unpaired radical electron, is studied self-consistently. In the absence of the side radical, the domain wall soliton is transformed into the soliton and antisoliton along the main chain with the increasing of λ. When the electron-phonon coupling along the main chain is larger than a critical value, a transition exists from a single soliton-like distortion ($\lambda < \lambda_c$) to a pair of soliton-like distortions ($\lambda > \lambda_c$) along the main chain. Such critical value λ_c depends mainly on the intersite Coulomb interactions. The spin density wave along the main chain is always localized around the center of soliton-like distortions. It is followed that the system, in which every odd site couples with one unpaired side radical, is still a stable ferromagnetic state, and that the soliton-like states are the main contributor of the ferromagnetic state of the system although the electron-phonon coupling λ is increased.

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