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# Spin correlation on the main chain of a quasi-one-dimensional polymer ferromagnet: a density matrix renormalization group study

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## Abstract
The spin correlation (SC) function on the main chain of a theoretical model for organic ferromagnets is studied by using a density matrix renormalization group method with both periodic boundary conditions and open boundary conditions (OBCs). It is found that the chain–radical interaction, the on-site electron–electron repulsion, and the electron–phonon coupling affect the SC greatly and play important roles in the stability of the ferromagnetic state. There exist some types of 'weak' OBC, diminishing the alternation of the SC.

## 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 ferromagnet [1–5], such as *m*-PDPC [1] and *p*-NPNN [2], have been discovered. These organic ferromagnets are expected to have unique features compared with usual ferromagnets, because the magnetic moments in these materials originate from the unpaired 2p electrons in molecular orbitals. For a class of quasi-one-dimensional organic ferromagnets, Ovchinnikov and Spector [6] proposed a simplified structure, shown in figure 1(a). Each side radical (R) contains one unpaired electron, and when it is attached to the main carbon chain in a definite way, ferromagnetic order is obtained. Further, the general features of quasi-one-dimensional organic ferromagnets can be illustrated by figure 1(b). Considering the antiferromagnetic correlation between itinerant $\pi$-electrons and the localized unpaired electron on the side radical, Yao *et al* proposed [7–9] a theoretical model for describing the organic ferromagnetic polymer, which consists of

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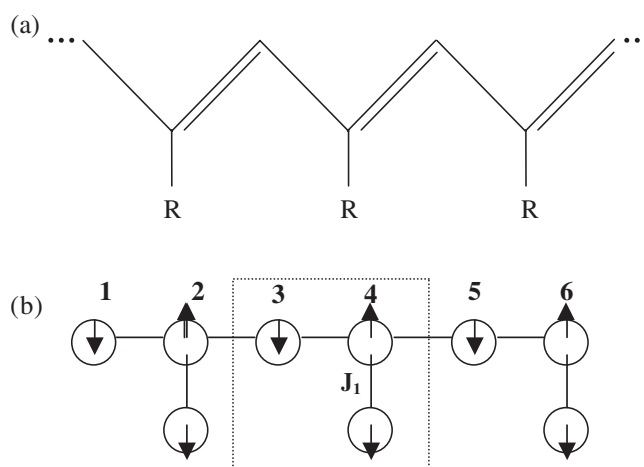
**Figure 1.** The quasi-one-dimensional organic ferromagnetic model under consideration here. The SDW on the main chain and the ferromagnetic order of the unpaired electrons on side radicals are displayed. The carbon atoms in the dotted rectangle form a unit cell of the polymer.

a Hubbard model describing the correlation of the $\pi$-electrons on the main chain and their itineracy. The localized unpaired electron in the radical is considered to have no freedom except as regards its spin.

The density matrix renormalization group (DMRG) technique [10] developed by White is a very powerful tool for dealing with low-dimensional systems with short-range interactions. This algorithm gives highly accurate results on ground state energies and static properties for systems much larger than those solvable by direct diagonalization [11–13]. Very recent work by us [14] has extended this algorithm to study of the magnetic structure of the organic magnetic systems.

In this paper, the spin correlation (SC) on the main chain is investigated on the basis of the structure of figure 1 by using a DMRG method with both periodic boundary conditions (PBCs) and open boundary conditions (OBCs). We will study the effects of several parameters (the chain–radical coupling, the on-site electron–electron (e–e) repulsion, and the electron–phonon (e–ph) coupling) on the SC function of the main chain, which is important to the stability of the ferromagnetic ground state. The effect of boundary conditions will also be involved. In section 2 we will give the model Hamiltonian and a brief description of the DMRG algorithm. Results and a discussion will be given in section 3.

## 2. The model Hamiltonian and the DMRG method

### 2.1. Model Hamiltonian

The Hamiltonian is written as

$$H = H_0 + H_1,$$

where $H_0$ is the Hamiltonian of the main chain and $H_1$ is the Hamiltonian related to the side radicals. We can write $H_0$ explicitly as follows:

$$H_0 = - \sum_{l,\sigma} [t_0 - \alpha(\mu_{l+1} - u_l)](C_{l,\sigma}^+ C_{l,\sigma} + \text{H.c.}) + \frac{k}{2} \sum_l (u_l - u_{l+1})^2 + U_0 \sum_l n_{l,\alpha} n_{l,\beta},$$

where $t_0$ is the hopping integral of the $\pi$-electron along the main chain, $\alpha$ is the e–ph coupling constant, and $k$ is the elastic constant of the lattice. $C_{l,\sigma}^+$ $(C_{l,\sigma})$ denotes the creation (annihilation) operator of a $\pi$-electron with spin $\sigma$ on the main chain and $u_l$ is the displacement of the $l$th carbon atom along the main chain. $U_0$ describes the Hubbard on-site e–e repulsion, and $n_{l,\sigma} = C_{l,\sigma}^+ C_{l,\sigma}$ $(\sigma = \alpha, \beta)$, where $\alpha$ and $\beta$ denote up spin and down spin, respectively.

The Hamiltonian $H_1$ can be written as follows:

$$H_1 = J_1 \sum_l \delta_l S_l \cdot S_{l_R},$$

where $J_1$ $(J_1 > 0)$ is the energy of exchange between the residual spin and $\pi$-electrons. We suppose that if the radical R bonds to the $l$th carbon atom of the main chain, then $\delta_l = 1$, and if not, then $\delta_l = 0$.

It is convenient to cast all quantities into dimensionless forms:

$$h = H/t_0, \qquad u = U_0/t_0, \qquad \lambda = 2\alpha^2/(\pi t_0 k)$$
$$y_l = (-1)^l (\alpha/t_0)(u_{l+1} - u_l), \qquad J = J_1/t_0.$$

Then, the Hamiltonian is transformed to the following:

$$h = -\sum_{l,\sigma}[1 - (-1)^l y_l](C_{l,\sigma}^+ C_{l+1,\sigma} + \text{H.c.}) + \frac{1}{\pi\lambda}\sum_l y_l^2 + u\sum_l n_{l,\alpha} n_{l,\beta} + J\sum_l \delta_l S_l \cdot S_{l_R}.$$

$\lambda$ is the e–ph coupling, which is dealt with classically, and $J$ is called 'chain–radical coupling' by us. The lattice configuration is optimized [14] using the Hellmann–Feynman theorem. The criterion for terminating the optimization is that the difference between two successive iterations is less than $10^{-8}$ for the displacement order parameter $y_l$.

## 2.2. The DMRG method

Following White [10], we give a brief description of the algorithm with reference to the present situation. For our model Hamiltonians, the dimension of the Hilbert space is of the order of more than $4^L$, where $L$ is the number of carbon atoms on the main chain. This severely limits the size of the lattice for direct diagonalization. The best that one can do is to find a truncated space which can describe the states of interest as accurately as possible. This is accomplished by keeping the eigenstates of a certain reduced density matrix with the highest weights. The basic step in the algorithm is the formation of a superblock from four blocks (figure 2). We start with the four-site main chain with two radicals shown in figure 2(a). Blocks 1 and 3, which are mirror images, come from the previous iteration. Blocks 1 and 2 are regarded as system blocks, blocks 3 and 4 as environment blocks. First one finds the ground state of the whole superblock, then traces out the environment blocks to form a reduced density matrix. Blocks 1 and 2 are combined to form a new block 1 by changing the previous basis to that formed by the eigenstates with some highest weights of the density matrix. Thus, each time the system block is enlarged by one atom (in even step, figure 2(b)) or one atom and the radical R bonds to it (in odd step, figure 2(a)). For finite systems, one first builds the superblock to the desired size, then increases the system block while reducing the environment block, so as to keep the total number of atoms unchanged. The procedure is repeated until some desired quantities converge. About 30–50 iterations are usually needed to reach convergence in the lattice configuration.

In the case of half-filling, the total electron number is $L + L/2 = 3L/2$ considered. By looping the up-spin number from 0 to $3L/2$, we find that the ground state is in the subspace where $S^z = (\pm 1/2) \times L/2$. We work in the subspace where $S^z = (-1/2) \times L/2$ for convenience.
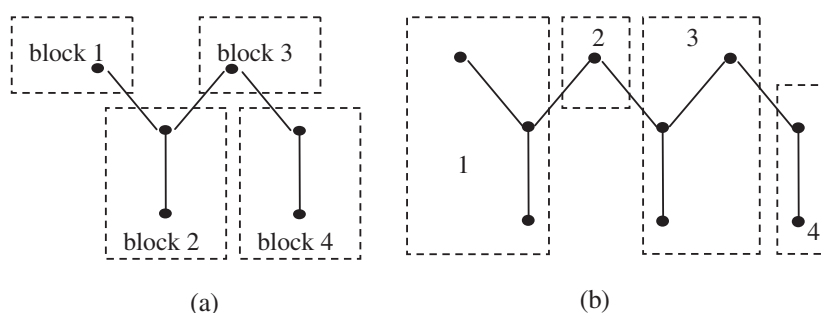
**Figure 2.** (a) The DMRG scheme for the odd step. Block 2 contains one atom and its nearest radical. (b) The scheme for the even step. Block 2 contains only one atom. Blocks 1 and 3 are mirror images. Block 4 always contains one atom and a radical.

To ensure that the sum of the weights is kept convergent to 1 as closely as possible (the truncation errors are $10^{-5}$), we keep 120 states for block 1. The number of states that we keep is limited by the memory of our computer. The rest of the eigenstates of the density matrix are discarded.

For a correlation function such as $\langle\psi|S_j^z S_k^z|\psi\rangle$, the evaluation depends on whether $j$ and $k$ are on the same block or not. Details can be found in [11].

## 3. Results and discussion

We consider a chain of 20 carbon atoms and 10 side radicals with both PBCs and OBCs. The results discussed in 3.1 and 3.2 are obtained with PBCs. In 3.3 we will demonstrate the effect of OBCs.

### 3.1. Effects of J and u on the spin correlation

Let us glance at the spin density on the main chain (figure 3) before studying the SC function, since this may be helpful for understanding the magnetic properties of the system. The two solid lines represent the spin density of the odd site and the even site respectively. The dotted line indicates that of the side radicals. From the figure we can see that there exists an antiferromagnetic (sign-alternating) spin density wave (SDW) on the main chain, and a ferromagnetic order of unpaired electrons of side radicals is established. This is also illustrated in figure 1. It is found that with increase of the chain–radical coupling $J$, the spin density of odd sites increases, while that of even sites decreases. After $J$ reaches about 1.4, the spin densities on every site almost cease to change; they tend towards a limit value very slowly with respect to their positions. For the even sites, the limit value is about 0.19; for the odd sites, it is $-0.39$ and $-0.3$ on a side radical. Moreover, because we work in the subspace where $S^z = (-1/2) \times L/2$ ($L = 20$), a unit cell (shown in figure 1) has a total spin of $-1/2$, which can be checked in figure 3.

Because of the PBC, the SC function of the main chain $\langle S_i S_{i+1}\rangle$ is a constant for every site $i$. Thus we can get a curve as a function of the chain–radical coupling $J$ (figure 4). One can see that the SC drops with increase of $J$. Similarly to the case for the spin density discussed before, there exists a critical interaction $J_m$ beyond which the SC will converge to a minimum. For example, in the case of $\lambda = 0.6$, $u = 4.0$ (the same as in figure 3), we get $J_m \approx 1.4$. This value is exactly the same as that of the spin density.
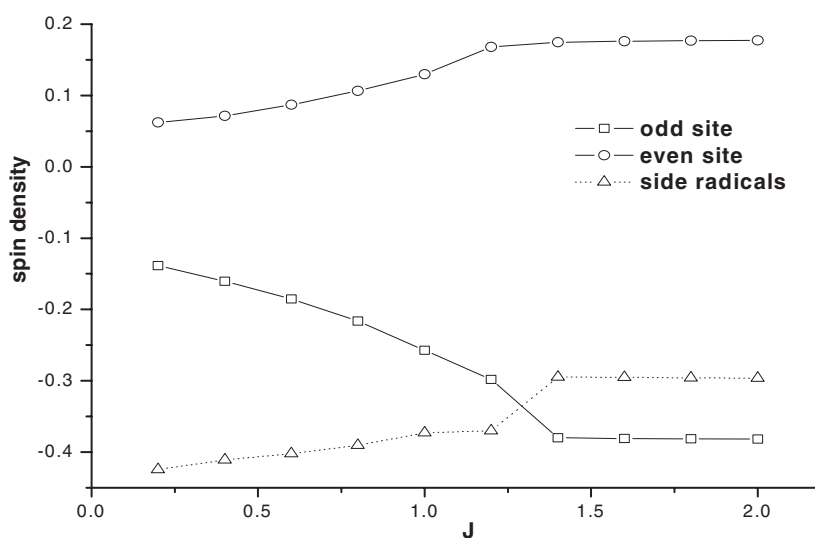
**Figure 3.** Spin density on every site as a function of chain–radical interaction $J$ ($u = 4.0$, $\lambda = 0.6$).
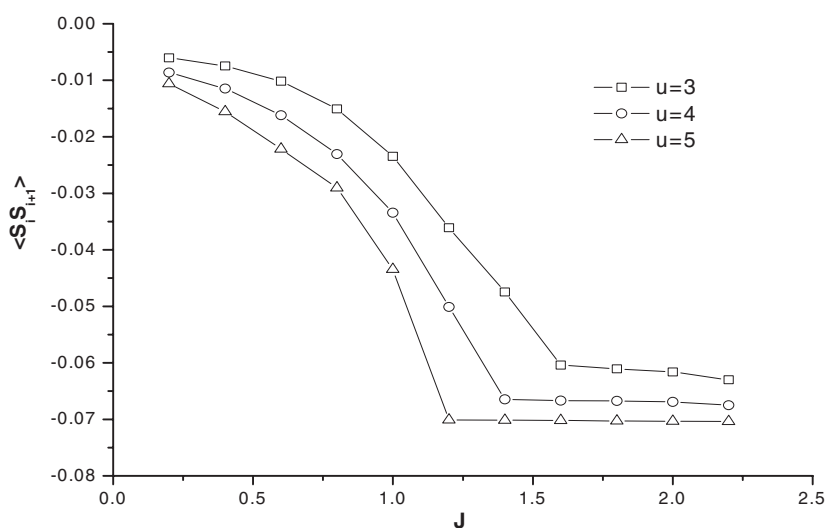


**Figure 4.** SC as a function of $J$ with different on-site e–e repulsions $u$ ($\lambda = 0.6$).

As for the on-site e–e repulsion, it is illustrated that different $u$ leads to different $J_m$. With increase of $u$, the critical value $J_m$ is reduced. This strongly suggests that $u$ favours decrease of the SC. That is to say, a larger $u$ can make the SC reach the minimum more quickly. Thus the relation between $J$ and $u$ is cooperative.

It should be stated that the SC is strongly related to the stability of the ferromagnetic ground state. With decrease of $\langle S_i S_{i+1} \rangle$, the ferromagnetic ground state of the system will become more stable. Thus we should select materials with large chain–radical coupling and e–e repulsion when designing such organic ferromagnets.
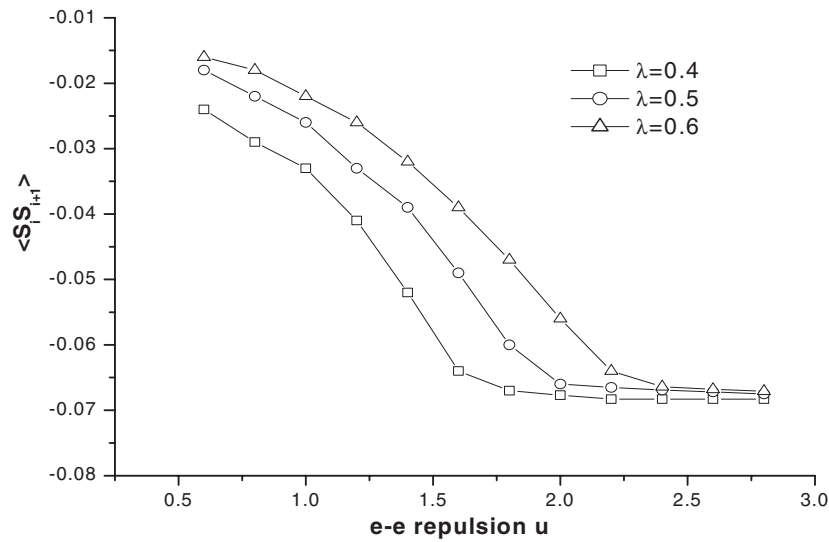
**Figure 5.** SC as a function of $u$ with different e–ph couplings $\lambda$ ($J = 3.0$).

### 3.2. Competition between $u$ and $\lambda$

Now we study the effect of on-site e–e repulsion $u$ and e–ph coupling $\lambda$ on the SC function (figure 5). It is found that the SC drops with increase of $u$. $u$ favours decreasing of SC; this is consistent with what we discussed in 3.1. And when $u$ reaches a critical value $u_m$, the SC will arrive at a minimum, just like in the situation in figure 4. In the present situation, when $\lambda$ increases, the critical value $u_c$ also increases. For example, $u_m$ is about 2.0 when $\lambda = 0.5$ and it grows to 2.5 for $\lambda = 0.6$. This suggests that $\lambda$ is unfavourable for decrease of the SC. Considering the discussion before, this means the $\lambda$ has an adverse effect on the stability of the ferromagnetic state, while for $u$ the opposite is true. Therefore, the competition between $u$ and $\lambda$ determines the stability of the ferromagnetic ground state.

### 3.3. What will happen when we use open boundary conditions?

For a DMRG method, one can expect to get a more accurate result using OBCs than using PBCs [10]. Thus, it is important to understand the effect of an OBC on the system. It is easily seen that the SC $\langle S_i S_{i+1} \rangle$ as a function of site index $i$ is never a constant (figure 6). An OBC causes a strong alternation in the SC, which decays very slowly. This effect is easily understood using the valence bond picture [11]. The system 'tries' to have strong single bonds (a low value of SC) at the outermost links, since that is the only way the end sites can participate in a bond.

If we desire the accuracy of OBCs but without alternation of the SC, which is absent in the bulk system, it is possible to considerably weaken the alternation using a 'weak' OBC. For this type of OBC, the boundary of the system must be preprocessed before calculation, hence its name. The result obtained from using a practicable version of such a 'weak' OBC is shown in figure 6(b). We increase the e–e repulsions $u$ of the four outermost sites (two for each end; they are exactly the mirror sites in the DMRG method) from their bulk value $u = 2.0$ to $u_1 = u_{19} = 5.0$ and $u_2 = u_{18} = 2.5$; obviously the alternation is nearly absent.
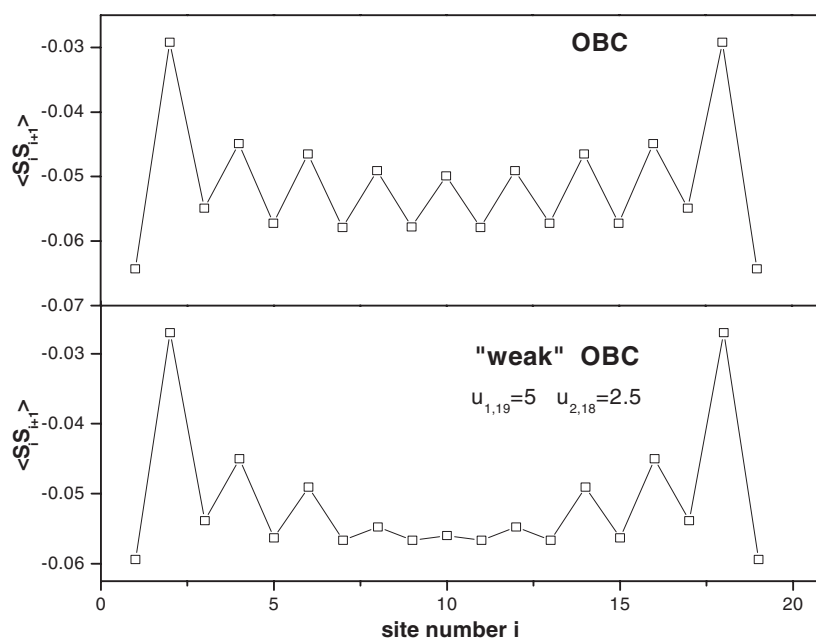
**Figure 6.** (a) SC with OBC ($u = 2.0$, $\lambda = 0.6$, $J = 3.0$). (b) A kind of 'weak' OBC. The four outermost site e–e repulsions are not 2.0.

## 4. Conclusions

We have studied the effects of several parameters (i.e. $u, \lambda$) on SC of the main chain in conjugated ferromagnetic polymers using a DMRG method with both PBCs and OBCs. This method has proven to be very accurate and powerful for studying quasi-one-dimensional systems. Our calculations show that $J$ and $u$ both favour decrease of the SC and thus favour the stability of the ferromagnetic ground state. It is also found that $\lambda$ has the opposite effect, which means that there is competition between $\lambda$ and $u$ (or $\lambda$ and $J$). In the case of OBCs, it is found that a strong alternation of the SC appears. And a practicable technique for diminishing the alternation by using a weak OBC has been proved to be effective.

Throughout this paper, we have been deeply convinced that, when the $\pi$-conjugated systems are set up in a particular way (figure 1), they can show ferromagnetic properties. Some species of organic ferromagnets [1, 2, 15] according with our model have been found experimentally. Moreover, as the calculation has shown, in order to obtain stable quasi-one-dimensional polymer ferromagnets, it is essential to enlarge the chain–radical interaction $J$ and the e–e repulsion $u$ while making the e–ph coupling $\lambda$ as small as possible.

## Acknowledgment

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