

Density matrix renormalization group studies on  $\pi$ -topology and spin alignment of an organic  $\pi$ -conjugated spin system

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 2093

(<http://iopscience.iop.org/0953-8984/16/12/018>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 14:09

Please note that [terms and conditions apply](#).

# Density matrix renormalization group studies on $\pi$ -topology and spin alignment of an organic $\pi$ -conjugated spin system

Q M Liu<sup>1,3</sup>, K L Yao<sup>1,2</sup>, Z L Liu<sup>1</sup> and Y Qin<sup>1</sup>

<sup>1</sup> Department of Physics and State Key Laboratory of Laser Technology, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

<sup>2</sup> The International Centre of Materials Physics, Chinese Academic of Science, Shenyang 110015, People's Republic of China

E-mail: onsunway@msn.com (Q M Liu) and klyao@hust.edu.cn

Received 16 January 2004

Published 12 March 2004

Online at [stacks.iop.org/JPhysCM/16/2093](http://stacks.iop.org/JPhysCM/16/2093) (DOI: 10.1088/0953-8984/16/12/018)

## Abstract

We carry out density matrix renormalization group (DMRG) calculations to study  $\pi$ -topology and spin alignment of an organic  $\pi$ -conjugated spin system in the Hubbard model. We discuss the spin correlation, the energy gap and the lattice configuration in half-filled and doped systems. It is confirmed that electronic doping can alter the spin state, and the spin alignment is influenced by the parity of the total site number  $N$ . The electron–electron interaction is in favour of the ferromagnetic stability of the system. For the half-filled odd case and the hole-doped even case, there exist strong ferromagnetic correlation and large energy gap in  $\pi$ -conjugated spin systems.

## 1. Introduction

The development of pure organic materials with ferromagnetic properties has been of long standing theoretical and experimental interest. To obtain high-spin organic materials, it is necessary to control spin–spin interactions of organic radicals. For the development of organic ferromagnets, organic radicals serve as spin containing units. The ferromagnetic coupling unit is responsible for the parallel alignment of adjacent spins. A number of prototypical one-dimensional polaronic ferromagnets were studied using oxidatively doped spin containing units to give polyradical cations [1]. These experimental results showed spin values greater than one half at very low spin concentrations, suggesting parallel alignment between adjacent radicals. However, at high-spin concentrations, above 1%, typically the spin values observed were well below one, which is most likely indicative of bipolaron formation and/or decomposition of the material. Many of the problems associated with the early prototypical oxidatively doped radical

<sup>3</sup> Author to whom any correspondence should be addressed.

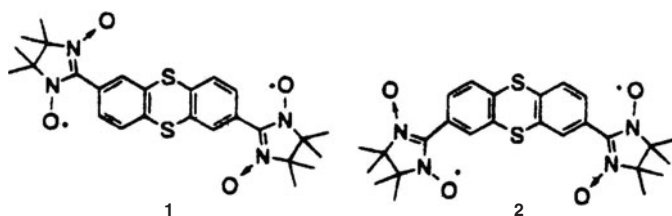


Figure 1. The structure of the thianthrene derivatives carrying two nitronyl nitroxide groups.

cation systems were resolved by the introduction of a doped radical anion spin containing unit [2]. Recently Izuoka and his co-workers [3] have succeeded in controlling intramolecular spin alignment by charge doping in a newly designed organic molecule, thianthrene bis(nitronyl nitroxide). They found that the mechanism of the spin alignment of the donor radicals in the singly oxidized state is totally different from that in the neutral state.

In the theoretical aspects, some modelling and computational studies have been developed. Most efforts have been made using the density functional theory (DFT) method to analyse the magnetic mechanism of organic materials. Recently Huai *et al* [4] have studied the spin alignment control in  $\pi$ -conjugated molecular magnets by charge doping by means of the exact diagonalization technique up to a total number of sites of 12. Though these efforts were made, the mechanism for controlling spin alignment by charge doping in the high-spin ground state of organic magnets has not yet been well elucidated. The density matrix renormalization group (DMRG) technique developed by White [5–7] has proved to be a very powerful tool to obtain highly accurate ground state static properties for low-dimensional systems and for systems much larger than those solvable by direct diagonalization. So we expect the DMRG method to solve the magnetic interaction of some models for designing and preparing the high-spin organic magnets. In this paper we will use this method with an open boundary condition to study the intramolecular spin alignment of the stable radicals through  $\pi$ -conjugation for the purely organic spin systems. We will also discuss the effects of doping on the total spin and the ferromagnetic interaction. In section 2, a theoretical model and a brief description of the computational process are given. In section 3 we calculate the spin correlation function, the energy gap, the lattice configuration and the total spin of the system. Finally we will give a brief summary of our results in section 4.

## 2. Theoretical model and computational method

According to the experimental results mentioned above, Izuoka *et al* [3] prepared thianthrene derivatives carrying two nitronyl nitroxide groups as a prototypical donor diradical as in figure 1. They found that two paramagnetically interacting unpaired electrons in the neutral species can be converted to a high-spin molecule through a ferromagnetic coupling which operates between the local spins on the side radical and a  $\pi$ -spin on the donor site generated upon one-electron oxidation. In order to further clarify the mechanism, we adopt a simplified theoretical model for the system with the  $\pi$ -electrons on the main chain and the two localized radical spins being located on both ends. The localized unpaired electron on the side radical is considered to have no freedom except its spin. Considering the electron–lattice coupling and the electron–electron interaction, we show the Hamiltonian form as follows:

$$H = - \sum_{i,\sigma} [t_0 + \alpha(u_i - u_{i+1})](c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.}) + U_0 \sum_i n_{i,\alpha} n_{i+1,\beta}$$

$$+ \frac{K}{2} \sum_i (u_i - u_{i+1})^2 - J_1 (S_{f_1} \cdot S_{R_1} + S_{f_N} \cdot S_{R_2}) \quad (1)$$

where  $t_0$  is the hopping integral of the  $\pi$ -electron along the main chain,  $\alpha$  is the electron–phonon coupling constant, and  $k$  is the elastic constant of the lattice.  $c_{i,\sigma}^\dagger$  ( $c_{i,\sigma}$ ) denotes the creation (annihilation) operator of a  $\pi$ -electron with spin  $\sigma$  on the main chain and  $u_i$  is the displacement of the  $i$ th site along the main chain.  $U_0$  describes the Hubbard on-site electron–electron repulsion, and  $n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$  ( $\sigma = \alpha, \beta$ ), where  $\alpha$  and  $\beta$  denote up spin and down spin, respectively.  $J_1$  is the exchange energy between the residual spin and the  $\pi$ -electrons.

It is convenient to cast all quantities into dimensionless forms:

$$h = H/t_0, \quad u = U_0/t_0, \quad J = J_1/t_0, \quad \lambda = \alpha^2/t_0k.$$

Then, the Hamiltonian is transformed to the following form:

$$h = - \sum_{i,\sigma} [1 + y(i)] (c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.}) + u \sum_i n_{i,\alpha} n_{i+1,\beta} + \frac{1}{2\lambda} \sum_i y(i)^2 - J (S_{f_1} \cdot S_{R_1} + S_{f_N} \cdot S_{R_2}) \quad (2)$$

where  $\lambda$  is the electron–phonon coupling parameter, and  $y(i)$  is treated classically and optimized by means of the Hellmann–Feynman theorem as shown in the following form:

$$y(i) = \left\langle \sum_{i,\sigma} (c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.}) \right\rangle.$$

The algorithm  $S_{f_i}$  ( $S_{f_N}$ ) denotes the Pauli matrix:

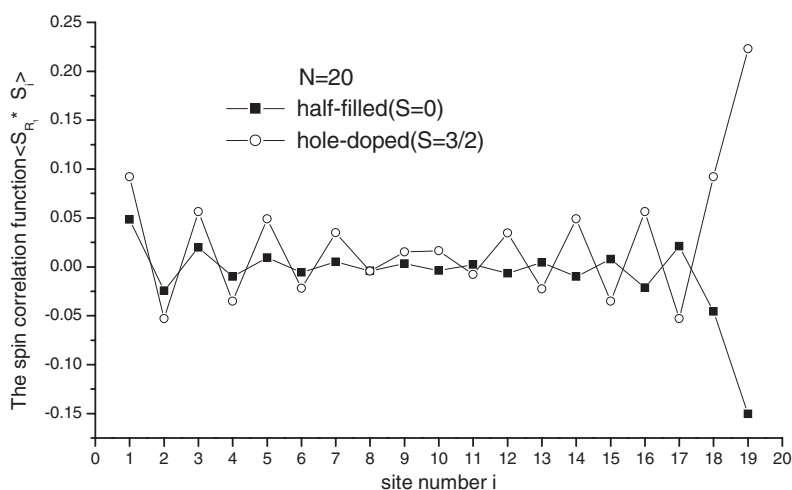
$$S_{f_i}^z = \frac{1}{2}(n_{1,\uparrow} - n_{1,\downarrow}), \quad S_{f_i}^+ = c_{1,\uparrow}^\dagger c_{1,\downarrow}, \quad S_{f_i}^- = c_{1,\downarrow}^\dagger c_{1,\uparrow}.$$

Following the above Hamiltonian and the topological structure of the theoretical model, we use an open boundary condition in the finite DMRG algorithm. For the Hubbard model Hamiltonian, the dimension of the Hilbert space is of the order of more than  $4^L$ , where  $L$  is the number of atoms of the system. Thus the exact diagonalization technique is limited to deal with small systems. However the DMRG method adopts a truncation procedure to solve larger systems. As is recognized, this method is one of the leading numerical means to study low-dimensional strongly correlated systems. In our work, we start with four sites of the main chain and two radicals distributed on both ends, and then systematically add two sites in the middle of the system for every iterative step to build up the total system. When the total number of site is even, the right block states are obtained by the reflection of the left block symmetrically. But for the odd sites system, the left–right block reflection symmetry commonly seen in DMRG calculations is broken. So we adopt the unsymmetrical enlargement procedure to construct the superblock of the system. The left block and the right block are separately increased in the same step.

For the estimation of the energy gap, the standard DMRG approach with one target state is considered to be inaccurate from the point of view of physics. Therefore, we constructed the reduced density with the help of a projection operator of the form [8]:

$$\rho = \frac{1}{2}(|\Psi_0\rangle\langle\Psi_0| + |\Psi_1\rangle\langle\Psi_1|)$$

where  $|\Psi_0\rangle$  and  $|\Psi_1\rangle$  denote the ground state and the excited state in the same spin subspace of the lowest energy state, respectively. In this way it is expected that the excited state information is recorded in the target state. For a correlation function, the evaluation depends on whether the corresponding two sites belong to the same block or not. In our work we also circulate the up spin electron number from 0 to the total electron number  $L$  in the case of half-filling and hole-doping to search for the subspace where the ground state and the first excited state are



**Figure 2.** The spin correlation function  $\langle S_{R_1} \cdot S_i \rangle$  with the total site number  $N = 20$  and electron–phonon coupling  $\lambda = 0.3$ .

located. Finally, the spin correlation function, the energy gap of the system and other related properties can be calculated by means of the ground state wavefunction after a few iterations of the finite DMRG algorithm. In addition, to check the accuracy of our calculations, we have carried out a DMRG calculation with 120 density matrix eigenvectors reserved after the energy converges for this truncation. The estimated truncation error is typically of the order of  $10^{-5}$ – $10^{-6}$  and the convergence precision of the energy is about  $10^{-6}$ – $10^{-9}$ . We have checked the accuracy of our DMRG calculations by comparing with the results of numerical exact diagonalization of 10 sites.

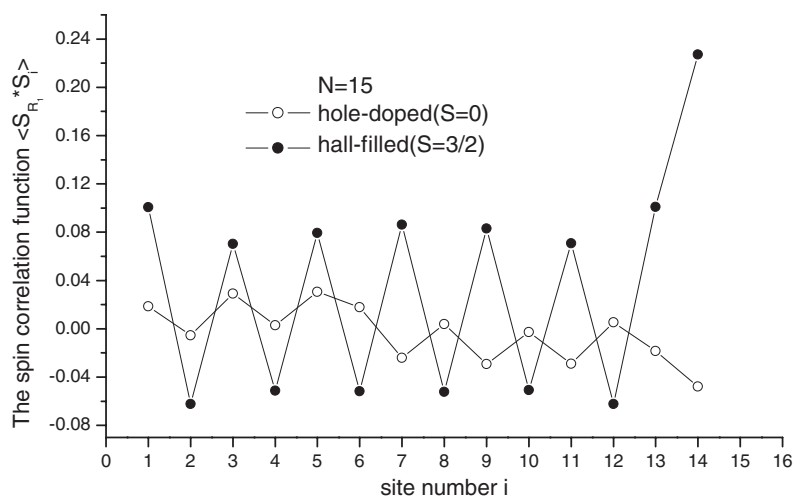
### 3. Results and discussions

Our studies are divided into two aspects:

- (1) the spin alignment by the ferromagnetic coupling between the  $\pi$ -electron and the radical in a purely organic  $\pi$ -conjugated spin system, and
- (2) the mechanism of an electronically controllable spin system for a high-spin hyperstructured molecule.

We have calculated the spin–spin correlation function, the energy gap and the dimerization  $y(i)$ , up to a maximum system size of 30 sites for  $\lambda$  values ranging from 0.1 to 0.5 by employing the finite system DMRG algorithm. In the whole calculation the Hubbard electron–electron interaction  $u$  is taken from 0.0 to 5.0 and  $J$  is set 1, which represents a relatively weak ferromagnetic intramolecular interaction [3].

First we discuss the spin–spin correlation function of one localized spin and other spins along the main chain and between two local spins. The results are shown in figures 2 and 3. From the two figures, it can be seen that the parity of the site number between the two side radicals and the hole-doping change to the spin alignment configurations. In the case of the half-filling system with even sites, the ground state is a spin singlet ( $S = 0$ ); when a hole is added to the system, the doped ground state is a spin quartet ( $S = 3/2$ ). It is also obvious to see the antiferromagnetic spin alignment for the half-filling case is mediated by the chain.

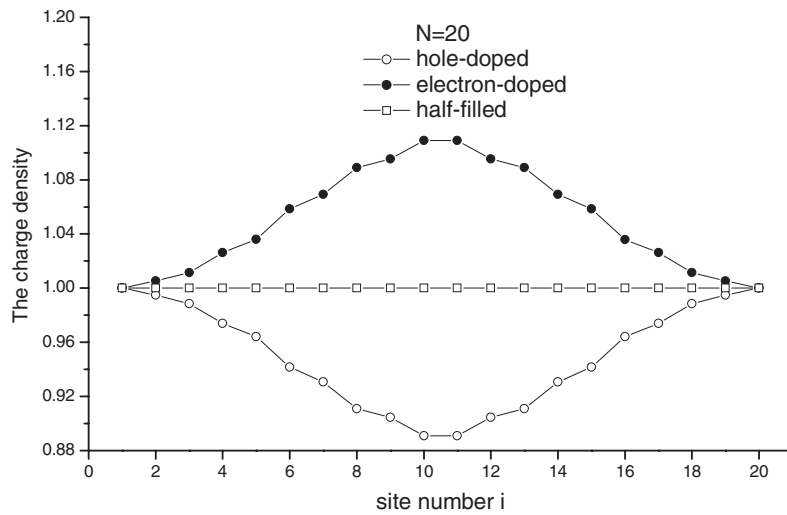


**Figure 3.** The spin correlation function  $\langle S_{R_1} \cdot S_i \rangle$  with the total site number  $N = 15$  and electron–phonon coupling  $\lambda = 0.3$ .

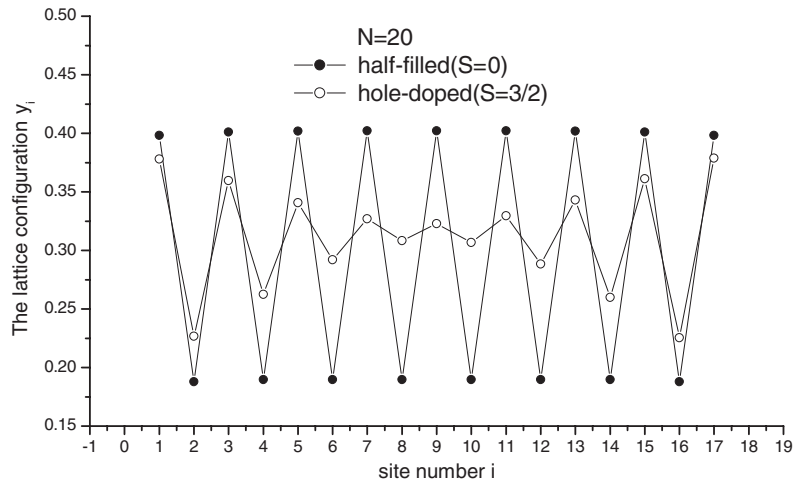
This is due to the spin polarization mechanism with the ferromagnetic correlation between the electron spins and the localized spin [4, 9]. For the ground state with odd sites, the spin quartet ( $S = 3/2$ ) becomes a spin singlet ( $S = 0$ ) when adding a hole into the half-filling system. Recent researchers also reported experimentally the first observation of a purely organic excited quartet ( $S = 3/2$ ) state and a quintet ( $S = 2$ ) state in  $\pi$ -conjugated spin systems [9]. It is suggested that the result is due to the spin alignment through  $\pi$ -conjugation between dangling stable radicals and the excited triplet ( $S = 1$ ) state of a phenyl- or diphenylanthracene derivative. Another study [10] indicated that the ground state triplet signals can be derived from the cation radicals of the donor radicals from ESR spectra of the singly oxidized donor radicals, the main reason is the presence of the ferromagnetic coupling between the generated  $\pi$ -spin and the localized unpaired electron on the radical unit. So the spin–spin correlation through  $\pi$ -conjugation and the ferromagnetic coupling play an important role for spin alignment in an organic spin system.

To further understand the spin alignment in  $\pi$ -conjugated spin systems, the charge density distribution is given as shown in figure 4. We can see that the charge density is uniformly distributed for the half-filling system with the total site number 20, and it is below 1 for the hole-doped system, and above 1 for the electron-doped system. So we think that doping has a collective effect on the system and alters the electron density mainly in the middle of the spin chain.

In order to study the stability of the high-spin ground state by electronically doping, we calculate the dimerization of the system along the main chain. The dimerization accompanied by a Peierls transition is also a unique feature in a one-dimensional system. In figure 5 we present the lattice configuration of the system with even sites. It can be seen that the half-filled system has a perfect dimerization duo to the Peierls instability while the hole-doped system exhibits weak lattice deformation especially around the middle of the lattice. It is believed that the electron–lattice interactions have an impact on the spin stability of the ground state [11, 12]. We also give the slightly different lattice configuration for the half-filled case of  $N = 30$  in figure 6 with a small electron–phonon coupling constant  $\lambda = 0.1$ . The strong dimerization on both sides is attributed to the effect of the localized spins.

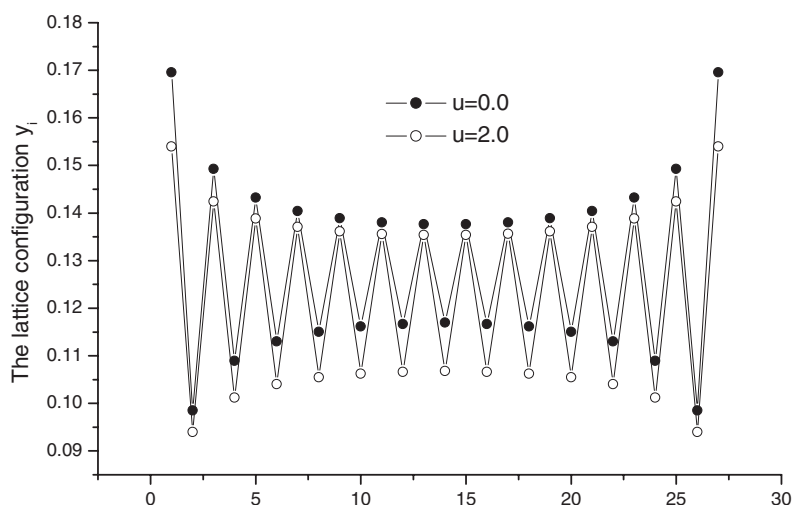


**Figure 4.** The charge density distribution for half-filled and doped cases with total site number  $N = 20$ .

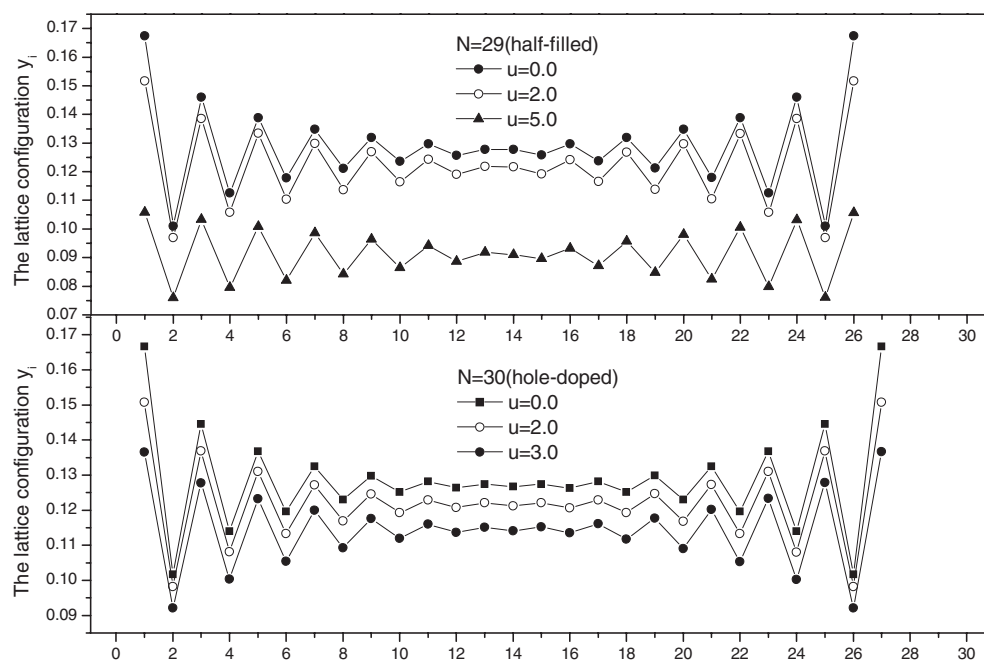


**Figure 5.** The lattice configuration  $y(i)$  along the main chain with electron–phonon coupling  $\lambda = 0.3$  and  $N = 20$ .

Next we discuss the effect on the ferromagnetic stability for different electron–electron ( $e$ – $e$ ) interaction and electron–phonon coupling. In figures 7 and 8 we show the dimerization and the spin–spin correlation function with different  $e$ – $e$  interaction for the half-filled case of  $N = 29$  and the hole-doped case of  $N = 30$ . It can be seen that these two systems have similar properties. The  $e$ – $e$  interaction increases the strength of the spin–spin correlation and decreases the dimerization. So the  $e$ – $e$  interaction is favourable for the ferromagnetic stability of the system. In addition, we also give the dependence of the energy gap and spin–spin correlation function on the electron–phonon coupling parameter  $\lambda$  for both the half-filled and the doped cases. From figure 9 it can be seen that the first excited state is in different spin subspace from the ground state. The electron–phonon coupling decreases the energy gap between the singlet



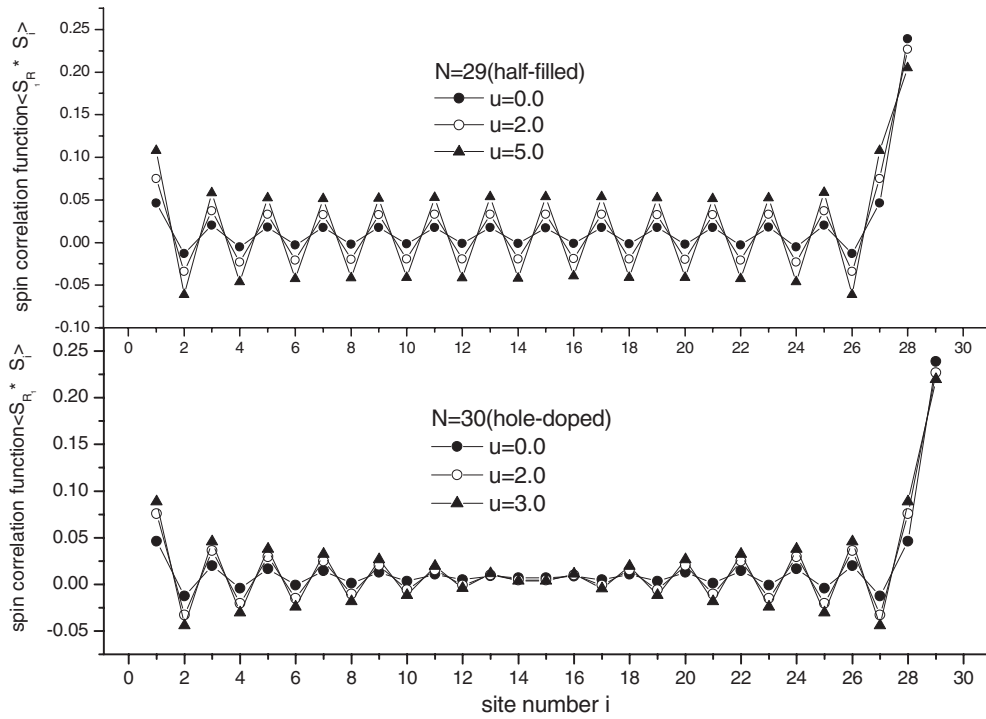
**Figure 6.** The lattice configuration  $y(i)$  along the main chain with electron–phonon coupling  $\lambda = 0.1$ ,  $N = 30$ ,  $u = 0.0$  and 2, respectively.



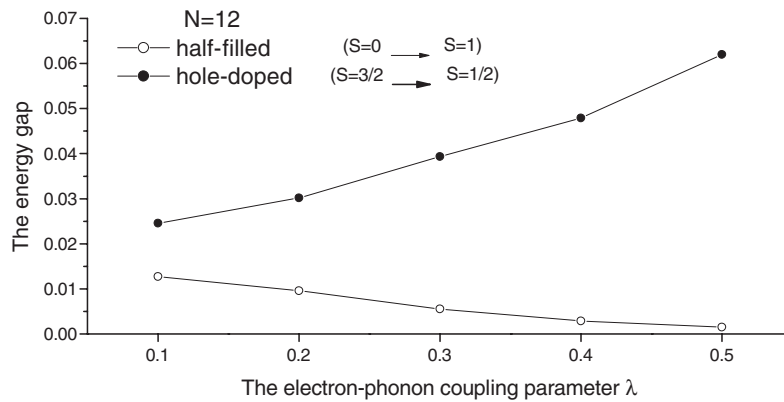
**Figure 7.** The lattice configuration  $y(i)$  along the main chain with electron–phonon coupling  $\lambda = 0.1$  for the half-filled  $N = 29$  and the hole-doped  $N = 30$  cases.

ground state and the excited state to zero value. However for the hole-doped even system, the energy gap between the quartet ground state and the doublet excited state gradually increases with the increase of  $\lambda$ . So it is argued that weak electron–lattice coupling is favourable to achieve stable spin alignment by electronic doping. In figure 10 we show the spin correlation as a function of  $\lambda$  for system sizes 12 and 20, respectively. It is found that the spin correlation





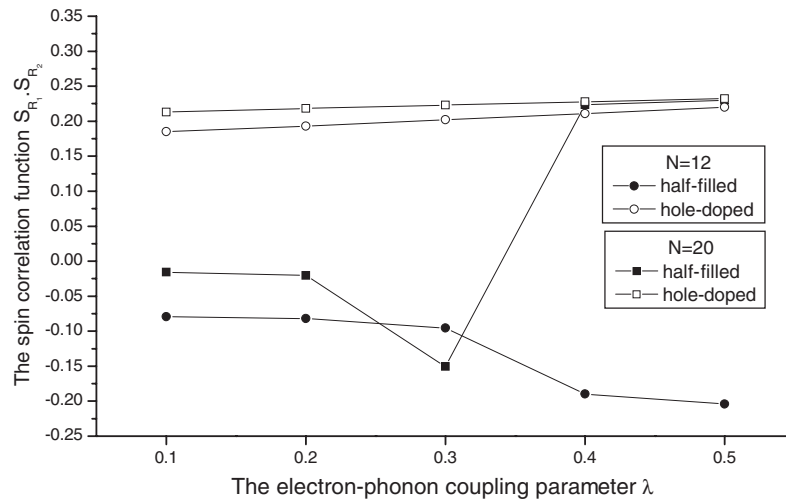
**Figure 8.** The spin correlation function  $\langle S_{R_1} \cdot S_i \rangle$  with the electron–phonon coupling  $\lambda = 0.1$  for the half-filled  $N = 29$  and the hole-doped  $N = 30$  cases.



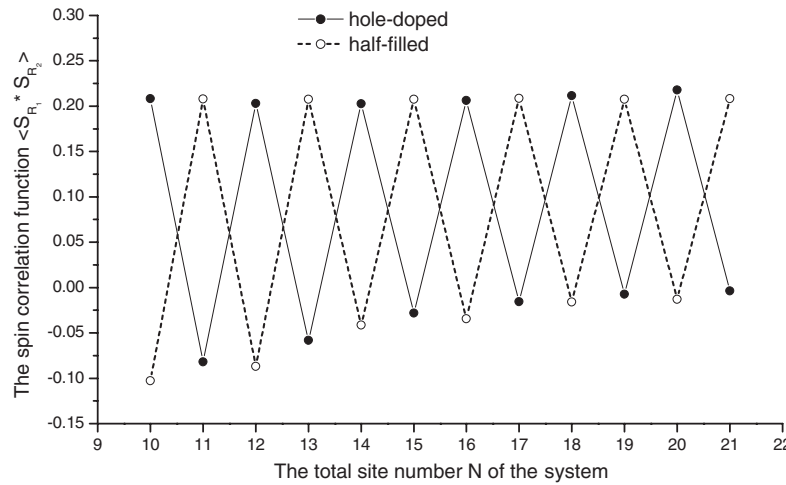
**Figure 9.** The energy gap between the ground state and the first excited state as a function of electron–phonon coupling  $\lambda$ .

becomes stronger for weak  $\lambda$ . This result is consistent with figure 9. But too large electron–phonon coupling  $\lambda$  will destroy the intrinsic spin alignment as shown in the 20 site case. So larger system size needs smaller  $\lambda$  for the stable spin alignment of organic spin systems.

At last, we discuss the size effect on the spin alignment. Figures 11 and 12 show the correlation between the localized spins and the energy with respect to the total site number  $N$  of the system. The electron–phonon coupling  $\lambda$  is set 0.3. For the half-filled system, the

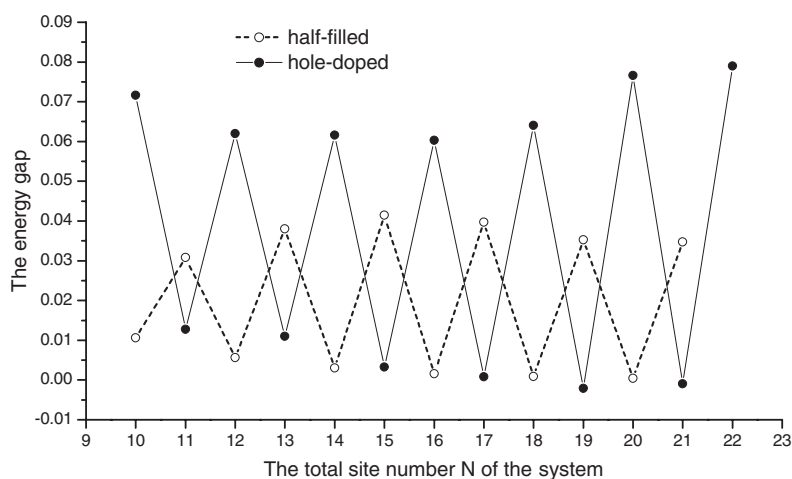


**Figure 10.** The spin correlation between two localized spins as a function of electron-phonon coupling  $\lambda$  for systems  $N = 12$  and  $20$ .



**Figure 11.** The spin correlation between two localized spins versus the total site number  $N$  of the system with electron-phonon coupling  $\lambda = 0.3$ .

spin correlation conforms to the result of the mean-field theory [13], and the spin alignment of the two localized spins located on both ends turns from antiparallel to parallel when the total site number  $N$  changes from even to odd, as expected from the spin polarization mechanism. However for the hole-doping case, the aforementioned spin alignment turns from parallel to antiparallel when the total site number  $N$  changes from even to odd. Furthermore, it is found that the spin correlation and the energy gap decrease and approach zero in the half-filled even case and the hole-doped odd case with the increase of the system size. However in the half-filled odd case and the hole-doped even condition, there is strong ferromagnetic correlation and a large energy gap in  $\pi$ -conjugated spin systems regardless of the size of the system involved in our discussion. So it can be deduced that the spin correlation and the energy gap disappear for relatively long half-filled even and hole-doped odd systems.



**Figure 12.** The energy gap between the ground state and the first excited state versus the total site number  $N$  of the system with electron–phonon coupling  $\lambda = 0.3$ .

#### 4. Conclusions

Intramolecular spin alignment and the exchange interactions through  $\pi$ -conjugation in purely organic spin systems are quite important in the field of molecule-based magnetism. In this paper we have studied the spin alignment mechanism in the simplified Hubbard model, which includes a one-dimensional main chain with two side radicals on both ends of the system. By use of the finite DMRG method with open boundary conditions, it is concluded that the topological nature of the  $\pi$ -electron and the ferromagnetic coupling between the  $\pi$ -electrons and the localized spin play an important role in spin alignment for organic spin systems. The electron–electron interaction is in favour of the stability of high-spin systems. It is also found that in the half-filled odd case and the hole-doped even case, there exist strong ferromagnetic correlation and a large energy gap in the  $\pi$ -conjugated spin systems. Our study will provide a theoretical basis for designing and preparing high-spin organic molecular materials.

#### Acknowledgments

This work was supported by the National Natural Science Foundation of China through grant nos 90103034 and 10174023.

#### References

- [1] Murray M M, Kaszynski P, Kaisaki D A, Chang W H and Dougherty D A 1994 *J. Am. Chem. Soc.* **116** 8152–61
- [2] Anderson K K and Dougherty D A 1998 *Adv. Mater.* **10** 688–69
- [3] Izuoka A, Hiraishi M, Abe T, Sugawara T, Sato K and Takui T 2000 *J. Am. Chem. Soc.* **122** 3234
- [4] Huai P, Shimoi Y and Abe S 2003 *Phys. Rev. Lett.* **90** 207203
- [5] White S R 1992 *Phys. Rev. Lett.* **69** 2863
- [6] White S R 1993 *Phys. Rev. B* **48** 10345
- [7] Noack R M, White S R and Scalapino D J 1994 *Phys. Rev. Lett.* **73** 882
- [8] Cheranocskii V O and Ozkan I 2001 *J. Magn. Magn. Mater.* **232** 156–62
- [9] Teki Y, Miyamoto S, Iimura K, Nakatsuji M and Miura Y 2000 *J. Am. Chem. Soc.* **122** 984
- [10] Sakurai H, Izuoka A and Sugawara T 2000 *J. Am. Chem. Soc.* **122** 9723
- [11] Duan Y F and Yao K L 2001 *Phys. Rev. B* **63** 134434
- [12] Wang W Z, Yao K L and Lin H Q 1997 *Chem. Phys. Lett.* **274** 221
- [13] Fang Z, Liu Z L, Yao K L and Li Z G 1995 *Phys. Rev. B* **51** 1304