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Study on the ferrimagnetic ground state of a phenylene molecule chain

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Abstract

The properties of the ferrimagnetic ground state of an *m*-phenylene molecule chain are studied with the Hubbard model. Within mean-field theory, the ferrimagnetic ground state with a total spin $S = 1$ per unit cell is obtained. The result shows that if the on-site electron–electron repulsion U at the radical sites and U_0 at the phenylene ring sites are different, the energy gap may disappear and the ferrimagnetic ground state becomes unstable. The spin configuration exhibits that the ferrimagnetic ground state results from the antiferromagnetic correlations between the nearest neighbors. Due to the cooperation and competition between the hopping integral and the on-site repulsion at different sites, the charge density and spin density can transfer between the radical sites and the phenylene ring sites.

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Keywords: Phenylene molecule; Ferrimagnetism; Spin density; Charge density

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1. Introduction

In the past decades, there have been increasing interests in magnetic interaction in organic solid since the synthesis of some organic molecule-based ferromagnetic compounds such as *p*-nitrophenyl nitronyl nitroxide (*p*-NPNN) [1–3], dupeyredioxyl (DTDA) [4–6], and 3-(4-chlorophenyl)-1,5-di-methyl-6-thioxoverdazyl (*p*-CDTV) [7]. Because these materials only consist of light elements such as H, C, N, and O, which do not involve spins of either d or f electrons in common ferromagnetic materials, the mechanism of ferromagnetism in organic polymers containing only π-electrons is, therefore, considerably challenging. McConnell [8] first proposed an intermolecular ferromagnetic interaction in organic molecules, which was based on the stacking of organic radicals. Nasu [9] investigated a quasi-one-dimensional (quasi-1D) organic ferromagnet called *m*-PDPC using a periodic Kondo–Hubbard model. With Hartree–

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Fock approximation (HFA), the ferromagnetic ground state has been obtained. For *p*-NPNN, ferromagnetic interaction is introduced by stable free radicals with localized spin structures [1]. The ferromagnetic behavior was described using the one-dimensional Heisenberg model [10]. For poly-BIPO[1,4-bis-(2,2,6,6-tetramethyl-4-piperidyl-butadiin], a simplified zigzag structure consisting of carbon atoms in the main chain and the side radicals was proposed [11]. Both π-electron in the main chain and the unpaired electron in the radicals were assumed to be localized and the ferromagnetism is attributed to the antiferromagnetic correlation between the neighboring spins. For this zigzag structure, the Kondo–Hubbard model or Hubbard model were also proposed and the ferromagnetic ground state was studied in HFA [12,13]. In recent articles [14–16], a polymer with bipartite lozenge lattice is also studied by means of HFA, the exact diagonalization, Monte Carlo simulation, rigorous theorem, and the cluster perturbation theory. The behaviour of the ferrimagnetic ground state have been studied in detail.

Among molecule-based magnetic compounds, polyradicals comprised of *m*-phenylene-bridged organic radicals are well known as building blocks of organic ferromagnets [17]. Experimentally, studies of magnetic interactions [18–23] show that some well-known organic magnetic molecules with the ferro(antiferro)magnetic ground state contain phenylene-bridged organic polyradicals. Theoretically, density function study of ferromagnetic interaction has been performed for *m*-phenylene molecules with various organic radical groups at *meta* position. The *meta*-isomers have usually more stable high-spin states with a parallel spin configuration than low-spin states with an antiparallel spin configuration between radical sites. Hence, organic high-spin dendrimers and polymers with the ferromagnetic ground state can be designed by linking various radicals through an *m*-phenylene unit. In order to confirm the possibility of designing this kind of ferromagnetic polymer, in this paper, we will study a simplified organic structure shown in Fig. 1, which is based on poly-(para)phenylene substituted at the meta-position by radicals. Generally, each of sites 2, 5 and 7 connects to an atom H, and each of the radical sites 4 and 8 is an atom group such as CH_2, NH, etc. We assume π-electron on the phenylene ring and unpaired electron on the radical sites are not completely localized and can be itinerant in this structure. The electron–electron correlation will be taken into account by the Hubbard model in this article. Although the molecules such as that in Fig. 1, have not been synthesized so far, we believe that the general studies of the ferromagnetism in this model structure can exhibit some interesting physics. In Fig. 1, the on-site repulsion U_0 at the phenylene ring may be quite different from U at the side radicals. The results in HFA show that in a large range of $U \neq U_0$, the spin is still $S = 1$ although the charge distribution is not homogeneous. But if U is much smaller than U_0, and the hopping integral t between the phenylene ring sites and the radical sites is smaller than t_0 between the phenylene ring sites, the ground state with spin $S = 1$ is unstable. The spin configuration shows that the antiferromagnetic correlation is different for different bonds and results in an unsaturated average spin.

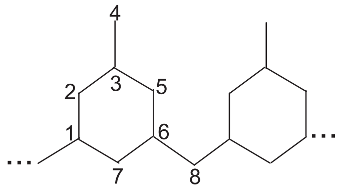

Fig. 1. An *m*-phenylene molecule chain with radicals.

The model Hamiltonian and the computational method will be given in the following section. In Section 3 we study the ground state, the phase diagram, the distribution of spin density and charge density. Finally, we summarize our results.

2. Model and computational method

The Hamiltonian is written as

$$H = -\sum_{\langle i,j\rangle,\sigma} t_{ij}(c^{\dagger}_{i,\sigma}c_{j,\sigma} + \text{h.c.}) + \frac{1}{2}\sum_{i,\sigma} U_i(n_{i,\sigma}n_{i,-\sigma}) + \sum_{i,\sigma} \mu_i n_{i,\sigma}. \quad (1)$$