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The gapless energy spectrum and spin-Peierls instability of 1D Heisenberg spin systems in polymeric complexes of transition metals and hypothetical carbon allotropes

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Abstract

We investigate the spin-Peierls instability of some periodic 1D Heisenberg spin systems having a gapless energy spectrum at different values of coupling J between the unit cells. Using the density-matrix renormalization group method we numerically study the dependence of critical exponents p of spin-Peierls transition of above spin systems on the value of J . In contrast to chain systems, we find significantly non-monotonous dependence $p(J)$ for three-legs ladder system. In the limit of weak coupling J we derive effective spin s chain Hamiltonians describing the low-energy states of the system considered by means of perturbation theory. The value of site spin s coincides with the value of the ground-state spin of the isolated unit cell of the system considered. This means that at small J values all the systems with the singlet ground state and the same half-integer value of s should have a similar critical behavior which is in agreement with our numerical study. The presence of gapped excitations inside the unit cells at small values of J should give, for our spin systems, at least one intermediate plateau in field dependence of magnetization at low temperatures. The stability of this plateau against the increase of the values of J and temperature is studied using the quantum Monte-Carlo method.

Keywords: low-dimensional magnets, Heisenberg spin Hamiltonian, spin-Peierls transition

(Some figures may appear in colour only in the online journal)



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1. Introduction

Quasi-1D materials like polymeric complexes of transition metals have attracted much attention due to their interesting physics and potential technological applications [1]. Another very promising direction of nano-engineering is the tuning of electronic and magnetic properties of low-dimensional carbon allotropes' fragments (graphene nanoribbons) through a partial substitution of carbon atoms in the corresponding network by various dopants [2, 3]. The graphene nanoribbons can also serve as components of numerous carbon allotropes as described in the recent survey [4] and in an extensive database [5] (unfortunately, the latter does not contain information about magnetic properties of the allotropes).

All these materials belong to the class of strongly correlated electron systems. This means that some of its properties cannot be described correctly in the frame of (effective) one-particle approximations like Hartree-Fock or DFT methods—those routinely implemented in all solid state quantum chemistry packages available to the students in the field [6]. The 1D extended electron systems may become unstable against the spin-Peierls transition (SPT), which leads to the distortion of the lattice structure (dimerization) and opening of an energy gap in the lowest energy excitation spectrum. The adequate description of this phenomenon requires thorough accounting of electron correlation effects and is a difficult problem, generally unresolved yet. Only for a uniform spin $s = 1/2$ Heisenberg chain there is a detailed trustable study of the instability against the dimerization on the base of density matrix renormalization group (DMRG) calculations [7].

In this work, we studied the energy spectrum and field dependence of magnetization of a special type of the Heisenberg spin systems on 1D lattices formed by interacting n -site unit cells each having a non-degenerate ground state with non-zero spin s_0 (except the trivial $2s_0 + 1$ degeneration).

For the case of weak interaction between unit cells we gave a detailed analysis of the lowest part of the excitation spectrum based on perturbation theory (PT) and the extended Lieb–Schultz–Mattis (LSM) theorem [8–11]. For the systems with half-integer value of the ground state spin of the isolated unit cell we established the existence of two types of lowest excitations: gapless and gapped. Such a character of the energy spectrum results in an intermediate plateau in the field dependence of the total magnetization at low temperatures. If, in addition, the whole system has a singlet ground state, it is unstable against the transition to the doubled unit-cell size (zero temperature SPT). On the other hand, we established the absence of such instability for the systems with macroscopic ground state spin (respectively, ferromagnetic or ferrimagnetic). As for an intermediate magnetization plateau, one of the well-known and studied examples of such a system is the strong coupling limit of the three-legs spin $s = 1/2$ ladder [12, 13]. This plateau is also a usual feature of 1D ferrimagnets [14] and some frustrated spin systems [15].

We also studied numerically the dependence of the lowest energy states of our model spin systems on the value of the interactions between the unit cells by means of finite and

infinite schemes of the DMRG method. On the basis of this numerical study we estimate critical exponents for the systems' ground-state energy in the context of possible spin-Peierls instability. In addition, we studied the dependence of intermediate magnetization plateau size on the interaction between the unit cells by the exact diagonalization for small lattice clusters and by the quantum Monte-Carlo method (QMC) based on stochastic series expansion approach [16].

Unfortunately, the last approach does not work properly for frustrated spin systems.

2. Model: Heisenberg spin Hamiltonians

Let us consider a model spin system on a periodic lattice formed by n -site unit cells, described by the following Heisenberg spin Hamiltonian

$$\mathbf{H} = \sum_{i=1}^N \mathbf{H}_i + \sum_{i=1}^{N-1} \mathbf{H}_{i,i+1}, \quad (1)$$

$$\mathbf{H}_i = \sum_{\langle k,l \rangle} J_{k,l} \mathbf{S}_{i,k} \mathbf{S}_{i,l}, \quad \mathbf{H}_{i,i+1} = \sum_{\langle \bar{k}, \bar{l} \rangle} J_{\bar{k}, \bar{l}} \mathbf{S}_{i,\bar{k}} \mathbf{S}_{i+1,\bar{l}}.$$

Here $\mathbf{S}_{i,k}$ is the spin operator on the k th site belonging to the i th unit cell of the lattice; $\langle k, l \rangle$ means a pair of neighbor sites of the lattice which belongs to the same unit cell; $\langle \bar{k}, \bar{l} \rangle$ corresponds to the interaction between neighboring unit cells through the sites with the numbers $\bar{k}$ and $\bar{l}$.

The finite fragments of some such spin systems formed by three-site unit cells with uniform one-site spins $s = 1/2$ are presented in figure 1.

Let us now assume that the unit cell has a nonzero total spin s_0 and only is $2s_0 + 1$ times trivially degenerate. In the absence of the interaction between the unit cells, the ground state of our system is $(2s_0 + 1)^N$ times degenerate. At specified value of z -projection of total spin M its wave function is a linear combination of the following functions:

$$\Phi_M \{m\} = \prod_{i=1}^N \varphi_{0,i}(m_i), \quad m_i = -s_0, -s_0 + 1, \dots, s_0, \quad M = \sum_{i=1}^N m_i$$

where $\varphi_{0,i}(m_i)$ is the ground-state wave function of i th isolated unit cell with the z -projection of the unit-cell spin m .

The weak interaction between unit cells lifts the degeneracy and can be described in the first PT order in the coupling parameters $J_{\bar{k}, \bar{l}}$ provided $\max(J_{\bar{k}, \bar{l}}) \ll \Delta = \varepsilon_1 - \varepsilon_0$, where ε_0 and ε_1 are the energies of the ground state and first excited state of the isolated unit cell, respectively. Similarly to [17] an application of the Wigner–Eckart theorem [18] leads to the following effective Hamiltonian for the low-energy states of the Hamiltonian (1):

$$\mathbf{H}_{\text{eff}} = N\varepsilon_0 + J_{\text{eff}} \sum_i^{N-1} \mathbf{S}_i \mathbf{S}_{i+1}, \quad J_{\text{eff}} = \sum_{\langle \bar{k}, \bar{l} \rangle} J_{\bar{k}, \bar{l}} \rho_{\bar{k}} \rho_{\bar{l}} \\ \rho_{\bar{k}} = \langle \varphi_{1,k}(s_0) | \mathbf{S}_{1,k}^z | \varphi_{1,k}(s_0) \rangle / s_0, \quad (2)$$

where $\mathbf{S}_i$ is a spin operator of unit cell total spin s_0 .

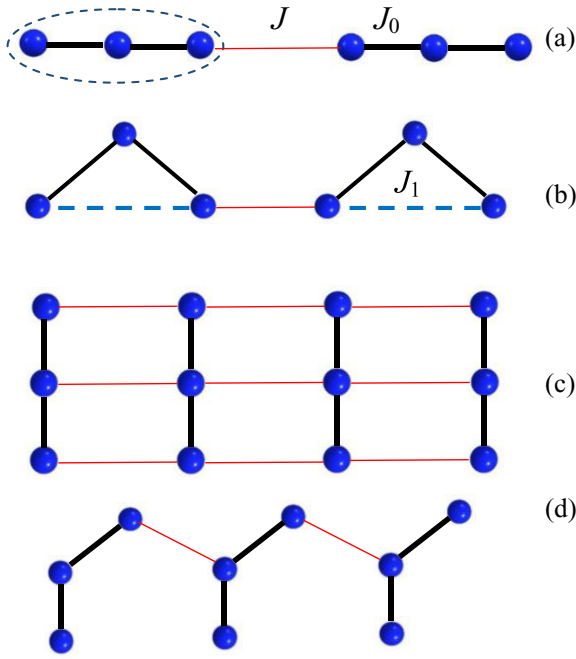


Figure 1. The fragments of 1D spin systems formed by weakly interacting three-site unit cells. Here the coupling parameters J_0 , J and J_1 correspond to black, thin red and dashed blue bonds, respectively. Systems (a), (c) and (d) are bipartite with nondegenerate ground state. For the system in panel (b), we consider only the case $J_0 \neq J_1$ in which the unit cell has a nondegenerate ground state.

Thus, the low-energy excitations of these spin systems with uniform spin coupling between unit cells ($J_{\vec{k},\vec{l}} = J$) are described by the effective spin-1/2 chain Hamiltonian.

$$\mathbf{H}_{\text{eff}} = J_{\text{eff}} \sum_i^{N-1} \mathbf{S}_i \mathbf{S}_{i+1}, \quad (3)$$

where effective coupling takes positive values for the systems depicted in figures 1(a)–(c) with $J_{\text{eff}} = 4J/9, J, J/9$, respectively, and the negative value for the system shown in figure 1(d): $J_{\text{eff}} = -2J/9$.

Note that a similar approach to the study of complex systems by the creation of effective low-energy Hamiltonians was proposed before [19, 20].

According to the Lieb theorem [21] the ground-state spin S_0 of the systems figures 1(a) and (c) takes a minimal value ($S_0 = 0$ for even N) at any values of coupling J . In the case of the system figure 1(d) this theorem gives the ground-state spin $S_0 = N/2$ at any values of J , which is in agreement with above PT treatment (negative sign of J_{eff}). For a frustrated system (like the one depicted in figure 1(b)) the Lieb theorem is not applicable and we may conclude only about the minimal value of S_0 at small values of coupling J . According to the extension of the Lieb–Schultz–Mattis (LSM) theorem [9, 10] all 1D bipartite spin-1/2 systems with odd number of spins in the unit cell have the gapless lowest-energy spectrum. Therefore, in the thermodynamic limit the exact energy spectra of the systems shown in figures 1(a), (c) and (d) have no gap at any value of the interaction between the unit cells.

Note that the system 1(b) can be treated as a linear fragment of an unconventional 2D carbon allotrope formed

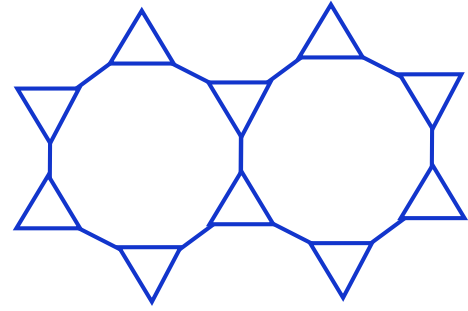


Figure 2. Finite fragments of a hypothetical 2D frustrated carbon network with triangular cycles.

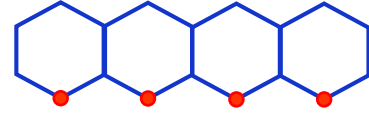


Figure 3. Finite polyacene fragments regularly doped by nonmagnetic heteroatoms (e.g. nitrogens—red balls).

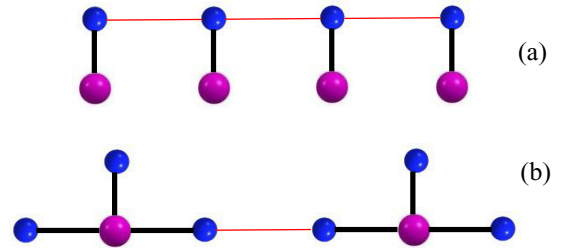


Figure 4. Finite fragments of 1D bimetallic magnets described by the Hamiltonian equation (3), which correspond to systems with 2-site (a) and 4-site (b) unit cells, respectively.

by the interacting triangular carbon cycles [22, 23] (see figure 2)—another unfortunate omission in the database [5]. At $J = 1$ the system 1(d) has the same magnetic sublattice as one of the simplest representatives of doped graphene nanoribbons—polyacene molecule with regularly distributed nonmagnetic heteroatoms as shown in figure 3.

It can be shown that the Hamiltonian equation (3) also describes the low-energy spectra of some bimetallic magnets having two types of site spins. The corresponding magnetic sublattices are shown on figure 4, where the small blue balls correspond to on-site spins $s_1 = 1/2$ and the big crimson balls correspond to the on-site spins $s_2 = 1$.

According to the extended Lieb theorem [24, 25] the ground-state spin of the unit cells for these systems equals 1/2.

The PT analysis gives for the system shown in figure 4(a) $J_{\text{eff}} = J/9$ and for that in figure 4(b) $J_{\text{eff}} = 25J/81$.

These two systems have even number of spins per unit cell. According to the extension of the LSM theorem [11], these systems have a gapless low-energy spectrum if the ground state of the isolated unit cell spin has a half-integer spin. Thus, the spin chains with pendant spins shown in figure 4 have gapless energy spectra at arbitrary interaction between the unit cells.

Note also that for $s_2 > 1$ the low-energy excitations of the system (4a) are described by the spin-chain Hamiltonian of type (3) with on-site spins $s = s_2 - 1/2$ and effective coupling

$J_{\text{eff}} = J \left(\frac{2s_2-1}{2s_2+1} \right)^2$. Similar consideration for the system (4b) yields the effective spin-chain Hamiltonian with on-site spins $s = |s_2 - 3/2|$ and effective coupling $J_{\text{eff}} = J \left(\frac{2s_2-3}{2s_2-1} \right)^2$.

The gapless energy spectrum of the bipartite systems with half-integer value of the ground-state spin of the unit cell s_0 may lead to their instability against the spin-Peierls transition if the corresponding gapless excitations have the spin S_0 and proper space symmetry. Therefore, according to the above PT analysis we may state that our systems have critical properties in the limit of small J only if the effective coupling J_{eff} is positive (all the above systems, except the case depicted in figure 1(d)). The detailed DMRG study of the critical behavior of the $s = 1/2$ linear alternating antiferromagnetic spin chain performed in [7] gives the critical exponent for the ground state energy per spin $p \approx 1.45$. The gapless character of the exact energy spectra of our 1D bipartite systems with the singlet ground state at any values of the coupling J may lead to similar criticality, and it is of interest to study the effect of increasing J on the critical exponents of above spin systems.

In the limit of weak coupling between the unit cells, all above periodic spin systems have two types of excitations. The first one is described by the antiferromagnetic spin-1/2 chain Hamiltonian. These excitations correspond to the value of total spin $S_1 \leq Ns_0$. Due to the finite size of fragments, there are also gapped excitations with the characteristic spin quantum number $S_2 = Ns_0 + 1$. Thus, at low temperatures the weak external magnetic field may increase the total system magnetization up to $M = S_1$. Further increase of M will be possible only due to the gapped excitations inside the fragments. In other words, our spin model should have at least one intermediate plateau in the field dependence of its magnetization at low temperatures. The increase of the interactions between the unit cells may change significantly the energy spectra of the above systems and destroy the intermediate magnetization plateau. We show the results of our numerical studies of this possibility numerically by QMC and exact diagonalization methods in the next section.

3. Numerical study

All the numerical calculations were carried out in dimensionless units, so, Boltzmann constant $k_B = 1$. Besides, intra-cell coupling parameters $J_0 = 1$ and $J_1 = 0.5$.

In order to study the possibility of the spin-Peierls transition in the periodical spin systems shown in figures 2 and 3 we consider a modified Hamiltonian equation (1) with the doubled unit cell.

$$\mathbf{H} = \sum_{i=1}^N \mathbf{H}_i + J \sum_{i=1}^{N-1} \left(1 + (-1)^i \delta \right) \mathbf{H}_{i,i+1}, \quad (4)$$

$$\mathbf{H}_i = \sum_{\langle k,l \rangle}^n \mathbf{S}_{i,k} \mathbf{S}_{i,l}, \quad \mathbf{H}_{i,i+1} = \sum_{\langle \bar{k}, \bar{l} \rangle}^n \mathbf{S}_{i,\bar{k}} \mathbf{S}_{i+1,\bar{l}}.$$

Let $E_o(\delta)$ be the non-degenerate ground state energy of the Hamiltonian (4). For the systems with the open ends the

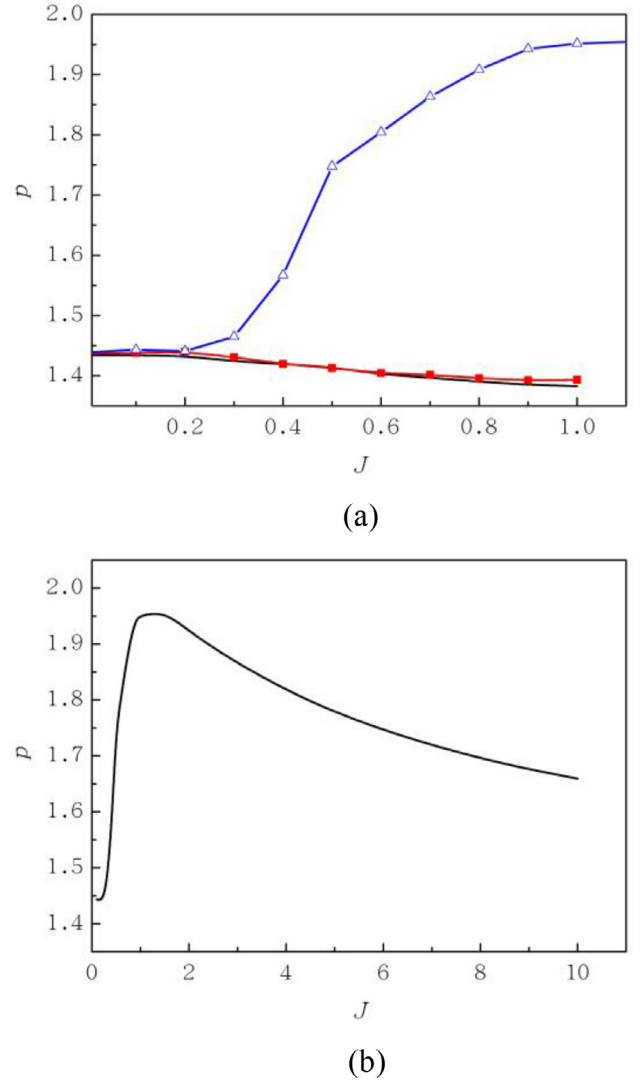


Figure 5. (a) The dependence of critical exponents for the ground state energy of the models shown in figure 1(a)—black curve, figure 1(b)—red boxes and figure 1(c)—blue triangles, on the value of the coupling parameter J ; (b) critical exponent $p(J)$ for the ladder model ground state energy shown in figure 1(c) in a wide region of the couplings J .

quantity $\Delta E = [E_o(\delta) + E_o(-\delta) - 2E_o(0)]/2$ does not depend on the sign of δ . It can be treated as the magnetic energy gain of the dimerized ground state with respect to the uniform ground state. The spin-Peierls instability of the corresponding periodic system in the thermodynamic limit can be associated with the dependence $\Delta E \sim |\delta|^p$, $1 < p < 2$ [7]. In order to estimate the values of critical exponent p we used finite and infinite algorithms of DMRG method at $0.1 \leq J \leq 1$ for five values of the parameter δ . Average number of optimized states in both approaches was equal to 50. The results of this study for the systems (a), (b) and (c) (see figure 1) are shown in figure 5.

In the limit of weak interaction between the unit cells all these systems have the lowest excitation spectra described by the Hamiltonian equation (3). Therefore for $J \ll 1$; $p \approx 1.45$, which is in a perfect agreement with our numerical simulation.

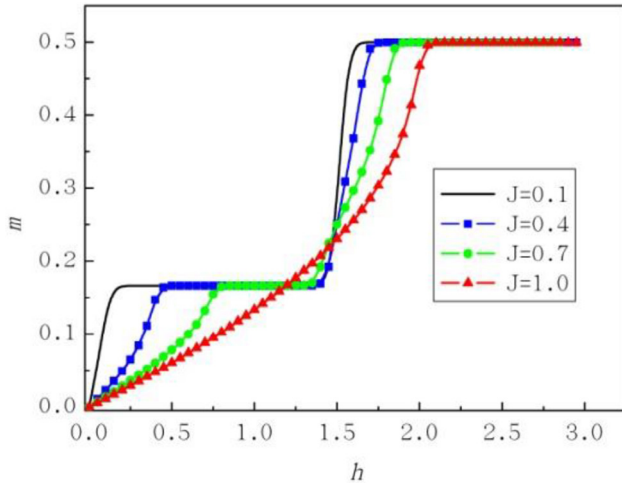


Figure 6. Intermediate plateau in the field dependence of magnetization per spin m for the system figure 1(a) at different values of coupling between unit cells J (in units of J_0).

It is of interest that for the three-legs ladder model the lowest excitation spectrum is described by the spin-1/2 chain Hamiltonian in two cases: at small values of J and in the limit $J \rightarrow \infty$ (in the last case we have a system of three isolated spin-1/2 chains). We performed the DMRG simulation for the spin-ladder model with $J > 1$ and found the decrease of the accuracy of this study in comparison with the case of weak interactions between ladder rings.

The resulting three-legs ladder model demonstrates significantly nonlinear dependence of the critical exponent p as a function of coupling J in agreement with above PT analysis. The maximum of $p(J)$ corresponds to maximal stability of the three-legs spin-ladder model against the dimerization (zero temperature spin-Peierls transition).

In order to check the accuracy of our DMRG numerical scheme we also estimated the critical exponent for the system (1d) with $J = 1$. In this case, due to the gapped character of the lowest excitations with total spin $S = S_0$ [26], we should have an analytical behavior of the quantity ΔE as a function of dimerization parameter δ , which corresponds to $p = 2$. Our DMRG study with 100 optimized states gave the estimate $p \approx 1.992$.

Now, let us consider the effect of the increase of coupling between unit cells on the intermediate plateau in field dependence of magnetization of the proposed 1D spin models. For the system figure 1(a) with the uniform on-site spins $s = 1/2$ we used the QMC method based on the stochastic series expansion approach [16], which permit us to consider rather large lattice clusters. In figure 6 we show the decrease of the plateau width on increasing the coupling J for the system in figure 1(a) at a temperature $T = 0.02J_0$ and system size $N = 150$ spins. A similar effect (not shown) was found for the system in figure 1(c) with $N = 300$ spins at the same temperature. Moreover, the increase of temperature destroys the intermediate magnetization plateau, as shown in figure 7 for the system in figure 1(a).

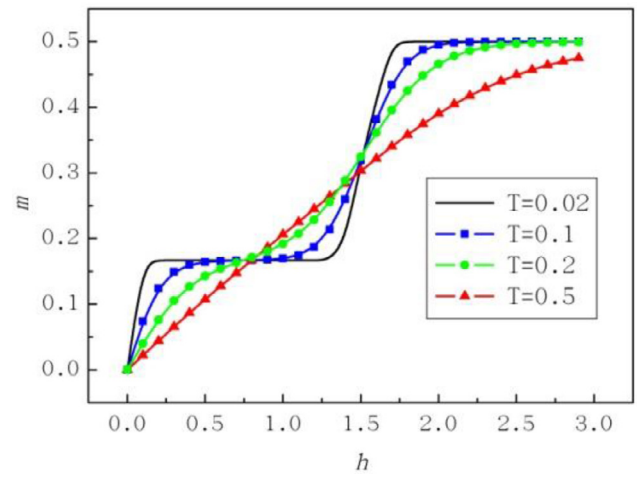


Figure 7. Intermediate plateau in the field dependence of the magnetization per spin m for the system figure 1(a) at different values of temperature (in units of J_0) and $J = 0.1J_0$ ($N = 150$ spins).

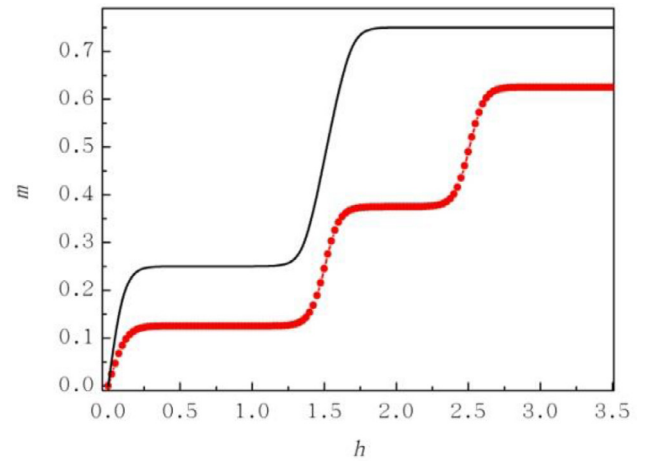


Figure 8. Field dependence of magnetization per spin m for systems (4a)—black curve and (4b)—red circles at the coupling $J = 0.1J_0$ and temperature $T = 0.05J_0$.

For the system (4b) with $s_2 = 1$ there are three excited states of isolated unit cells with total spin $S = 3/2$ and one excited state with $S = 5/2$. According to the above analysis, this leads to the appearance of two intermediate magnetization plateaus at small values of coupling J and low temperatures. Unfortunately, for the mixed spin systems shown in Figures 4(a) and (b) the QMC did not give reliable results. Therefore, for the simulation of the finite temperature thermodynamics of these models we used the exact diagonalization of small cluster models formed by 8 and 12 spins. The results of our numerical simulation demonstrate very weak dependence of magnetization on cluster size at specified values of parameters. For 12 spins cluster the field dependence of magnetization per spin $m(h)$ is given in figure 8.

We also performed DMRG calculations for the dependence $m(h)$ at zero temperature by means of finite DMRG scheme

(system size is 160 spins and 50 optimized states). The results of this simulation are very close to the above exact diagonalization study and therefore are not presented here.

4. Conclusion

We studied the spin-Peierls instability of the periodic 1D Heisenberg spin systems formed by unit cells having half-integer ground state spin at different values of the coupling J between cells. We suppose that similar to antiferromagnetic spin $\frac{1}{2}$ Heisenberg chain the ground state energies of the systems considered have power law dependence of critical exponents p and estimated these exponents using DMRG calculations. We checked the adequacy of our DMRG approach by the estimation of p for the system (1d) with the macroscopic ground state spin S_0 . According our previous study this spin chain has gapped excitations in the sector $S = S_0$ and is stable against a spin-Peierls transition. Our DMRG estimate $p \approx 1.992$ is in a good agreement with the above conclusion. Gapless character of the energy spectra of the systems considered results also in interesting magnetic behavior at low temperatures like intermediate magnetization plateau. We hope to extend our analysis on more complicated 1D systems like graphene nanoribbons with defects and/or embedded heteroatoms proposed in the seminal work [27].

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