Size-dependent low-energy excitations in an alternating spin-1/spin-$\frac{1}{2}$ antiferromagnetic chain: Spin-wave theory and density-matrix renormalization-group studies

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We study the properties of the ground state and the low-lying excited states of an alternating spin-1 and spin-$\frac{1}{2}$ antiferromagnetic chain with ferromagnetic next-nearest-neighbor coupling with a variety of methods, namely, spin-wave analysis, density-matrix renormalization-group (DMRG) method, and exact-diagonalization method. The ground state of this model with $2N$ spins is ferrimagnetic with the total spin $S_G=N/2$ for all parameter values. In the long chain limit, a gapless excitation is found with characteristics of goldstone mode of the ferromagnetic order with total spin $S=S_G-1$. The lowest gapped excitation, however, exists in the total spin $S=S_G+1$ sector. Interestingly, we find that with the increase in ferromagnetic coupling, spin-wave gapped excitation becomes lower than the massless mode for the large wave numbers. Correspondingly, from DMRG analysis we find that the excitation in the total spin $S=S_G+1$ is lower than that in the total spin $S=S_G-1$ when the size of the chain is short and the ferromagnetic interaction is large. Characteristics of these excitations are also reflected in the low temperature thermodynamic quantities, where the low-energy properties are strongly affected by the system size and the coupling strength.

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The low-dimensional quantum spin systems have attracted much attention in the last decades and have remained in the forefront of research in condensed matter physics. This is primarily because these systems offer a great many variety of exotic quantum phenomena such as spin-Peierls instability and Haldane's conjecture. These properties are difficult to obtain in higher-dimensional analogs. This is particularly due to various topological factors that arise in one dimension. Since Haldane's conjecture,[1] there have been numerous studies on quantum spin chains with antiferromagnetic interactions, where a kind of dimerization, the so-called valence bond solid formation, plays an important role. The effects of the spin anisotropy, competing interactions, etc., have also been extensively studied.[2–9] In parallel, experimental synthesis and characterization of a large class of materials have been carried out, which have provided the support and have raised the quest for more interesting questions. Among these studies, the systems with unique spins and different spins in the unit cell have been found to give rise to novel quantum phases and unusual thermodynamic properties.[10–20] It has also been pointed out that the mixture of ferromagnetic and antiferromagnetic interactions[21–23] provides interesting properties. Many such low-dimensional molecular magnetic structures have also been synthesized.[24,25] Particularly, the systems with different spin magnitudes and topological constraints are very interesting. Most often, these systems contain two transition metal ions in one unit cell. One such class of systems has general formula $AB(\mathrm{pbaOH})(\mathrm{H_2O})_3\cdot 2\mathrm{H_2O}$ with pbaOH=2-hydroxy-1, 3-propylenebis(oxamato) and A, B are the transition metal ions with varying spins (A, B=Cu, Mn, Fe, Co, Ni). The simplest of such systems is $\mathrm{NiCu(pba)(H_2O)_3(2H_2O)}$ with pba=1,3 propylenebis (oxamato),[24,26] where the $S=1$ spin of the Ni^{2+} ion and $S=\frac{1}{2}$ of the Cu^{2+} ion constitute a chain with alternating spins. The zigzag nature of such chains may have antiferromagnetic exchange between nearest neighbors and weak ferromagnetic coupling between distant neighbor spins of the same sublattice. While alternating spin chains with nearest-neighbor antiferromagnetically coupling have been studied extensively, the explicit inclusion of ferromagnetic coupling between the spins of the same sublattice has received scarce attention. The ground state of an alternating spin chain with antiferromagnetic coupling between the nearest neighbors is a ferrimagnet with opposite spins in the sublattices. Inclusion of ferromagnetic interaction seems simply assist the ferrimagnetic order, but we find that it causes different effects in a short range chain. As will be shown later the explicit inclusion of ferromagnetic coupling between the next-nearest-neighbor spins gives rise to a different type of excitations which depends on the system size.

In what follows, we consider a chain of alternating spin-1 and spin-$\frac{1}{2}$ sites, where the nearest-neighbor sites interact antiferromagnetically and the interactions between the next-nearest neighbors are explicitly kept as ferromagnetic. The present model can also be viewed as two ferromagnetic chains of spin-1 and spin-$\frac{1}{2}$ with intrachain coupling constant J' coupled by an antiferromagnetic interchain coupling J. The corresponding Hamiltonian is

$$H=\sum_n J(S_{1,n}\cdot S_{2,n}+S_{2,n}\cdot S_{1,n+1}) - \sum_n J'(S_{1,n}\cdot S_{1,n+1}+S_{2,n}\cdot S_{2,n+1}), \quad (1)$$

where n denotes the number of the unit cell and $S_{1,n}$ and $S_{2,n}$ are spin-1 and spin-$\frac{1}{2}$ sites, respectively, at the unit cell n. The exchange integrals J and J' are both positive. Here, we consider N unit cells with $2N$ spins. The sum is over the total

number of unit cells and we use periodic boundary conditions with $S_{1,N+1}=S_{1,1}$.

We calculate the ground state properties, low-energy excited states, and the thermodynamic quantities by a number of methods, namely, spin-wave theory, exact-diagonalization method, and also the density-matrix renormalization-group (DMRG) methods.

Using the Holstein-Primakoff-type spin-wave theory,[27–29] we analyze the leading order corrections to the classical ground state where the z components of the spin-1 and spin-$\frac{1}{2}$ sites are S_1 and $-S_2$, respectively. By expanding the Hamiltonian up to quadratic order and taking the Fourier transform, followed by the Bogoliubov transformation,

$$c_k = a_k \cosh\,\theta_k + b_{-k}^{\dagger} \sinh\,\theta_k, \tag{2}$$

$$d_k = \hat{b}_{-k} \cosh\,\theta_k + \hat{a}_k^{\dagger} \sinh\,\theta_k, \tag{3}$$

we obtain the spin-wave Hamiltonian in the diagonal form,

$$H = -2NJS_1S_2 - NJ'(S_1^2 + S_2^2) + \sum_k [E_{1k}c_k^{\dagger}c_k + E_{2k}d_k^{\dagger}\hat{d}_k + E_{0k}], \tag{4}$$

where E_{1k} and E_{2k} are two different modes of energies and E_{0k}, the zero-point energy. These are given by

$$E_{1k} = (-S_1 + S_2)[J - J' + J'\cos(k)] + E_k,$$

$$E_{2k} = (S_1 - S_2)[J - J' + J'\cos(k)] + E_k,$$

$$E_{0k} = (S_1 + S_2)[-J + J' + J'\cos(k)] + E_k,$$

where

$$E_k = \sqrt{(S_1 + S_2)^2[J + J' - J'\cos(k)]^2 - 4J^2S_1S_2\cos^2\left(\frac{k}{2}\right)}.$$

We find that the energy E_{1k} is the gapless mode and belongs to the state with total spin $S=S_G-1$, whereas E_{2k} is a gapfull mode and belongs to the state of the total spin $S=S_G+1$.

The dispersion relations for the two excitation modes, E_{1k} and E_{2k}, are plotted in Fig. 1. As can be seen, both E_{1k} and E_{2k} are positive for all the momenta spanning 0 to π. Therefore, the ground state $|\psi_0\rangle$ is given by the state in which $\langle c_k^{+}c_k\rangle=\langle d_k^{+}d_k\rangle=0$. From the energy spectrum of spin-wave analysis, we find that the modes corresponding to the energy E_{1k} are gapless at $k=0$ and E_{2k} are gapped for all values of k with a minimum gap of magnitude $2J(S_1-S_2)$ at $k=0$ for all values of J'. At $k=0$, the energies for both the modes are independent of the J' value since the term containing J' vanishes as $\cos(k)=1$ for $k=0$, which is clear from the given expressions for E_{1k} and E_{2k}. Hence, these energies for both the modes only depend on the J value at $k=0$ and for other values of k it depends on both the parameters J and J'. The energy to the mode E_{1k} increases with J, which suggests that this mode is hardened by the antiferromagnetic interaction. This naturally means that the ferrimagnetic order is supported by both ferromagnetic and antiferromagnetic interactions.

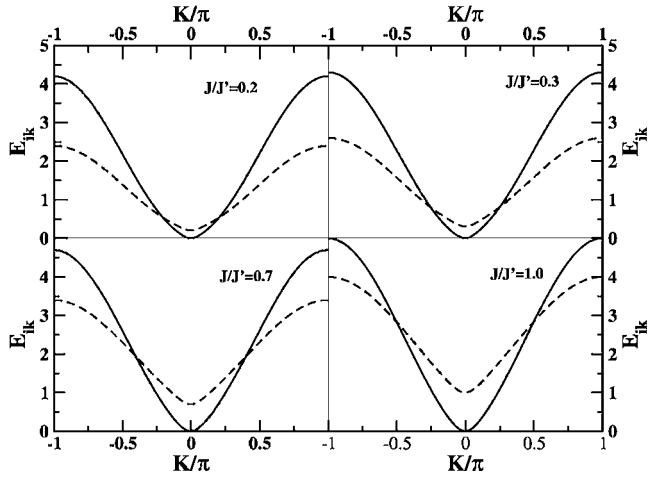

FIG. 1. The two branches of the spin-wave dispersion curves, E_{1k} and E_{2k}, in units of J' as a function of k. The solid line is for E_{1k} mode and the dashed line is for E_{2k} mode for $J/J'=0.2$, 0.3, 0.7, and 1.0.

Let us now consider the nature and characteristics of these two excitation modes. Since the present model has no frustration, from the Lieb-Mattis theorem,[34] we know that the ground state is in the sector of the total spin $S=N/2$. The corresponding classical picture is given in Fig. 2(a). Because of the quantum fluctuations, mainly the exchange of the pair $(S_1=1,S_2=-1/2)\leftrightarrow(S_1=0,S_2=1/2)$ reduces the ground state spin of the system [Fig. 2(a′)]. In fact, the ground state expectation values of S_1^z and S_2^z depend on the antiferromagnetic coupling (J). In our spin-wave study, these values are

$$\langle S_1^z\rangle = 0.816 \quad \text{and} \quad \langle S_2^z\rangle = -0.316, \tag{5}$$

for $J=1.0$. In Fig. 1, the two branches of excitations are shown for $J/J'=0.2$, 0.3, 0.7, and 1.0. The gapless excitation has a total spin $S=N/2-1$. This excitation corresponds to the configuration depicted in Fig. 2(b). In order to move the flipped spin to obtain the state with $S=N/2-1$, we need to prepare a flipped pair as indicated in Fig. 2(b′). Thus, the intermediate state energy for this motion is $4J'+4J+E_G$. On the other hand, the massive excitation in the spin-wave spectrum is in the total spin $S=N/2+1$. This excitation corresponds to the configuration depicted in Fig. 2(c). In order to move the flipped spin to obtain the state with the total spin $S=N/2+1$, we need to prepare a flipped pair as indicated in Fig. 2(c′). In this configuration, the intermediate energy is $3J'+6J+E_G$. From the comparison of both the intermediate excitation energies, we find that for small J/J', the latter one is favorable. Since the excitation mode with the total spin $S=N/2-1$ gives the massless mode of the present model in the long chain limit, the mode with the total spin $S=N/2+1$ must be the lowest excitation in the short chain limit.

We have studied this situation by DMRG. By computing the lowest energies in different magnetization sectors, we estimate the magnetization of the ground state and the low-lying excited states for a number of coupling parameters with varying chain length up to 60 sites. The DMRG procedure follows the same steps as for the systems described in pre-

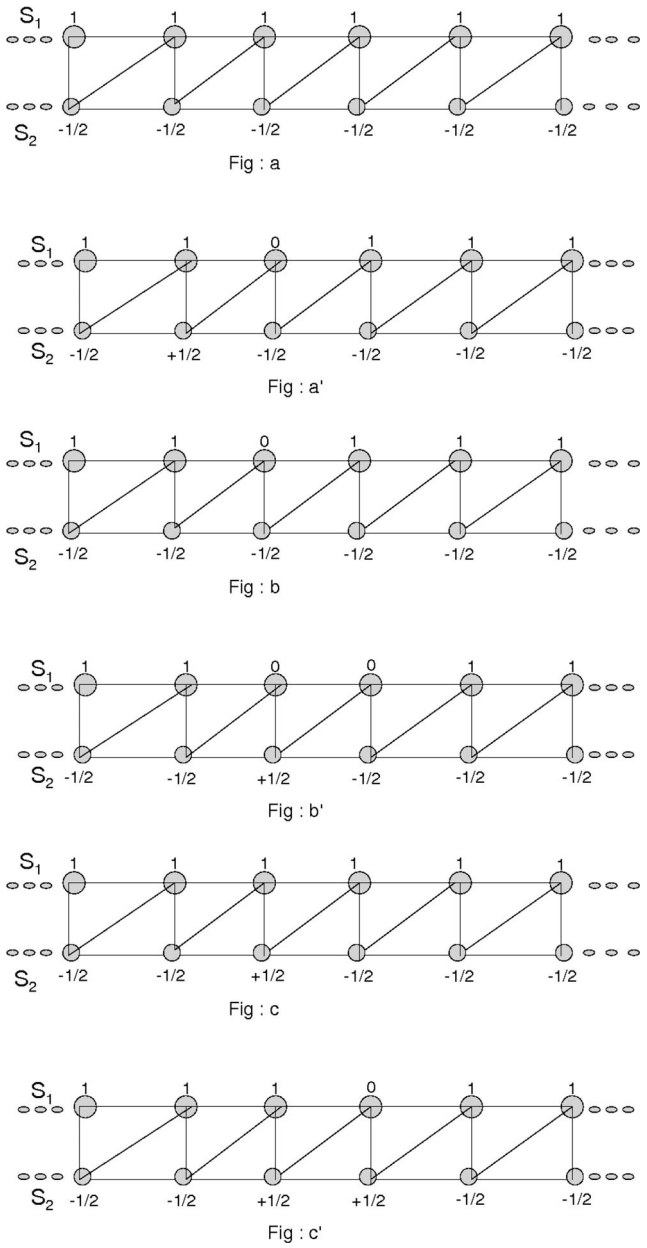

FIG. 2. Schematic spin configurations of (a) the classical ground state, (a′) the classical ground state with a pairwise flip, (b) the spin configuration with the magnetization S_G-1, (b′) the spin configuration as in (b) with a pairwise flip, (c) the spin configuration with the magnetization S_G+1, and (c′) the spin configuration as in (c) with a pairwise flip.

vious papers[4,30,31] except the fact that now the systems do not have the symmetry between the left and right halves. The ground state of the system is confirmed to be ferrimagnetic with total spin $S_G=N/2$ and $M_s=N(S_1-S_2)$ for all the coupling strengths.

Figure 3 presents the ground state energy per site as a function of J/J'. For $J/J'=0.1$, its value obtained from DMRG calculations is −0.6825, while the spin-wave analysis gives a value of −0.6559. The E_0 values obtained from the spin-wave analysis is higher than the DMRG value for all J/J', as expected since quantum fluctuations are not fully

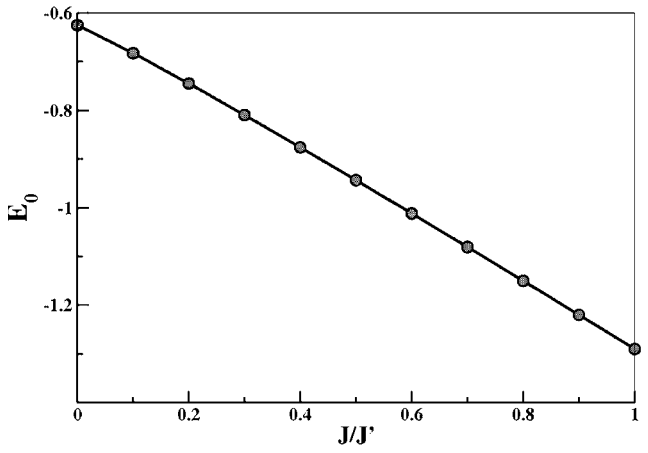

FIG. 3. The ground state energy per site (E_0) in units of J', as a function of J/J', for alternating spin-1/spin-$\frac{1}{2}$ chain.

included in spin-wave calculations. The ground state energy per site for this alternating spin system at all coupling strength lies between the values for the pure spin-$\frac{1}{2}$ uniform chain (−0.443 147J) (Ref. 32) and the pure spin-1 uniform chain (−1.401 484J) (Ref. 33).

Next, we calculate the excitation gaps to these states from the ground state for various values of J/J' and various sizes of the system, from 8 to 60 sites. When there is no explicit inclusion of ferromagnetic coupling between next-nearest neighbors ($J'=0.0$), it is known that the state with spin $S=S_G-1$ is the lowest excitation and is gapless in the long chain limit, whereas the state with spin $S=S_G+1$ is the lowest gapped excitation.[4]

In Fig. 4, we present the excitation gaps as a function of size of the system for four different values of J/J' (0.2, 0.3, 0.7, and 1.0). As can be seen in the Fig. 4, when the antiferromagnetic interaction is relatively weak ($J/J'=0.2$), for short chains, the lowest excitation is no more the state with $S=S_G-1$ which is the gapless mode in the infinite chain. As we decrease J/J', the ferromagnetic interaction becomes dominant and this dependence becomes more significant. This inversion of the order of the excited state energy in short chains reflects the fact that the E_{1k} and E_{2k} modes of the spin-wave spectrum cross at large k. In short chains, the boundary effect causes an increase of the energy of the extended mode E_{1k} more strongly than the localized mode E_{2k}, and thus we have this change-over of the excited state energies. We also found that the excitation in the sector $S=S_G+2$ exists above that of $S=S_G+1$.

Very interestingly, there is a competition among the excitations, depending on the size of the system and the antiferromagnetic coupling strength. Generally, when the size of the system increases, the energies corresponding to the $S=S_G+1$ and $S=S_G+2$ states increase, while the energy to the $S=S_G-1$ state gradually decreases. As a result, at a particular size of the system, there is a crossover among the energies. At large sized system, irrespective of antiferromagnetic coupling, the state with spin $S=S_G-1$ becomes the lowest excitation, while $S=S_G+1$ becomes the second higher excitation and the state with $S=S_G+2$ becomes the highest excitation. We find this tendency for all values of J/J', al-

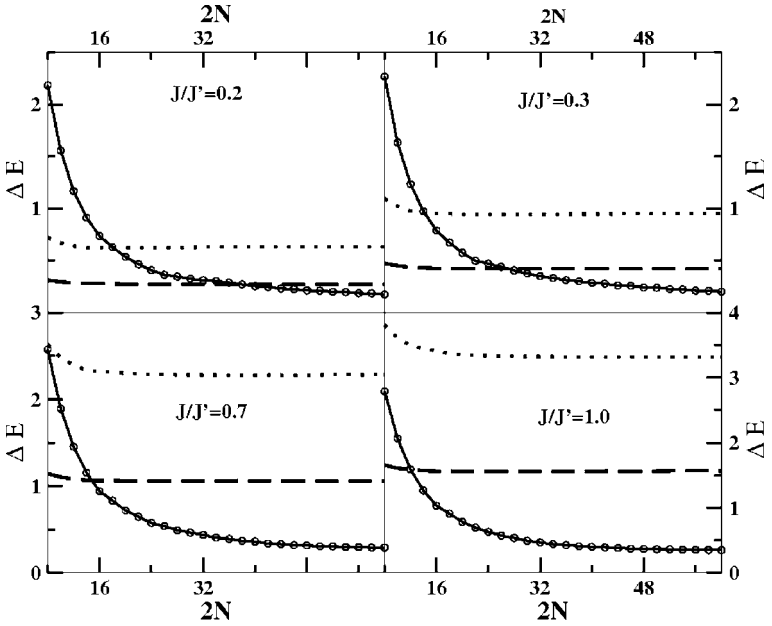

FIG. 4. Excitation gaps as a function of the size of the system ($2N$) for $J/J'=0.2$, 0.3, 0.7, and 1.0. The solid line with circles represents the gap to the state $S=S_G-1$. The dashed line and the dotted line represent the gap to the excitations $S=S_G+1$ and $S=S_G+2$, respectively.

though precisely speaking, when the antiferromagnetic interaction is strong, the state with $S=S_G-1$ is the lowest excitation at all sizes.

From the view of the low-energy excitations described above, we carried out calculations of the thermodynamic properties at different parameter regimes by exact diagonalization. We obtained all eigenvalues and eigenstates of the Hamiltonian in the Fock space basis for fixed M_s sectors for a ring of $2N=12$ sites, and obtained the canonical partition function Z for the 12 site ring:

$$Z=\sum_i \exp^{-\beta[E_i-B(M_s)_i]}, \tag{6}$$

where the sum is over all the energy levels in all M_s sectors. E_i and $(M_s)_i$ are the energy and z component of the total spin of the state i, B is the magnetic field along the z direction, and $\beta=J/k_BT$ with k_B the Boltzmann constant and T the temperature, respectively. Hereafter, we measure the temperature in units of k_B and will not explicitly write k_B. The field-induced magnetization $\langle M\rangle$ is defined as

$$\langle M\rangle=\frac{\sum_i (M_s)_i \exp^{-\beta[E_i-B(M_s)_i]}}{Z}. \tag{7}$$

The magnetic susceptibility χ, which is the fluctuation in magnetization, is thus defined as

$$\chi=\beta[\langle M^2\rangle-\langle M\rangle^2]. \tag{8}$$

In order to make clear the ordering property, we study $\langle M^2\rangle$, i.e., χT instead of χ. The dependence of χT is shown in Fig. 5 for various values of the coupling constants.

The value of $\chi T/(2N)$ is $\frac{S_G(S_G+1)}{6N}$ at $T=0$ which represents the ferrimagnetic order. When the ferromagnetic interaction is strong, i.e., for small J/J', the lowest-energy excitation is to a state with $S=S_G+1$, which is accessed at low temperature, and thereby χT increases with T. If we decrease the antiferromagnetic interaction, the enhancement of χT at low T becomes larger. On the other hand, for larger values of J/J', i.e., $J/J'=1.0$ and 2.0, the excitation with $S=S_G-1$ is the lowest excitation. At low temperatures, the population of this state reduces the χT value. In all the cases, χT approaches the Curie value, i.e., 11/24, averaged for spin-1 and spin-$\frac{1}{2}$ moments at high temperature limit, which is shown in the inset of the Fig. 5.

In conclusion, we have studied the ground state and low-lying excited states of the spin-1 and spin-$\frac{1}{2}$ alternating chains with nearest-neighbor antiferromagnetic and next-nearest-neighbor ferromagnetic interactions by applying the spin-wave theory and DMRG methods. Both methods predict that the ground state of the system is ferrimagnetic with

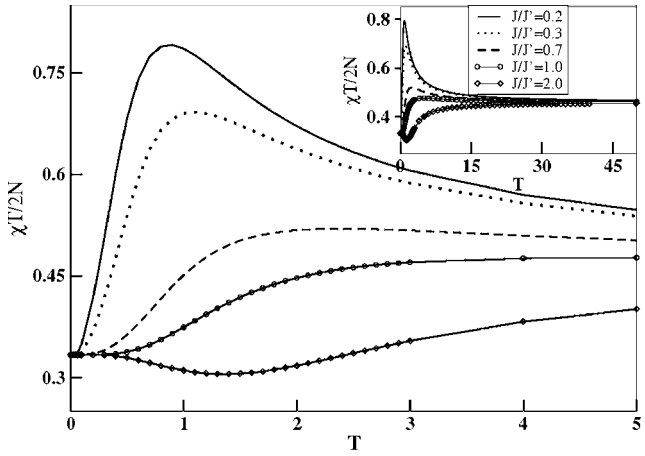

FIG. 5. Magnetic susceptibility multiplied by $T(\chi T)$ as a function of temperature (T). The solid line represents χT for $J/J'=0.2$, the dotted line for $J/J'=0.3$, the dashed line for $J/J'=0.7$, the solid line with circles for $J/J'=1.0$, and the solid line with diamonds for $J/J'=2.0$.

total spin $S_G=N/2$, and there exist composite excitations of the state with $S=S_G\pm1$. The state of $S=S_G-1$ is gapless in the infinite long chain limit and the one with $S=S_G+1$ has a finite lowest gap. We find that the size of the system and the antiferromagnetic coupling play a crucial role in the relative ordering of the low-energy excitations, which is reflected in their thermodynamic properties.

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