On effects of regular S=1 dilution of S=1/2 antiferromagnetic
Heisenberg chains by a quantum Monte Carlo simulation

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The effects of regular S=1 dilution of S=1/2 isotropic antiferromagnetic chain are investigated by the quantum Monte Carlo loop/cluster algorithm. Our numerical results show that there are two kinds of ground-state phases which alternate with the variation of $S^2 = 1$ concentration. When the effective spin of a unit cell is half-integer, the ground state is ferrimagnetic with gapless energy spectrum and the magnetism becomes weaker with decreasing of the $S^1$ concentration $\rho = 1/M$. While it is integer, a non-magnetic ground state with gaped spectrum emerges and the gap gradually becomes narrowed as fitted by a relation of $\Delta \approx 1.25\sqrt{\rho}$.

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I. INTRODUCTION

The effects of substitutions of magnetic impurities on the antiferromagnetic spin chain have attracted great interests in the past decade. It has been shown theoretically that the ground state properties vary with different dilution cases. For the random substitutions, the most interested case is of the $S=1/2$ impurities in Haldane chain $H_2$. For example, inelastic neutron scattering experiment on the compound Y$_2$BaNiO$_5$ substituting Ca$^{2+}$ for Ni$^{2+}$ show a substantial increase of the spectral function below the Haldane gap to indicate the creation of states below the energy of the spin gap. This effects are also studied by numerical works by S. Wessel [2]. For regular substitutions, these systems are the mixed-spin chains which have been extensively studied by many authors in the past a few years. Analytical methods of non-linear sigma model, mean field theory and spin-wave method [4, 5, 6, 7] as well as numerical works by density matrix renormalization group [8] and quantum Monte Carlo [9, 10] have been applied extensively for such systems. So far, it is well known that the topology of spin arrangements in the mixed chains plays an essential role on the ground state properties and thermodynamics in the mixed-spin systems.

Experimently, many Quasi-1D mixed-spin materials have been synthesized in the past two decades, such as ACu(pba)(H$_2$ O)$_3$ $\cdot$ nH$_2$ O (where pba=1,3-propylenebis(oxamato), pbaOH=2-hydroxo-1,3-propylenebis and A= Ni,Fe,Co,Mn,Zn). These materials contains two different transition metal ions per unit cell, and their properties were studied as ferrimagnetic chains [11, 12, 13, 14, 15, 16]. The experiment results imply that the magnetic properties of the mixed-spin compounds can all be described by a Heisenberg model with nearest-neighbor antiferromagnetic coupling as

$$H = \sum_{i=1}^{N} J_i S_i \cdot S_{i+1},$$

where $S_i$ denotes a spin-$S$ moment at site $i$, $N$ is system size and $J_i > 0$. T. Fukui and N. Kawakami [17] have studied spin chain composed by a periodic array of impurities $S^1$ embedded in the host $S^2 \neq S^1$ spin chain with the period $M$, i.e.,

$$S^1 \otimes S^2 \otimes S^2 \otimes \ldots \otimes S^2 \otimes S^1 \otimes S^2 \otimes \ldots \otimes S^2.$$  

The dilutions of the model denoted by the impurity concentration $\rho$ has two limits: (i) $\rho = 0$, the undoped pure antiferromagnetic $S^2$ chain, it has a non-magnetic ground state; (ii) $\rho = 0.5$, the alternating spin chain of $S^1$ and $S^2$. According to Marshall theorem and Lieb-Schultz-Mattis (LSM) theorem [18], ground state of the doped cases are specified by the spin quantum number $S = 0(|S_1 - S_2|N/M)$ for $M = odd$ or $even$, it is either a spin singlet or ferrimagnetic. If the effective spin in a unit composed of $M$ spins $S_{eff}$ is half-integer,
so the system has a gapless energy spectrum. But when \( S_{\text{eff}} \) is integer, LSM theorem fails to predict the energy spectrum to be gaped or gapless. By applying non-linear \( \sigma \) model, it is found that the system has an energy gap when the \( S_{\text{eff}} \) is integer \([2, 3]\). But details of ground state properties and thermodynamics can not be given by non-linear \( \sigma \) model analyses.

The authors of present paper have recently studied the model (1) with the case of \( S^1 = 1/2 \) and \( S^2 = 1 \) by applying quantum Monte Carlo simulations \([13]\), where the numerical results reveal different non-trivial magnetic properties happeneden between two kinds of diluting cases, i.e. for odd \( S^2 = 1 \) spins in a unit, system has magnetic ground state and it shows ferromagnetic features; while for even \( S^2 = 1 \) spins in a unit, systems behave non-magnetic ground states with antiferromagnetic-like features. For both the odd — even cases, the ground states are gapless steadily. And the system gradually transits from the ferrimagnetic ground state of the alternating \( S^1\)-\( S^2 \) chain to the disordered ground state of pure \( S = 1 \) chain in two different tendencies. In this Letter, we study an opposite case with \( S^1 = 1 \) and \( S^2 = 1/2 \). Previous analytical work predicted that if odd \( S^2 = 1/2 \) spins in a unit, the effective spin \( S_{\text{eff}} \) is half-integer, the ground state is ferrimagnetic with a gapless energy spectrum; while if even \( S^2 = 1/2 \) in a unit, \( S_{\text{eff}} \) is integer, the ground state is non-magnetic and the system has an energy gap. Our numerical study will focus on how the ground state properties depend on the concentration and the finite temperature magnetic properties evolve with decreasing of the \( S^1 = 1 \) concentration \( \rho \).

II. CALCULATION AND RESULTS

We use the efficient continuous imaginary time version of loop cluster algorithm to perform the quantum Monte Carlo simulation \([13]\), which has been successfully applied for the other mixed-spin chains \([18, 20]\). We confine our calculation to isotropic antiferromagnetic coupling cases, i.e. \( J_z = J > 0 \) in equation \([4]\), and the positions of spin \( S^1 = \frac{1}{2} \) and \( S^2 = 1 \) are arranged as represented in equation \([2]\) with \( M \) taking the values from 2 to 11. We carry out \( 10^6 \) Monte Carlo steps for measuring physical quantities after \( 10^3 \) Monte Carlo steps for the thermalization. In order to clearly explore the ground state properties, the simulations are performed at the very low temperature \( \beta = 1/T = 200 \) for system sizes \( L > 200 \) in condition of even number of unit. The physical quantities we measure are the ground state energy \( E_G \), the uniform magnetic susceptibility \( \chi_u \) and staggered susceptibility \( \chi_s \) by using the improved estimators in the loop cluster algorithm, e.g.,

\[
< \chi > = \frac{\beta}{4V} \left\langle \sum_{\text{cluster}} w_t(c)^2 \right\rangle_{\text{MC}},
\]

\[
< \chi_s > = \frac{1}{4V \beta} \left\langle \sum_{\text{cluster}} |C|^2 \right\rangle_{\text{MC}},
\]

where \( w_t(c) \) is winding number of cluster \( c \), and \( |C| \) is the cluster size. The magnetization and staggered magnetization are estimated by

\[
< M^2 > = \left\langle 3 \left( \sum_i S_i^z \right)^2 \right\rangle_{\text{MC}},
\]

and

\[
< M_s^2 > = \left\langle 3 \left( \sum_i (-1)^i S_i^z \right)^2 \right\rangle_{\text{MC}}.
\]

The energy gap \( \Delta \) is also estimated in the way given by Todo, \([21]\)

\[
\Delta = \lim_{L \to \infty} \frac{1}{\xi_{\tau,0}(L)},
\]

where \( \xi_{\tau,0} \) is the correlation length in the imaginary time direction.

The results for magnetizations and uniform susceptibility are plotted in Fig. \([1]\) and Fig. \([2]\).

We find that the magnetic properties are apparently different for two cases of \( M = \text{odd} \) and \( M = \text{even} \). When \( M = \text{even} \), the magnetization is finite and approaches zero linearly with decreasing of \( \rho \). While \( M = \text{odd} \), the magnetization remains almost at zero value. On the other hand, it can be observed from our results that the uniform susceptibilities \( \chi_u \) is finite for \( M = \text{even} \), but it vanishes when \( M = \text{odd} \).

Thus there is magnetic long-range order (LRO) in the ground state when \( M = \text{even} \), but the order is absent when \( M = \text{even} \).

We further estimate the staggered magnetization and its susceptibility as a function of concentration shown in Fig. \([3]\) and Fig. \([4]\) respectively. The two observables are both finite for \( M = \text{odd} \) and \( M = \text{even} \) cases, but the data for the cases of \( M = \text{even} \) have much stronger values than the cases of \( M = \text{odd} \).

In order to confirm the results observed above, we begin to investigate the finite temperature uniform magnetic susceptibility. As
FIG. 1: The magnetization versus $\rho = 1/M$, i.e. the diluting concentration of $S^1$. The filled squares present the cases of $M = \text{even}$ and the empty squares for $M = \text{odd}$.

FIG. 2: The magnetic susceptibility versus $\rho = 1/M$. The filled diamonds are for the cases of $M = \text{even}$ and the empty diamonds for $M = \text{odd}$.

FIG. 3: The staggered magnetization versus $\rho = 1/M$. The filled triangles are for the cases of $M = \text{even}$ and empty ones for $M = \text{odd}$.

FIG. 4: The staggered susceptibility versus $\rho = 1/M$. The filled triangles are for the cases of $M = \text{even}$ and empty ones for $M = \text{odd}$.

displayed in Fig. 5 one can easily find that $\chi_u$ diverges when the temperature $T = 1/\beta$ goes to zero in the cases $M = \text{even}$. This is the typical behavior of a system with magnetic LRO. In the cases $M = \text{odd}$, all the $\chi_u$ approach zero when $T \to 0$, a remarkable evidence to reveal the existence of the energy gap.

Up to now, our results verify numerically that there are magnetic LRO and antiferromagnetic LRO in the ground states when $M = \text{even}$. They clearly show that the ground states are ferrimagnetic in such cases. While for $M = \text{odd}$, there should exist of spin liquid phases denoted by the vanish of the magnetizations. Consequently we believe our numerical results consist correctly with the previous analytical predictions. More important, one can easily see that the magnetism decreases with decreasing of impurity concentration in the case of $M = \text{even}$. But there is not notable change of the magnetic properties when the $S^1 = 1$ concentration decreases as $M = \text{odd}$.

Next, we consider the feature of the energy gap $\Delta$ on different regular dilutions. Not surprised for us, the energy gap is closed when $M$ is $\text{even}$ and it opens again while $M$ is $\text{odd}$ as shown in Fig. 6. These results is consist with the prediction by non-linear $\sigma$ model and LSM theorem [4, 5]. It is interesting that the energy gap $\Delta$ tends to be narrow as decreasing of $S^1 = 1$ concentration when $M = \text{odd}$. We confirm such behavior by fitting $\Delta$ to the curve of $1.25 \sqrt{\rho}$ as one can see in Fig. 6.

Moreover, we show the finite-size effect of $\Delta$ results for several cases with $L$ increasing in Fig. 7. In our estimations, although the gaps are not exact closed for $M = \text{even}$ due to the finite-size simulations, we find the data of the gaps decrease fast than $L^{-1}$, so it is obvious that the gaps will trend to zero as $L \to \infty$. For the cases $M = \text{odd}$, where the gap opens all the time, there is almost no finite-size effect.

In order to identify the ground state phases, we calculate the valence-bond-solid (VBS) [22]...
order parameter

\[ z = \exp \left( \frac{2\pi}{N} \sum_{j=1}^{N} j S_j^z \right), \]  \hspace{1cm} (8)

According to the LSM theorem, \( z \) vanishes in the gapless phase as system size \( N \to \infty \). On the other hand, one expects that \( z \) varies in between \( \pm 1 \) but \( z \neq 0 \) in a given gaped phase. In exact VBS states, \( z = \pm 1 \). Our calculations are plotted in Fig. 8. It is clear that \( z \approx -1 \) for all cases of \( M = odd \) to present the system located in a VBS phase; while \( z \approx 0 \), it reveals the gapless energy spectrum for all \( M = even \) cases.

Especially, all these ground state phases can be understood under the scenario of VBS picture. In VBS picture, each impurity \( S^z = 1 \) can be regarded as two spin-1/2 in a triplet state, these two spin-1/2 can form singlet with their nearest neighbor \( S=1/2 \) spin due to the antiferromagnetic coupling. When \( M = odd \), each unit have even number of spin-1/2 host spins, so they can fall into singlets with their nearest neighbors including the two spin-1/2 of \( S=1 \) to induce the VBS order as seen in Fig. 9(a). As a result, the system now shows a gaped energy spectrum. But for \( M = even \), odd number of spin-1/2 exist in a unit and there will be an active spin which is not used to form singlet as shown in Fig. 9(b), thus there is no VBS order and the system emerges no spin gap. Our results of the VBS order parameter \( z \) clearly verify this picture, \( z \approx -1 \) when \( M = odd \) and \( z \approx 0 \) when \( M = even \) as shown in Fig. 8. At last, we note that the VBS phase is stable with the variation of \( S^z = 1 \) concentration \( \rho \) when \( M = odd \).
FIG. 9: The illustrations of VBS picture. The dashed ellipses present the spin $S = 1$, filled circles present the $S = 1/2$ and empty circles present the active $S = 1/2$ spins. (a) for $M = odd$ and (b) for $M = even$. The empty circles in (b) present the active spin-1/2.

III. DISCUSSION AND CONCLUSION

Our Monte Carlo study verifies that two branches of different magnetic behaviors emerge in cases of regular $S=1$ diluted $S=1/2$ host chains. According Marshall theorem, the cases with $M = even$ have the ferrimagnetic ground states which can be specified by quantum number $S_{total} = |S_1 - S_2|N/M$, so the magnetization per site is finite and it decreases linearly as a function of $\rho$ to $M = 0$, the case of the pure $S=1/2$ antiferromagnetic Heisenberg chain. This feature can be easily observed from our results in Fig. 4 and Fig. 5. When $M$ is odd, the ground state is singlet with $S_{total} = 0$, thus the magnetization per site keeps zero and this is a non-magnetic state. As observed in our simulations there is no notable variations of the ground state magnetic properties in the cases of $M = odd$.

To compare our ground state results of the model in this Letter for $S^1 = 1$ and $S^2 = 1/2$ (system I) with the one we studied previously [18] when $S^1 = 1/2$ and $S^2 = 1$ (system II), we collect the main points of the numerical calculations in Table I. One can easily see that both systems behave with two kinds of different ground state phases, magnetic or non-magnetic, respectively. If $M = even$, the ground states are ferrimagnetic for both system I and system II, and their magnetizations and staggered magnetizations are all finite and decrease linearly with decreasing of impurity concentration. However, for the cases of $M = odd$, there appears VBS order in system I which is gapped, but the order is absent in system II where the spin arrangements can not induce such order, so the gap is constantly closed. This feature reveals that this topological order plays an important role to the behavior of the energy gap in the mixed-spin system. We believe that the fitted relation of $\Delta \approx 1.25\sqrt{\rho}$, to denote the energy gap as function of $S^1 = 1$ concentration, provides a good stuff to study how the topological order affects the energy gap in the mixed-spin systems.

In conclusion, we have studied the ground state and finite temperature magnetic properties of the regular $S^1 = 1$ diluted in $S^2 = 1/2$ antiferromagnetic chain. Our calculations show that there exist different phases in the ground state as a function of $S^1$ concentration. When there is one $S^1$ impurity and odd number of host $S^2$ spins in a unit cell, the ground states are ferrimagnetic and the system has a gapless energy spectrum. The ferrimagnetism becomes weaker as the impurity concentration reduced. While for one $S^1$ and even number of $S^2$ in one unit cell, the ground state is a VBS phase where there is a gaped energy spectrum and the energy gap gradually approaches to zero with decreasing the concentration $\rho$. An interesting observation is that the behavior of the energy gap can be numerically well fitted by $\Delta \approx 1.25\sqrt{\rho}$. Further analytical work, for example using the mean-field theory [6], is required to explain why such dependence of the energy gap exist in VBS phases.

| $S_{eff}$ | $I$. $S^1 = 1, S^2 = 1/2$ | $II$. $S^1 = 1/2, S^2 = 1$ |
|-----------|--------------------------|---------------------------|
| $M = odd$ | $M = even$ | $M = odd$ | $M = even$ |
| $<M>_{\text{even}}$ | zero | finite | zero | finite |
| $\chi_u$ | zero | large | small | large |
| $<M_s>$ | finite | finite | finite | finite |
| $\Delta$ | gaped | gapless | gapless | gapless |
| $z$ | -1.0 | 0.0 | 0.0 | 0.0 |

TABLE I: Comparison of ground state properties of two model, where $S_{eff}$ is effective spin in a unit, $<M>$ is magnetization, $<M_s>$ is staggered magnetization, $\chi_u$ is uniform susceptibility, $\chi_s$ is staggered susceptibility, $\Delta$ is energy gap and $z$ is VBS order parameter.

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