Successive valence-bond-state transitions in quantum mixed spin chains

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We study quantum mixed-spin chains consisting of two integer spins S^1 and two half integer spins S^2 arrayed as S^1-S^1-S^2-S^2 in a unit cell with antiferromagnetic nearest-neighbor couplings J_1 (J_2) between the spins of equal (different) magnitudes. By varying the ratio of two competing couplings, $\alpha = J_2/J_1$, the systems undergo successive quantum phase transitions between different valence-bond-solid (VBS) states accompanied by the vanishing of the energy gap. By a quantum Monte Carlo simulation with an improved loop cluster algorithm, we find one critical point $\alpha_c = 0.762(1)$ in a 1-1-$\frac{1}{2}$-$\frac{1}{2}$ chain and two critical points $\alpha_{c1} = 0.479(1)$ and $\alpha_{c2} = 1.318(1)$ in a 1-1-$\frac{3}{2}$-$\frac{3}{2}$ chain, respectively. The calculated expectation values of the Lieb-Shultz-Mattis twist operator show the characteristic features of the single VBS transition in the 1-1-$\frac{1}{2}$-$\frac{1}{2}$ chain and two successive VBS transitions in the 1-1-$\frac{3}{2}$-$\frac{3}{2}$ chain at these critical points.

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Quantum spin chains have been continuously attracting research interest in both theoretical and experimental condensed-matter physics. The interplay of local spin configurations and one-dimensional (1D) quantum fluctuations leads to a rich variety of exotic magnetic phenomena. One of the most famous results is the Haldane conjecture which states that at zero temperature the half-odd-integer antiferromagnetic Heisenberg chains should have gapless spectra with algebraic decay of correlations, and the integer spin ones should be gapped with an exponential decay of correlations.[1] For $S=1$, this conjecture was confirmed by many numerical[2] and experimental studies.[3] The similar gapped phases exist also in an $S=1$ antiferromagnetic Heisenberg chain with biquadratic interaction,[4] as well as in a variety of spin chains or spin ladders with bond alternation and other competing interactions.[5–7] Though the gapped phases fall into a catalog of a generic valence-bond-solid (VBS) picture, they are basically separated by some massless boundaries. Theoretically, it is quite interesting to distinguish the different VBS states and to demonstrate the phase transitions among them.

In last two decades, many quasi-1D mixed-spin materials,[8–10] such as $A\mathrm{Cu}(pba)(\mathrm{H_2O})_3\cdot n(\mathrm{H_2O})$ and $A\mathrm{Cu}(pba\mathrm{OH})(\mathrm{H_2O})_3\cdot n\mathrm{H_2O}$ (where pba=1,3-propylenebis (oxamato), pbaOH=2-hydroxo-1,3-propylenebis, and A =Ni, Fe, Co, Mn, Zn), have been synthesized. These materials are quasi-1D bimetallic molecular magnets containing two different transition-metal ions per unit cell alternatingly distributed on the lattice.[11] The model Hamiltonians describing these systems are the antiferromagnetic mixed chains with a periodic array of the unit cells involving two different spins S^1 and S^2. The periodic chains with complicated local spin configurations in a unit cell will in general result in variations of energy gaps and magnetizations. Owing to the translational invariance of the systems with respect to each unit cell, a necessary condition for the gap formation in zero field is obtained so that the magnetization per unit cell should be integers. This can be shown by applying a twist operator on the ground state, $U \equiv \exp[i(2\pi/N)\Sigma_{j=1}^{N} jS_j^z]$, as was first proposed by Lieb, Schultz, and Mattis,[12] and generalized later by Affleck and Lieb,[13] and Oshikawa, Yamanaka, and Affleck.[14] In the simplest case, each unit cell involves two spins, denoted by S^1-S^2. For integer S^1 and half integer S^2, this mixed chain is a quantum ferrimagnet and its ground state is gapless and magnetic.[15–17] In order to explore the mixed chain with a nonmagnetic ground state, one considers the case with two S^1 and two S^2 spins arrayed alternatively, i.e., each unit cell involves four spins denoted by S^1-S^1-S^2-S^2. The model Hamiltonian is

$$H=\sum_{l=1}^{N/4}\left(J_1 S_{4l-3}^1\cdot S_{4l-2}^1+J_2 S_{4l-2}^1\cdot S_{4l-1}^2 + J_1 S_{4l-1}^2\cdot S_{4l}^2+J_2 S_{4l}^2\cdot S_{4l+1}^1\right) \quad (1)$$

as represented in Fig. 1.

In the case with $S^1=1$, $S^2=1/2$, the model was studied by quantum Monte Carlo (QMC) simulation[18] and the nonlinear σ model (NLSM),[19,20] respectively. The ground state of the system is nonmagnetic with gapped excitations. The gap varies as a function of the parameter $\alpha = J_2/J_1$, and vanishes at a critical point α_c. This signals a quantum phase transition between two different VBS states, as shown schematically in Fig. 2. The VBS states of Figs. 2(a) and 2(b) are exact in the limiting cases $\alpha \to 0$ and $\alpha \to \infty$, respectively, and are approximately correct in the corresponding regions separated by α_c. The massless point α_c predicted analytically by the NLSM is 0.5,[20] while it is 0.77 calculated numerically by QMC simulations.[18] In general, the NLSM estimates quantitatively deviate from the actual values,[21] but further numerical studies are needed to confirm the previous numerical results. Moreover, the numerical investigations for

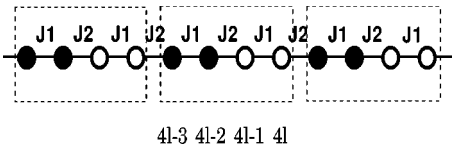

FIG. 1. Graphical representation of the Hamiltonian, Eq. (1). The black and white circles represent spins S^1 and S^2, respectively.

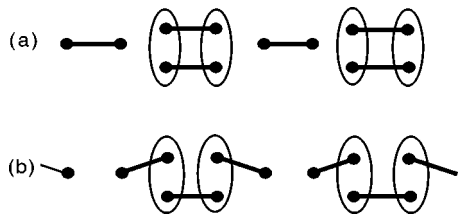

FIG. 2. The valence-bond-solid picture of the 1-1-$\frac{1}{2}$-$\frac{1}{2}$ model ground state (a) for $\alpha<\alpha_c$ and (b) for $\alpha>\alpha_c$. The solid circles represent the $S=\frac{1}{2}$ spin, and two $S=\frac{1}{2}$ spins connected by the solid line form a singlet pair. Each open ellipse surrounding two $S=\frac{1}{2}$ spins represents an operation of constructing a $S=1$ spin from these $S=\frac{1}{2}$ spins by symmetrizing them.

characterizing the different VBS states as well as the phase transitions in nonmagnetic mixed-spin systems are still lacking.

In this paper, we consider the model Hamiltonian, Eq. (1), in the cases of $S^1=1$, $S^2=1/2$ and $S^1=1$, $S^2=3/2$, respectively. The former enables us to check our numerical scheme and the latter is the minimal model for successive transitions in mixed-spin chains. To determine the massless points we first calculate the energy gaps and low-temperature susceptibilities. Then, in order to determine the phase transitions and characterize the different VBS states in a more precise way, we calculate the expectation value of the Lieb-Schultz-Mattis twist operator on the ground state,

$$z \equiv \left\langle \exp\left[i \frac{2\pi}{N} \sum_{j=1}^{N} j S_j^z \right] \right\rangle. \tag{2}$$

Here, z serves as an order parameter equivalent to the string order parameter in the usual Haldane phase.[22] According to the theorem of Lieb-Schultz-Mattis, z vanishes in the gapless phase as system size $N\rightarrow\infty$. On the other hand, in a given gapped phase, one expects that z varies between ± 1, but $z \neq 0$. In exact VBS states, $z=\pm 1$, the sign depends on the number of valence bonds at the boundary. Recently, Nakamura and Todo have shown that z is more direct than the string order parameter in detecting VBS states of the gapped phases as well as their boundaries in the bond-alternating Heisenberg spin chains and $S=1/2$ two-leg frustrated ladder.[23] We find that this new order parameter can be also used to detect the two different VBS states in the 1-1-$\frac{1}{2}$-$\frac{1}{2}$ chain. Extending the investigations to other higher spins, we find that the 1-1-$\frac{3}{2}$-$\frac{3}{2}$ chain is more interesting, since it provides a minimal model system to study the successive VBS transitions in mixed-spin chains. Our results are briefly stated below. For the 1-1-$\frac{1}{2}$-$\frac{1}{2}$ chain, the evidence for the massless point from the vanishing of the energy gap, the finite zero-temperature susceptibility, and the zero of the z parameter converge at $\alpha_c=0.762(1)$, very close to the previous numerical result given in Ref. 18. For the 1-1-$\frac{3}{2}$-$\frac{3}{2}$ chain, the three kinds of evidence fit perfectly and show that there are two massless points at $\alpha_{c1}=0.479(1)$ and $\alpha_{c2}=1.318(1)$, respectively. The three gapped phases by which they are separated are thus represented by three different VBS states

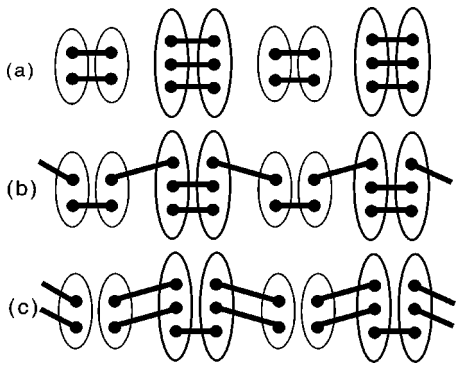

FIG. 3. The valence-bond-solid picture of the $\frac{3}{2}$-$\frac{3}{2}$-1-1 model ground state (a) for $\alpha<\alpha_{c1}$, (b) for $\alpha_{c1}<\alpha<\alpha_{c2}$, and (c) for $\alpha>\alpha_{c2}$. The solid circles represent the $S=\frac{1}{2}$ spin, and two $S=\frac{1}{2}$ spins connected by the solid line form a singlet pair. Each open ellipse surrounding two or three $S=\frac{1}{2}$ spin represents an operation of constructing a $S=1$ or $S=\frac{3}{2}$ spin from these $S=\frac{1}{2}$ spins by symmetrizing them.

as shown in Fig. 3. Moreover, z varies continuously as a function of α between ± 1, vanishing only at the two massless points.

Our numerical results are determined as accurately as possible by employing the QMC method based on the loop cluster algorithm.[24,25] This algorithm is fully ergordic and drastically reduces the autocorrelation time, especially at low temperatures. Furthermore, by using the continuous-time version of the algorithm and the improved estimators,[26] it can be used to study rather large systems and estimate the physical quantities within satisfactory accuracy. More recently, Harada *et al.*[27] and Todo and Kato[28] have developed this algorithm for the quantum spin systems with an arbitrary spin size, while the Haldane-type gap is directly related to the correlation length $\xi_{\tau,0}$ in the imaginary time direction and can be precisely estimated by

$$\triangle = \lim_{N\rightarrow\infty} \frac{1}{\xi_{\tau,0}(L)} \tag{3}$$

without further extrapolation procedures.[28] Their strategy is improved in our QMC study of the mixed chains. We first perform 10^3 Monte Carlo steps for thermalization, and then Monte Carlo averages 10^5 times. To test the efficiency of our program, we calculate several physical quantities of different models including a pure spin-1 chain and the mixed-spin chains 1-$\frac{1}{2}$ and 1-$\frac{3}{2}$, respectively. A comparison of our numerical results with previous ones obtained by the QMC or density-matrix renormalization-group (DMRG) method is listed in Table I.

Our program is then used to reexamine the mixed chain 1-1-$\frac{1}{2}$-$\frac{1}{2}$, without using the least-squares fittings. The energy gap has a deep dip very close to $\alpha=0.762$. At this point, the susceptibility of the low-temperature saturates at $\chi=0.324$. The lowest temperature is $k_BT=0.01$ (set as $J_1=1$) in our QMC calculation, while it is 0.05 in Ref. 18. Since the energy gap and low-temperature susceptibility have been reported in Ref. 18, we only list the new results in Fig. 4, i.e.,

TABLE I. Comparison of ours and other previous numerical results. e_g is the ground-state energy per cell, $\triangle$ is the energy gap, and χ_s is the staggered magnetic susceptibility of the pure S=1 chain. DMRG results are from Ref. 2 and Ref. 17, and QMC results are from Ref. 28.

Model	Previous results	Our results
Pure $S=1$ chain	$e_g=-1.4015$ (DMRG)	$e_g=-1.401\,38$
Pure $S=1$ chain	$\triangle=0.411\,27$ (QMC)	$\triangle=0.4113$
Pure $S=1$ chain	$\chi_s=18.4028$ (QMC)	$\chi_s=18.413$
Mixed $\frac{1}{2}$-1 chain	$e_g=-1.4541$ (DMRG)	$e_g=-1.4537$
Mixed $\frac{3}{2}$-1 chain	$e_g=-3.8619$ (DMRG)	$e_g=-3.8616$

the parameter z. Notice that z is complex in general, but its imaginary part vanishes in the large-N limit. Thus it is sufficient to calculate the real part of z in the following. The calculated (real part of) z changes sign accurately at this point (within accuracy of 10^{-3}, i.e., up to the last digit), showing a phase transition between the two different VBS states. Thus the very location of the massless point $\alpha_c=0.762(1)$ should be more precise than $\alpha_c=0.77$ obtained in Ref. 18.

Now we turn to the main results of this paper for the mixed chain 1-1-$\frac{3}{2}$-$\frac{3}{2}$. The ground-state energy e_g (per site) and energy gap Δ are calculated as functions of α for the system size from $N=16$ to $N=200$ and temperature $k_BT=0.01$. The ground-state energy shows almost no N dependence while the energy gap shows rather weak N dependence for large N. For $N=200$, the α dependence of Δ is shown in Fig. 5, where two dips are located around at 0.479 and 1.318, respectively. To convince us that these two points are critical ones, we observe that at these two points, Δ approaches zero between $1/N$ and $1/\sqrt{N}$ for large N. Analytically, the existence of the massless points in the mixed chains are expected within the nonlinear σ-model approach,[20] where the massless points satisfy

$$\frac{1}{J_2}=\frac{1-t_2}{2t_1}\frac{1}{J_1}+\frac{1-t_1}{2t_1}\frac{S^2}{S^1}, \tag{4}$$

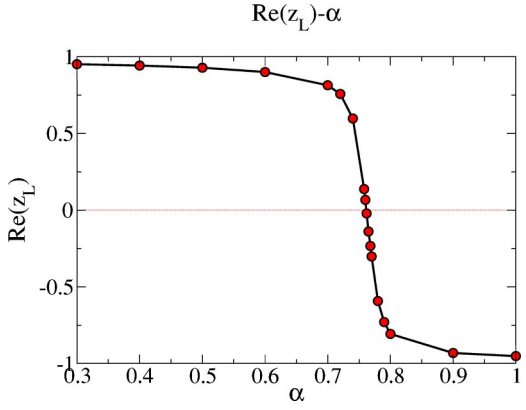

FIG. 4. The order parameter z as function of α in the 1-1-$\frac{1}{2}$-$\frac{1}{2}$ chain.

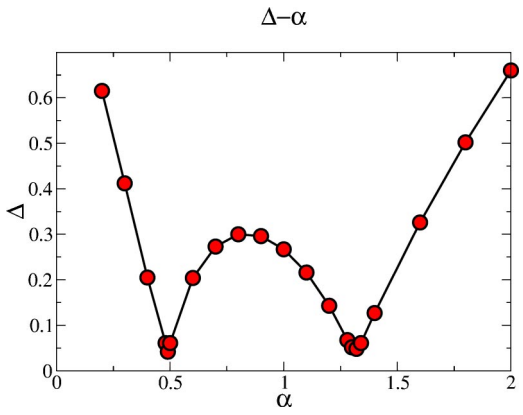

FIG. 5. The energy gap Δ of the 1-1-$\frac{3}{2}$-$\frac{3}{2}$ chain. The result is obtained for system size $N=200$ at temperature $k_BT=0.01$.

with $t_1=2n-1/4S^1$, $t_2=2n-1/4S^2$ for positive integer n. For antiferromagnetic couplings and $S^1=\frac{3}{2}$, $S^2=1$, one obtains two vanishing points $\alpha=0.255$ and $\alpha=1.714$, respectively, quantitatively different from ours.

The thermodynamics of the 1-1-$\frac{3}{2}$-$\frac{3}{2}$ chain are calculated by varying temperatures from $k_BT=2.0$ to $k_BT=0.02$ with size $N=200$ fixed. The result of magnetic susceptibility is shown in Fig. 6. When α deviates from 0.479 and 1.318 (all within the same accuracy of 10^{-3}), the susceptibility approaches zero as the temperature decreases. But it is at about $\chi=0.090$ and $\chi=0.050$ per site at temperature $k_BT=0.02$ at these two points that significantly shows the criticality.

The ground-state energy per site is continuous on the parameter α, and the previous results imply that at zero temperature the ground state of the system undergoes two successive phase transitions of second order at $\alpha_{c1}=0.479(1)$ and $\alpha_{c2}=1.318(1)$, respectively. To give a general VBS picture of the transitions, one first notices that in the limiting case $\alpha\to 0$, the valence bonds are composed of two nearest $S^1=1$ and $S^2=3/2$ spins, respectively, each of them with two and three numbers of bonds. This VBS state is denoted by (2,0,3); see Fig. 3(a). In the opposite limit, $\alpha\to\infty$, the bonds of two nearest $S^1=1$ spins are completely broken, and the bonds of two nearest $S^2=3/2$ spins are partially broken, thus forming new bonds between the nearest spins $S^1=1$ and

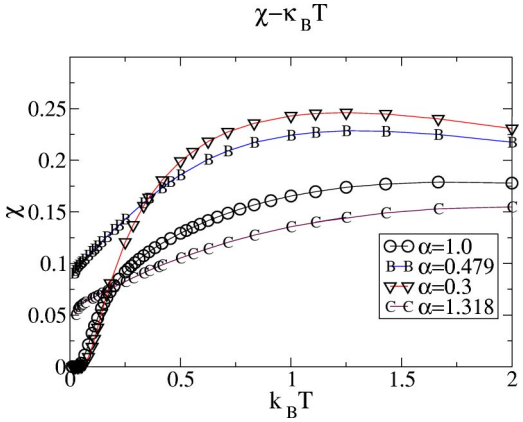

FIG. 6. Magnetic susceptibility versus temperature k_BT.

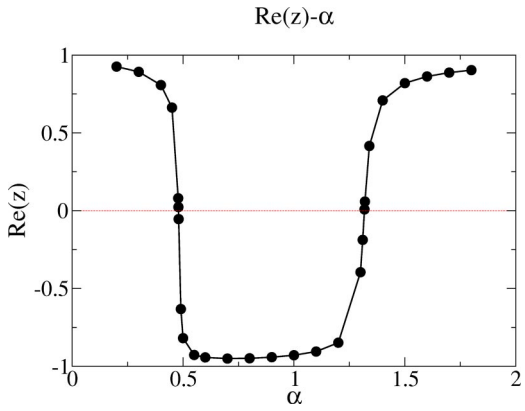

FIG. 7. The order parameter z as a function of α in the 1-1-$\frac{3}{2}$-$\frac{3}{2}$ chain.

$S^2=3/2$. There remains an unbroken bond for two nearest $S^2=3/2$ spins. This VBS state is denoted by (0,2,1); see Fig. 3(c). We have also calculated the nearest-neighbor two-spin correlation functions,

$$\omega_{11}=\langle S^1\cdot S^1\rangle, \quad \omega_{12}=\langle S^1\cdot S^2\rangle, \quad \omega_{22}=\langle S^2\cdot S^2\rangle, \quad (5)$$

for α from 0 to 2 at $k_BT=0.01$ and $N=200$. It is found that $\omega_{11}(\omega_{22})/\omega_{12}$ are enhanced/suppressed for small α and suppressed/enhanced for large α. This shows that as α varies from 0 to ∞, the valence bond states (2,0,3) and (0,2,1) are approximately correct in two sides, but should be replaced by a new valence bond in the intermediate value of α. In Fig. 3, one expects the intermediate phase with one nearest S^1 bond, one nearest S^1-S^2 bond, and two nearest S^2 bonds, respectively, denoted by (1,1,2).

To characterize the VBS states in the 1-1-$\frac{3}{2}$-$\frac{3}{2}$ chain in a more precise way, we calculate the order parameter z defined by Eq. (2) for $N=200$, $k_BT=0.01$. The result is plotted in Fig. 7. Again, within accuracy up to the last digit, we find that z vanishes only at the two isolated points $\alpha_{c1}=0.479(1)$, $\alpha_{c2}=1.318(1)$, respectively. The three regions (I) $0<\alpha<\alpha_{c1}$, (II) $\alpha_{c1}<\alpha<\alpha_{c2}$, and (III) $\alpha_{c2}<\alpha<2$ are all gapped phases. Though our QMC calculations are limited in $0<\alpha<2$, region III may extend to $\alpha\to\infty$. In regions I and III, z is positive, while it is negative in region II. Therefore, as α increases, z varies between ±1, changing its sign each time it enters the neighboring regions, while vanishing accurately at the two isolated boundaries. Figure 7 shows also that there is only one intermediate gapped phase in the 1-1-$\frac{3}{2}$-$\frac{3}{2}$ chain, confirming the general picture of Fig. 3.

Our numerical results, though obtained for two simple cases with $S^1=1$ and $S^2=1/2,3/2$ by QMC simulations, are very helpful for understanding the general picture of phase transitions between different VBS states in quantum antiferromagnetic mixed-spin chains described by Hamiltonian (1) with arbitrary S^1 and S^2. We predict that as $\alpha=J_2/J_1$ varies, the systems undergo successive VBS quantum phase transitions. There are $2\min(S^1,S^2)+1$ numbers of gapped phases characterized by different VBS states, each denoted by $(2S^1\text{-}m,\ m,\ 2S^2\text{-}m)$, with $m=0,1,\ldots,$ with $2\min(S^1,S^2)$ the number of $(S^1\text{-}S^2)$ valence bonds in a unit cell. The gapped phases are separated by $2\min(S^1,S^2)$ numbers of critical points α_{ci} accompanied by the vanishing of the energy gap. Their positions can be accurately determined by QMC simulations or other numerical methods. The successive VBS transitions can be characterized by the expectation value of the twist operator, z, which varies between ±1 [keeping the signs $(-1)^m$ in mth gapped phases] and vanishes exactly at the critical points.

In summary, we have studied the quantum antiferromagnetic mixed chains 1-1-$\frac{1}{2}$-$\frac{1}{2}$ and 1-1-$\frac{3}{2}$-$\frac{3}{2}$ by QMC simulations based on the loop cluster algorithm. The results for the 1-1-$\frac{1}{2}$-$\frac{1}{2}$ chain not only confirm with better accuracy the previous numerical (QMC) ones, but also exhibit clearly the phase transition between the two different VBS states. For the 1-1-$\frac{3}{2}$-$\frac{3}{2}$ chain, besides the twist operator, the energy gap and the low-temperature susceptibility suggest the existence of two massless points, which are located at $\alpha_{c1}=0.479(1)$ and $\alpha_{c2}=1.318(1)$, respectively. The gapped phases by which they are separated can be represented by three different VBS states as shown in Fig. 3. Furthermore, the order parameter z changes the sign for two neighboring phases and vanishes only at the critical points. It is straightforward to expect similar successive VBS transitions in the mixed-spin chains with arbitrary S^1 and S^2.

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