Parity-dependent phase diagrams in spin-cluster two-leg ladders

Zongsheng Zhou,1 Fuzhou Chen,1 Yin Zhong,1 Hong-Gang Luo,1,2 and Jize Zhao1, *

1Center for Interdisciplinary Studies & Key Laboratory for Magnetism and Magnetic Materials of the MoE, Lanzhou University, Lanzhou 730000, China
2Beijing Computational Science Research Center, Beijing 100084, China

Motivated by the recent experiment on K₂Cu₃O(SO₄)₃, an edge-shared tetrahedral spin-cluster compound [M. Fujihala et al., Phys. Rev. Lett. 120, 077201 (2018)], we investigate two-leg spin-cluster ladders with the plaquette number \( n_p \) in each cluster up to six by the density-matrix renormalization group method. We find that the phase diagram of such ladders strongly depends on the parity of \( n_p \). For even \( n_p \), the phase diagram has two phases, one is the Haldane phase, and the other is the cluster rung-singlet phase. For odd \( n_p \), there are four phases, which are a cluster-singlet phase, a cluster rung-singlet phase, a Haldane phase and an even Haldane phase. Moreover, in the latter case the region of the Haldane phase increases while the cluster-singlet phase and the even Haldane phase shrink as \( n_p \) increases. We thus conjecture that in the large \( n_p \) limit, the phase diagram will become independent of \( n_p \). By analysing the ground-state energy and entanglement entropy we obtain the order of the phase transitions. In particular, for \( n_p = 1 \) there is no phase transition between the even Haldane phase and the cluster-singlet phase while for other odd \( n_p \) there is a first-order phase transition. Our work provides comprehensive phase diagrams for these cluster-based models and may be helpful to understand experiments on related materials.

I. INTRODUCTION

An integer is either even or odd, which is known as the parity. The properties of some physical systems associated with different parity may be fundamentally different. A well-known example stems from Haldane’s conjecture that the lowest excitation of spin chains with integer spin is gapful while those with half integer spin is gapless. Correspondingly, the lowest excitation of spin-\( \frac{1}{2} \) ladders with even legs are gapful but those with odd legs are gapless. This conjecture was soon confirmed by various numerical and experimental works and therefore the gapful phase is called Haldane phase. Recently, further theoretical works show that the Haldane phase for spin chains with odd integer spins and even integer spins are actually different. The former one is protected by some symmetries, such as time-reversal, space inversion but the latter is not although edge states may exist in both of them. Hereafter, following literature, we will just call the former one as Haldane (HP) phase but the latter one as even Haldane (EHP) phase. Now we know that the HP phase is actually a symmetry-protected topological phase. These theoretical progresses have stimulated extensive efforts to search for such topologically nontrivial phase in quasi-one dimensional materials as well as artificial structures and the Haldane phase has been reported in a variety of experiments.

Very recently, experimental evidence for the Haldane phase in spin-cluster materials was first reported in the compound K₂Cu₃O(SO₄)₃ by M. Fujihala et al. This compound consists of edge-shared tetrahedral spin clusters. Spin-\( \frac{1}{2} \) Cu⁺ sits at the corner of the tetrahedron. These clusters are connected via SO₄²⁻ along the b axis. In other directions, they are connected via nonmagnetic ions/or no exchange path is allowed and thus interactions can be neglected. These identify K₂Cu₃O(SO₄)₃ as a quasi one-dimensional compound. Various experiments from the magnetic susceptibility, magnetization, heat capacity, neutron scattering reveal that its ground state is an HP phase. In addition to K₂Cu₃O(SO₄)₃, some other cluster-type one-dimensional materials have also been reported, such as Cu₂Te₂O₅X₂ with \( X = \text{Cl, Br} \). These experiments call for a systematical investigation on the low-energy properties of spin-cluster ladders.

For this purpose, we study a Hamiltonian written as follows

\[
\mathcal{H} = \sum_{k=1}^{L_c} \mathcal{H}^{(k)}_{\text{intra}} + \sum_{k=1}^{L_c-1} \mathcal{H}^{(k,k+1)}_{\text{inter}}
\]

where \( L_c \) is the number of clusters. The Hamiltonian has two parts, the first is the interaction within one cluster, and the other is the interaction between two nearest-neighbor clusters. Such intra-cluster and inter-cluster Hamiltonians are given by:

\[
\mathcal{H}^{(k)}_{\text{intra}} = J_{\perp} \sum_{j=1}^{n_p+1} \mathbf{S}_{1,j}^{(k)} \cdot \mathbf{S}_{2,j}^{(k)} + J_{\parallel} \sum_{i=1}^{n_p} \sum_{j=1}^{n_p} \mathbf{S}_{i,j}^{(k)} \cdot \mathbf{S}_{i,j+1}^{(k)} + J_c \sum_{j=1}^{n_p} \sum_{a=0,1} \mathbf{S}_{1,j+a}^{(k)} \cdot \mathbf{S}_{2,j+1-a}^{(k)}
\]

\[
\mathcal{H}^{(k,k+1)}_{\text{inter}} = J_{\text{inter}} \sum_{i=1,2} \mathbf{S}_{i,n_p+1}^{(k)} \cdot \mathbf{S}_{i,1}^{(k+1)}
\]

where \( \mathbf{S}_{i,j}^{(k)} \) is the spin operator in the \( k \)th cluster with the leg index \( i \) and rung index \( j \). \( n_p \) is the plaquette number within one cluster, which is one to one correspondence to the tetrahedron number within one cluster in compounds. A schematic representation of the model...
and the couplings $J_L$, $J_\|$, $J_c$ and $J_{\text{inter}}$ is plotted in Fig. 1. This model was proposed\textsuperscript{26} for K$_2$Cu$_3$O (SO$_4$)$_3$, where $n_p$ takes 2 and $J_c = J_\|$ due to the symmetry of a tetrahedron. Although in known compounds, $n_p$ is limited to 1 or 2, in our theoretical work we will consider general $n_p$ and extrapolate our conclusions to the large $n_p$ limit. Moreover, for simplicity, we assume that $J_c = J_\|$ is satisfied for all $n_p$ and set $J_{\text{inter}} = 1$ as the energy unit.

To study the low-energy properties of Hamiltonian (1), we resort to the state-of-art numerical algorithm, density-matrix renormalization group (DMRG)\textsuperscript{34-37}. In our calculations, we keep up to 3000 states thus the largest truncation error is smaller than $10^{-10}$. We find that the phase diagrams of this model depend strongly on the parity of $n_p$. For even $n_p$, we have two phases, and for odd $n_p$, we have four phases. The particular features for $n_p = 1$ and large $n_p$ are also discussed. The rest of the paper is organized as follows. In Sec. II, we present the phase diagram for even $n_p$. In Sec. III, we present the phase diagram for odd $n_p$. In Sec. IV, we show the results in the large $n_p$ limit and in Sec. V we conclude our work.

II. PHASE DIAGRAM FOR EVEN $n_p$

In this section, we will discuss the phase diagrams for even $n_p$. In Fig. 2, we show our results for $n_p = 2, 4$ and 6. We find two phases, which are an HP phase and a CRS phase. The former is common in spin-1 chains and two-leg ladders\textsuperscript{12,38,39}. The latter is a trivial product state of singlets. In this phase, each rung within a cluster forms a singlet. But at the edge the situation may be different, depending on the coupling $J_\|$ and $J_L$. For example, when $J_\|, J_L \ll 1$, the two spins connected by $J_{\text{inter}}$ form a singlet while $J_L \gg 1$ each rung is a singlet. Although these edge spin configurations may be different, we find no phase transition.

The phase diagram and the phase boundary can be determined by the ground-state energy, the entanglement entropy and entanglement spectrum. Now we turn to discuss our steps. In our DMRG simulations, we split the ladder into two halves. One is the system and the other is the environment. After tracing out the freedom of the environment, we obtain the reduced density matrix $\rho$. The entanglement entropy is defined as $S = -\sum_i \rho_i \ln \rho_i$ with $\rho_i$ the eigenvalues of $\rho$. The entanglement spectrum $\xi_i = -\ln \rho_i$ is thus readily available. In the following we will illustrate our procedure that determines the phase boundaries. It’s obvious that the phase boundary for $n_p = 2$ and for other even $n_p$ it is similar.

In Fig. 3 (a), we plot the energy of the ground state and the first excited state for $L_c = 16$ as a function of $J_\|$. An energy-level cross occurs at $J_\| = 3.1571(2)$, and this signals a first-order phase transition between the HP phase and the CRS phase. We checked other $L_c$ and confirmed our conclusion and we also find that the transition point is almost independent on $L_c$. Moreover, we calculate the excitation gap and find that both phases are gapful. In particular, in the CRS phase the gap may correspond to the breaking of the singlet. We should mention that because the CRS is a product state of singlets it is difficult to calculate the excited state for large $L_c$. To avoid this difficulty, we will focus on the ground state in large $L_c$ and study the entanglement entropy and entanglement spectrum. In Fig. 3(b), we show that the entanglement entropy $S$ for $L_c = 24$. In this case, the length of the system and the environment is equal. We observe a jump of $S$. This is interpreted as a first-order phase transition. Moreover, such jump occurs at $J_\| = 3.1570(1)$. These are well consistent with our conclusion from Fig. 3 (a). Such phase transition is also reflected in the entanglement spectrum. As we show in Fig. 3 (c), the degeneracy of the entanglement spectrum is different in the two phases. In the HP phase, all the entanglement spectrum are even-fold degenerate, which is a characteristic feature of the symmetry-protected topological phase\textsuperscript{18,42-47}. However, in the CRS phase, some of the entanglement spectrum are even-fold degenerate and others are odd-fold degenerate. Moreover, we find that in the CRS phase the lowest spectrum is nondegenerate and it is nearly zero, which indicates that the
corresponding eigenvalue of the reduced density matrix is very close to 1. This provides us strong evidence that the ground state in the given parameters is a product state of the system and the environment. During our DMRG sweep, the ladder is splitted into the system and the environment at different positions. By analysing the entanglement entropy of such different division, we can further determine the unit of such product state.

III. PHASE DIAGRAM FOR ODD $n_p$

When $n_p$ is odd the phase diagrams Fig. 4 are different from those for even $n_p$. In addition to the HP phase and the CRS phase, we find two more phases. One is the cluster singlet (CS) phase and the other is the even Haldane phase (EHP). In the CS phase, the intra-cluster interaction $J_\parallel$ is dominant and each cluster is a singlet. The dominant term in the ground state is the product state of these singlets. As we explain in Sec. I, the EHP phase is different from the HP phase. Particularly, it is not protected by symmetries. Therefore, it can evolve into a product state accompanied with a phase transition or without a phase transition\(^{18}\). $n_p = 3, 5$ belong to the former case. There is a first-order phase transition between the EHP phase and the CRS phase. But $n_p = 1$ belongs to the latter case, i.e., there is no phase transition between the EHP phase and the CRS phase, agreeing with previous works\(^{48,49}\). Even so, these two phases can be distinguished by their edge states. To show this, we calculate low-energy states under both periodic boundary condition (PBC) and open boundary condition (OBC). We find that under both PBC and OBC the ground state of the CRS phase is unique. The ground state of the EHP phase is unique under PBC but it is nine-fold degenerate under OBC, demonstrating the existence of an effective edge spin with spin-1.

Similar to those with even $n_p$, the phase diagrams with odd $n_p$ are determined as well by the energy of the ground state and first excited state, the entanglement entropy and the entanglement spectrum. We demonstrate this for $n_p = 3$ in Fig. 5 and Fig. 6. Let us first see Fig. 5. For simplicity, we fix $J_\perp = -3$. In panel (a), we show the entanglement entropy $S$ for $L_c = 40$ as a function of $J_\parallel$. Two sharp peaks are clearly observed, suggesting phase transitions at these two points. Moreover, contrary to that in Fig. 3, there is no discontinuity, and this suggests a continuous phase transition. In the thermodynamic limit, these two peaks are at $J_\parallel = 0.216(2)$ and $1.406(2)$. In panel (b), we show the excitation gap for various $L_c$ and two minimums are found. In the inset, we show the extrapolation of the excitation gaps at $J_\parallel = 0.216$ and $J_\parallel = 1.406$ for various sizes. In the thermodynamic limit they become gapless. We also check that the phases are gapful. These results are in good agreement with those obtained from the entanglement entropy. Since a characteristic feature of the HP phase is the even-fold-degenerate entanglement spectrum, we calculate them with equal system length and environment length. As we show in panel (c), the spectrum are indeed even-fold degenerate in the HP phase but in the EHP phase and CS phase they are not. Moreover, we calculate the excita-
and its phase diagram is already known. It occurs, suggesting a first-order phase transition. The level-crossing suggests a first-order phase transition. In Fig. 6, the two lowest energies are shown near the phase-transition points. For simplicity, we take \( J_\parallel = 0.4, 1.0 \) and \( 3.0 \), corresponding to the EHP to CRS, HP to CRS and CS to CRS transitions. In all three cases, a level-crossing occurs, suggesting a first-order phase transition.

FIG. 5. The entanglement entropy \( S \), the excitation gap \( \Delta \) and the entanglement spectrum \( \xi_i \) for \( n_p = 3 \) are plotted as a function of \( J_\perp \). In our calculation, \( J_\perp = -3 \) is fixed and the periodic boundary condition is employed. (a) The two peaks in the entanglement entropy suggest two phase transitions. \( L_c = 40 \) in this panel. (b) The excitation gap for \( L_c = 20, 30 \) and 40. Inset: in the thermodynamic limit, the excitation gap at the two dips closes and at other points it remains finite. (c) The entanglement spectrum in three phases. In the HP phase, they are even-fold degenerate.

FIG. 6. The ground-state energy \( E_0 \) and the first excited-state energy \( E_1 \) for \( L_c = 8, n_p = 3 \) are plotted as a function of \( J_\perp \). The level-crossing suggests a first-order phase transition.

Now, we have the phase diagrams for various \( n_p \). From Fig. 2 and 4, it is obvious that these phase diagrams depend on the parity of \( n_p \). For even \( n_p \), the phase diagram has an HP phase and a CRS phase. But for odd \( n_p \), there are four phases, an HP phase, a CRS phase, a CS phase and an EHP phase. Moreover, our results show that the region of the CS and EHP phases become smaller as \( n_p \) increases. Therefore, we expect that in the large \( n_p \) limit the phase diagrams will include only an HP phase and a CRS phase. For small \( n_p \), Hamiltonian (3) can not be neglected even if \( J_{\text{inter}} \) is much smaller in comparison with \( J_\parallel \) or \( J_\perp \) because it connects the two nearest-neighbor clusters. However, in the large \( n_p \) limit, the bulk properties are determined solely by Hamiltonian (2). Hamiltonian (3) only have some edge effect and thus can be neglected.

First, we consider the properties of Hamiltonian (2) and try to gain some insight from them. Actually, Hamiltonian (2) in the large \( n_p \) limit has been extensively studied and its phase diagram is already known. It includes an HP phase and a rung-singlet(RS) phase. A first-order phase transition is exactly known to occur at \( J_{\perp}/J_{\parallel} = 1.401 \ldots \).

To verify our analysis, let us examine the phase boundary in Fig. 2 and 4. We notice that when \( J_\perp \) is large enough the phase boundary is almost linear to \( J_{\parallel} \). This means that \( J_{\perp}/J_{\parallel} \) is nearly a constant. In the large \( n_p \) limit, we also expect that the phase transition depends only on \( J_{\perp}/J_{\parallel} \). In Fig. 7, we extrapolate \( J_{\perp}/J_{\parallel} \) as a quadratic polynomial of \( 1/n_p \) to the large \( n_p \) limit and obtain \( J_{\perp}/J_{\parallel} = 1.40(3) \), and this agrees well with the expected transition point \( J_{\perp}/J_{\parallel} = 1.401 \ldots \). Moreover, in the large \( n_p \) limit, the edge configuration can be neglected and CRS phase becomes RS phase. These provide strong numerical evidence supporting our analysis.

IV. LARGE \( n_p \) LIMIT
V. CONCLUSIONS

In conclusion, we study cluster-based two-leg ladders with the plaquette number $n_p$ up to six. These models are direct extensions of the model proposed for an edge-shared tetrahedral spin-cluster compound $\text{K}_2\text{Cu}_3\text{O} (\text{SO}_4)_3$. The numerically exact ground-phase phase diagrams are mapped out by using density-matrix renormalization group method. We find that they are closely associated with the parity of $n_p$. For even $n_p$, there are two phases in the phase diagram which includes an HP phase and a CSR phase. For odd $n_p$, in addition to the HP phase and the CRS phase, there are two more phases, which are a CS phase and an EHP phase. Moreover, the region of such two phases shrinks as $n_p$ increase, which leads to our conjecture that in the large $n_p$ limit they may disappear\(^{50}\). By extrapolating the phase transition point to the large $n_p$ limit, we can reproduce the phase transition point of the Hamiltonian without intercluster coupling (i.e. $J_{\text{inter}} = 0$), which confirms our conjecture. By analysing the energy and entanglement entropy, we determine the order of the phase transitions. The transition from HP phase to CS phase or to EHP phases in odd $n_p$ are continuous. There is no phase transition from the EHP phase to the CRS phase for $n_p = 1$, and all other phase transitions are first order.

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