Coexistence of valence-bond formation and topological order in the Frustrated Ferromagnetic $J_1$-$J_2$ Chain

Cléo Efthimia Agrapidis,1 Stefan-Ludwig Drechsler,1 Jeroen van den Brink,1,2 and Satoshi Nishimoto1,2

1Institute for Theoretical Solid State Physics, IFW Dresden, 01069 Dresden, Germany
2Department of Physics, Technical University Dresden, 01069 Dresden, Germany

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Frustrated one-dimensional magnets are known as ideal playgrounds for new exotic quantum phenomena to emerge. We consider one of the most elementary frustrated magnetic chains: the spin-$\frac{1}{2}$ ferromagnetic ($J_1$) Heisenberg chain with next-nearest-neighbor antiferromagnetic ($J_2$) interactions. On the basis of density-matrix renormalization group calculations we find its ground state at $J_2/|J_1| > 1/4$ to be a valence bond solid (VBS) that is characterised by an emergent spin-singlet dimerization between third-neighbour sites. The VBS is the consequence of spontaneous symmetry breaking through order by disorder. Quite interestingly, this VBS state has a Affleck-Kennedy-Lieb-Tasaki-type topological order and has a spin gap which reaches its maximum $\sim 7 \times 10^{-3}|J_1|$ around the most frustrated region $J_2/|J_1| = 0.6$. This is the first example of a frustrated spin chain in which quantum fluctuations induce gapped topological order.

Introduction. — The one-dimensional quantum world of spin-chain systems connects some of the most advanced concepts from many-body physics, such as integrability and symmetry-protected topological order [1], with the measurable physical properties of real materials. An example is the presence of the Haldane phase [2] in spin-1 chains, which is a topological ground state protected by global $Z_2 \times Z_2$ symmetry [3,4]. On the other hand frustrated magnets, in which a macroscopic number of quasi-degenerate states compete with each other, are an ideal playground for the emergence of exotic phenomena [5]. For instance, the interplay of frustration and fluctuations leads to unexpected condensed matter orders at low temperatures by spontaneously breaking of either a continuous or discrete symmetry order by disorder [6]. One of the simplest systems that shares both these features – geometric frustration and one-dimensionality – is the so-called $J_1$-$J_2$ chain, the Hamiltonian of which is given by

$$H = J_1 \sum_i S_i \cdot S_{i+1} + J_2 \sum_i S_i \cdot S_{i+2},$$

where $S_i$ is spin-$\frac{1}{2}$ operator at sites $i$, $J_1$ is nearest-neighbor (NN) and $J_2$ is next-nearest-neighbor (NNN) interactions. This chain system can be also represented as a zigzag ladder [Fig.1(a)] or a diagonal ladder [Fig.1(b)(c)]. The NNN interaction is assumed to be antiferromagnetic (AFM), i.e. $J_2 > 0$, inducing geometrical frustration. The frustration is parametrised as $\alpha = J_2/|J_1|$. The magnetic properties are quite different between the cases of ferromagnetic (FM) $J_1 < 0$ and AFM $J_1 > 0$, where we denote the systems as “FM $J_1$-$J_2$ chain” and “AFM $J_1$-$J_2$ chain”, respectively. In this Letter, we restrict ourselves to the FM $J_1$-$J_2$ chain, which is used as a standard magnetic model for quasi-one-dimensional edge-shared cuprates such as Li$_2$CuO$_2$ [7], LiCuSbO$_4$ [8], LiCuVO$_4$ [9], Li$_2$ZrCuO$_2$ [10], Rb$_2$CuMo$_3$O$_8$ [11] and PbCuSO$_4$(OH)$_2$ [12]. Especially, multi-magnons bound state [13] and multipolar ordering [14] under magnetic field have been established both theoretically and experimentally in this context.

The ground state of the AFM $J_1$-$J_2$ chain is well understood [15,17], assisted by the exact solution of the Majumdar-Ghosh model for $\alpha = 0.5$ [18]; but surprisingly the ground and excited state properties of the FM $J_1$-$J_2$ chain are still not completely identified. It is known that a phase transition occurs at $\alpha = \frac{1}{4}$ [19,20] from a FM to an incommensurate spiral state [21,22] with dimerization order [23]. But the quantitative estimation of spin gap (if it exists) and its numerical confirmation have been a long standing challenge - so far there is only a field-theoretical predictions of an exponentially small spin gap for $\alpha \gtrsim 3.3$ [24,25].

Our aim is to determine the ground state and spin gap of the
FM $J_1$-$J_2$ chain. To this end, we calculated various quantities including spin gap, string order parameter, several dimerization order parameters, dimer-dimer correlation function, spin-spin correlation function, and entanglement entropy using the density-matrix renormalization group (DMRG) technique [26]. First, we verify the existence of a finite spin gap at $\alpha > \frac{1}{2}$ and find its maximum around $\alpha = 0.6$. Next, we show that the ground state is a valence bond solid (VBS) state with spin-singlet formations between third-neighbor sites (which we refer to as the “$D_3$-VBS state”), which leads to the finite spin gap. The leading mechanism for the emergence of this ordered state is magnetic frustration, which is characterized by the presence of strong quantum fluctuations, thus we are observing the formation of order by disorder. Remarkably, this VBS state is associated with an Affleck-Kennedy-Lieb-Tasaki (AKLT) [27]-like topological hidden order. We confirm the robustness of the $D_3$-VBS state by considering an adiabatic connection of the ground state to the enforced third-neighbor dimerized state.

Method. — We employ the DMRG method, which is one of the most powerful numerical techniques for studying 1D quantum systems. Open boundary conditions (OBC) are applied unless stated otherwise. Besides, both edged $J_1$’s (denoted as $J_1^{\text{edge}}$) are taken to be zero in the open chain. This has an important physical implication which will be clarified in the following. This enables us to calculate ground-state and low-lying excited-state energies, as well as static quantities, quite accurately for very large systems. This puts us in the position to carry out an accurate finite-size-scaling analysis to obtain energies and quantities in the thermodynamic limit. We keep up to $m = 6000$ density-matrix eigenvalues in the renormalization procedure. Moreover, several chains with length up to $L = 800$ are studied to perform finite size scaling. This way, we are able to obtain accurate results with error in the energy $\Delta E/L < 10^{-11}$. In some cases we study larger systems up to $L = 3000$ to estimate the decay length of the spin-spin correlation function and entanglement entropy.

Spin gap. — Although the existence of a tiny spin gap was predicted by the field-theoretical analyses [24,25], it has not been numerically detected so far. In our DMRG calculations, the spin gap $\Delta$ is defined as the energy difference between the singlet ground state and the triplet first excited state:

$$\Delta(L) = E_0(L, S^z = 1) - E_0(L, S^z = 1); \quad \Delta = \lim_{L \to \infty} \Delta(L),$$

where $E_0(L, S^z)$ is the ground state energy of a system of size $L$ and total spin $z$ component $S^z$. As mentioned above, we set $J_1^{\text{edge}} = 0$; otherwise, one cannot measure correctly the excitation energy for the bulk system (see the Supplemental Material for details). Fig. 2 shows the spin gap in the thermodynamic limit as a function of $\alpha$. It is compared to that for the AFM $J_1$-$J_2$ chain in the inset of Fig. 2. For the FM $J_1$-$J_2$ chain a finite spin gap is clearly observed in a certain $\alpha$ region, although it is about two orders of magnitude smaller than that for the AFM $J_1$-$J_2$ chain. The spin gap seems to grow continuously from $\alpha = \frac{1}{2}$ reaching its maximum $\Delta \simeq 0.007 |J_1|$ around $\alpha = 0.6$, which is within the most highly-frustrated region. This already suggests that the origin of the spin gap is a frustration-induced long-range order, and the result of order by disorder.

Valence bond solid state. — Having established the existence of a finite spin gap for $\alpha > \frac{1}{2}$, we investigate a possible mechanism leading to it. It is known that a spontaneous FM dimerization is driven along $J_1$ bonds [24,25] and an emergent effective spin-1 degrees of freedom is created with the dimerized two spin-$\frac{1}{2}$’s [23]. If the system (1) can be mapped onto a $S = 1$ Heisenberg chain, the finite spin gap might be interpreted as a Haldane gap with a VBS state [27]. However, it is not trivial whether an arbitrary set of valence bonds between the neighboring effective $S = 1$ sites leads to a finite spin gap [see Fig. 1(b)]. To investigate the stability of VBS state, we examine the string order parameter [23]:

$$O_{\text{string}}^2 = - \lim_{|k - j| \to \infty} \left( \sum_{j=1}^{-1} \exp(i\pi \sum_{l=k+2}^{2} S_{j}^z) (S_{j}^z + S_{j+1}^z) \right).$$

(3)

For our system (1), Eq. (1) can be simplified as $O_{\text{string}}^2 = - \lim_{|k - j| \to \infty} \left( \sum_{j=1}^{-1} (S_{k}^z + S_{k+1}^z) \prod_{l=k+2}^{2} (S_{j}^z + S_{j+1}^z) \right)$ (see Supplemental Material). The two-fold degeneracy of the ground state is lifted under OBC and the value of $O_{\text{string}}^2$ is different for even and odd $j$ ($k$). We thus take their average obtained with $(k, j) = (\frac{k}{2}, \frac{j}{2})$ and $(k, j) = (\frac{k+1}{2}, \frac{j}{2} - 1)$. We confirm the validity of this method by checking the agreement of the OBC results with those obtained under periodic boundary conditions keeping $|k - j| = \frac{L}{2}$. In Fig. 3(a) the string order parameter in the thermodynamic limit is plotted as a function of $\alpha$. The finite value of $O_{\text{string}}^2$ suggests the formation of a VBS state with a hidden topological long-range order. The string order vanishes
when approaching $\alpha = \frac{1}{4}$, indicating a second-order phase transition at the FM critical point. With increasing $\alpha$, it goes through a maximum at $\alpha \simeq 0.55$, which is roughly consistent with the maximum position of the spin gap, and tends slowly towards zero in the limit $\alpha \to \infty$. The maximum value $\mathcal{O}_{\text{string}} \sim 0.06$ is much smaller than $\mathcal{O}_{\text{VBS}}^\alpha = \frac{1}{8} \simeq 0.4444$ for the perfect VBS state for the AKLT model [27] and $\mathcal{O}_{\text{string}}^\alpha \simeq 0.3743$ for the $S = 1$ Heisenberg chain [28]. This means that our VBS state is very fragile which is a reason why it is so difficult to detect the spin gap numerically.

Furthermore, the criticality of a 1D system can be definitely identified by its entanglement structure. We use the von Neumann entanglement entropy of the subsystem with length $l$, $S_L(l) = -\text{Tr}_l \rho_l \log \rho_l$, where $\rho_l = \text{Tr}_{L-l} \rho$ is the reduced density matrix of the subsystem and $\rho$ is the full density matrix of the whole system. A gapped state is characterized by a saturation of $S_L(l)$ as as function of $l$ [30]. In Fig. 3b) the entanglement entropy is plotted as a function of $l$ with fixed whole system length $L = 2000$. We can clearly see the saturation behavior indicating a gapped ground state. The saturation value is slightly split depending on whether the system is divided inside or outside the effective $S = 1$ site. In a VBS state, $S_L(l)$ approaches the saturation value $S_L^\text{sat}$ exponentially, i.e., $S_L(l) \sim S_L^\text{sat} - a \exp(-l/\xi_{\text{ent}})$; while the spin-spin correlation decays with distance exponentially, i.e., $|\langle S_0^z S_j^z \rangle| \sim \exp(-r/\xi_{\text{corr}})$ [31]. For the AKLT VBS state $\xi_{\text{ent}}$ and $\xi_{\text{corr}}$ must coincide, which is indeed what we observe numerically in the $D_3$-VBS state. [See Fig. 3c)] For technical reasons, we could determine the spin gap only for $\alpha \leq 0.85$. However, since $\xi_{\text{corr}} \cdot (\Delta/J_2) = \text{const}.$ is expected in the large $\alpha$ regime, a tiny but finite gap is expected up to $\alpha = \infty$. The above analysis makes clear that a gap opens due to the formation of a VBS state but it is not yet obvious how the VBS structure is formed.

Dimerization order. — We can determine a more specific VBS structure by considering the possibility of longer-range dimerization orders. The dimerization order parameter between sites distant $\delta$ is defined as

$$O_{\text{dimer}}(\delta) = \lim_{L \to \infty} |\langle S_{i-\delta} \cdot S_i \rangle - \langle S_i \cdot S_{i+\delta} \rangle|, \quad (4)$$

where we take $i = L/2$ for $\delta = 1$ and $i = L/2 - 1$ for $\delta = 2,3$ (the extrapolated value in the thermodynamic limit does not depend on these choices). If $O_{\text{dimer}}(\delta)$ is finite for $\delta$, it signifies a long-range dimerization order associated with translational symmetry breaking to period of $4 - 2(\delta \text{ mod } 2)$. For the case of $\delta = 2$ we verified that $O_{\text{dimer}}(2)$ goes to zero in the thermodynamic limit (See Supplemental Material). Thus, the possibility of a VBS state with dimerization along two $J_2$ chains is excluded. Whereas for $\delta = 1$ and 3, $O_{\text{dimer}}(\delta)$ is finite. In Fig. 3a) the values of $O_{\text{dimer}}(1)$ and $O_{\text{dimer}}(3)$ in the thermodynamic limit are plotted as a function of $\alpha$. Remarkably, $O_{\text{dimer}}(3)$ is significantly larger than $O_{\text{dimer}}(1)$ despite the longer distance. Moreover, though FM dimerization between fifth-neighbors and AFM dimerization between seventh-neighbor may be finite, we expect them to be much smaller than the values reported in Fig. 4a). We also find that $\langle S_i \cdot S_{i+3} \rangle$ is always negative at $\alpha > \frac{1}{4}$ suggesting that a VBS ground state with the third-neighbor valence bonds, i.e., $D_3$-VBS state, is stabilized as shown in Fig. 3c).

In order to further prove the $D_3$-VBS picture, we calculate the dimer-dimer correlation function defined as

$$\langle D_3(i)D_3(j) \rangle - \langle D_3 \rangle^2, \quad (5)$$

FIG. 3. String-order parameter as a function of $\alpha$. Red (blue) line refers to open (periodic) boundary conditions. (b) Entanglement entropy as a function of the subsystem length $l$. (c) Inverse of the decay length estimated from the spin-spin correlation ($\xi_{\text{corr}}$) and the entanglement entropy ($\xi_{\text{ent}}$) as a function of $\alpha$. Red line is a fit with the exponential function $1/\xi_{\text{corr}} = 0.13 \exp(-0.35\alpha)$.

FIG. 4. (a) Dimer order parameters for the NN (red line) and third-neighbor (blue line) bonds as a function of $\alpha$. (b) Dimer-dimer correlation $\langle D_3(i)D_3(i) \rangle$ as a function of distance $|i - j|$ for several values of $\alpha$. To see the net correlation the product of expectation values $\langle D_3 \rangle^2$ is subtracted.
the S function yields $\Delta_D$ where sites 1 and 3 of the diagonal ladder [Fig. 1(c)]. A spin-singlet is formed between $|\alpha\rangle$ in the first-neighbor sites (J$_i$) and $|\alpha\rangle$ in the third-neighbor sites (J$_{i+3}$) for different values of J$_i$. The third-neighbor valence bond is locally stabilized in a S$_3$-VBS state with the AKLT-like topological hidden order. This is similar to the ground state of the AKLT model but the symmetric operation between two spin-1/2’s within the effective S = 1 site, i.e., |↑⟩|↓⟩ + |↓⟩|↑⟩, is not explicitly included (see also the Supplemental Material).

Consequently, two terms in Eq. (5) correspond to two-fold degenerate $\Delta_0$ with $S$ = 1 rungs as in Fig. 1(c), the $D_3$-VBS state may be interpreted as a symmetry protected state [1] with a plaquette unit including two effective $S$ = 1 rungs.

Matrix product state. — Our VBS wave function can be expressed as the matrix product state

$$|\text{VBS}\rangle = \frac{1}{\sqrt{2}} \left[ \text{Tr} \prod_{i \text{ odd}} g_i + \text{Tr} \prod_{i \text{ even}} g_i \right]$$

with

$$g_i = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} |\uparrow\rangle_i+1 |\downarrow\rangle_i \\ |\downarrow\rangle_i+1 |\uparrow\rangle_i \end{pmatrix}$$

where $|\alpha\rangle$ denotes the spin state of effective $S$ = 1 site created by the original two $S = 1/2$ sites (i, i+1).

This is similar to the ground state of the AKLT model but the symmetric operation between two spin-1/2’s within the effective S = 1 site, i.e., |↑⟩|↓⟩ + |↓⟩|↑⟩, is not explicitly included (see also the Supplemental Material). Alternatively, two terms in Eq. (5) correspond to two-fold degenerate states. The Lieb-Schultz-Mattis theorem is thus satisfied. A schematic picture of one is shown in Fig. 1(d), in which every site forms a singlet pair with the third neighbor site. In fact, setting $J_1^{\text{edge}} = 0$ corresponds to an explicit replacement of S = 1 spin at the each end by $S = 1/2$ spin in our effective S = 1 chain [34]. It removes the degeneracy due to the edge spin state and enables us to calculate the spin gap with the DMRG method.

In analogy with the AKLT state, the essential physics of our $D_3$-VBS state should be explained by extracting a single plaquette including two effective S = 1 sites, i.e., four S = 1/2 sites. The plaquette is sketched in the inset of Fig. 5(b). The third-neighbor valence bond is locally stabilized in a S = 1 rungs. The excitation energy can be qualitatively estimated from the excitation energy to a state with $|\sum_{i=1}^4 S_i| = 2$, i.e., $S^{\text{tot}} = 2$, sector which is projected out from the ground state as in the AKLT model. We plot the excitation energy as a function of a $\Delta$. We can see that the tendency of $\Delta$ is qualitatively reproduced by the single plaquette: With increasing $\Delta$, the gap starts to increase at $\alpha = 1/2$, goes through the maximum at $\alpha = 0.5$, and then decreases slowly at larger $\alpha$.

Conclusion. — We studied the frustrated FM J$_1$-J$_2$ chain using the DMRG technique. Based on the results of string order parameter, dimerization order parameters, dimer-dimer correlation function, and entanglement entropy, we find a second order phase transition at $\alpha = 1/2$ from a FM state to a third-neighbor VBS state with the AKLT-like topological hidden order. This provides a simple realization of coexistence of spontaneous symmetry breaking and topological order, or rather, topological order caused by spontaneous symmetry breaking: Frustration leads to dimerization, i.e. breaking of translational symmetry, which in turns leads to the observed VBS state. This means the ordered state is due to the quantum fluctuations typical of magnetic frustration – order by disorder.
The emergence of spontaneous third-neighbor VBS formation was further confirmed by the observation of an adiabatic connection of the ground state to an enforced third-neighbor dimerized state. Originated from the VBS state, the spin gap opens at \( \alpha = \frac{1}{4} \) and reaches its maximum \( \Delta \approx 0.007|J_1| \), which is about two orders of magnitude smaller than that for the AFM \( J_1-J_2 \) chain, at \( \alpha \approx 0.6 \). A typical value for \( J_1 \) in cuprates is \( J_1 = -200K \), which leads to a gap closing at external magnetic field \( \simeq 1 \) T. Since the correlation length of spin-spin correlation seems to diverge at \( \alpha = \infty \), a tiny but finite spin gap may be present up to \( \alpha = \infty \).

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SUPPLEMENTAL MATERIAL

DERIVATION OF THE STRING ORDER PARAMETER FOR NUMERICAL CALCULATIONS

The string order parameter for a spin $S = 1$ chain is defined as

$$O_{\text{string}}^z = -\lim_{|k-j|\to\infty} \langle \langle \hat{S}_k^z \rangle \exp(i\pi \sum_{l=k+1}^{j-1} \hat{S}_l^z) \langle \hat{S}_j^z \rangle \rangle,$$

(1)

where $\hat{S}_i^z$ is the $z$-component of a spin-1 operator at site $i$. In our system, the resultant spin of two $S = 1/2$ spins forming a spin-triplet pair is regarded as an effective $S = 1$ spin. Hence, Eq. (1) can be rewritten in term of $S = 1/2$ spins as

$$O_{\text{string}}^z = -\lim_{|k-j|\to\infty} \langle \langle S_k^z + S_{k+1}^z \rangle \exp(i\pi \sum_{l=k+2}^{j-1} S_l^z) \langle S_j^z + S_{j+1}^z \rangle \rangle,$$

(2)

where $S_i^z$ is the $z$-component of a spin-1/2 operator at site $i$. Considering that the $z$-component of a spin-1/2 spin can only take the values $S^z = \pm 1/2$, we have

$$\exp(i\pi S_i^z) = i \sin(\pm \pi/2) = \pm i,$$

since $\cos(\pm \pi/2) = 0$. Taking pairs of spins $S_i^z S_{i+1}^z$ (within an effective spin-1 site), we get a relation

$$\exp[i\pi (S_i^z + S_{i+1}^z)] = -4S_i^z S_{i+1}^z,$$

where the coefficient 4 accounts for renormalizing the 1/4 factor from multiplying two spin-1/2’s. Finally, we obtain a simplified string order parameter:

$$O_{\text{string}}^z = -\lim_{|k-j|\to\infty} (-4)^{-k-2} \langle (S_k^z + S_{k+1}^z) \prod_{l=k+2}^{j-1} S_l^z \rangle \langle S_j^z + S_{j+1}^z \rangle,$$

(3)

which is expressed only by products of $S^z$. 
BOUNDARY CONDITION ON $J_1$ BONDS

Fig. 6. Expectation value of the $z$-component of local spin $\langle S_z^i \rangle$ as a function of site position $i$ at $\alpha = 0.6$ with $L = 600$ for (a) $J_{\text{edge}}^1 = -1$ and (b) $J_{\text{edge}}^1 = 0$.

In our open chain, we set the $J_1$ bonds at the chain edges to be zero, i.e., $J_{\text{edge}}^1 = 0$. As written in the main text, it corresponds to an explicit replacement of $S = 1$ spin at each end by $S = \frac{1}{2}$ spin in the 1D $S = 1$ Heisenberg model. It is known that this procedure is necessary to numerically calculate the spin gap as a singlet-triplet excitation. To illustrate it in our model, we plot the value of the spin $z$-component, i.e. $S_z^i$, in the $S_z = 1$ excited triplet state as a function of site position $i$ at $\alpha = 0.6$ for $L = 600$. As shown in Fig. 6(a), when we naively keep $J_{\text{edge}}^1 = -1$, the spin flipped from the singlet ground state (spinon) is mostly localized around the chain edges. It resembles the fact that a residual $S = 1/2$ edge spin (out of a valence bond) in the 1D $S = 1$ Heisenberg model can be flipped without energy cost. If such a situation happens, the excitation energy, i.e. the spin gap, is zero or significantly underestimated. It thus prevents us from estimating the bulk spin gap correctly. Whereas in the case of $J_{\text{edge}}^1 = 0$, the flipped spin is distributed inside the system as seen in Fig. 6(b). Therefore, we can obtain the spin gap after an extrapolation of the singlet-triplet excitation energy to the thermodynamic limit.

Additionally, we have to exclude the possibility that artificially setting $J_{\text{edge}}^1 = 0$ puts the system in an excited state. To study it, we compare the lowest energies at $\alpha = 0.6$ for the two different values of $J_{\text{edge}}^1$ in Fig. 7 as a function of $1/L$. We see that at finite $L$ the energy for $J_{\text{edge}}^1 = 0$ is rather lower than that for $J_{\text{edge}}^1 = -1$. A linear fitting yields $E_0/L(J_{\text{edge}}^1 = -1) = -0.2874202246$, while for $J_{\text{edge}}^1 = 0$ it yields $E_0/L(J_{\text{edge}}^1 = 0) = -0.2874200731$. They coincide perfectly in the thermodynamic limit ($1/L = 0$) This means that the bulk ground state does not depend on the choice of $J_{\text{edge}}^1$. 

Fig. 7. Finite-size scaling of the lowest energy for $J_{\text{edge}}^1 = -1$ and $J_{\text{edge}}^1 = 0$ at $\alpha = 0.6$. A linear fitting is performed in both cases.
In Fig. 8 we present three examples for the finite-size scaling of the spin gap. Below $\alpha \simeq 0.6$ the data points align well so that a second-order polynomial fitting works. Above $\alpha \simeq 0.6$ the data points oscillate reflecting the incommensurate structure and the fitting becomes more difficult. Therefore, we perform both linear and second-order polynomial fittings and the difference in the obtained values is put as an error bar in Fig. 2 of the main text. For $\alpha > 0.85$, the oscillation is a crucial problem in the scaling and we could not perform a reasonable fitting.
EXCLUSION OF THE POSSIBILITY OF VALENCE BONDS FORMATION ON $J_2$ BONDS

FIG. 9. Finite-size scaling of the dimerization order parameter for the formation of valence bonds along two $J_2$ chains at $\alpha = 0.6$. The formation of valence bonds along two $J_2$ chains is sketched in (b).

The order parameter for spontaneous dimerization along the two $J_2$ chains is defined as

$$O_{\text{dimer}}(2) = \lim_{L \to \infty} \langle |S_{L/2-2}S_{L/2} - S_{L/2}S_{L/2+2}| \rangle.$$  (4)

In the limit of $L \to \infty$, $O_{\text{dimer}}(2)$ vanishes, as seen in Fig. 9(a). This clearly indicates the absence of long-range dimerization order along the two $J_2$ chains like in Fig. 9(b). Thus, this VBS state is excluded from the candidate for the ground state for the FM $J_1$-$J_2$ chain.
DIMER-DIMER CORRELATION FUNCTION FOR THE THIRD-NEIGHBOR BONDS

In the main text, we show the saturation of dimer-dimer correlations for the third-neighbor bonds, $\langle D_3(i)D_3(j) \rangle - \langle D_3 \rangle^2$ with $D_3(i) = S_i \cdot S_{i+3}$, at $\alpha = 0.4$, 0.6, and 0.8. However, only the correlations for dimer pairs forming valence bond as in Fig. 10(a) are shown in the manuscript. It would be informative to see the correlation between the other third-neighbor bond pairs. As expected, the correlation between third-neighbor pairs without valence bond saturates to a negative value [Fig. 10(c)] and that between third-neighbor pairs with and without valence bond vanishes [Fig. 10(b)].

FIG. 10. Dimer-dimer correlation functions for the three different kinds of third-neighbor bonds pairs at $\alpha = 0.6$. 
We consider a single plaquette of the diagonal ladder representation as depicted in the inset of Fig. 11. A single plaquette includes two effective $S = 1$ sites; $(1, 2)$ and $(3, 4)$. In the $S_{\text{tot}} = 1$ sector the antiferromagnetic spin-spin correlation between sites 1 and 4 is much stronger than that between sites 1 and 3 for $\alpha > 1/4$. This clearly indicates a spin-singlet formation between sites 1 and 4, which corresponds to the third-neighbor valence bond in our $D_3$-VBS state. Each of the remaining two $S = 1/2$ spins on sites 2 and 3 forms another spin-singlet with a $S = 1/2$ spin in the neighboring plaquette.
MATRIX PRODUCT EXPRESSION OF THE $D_3$-VBS STATE

The $D_3$-VBS wave function is expressed as a matrix product state

$$|VBS⟩ = \frac{1}{\sqrt{2}} \left[ \text{Tr} \prod_{i \text{ odd}} g_i + \text{Tr} \prod_{i \text{ even}} g_i \right]$$

with

$$g_i = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} |↑⟩_{i+1} |↑⟩_{i} & |↑⟩_{i+1} |↓⟩_{i} \\ |↓⟩_{i+1} |↑⟩_{i} & |↓⟩_{i+1} |↓⟩_{i} \end{pmatrix}$$

where $|a⟩_i|b⟩_i$ ($a,b = ↑, ↓$) denotes the spin state of the effective $S = \frac{1}{2}$ site created by the original $S = \frac{1}{2}$ sites $(i, i+1)$. Let us perform a part of the product between two effective $S = 1$ sites:

$$\begin{pmatrix} |↑⟩_{i+1} |↑⟩_{i} & |↑⟩_{i+1} |↓⟩_{i} \\ |↓⟩_{i+1} |↑⟩_{i} & |↓⟩_{i+1} |↓⟩_{i} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} |↑⟩_{i+3} |↑⟩_{i+2} & |↑⟩_{i+3} |↓⟩_{i+2} \\ |↓⟩_{i+3} |↑⟩_{i+2} & |↓⟩_{i+3} |↓⟩_{i+2} \end{pmatrix}$$

$$= \begin{pmatrix} |↑⟩_{i+1} |↑⟩_{i+2} & |↑⟩_{i+1} |↓⟩_{i+2} \\ |↓⟩_{i+1} |↑⟩_{i+2} & |↓⟩_{i+1} |↓⟩_{i+2} \end{pmatrix} \otimes \left( |↑⟩_{i} |↓⟩_{i+3} - |↓⟩_{i} |↑⟩_{i+3} \right).$$

A spin-singlet is formed between $S = 1/2$ spins at sites $i$ and $i+3$, namely, between third-neighbor sites. Since the resultant $2 \times 2$ matrix has the same form as before, this matrix product state can be extended up to an arbitrary length.