Valence bond solid and possible deconfined quantum criticality in an extended kagome lattice Heisenberg antiferromagnet

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We present numerical evidence for the emergence of an extended valence bond solid (VBS) phase at $T = 0$ in the kagome $S = 1/2$ Heisenberg antiferromagnet with ferromagnetic further-neighbor interactions. The VBS is located at the boundary between two magnetically ordered regions and extends close to the nearest-neighbor Heisenberg point. It exhibits a diamond-like singlet covering pattern with a 12-site unit-cell. Our results suggest the possibility of a direct, possibly continuous, quantum phase transition from the neighboring magnetically ordered phase into the VBS phase. Moreover, a second phase which breaks lattice symmetries, and is of likely spin-nematic type, is found close to the transition to the ferromagnetic phase. The results have been obtained using numerical Exact Diagonalization. We discuss implications of our results on the nature of nearest-neighbor Heisenberg antiferromagnet.

Introduction — We expect the unexpected when strong electron interactions meet geometric frustration. The emergence of novel exotic states of matter in frustrated quantum magnets is intensely studied in experiments, theory, and numerical computations. Several materials and theoretical models exhibit a lack of magnetic ordering even at lowest temperatures. Instead, genuine quantum many-body states, like quantum spin liquids [1, 2] or valence bond solids (VBS) can be observed [3–6].

The nearest-neighbor kagome lattice Heisenberg spin 1/2 antiferromagnet arguably remains one of the most puzzling conundrums in frustrated magnetism. Various scenarios on the nature of its ground state have been proposed. It has been found early, that a VBS is energetically competitive [7–11]. However, more recent numerical studies suggest, that different spin disordered states are a more likely scenario. Several density-matrix renormalization group (DMRG) studies later suggested the possibility of a gapped spin liquid ground state [12, 13]. More recently, variational Monte Carlo and tensor network studies also suggested a gapless spin liquid state being realized [14–18]. While conclusion on the nature of its ground state has not unanimously been reached to date [19], several exotic new states of matter have been clearly identified in close proximity to the nearest-neighbor model [20–23]. Among those, a chiral spin liquid has been found in an extended Heisenberg model with antiferromagnetic second and third nearest-neighbor interactions [21–23]. The classical ground state phase diagram of this model has previously been established [24, 25]. A phase transition between two magnetic orders has been found for antiferromagnetic interactions. In the quantum case, the chiral spin liquid phase is located at the transition line between these two magnetic phases and extends close to the nearest-neighbor point. The classical phase diagram also contains a phase transition line between two types of coplanar magnetic orders for ferromagnetic second and third nearest-neighbor interactions. Given that some frustrated kagome materials involving both magnetic and antiferromagnetic couplings are known to exist [26, 27], there is a strong interest to explore whether novel phases also emerge at or in the vicinity of the classical transition line at $J_3 = 2J_2 < 0$.

Here, we investigate the kagome spin 1/2 Heisenberg antiferromagnet with additional ferromagnetic second and third nearest-neighbor interactions. We present conclusive numerical evidence for the appearance of a diamond VBS phase in an extended parameter range. The VBS phase is located in the vicinity of the classical transition line between the $q = 0$ and $\sqrt{3} \times \sqrt{3}$ magnetic orders. Interestingly, the phase extends close up to the nearest-neighbor Heisenberg point.

![FIG. 1. (a) Approximate phase diagram of the extended kagome Heisenberg model Eq. (1) for $J_1 > 0$ and $J_2, J_3 \leq 0$ as obtained from ED on a 36-site simulation cluster. Between two regions of magnetic $q = 0$ and $\sqrt{3} \times \sqrt{3}$ order a diamond VBS and a spin nematic phase are emerging. Different colors denote the quantum numbers of the first excited state. Green: $S = 1$, $\Gamma.D6.A2$ or $\Gamma.D6.E2$. Blue: $S = 1$, $\Gamma.D6.B1$ or $K.D3.A1$. Pink: $S = 0$, $M.D2.A2$. Orange: $S = 0$, $M.D2.A1$. Yellow: $S = 2$, $\Gamma.D6.A1$. Gray: $S = 0$, various space group sectors. Gray lines are a guide to the eye. (b) Coupling geometry for the Hamiltonian Eq. (1). (c) Structure of the diamond VBS with a 12-site unit cell. Dimer coverings on the diamond structure are in resonance.](https://example.com/fig1.png)
Model and phase diagram — We consider the Hamiltonian,

\[ H = J_1 \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle \langle i,j \rangle \rangle} \vec{S}_i \cdot \vec{S}_j + J_3 \sum_{\langle \langle \langle i,j \rangle \rangle \rangle} \vec{S}_i \cdot \vec{S}_j, \]

on a kagome lattice geometry, where \( \vec{S}_i = (S_i^x, S_i^y, S_i^z) \) denotes spin 1/2 operators, \( \langle \ldots \rangle \) and \( \langle \langle \ldots \rangle \rangle \) denotes the sum over nearest- and second-nearest-neighbor sites, and \( \langle \langle \langle \ldots \rangle \rangle \rangle \) denotes sum over third nearest-neighbor interactions only across the hexagons of the kagome lattice, cf. Fig. 1(b). In the following, we set \( J_1 = 1 \) and focus on the case of ferromagnetic couplings \( J_2 < 0 \) and \( J_3 < 0 \).

Our results are obtained by Exact Diagonalization (ED) calculations on a \( N = 36 \) site kagome lattice with periodic boundary conditions [28]. Its Brillouin zone features the \( \mathbf{K} \) and \( \mathbf{M} \) points and is hence suited to stabilize both the \( \sqrt{3} \times \sqrt{3} \) and \( \mathbf{q} = 0 \) order. We detect ordering by investigating suitably chosen order parameters and performing tower-of-states analysis, i.e. comparing quantum numbers of finite-size energy eigenstates with theoretical predictions. The order parameters of the ground state and finite-size energy spectra are calculated on a grid for \( J_2 \in [-1, 0] \) with spacing 0.05 and \( J_3 \in [-2, 0] \) with spacing 0.1.

For classical Heisenberg spins the phase diagram of this model has been established in Ref. [25]. The \( \sqrt{3} \times \sqrt{3} \) magnetic phase is separated from the \( \mathbf{q} = 0 \) magnetic phase by a critical line located at \( J_3 = 2J_2 \). For \( J_3 < -2 \) and \( J_2 < -1 \) a ferromagnetic state is stabilized.

In Fig. 1 we present a first exploration of the quantum (\( S = 1/2 \)) phase diagram based on a map organized by the quantum numbers of the first excitation above the ground state. The assignment of the phases is performed based on a tower-of-states analysis for different candidate phases. According to this rationale, the blue region indicates the \( \sqrt{3} \times \sqrt{3} \) magnetic order, the green region indicates the \( \mathbf{q} = 0 \) magnetic order and the pink region the VBS phase. The nematic phase extends in the yellow and orange region, where two different quantum numbers are the first excitation. The gray lines serve as a guide to the eye and determine approximate phase boundaries. Apart from the expected \( \sqrt{3} \times \sqrt{3} \) and \( \mathbf{q} = 0 \) collinear magnetic order phases, we find an unanticipated diamond VBS and a lattice symmetry breaking spin nematic phase located in the vicinity of the classical transition line. In Fig. 2 we corroborate the spectroscopy picture with an analysis of corresponding order parameters. The spin nematic phase extends close to the classical ferromagnetic phase, while the VBS phase extends close to the nearest-neighbor point. We now proceed to characterize the reported phases in more detail.

Magnetic order — The \( \mathbf{q} = 0 \) and \( \sqrt{3} \times \sqrt{3} \) magnetic phases break spin rotational SU(2) symmetry and exhibit patterns of magnetic ordering shown in the supplementary material [29]. We consider the static spin structure factor,

\[ S(\mathbf{q}) = \frac{1}{N} \sum_{k,l=1}^{N} e^{-i\mathbf{q} \cdot (\mathbf{r}_k - \mathbf{r}_l)} \langle \vec{S}_{k} \cdot \vec{S}_{l} \rangle. \]

For the two magnetic orders, the structure factor is peaked at the points

\[ \mathbf{M}' = (2\pi, 2\pi/\sqrt{3}) \quad \text{for} \quad \mathbf{q} = 0 \text{ order}, \]
\[ \mathbf{K}' = (8\pi/3, 0) \quad \text{for} \quad \sqrt{3} \times \sqrt{3} \text{ order}, \]

in the extended Brillouin zone, cf. [24]. Hence, \( S(\mathbf{M}') \) and \( S(\mathbf{K}') \) shown in Fig. 2(a) and (b) identify both magnetic phases, respectively. The regions where these structure factors are peaked coincide with the blue and green regions in Fig. 1. The blue region in Fig. 1(a) is given by the points, where the first excitation is a triplet, \( S = 1 \), state with KD.3.A1 or \( \Gamma.D6.B1 \) space group quantum numbers [29, 30]. In the green region in Fig. 1(a), the triplet states, \( S = 1 \), with \( \Gamma.D6.A2 \) and \( \Gamma.D6.E2 \) space group quantum numbers are the first excitation. Thus, the spin structure factor and energy spectroscopy yield consistent results on the extent of these two phases.
Diamond VBS phase — To identify the VBS and the lattice symmetry breaking spin-nematic phase we consider the connected dimer correlations,

\[ D_{kl} = \langle \langle \hat{S}_k \cdot \hat{S}_l \rangle \rangle - \langle \hat{S}_k \rangle \langle \hat{S}_l \rangle, \]

where the sites 0 and 1 are an arbitrary nearest-neighbor bond chosen as reference. These correlations are long-ranged in the VBS phase and exhibit specific patterns of positive and negative correlation that can be predicted for model VBS state. The sign structure of these correlations serves as a first fingerprint of the particular VBS phase realized. For the diamond VBS state the expected sign structure of the dimer correlations are shown in Fig. 3(a). Thereby, we define an order parameter of the VBS phase,

\[ O_{\text{VBS}} = \frac{1}{N} \sum_{(k,l)} \theta_{\text{VBS}}^{kl} D_{kl}, \]

where \( \theta_{\text{VBS}}^{kl} = \pm 1 \) denotes the sign as defined in Fig. 3(a).

This diamond VBS parameter \( O_{\text{VBS}} \) is shown in Fig. 2(c), indicating the extent of the VBS phase. It is located between the two magnetic orders and extends basically along the whole classical critical line from \( J_2 = -1 \) to \( J_3 = 0 \). The region of pronounced \( O_{\text{VBS}} \) also coincides with the pink region in Fig. 1. There, the first excited state is a singlet \( S = 0 \) state with M.D2.A2 space group quantum number.

The precise nature of the reported VBS itself requires some more care. There are two basic candidate VBS model states with a twelve site unit cell [12, 31–33]. A pinwheel VBS, where all dimers are static and the pinwheels all share the same orientation. This particular state is eightfold degenerate, a factor four from the translations and a factor two from the pinwheel orientation. On the other hand, like in many other VBS scenarios, there is a resonant version of this VBS, where we consider resonances involving eight-site loops in the shape of a diamond lozenge. A fully packed state of non-overlapping resonances is shown in Fig. 1(c). This state is actually twelve-fold degenerate, a factor four from the translations, and a factor three from the orientations of the diamond lozenges. The dimer-dimer correlations in these two model states are identical, so that dimer correlations can not distinguish the two states. However the spectral decomposition [29] reveals that beyond some common levels the diamond VBS features a characteristic spin singlet \( \Gamma \text{D6.E2} \) level, while the pinwheel VBS comes with a characteristic \( \Gamma \text{D6.A2} \) level. A close inspection of the energy spectrum of the VBS phase in Fig. 3(c) reveals a low-lying spin singlet \( \Gamma \text{D6.E2} \) level, and the absence of a low-lying \( \Gamma \text{D6.A2} \) level, thus clarifying the presence of a diamond VBS phase in this parameter region.

Spin nematic-plaquette phase — The dimer correlations also exhibit a different peculiar sign structure in another parameter region, as shown for \( J_2 = -1 \) and \( J_3 = -2 \) in Fig. 4(a). We see characteristic positively correlated hexagon patterns suggesting a \( 2 \times 2 \) unit cell superstructure. However we are unaware of a singlet VBS model state exhibiting such a correlation pattern. We analogously define an order parameter for this lattice symmetry breaking pattern,

\[ O_{\text{nem}} = \frac{1}{N} \sum_{(k,l)} \theta_{\text{nem}}^{kl} D_{kl}, \]

where \( \theta_{\text{nem}}^{kl} = \pm 1 \) is defined according to Fig. 4(c). The region in parameter space where its signal is strong is shown in Fig. 1(d).

Since we are unaware of a singlet VBS with this structure, and due to the vicinity of the ferromagnet, we explore the possibility of a phase with additional spin-nematic character, for example of quadrupolar type [34]. Several examples of frustrated ferromagnets giving rise to spin nematic phases have
be discussed [35–38]. In Fig. 4(b) we display the quadrupolar bond correlations,

$$Q_{kl} \equiv \langle (S^+_k S^+_l)(S^-_l S^-_o) \rangle,$$

exhibiting sizeable correlations. We notice a peculiar hexagon-ring sign structure, where the correlations on hexagons surrounding the middle hexagon are negative, while correlations on the other hexagons are positive. In Fig. 4(d) we show an energy spectrum resolved by total $S^z$ and we can see a low-lying $S = 2$ level, which could be due to the quadrupolar character. The lowest singlet excited state is a M.D2.A1 level, which is in agreement with the reported $2 \times 2$ hexagon plaquette superstructure. So we see quite strong evidence for a novel phase, distinct from the other reported phases, but a detailed characterization of the phase has to be left for future research.

Discussion and Outlook—We have explored the appearance of two unexpected phases along the classical transition line in the $S = 1/2$ kagome Heisenberg antiferromagnet with competing ferromagnetic further neighbor couplings. The first phase is a diamond VBS with a twelve site unit cell. This VBS or variants thereof have been seen in quantum dimer models [11, 32, 33, 39, 40] and hinted at by fluctuations or weak correlations in quantum spin models at the nearest-neighbor point ($J_2 = J_3 = 0$) in Refs. [12, 19]. We have now firmly established this VBS phase in the extended model (1). The location of this VBS phase in the immediate vicinity of the $q = 0$ magnetic order, and the apparent second-order nature of the phase transition between the two phases in exact diagonalization, places this transition into a contender role for an example of a deconfined quantum critical transition, with possibly deconfined spin excitations at the transition [41]. Recent analytical work on the triangular lattice [42] and the analysis of the matching VBS and Néel monopoles in the Dirac spin liquid [43] combined with our numerical results renders this scenario at least plausible. It will also be important to work out the connection between the VBS phase and the Dirac spin liquid state, which is currently a prime candidate to describe the kagome antiferromagnet at small antiferromagnetic $J_2$ coupling [14–18], before entering the $q = 0$ magnetic ordered phase.

This part of the phase diagram is then separated by a likely first order phase transition from the $\sqrt{3} \times \sqrt{3}$ magnetically ordered phase and the lattice symmetry breaking spin nematic phase close to the ferromagnetic phase. The precise nature of the latter phase is left for future studies.

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Supplementary material to “Valence bond solid in extended kagome lattice Heisenberg antiferromagnet”

Simulation cluster geometry and symmetries

We use a 36 site kagome lattice with periodic boundary conditions shown in Fig. S1(a). The cluster features sixfold rotational symmetry and spatial reflection symmetry. In reciprocal space, it features the K and M point, cf. Fig. S1(b), which are necessary to stabilize the $\sqrt{3} \times \sqrt{3}$ magnetic order and the diamond valence bond solid (VBS) state.

We use the following naming convention when referring to irreducible representations of the space group,

$$\mathbf{q}, \mathcal{L}_\mathcal{G}, \rho,$$

(S1)

where $\mathbf{q}$ denotes the reciprocal lattice vector, so one of $\Gamma, \chi, M, K$ in the case of the 36 site cluster in Fig. S1. $\mathcal{L}_\mathcal{G}$ denotes the little group of the crystal momentum $\mathbf{q}$. The names $D_k$: ($k = 1, 2, 3, 6$) denote the dihedral groups of order $2k$, comprised of $k$-fold rotational symmetry plus an additional spatial reflection symmetry. $\rho$ denotes the irreducible representation of the little group, according to the standard Mulliken naming convention introduced in Ref [44].

Exact Diagonalizations are performed in the symmetrized bases with respect to the irreducible representations of the space group. Moreover, we employ $S_z$ conservation and the C2 spin-flip symmetry,

$$[H, F] = 0 \text{ where } F |\sigma_1, \ldots, \sigma_N\rangle = -|\sigma_1, \ldots, -\sigma_N\rangle.$$

(S2)

Even (odd) spin-flip symmetry sectors correspond to even (odd) total spin $S$, if the number of lattice sites is a multiple of 4. Details on the Exact Diagonalization method employed are explained in Ref. [28].

Ordering and tower-of-states analysis

We show the two types of magnetic ordering encountered in the main text in Fig. S2. The spin structure factor of those two orders is peaked at different locations in the extended Brillouin zone, cf. Ref. [24]. In the thermodynamic limit, antiferromagnetic SU(2) symmetry breaking yields degenerate ground states in all total spin sectors $S$, which manifest itself on a finite lattice as the tower-of-states. The quantum numbers of these states can be derived analytically and compared to numerical calculations, see Ref [45]. We state the results of this derivation for the $\mathbf{q} = 0$ and $\sqrt{3} \times \sqrt{3}$ in table S1.

We considered two VBS with different pattern of valence bond configurations. The diamond VBS in Fig. S3(a) has resonant dimer patterns on the “diamond” structure, whereas the so-called pinwheel VBS realizes only one of the two states. The sign of dimer correlation patterns of both VBS are identical, and hence these two states cannot be distinguished by this order parameter. The quantum numbers of the degenerate ground states, however, are different for those two states. These quantum numbers can also be derived by investigating the representation theory of the space symmetry group acting on the VBS ansätzte, cf. Refs. [45, 46]. We state the result of our derivation in table S1. The two VBS configurations can be distinguished by the appearance of a $\Gamma$.D6.E2 states in the degenerate ground state manifold, which is not present in the pinwheel VBS case.
| $q = 0$ order | $\sqrt{3} \times \sqrt{3}$ order |
|----------------|--------------------------|
| $\Gamma$.D6.A1, $\Gamma$.D6.A2 | $\Gamma$.D6.A1, $\Gamma$.D6.B1, K.D3.A1 |
| 0 | 1 | 0 | 0 | 1 | 0 | 0 |
| 1 | 0 | 1 | 1 | 0 | 1 | 1 |
| 2 | 1 | 0 | 2 | 1 | 0 | 2 |
| 3 | 1 | 2 | 2 | 1 | 2 | 2 |

Diamond VBS ($S = 0$):
$\Gamma$.D6.A1, $\Gamma$.D6.A2, $2 \times \Gamma$.D6.E2, M.D2.A1, M.D2.A2

Pinwheel VBS ($S = 0$):
$\Gamma$.D6.A1, $\Gamma$.D6.A2, M.D2.A1, M.D2.A2

TABLE S1. Quantum numbers constituting the tower-of-states of the $q = 0$ and $\sqrt{3} \times \sqrt{3}$ magnetic ordering and quantum numbers of the degenerate $S = 0$ states of the pinwheel and diamond VBS state.