Valence-bond crystal in the extended Kagome spin-$\frac{1}{2}$ quantum Heisenberg antiferromagnet: A variational Monte Carlo approach

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Introduction. It is well known that, on the nonbipartite two-dimensional Kagomé lattice, the combination of low spin ($S = 1/2$), low coordination number ($z = 4$), and frustrating anti-ferromagnetic (AF) exchange interactions lead to extremely strong quantum fluctuations. It is, however, a widely debated and long-standing theoretical issue whether the ground state of the nearest-neighbor (n.n.) spin-1/2 quantum Heisenberg antiferromagnet (QHAF) on the Kagomé lattice is a spin disordered state (quantum spin liquid),1,2 which preserves spin rotation and lattice space group symmetry, or instead a valence bond crystal (VBC).3–7 which breaks lattice symmetries. On the experimental side, studies on a nearly perfect spin-1/2 Kagomé compound, Herbstsmithite ZnCu$_3$(OH)$_6$Cl$_2$,8–15 reveal the absence of any spin ordering down to 50 mK despite a sizable n.n. AF exchange coupling ($J \approx 180 K$) between spin-1/2 moments of Cu$^{2+}$. In particular, Raman spectroscopic data on Herbstsmithite points towards a gapless, algebraic spin liquid state.16 This lends support to the view that the ground state of the n.n. spin-1/2 QHAF model on the Kagomé lattice is a long-range resonating-valence bond state. Within a class of variational projected wave functions, a particular gapless spin liquid belonging to the class of algebraic spin liquids, the U(1) Dirac state, has been claimed to possess the lowest energy.17,18 In such a state, the (mean-field) Fermi surface collapses to two points, where the spectrum becomes relativistic with Dirac conical excitations. On the contrary, a recent study of the n.n. spin-1/2 QHAF model using density-matrix renormalization group (DMRG)19 establishes the ground state to be a singlet-gapped spin liquid, supposedly with a $Z_2$ low-energy gauge structure.

From the experimental point of view, the weak ferromagnetism observed in Herbstsmithite has been attributed to the ferromagnetic (FM) nature of the next-nearest-neighbor (n.n.n.) coupling between Cu$^{2+}$ ions in the Kagomé layers. This model was investigated in Ref. [20] by using projected wave functions and it has been found that, above a certain critical n.n.n. FM coupling, a gapless spin liquid with a large circular spinon Fermi surface, named here as uniform projected Fermi sea (PFS), is stabilized as opposed to the U(1) Dirac state. Furthermore, this state undergoes a small dimerization, which lowers slightly its energy. The same n.n.n. FM model was also recently investigated using a quantum dimer model approach in Ref. [21], showing consistently that a 36-site cell VBC order is favored.

In this Rapid Communication, we revisit the spin-1/2 QHAF with the inclusion of n.n.n. exchange interactions using a more extended variational space of projected wave functions that may be optimized by using the technique of Ref. [22]. In the following, we will limit to non-magnetic variational states and, therefore, we will not consider possible instabilities toward magnetically ordered states.23 Our main result is that the addition of ferromagnetic n.n.n. exchange coupling leads to the stabilization of a 36-site unit cell VBC (in agreement with the results of Ref. [21]) over an extended ferromagnetic region which starts from a very weak coupling. Although being a dimerization of the uniform PFS, our VBC does not arise from a local instability of the latter. In other words, it is not trivially connected to it in the variational parameter landscape; instead it possesses a non-trivial flux pattern and dimerization. Moreover, we find that the level crossing between the PFS and the U(1) Dirac state (once suitably extended with n.n.n. hopping) occurs at nearly twice the value previously reported.20 For AF n.n.n. exchange coupling, the inclusion of n.n.n. hoppings in the U(1) Dirac state leads to a considerable lowering in energy, which becomes more pronounced with increasing the AF coupling. Moreover, no VBC order is found in the AF n.n.n. coupling region.

Model and wave function. The Hamiltonian for spin-
1/2 quantum Heisenberg $J_1-J_2$ model is
\[
\hat{H} = J_1 \sum_{\langle ij \rangle} \hat{S}_i \cdot \hat{S}_j + J_2 \sum_{\langle\langle ij \rangle\rangle} \hat{S}_i \cdot \hat{S}_j \tag{1}
\]
where \(\langle ij \rangle\) and \(\langle\langle ij \rangle\rangle\) denote sums over n.n. and n.n.n. neighbor sites, respectively. In the following, we will consider \(J_1 > 0\) and both FM and AF superexchange \(J_2\); all energies will be given in units of \(J_1\).

The variational wave functions are defined by projecting non-correlated fermionic states:
\[
\Psi_{\text{VMC}}(\chi_{ij}, \Delta_{ij}, \mu) = \mathcal{P}_G \Psi_{\text{MF}}(\chi_{ij}, \Delta_{ij}, \mu),
\]
where \(\mathcal{P}_G = \prod_i (1 - n_{i,\uparrow} n_{i,\downarrow})\) is the full Gutzwiller projector enforcing the one fermion per site constraint. Here, \(\Psi_{\text{MF}}(\chi_{ij}, \Delta_{ij}, \mu)\) is the ground state of mean-field Hamiltonian containing chemical potential, hopping, and pairing terms:
\[
\mathcal{H}_{\text{MF}} = \sum_{i,j,\alpha}(\chi_{ij} + \mu \delta_{ij}) c_{i,\alpha}^\dagger c_{j,\alpha} + \Delta_{ij} c_{i,\alpha}^\dagger c_{j,-\alpha}^\dagger + \text{h.c.} \tag{3}
\]

In this work, all states that we consider include hopping terms only, i.e., \(\chi_{ij}\) up to second neighbors. The effect of including BCS pairing terms is discussed at the end of this Rapid Communication. Cases in which the translational symmetry is explicitly broken will also be considered, so as to include VBC states.

Different spin-liquid and VBC phases correspond to different patterns of distribution of \(\chi_{ij}\) and \(\Delta_{ij}\) on the lattice bonds; they are the ansatz of a given state and serve as the variational parameters that are optimized within the variational Monte Carlo scheme to find the energetically best state.\(^{22}\) It is worth mentioning that this method allows us to obtain an extremely accurate determination of variational parameters. All parameters belonging to one class (i.e., with the same magnitude) are generically labelled as \(\chi_\lambda\).

Results. We have performed our variational calculations on a 576-site (i.e., \(36 \times 4 \times 4\)) cluster with mixed periodic-antiperiodic boundary conditions. Such a cluster accommodates all possible VBC supercells proposed in the literature. In addition, it ensures non-degenerate wave functions at half-filling.

For n.n. spin-1/2 QHAF, among the class of n.n. translationally symmetric, non-chiral, gapless spin liquids, the \(U(1)\) Dirac state is given by the ansatz in Fig. 1.(a). Due to flux \(\varphi\) being 0 and \(\pi\) (\(\varphi = \prod_{\text{plaque}} \chi_\lambda\)) through the triangles and hexagons respectively, it is denoted as \([0, \pi]\). Its energy per site is \(E/J_1 = -0.42866(1)\). The n.n. uniform PFS state has no flux through any plaquette and is therefore denoted as \([0, 0]\), its energy per site is \(E/J_1 = -0.41197(1)\).\(^{17,18}\) In this work we study only gapless states in particular those with a \(U(1)\) low energy gauge structure. However, we believe that by performing a case by case projected wave function study of all possible (a few hundred) \(Z_2\) spin liquids on the Kagomé lattice, one can identify variationally the state found in Ref.\(^{[19]}\) using DMRG.

With the aim of investigating the effect of an additional n.n.n. exchange coupling (of both AF and FM type), we first extend the \([0, \pi]\) and \([0, 0]\) states. While previous studies,\(^{20}\) considered wave functions with n.n. couplings only, here we include in addition n.n.n. couplings in the mean-field Hamiltonian (3), which also leads to space group symmetric, non-chiral, gapless spin liquids, see Fig. 1. Two new plaquettes (triangles \(abc\) and \(acd\) in Fig. 1) appear upon the inclusion of n.n.n. couplings. Space group symmetric, non-chiral spin liquids may now be labelled by four fluxes (but only three are independent) (i.e., by \(\{\alpha, \beta, \gamma, \delta\}\): \(\alpha\) and \(\beta\) are fluxes through original triangles and hexagons, respectively; \(\gamma\) and \(\delta\) instead are fluxes through triangles \(abc\) and \(acd\), respectively).

The only possible states built upon the \([0, \pi]\) state are \([0, \pi; \pi, 0]\) or \([0, \pi; 0, \pi]\) and those upon the \([0, 0]\) state are \([0, 0; \pi, \pi]\) or \([0, 0; 0, 0]\) (see Fig. 1). Notice that for both DSL and PFS, the two states with different \(\gamma\) and \(\delta\) fluxes are related by a change of sign in \(\chi_{n,n,n}\). The energetically lower states will depend upon the actual value of the ratio \(J_2/J_1\). This extension does not modify the topological properties associated with the wave functions, such as...
as the Dirac spectrum and the large spinon Fermi surface. Most importantly, the inclusion of n.n.n. hopping parameters leads to lowering of the variational energies, via an optimal tuning of $χ_{n.n.n}$ as a function of $J_2$ [see Fig. 2(a)]. It is important to note that we purposely restrict our calculations to small enough $J_2/J_1$, since for larger n.n.n. couplings (of both AF and FM type), it is probable that Néel states are energetically favored, and consequently our treatment becomes insufficient.

Point D in Figs. 2(b) and 3 marks a transition between the $[0, 0; 0, \pi]$ and $[0, \pi; \pi, 0]$ states, and point E, the transition between $[0, \pi; 0, \pi]$ and $[0, \pi; 0, 0]$ states, both occurring at $J_2 \neq 0$. Therefore, we find a finite $χ_{n.n.n}$ even for the n.n. spin-1/2 QHAF [see points F and G in Fig. 2(b)]. We mention that these extended wave functions with n.n.n. hoppings lead to slightly lower energies, namely $E/J_1 = -0.42872(1)$ for the $[0, \pi; 0, \pi]$ state and $E/J_1 = -0.41209(1)$ for the $[0, 0; 0, \pi]$ state.

Due to negative n.n.n. spin-spin correlations of $[0, \pi]$ state and positive for the $[0, 0]$ state, a level crossing occurs at $J_2/J_1 \approx -0.16$ [see point B in Fig. 3]. However, the addition of the n.n.n. hopping shifts the level crossing between the reference spin liquids, the $[0, 0; 0, 0]$ and $[0, \pi; 0, \pi]$ states to $J_2/J_1 \approx -0.335$ (see point A in Fig. 3). The question of global and local instability of these spin-liquid states towards a VBC ordering is now thoroughly addressed. In contrast to previous studies, which aimed at checking only the local instabilities of spin liquids towards various dimerization patterns via the imposition of a small bond amplitude modulation (5%-10%) of $χ$, we make a complete optimization of the parameters to detect a possible stabilization of VBC states.

In the 12-site supercell, all bonds connected by $D_6$ operations have same magnitude [see Fig. 4(a)], leading to three classes of different bonds. In the 18-site supercell [see Fig. 4(b)], there are only two classes of bonds. In the 36-site supercell with n.n. couplings [see Fig. 4(c)], there are six classes, given the $D_6$ symmetry about the hexagon C. By adding n.n.n. bonds and preserving this symmetry, we obtain six more independent bonds [see Fig. 4(d)]

In our analysis, we start from a large number of arbitrary different points (amplitude modulation of $χ$) in the variational space and thoroughly scan the landscape. As a consequence we find that for the n.n. spin-1/2 QHAF, the $[0, \pi]$, and $[0, 0]$ states are locally and globally stable with respect to 12-site, 18-site, and 36-site supercell dimerizations. Indeed, the optimization procedure always gives back the uniform $|χ|=1$ state. We bring attention to the fact, that the 36-site supercell considered by us has a much larger variational space (six different hoppings) as compared to the ones studied in literature, which considered a dimerization only along the hexagon P in Fig. 4(c).

Upon the inclusion of a finite FM $J_2$, we detect the appearance of another competing state with broken symmetries which is stabilized and is the lowest in energy for
We finish by considering the case of an AF $J_2$ coupling. Our study reveals the absence of symmetry breaking, instead we find a gapless state with Dirac fermions, the $[0, \pi; \pi, 0]$ state. Upon optimizing $\chi_{n.n.n.}/\chi_{n.n.}$, this state gets a significantly lower energy than the n.n. $[0, \pi]$ state, this gain becoming more pronounced for larger $J_2$. In contrast, we find a different VBC wave function, which is stabilized starting from a very weak FM n.n. coupling. As mentioned above, this state possesses a very large 36-site modulation, leading to a significant large gain in energy.

In summary, we investigated the spin-1/2 QHAF on the Kagomé lattice by using improved variational wave functions. We found that a VBC is stabilized when a n.n.n. ferromagnetic superexchange coupling is considered. This state possesses a non-trivial distribution of hopping parameters and flux pattern.
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