Valence bond phases in $S = 1/2$
Kane–Mele–Heisenberg model

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Received 30 July 2014, revised 11 September 2014
Accepted for publication 17 September 2014
Published 22 October 2014

Abstract

The phase diagram of the Kane–Mele–Heisenberg model in a classical limit [47] contains disordered regions in the coupling space, as the result of competition between different terms in the Hamiltonian, leading to frustration in finding a unique ground state. In this work we explore the nature of these phases in the quantum limit, for a $S = 1/2$. Employing exact diagonalization in $S_z$ and nearest neighbour valence bond bases, and bond and plaquette valence bond mean field theories, we show that the disordered regions are divided into ordered quantum states in the form of plaquette valence bond crystals and staggered dimerized phases.

Keywords: Kane–Mele–Heisenberg model, plaquette valence bond solid, staggered dimerized solid

(Some figures may appear in colour only in the online journal)

1. Introduction

2D frustrated spin systems with $S = 1/2$ have recently received a lot of attention, due to their potential for realizing the quantum spin liquid (QSL), a magnetically disordered state which respects all the symmetries of the systems, even at absolute zero temperature [1]. The spin model, which recently attracted much interest, is the Heisenberg model with first and second anti-ferromagnetic exchange interactions, the $J_1 - J_2$ model, in a honeycomb lattice. The lowest coordination number ($z = 3$) in 2D, being the unique peculiarity of a honeycomb, makes this lattice a promising candidate to host QSL. It is known that the classical $J_1 - J_2$ model does not show any long range ordering at $T = 0$ for $1/2 < J_2/J_1 < 0.5$, because of a high degeneracy in the energy of the ground state [2]. However, thermal fluctuations can lower the free energy of some specific spiral states within the ground state manifold [3], a phenomenon called thermal order by disorder [4]. To date, many efforts have been devoted to gaining an insight into the quantum nature of this disordered region for $S = 1/2$ systems. Some of these works support the existence of QSL [5–10] for $0.2 \lesssim J_2/J_1 \lesssim 0.5$, while others suggest a translational broken symmetry state with plaquette valence bond ordering for $0.2 \lesssim J_2/J_1 \lesssim 0.35$ which transforms to a nematic staggered dimerized state when the ratio $J_2/J_1$ rises to lay within $0.35 \lesssim J_2/J_1 \lesssim 0.5$ [11–18]. For $J_2/J_1 > 0.5$, a long ranged collinear ordered ground state is proposed [13, 18].

The speed of progress in the field of topological insulators (TI) [19–26], has drawn the attention of physicists into the study of effective spin models in the strong coupling limit of TI models. The Kane–Mele–Hubbard model is an example of such a model which was recently studied by various methods [27–46]. The strong coupling limit of the Kane–Mele–Hubbard model is effectively described by an XXZ model, also called the Kane–Mele–Heisenberg (KMH) model [27]. A classical phase diagram of the KMH model contains six regions in the coupling space [47]. In three regions the model is long-range ordered, planar Néel state in a honeycomb plane (phase I), commensurate spiral states in the plane normal to a honeycomb lattice (phase VI) and collinear states along a perpendicular to...
The Kane–Mele–Hubbard model is described by the following Hamiltonian

\[ H = -t \sum_{\langle ij \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + i \lambda \sum_{\langle\langle ij \rangle\rangle, \sigma} v_{ij} c_{i\sigma}^\dagger c_{j\sigma}^\dagger c_{j\sigma}^\dagger c_{i\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow}, \]

in which \( \langle \cdot \cdot \rangle \) and \( \langle \langle \cdot \cdot \rangle \rangle \) denote the nearest and next nearest neighbour sites in a honeycomb lattice. The first term represents the hopping between nearest neighbour atoms, while the second term, with \( v_{ij} = \pm 1 \) being an anti-symmetric tensor, denotes the hopping between the second neighbours arising from the spin–orbit coupling. The last term is the onsite Hubbard term, in which \( U > 0 \) denotes the Coulomb repulsion energy between two electrons within a single atom. In a strong coupling limit, where \( U \) is much larger than \( t \) and \( \lambda \), the model can be effectively described by a \( S = 1/2 \) spin Hamiltonian, namely the KMH model \[ 27 \]

\[ H_{\text{KMH}} = J_1 \sum_{\langle ij \rangle} S_i \cdot S_j + J_2 \sum_{\langle\langle ij \rangle\rangle} S_i \cdot S_j \]

\[ + g_2 \sum_{\langle\langle ij \rangle\rangle} \left( -S_i^x S_j^x - S_i^y S_j^y + S_i^z S_j^z \right), \]

in which \( J_1 = 4t^2/U - 16t^4/U^3 \), \( J_2 = 4t^4/U^3 \) and \( g_2 = 4\lambda^2/U \) are the first and second neighbour exchange couplings.

3. Exact diagonalization

To gain an insight into the fate of the classically disordered region of the KMH model in the quantum limit, we employ the exact diagonalization method in both \( S \) and nearest neighbour valence bond (NNVB) bases. NNVB, a basis composed of the products of the nearest neighbour singlet pairs of \( S = 1/2 \) spins, provides a natural framework for characterizing the features of the disordered quantum ground states. The spin disordered states, such as resonating valence bond (RVB) and spin liquid and plaquette valence bond crystal (PVBC) receive most of their components from the Hilbert space spanning only by a NNVB basis. Therefore, comparing the results of ED within \( S \), with those obtained by the NNVB basis, would be a guideline to learn about the nature of the ground state in the classically degenerated phases III and IV.

Let us expand the ground state wave function in terms of NNVB states as

\[ |\psi_0\rangle = \sum_\alpha a(\alpha) |\alpha\rangle, \]

where \( |\alpha\rangle \) denotes all possible configurations \( \alpha \) of NNVBs:

\[ |\alpha\rangle = \prod_{\langle ij \rangle, \alpha} (i_{ij} j_{i\downarrow} - i_{ij} j_{i\uparrow}). \]

First, we have to enumerate the basis \( |\alpha\rangle \) to construct a numerical representation of the Hamiltonian matrix in this basis. To determine the basis, the exact Pfaffian representation of the RVB wave function is employed \[ 49 \]. In this method

honeycomb plane (phase II) (see figure 1). In the other three regions the system is disordered, the ground state is infinitely degenerate and characterized by a manifold of incommensurate wave-vectors. These phases are, planar spiral (phase III), vertical spiral states (phase IV) and non-coplanar states (phase V, being out of range not shown in figure 1). The quantum phase diagram of the KMH model remains unexplored, apart from a Schwinger boson and Schwinger fermion study \[ 48 \], where a chiral spin liquid state was proposed for a narrow region but with large values of second neighbour exchange \( J_2 \).

Our aim in this work, is to understand the nature of the quantum ground state of a \( S = 1/2 \) KMH model for intermediate values of \( J_2 \), mostly in phases III and IV, where it is classically disordered. For this purpose, we use exact diagonalization as well as valence bond and plaquette mean field theories.

The paper is organized as follows. In section 2 the KMH model is introduced. The quantum ground state properties of the classically disordered phases are investigated, using ED for a finite lattice in section 3 and bond operator and plaquette valence bond mean field theories in section 4. Section 5 is devoted to the conclusions. The details of the bond operator and plaquette mean field theories are given in the appendices A and B, respectively.
and overlaps. The radii of the circles are proportional to the magnitude of the

To investigate the region in coupling space where this ordering

for the whole

basis (\(N\) = 24 lattice points and \(J_1 = 1\)). The radii of the circles are proportional to the magnitude of the overlaps.

one expresses the RVB wave function as the Pfaffian of an antisymmetric matrix whose dimension is equal to the number of the lattice points. The dimension of Hilbert space corresponding to the NNVB basis is much smaller than that for the whole \(S_z = 0\) basis, so that the Hamiltonian matrix can be fully diagonalized with standard library routines. Note that since the NNVB components (\(c_{\alpha}^{\beta}\)) are not orthonormal, one needs to solve the generalized eigenvalue problem

\[
\det[H - \epsilon O] = 0,
\]

where \(O = \langle c_{\beta}^{\gamma} | c_{\alpha}^{\delta} \rangle\) denotes the overlap matrix between different NNVB configurations.

We begin with the calculation of relative error in ground state energy between the exact and NNVB basis, \((E_0^{\text{NNVB}} - E_0^{\text{ED}})/E_0^{\text{ED}}\) and also the overlap of the corresponding ground state wave functions. From now on we set \(J_1 = 1\). Figures 1 and 2 show the relative errors (in percentages) and the overlapping of the ground state wave functions, respectively, for a system consisting of \(N = 24\) lattice points. Relative error and wave function overlaps indicate that the best match between the ground states, obtained by the two bases, occurs mostly in the classically disordered Phase III and also in a large part of phase IV.

Now we proceed to inspect the possible orderings in the coupling space by defining appropriate structure functions. Since the spin–orbit coupling is small for real materials, we limit ourselves to \(0 < g_2 < 0.2\) and \(0 < J_2 < 0.6\). For small values of \(J_2\), the classical ground state is a planar Néel state. To investigate the region in coupling space where this ordering is extended, we calculate a structure function corresponding to it in terms of spin–spin correlation functions as

\[
S^{\text{xy}}_{\text{Néel}} = \frac{1}{N^2} \left( \sum_{i,j \in \text{Ann}B} (S_i^x S_j^x + S_i^y S_j^y) - \sum_{i \in A, j \in B} (S_i^x S_j^x + S_i^y S_j^y) \right).
\]

in which \(N\) is the number of lattice points and \(A, B\) denote the two sublattices of the honeycomb.

The obtained structure function for Néel-xy is depicted in figure 3, indicating that the Néel ordering in the honeycomb plane extends to \(J_2 \sim 0.2\) for \(g_2 = 0\) and stretches up to \(J_2 \sim 0.3\) as \(g_2\) tends to 0.2.

Now we seek the features of the disordered quantum ground state, where Néel ordering vanishes and we will see whether they break any symmetries of the lattice. The proposed \(SU(2)\) symmetric ground states, breaking the symmetries of the honeycomb lattice, are the staggered dimerized (SD) or nematic valence bond solid, which breaks the \(C_3\) rotational symmetry and the plaquette valence bond crystal (PVBC) which breaks the translational symmetry of the honeycomb lattice (figure 4). The structure functions for SD and PVBC can be defined in terms of dimer–dimer correlations as

\[
S_{\lambda} = \frac{1}{N_b} \sum_{\alpha} \epsilon_{\alpha} \langle c_{\alpha'} \rangle C(\alpha, \alpha'),
\]

where \(N_b\) denotes the number of bonds and \(C(\alpha, \alpha')\) is the dimer–dimer correlation given by

\[
C(\alpha, \alpha') = 4((\langle S_i S_j \rangle (\langle S_i S_j \rangle)^2) - \langle (S_i S_j) \rangle^2),
\]

where \(\alpha' = (k, l)\) and \(\alpha = (i, j)\) denote the reference bond relative to which the correlations are calculated. \(\epsilon_{\alpha} (\alpha')\) is the phase factor, appropriately defined for each of the two states \(\lambda = SD, PVBC\) [50].

The two structure functions, calculated exactly in \(S_\lambda\) basis for \(N = 24\), are represented in figure 5, where the radii of the

![Figure 2](image-url)  
Figure 2. Overlap between the normalized ground state wave functions, obtained by diagonalization in the NNVB basis (\(\psi_0^{\text{NNVB}}\)) and \(S_z\) basis (\(\psi_0^{\text{ED}}\)) in \(g_2 - J_2\), for \(N = 24\) lattice points and \(J_1 = 1\). The radii of the circles are proportional to the magnitude of the overlaps.

![Figure 3](image-url)  
Figure 3. Structure function planar Néel, calculated by exact diagonalization in \(S_z\) basis for \(N = 24\) lattice points. The radii of the circles are proportional to the magnitude of the structure function (magnified by a factor of 1000) for each point in the coupling space. (b) A schematic representation of the Néel-xy state, proposed for phase I.
Figure 4. A schematic representation of (a) staggered dimerized (SD) and (b) plaquette valence bond crystal (PVBC).

Figure 5. (a) Plaquette valence bond crystal and (b) staggered dimerized structure functions, calculated by exact diagonalization in the $S_z$ basis for $N = 24$ lattice points. The radii of the circles are proportional to the magnitude of the structure function (magnified by a factor of 1000) calculated for each point in the coupling space. The black and white circles denote the strength of the aforementioned orderings for each set of couplings $(g_2, J_2)$. Figure 5(a) shows that in most parts of phases III and IV, where the ground state is well described by the NNVB basis, the PVBC structure function is remarkably large, while for $J_2 \gtrsim 0.4$, it falls down abruptly. On the other hand, figure 5(b) shows the sudden growth of the SD structure function for $J_2 \gtrsim 0.4$, an indication of first order phase transition between the PVBC and SD states. One can also see from this figure, that for the range of coupling under study, the SD ordering is well developed inside phase II, for which a collinear ordering perpendicular to the honeycomb plane is found in the classical limit. The structure function corresponding to collinear-$z$ ordering, for which a possible configuration is depicted in figure 6(b), can be defined as

$$S_{COL}^z = \frac{1}{N^2} \sum_{i,j} e^{i q \cdot (r_i - r_j)} \langle S_i^z S_j^z \rangle,$$

in which $q = (\pi, \pi/\sqrt{3})$, $r_i$ denotes the translational vector of a triangular Bravais lattice and the unit cell is chosen so as to contain two parallel spins. Figure 6(a) displays the values of $S_{COL}^z$ obtained from the ED calculation. The magnitudes of this structure function, being very small compared to those corresponding to SD ordering, verify the alternation of SD ordering instead of the collinear-$z$ state in phase II, at least for $g_2 < 0.4$.

The results in this section are summarized in a finite lattice quantum phase diagram, represented in figure 7.

4. Bond operator method

Inspired by ED calculation on the finite system, in this section we employ bond operator as well as plaquette operator mean-
field theories to investigate the regions of the stability of the PVBC and SD phases and the transition between them, for the infinite lattice.

The bond operator formalism is introduced by Chubukov [51] and Sachdev and Bhatt [52], for describing the disordered phases of a frustrated spin Hamiltonian. In this formalism, a couple of \( S = 1/2 \) spin operators belonging to a bond are represented in terms of the components of their summation, with a Hilbert space consisting of one singlet |s⟩ and three triplet states, |t₁⟩, |t₂⟩ and |t₃⟩. Introducing the singlet and triplet creation operators out of vacuum |0⟩,

\[
|s⟩ = s^z|0⟩ = \frac{1}{\sqrt{2}}(|↑↓⟩ - |↓↑⟩),
\]

\[
|t₁⟩ = t_1^z|0⟩ = \frac{-1}{\sqrt{2}}(|↑↑⟩ - |↓↓⟩),
\]

\[
|t₂⟩ = t_y|0⟩ = \frac{i}{\sqrt{2}}(|↑↑⟩ + |↓↓⟩),
\]

\[
|t₃⟩ = t_z|0⟩ = \frac{1}{\sqrt{2}}(|↑↓⟩ + |↓↑⟩),
\]

one can express a spin residing on site \( n \), in terms of these basis states as \( S_n = \sum_{\mu, \nu} |\mu⟩⟨\nu| \). Here |\mu⟩ and |\nu⟩ can be each of the above four states. Evaluation of the matrix elements \( ⟨\mu | S_n | \nu⟩ \), gives rise to the representation of the spin operator in terms of the bosonic bond operators,

\[
S_n^z = (\frac{-1}{2})^n (s^z t_μ + t_μ^z s^z) - i \frac{1}{2} ε_{αβγ} t_α^z t_β t_γ^z,
\]

where \( α, β \) and \( γ \) stand for \( x, y \) and \( z \) and \( ε \) is the totally anti-symmetric tensor. Moreover, the fact that each bond is either in a singlet or triplet state, leads to the following constraint

\[
s^z s + \sum_α t_α^z t_α = 1
\]

Now, considering a SD configuration illustrated in figure 4,(a), the spin Hamiltonian (2) can be decomposed into the inter and intra bond terms given by equation (A1). Using the spin representations (10), we achieve a bosonic Hamiltonian in terms of singlet and triplet operators, in which all the singlets are considered to be condensed. Then, keeping only the quadratic triplet terms as an approximation enables us to diagonalize the resulting Hamiltonian by the use of Bogoliubov transformations. Finally, minimization of the total energy subjected to the constraint (11), provides us with a set of self consistent equations. The numerical solution of these equations gives the energy of the corresponding dimerized configuration. The details of the derivation of the self-consistent equations are given in appendix A.

In order to find the energy of a plaquette ordered state, we rewrite the spin Hamiltonian (2) in terms of the plaquette operators defining, based on the eigenstates of the KMH Hamiltonian, for a single hexagon. In the absence of the Kane–Mele term, i.e. \( g_2 = 0 \), the commutation relation \([H, S^z]^2 = 0\), enables us to label each eigenstate of such a Hamiltonian by the eigenvalues of the \( S^z \) operator. The ground state is then found to be a spin singlet, invariant under rotation by 60°, up to \( J_2/J_1 = 0.5 \). This ground state is predominantly expressed by the symmetric combination of two Kekulé structures, implying that the ground state of \( J_1 - J_2 \) within a hexagon is a s-wave singlet, in contrast to the f-wave singlet (the anti-symmetric superposition of two Kekulé structures) proposed in [16]. The first excited states are also found to be a triplet for \( 0 < J_2/J_1 < 0.25 \) and are replaced by a f-wave singlet state for \( J_2/J_1 > 0.25 \).

Now, we proceed to represent the spin operators in terms of the eigenstates of the \( J_1 - J_2 \) Hamiltonian within a hexagon. The spin operators connect the s-wave ground state singlet only to the triplet excited states, hence, we need to find the ground state of the full Hamiltonian in the subspace of the Hilbert space consisting of a s-wave singlet and triplet states. Therefore the relevant matrix elements are

\[
d_{n,m} = ⟨s_1|S_{na}|t_{ma}⟩,
\]

in which |\( s_1 \rangle \) and |\( t_{ma} \rangle \) are the s-wave singlet and triplet excited states, respectively. These states can be represented in terms of the creation and annihilation operators, as

\[
s_1^z|0⟩ = |S_{tot} = 0; S_z = 0⟩,
\]

\[
t₁^z|0⟩ = \frac{-1}{\sqrt{2}}(|S_{tot} = 1; S_z = 1⟩ - |S_{tot} = 1; S_z = -1⟩),
\]

\[
t₂^z|0⟩ = \frac{i}{\sqrt{2}}(|S_{tot} = 1; S_z = 1⟩ + |S_{tot} = 1; S_z = -1⟩),
\]

\[
t₃^z|0⟩ = |S_{tot} = 1; S_z = 0⟩.
\]

We can represent the spin at site \( n \) as

\[
S_{na} = \sum_m d_{n,m}(s_1^z t_{ma} + t_1^z t_{ma} s_1).
\]

Restricting to the reduced Hilbert space, requires the following constraint

\[
s_1^z s_1 + \sum_{m, α} t_α^z t_{ma} = 1
\]

The procedure similar to the bond operator method leads to a set of self-consistent equations from which we can calculate the ground state energy corresponding to the plaquette ordered state. For more details we refer the reader to appendix B.

Figure 8, shows two plots of energy per spin for SD and PVBC states as a function of \( J_2 \) for \( g_2 = 0 \) (top panel) and \( g_2 = 0.05 \) (bottom panel). Both plots illustrate the crossing of PVBC and SD energies as \( J_2 \) is increased. For \( g_2 = 0 \), the transition point between PBVC to SD is at \( J_2 \sim 0.31 \) and increases a little by increasing the value of \( g_2 \). The crossing of the two energies indicates that it is a first order transition.

As the final result, the bond and plaquette operator phase diagrams of the KMH model are represented in figure 9, showing that for \( J_2 \leq 0.3 \), i.e. the classical phase III and the lower part of the classical phase IV, the ground state is a PVBC while for the upper part of phase IV and also inside the classical phase II, the ground state is described by an SD state, in qualitative agreement with the ED results for the finite lattice.
In summary, we explored the quantum phase diagram of the $S = 1/2$ KMH model, using exact diagonalization for a finite lattice and bond operator and plaquette operator methods for the infinite system size, with a focus on the regions of coupling space with high classical degeneracy. Here, we found that the Néel, PVBC and SD orderings obtained for the $J_1 - J_2$ Heisenberg model, adiabatically continues to the phase space of the KMH model. The effect of the spin–orbit term $g_2$, which reduces the $O_3$ symmetry of the Heisenberg model to $O_2$ for KMH, is to convert the isotropic Néel ordered (for $0 < J_2 < 0.2$) state to a planar Néel ordering in the honeycomb plane. Moreover, the s-wave PVBC ordered state which is found to be the ground state of the $J_1 - J_2$ model, for $0.2 < J_2/J_1 < 0.35$, continues adiabatically into the classical phase III and the lower part of phase IV. It is worth mentioning that the Kane–Mele (KM) term, not commuting with $S^2$, mixes the singlet and triplet sectors. However for small values of KM coupling, $g_2$, the singlet–triplet transition matrix elements are very small, hence the ground state can be well approximated by a s-wave singlet plaquette ordering state. For $0.35 < J_2/J_1 < 0.5$, the SD ordering obtained for the isotropic model extends toward the upper part of phase IV and also into the classically ordered phase II for $g_2 < 0.2$. Our work highlights the significance of quantum fluctuations for the $S = 1/2$ KMH model, in melting down the classically ordered state into purely quantum ground states.

Appendix A. Self-consistent equation of bond operator mean field theory

The spin Hamiltonian (2) for an SD configuration can be rewritten as

$$H = J_1 \sum_{\langle ij \rangle \text{bond}} S_i S_j + (J_2 - g_2) \sum_{\langle ij \rangle \text{bond}} S_i S_j + g_2 \sum_{\langle ij \rangle \text{bond}} S_i^z S_j^z.$$

(A1)

Inserting the spin representations (10) into this Hamiltonian, assuming that all the singlets are condensed (this means replacing $s$ and $s^\dagger$ with the c-number $s$), keeping only the quadratic terms, incorporating the constraint (11) by a Lagrange multiplier $\mu$ and finally the Fourier transformation, we obtain the following quadratic Hamiltonian in terms of the momentum space triplet operators

$$H[2]_{BO} = -N_b \frac{3}{4} J_1 \bar{\sigma}^z - N_b \mu \bar{\sigma}^z + N_b \mu$$

$$+ \sum_{k} \left[ (G_k + F_k^1) (t_{k,x} t_{k,x} + t_{-k,x} t_{-k,x}) + (G_k + F_k^1) (t_{k,y} t_{k,y} + t_{-k,y} t_{-k,y}) + (G_k + F_k^1) (t_{k,z} t_{k,z} + t_{-k,z} t_{-k,z}) + (F_k + F_k^1) (t_{k,\bar{x}} t_{k,\bar{x}} + t_{-k,\bar{x}} t_{-k,\bar{x}}) + (F_k + F_k^1) (t_{k,\bar{y}} t_{k,\bar{y}} + t_{-k,\bar{y}} t_{-k,\bar{y}}) + (F_k + F_k^1) (t_{k,\bar{z}} t_{k,\bar{z}} + t_{-k,\bar{z}} t_{-k,\bar{z}}) \right].$$

(A2)

where $N_b$ is the number of bonds and

$$G_k = \frac{J_1}{4} - \frac{\mu}{4} - \frac{\bar{\sigma}^z}{4} J_1 (\epsilon_k + \epsilon_{-k}) + \frac{\bar{\sigma}^z}{4} J_2 (\eta_k + \eta_{-k})$$

$$F_k = -\frac{\bar{\sigma}^z}{4} J_1 (\epsilon_k + \epsilon_{-k}) - \frac{\bar{\sigma}^z}{4} J_2 (\eta_k + \eta_{-k})$$

$$F_k^1 = -\frac{\bar{\sigma}^z}{4} g_2 (\eta_k + \eta_{-k})$$

$$F_k^2 = \frac{\bar{\sigma}^z}{4} g_2 (\eta_k + \eta_{-k}).$$

(A3)

In the above relations $\epsilon_k$ and $\eta_k$ are defined as

$$\epsilon_k = e^{-ikx} + e^{-ik(x+y)}$$

$$\eta_k = 2 [\cos(k_x) + \cos(k_y) + \cos(k_x + k_y)].$$

(A4)
Using appropriate Bogoliubov transformations, the Hamiltonian (A2) can be diagonalized as

\[ H_{\text{BO}}^{[2]} = N_F \left( -\frac{3}{4} J_3 s^2 - \mu s^2 + \mu \right) + \sum_{k>0} (\omega_{k,x} + \omega_{k,y} + \omega_{k,z} - 3 G_k - 2 F_k^1 - F_k^2) + \sum_{k>0} \omega_{k,x} y_{k,x} + \sum_{k>0} \omega_{k,y} y_{k,y} + \sum_{k>0} \omega_{k,z} y_{k,z}, \]

in which

\[ \omega_{k,x} = \omega_{k,y} = \sqrt{(G_k + F_k^1)^2 - (F_k + F_k^2)^2}, \]

\[ \omega_{k,z} = \sqrt{(G_k + F_k^2)^2 - (F_k + F_k^2)^2}, \]

are the triplon dispersions and

\[ \epsilon_g = \left( -\frac{3}{4} J_3 s^2 - \mu s^2 + \mu \right) + \sum_{k>0} (\omega_{k,x} + \omega_{k,y} + \omega_{k,z} -3 G_k - 2 F_k^1 - F_k^2), \]

gives the ground state energy per bond. The ground state energy depends on the parameters \( \mu \) and \( \bar{s} \) and can be determined self-consistently from the saddle-point conditions

\[ \frac{\partial \epsilon_g}{\partial \mu} = -\bar{s}^2 + 1 - 2 \sum_{k>0} \frac{(G_k + F_k^1)}{\omega_{k,x}}, \]

\[ \frac{\partial \epsilon_g}{\partial \bar{s}^2} = -\frac{3}{4} J_3 - \mu + 2 \sum_{k>0} \left( -\frac{J_1}{4} (\epsilon_k + \epsilon_{-k}) + \frac{(J_2 - g_2)}{4} (\eta_k + \eta_{-k}) \right) \times \frac{(G_k - F_k^1)}{\omega_{k,x}} - 1, \]

\[ \times \left( \frac{J_1}{4} (\epsilon_k + \epsilon_{-k}) + \frac{(J_2 - g_2)}{4} (\eta_k + \eta_{-k}) \right) \times \frac{(G_k - F_k^2)}{\omega_{k,z}} - 1 = 0. \]

Appendix B. Self consistent equations of plaquette mean field theory

Considering the PVBC ordering shown in figure 4(b), the Hamiltonian (2) can be rewritten as

\[ H = J_1 \sum_{(ij) \in \text{PL}} S_i S_j + (J_2 - g_2) \sum_{(ij) \in \text{PL}} S_i S_j + 2 g_2 \sum_{(ij) \in \text{PL}} S_i^2 S_j^2 + J_1 \sum_{(ij) \notin \text{PL}} S_i S_j + (J_2 - g_2) \sum_{(ij) \notin \text{PL}} S_i S_j. \]

The Hamiltonian of a single hexagonal block can be represented in terms of creation and annihilation operators as

\[ H_{\text{PL}} = \sum_p \epsilon_{p,s} s_p^\dagger + \sum_m \epsilon_{m} t_m^\dagger t_m, \]

where \( \epsilon_p \) and \( \epsilon_m \) are evaluated numerically by diagonalizing the KHIM Hamiltonian in the \( S_Z = 0 \) basis in a hexagon. Re-expressing the Hamiltonian equation (B1) in these new singlet and triplet operators and, incorporating the constraint (15), using the Bogoliubov transformation and assuming the condensation of singlets, we arrive at the following diagonalized Hamiltonian in the space

\[ H_{\text{PL}}^{[2]} = N_F \left( -\frac{3}{4} s^2 e_s - \mu s^2 + \mu \right) + \sum_{k>0} (\omega^x_{s,k} + \omega^y_{s,k} + \omega^z_{s,k} - 3 G_{s,k} - 2 G^1_{s,k} - G^2_{s,k}) + \sum_{k>0} \omega^x_{s,k} y^x_{s,k} + \sum_{k>0} \omega^y_{s,k} y^y_{s,k} + \sum_{k>0} \omega^z_{s,k} y^z_{s,k}, \]

which solution provides us with the ground state energy of the PVBC state.
