Cluster Mott insulator and two Curie-Weiss regimes on an anisotropic Kagome lattice

Gang Chen,1 Hae-Young Kee,1,2 and Yong Baek Kim1,2,3

1Department of Physics, University of Toronto, Toronto, Ontario, M5S1A7, Canada
2Canadian Institute for Advanced Research/Quantum Materials Program, Toronto, Ontario M5G 1Z8, Canada
3School of Physics, Korea Institute for Advanced Study, Seoul 130-722, Korea

(Dated: April 10, 2015)

Motivated by recent experiments on the quantum-spin-liquid candidate material LiZn2Mo3O8, we study a single-band extended Hubbard model on an anisotropic Kagome lattice with the 1/6 electron filling. Due to the partial filling of the lattice, the inter-site repulsive interaction is necessary to generate Mott insulators, where electrons are localized in clusters, rather than at lattice sites. It is shown that these cluster Mott insulators are generally U(1) quantum spin liquids with spinon Fermi surfaces. The nature of charge excitations in cluster Mott insulators can be quite different from conventional Mott insulator and we show that there exists a novel cluster Mott insulator where charge fluctuations around the hexagonal cluster induce a plaquette charge order (PCO). The spinon excitation spectrum in this spin-liquid cluster Mott insulator is reconstructed due to the PCO so that only 1/3 of the total spinon excitations are magnetically active. Based on these results, we propose that the two Curie-Weiss regimes of the spin susceptibility in LiZn2Mo3O8 may be explained by finite-temperature properties of the cluster Mott insulator with the PCO as well as fractionalized spinon excitations. Existing and possible future experiments on LiZn2Mo3O8, and other Mo-based cluster magnets are discussed in light of these theoretical predictions.

I. INTRODUCTION

If there is no spontaneous symmetry breaking, the ground state of a Mott insulator with odd number of electrons per unit cell may be a quantum spin liquid (QSL). QSL is an exotic quantum phase of matter with a long-range quantum entanglement and is characterized by fractionalized spin excitations and an emergent gauge structures at low energies. It has been suggested that some frustrated Mott insulating systems which are proximate to Mott transitions may provide physical realizations of QSL. Several QSL candidate materials, such as the 2D triangular lattice organic materials κ-(ET)2Cu2(CN)8 and EtMe3Sb[Pd(dmit)2]2, and a 3D hyperkagome system Na4Ir3O8 [14,15], are expected to be in this weak Mott regime. These weak Mott-insulator U(1) QSLs are obtained as a deconfined phase of an emergent U(1) lattice gauge theory, where the electron is fractionalized into spin-carrying spinons and charged bosons. The charge excitations are gapped and the low-energy physics of the QSLs is described by a spinon Fermi surface coupled to the U(1) gauge field.

Recently LiZn2Mo3O8 has been proposed as a new candidate material for QSL ground state [13,14]. Besides the usual QSL phenomenology [13,14], the experiments reveal two Curie-Weiss regimes of the spin susceptibility at finite temperatures. The low temperature Curie-Weiss regime is governed by a much smaller Curie-Weiss temperature than the high temperature one and a reduced Curie constant which is 1/3 of the high temperature counterpart. In this work, to understand how one can achieve the QSL phenomenology and the puzzling two Curie-Weiss regimes in this material, we consider a 1/6-filled extended Hubbard model with nearest-neighbor repulsions on an anisotropic Kagome lattice. We propose a U(1) QSL with spinon Fermi surfaces and a plaquette charge order (PCO) as a possible ground state for this model. The Mott insulators in partially filled systems arise due to large nearest-neighbor repulsions and localization of the charge degrees of freedom in certain cluster units. Hence such Mott insulators are called "cluster Mott insulators" (CMI) [17].

The single-band extended Hubbard model is defined on the anisotropic Kagome lattice of the Mo sites (see Fig. 1) and is given by

\[ H = \sum_{\langle ij \rangle \in U} \left[ -t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + V_{ij} n_i n_j \right] + [u \leftrightarrow d, 1 \leftrightarrow 2] \]

\[ + \sum_i \frac{U}{2} (n_i - 1)^2, \]

FIG. 1. (Color online.) (a) The electron configuration in the CMI without the PCO when \( V_2 \ll t_1 \) and \( V_1 \gg t_2 \). (b) The electron configuration in the CMI with the PCO. Three electrons hop resonantly in each hexagon that is marked by a (red) circle. These marked hexagons form an emergent triangular lattice (with lattice vectors \( a_1, a_2 \)).
where the spin index $\sigma (=\uparrow, \downarrow)$ is implicitly summed, $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) creates (annihilates) an electron with spin $\sigma$ at lattice site $i$, and $t_1$, $V_1$ and $t_2$, $V_2$ are the nearest-neighbor electron hopping and interaction in the up-pointing triangles (denoted as ‘u’) and the down-pointing triangles (denoted as ‘d’), respectively. $n_i = \sum_\sigma c_{i\sigma}^\dagger c_{i\sigma}$ is the electron occupation number at site $i$. Since there exists only one unpaired electron in each Kagome lattice unit cell, the electron filling for this Hubbard model is 1/6.

Although the down-triangles are larger in size than the up-triangles in LiZn$_2$Mo$_3$O$_8$, because of the large spatial extension of the 4$d$ Mo electron orbitals we think it is necessary to include the inter-site repulsion $V_2$ for the down-triangles. For LiZn$_2$Mo$_3$O$_8$ we expect $t_1 > t_2$ and $U > V_1 \sim V_2$. Because of the 1/6 electron filling, although the Hubbard $U$ is the largest energy scale, it alone can only remove double electron occupation on a single lattice site and cannot localize the electron. We need $V_1$ and $V_2$ to localize the electrons in the (elementary) triangles of the Kagome lattice instead of the lattice sites.

Let us first explain the electron localization in the absence of $V_2$. Clearly, as $t_2$ is the hopping between the up-triangles, when $V_1 \gg t_2$, the electrons are localized on the up-triangles with one electron per up-triangle (see Fig. 1a). In this picture, the localized electron can hop freely among the three lattice sites within each up-triangle and gain local kinetic energy $\sim O(t_1)$ while the electron number on the down-triangle is strongly fluctuating. After $V_2$ is introduced, as $V_2$ increases, the configuration with more than one electrons on the down-triangles (like the one in Fig. 1a) becomes less favorable energetically. When the interaction energy cost ($\sim O(V_2)$) on the down-triangle overcomes the local kinetic energy gain $\sim O(t_1)$, the electron number on each down-triangle is also fixed to one and the electrons can no longer move freely within each up-triangle. Instead, the electrons develop a collective motion. For instance, in Fig. 1b, the three electrons on the hexagon at position $\mathbf{R}$ can tunnel between the configuration occupying sites 1,3,5 and the other configuration occupying sites 2,4,6. This collective electron tunnelling process preserves the electron number on each triangle and occurs below the Mott gap. We show this collective electron tunnelling gives rise to a long-range PCO that breaks the lattice symmetry spontaneously. With the PCO, the electrons are preferentially tunnelling back and forth on the hexagons that are marked with a (red) circle (see Fig. 1b). We will refer these special hexagons as “resonating” hexagons. On these resonating hexagons, the three electrons form a linear superposition state of the two electron configurations with sites 1,3,5 or sites 2,4,6 occupied. We emphasize and will show in Sec. II that the emergence of the PCO in the CMI is a quantum effect and cannot be obtained from the classical treatment of the electron interaction.

With the PCO, 1/3 of the elementary hexagons become resonating. As shown in Fig. 1b, these resonating hexagons form an emergent triangular lattice (ETL). The PCO triples the original unit cell of the Kagome lattice, and the localized electron number in the enlarged unit cell now becomes 3, which is odd. According to Hastings’ theorem[1], the CMI with the PCO is not connected to a trivial band insulator and the QSL is expected. In the resulting U(1) QSL, we obtain 9 mean-field spinon sub-bands, compared to the 3 spinon bands in the U(1) QSL for the CMI without the PCO. The 9 mean-field spinon sub-bands are obtained by splitting the 3 spinon bands of the CMI without the PCO, and this is the reason why we use the term “sub-bands”. A direct band gap separates the lowest spinon sub-band from other spinon sub-band in the presence of the PCO. The lowest spinon sub-band is completely filled by 2/3 of the spinons, leaving the remaining 1/3 of the spinons to partially fill the second and third lowest spinon sub-band. Because of the band gap, the only active degrees of freedom at low energies are the spinons in the partially filled spinon sub-band, and the fully-filled lowest spinon sub-band is inert to external magnetic field at low temperatures as long as the PCO persists. Therefore, only 1/3 of the magnetic degrees of freedom are active at low temperatures. If one then considers the local moment formation starting from the band filling picture of the spinons (just like electrons occupying the same band structure) only the 1/3 of the spinons from the partially filled upper bands would participate in the local moment formation. This means the CMI with the PCO would be continuously connected to the Curie-Weiss regime with the 1/3 Curie constant at finite temperature (compared to the case when all spinons can participate in the local moment formation). This would explain the two Curie-Weiss regimes in the spin susceptibility data of LiZn$_2$Mo$_3$O$_8$. More precise connection to the existing experiments is discussed later.

The rest of the paper is structured as follows. In Sec. II, we show the CMI develops the PCO in the charge sector when every triangle contains only one electron. We generalize the Levin-Wen variational string wavefunction approach[12] to study the reconstruction of the spinon band structure by the PCO in Sec. III. In Sec. IV, we explain the consequence of this reconstructed spinon band structure and discuss the low-temperature magnetic susceptibility. In Sec. V, we connect our theory to the experiments on LiZn$_2$Mo$_3$O$_8$, suggest possible future experiments, and discuss other Mo based cluster magnets.

II. THE EMERGENCE OF THE PLAQUETTE CHARGE ORDER

As a preparation step, we first employ the standard slave-rotor representation and map the low-energy charge sector Hamiltonian into a quantum dimer model on the dual honeycomb lattice. With the quantum dimer model, we then show the system should develop the PCO.

Using standard slave-rotor representation[12], we first express the electron operator, $c_{i\sigma}^\dagger = f_{i\sigma}^r e^{i\theta_\sigma}$, where the
respectively, spinon and rotor sectors, we obtain the following two change in Eq. (6). The (blue) solid ball represents the electron that contribute to the ring electron hopping or the ring fermionic spinon \((e^{i\theta_i})\) carries the electron charge and the to the ring exchange in Eq. (6). The (blue) solid ball represents the electron or the charge rotor.

bosonic rotor \((e^{i\theta_i})\) carries the electron charge and the fermionic spinon \((f^\dagger_{i\sigma})\) carries the spin quantum number. To constrain the enlarged Hilbert space, we introduce an angular momentum variable \(L_i^z, L_i^z = \sum_{\sigma} f^\dagger_{i\sigma} f_{i\sigma} - 1/2\), where \(L_i^z\) is conjugate to the rotor variable with \([\theta_i, L_j^z]\) = \(i\delta_{ij}\). Moreover, since the on-site interaction \(U\) is assumed to be the largest energy scale, in the large \(U\) limit the double electron occupation is always suppressed. Hence, the angular momentum variable \(L_i^z\) primarily takes \(L_i^z = 1/2\) \((-1/2\)) for a singly-occupied (empty) site.

Via a decoupling of the electron hopping term into the spinon and rotor sectors, we obtain the following two coupled Hamiltonians for the spin and charge sectors, respectively,

\[
H_s = -\sum_{(ij)} t^\text{eff}_{ij} f^\dagger_{i\sigma} f_{j\sigma} + \text{h.c.} - \sum_i h_i f^\dagger_{i\uparrow} f_{i\uparrow}, \tag{2}
\]

\[
H_c = \sum_{(ij)} [-2J^\text{eff}_{ij}\cos(\theta_i - \theta_j) + V_{ij}(L_i^z + \frac{1}{2})
\times (L_j^z + \frac{1}{2}) + \frac{1}{2}]} + \sum_i \frac{1}{2}(L_i^z)^2 + h_i(L_i^z + \frac{1}{2})], \tag{3}
\]

where \(t^\text{eff}_{ij} = t_{ij}\langle e^{i\theta_i - i\theta_j} \rangle = \langle |t^\text{eff}_{ij}| e^{i\alpha_{ij}} \rangle = t_{ij} \sum_{\sigma} \langle f^\dagger_{i\sigma} f_{j\sigma} \rangle = J_{ij}^\text{eff} e^{-i\alpha_{ij}}\) and \(t_{ij} = t_1\) (i.e., \(V_{ij} = V_1\) \((V_2)\) for the bond \(ij\) on the up-triangles (down-triangles). \(h_i\) is a Lagrange multiplier that imposes the Hilbert space constraint. Here, we have chosen the mean-field ansatz to respect the symmetries of the Kagome lattice. The Hamiltonians \(H_s\) and \(H_c\) are invariant under an internal U(1) gauge transformation, \(f^\dagger_{i\sigma} \rightarrow f^\dagger_{i\sigma} e^{-i\chi_i}, \theta_i \rightarrow \theta_i + \chi_i,\) and \(\alpha_{ij} \rightarrow \alpha_{ij} + \chi_i - \chi_j.\)

We now focus on the charge sector and study the low energy physics of the charge sector. From the previous slave-rotor formulation, the charge sector Hamiltonian is given by

\[
H_c = \sum_{(ij)} -2J^\text{eff}_{ij}\cos(\theta_i - \theta_j) + V_{ij}(L_i^z + \frac{1}{2}) (L_j^z + \frac{1}{2})
\]

\[
+ \sum_i h_i(L_i^z + \frac{1}{2}), \tag{4}
\]

where we have dropped the \(U\) interaction term with the understanding that \(L_i = \pm 1/2\) in the large \(U\) limit. This charge sector Hamiltonian can be thought as a Kagome lattice spin-1/2 XXZ model in the presence of an external magnetic field upon identifying the rotor operators as the effective spin ladder operators, \(e^{\pm i\theta_i} = L_i^\pm\) where \(L_i^\pm = \mp \frac{1}{2}\) \((L_i^\pm = \pm \frac{1}{2}\)). Thus the corresponding effective spin-L model reads

\[
H_c = \sum_{(ij)} [-2J^\text{eff}_{ij}(L_i^+ L_j^- + h.c.) + V_{ij} L_i^z L_j^z]
\]

\[
+ h \sum_i L_i^z, \tag{5}
\]

in which we have made a uniform mean-field approximation such that \(h_i = 3(V_1 + V_2) \equiv \bar{h}\). The 1/6 electron filling is equivalent to \(N_s^{-1}\sum L_i^z = -1/6\), where \(N_s\) is the total number of Kagome lattice sites.

As we explained in Sec. \(A\) when \(V_1 (V_2)\) is large enough compared to \(t_2\) \((t_1)\), the electron number on each triangle, both up-triangle and down-triangle, is fixed to be one. The electron occupation configuration that satisfies this condition is highly degenerate. The presence of the electron hopping, i.e., \(L_i^+ L_j^-\), lifts this classical degeneracy and the effective interaction can be obtained from a third-order degenerate perturbation theory. The resulting effective ring exchange Hamiltonian is given as

\[
H_{c,\text{ring}} = -\sum_{\bigcirc} J_{\text{ring}}(L_i^+ L_j^- L_k^+ L_3^- L_4^+ L_5^- L_6^- + h.c.), \tag{6}
\]

where “\(\bigcirc\)” refers to the elementary hexagon of the Kagome lattice. \(J_{\text{ring}} = 6(J^\text{eff})^3/V_1^2 + 6(J^\text{eff})^3/V_2^2\) and \(1, \cdots, 6\) are the 6 vertices on the perimeter of the elementary hexagon (see Fig. [2]). This ring Hamiltonian in Eq. [6] describes the collective tunnelling of three electron charges between A and B configurations in Fig. [2].

FIG. 2. (Color online.) The two collective hopping processes that contribute to the ring electron hopping or the ring exchange in Eq. (6). The (blue) solid ball represents the electron or the charge rotor.

FIG. 3. (Color online.) The anisotropic Kagome lattice and the dual honeycomb lattice (in gray).
We now map \(H_{\text{c,ring}}\) into a quantum dimer model on the dual honeycomb lattice that is formed by the centers of the triangles on the Kagome lattice (see Fig. 3). As depicted in Fig. 2, a dimer is placed on the corresponding link if the center of the link (or the Kagome lattice site) is occupied by an electron charge. The rotor operator \(L^\pm_i\) simply adds or removes the charge dimer. So \(H_{\text{c,ring}}\) is mapped into the quantum dimer model with only a resonant term,

\[
H_{\text{c,ring}} = -J_{\text{ring}} \sum_{\text{O}} (|\text{O}_A\rangle\langle\text{O}_B| + |\text{O}_B\rangle\langle\text{O}_A|) \tag{7}
\]

where \(|\text{O}_A\rangle\) and \(|\text{O}_B\rangle\) refer to the two charge dimer covering configurations in the elementary hexagon “O” of the dual honeycomb lattice as shown in Fig. 3.

In Ref. [13] Moessner, Sondhi and Chandra studied the phase diagram of the quantum dimer model on the honeycomb lattice quite extensively. In the case with only the resonant term of our model in Eq. (7), they found a translational symmetry breaking phase with a plaquette dimer order, in which the system preferentially gains dimer resonating (or kinetic) energy through the resonating hexagons on the dual honeycomb lattice (see Fig. 4a).

The dimers on resonating hexagons form a linear superposition of the dimer covering configurations \(|\text{O}_A\rangle\) and \(|\text{O}_B\rangle\). This indicates that our model is unstable to translational symmetry breaking. The plaquette dimer order of the quantum dimer model is then mapped back to the plaquette charge order (PCO) on the Kagome lattice (see Fig. 3). Just like the resonating dimers, the three electron charges on the resonating hexagons also form a linear superposition of two occupation configurations in Fig. 3. This is a quantum mechanical effect and cannot be obtained by treating the inter-site electron interactions \(V_1\) and \(V_2\) in a classical fashion. Moreover, this PCO can be regarded as a local charge resonating valence bond (RVB) state which contrasts with the spin singlet RVB of Anderson [20,21].

We note that similar type of PCO has been obtained for extended Hubbard models with fermions or hard-core bosons on an isotropic Kagome lattice with 1/3 and 2/3 fillings in certain parameter regimes in previous studies [22–26].

With the PCO, the electrons are preferentially hopping around the perimeters of the resonating hexagons on the Kagome lattice. These resonating hexagons are periodically arranged, forming an emergent triangular lattice (see Fig. 4b). Due to the translational symmetry breaking, this emergent triangular lattice (ETL) has an enlarged unit cell that includes 9 sublattices compared to 3 sublattices in a Kagome lattice (see Fig. 5).

III. THE SPINON BAND STRUCTURE

In Sec. III using a slave-rotor approximation, we have shown that the system is unstable to the development of the PCO in the CMI where both up-triangle and down-triangle contain only one electron. Although our result is obtained by first starting from a translationally invariant mean-field ansatz, as we argue below, the PCO breaks the translational symmetry of the spinon mean-field state and the modified spinon band structure makes the PCO even more stable [27].

A. Spin charge coupling in the CMI with the PCO

To understand how the PCO in the charge sector influences the spinon sector, we first consider the low-energy effective ring hopping model in the CMI where both up-triangle and down-triangle contain only one electron,

\[
H_{\text{ring}} = - \sum_{\text{L}} \sum_{\alpha\beta\gamma} \left[ K_1 (c_{i\alpha}^\dagger c_{6\alpha}^\dagger c_{4\beta}^\dagger c_{3\gamma} c_{2\gamma} + \text{h.c.}) + K_2 (c_{i\alpha}^\dagger c_{2\alpha}^\dagger c_{3\beta}^\dagger c_{4\gamma}^\dagger c_{6\gamma} + \text{h.c.}) \right], \tag{8}
\]

where \(K_1 = 6t_1^2/V^2_2\) and \(K_2 = 6t_2^2/V^2_2\) are readily obtained from the third-order degenerate perturbation theory. Here, \(\alpha, \beta, \gamma = \uparrow, \downarrow, \text{ and } "1, \ldots, 6"\) are the 6 vertices in the elementary hexagon of the Kagome lattice.

Using the slave-rotor representation in Sec. III for the electron operator \(c_{i\alpha} = f_{i\alpha}^\dagger e^{i\theta_i} \equiv f_{i\alpha}^\dagger L^\dagger_i\), the ring hopping model \(H_{\text{ring}}\) can be decoupled as

\[
H_{\text{ring}} = - \sum_{\text{L}} \left[ K_1 (L^\dagger_1 L^\dagger_2 L^\dagger_3 L^\dagger_4 L^\dagger_5 L^\dagger_6 \times M_{165432} + \text{h.c.}) + K_2 (L^\dagger_1 L^\dagger_2 L^\dagger_3 L^\dagger_4 L^\dagger_5 L^\dagger_6 \times M_{123456} + \text{h.c.}) \right] \tag{9}
\]

\[
\equiv - \sum_{\text{O}} \left[ K_1 (|\text{O}_A\rangle\langle\text{O}_B| M_{165432} + |\text{O}_B\rangle\langle\text{O}_A| M_{165432}^* ) + K_2 (|\text{O}_A\rangle\langle\text{O}_B| M_{123456} + |\text{O}_B\rangle\langle\text{O}_A| M_{123456}^* ) \right], \tag{10}
\]

where \(|\text{O}_A\rangle\) and \(|\text{O}_B\rangle\) are the two charge dimer coverings in Fig. 2. Here we are focusing on the charge sector and...
We expect the mean-field ground state, which we explain below. For the charge sector is influenced by the spinon sector. By doing this, we can study how directly couple the charge sector quantum dimer model $\mathcal{M}$. We take the enlarged unit cell of the ETL to understand how the spinon band structure is modified. Thereby, we spontaneously break the translational symmetry of the Kagome lattice, the result of the renormalized couplings, and this would immediately imply the system should develop the PCO and spontaneously break the translational symmetry of the Kagome lattice. In turn, the breaking of lattice symmetry by the PCO would then influence the spinon sector. To understand how the spinon band structure is modified by the underlying PCO in the charge sector and how the modified spinon band structure feeds back to the charge sector, we take the enlarged unit cell of the ETL and introduce the following spinon mean-field (hopping) Hamiltonian (see Fig. 5a),

$$
\hat{H}_s = \sum_{\mathbf{R}} -\tilde{t}_1 \left[ f_{1\alpha}^\dagger \bar{R} f_{6\sigma} + f_{2\beta}^\dagger \bar{R} f_{3\sigma} + f_{4\gamma}^\dagger \bar{R} f_{5\sigma} + h.c. \right] \\
-\tilde{t}_2 \left[ f_{1\alpha}^\dagger f_{2\sigma} + f_{2\beta}^\dagger f_{3\sigma} + f_{4\gamma}^\dagger f_{5\sigma} + h.c. \right] \\
-\tilde{t}_1' \left[ f_{1\alpha}^\dagger f_{7\sigma} + f_{2\beta}^\dagger f_{8\sigma} + f_{3\gamma}^\dagger f_{9\sigma} + f_{5\alpha}^\dagger f_{8\sigma} + f_{5\beta}^\dagger f_{9\sigma} + h.c. \right] \\
+ f_{9\alpha}^\dagger f_{9\sigma} + f_{9\beta}^\dagger f_{9\sigma} + f_{9\gamma}^\dagger f_{9\sigma} + h.c. \right] \\
-\tilde{t}_2' \left[ f_{9\alpha}^\dagger f_{9\sigma} + f_{9\beta}^\dagger f_{9\sigma} + f_{9\gamma}^\dagger f_{9\sigma} + h.c. \right] \\
+ f_{1\alpha}^\dagger f_{1\alpha} + f_{2\beta}^\dagger f_{2\beta} + f_{3\gamma}^\dagger f_{3\gamma} + f_{4\alpha}^\dagger f_{4\alpha} + f_{4\beta}^\dagger f_{4\beta} + f_{4\gamma}^\dagger f_{4\gamma} + h.c. \right]
$$

(11)

where the lattice sites $i, j, k, l, m, n$ are arranged either clockwise or anti-clockwise and $M_{ijklmn}$ is the complex conjugate of $M_{ijklmn}$. What we did in Eq. (10) is to directly couple the charge sector quantum dimer model with the spinon sector. By doing this, we can study how the charge sector is influenced by the spinon sector.

The parameter $M_{ijklmn}$ is evaluated in the spinon mean-field ground state, which we explain below. For a time-reversal invariant system, we expect $M_{ijklmn} = M^*_{ijklmn}$. If we assume the spinon sector respects the translational invariance of the Kagome lattice, the resulting charge sector model would be equivalent to $H_{\text{ring}}$ in Eq. (5) and also to the quantum dimer model in Eq. (7) except for the renormalized couplings, and this would immediately imply the system should develop the PCO and spontaneously break the translational symmetry of the Kagome lattice. In turn, the breaking of lattice symmetry by the PCO would then influence the spinon sector.

To understand how the spinon band structure is modified by the underlying PCO in the charge sector and how the modified spinon band structure feeds back to the charge sector, we take the enlarged unit cell of the ETL and introduce the following spinon mean-field (hopping) Hamiltonian (see Fig. 5a),

$$
\hat{H}_s = \sum_{\mathbf{R}} -\tilde{t}_1 \left[ f_{1\alpha}^\dagger \bar{R} f_{6\sigma} + f_{2\beta}^\dagger \bar{R} f_{3\sigma} + f_{4\gamma}^\dagger \bar{R} f_{5\sigma} + h.c. \right] \\
-\tilde{t}_2 \left[ f_{1\alpha}^\dagger f_{2\sigma} + f_{2\beta}^\dagger f_{3\sigma} + f_{4\gamma}^\dagger f_{5\sigma} + h.c. \right] \\
-\tilde{t}_1' \left[ f_{1\alpha}^\dagger f_{7\sigma} + f_{2\beta}^\dagger f_{8\sigma} + f_{3\gamma}^\dagger f_{9\sigma} + f_{5\alpha}^\dagger f_{8\sigma} + f_{5\beta}^\dagger f_{9\sigma} + h.c. \right] \\
+ f_{9\alpha}^\dagger f_{9\sigma} + f_{9\beta}^\dagger f_{9\sigma} + f_{9\gamma}^\dagger f_{9\sigma} + h.c. \right] \\
-\tilde{t}_2' \left[ f_{9\alpha}^\dagger f_{9\sigma} + f_{9\beta}^\dagger f_{9\sigma} + f_{9\gamma}^\dagger f_{9\sigma} + h.c. \right] \\
+ f_{1\alpha}^\dagger f_{1\alpha} + f_{2\beta}^\dagger f_{2\beta} + f_{3\gamma}^\dagger f_{3\gamma} + f_{4\alpha}^\dagger f_{4\alpha} + f_{4\beta}^\dagger f_{4\beta} + f_{4\gamma}^\dagger f_{4\gamma} + h.c. \right]
$$

(12)

such that the influence of the charge sector on the spinon sector is captured.

In the presence of the PCO, we expect $\tilde{t}_1 > \tilde{t}_1'$ and $\tilde{t}_2 > \tilde{t}_2'$ due to the presence of the PCO. According to Eqs. (13), (14), (15) and (16), the presence of the PCO would enhance the bonding of the charge rotors and then the spinon hoppings in the resonating hexagons and weakens the ones in the non-resonating hexagons. The enhanced spinon hoppings in the resonating hexagons further strengthen the couplings of the $H_{\text{ring}}$ in the resonating hexagons through $M_{ijklmn}$ in Eq. (10). Thus the PCO would become more stable if the coupling between spinon and charge excitations is switched on.

### B. Generalized Levin-Wen’s variational dimer wavefunction approach and the spinon band structure in the presence of the PCO

We now consider the combination of the spinon hopping model $\hat{H}_s$ in Eq. (12) with the ring hopping model $H_{\text{ring}}$ in Eq. (10). It was pointed by Levin and Wen that quantum dimer model is an example of string-net models. In Ref. 18, Levin and Wen developed a variational string wavefunction approach (or string mean-field theory) to describe the properties of quantum dimer model. To make the nomenclature consistent, we refer Levin-Wen’s variational string wavefunction approach as variational dimer wavefunction approach in the following. Since the charge sector is described by a quantum dimer model, we can extend Levin-Wen’s variational string wavefunction approach to solve the coupled charge and spinon problem in Sec. III A. In Levin and Wen’s original work, the variational dimer wavefunction approach was designed for pure quantum dimer model. The new ingredients of our problem are the presence of the spinon degrees of freedom, and the coupling and the mutual feedback between the spinons and charge dimers.

We describe below the variational dimer wavefunction approach that is used to optimize the Hamiltonian $\hat{H}_{\text{ring}}$ in Eq. (10) for the charge dimers. Following Levin and Wen, the variational dimer wavefunction is parametrized by a set of variational parameters $\{z_i\}$ where $z_i$ is defined on each link of the dual honeycomb lattice. Here the links on the dual honeycomb lattice are also parametrized by the Kagome lattice sites that are located at the centers of...
the links. These variational parameters \( z_i \) are also termed as string (or dimer) fugacity by Levin and Wen. For each set of \( \{ z_i \} \), the variational dimer wavefunction is given by

\[
\Psi(\{ z_i \}) = \prod_i \frac{|0_i\rangle + z_i|1_i\rangle}{(1 + |z_i|^2)^{\frac{1}{2}}},
\]

(17)

where \(|0_i\rangle\) and \(|1_i\rangle\) define the absence and presence of the electron charge at the Kagome lattice site \( i \) or the dimer on the corresponding link on the dual honeycomb lattice, respectively. Moreover, we have the following relations by definition,

\[
n_i|0_i\rangle = 0, \quad n_i|1_i\rangle = |1_i\rangle, \quad L_i^+|0_i\rangle = |1_i\rangle, \quad L_i^-|1_i\rangle = |0_i\rangle,
\]

(18)

(19)

where \( n_i \) counts the electron number (or the number of dimers) at site \( i \).

We employ the symmetry of the PCO to reduce the number of free variational parameters in the dimer wavefunction \( \Psi(\{ z_i \}) \). Using the symmetries of the ETL, we find that only two variational parameters are needed

\[
z_1(R) = z_2(R) = z_3(R) = z_4(R)
\]

\[
z_5(R) = z_6(R) = z_7(R) = z_8(R) = z_9(R) \equiv z,
\]

(20)

(21)

where \( z_\mu(R) (\mu = 1, 2, \ldots, 9) \) refers to the variational parameter of the \( \mu \)th sublattice at the unit cell \( R \) (see Fig. 5). We have reduced the set of variational parameters in the variational dimer wavefunction to \( z \) and \( \tilde{z} \). Moreover, \( z \) and \( \tilde{z} \) are not independent from each other. This is because of the charge localization constraint, i.e. every triangle contains only one electron. In terms of the dimer language, this constraint is that every dual honeycomb lattice site is connected by only one dimer. To satisfy this constraint, we only need to require

\[
\langle n_1(R) \rangle + \langle n_6(R) \rangle + \langle n_7(R) \rangle = 1,
\]

(22)

where the expectation value is taken for the variational wavefunction \( \Psi(\{ z_i \}) \). This relation connects \( \tilde{z} \) to \( z \).

For the quantum dimer model \( H_{c, \text{ring}} \) in Eq. (7), variational (or mean-field) phase is obtained by evaluating the Hamiltonian \( H_{c, \text{ring}} \) with respect to \( \Psi(\{ z_i \}) \) and optimizing the energy by varying \( z \). This static variational approach, however, cannot directly produce the plaquette ordered phase of the quantum dimer model. What it gives is a translationally invariant variational ground state. To obtain the right result, Levin and Wen developed a dynamical variational approach. Namely, for each static variational ground state, one checks the stability of the variational phase by considering the quantum fluctuation of this phase. In the model that Levin and Wen were considering, they found some modes in a translationally invariant variational ground state can become unstable and drive a dimer crystal ordering. We expect similar physics should happen to our quantum dimer model \( H_{c, \text{ring}} \).

Unfortunately, the dynamical variational approach by Levin and Wen is not a self-consistent variational approach and cannot be extended to the combined spinon and charge dimer problem that we are interested in here. Since we know our quantum dimer model \( H_{c, \text{ring}} \) gives the ground state with the PCO and we have argued that coupling the charge (dimer) with the spinons makes the PCO even more stable in Sec. III A, we now introduce the PCO into the system by explicitly breaking the lattice symmetry. That is, we modify the ring hoppings \( K_1 \) and \( K_2 \) in \( H_{\text{ring}} \) of Eq. (9). For the resonating hexagons, we change

\[
K_1 \to K_1(1 + \delta), \quad K_2 \to K_2(1 + \delta),
\]

(23)

and for the non-resonating hexagons, we use

\[
K_1 \to K_1(1 - \delta), \quad K_2 \to K_2(1 - \delta),
\]

(24)

where \( \delta \) (with \( \delta > 0 \)) is a phenomenological parameter that breaks an appropriate lattice symmetry for the PCO. This modification of the ring hoppings captures the spatial modulation of the energy in the system when the PCO is present. This phenomenological way of introducing the PCO is very similar in spirit to Henley’s approach to the order by disorder, where a phenomenological interaction is introduced into the energy or the free energy to model the ground state selection due to the quantum fluctuation.

We now solve the combined Hamiltonian of \( H_s \) and \( H_{\text{ring}} \) with the modified ring hoppings self-consistently. This self-consistent approach is expected to underestimate the PCO for any fixed \( \delta \) and thus underestimates the reconstruction of the spinon band structure due to the PCO. Nevertheless, to understand the generic features of the spinon band structure reconstruction in the presence of the PCO, we can simply vary the phenomenological parameter \( \delta \) and study the spinon band structure from this self-consistent approach.

The evolution of the mean-field spinon band structure is depicted in Fig. [9]. When \( \delta = 0 \), there is no PCO and the symmetry of the Kagome lattice is preserved. The spinon band structure contains 3 bands in the 1st BZ1 of the Kagome lattice (BZ1 in Fig. [1]). The 3 spinon bands are well separated in energy and have no direct nor indirect overlap, and we can simply focus on the lowest band as the spinons only fill half of the lowest band. So in Fig. [5] we only need to plot the evolution of the lowest spinon band. In Fig. [6], we have more folded the lowest spinon band onto the 1st BZ1 zone of the ETL (BZ2 in Fig. [1]) and obtain 3 spinon sub-bands. We use “spinon sub-bands” to refer the spinon bands plotted in the BZ2 of the ETL.

In the presence of the PCO for a finite \( \delta \), the system has 9 sublattices (see Fig. [5]), the 3 spinon bands at \( \delta = 0 \) are further split into 9 spinon sub-bands, and the lowest spinon band at \( \delta = 0 \) is split into 3 spinon sub-bands.

We now explain the evolution of the spinon bands as the PCO is enhanced by increasing the variational parameter \( \delta \). At \( \delta = 0 \), there is no PCO, and the 2nd and
Because of the direct band gap, the lowest spinon sub-band is fully filled by 2/3 of the spinon numbers. A fully-filled spinon is inert to an external magnetic field, and thus, only the 1/3 of the spinons from the partially filled upper sub-bands contribute to the local moment, and thus, only the 1/3 of the spinons from the partially filled upper sub-bands contribute to the local moment, and thus the internal U(1) gauge field is expected to be in the deconfining phase. and we obtain U(1) QSL for the ground state.

IV. THERMAL TRANSITION AND SPIN SUSCEPTIBILITY

Because the PCO breaks the lattice symmetry, this implies that there exists a thermal phase transition at a finite temperature which destroys the PCO and restores the lattice symmetry. This thermal transition is expected to occur at $T^\ast \sim O(\xi_1) = O(t_1^2/N_{\Delta}^2)$ (because $\xi_1 \gg \xi_2$) when the local electron resonance in the elementary hexagons loses the quantum phase coherence.

Based on the understanding of the spinon band structure in Sec. III, we describe the behavior of the spin susceptibility in the low temperature regime with the PCO ($T < T^\ast$) and in the high temperature regime without the PCO ($T > T^\ast$). Since the U(1) QSL ground state has spinon Fermi surfaces, we expect a finite (Pauli-like) spin susceptibility in the zero temperature limit. At finite temperatures, one should recover the Curie-Weiss law for the spin susceptibility. What are the Curie constant and the Curie-Weiss temperature that characterize the Curie-Weiss law for $T < T^\ast$ and $T > T^\ast$? The Curie constant measures the number of the active local moments. Let us now consider the local moment formation regime for $T < T^\ast$. As long as the PCO is not destroyed by thermal fluctuations which is the case for $T < T^\ast$, the direct band gap between the lowest spinon sub-band and upper sub-bands would be present, and the lowest spinon sub-band is fully filled by 2/3 of the spinon numbers. A fully-filled spinon is inert to an external magnetic field, and thus, only the 1/3 of the spinons from the partially filled upper sub-bands contribute to the local moment, and thus, only the 1/3 of the spinons from the partially filled upper sub-bands contribute to the local moment, which comprise 1/3 of the total number of electrons in the system. Therefore, the low temperature Curie constant in a DC susceptibility measurement for $T < T^\ast$ is

$$C_L = \frac{g^2 \mu_B^2 s(s + 1) N_{\Delta}}{3k_B}$$

(25)

where $g \approx 2$ is the Landé factor, $s = 1/2$, and $N_{\Delta}$ is the total number of up-triangles in the system. From the electron filling fraction, we know $N_{\Delta}$ equals the total electron number $N_e$. Because only 1/3 of the total spins are responsible for the low-temperature magnetic properties, the Curie constant is only 1/3 of the one at very high temperatures where all the electron spins are supposed to be active.

For $T > T^\ast$, the PCO is destroyed by thermal fluctuation, and the direct band gap between the lowest spinon sub-band and the upper spinon sub-bands is closed. All the localized electrons are active and contribute to the local moment, and thus the Curie constant in this high temperature regime is

$$C_H = \frac{g^2 \mu_B^2 s(s + 1)}{3k_B} N_{\Delta},$$

(26)
which is 3 times the low temperature one, $c^L$.

As for the Curie-Weiss temperature, it is hard to make a quantitative prediction from the spinon Fermi surface. But it is noted that the Curie-Weiss temperature is roughly set by the bandwidth of the active spinon bands in the QSL phase. At low temperature PCO phase, the active spinon bands are the partially-filled upper spinon sub-bands on the ETL (see Fig. 6c). As one can see from Fig. 6c, the bandwidth of the active spinon bands is significantly reduced when the PCO is present compared to Fig. 6a when the PCO is absent. As a result, we expect a much reduced Curie-Weiss temperature in the presence of the PCO at $T < T^*$ compared to the case in the absence of the PCO at $T > T^*$. In the absence of the PCO at $T > T^*$, as all the spinon sub-bands are active, the Curie-Weiss temperature is set by the total spinon bandwidth in Fig. 6a.

\section{V. DISCUSSION}

\subsection{A. Applications to LiZn$_2$Mo$_3$O$_8$}

As we discuss in Sec. \[\text{14}\], the CMI with the PCO provides two Curie-Weiss regimes in spin susceptibility. Armed with these results, we here propose that the Mo system in LiZn$_2$Mo$_3$O$_8$ may be in the CMI with the PCO at low temperatures. Because the PCO triples the unit cell, the thermal transition at $T^*$ is found to be first order in a Landau theory analysis for a clean system.\[25\] In reality, LiZn$_2$Mo$_3$O$_8$ is influenced by various disorders or impurities (e.g. the mixed Li/Zn sites and mobile Li ions). For example, impurities would broaden the charge ordering transition.\[26\] This may explain why a sharp transition is not observed in the experiments.\[26\] Nevertheless, the experiments do observe a peak around 100K in heat capacity which might be related to the smeared-out phase transition.

Based on the fact that there is no obvious ordering down to $\sim 0.1K$ for LiZn$_2$Mo$_3$O$_8$ and the apparent gapless spin excitation in neutron scattering,\[13,15\] we further propose that the system is in the U(1) QSL with spinon Fermi surfaces (as well as the PCO) of the CMI that is obtained in Sec. \[11b\]. With the spinon Fermi surfaces, we expect the usual behaviors of a 2D U(1) QSL with spinon Fermi surfaces would show up. That is, the specific heat $C_v \sim T^{2/3}$, and a Pauli-like spin susceptibility in the low temperature limit.\[26\] The crossover in the behavior of the spin susceptibility from the local moment Curie-Weiss regime to the Pauli-like behavior is expected to happen at the temperature set by the bandwidth of active spinon bands (see Sec. \[11b\]), or equivalently, by the low-temperature Curie-Weiss temperature below $T^*$. This crossover temperature should be very low because of the suppressed Curie-Weiss temperature at low temperatures. As a result, the Pauli-like spin susceptibility may be smeared out by various extrinsic factors like local magnetic impurities at very low temperatures. Likewise, even though the $C_v/T$ experiences a upturn below 10K in the absence of external magnetic fields, it is likely that the nuclear Schottky anomalies may complicate the specific heat data.

On the other hand, the apparently gapless spectrum of the spin excitations in the inelastic neutron scattering measurement\[12\] is certainly consistent with the gapless spinon Fermi surface of our U(1) QSL. Moreover, the measurements of relaxation rate from both NMR ($1/(T\lambda T)$) and $\mu$SR ($\lambda^{-1}$) also indicate gapless spin-spin correlation.\[12\] In our U(1) QSL, the reduction of the spinon bandwidth due to the PCO increases the density of the low-energy magnetic excitations. This would lead to a low-temperature upturn of the spin-lattice relaxation, which is in fact observed in NMR and $\mu$SR experiments.\[24\]

A direct measurement of the PCO at low temperatures is crucial for our theory. To this end, a high resolution X-ray scattering measurement and NQR (nuclear quadrupole resonance) can be helpful. Moreover, the presence of local quantum entanglement within the resonant hexagon may be probed optically by measuring the local exciton excitations. Furthermore, if the system is in a U(1) QSL with a spinon Fermi surface, the low-temperature thermal conductivity can be an indirect probe of the low-energy spinon excitation, and a direct measurement of the correlation of the emergent U(1) gauge field might be possible because the strong spin-orbit coupling of the Mo atoms can enhance the coupling between the spin moment and the spin texture.\[24\]

A previous work on LiZn$_2$Mo$_3$O$_8$ has proposed a theory based on varying spin exchange interaction from the emergent lattice that is caused by the lattice distortion.\[25\] In contrast, our work here is purely based on the electron degrees of freedom and their interactions.

\subsection{B. Other Mo based cluster magnets}

The compounds that incorporate the Mo$_3$O$_{13}$ cluster unit represent a new class of magnetic materials called “cluster magnets”. Several families of materials, such as \[\text{M}_2\text{Mo}_3\text{O}_8\] ($\text{M} = \text{Mg, Mn, Fe, Co, Ni, Zn, Cd}$), \[\text{LiRMo}_3\text{O}_8\] ($\text{R} = \text{Sc, Y, In, Sm, Gd, Tb, Dy, Ho, Er, Yb}$) and other related variants fall into this class. The magnetic properties of most materials have not been carefully studied so far. In Tab. \[\text{I}\] we list three cluster magnets with

| [Mo-Mo]$_{\text{u}}$ | [Mo-Mo]$_{\text{d}}$ | $\lambda$ e$^{-}$/Mo$_3$ | Ref |
|---------------------|---------------------|-----------------------|-----|
| LiZn$_2$Mo$_3$O$_8$  | 2.6Å  | 3.2Å  | 1.23 | 7 \[13\]  |
| Li$_2$InMo$_3$O$_8$  | 2.54Å  | 3.25Å  | 1.28 | 7 \[36\]  |
| ScZnMo$_3$O$_8$     | 2.58Å  | 3.28Å  | 1.27 | 7 \[37\]  |

\[\text{TABLE I. Mo-Mo bond lengths, anisotropic parameters ($\lambda$) and number of electrons per Mo$_3$O$_{13}$ cluster for three different cluster magnets. The electron number is counted from stoichiometry.}\]
odd number of electrons in the Mo$_3$O$_{13}$ cluster unit. We introduce a phenomenological parameter $\lambda$ to characterize the anisotropy of the Mo Kagome lattice, which is defined as the ratio between inter-cluster (or down-triangle) and intra-cluster (or up-triangle) Mo-Mo bond lengths,

$$
\lambda = \frac{[\text{Mo-Mo}]_d}{[\text{Mo-Mo}]_u}.
$$

(27)

Large anisotropy tends to reduce the interaction $V_2$ and increase the hopping $t_1$ so that the systems are more likely to be in the regime where the electron is only localized on the up-triangle while the electron number on the down triangle is strongly fluctuating (see Fig. 1). In such a regime, there is no PCO, each localized electron on the up-triangle forms a local spin-$1/2$ moment, and these local spin-$1/2$ moments form a triangular lattice. If the system is in the weak Mott regime like the organics, the up-triangle forms a local spin-1/2 moment, and these local spin-$1/2$ moments form a triangular lattice. If the system is in the weak Mott regime like the organics, the up-triangle forms a local spin-1/2 moment, and these local spin-$1/2$ moments form a triangular lattice. If the system is in the weak Mott regime like the organics, the up-triangle forms a local spin-1/2 moment, and these local spin-$1/2$ moments form a triangular lattice. If the system is in the weak Mott regime like the organics, the up-triangle forms a local spin-1/2 moment, and these local spin-$1/2$ moments form a triangular lattice. If the system is in the weak Mott regime like the organics, the up-triangle forms a local spin-1/2 moment, and these local spin-$1/2$ moments form a triangular lattice.

Below 25K, the spin susceptibility of Li$_2$InMo$_3$O$_8$ saturates to a constant, which is consistent with the Pauli-like spin susceptibility for a spinon Fermi surface U(1) QSL. Besides the structural and spin susceptibility data, very little is known about Li$_2$InMo$_3$O$_8$. Thus, more experiments are needed to confirm the absence of magnetic ordering in Li$_2$InMo$_3$O$_8$ and also to explore the magnetic properties of ScZnMo$_3$O$_8$ and other cluster magnets.

**Acknowledgements.** We thank A. Essin, A. Burkov, L. Balents and M. Hermele for helpful discussion, and especially T. McQueen and P. A. Lee for email correspondence and conversation that helps clarify some details of our theory. This work was supported by the NSERC, CIFAR, and Centre for Quantum Materials at the University of Toronto. We also acknowledge NSF grant no. PHY11-25915 for supporting the visitor program at the Kavli Institute for Theoretical Physics during the workshop “Frustrated Magnetism and Quantum Spin Liquids”, where the current work was initiated.

* chqget@gmail.com

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