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Spin-orbital liquids in non-Kramers magnets on the kagome lattice

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Localized magnetic moments with crystal-field doublet or pseudospin-$\frac{1}{2}$ may arise in correlated insulators with even number of electrons and strong spin-orbit coupling. Such a non-Kramers pseudospin-$\frac{1}{2}$ is the consequence of crystalline symmetries as opposed to the Kramers doublet arising from time-reversal invariance, and is necessarily a composite of spin and orbital degrees of freedom. We investigate possible spin-orbital liquids with fermionic spinons for such non-Kramers pseudospin-$\frac{1}{2}$ systems on the kagome lattice. Using the projective symmetry group analysis, we find 10 phases that are not allowed in the corresponding Kramers systems. These phases are allowed due to unusual action of the time-reversal operation on non-Kramers pseudospins. We compute the spin-spin dynamic structure factor that shows characteristic features of these non-Kramers spin-orbital liquids arising from their unusual coupling to neutrons, which is therefore relevant for neutron scattering experiments. We also point out possible anomalous broadening of Raman scattering intensity that may serve as a signature experimental feature for gapless non-Kramers spin-orbital liquids.

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I. INTRODUCTION

The low-energy magnetic degrees of freedom of a Mott insulator, in the presence of strong spin-orbit coupling, are described by states with entangled spin and orbital wave functions.[1,2] In certain crystalline materials, for ions with even numbers of electrons, a low-energy spin-orbit entangled “pseudospin”-$\frac{1}{2}$ may emerge, which is not protected by time-reversal symmetry (Kramers degeneracy)[3] but rather by the crystal symmetries.[4,5] Various phases of such *non-Kramers* pseudospin systems on geometrically frustrated lattices, particularly various quantum paramagnetic phases, are of much recent theoretical and experimental interest in the context of a number of rare-earth materials including frustrated pyrochlores[6–10] and heavy-fermion systems.[11,12]

In this paper, we explore *spin-orbital liquids* that may emerge in these systems due to the unusual transformation of the non-Kramers pseudospins under the time-reversal transformation. Contrary to Kramers spin-$\frac{1}{2}$, where the spins transform as $\mathbf{S} \rightarrow -\mathbf{S}$ under time reversal,[3] here only one component of the pseudospin operators changes sign under time reversal: $\{\sigma^1,\sigma^2,\sigma^3\} \rightarrow \{\sigma^1,\sigma^2,-\sigma^3\}$.[4,5] This is because, due to the nature of the wave-function content, the σ_3 component of the pseudospin carries a dipolar magnetic moment while the other two components carry quadrupolar moments of the underlying electrons. Hence, the time-reversal operator for the non-Kramers pseudospins is given by $\mathcal{T} = \sigma^1 K$ (where K is the complex conjugation operator), which allows for different spin-orbital liquid phases. Since the magnetic degrees of freedom are composed out of wave functions with entangled spin and orbital components, we prefer to refer to the above quantum paramagnetic states as spin-orbital liquids, rather than spin liquids.

Since the degeneracy of the non-Kramers doublet is protected by crystal symmetries, the transformation properties of the pseudospin under various lattice symmetries intimately depend on the content of the wave functions that make up the doublet. To this end, we focus our attention on the example of praseodymium ions (Pr^{3+}) in a local D_{3d} environment, which is a well-known non-Kramers ion that occurs in a number of materials with interesting properties.[6–8] Such an environment typically occurs in praseodymium pyrochlores given by the generic formulas $\mathrm{Pr}_2TM_2\mathrm{O}_7$, where TM (= Zr, Sn, Hf, or Ir) is a transition metal. In these compounds, the Pr^{3+} ions host a pair of $4f$ electrons which form a $J=4$ ground-state manifold with $S=1$ and $L=5$, as expected due to Hund’s rules. In terms of this local environment, we have a ninefold degeneracy of the electronic states.[5] This degeneracy is broken by the crystalline electric field. The oxygen and TM ions form a D_{3d} local symmetry environment around the Pr^{3+} ions, splitting the ninefold degeneracy. A standard analysis of the symmetries of this system (see Appendix A) shows that the $J=4$ manifold splits into three doublets and three singlets ($\Gamma_{j=4} = 3E_g + 2A_{1g} + A_{2g}$) out of which one of the doublets is found to have the lowest energy, usually well separated from the other crystal-field states.[5] This doublet (details in Appendix A), formed out of a linear combination of the $J_z = \pm 4$ with $J_z = \pm 1$ and ± 2 states, is given by

$$|\pm\rangle = \alpha|m=\pm 4\rangle \pm \beta|m=\pm 1\rangle - \gamma|m=\mp 2\rangle. \quad (1)$$

The non-Kramers nature of this doublet is evident from the nature of the “spin”-raising and -lowering operators within the doublet manifold; the projection of the angular-momentum-raising and -lowering operators to the space of doublets is zero ($\mathcal{P}J^{\pm}\mathcal{P}|\sigma\rangle = 0$ where $\mathcal{P}$ projects into the doublet manifold). However, the projection of the J^z operator to this manifold is nonzero, and describes the z component of the pseudospin (σ^3). In addition, there is a nontrivial projection of the quadrupole operators $\{J^{\pm},J^z\}$ in this manifold. These have off-diagonal matrix elements, and are identified with the pseudospin-raising and -lowering operators ($\sigma^{\pm} = \sigma^1 \pm i\sigma^2$).

In a pyrochlore lattice, the local D_{3d} axes point to the center of the tetrahedra.[5] On looking at the pyrochlore lattice along the [111] direction, it is found to be made out of alternate layers of kagome and triangular lattices. For each kagome

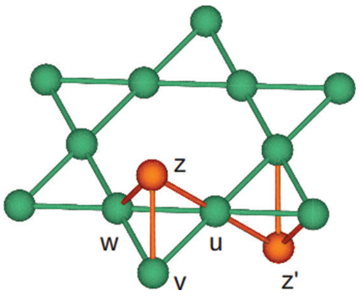


FIG. 1. (Color online) A kagome layer, in the pyrochlore lattice environment. We consider sites labeled z and z' replaced by nonmagnetic ions, decoupling the kagome layers. The local axis at the u, v, and w sites point towards the center of the tetrahedron on which these lie.

layer (shown in Fig. 1), the local D_{3d} axes make an angle of $\cos^{-1}(\sqrt{2/3})$ with the plane of the kagome layer. We imagine replacing the Pr^{3+} ions from the triangular lattice layer with nonmagnetic ions so as to obtain decoupled kagome layers with Pr^{3+} ions on the sites. The resulting structure is obtained in the same spirit as the now well-known kagome compound Herbertsmithite was envisioned. As long as the local crystal field has D_{3d} symmetry, the doublet remains well defined. A suitable candidate nonmagnetic ion may be isovalent but nonmagnetic La^{3+}. Notice that the most extended orbitals in both cases are the fifth-shell orbitals, and the crystal field at each Pr^{3+} site is mainly determined by the surrounding oxygens and the transition-metal element. Hence, we expect that the splitting of the non-Kramers doublet due to the above substitution would be very small and the doublet will remain well defined. In this work, we shall consider such a kagome lattice layer and analyze possible Z_2 spin-orbital liquids, with gapped or gapless fermionic *spinons*.

The rest of the paper is organized as follows. In Sec. II, we begin with a discussion of the symmetries of the non-Kramers system on a kagome lattice and write the most general pseudospin model with pseudospin exchange interactions up to second nearest neighbors. In Sec. III, we formulate the projective symmetry group (PSG) analysis for singlet and triplet decouplings. Using this, we demonstrate that the non-Kramers transformation of our pseudospin degrees of freedom under time reversal leads to a set of 10 spin-orbital liquids which can not be realized in the Kramers case. In Sec. IV, we derive the dynamic spin-spin structure factor for two representative spin liquids for the case of both Kramers and non-Kramers doublets, demonstrating that experimentally measurable properties of these two types of spin-orbital liquids differ qualitatively. Finally, in Sec. V, we discuss our results, and propose an experimental test which can detect a non-Kramers spin-orbital liquid. The details of various calculations are discussed in different appendixes.

II. SYMMETRIES AND THE PSEUDOSPIN HAMILTONIAN

Since the local D_{3d} axes of the three sites in the kagome unit cell differ from each other, a general pseudospin Hamiltonian is not symmetric under *continuous* global pseudospin rotations. However, it is symmetric under various symmetry transformations of the kagome lattice as well as time-reversal symmetry. Such symmetry transformations play a major role in the remainder of our analysis. We start by describing the effect of various lattice symmetry transformations on the non-Kramers doublet.

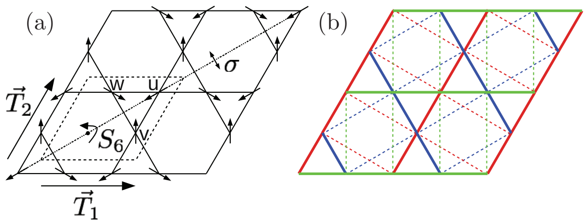


FIG. 2. (Color online) (a) The symmetries of the kagome lattice. Also shown are the labels for the sublattices and the orientation of the local z axis. (b) Nearest- and next-nearest-neighbor bonds. Colors refer to the phases $\phi_{r,r'}$ and $\phi'_{r,r'}$, with these being 0 on blue bonds, 1 on green bonds, and 2 on red bonds.

We consider the symmetry operations that generate the space group of the above kagome lattice. These are [as shown in Fig. 2(a)] as follows:

(i) T_1, T_2: generate the two lattice translations.

(ii) $\sigma = C_2' I$: (not to be confused with the pseudospin operators which come with a superscript) where I is the three-dimensional inversion operator about a plaquette center and C_2' refers to a twofold rotation about a line joining two opposite sites on the plaquette.

(iii) $S_6 = C_3^2 I$: where C_3 is the threefold rotation operator about the center of a hexagonal plaquette of the kagome lattice.

(iv) $T = \sigma_1 K$: time reversal.

Here, we consider a three-dimensional inversion operator since the local D_{3d} axes point out of the kagome plane. The above symmetries act nontrivially on the pseudospin degrees of freedom, as well as the lattice degrees of freedom. The action of the symmetry transformations on the pseudospin operators is given by

$$\begin{aligned} S_6 &: \{\sigma^3,\sigma^+,\sigma^-\} \to \{\sigma^3,\bar{\omega}\sigma^+,\omega\sigma^-\},\\ T &: \{\sigma^3,\sigma^+,\sigma^-\} \to \{-\sigma^3,\sigma^-,\sigma^+\},\\ C_2' &: \{\sigma^3,\sigma^+,\sigma^-\} \to \{-\sigma^3,\sigma^-,\sigma^+\},\\ T_1 &: \{\sigma^3,\sigma^+,\sigma^-\} \to \{\sigma^3,\sigma^+,\sigma^-\},\\ T_2 &: \{\sigma^3,\sigma^+,\sigma^-\} \to \{\sigma^3,\sigma^+,\sigma^-\} \end{aligned} \tag{2}$$

($\omega = \bar{\omega}^{-1} = e^{i\frac{2\pi}{3}}$). Operationally, their action on the doublet $(|+\rangle|-\rangle)$ can be written in form of 2×2 matrices. The translations T_1, T_2 act trivially on the pseudospin degrees of freedom, and the remaining operators act as

$$T = \sigma_1 K, \quad \sigma = \sigma_1, \quad S_6 = \begin{bmatrix} \bar{\omega} & 0 \\ 0 & \omega \end{bmatrix}, \tag{3}$$

where K refers to complex conjugation. The above expressions can be derived by examining the effect of these operators on the wave function describing the doublet [Eq. (1)].

We can now write the most generic pseudospin Hamiltonian allowed by the above lattice symmetries that is bilinear in pseudospin operators. The form of the time-reversal symmetry restricts our attention to those products which are formed by a pair of σ^3 operators or those which mix the pseudospin-raising and -lowering operators. Any term which mixes σ^3 and $\sigma^\pm$ changes sign under the symmetry, and can thus be excluded. Under the C_3 transformation about a site, the terms $C_3 : \sigma_r^3 \sigma_{r'}^3 \rightarrow \sigma_{C_3(r)}^3 \sigma_{C_3(r')}^3$ and $C_3 : \sigma_r^+ \sigma_{r'}^- \rightarrow \sigma_{C_3(r)}^+ \sigma_{C_3(r')}^-$. However, the term $\sigma_r^+ \sigma_{r'}^+$ (and its Hermitian conjugate) gain additional phase factors when transformed; under the C_3 symmetry transformation, this term becomes $C_3 : \sigma_r^+ \sigma_{r'}^+ \rightarrow \bar{\omega} \sigma_{C_3(r)}^+ \sigma_{C_3(r')}^+$. In addition, under the σ symmetry, this term transforms as $\sigma : \sigma_r^+ \sigma_{r'}^+ \rightarrow \sigma_{\sigma(r)}^- \sigma_{\sigma(r')}^-$. Thus, the Hamiltonian with spin-spin exchange interactions up to next-nearest neighbor is given by

$$\begin{aligned} H_{\text{eff}} = J_{nn} \sum_{\langle r,r' \rangle} \Big[& \sigma_r^3 \sigma_{r'}^3 + 2(\delta \sigma_r^+ \sigma_{r'}^- + \text{H.c.}) \\ & + 2q \Big(e^{\frac{2\pi i \phi_{r,r'}}{3}} \sigma_r^+ \sigma_{r'}^+ + \text{H.c.} \Big) \Big] \\ & + J_{nnn} \sum_{\langle\langle r,r' \rangle\rangle} \Big[\sigma_r^3 \sigma_{r'}^3 + 2(\delta' \sigma_r^+ \sigma_{r'}^- + \text{H.c.}) \\ & + 2q' \Big(e^{\frac{2\pi i \phi'_{r,r'}}{3}} \sigma_r^+ \sigma_{r'}^+ + \text{H.c.} \Big) \Big], \end{aligned} \tag{4}$$

where ϕ and ϕ' take values 0, 1, and 2 depending on the bonds on which they are defined [Fig. 2(b)]. The above Hamiltonian is similar in form to that derived in Ref. 5 with one difference: the coupling δ, in the present case, is allowed to be complex due to the lowered symmetry.

III. SPINON REPRESENTATION OF THE PSEUDOSPINS AND PSG ANALYSIS

Having written the pseudospin Hamiltonian, we now discuss the possible spin-orbital liquid phases. We do this in two stages in the following sections.

A. Slave-fermion representation and spinon decoupling

In order to understand these phases, we will use the fermionic slave-particle decomposition of the pseudospin operators. At this point, we note that the pseudospins satisfy $S = \frac{1}{2}$ representations of an "SU(2)" algebra among their generators (not to be confused with the regular spin rotation symmetry). We represent the pseudospin degrees of freedom in terms of a fermion bilinear. This is very similar to usual slave-fermion construction for spin liquids.[13,14] We take

$$\sigma_j^\mu = \tfrac{1}{2} f_{j\alpha}^\dagger [\rho^\mu]_{\alpha\beta} f_{j\beta}, \tag{5}$$

where $\alpha,\beta = \uparrow,\downarrow$ is defined along the local z axis and f ($f^\dagger$) is an $S = \frac{1}{2}$ fermionic annihilation (creation) operator. Following standard nomenclature, we refer to the f ($f^\dagger$) as the spinon annihilation (creation) operator, and note that these satisfy standard fermionic anticommutation relations. The above spinon representation, along with the single-occupancy constraint

$$f_{i\uparrow}^\dagger f_{i\uparrow} + f_{i\downarrow}^\dagger f_{i\downarrow} = 1, \tag{6}$$

form a faithful representation of the pseudospin-$\frac{1}{2}$ Hilbert space. The above representation of the pseudospins, when used in Eq. (4), leads to a quartic spinon Hamiltonian. Following standard procedure,[13,14] this is then decomposed using auxiliary fields into a quadratic spinon Hamiltonian (after writing the corresponding Euclidian action). The mean-field description of the phases is then characterized by the possible saddle-point values of the auxiliary fields. There are eight such auxiliary fields per bond, corresponding to

$$\chi_{ij} = \langle f_{i\alpha}^\dagger f_{j\alpha} \rangle^*; \quad \eta_{ij} = \langle f_{i\alpha} [i\tau^2]_{\alpha\beta} f_{j\beta} \rangle^*; \tag{7a}$$

$$E_{ij}^a = \langle f_{i\alpha}^\dagger [\tau^a]_{\alpha\beta} f_{j\beta} \rangle^*; \quad D_{ij}^a = \langle f_{i\alpha} [i\tau^2 \tau^a]_{\alpha\beta} f_{i\beta} \rangle^*, \tag{7b}$$

where τ^a ($a = 1,2,3$) are the Pauli matrices. While Eq. (7a) represents the usual singlet spinon hopping (particle-hole) and pairing (particle-particle) channels, Eq. (7b) represents the corresponding triplet decoupling channels. Since the Hamiltonian [Eq. (4)] does not have pseudospin rotation symmetry, both the singlet and the triplet decouplings are necessary.[15,16]

From this decoupling, we obtain a mean-field Hamiltonian which is quadratic in the spinon operators. We write this compactly in the following form[16] [subject to the constraint Eq. (6)]:

$$H_0 = \sum_{ij} J_{ij} \vec{f}_i^{\,\dagger} U_{ij} \vec{f}_j, \tag{8}$$

$$\vec{f}_i^{\,\dagger} = [\, f_{i\uparrow}^\dagger \quad f_{i\downarrow} \quad f_{i\downarrow}^\dagger \quad -f_{i\uparrow} \,], \tag{9}$$

$$U_{ij} = \xi_{ij}^{\alpha\beta} \Sigma^\alpha \Gamma^\beta, \tag{10}$$

$$\Sigma^\alpha = \rho^\alpha \otimes I, \quad \Gamma^\beta = I \otimes \tau^\beta, \tag{11}$$

where ρ^α are the identity (for $\alpha = 0$) and Pauli matrices ($\alpha = 1,2,3$) acting on pseudospin degrees of freedom, and τ^α represents the same in the gauge space. We immediately note that

$$[\Sigma^\alpha, \Gamma^\beta] = 0 \, \forall \, \alpha,\beta. \tag{12}$$

The requirement that H_0 be Hermitian restricts the coefficients ξ_{ij} to satisfy

$$\xi_{ij}^{00}, \xi_{ij}^{ab} \in \text{Im}; \quad \xi_{ij}^{a0}, \xi_{ij}^{0b} \in \text{Re} \tag{13}$$

for $a,b \in \{1,2,3\}$. The relations between ξ_{ij}'s and $\{\chi_{ij}, \eta_{ij}, \mathbf{E}_{ij}, \mathbf{D}_{ij}\}$ are given in Appendix C.[16] As a straightforward extension of the SU(2) gauge theory formulation for spin liquids,[13,17] we find that H_0 is invariant under the gauge transformation

$$\vec{f}_j \rightarrow W_j \vec{f}_j, \tag{14}$$

$$U_{ij} \rightarrow W_i U_{ij} W_j^\dagger, \tag{15}$$

where the W_i matrices are SU(2) matrices of the form $W_i = e^{i \vec{\Gamma} \cdot \vec{a}_i}$ [$\vec{\Gamma} \equiv (\Gamma^1, \Gamma^2, \Gamma^3)$]. Noting that the physical pseudospin operators are given by

$$\vec{\sigma}_i = \tfrac{1}{4} \vec{f}_i^{\,\dagger} \vec{\Sigma} \vec{f}_i, \tag{16}$$

Eq. (12) shows that the spin operators, as expected, are gauge invariant. It is useful to define the "Σ components" of the U_{ij} matrices as follows:

$$U_{ij} = \mathcal{V}_{ij}^\alpha \Sigma^\alpha, \tag{17}$$

where

$$\mathcal{V}_{ij}^\alpha = \xi_{ij}^{\alpha\beta} \Gamma^\beta = \begin{bmatrix} \mathcal{J}_{ij}^\alpha & 0 \\ 0 & \mathcal{J}_{ij}^\alpha \end{bmatrix} \tag{18}$$

and

$$\mathcal{J}^{\alpha}_{ij} = \begin{bmatrix} \xi^{\alpha 0}_{ij} + \xi^{\alpha 3}_{ij} & \xi^{\alpha 1}_{ij} - i\xi^{\alpha 2}_{ij} \\ \xi^{\alpha 1}_{ij} + i\xi^{\alpha 2}_{ij} & \xi^{\alpha 0}_{ij} - \xi^{\alpha 3}_{ij} \end{bmatrix}. \tag{19}$$

Under global spin rotations, the fermions transform as

$$\vec{f}_i \to V\vec{f}_i, \tag{20}$$

where V is an SU(2) matrix of the form $V = e^{i\vec{\Sigma}\cdot\vec{b}}$ ($\vec{\Sigma} \equiv \{\Sigma^1,\Sigma^2,\Sigma^3\}$). So, while $\mathcal{V}^0_{ij}$ (the singlet hopping and pairing) is invariant under spin rotation, $\{\mathcal{V}^1_{ij},\mathcal{V}^2_{ij},\mathcal{V}^3_{ij}\}$ transforms as a vector as expected since they represent triplet hopping and pairing amplitudes.

B. PSG classification

We now classify the non-Kramers spin-orbital liquids based on projective representation similar to that of the conventional quantum spin liquids.[13] Each spin-orbital liquid ground state of the quadratic Hamiltonian [Eq. (11)] is characterized by the mean-field parameters (eight on each bond, $\chi,\eta,E^1,E^2,E^3,D^1,D^2,D^3$ or, equivalently, U_{ij}). However, due to the gauge redundancy of the spinon parametrization [as shown in Eq. (15)], a general mean-field *Ansatz* need not be invariant under the symmetry transformations on their own but may be transformed to a gauge-equivalent form without breaking the symmetry. Therefore, we must consider its transformation properties under a projective representation of the symmetry group.[13] For this, we need to know the various projective representations of the lattice symmetries of the Hamiltonian [Eq. (4)] in order to classify different spin-orbital liquid states.

Operationally, we need to find different possible sets of gauge transformations $\{GG\}$ which act in combination with the symmetry transformations $\{SG\}$ such that the mean-field *Ansatz* U_{ij} is invariant under such a combined transformation. In the case of spin rotation invariant spin liquids (where only the singlet channels χ and η are present), the above statement is equivalent to demanding the following invariance:

$$U_{ij} = [G_S S]\,U_{ij}\,[G_S S]^{\dagger} = G_S(i)U_{S(i)S(j)}G^{\dagger}_S(j), \tag{21}$$

where $S \in SG$ is a symmetry transformation and $G_S \in GG$ is the corresponding gauge transformation. The different possible $\{G_S|\forall S \in SG\}$ give the possible algebraic PSGs that can characterize the different spin-orbital liquid phases. To obtain the different PSGs, we start with various lattice symmetries of the Hamiltonian. The action of various lattice transformations[18] is given by

$$\begin{aligned} T_1 &: (x,y,s) \to (x+1,y,s); \\ T_2 &: (x,y,s) \to (x,y+1,s); \\ \sigma &: (x,y,u) \to (y,x,u), \\ &\quad (x,y,v) \to (y,x,w), \\ &\quad (x,y,w) \to (y,x,v); \\ S_6 &: (x,y,u) \to (-y-1,x+y+1,v), \\ &\quad (x,y,v) \to (-y,x+y,w), \\ &\quad (x,y,w) \to (-y-1,x+y,u), \end{aligned} \tag{22}$$

where (x,y) denotes the lattice coordinates and $s \in \{u,v,w\}$ denotes the sublattice index (see Fig. 2).

In terms of the symmetries of the kagome lattice, these operators obey the following conditions:

$$\begin{aligned} T^2 = \sigma^2 = (S_6)^6 &= e, \\ g^{-1}T^{-1}gT &= e \quad \forall\, g \in SG, \\ T_2^{-1}T_1^{-1}T_2T_1 &= e, \\ \sigma^{-1}T_1^{-1}\sigma T_2 &= e, \\ \sigma^{-1}T_2^{-1}\sigma T_1 &= e, \\ S_6^{-1}T_2^{-1}S_6T_1 &= e, \\ S_6^{-1}T_2^{-1}T_1S_6T_2 &= e, \\ \sigma^{-1}S_6\sigma S_6 &= e. \end{aligned} \tag{23}$$

In addition, these commutation relations are valid in terms of the operations on the pseudospin degrees of freedom, as can be verified from Eq. (3).

In addition to the conditions in Eq. (23), the Hamiltonian is trivially invariant under the identity transformation. The invariant gauge group (IGG) of an *Ansatz* is defined as the set of all pure gauge transformations G_I such that $G_I : U_{ij} \to U_{ij}$. The nature of such pure gauge transformations immediately dictates the nature of the low-energy fluctuations about the mean-field state. If these fluctuations do not destabilize the mean-field state, we get stable spin-liquid phases whose low-energy properties are controlled by the IGG. Accordingly, spin liquids obtained within projective classification are primarily labeled by their IGGs and we have Z_2,U(1), and SU(2) spin liquids corresponding to IGGs of Z_2,U(1), and SU(2), respectively. In this work, we concentrate on the set of Z_2 "spin liquids" (spin-orbital liquids with a Z_2 IGG).

We now focus on the PSG classification. As shown in Eq. (2), in the present case, the pseudospins transform nontrivially under different lattice-symmetry transformations. Due to the presence of the triplet decoupling channels, the non-Kramers doublet transforms nontrivially under lattice symmetries [Eq. (3)]. Thus, the invariance condition on the U_{ij}'s is not given by Eq. (21), but by a more general condition

$$U_{ij} = [G_S S]U_{ij}[G_S S]^{\dagger} = G_S(i)\phi_S[U_{S(i)S(j)}]G^{\dagger}_S(j). \tag{24}$$

Here,

$$\phi_S[U_{S(i)S(j)}] = \mathcal{D}_S U_{S(i)S(j)} \mathcal{D}^{\dagger}_S, \tag{25}$$

and $\mathcal{D}_S$ generates the pseudospin rotation associated with the symmetry transformation (S) on the doublet. The matrices $\mathcal{D}_S$ have the form

$$\mathcal{D}_{S_6} = -\frac{1}{2}\Sigma^0 - \frac{i\sqrt{3}}{2}\Sigma^3, \tag{26}$$

$$\mathcal{D}_\sigma = \mathcal{D}_T = i * \Sigma^1, \quad \mathcal{D}_{T_1} = \mathcal{D}_{T_2} = \Sigma^0. \tag{27}$$

Under these constraints, we must determine the relations between the gauge transformation matrices $G_S(i)$ for our set of *Ansätze*. The additional spin transformation [Eq. (25)] does not affect the structure of the gauge transformations, as the gauge and spin portions of our *Ansätze* are naturally separate [Eq. (12)]. In particular, we can choose to define our gauge transformations such that

$$G_S : U_{ij} = G_S : \xi_{ij}^{\alpha\beta}\Sigma^\alpha\Gamma^\beta \to \xi_{ij}^{\alpha\beta}\Sigma^\alpha G_S^\dagger(i)\Gamma^\beta G_S(j), \quad (28)$$

$$S : U_{ij} = S : \xi_{ij}^{\alpha\beta}\Sigma^\alpha\Gamma^\beta \to \xi_{S(i)S(j)}^{\alpha\beta}\mathcal{D}_S\Sigma^\alpha\mathcal{D}_S^\dagger\Gamma^\beta, \quad (29)$$

where we have used the notation $G_S : U_{ij} \equiv G_S^\dagger(i)U_{ij}G_S(j)$ and so forth. As a result, we can build on the general construction of Lu *et al.*[18] to derive the form of the gauge transformation matrices. The details are given in Appendix B.

A major difference arises when examining the set of algebraic PSGs for Z_2 spin liquids found on the kagome lattice due to the difference between the structure of the time-reversal-symmetry operation on the Kramers and non-Kramers pseudospin-$\frac{1}{2}$. In the present case, we find there are 30 invariant PSGs leading to 30 possible spin-orbital liquids. This is in contrast with the Kramers case analyzed by Lu *et al.*,[18] where 10 of the algebraic PSGs can not be realized as invariant PSGs, as all bonds in these *Ansätze* are predicted to vanish identically due to the form of the time-reversal operator, and hence there are only 20 possible spin liquids. However, with the inclusion of spin-triplet terms and the non-Kramers form of our time-reversal operator, these *Ansätze* are now realizable as invariant PSGs as well. The time-reversal operator, as defined in Appendix B, acts as

$$T : \xi_{ij}^{\alpha\beta}\Sigma^\alpha\Gamma^\beta \to \tilde{\xi}_{ij}^{\alpha\beta}\Sigma^\alpha\Gamma^\beta, \quad (30)$$

where $\tilde{\xi}^{\alpha\beta} = \xi^{\alpha\beta}$ if $\alpha \in \{1,2\}$ and $\tilde{\xi}^{\alpha\beta} = -\xi^{\alpha\beta}$ if $\alpha \in \{0,3\}$. The projective implementation of the time-reversal symmetry condition [Eq. (23)] takes the form (see Appendix B)

$$[G_T(i)]^2 = \eta_T I \forall\, i, \quad (31)$$

where $G_T(i)$ is the gauge transformation associated with time-reversal operation and $\eta_T = \pm 1$ for a Z_2 IGG.

Therefore, the terms allowed by the time-reversal symmetry to be nonzero are, for $\eta_T = 1$,

$$\xi^{10},\ \xi^{11},\ \xi^{12},\ \xi^{13},\ \xi^{20},\ \xi^{21},\ \xi^{22},\ \xi^{23}, \quad (32)$$

and for $\eta_T = -1$, with the choice $G_T(i) = i\Gamma^1$ (see Appendix B),

$$\xi^{02},\ \xi^{03},\ \xi^{10},\ \xi^{11},\ \xi^{20},\ \xi^{21},\ \xi^{32},\ \xi^{33}. \quad (33)$$

This contrasts with the case of Kramers doublets, in which no terms are allowed for $\eta_T = +1$, and for $\eta_T = -1$ the allowed terms are

$$\xi^{02},\ \xi^{03},\ \xi^{12},\ \xi^{13},\ \xi^{22},\ \xi^{23},\ \xi^{32},\ \xi^{33}. \quad (34)$$

Further restrictions on the allowed terms on each link arise from the form of the gauge transformations defined for the symmetry transformations. All nearest-neighbor bonds can then be generated from U_{ij} defined on a single bond, by performing appropriate symmetry operations.

Using the methods outlined in earlier works (Refs. 13 and 18), we find the *minimum* set of parameters required to stabilize Z_2 spin-orbital liquids. We take into consideration up to second-neighbor hopping and pairing amplitudes (both singlet and triplet channels). The results are listed in Table I.

The spin-orbital liquids listed from 21–30 are not allowed in the case of Kramers doublets and, as pointed out before, their existence is solely due to the unusual action of the time-reversal-symmetry operator on the non-Kramers spins. Hence, these 10 spin-orbital liquids are qualitatively different phases that may appear in these systems. Of these 10 phases, only *two* (labeled as 21 and 22 in Table I) require next-nearest-neighbor amplitudes to obtain a Z_2 spin-orbital liquid. For the other 8, nearest-neighbor amplitudes are already sufficient to stabilize a Z_2 spin-orbital liquid.

TABLE I. Symmetry-allowed terms: We list the terms allowed to be nonzero by symmetry, for the 30 PSGs determined by Lu *et al.* (Ref. 18). The PSGs listed together are those with $\eta_{12} = \pm 1$ and all other factors equal. Included are terms allowed on nearest- and next-nearest-neighbor (NN and NNN, respectively) bonds, as well as chemical potential terms Γ which can be nonzero on all sites for certain spin-orbital liquids. Also included is the distance of bond up to which we must include in order to gap out the gauge fluctuations to Z_2 via the Anderson-Higgs mechanism (Ref. 13). Only PSGs 9 and 10 can not host Z_2 spin-orbital liquids with up to second-nearest-neighbor bonds.

No.	Λ_s	NN	NNN	Z_2
1–2	Γ^2,Γ^3	$\xi^{10},\xi^{21},\xi^{02},\xi^{03},\xi^{32},\xi^{33}$	$\xi^{10},\xi^{21},\xi^{02},\xi^{03},\xi^{32},\xi^{33}$	NN
3–4	0	$\xi^{10},\xi^{21},\xi^{02},\xi^{03},\xi^{32},\xi^{33}$	ξ^{10},ξ^{21}	NN
5–6	Γ^3	$\xi^{10},\xi^{21},\xi^{02},\xi^{03},\xi^{32},\xi^{33}$	$\xi^{10},\xi^{21},\xi^{03},\xi^{33}$	NN
7–8	0	ξ^{11},ξ^{20}	$\xi^{11},\xi^{20},\xi^{02},\xi^{03},\xi^{32},\xi^{33}$	NNN
9–10	0	ξ^{11},ξ^{20}	ξ^{11},ξ^{20}	
11–12	0	ξ^{11},ξ^{20}	$\xi^{10},\xi^{11},\xi^{02},\xi^{32}$	NNN
13–14	Γ^3	$\xi^{10},\xi^{11},\xi^{03},\xi^{33}$	$\xi^{10},\xi^{21},\xi^{02},\xi^{03},\xi^{32},\xi^{33}$	NN
15–16	Γ^3	$\xi^{10},\xi^{11},\xi^{03},\xi^{33}$	$\xi^{10},\xi^{21},\xi^{03},\xi^{33}$	NN
17–18	0	$\xi^{10},\xi^{11},\xi^{03},\xi^{33}$	$\xi^{10},\xi^{11},\xi^{02},\xi^{32}$	NN
19–20	0	$\xi^{10},\xi^{11},\xi^{03},\xi^{33}$	ξ^{10},ξ^{21}	NN
21–22	0	$\xi^{10},\xi^{21},\xi^{22},\xi^{23}$	$\xi^{10},\xi^{21},\xi^{22},\xi^{23}$	NNN
23–24	0	$\xi^{10},\xi^{21},\xi^{22},\xi^{23}$	$\xi^{10},\xi^{11},\xi^{12},\xi^{23}$	NN
25–26	0	$\xi^{11},\xi^{12},\xi^{13},\xi^{20}$	$\xi^{13},\xi^{20},\xi^{21},\xi^{22}$	NN
27–28	0	$\xi^{11},\xi^{12},\xi^{13},\xi^{20}$	$\xi^{10},\xi^{11},\xi^{13},\xi^{22}$	NN
29–30	0	$\xi^{11},\xi^{12},\xi^{13},\xi^{20}$	$\xi^{11},\xi^{12},\xi^{13},\xi^{20}$	NN

It is interesting to note (see following) that *bond-pseudospin-nematic* order [Eqs. (35) and (36)] can signal spontaneous time-reversal-symmetry breaking. Generally, since the triplet decouplings are present, the bond-nematic order parameter for the pseudospins[19,20]

$$\mathcal{Q}_{ij}^{\alpha\beta} = \langle \left(S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha\right)/2 - \delta^{\alpha\beta}(\vec{S}_i \cdot \vec{S}_j)/3\rangle, \tag{35}$$

as well as vector chirality order

$$\vec{\mathcal{J}}_{ij} = \langle \vec{S}_i \times \vec{S}_j \rangle, \tag{36}$$

are nonzero. Since the underlying Hamiltonian (4) generally does not have pseudospin rotation symmetry, the above nonzero expectation values do not spontaneously break any pseudospin rotation symmetry. However, because of the unusual transformation property of the non-Kramers pseudospins under time reversal, the operators corresponding to $\mathcal{Q}_{ij}^{13}, \mathcal{Q}_{ij}^{23}, \mathcal{J}_{ij}^{1}, \mathcal{J}_{ij}^{2}$ are odd under time reversal, a symmetry of the pseudospin Hamiltonian. Hence, if any of the above operators gain a nonzero expectation value in the ground state, then the corresponding spin-orbital liquid breaks time-reversal symmetry. While this can occur in principle, we have checked explicitly (see Appendix C) that in all the spin-orbital liquids discussed above, the expectation values of these operators are identically zero. This provides a nontrivial consistency check on our PSG calculations.

Having identified the possible Z_2 spin-orbital liquids, we can now study typical dynamic spin structure factors for these spin-orbital liquids. In the next section, we examine the typical spinon band structure for different spin-orbital liquids obtained above and find their dynamic spin structure factor.

IV. DYNAMIC SPIN STRUCTURE FACTOR

The dynamic spin structure factor is given by

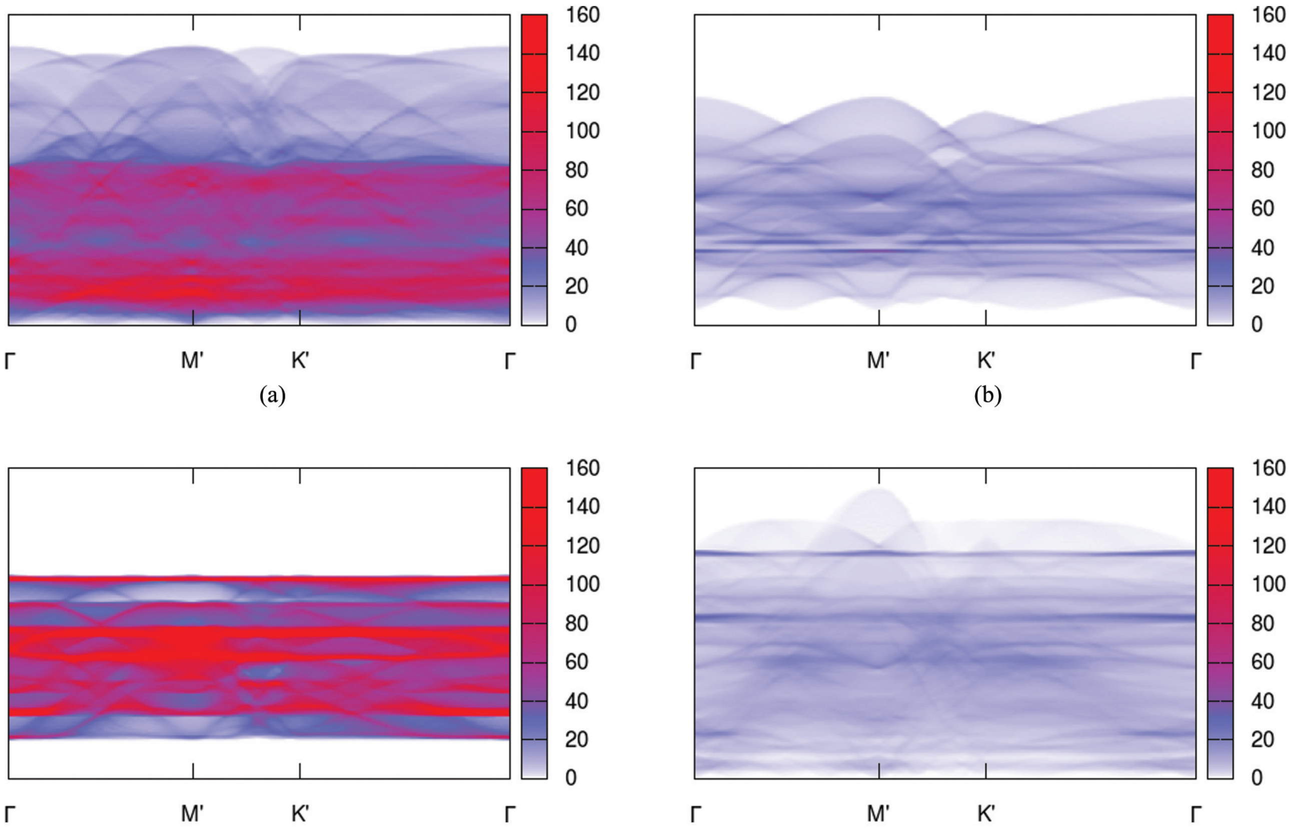
$$S(q,\omega) = \int \frac{dt}{2\pi} e^{i\omega t} \sum_{ij} e^{i\boldsymbol{q}\cdot(\boldsymbol{r}_i - \boldsymbol{r}_j)} \sum_{a=1,2,3} \langle \sigma_i^a(t)\sigma_j^a(0)\rangle. \tag{37}$$

Here, we show it for two of the candidates and restrict ourselves pointing out the qualitative differences between the Kramers and non-Kramers spin-orbital liquids. More quantitative differences require careful analysis of the corresponding spin-liquid ground state within self-consistent mean-field theory or other sophisticated numerical techniques, which is beyond the scope of this work. We choose spin liquids nos. 5 and 17 to demonstrate these qualitative differences. Both of these can be realized for the case of Kramers and non-Kramers spins and hence we can use them to contrast the general features for the two types. While the choice of the two spin liquids is arbitrary, the features discussed here are generally applicable to the other cases.

In Eq. (37), the pseudospin variables are defined in a global basis (with the z axis perpendicular to the kagome plane). In computing the structure factor for the non-Kramers example, we include only the σ^3 components of the pseudospin operator in the local basis since only the z components carry magnetic dipole moment (see discussion before). Hence, only this component couples linearly to neutrons in a neutron scattering experiment (see also the comments at end of this section). Equation (37) fails to be periodic in the first Brillouin zone of the kagome lattice,[15] as the term $r_i - r_j$ in Eq. (37) is a half-integer multiple of the primitive lattice vectors when the sublattices of sites i and j are not equal. As such, we examine the structure factor in the extended Brillouin zone, which consists of those momenta of length up to double that of those in the first Brillouin zone. We plot the structure factor along the cut $\Gamma \rightarrow M' \rightarrow K' \rightarrow \Gamma$, where $M' = 2M$ and $K' = 2K$.

We find that the structure factor generally has greater intensity in the case of a Kramers spin liquid in comparison to their non-Kramers counterparts. This is expected due to the fact that the moment of the scattering particle (viz. neutron) couples with all components in the case of the spins, rather than simply the z component for the pseudospins. We also note that the presence of different sets of mean-field parameters allowed by the respective PSGs of the Kramers and non-Kramers spin-orbital liquids may change the qualitative as well as quantitative features of the spinon dispersion including the presence or absence of a spinon gap. Some of these qualitative differences are immediately visible in the structure factor. For example, in the case of spin liquid no. 5, the Kramers spectrum is gapped while the non-Kramers spectrum is gapless in the same parameter regime. This is clearly visible in the corresponding structure factors [Figs. 3(c) and 3(d)]. Qualitative and quantitative differences such as these, which can be observed in these structure factors between Kramers and non-Kramers spin-orbital liquids, provide one possible distinguishing experimental signature of these states.

Before ending, we would like to point out a curious feature of the effect of the fluctuations about the mean-field states in the case of non-Kramers spin liquids only. In the absence of pairing channels (both singlet and triplet) the IGG is U(1). In this case, the fluctuations of the gauge field about the mean field are related to the scalar pseudospin chirality $\vec{S}_1 \cdot \vec{S}_2 \times \vec{S}_3$, where the three sites form a triangle.[21] Such fluctuations are gapless in a U(1) spin liquid. It is interesting to note that the scalar spin chirality is odd under time-reversal symmetry and it has been proposed that such fluctuations can be detected in neutron scattering experiments in the presence of spin rotation symmetry breaking.[22] In the present case, however, due to the presence of spinon pairing, the IGG is broken down to Z_2 and the above gauge fluctuations are rendered gapped through the Anderson-Higgs mechanism.[13] In addition to the above gauge fluctuations, because of the triplet decouplings which break pseudospin rotational symmetry, there are bond quadrupolar fluctuations of the pseudospins $\mathcal{Q}_{ij}^{\alpha\beta}$ [Eq. (35)], as well as vector chirality fluctuations $\vec{\mathcal{J}}_{ij}$ [Eq. (36)] (Refs. 19 and 20) on the bonds. These nematic and vector chirality fluctuations are gapped because the underlying pseudospin Hamiltonian [Eq. (4)] breaks pseudospin rotation symmetry. However, we note that because of the unusual transformation of the non-Kramers pseudospins under time reversal (only the z component of pseudospins being odd under time reversal), certain quadrupolar operators [see Eqs. (35) and (36)], namely, $\mathcal{Q}_{ij}^{13}, \mathcal{Q}_{ij}^{23}, \mathcal{J}_{ij}^{1}$, and $\mathcal{J}_{ij}^{2}$, are odd under time reversal. Hence, while their mean-field expectation values are zero (see above), the fluctuations of these quantities can in principle linearly couple to the neutrons in addition to the z component of the pseudospins. In a typical neutron scattering experiment,



(a) (b)

(c) (d)

FIG. 3. (Color online) The spin structure factor for an *Ansatz* in spin liquid nos. 17 [(a) and (b)] and 5 [(c) and (d)]. (a) and (c) are the Kramers spin liquids whereas (b) and (d) are the corresponding non-Kramers spin liquids (see text for detailed discussion).

these contributions should also be present along with the contribution from the spin structure factor. We have, however, not shown them in this work in Fig. 3.

V. DISCUSSION AND POSSIBLE EXPERIMENTAL SIGNATURE OF NON-KRAMERS SPIN-ORBITAL LIQUIDS

In this work, we have outlined the possible Z_2 spin-orbital liquids, with gapped or gapless fermionic spinons, that can be obtained in a system of non-Kramers pseudospin-$\frac{1}{2}$'s on a kagome lattice of Pr^{+3} ions. We find a total of 30, 10 more than in the case of corresponding Kramers system, allowed within PSG analysis in the presence of time-reversal symmetry. The larger number of spin-orbital liquids is a result of the difference in the action of the time-reversal operator, when realized projectively. We note that the spin-spin dynamic structure factor can bear important signatures of a non-Kramers spin-orbital liquid when compared to their Kramers counterparts. Our analysis of the number of invariant PSGs leading to possibly different spin-orbital liquids that may be realizable in other lattice geometries will form interesting future directions.

We now briefly discuss an experiment that can play an important role in determining non-Kramers spin-orbital liquids. Since the non-Kramers doublets are protected by crystalline symmetries, lattice strains can linearly couple to the pseudospins. As we discussed, the transverse (x and y) components of the pseudospins $\{\sigma^1,\sigma^2\}$ carry quadrupolar moments and hence are even under the time-reversal transformation. Further, they transform under an E_g irreducible representation of the local D_{3d} crystal field. Hence, any lattice strain which has this symmetry can linearly couple to the above two transverse components. It turns out that in the crystal type of which we are concerned, there is indeed such a mode related to the distortion of the oxygen octahedra. Symmetry considerations show that the linear coupling is of the form $E_{g1}\sigma^1 + E_{g2}\sigma^2$ ($\{E_{g1},E_{g2}\}$ being the two components of the distortion in the local basis). The above mode is Raman active. For a spin liquid, we expect that as the temperature is lowered, the spinons become more prominent as deconfined quasiparticles. So, the Raman active phonon can efficiently decay into the spinons due to the above coupling channel. If the spin liquid is gapless, then this will lead to anomalous broadening of the above Raman mode as the temperature is lowered, which, if observed, can be an experimental signature of the non-Kramers spin-orbital liquid. The above coupling is forbidden in Kramers doublets by time-reversal symmetry and hence no such anomalous broadening is expected.

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APPENDIX A: CRYSTAL-FIELD EFFECTS

In this appendix, we explore the breaking of the $J = 4$ spin degeneracy by the crystalline electric field. The oxygen and TM ions form a D_{3d} local symmetry environment around the Pr^{3+} ions, splitting the ground-state degeneracy of the electrons. This symmetry group contains six classes of elements: E, $2C_3$, $3C_2'$, i, $2S_6$, and $3\sigma_d$, where the C_3 are rotations by $2\pi/3$ about the local z axis, the C_2' are rotations by π about axis perpendicular to the local z axis, i is inversion, S_6 is a rotation by $4\pi/3$ combined with inversion, and σ_d is a reflection about the plane connecting one corner and the opposing plane, running through the Pr molecule about which this is measured (or, equivalently, a rotation about the x axis combined with inversion). For our $J = 4$ manifold, these have characters given by

$$\chi^{(4)}(E) = 2 * 4 + 1 = 9 = \chi^{(4)}(i), \tag{A1}$$

$$\chi^{(4)}(C_3) = \chi^{(4)}\left(\frac{2\pi}{3}\right) = \frac{\sin(3\pi)}{\sin(\pi/3)} = 0 = \chi^{(4)}(S_6), \tag{A2}$$

$$\chi^{(4)}(\sigma_d) = \chi^{(4)}(\pi) = \frac{\sin(9\pi/2)}{\sin(\pi/2)} = 1 = \chi^{(4)}(C_2'), \tag{A3}$$

where the latter equalities are given by the fact that our $J = 4$ manifold is inversion symmetric. Thus, decomposing this in terms of D_{3d} irreps, our $J = 4$ manifold splits into a sum of doublet and singlet manifolds as

$$\Gamma_{J=4} = 3E_g + 2A_{1g} + A_{2g}. \tag{A4}$$

To examine this further, we need to consider the matrix elements of the crystal-field potential between the states of different angular momenta. We know that this potential must be invariant under all group operations of D_{3d}, so we can examine the transformation properties of individual matrix elements $\langle m|V|m'\rangle$. Under the C_3 operation, these states of fixed m transform as

$$C_3|m\rangle = e^{\frac{2\pi i m}{3}}|m\rangle = \omega^m|m\rangle \quad (\omega = e^{\frac{2\pi i}{3}}) \tag{A5}$$

and thus the matrix elements transform as

$$C_3 : \langle m|V|m'\rangle \to \langle m|(C_3)^{-1}VC_3|m'\rangle = \omega^{m'-m}\langle m|V|m'\rangle. \tag{A6}$$

By requiring that this matrix be invariant under this transformation, we can see that this potential only contains matrix elements for mixing of states which have the z component of angular momentum which differ by 3. Thus, our eigenstates are mixtures of the $|m = 4\rangle$, $|m = 1\rangle$, and $|m = -2\rangle$ states, of the $|m = 3\rangle$, $|m = 0\rangle$, and $|m = -3\rangle$ states, and of the $|m = -4\rangle$, $|m = -1\rangle$, and $|m = 2\rangle$ states.

In addition to this, we have the transformation properties

$$T|m\rangle = (-1)^m|-m\rangle \tag{A7}$$

and

$$\sigma|m\rangle = (-1)^m|-m\rangle. \tag{A8}$$

Inversion acts trivially on these states, as we have even total angular momentum. Thus, our time-reversal and lattice-reflection (about one axis) symmetries give us doublet states of eigenstates $\alpha|m = 4\rangle + \beta|m = 1\rangle - \gamma|m = -2\rangle$ and $\alpha|m = -4\rangle - \beta|m = -1\rangle - \gamma|m = 2\rangle$ (with $\alpha, \beta, \gamma \in \mathrm{Re}$ in order to respect the time-reversal symmetry) for the three eigenstates of V in these sectors. The eigenstates of the $|m = 3\rangle$, $|m = 0\rangle$, and $|m = -3\rangle$ portion of V must therefore split into three singlet states, by our representation theory argument (A4). Due to the expected strong Ising term in our potential, we expect the eigenstate with maximal J to be the ground state, meaning that to analyze the properties of this ground state we are interested in a single doublet state, one with large α (close to one). We will restrict ourselves to this manifold from this point forward, and define the two states in this doublet as

$$|+\rangle = \alpha|m = 4\rangle + \beta|m = 1\rangle - \gamma|m = -2\rangle, \tag{A9}$$

$$|-\rangle = \alpha|m = -4\rangle - \beta|m = -1\rangle - \gamma|m = 2\rangle. \tag{A10}$$

APPENDIX B: GAUGE TRANSFORMATIONS

We begin by describing the action of time reversal on our *Ansatz*. The operation is antiunitary, and comes with a spin transformation σ^1 in the case of non-Kramers doublets. As a result, the operation acts as $T : \xi_{ij}^{\alpha\beta}\Sigma^\alpha\Gamma^\beta \to \xi_{ij}^{\alpha\beta *}\Sigma^1\Sigma^{\alpha *}\Sigma^1\Gamma^{\beta *}$. However, we can simplify this considerably by performing a gauge transformation in addition to the above transformation, which yields the same transformation on any physical variables. The gauge transformation we perform is $i\Gamma^2$, which changes the form of the time-reversal operation to $T : \xi_{ij}^{\alpha\beta}\Sigma^\alpha\Gamma^\beta \to \xi_{ij}^{\alpha\beta *}\Sigma^1\Sigma^{\alpha *}\Sigma^1\Gamma^2\Gamma^{\beta *}\Gamma^2 = \tilde{\xi}_{ij}^{\alpha\beta}\Sigma^\alpha\Gamma^\beta$, where $\tilde{\xi}^{\alpha\beta} = \xi^{\alpha\beta}$ if $\alpha \in \{1,2\}$ and $\tilde{\xi}^{\alpha\beta} = -\xi^{\alpha\beta}$ if $\alpha \in \{0,3\}$.

On the kagome lattice, the allowed form of the gauge transformations has been determined by Lu *et al.*[18] For completeness, we will reproduce that calculation, valid also for our spin-triplet *Ansatz*, here. The relations between the gauge transformation matrices

$$[G_T(i)]^2 = \eta_T I, \tag{B1}$$

$$G_\sigma[\sigma(i)]G_\sigma(i) = \eta_\sigma I, \tag{B2}$$

$$G_{T_1}^\dagger(i)G_T^\dagger(i)G_{T_1}(i)G_T\left[T_1^{-1}(i)\right] = \eta_{T_1T}I, \tag{B3}$$

$$G_{T_2}^\dagger(i)G_T^\dagger(i)G_{T_2}(i)G_T\left[T_2^{-1}(i)\right] = \eta_{T_2T}I, \tag{B4}$$

$$G_\sigma^\dagger(i)G_T^\dagger(i)G_\sigma(i)G_T[\sigma^{-1}(i)] = \eta_{\sigma T}I, \tag{B5}$$

$$G_{S_6}^\dagger(i)G_T^\dagger(i)G_{S_6}(i)G_T\left[S_6^{-1}(i)\right] = \eta_{S_6T}I, \tag{B6}$$

$$G_{T_2}^\dagger\left[T_1^{-1}(i)\right]G_{T_1}^\dagger(i)G_{T_2}(i)G_{T_1}\left[T_2^{-1}(i)\right] = \eta_{12}I, \tag{B7}$$

$$\begin{aligned} &G_{S_6}\left[S_6^{-1}(i)\right]G_{S_6}\left[S_6^{-2}(i)\right]G_{S_6}\left[S_6^{3}(i)\right] \\ &\quad\times G_{S_6}\left[S_6^{2}(i)\right]G_{S_6}[S_6(i)]G_{S_6}(i) = \eta_{S_6}I, \end{aligned} \tag{B8}$$

$$G_\sigma^\dagger\left[T_2^{-1}(i)\right]G_{T_2}^\dagger(i)G_\sigma(i)G_{T_1}[\sigma(i)] = \eta_{\sigma T_1}I, \tag{B9}$$

$$G_\sigma^\dagger\left[T_1^{-1}(i)\right]G_{T_1}^\dagger(i)G_\sigma(i)G_{T_2}[\sigma(i)] = \eta_{\sigma T_2}I, \tag{B10}$$

$$G_\sigma^\dagger[S_6(i)]G_{S_6}[S_6(i)]G_\sigma(i)G_{S_6}[\sigma(i)] = \eta_{\sigma S_6} I, \quad \text{(B11)}$$

$$G_{S_6}^\dagger\big[T_2^{-1}(i)\big]G_{T_2}^\dagger(i)G_{S_6}(i)G_{T_1}\big[S_6^{-1}(i)\big] = \eta_{S_6 T_1} I, \quad \text{(B12)}$$

$$\begin{aligned} &G_{S_6}^\dagger\big[T_2^{-1}T_1(i)\big]G_{T_2}^\dagger[T_1(i)]G_{T_1}[T_1(i)] \\ &\quad\times G_{S_6}(i)G_{T_2}\big[S_6^{-1}(i)\big] = \eta_{S_6 T_2} I \end{aligned} \quad \text{(B13)}$$

are valid for our case as well, due to the decoupling of spin and gauge portions of our *Ansätze*. In the above, the relations are valid for all lattice sites $i = (x,y,s)$, I is the 4×4 identity matrix, and the G_S matrices are gauge transformation matrices generated by exponentiation of the Γ matrices. The η's are ± 1, the choice of which characterize different spin-liquid states.

We turn next to the calculation of the gauge transformations. We look first at the gauge transformations associated with the translations. We can perform a site-dependent gauge transformation $W(i)$, under which the gauge transformations associated with the translational symmetries transform as

$$G_{T_1}(i) \to W(i)G_{T_1}(i)W^\dagger(i - \hat{x}), \quad \text{(B14)}$$

$$G_{T_2}(i) \to W(i)G_{T_2}(i)W^\dagger(i - \hat{y}). \quad \text{(B15)}$$

As such, we can choose a gauge transformation $W(i)$ to simplify the form of G_{T_1} and G_{T_2}. Using such a transformation, along with condition (B7), we can restrict the form of these gauge transformations to be

$$G_{T_1}(i) = \eta_{12}^{i_y} I, \quad G_{T_2}(i) = I. \quad \text{(B16)}$$

To preserve this choice, we can now only perform gauge transformations which are equivalent on all lattice positions $[W(x,y,s) = W(s)]$ or transformations which change the shown matrices by an IGG transformation.

Next, we look at adding the reflection symmetry σ. Given our formulas for G_{T_1} and G_{T_2}, along with the relations between the gauge transformations, we have that

$$G_\sigma^\dagger\big[T_2^{-1}(i)\big]G_\sigma(i)\eta_{12}^x = \eta_{\sigma T_1} I, \quad \text{(B17)}$$

$$G_\sigma^\dagger\big[T_1^{-1}(i)\big]G_\sigma(i)\eta_{12}^y = \eta_{\sigma T_2} I. \quad \text{(B18)}$$

Defining $G_\sigma(0,0,s) = g_\sigma(s)$, we have, by repeated application of the above,

$$G_\sigma(0,y,s) = \eta_{\sigma T_1}^y g_\sigma(s), \quad \text{(B19)}$$

$$G_\sigma(x,y,s) = \eta_{\sigma T_1}^y \eta_{12}^{xy} \eta_{\sigma T_2}^x g_\sigma(s). \quad \text{(B20)}$$

Next, using

$$G_\sigma[\sigma(i)]G_\sigma(i) = \eta_\sigma I, \quad \text{(B21)}$$

we find that

$$\begin{aligned} \eta_\sigma I &= G_\sigma[y,x,\sigma(s)]G_\sigma(x,y,s) \quad \text{(B22)} \\ &= (\eta_{\sigma T_1}\eta_{\sigma T_2})^{x+y} g_\sigma[\sigma(s)]g_\sigma(s). \quad \text{(B23)} \end{aligned}$$

Since this is true for all x and y, $\eta_{\sigma T_1}\eta_{\sigma T_2} = 1$ and thus $\eta_{\sigma T_1} = \eta_{\sigma T_2}$ and $g_\sigma[\sigma(s)]g_\sigma(s) = \eta_\sigma I$ [where $\sigma(u) = u, \sigma(v) = w$ and $\sigma(w) = v$]. Our final form for the gauge transformation is

$$G_\sigma(x,y,s) = \eta_{\sigma T_1}^{x+y} \eta_{12}^{xy} g_\sigma(s). \quad \text{(B24)}$$

Next, we look at adding the S_6 symmetry to our calculation. We can do an IGG transformation, taking $G_{T_1}[T_1(i)]$ to $\eta_{S_6 T_2} G_{T_1}[T_1(i)]$, with the net effect being that $\eta_{S_6 T_2}$ becomes one (previous calculations are unaffected). We now have that

$$G_{S_6}^\dagger\big[T_2^{-1}T_1(i)\big]G_{S_6}(i)\eta_{12}^y = I, \quad \text{(B25)}$$

$$G_{S_6}^\dagger\big[T_2^{-1}(i)\big]G_{S_6}(i)\eta_{12}^{-x-1} = \eta_{S_6 T_1} I \quad (s = u,v), \quad \text{(B26)}$$

$$G_{S_6}^\dagger\big[T_2^{-1}(i)\big]G_{S_6}(i)\eta_{12}^{-x} = \eta_{S_6 T_1} I \quad (s = w). \quad \text{(B27)}$$

Defining $G_{S_6}(0,0,s) = g_{S_6}(s)$, we find that

$$G_{S_6}(n, -n,s) = \eta_{12}^{n(n-1)/2} g_{S_6}(s), \quad \text{(B28)}$$

$$G_{S_6}(x,y,s) = \eta_{12}^{x(x-1)/2+y+xy} \eta_{S_6 T_1}^{x+y} g_{S_6}(s) \quad (s = u,v), \quad \text{(B29)}$$

$$G_{S_6}(x,y,s) = \eta_{12}^{x(x-1)/2+xy} \eta_{S_6 T_1}^{x+y} g_{S_6}(s) \quad (s = w). \quad \text{(B30)}$$

Using the commutation relation between the σ and S_6 gauge transformations, we find that

$$\begin{aligned} \eta_{\sigma S_6} I &= \eta_{\sigma T_1}^y \eta_{12}^y \eta_{S_6 T_1}^y g_\sigma^\dagger(v)g_{S_6}(v)g_\sigma(u)g_{S_6}(u) \quad \text{(B31)} \\ &= \eta_{\sigma T_1}^y \eta_{12}^y \eta_{S_6 T_1}^y \eta_\sigma g_\sigma(w)g_{S_6}(v)g_\sigma(u)g_{S_6}(u), \quad \text{(B32)} \end{aligned}$$

giving us that $\eta_{\sigma T_1}\eta_{12}\eta_{S_6 T_1} = 1$ and $g_\sigma(u)g_{S_6}(u)g_\sigma(w)g_{S_6}(v) = \eta_{\sigma S_6}\eta_\sigma I$. A similar calculation on a different sublattice gives us

$$\begin{aligned} \eta_{\sigma S_6} I &= \eta_{\sigma T_1}^y \eta_{12}^y \eta_{S_6 T_1}^y g_\sigma^\dagger(w)g_{S_6}(w)g_\sigma(v)g_{S_6}(w) \quad \text{(B33)} \\ &= \eta_{\sigma T_1}^y \eta_{12}^y \eta_{S_6 T_1}^y \eta_\sigma g_\sigma(v)g_{S_6}(w)g_\sigma(v)g_{S_6}(w), \quad \text{(B34)} \end{aligned}$$

giving us $[g_\sigma(v)g_{S_6}(w)]^2 = \eta_{\sigma S_6}\eta_\sigma I$. A Z_2 (IGG) gauge transformation of the form $W(x,y,s) = \eta_{\sigma T_1}^y$ changes $\eta_{\sigma T_1}$ to 1. Using the cyclic relation of the gauge transformations related to the S_6 operators, we find

$$\eta_{S_6} I = \eta_{12}[g_{S_6}(w)g_{S_6}(v)g_{S_6}(u)]^2, \quad \text{(B35)}$$

giving us that

$$[g_{S_6}(w)g_{S_6}(v)g_{S_6}(u)]^2 = \eta_{S_6}\eta_{12} I. \quad \text{(B36)}$$

Next, we turn to the time-reversal symmetry. Similar methods to the above give us that

$$[G_T(i)]^2 = \eta_T I, \quad \text{(B37)}$$

$$G_T^\dagger(i)G_T(i + \hat{x}) = \eta_{T_1 T} I, \quad \text{(B38)}$$

$$G_T^\dagger(i)G_T(i + \hat{y}) = \eta_{T_2 T} I. \quad \text{(B39)}$$

The first of these relations tells us that $G_T(i)$ is either the identity (for $\eta_T = 1$) or $i\vec{a} \cdot \vec{\Gamma}$ (for $\eta_T = -1$, where $|\vec{a}| = 1$). Defining $G_T(0,0,s) = g_T(s)$,

$$G_T(x,y,s) = \eta_{T_1 T}^x \eta_{T_2 T}^y g_T(s) \quad \text{(B40)}$$

and further, using the commutation relations between the σ and T gauge transformations and the S_6 and T gauge transformations,

$$g_\sigma^\dagger(s)g_T^\dagger(s)g_\sigma(s)g_T[\sigma(s)]\eta_{T_1 T}^{x+y}\eta_{T_2 T}^{x+y} = \eta_{\sigma T} I, \quad \text{(B41)}$$

$$g_{S_6}^\dagger(s)g_T^\dagger(s)g_{S_6}(s)g_T\big[S_6^{-1}(s)\big]\eta_{T_1 T}^{f_1(i)}\eta_{T_2 T}^{f_2(i)} = \eta_{S_6 T} I. \quad \text{(B42)}$$

Because this is true for all x and y, and $f_1(i)$ is not equal to $f_2(i)$, $\eta_{T_1 T} = \eta_{T_2 T} = 1$. If $G_T(i) = i\vec{a} \cdot \vec{\Gamma}$, we perform a gauge transformation W on $G_T(i)$ such that $W^\dagger G_T(i)W = i\Gamma^1$ (as this is the same on all sites, it does not affect our gauge

TABLE II. We list the solutions of Eqs. (B43)–(B54), along with a set of gauge transformations which realize these solutions.

No.	η_T	$\eta_{\sigma T}$	$\eta_{S_6 T}$	η_σ	$\eta_{\sigma S_6}$	η_{S_6}	η_{12}	$g_\sigma(u)$	$g_\sigma(v)$	$g_\sigma(w)$	$g_{S_6}(u)$	$g_{S_6}(v)$	$g_{S_6}(w)$
1,2	-1	1	1	1	1	±1	±1	Γ^0	Γ^0	Γ^0	Γ^0	Γ^0	Γ^0
3,4	-1	1	1	1	-1	∓1	±1	Γ^0	Γ^0	Γ^0	Γ^0	$-\Gamma^0$	$i\Gamma^1$
5,6	-1	1	-1	1	-1	∓1	±1	Γ^0	Γ^0	Γ^0	$i\Gamma^3$	$i\Gamma^3$	$i\Gamma^3$
7,8	-1	1	1	-1	-1	∓1	±1	$i\Gamma^1$	Γ^0	$-\Gamma^0$	Γ^0	$i\Gamma^1$	Γ^0
9,10	-1	1	1	-1	1	±1	±1	$i\Gamma^1$	Γ^0	$-\Gamma^0$	Γ^0	$-i\Gamma^1$	$i\Gamma^1$
11,12	-1	1	-1	-1	1	∓1	±1	$i\Gamma^1$	Γ^0	$-\Gamma^0$	$i\Gamma^3$	$-i\Gamma^2$	$i\Gamma^3$
13,14	-1	-1	-1	-1	-1	∓1	±1	$i\Gamma^3$	$i\Gamma^3$	$i\Gamma^3$	$i\Gamma^3$	$i\Gamma^3$	$i\Gamma^3$
15,16	-1	-1	1	-1	1	±1	±1	$i\Gamma^3$	$i\Gamma^3$	$i\Gamma^3$	Γ^0	Γ^0	Γ^0
17,18	-1	-1	1	-1	1	∓1	±1	$i\Gamma^3$	$i\Gamma^3$	$i\Gamma^3$	Γ^0	Γ^0	$i\Gamma^1$
19,20	-1	-1	-1	-1	1	∓1	±1	$i\Gamma^3$	$i\Gamma^3$	$i\Gamma^3$	$i\Gamma^3$	$-i\Gamma^3$	$i\Gamma^3$
21,22	1	1	1	1	1	±1	±1	Γ^0	Γ^0	Γ^0	Γ^0	Γ^0	Γ^0
23,24	1	1	1	1	-1	∓1	±1	Γ^0	Γ^0	Γ^0	Γ^0	$-\Gamma^0$	$i\Gamma^3$
25,26	1	1	1	-1	-1	∓1	±1	$i\Gamma^3$	Γ^0	$-\Gamma^0$	Γ^0	$i\Gamma^3$	Γ^0
27,28	1	1	1	-1	1	∓1	±1	$i\Gamma^3$	Γ^0	$-\Gamma^0$	Γ^0	$-i\Gamma^3$	$i\Gamma^1$
29,30	1	1	1	-1	1	±1	±1	$i\Gamma^3$	Γ^0	$-\Gamma^0$	Γ^0	$-i\Gamma^3$	$i\Gamma^3$

fixing for the translation gauge transformations). Collecting the necessary results for further use,

$$G_{T_1}(x,y,s) = \eta_{12}^{y} I, \tag{B43}$$

$$G_{T_2}(x,y,s) = I, \tag{B44}$$

$$G_\sigma(x,y,s) = \eta_{12}^{xy} g_\sigma(s), \tag{B45}$$

$$G_{S_6}(x,y,s) = \eta_{12}^{xy+(x+1)x/2} g_{S_6}(s), \quad s = u,v \tag{B46}$$

$$G_{S_6}(x,y,s) = \eta_{12}^{xy+x+y+(x+1)x/2} g_{S_6}(s), \quad s = w \tag{B47}$$

$$G_T(s) = I = g_T(s), \quad \eta_T = 1, \tag{B48}$$

$$G_T(s) = i\Gamma^1 = g_T(s), \quad \eta_T = -1, \tag{B49}$$

$$g_\sigma[\sigma(s)] g_\sigma(s) = \eta_\sigma I, \tag{B50}$$

$$g_\sigma(u) g_{S_6}(u) g_\sigma(w) g_{S_6}(v) = [g_\sigma(v) g_{S_6}(w)]^2 = \eta_{\sigma S_6} \eta_\sigma I, \tag{B51}$$

$$[g_{S_6}(w) g_{S_6}(v) g_{S_6}(u)]^2 = \eta_{S_6} \eta_{12} I, \tag{B52}$$

$$g_\sigma(s) g_T[\sigma(s)] = \eta_{\sigma T} g_T(s) g_\sigma(s), \tag{B53}$$

$$g_{S_6}(s) g_T[S_6^{-1}(s)] = \eta_{S_6 T} g_T(s) g_{S_6}(s). \tag{B54}$$

We also have the gauge freedom left to perform a gauge rotation arbitrarily at all positions for $\eta_T = 1$ or an arbitrary gauge rotation about the x axis for $\eta_T = -1$.

The solution to the above equations is derived in detail by Lu *et al.*[18] and as such we simply list the results in Table II. The basic method of obtaining these solutions is as follows: for each choice of Z_2 parameter set, we determine whether there is a choice of gauge matrices $\{g_S\}$ which satisfy Eqs. (B43)–(B54). In order to do so, we determine the allowed forms of the g_S matrices from the equations, then use the gauge freedom on each site to fix the form of these. Of particular note is the fact that in the consistency equations for the g matrices, the terms η_{12} and η_{S_6} only appear multiplied together, meaning that for any choice of the gauge matrices g_S we can choose $\eta_{12} = \pm1$, which fixes the form of η_{S_6}.

APPENDIX C: RELATION AMONG THE MEAN-FIELD PARAMETERS

The relation among the different singlet and triplet parameters in terms of ξ_{ij} is given by

$$\begin{aligned}
&\chi_{ij} = \xi_{ij}^{00} + \xi_{ij}^{03}; \quad \eta_{ij} = -\xi_{ij}^{01} + i\xi_{ij}^{02};\\
&E_{ij}^1 = \xi_{ij}^{10} + \xi_{ij}^{13}; \quad E_{ij}^2 = \xi_{ij}^{20} + \xi_{ij}^{23}; \quad E_{ij}^3 = \xi_{ij}^{30} + \xi_{ij}^{33};\\
&D_{ij}^1 = -\xi_{ij}^{11} + i\xi_{ij}^{12}; \quad D_{ij}^2 = -\xi_{ij}^{21} + i\xi_{ij}^{22};\\
&D_{ij}^3 = -\xi_{ij}^{31} + i\xi_{ij}^{32}.
\end{aligned} \tag{C1}$$

Using these, we can derive the form of the bond-nematic order parameter and vector chirality order parameters, which are given in terms of the mean-field parameters[19] as

$$\begin{aligned}
\mathcal{Q}_{ij}^{\mu,\nu} &= -\frac{1}{2}\left(E_{ij}^{\mu} E_{ij}^{*\nu} - \frac{1}{3}\delta^{\mu,\nu}|\vec{E}_{ij}|^2\right) + \text{H.c.}\\
&\quad - \frac{1}{2}\left(D_{ij}^{\mu} D_{ij}^{*\nu} - \frac{1}{3}\delta^{\mu,\nu}|\vec{D}_{ij}|^2\right) + \text{H.c.},\\
\mathcal{J}_{ij}^{\lambda} &= \frac{i}{2}\left(\chi_{ij} E_{ij}^{*\lambda} - \chi_{ij}^{*} E_{ij}^{\lambda}\right) + \frac{i}{2}\left(\eta_{ij} D_{ij}^{*\lambda} - \eta_{ij}^{*} D_{ij}^{\lambda}\right),
\end{aligned} \tag{C2}$$

where our definition of η_{ij} differs by a factor of (-1) from that of the cited work. We rewrite this in terms of our variables, finding

$$\begin{aligned}
\mathcal{Q}_{ij}^{\mu\nu} &= -\xi_{ij}^{\mu 0}\xi_{ij}^{\nu 0} + \sum_a \xi_{ij}^{\mu a}\xi_{ij}^{\nu a}\\
&\quad + \frac{\delta^{\mu\nu}}{3}\sum_b \left(\left(\xi_{ij}^{b0}\right)^2 - \sum_a \left(\xi_{ij}^{ba}\right)^2\right),\\
\mathcal{J}_{ij}^{\lambda} &= i\left(\xi_{ij}^{00}\xi_{ij}^{\lambda 0} - \sum_a \xi_{ij}^{0a}\xi_{ij}^{\lambda a}\right).
\end{aligned} \tag{C3}$$

In particular, we find that $\mathcal{J}^1$, $\mathcal{J}^2$, $\mathcal{Q}^{13}$, and $\mathcal{Q}^{23}$ must be zero for all non-Kramers spin liquids, as the terms allowed by symmetry in Eqs. (32) and (33) do not allow nonzero values for these order parameters.

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