Ground state phase diagram of dipolar-octupolar pyrochlores

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The “dipolar-octupolar” pyrochlore oxides R\textsubscript{2}M\textsubscript{2}O\textsubscript{7} (R= Ce, Sm, Nd; M= Zr, Hf, Ti, Sn, Pb) \textsuperscript{27–44} constitute an opportunity in this context, with their low energy physics being described by a simple XYZ Hamiltonian \textsuperscript{45, 46}. Experimentally, Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} \textsuperscript{27, 28} and Ce\textsubscript{2}Sn\textsubscript{2}O\textsubscript{7} \textsuperscript{29, 30} pyrochlores have been highlighted recently as QSL candidates. Neutron scattering results for Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} bear encouraging similarity to predictions for a U(1) quantum spin liquid \textsuperscript{30, 47}.

In this Letter, we calculate the ground state phase diagram of Eq. (1) by combining Cluster Mean Field Theory (CMFT), a cluster variational extension to CMFT (CVAR) \textsuperscript{52} and Exact Diagonalization (ED). Where the results can be compared with available QMC results \textsuperscript{55}, they agree well. The final result for the phase diagram is the ground state phase diagram of dipolar-octupolar pyrochlores. Combining cluster mean field theory, variational arguments and exact diagonalization we discover multiple U(1) QSL phases which together occupy a large fraction of the parameter space. These results give a comprehensive picture of the ground state physics of an important class of QSL candidates and support the possibility of a U(1) QSL ground state in Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} and Ce\textsubscript{2}Sn\textsubscript{2}O\textsubscript{7}.

\textsuperscript{1}QSL ground state in Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} and Ce\textsubscript{2}Sn\textsubscript{2}O\textsubscript{7} bear encouraging similarity to predictions for a U(1) quantum spin liquid. The thing which can be divided out and \textsuperscript{2}QSL ground states have not gone unrewarded. On the theory side, it has been realized that an enormous diversity of QSL states are possible \textsuperscript{1, 2} and several physically relevant models are now known to have QSL ground states \textsuperscript{3–11}. In experiment, many candidate materials have been established, exhibiting spin liquid like properties at low temperature \textsuperscript{12–16}. What has yet to be achieved is the combination of a material with an experimentally robust QSL state, with theoretical understanding of the microscopic interactions which give rise to that state and what kind of spin liquid they produce. Some materials studied as potential QSLs actually order at low temperature \textsuperscript{17–19}, and others give rise to that state and what kind of spin liquid \textsuperscript{20–23}. Meanwhile, the relevant theoretical models are often complicated, possessing many free parameters \textsuperscript{24–26}. Meanwhile, the relevant theoretical models are often complicated, possessing many free parameters \textsuperscript{24–26}.

“Dipolar-octupolar” (DO) pyrochlores R\textsubscript{2}M\textsubscript{2}O\textsubscript{7} (R= Ce, Sm, Nd; M= Zr, Hf, Ti, Sn, Pb) \textsuperscript{27–44} constitute an opportunity in this context, with their low energy physics being described by a simple XYZ Hamiltonian \textsuperscript{45, 46}. Experimentally, Ce\textsubscript{2}Sn\textsubscript{2}O\textsubscript{7} \textsuperscript{27, 28} and Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} \textsuperscript{29, 30} pyrochlores have been highlighted recently as QSL candidates. Neutron scattering results for Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} bear encouraging similarity to predictions for a U(1) quantum spin liquid \textsuperscript{30, 47}.

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\[
\tilde{J}_z = \tilde{J} \cos(\phi) \sin(\psi), \quad \tilde{J}_\theta = \tilde{J} \sin(\phi) \sin(\psi), \quad \tilde{J}_\tilde{z} = \tilde{J} \cos(\psi)
\]

We find four U(1) spin liquid phases, occupying a large combined portion of the parameter space, competing

\[
\mathcal{H} = \sum_{\langle ij \rangle} \left[ \left( \sum_{\alpha=x,y,z} J_\alpha \tau_i^\alpha \tau_j^\alpha \right) + J_{xz} \left( \tau_i^x \tau_j^x + \tau_i^z \tau_j^z \right) \right] \quad (1)
\]

\[
\mathcal{H} = \sum_{\langle ij \rangle} \sum_{\alpha=x,y,z} J_\alpha \tau_i^\alpha \tau_j^\alpha. \quad (2)
\]

An understanding of dipolar-octupolar pyrochlores and their potential to realize QSL ground states requires understanding of the ground state phase diagram of Eq. (2). Certain limits of the parameter space of Eq. (2) have been well studied, namely: the perturbative limit where one exchange parameter dominates the other two \textsuperscript{4, 47, 49}, the XXZ limit where two of the three exchange parameters are equal \textsuperscript{5, 50–54} and the region of parameter space without a sign problem for Quantum Monte Carlo (QMC) \textsuperscript{5, 45, 53–55}. However, there is no reason to expect materials of interest to fall into one of these limits, so a global phase diagram is needed.

In this Letter, we calculate the ground state phase diagram of Eq. (1) by combining Cluster Mean Field Theory (CMFT), a cluster variational extension to CMFT (CVAR) \textsuperscript{52} and Exact Diagonalization (ED). Where the results can be compared with available QMC results \textsuperscript{55}, they agree well. The final result for the phase diagram is shown in Fig. 1, with the parameter space expressed in terms of an overall scale \textsubscript{J} which can be divided out and two angles \phi, \psi:

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FIG. 1. Ground state phase diagram of the XYZ model [Eq. (2)] on the pyrochlore lattice (inset), describing dipolar-octupolar pyrochlores. The three exchange parameters \( \tilde{J}_{\alpha} \) are represented in terms of an overall scale \( \tilde{J} \) and two angular variables \( \phi, \psi \) [Eq. (3)]. The phase diagram features “all in/all out” (AIAO) and octupolar ordered phases, and four distinct U(1) QSLs. These four QSLs are distinguished by whether the emergent electric field of the low energy gauge theory transforms like a magnetic dipole or octupole, and by the flux penetrating elementary plaquettes in the ground state (0 or \( \pi \)). The phase diagram is obtained by combining Cluster Mean Field Theory (CMFT), a cluster variational (CVAR) calculation and Exact Diagonalization (ED) as described in the text.

with an antiferromagnetic “all in/all out” (AIAO) phase and octupolar order. The four U(1) QSLs all host gapless photons and gapped fractionalized charges, and are thus realizations of emergent electromagnetism [4, 6, 47, 49]. They are labelled dipolar/octupolar-U(1) dipolar-octupolar label referring to whether the emergent electric field transforms like a magnetic dipole or octupole [56], and the \( 0/\pi \) subscript referring to the U(1) flux penetrating elementary plaquettes in the ground state.

In what follows, we explain the calculations leading to Fig. 1, beginning with the CMFT, followed by the CVAR and ED.

In calculating the phase diagram it is useful to note that Eq. (2) has some dualities in which the exchange parameters can be permuted by a unitary transformation acting on \( \mathcal{H} \). Specifically:

\[
\mathcal{H}(\tilde{J}_x, \tilde{J}_y, \tilde{J}_z) = U_{\gamma_y/3,111} \mathcal{H}(\tilde{J}_x, \tilde{J}_y, \tilde{J}_z) U_{\gamma_y/3,111}^\dagger
\]

\[
\mathcal{H}(\tilde{J}_y, \tilde{J}_x, \tilde{J}_z) = U_{\gamma_x/2,001} \mathcal{H}(\tilde{J}_x, \tilde{J}_y, \tilde{J}_z) U_{\gamma_x/2,001}^\dagger
\]

where \( U_{\gamma_y/3,111} \) represents a global rotation by an angle \( \gamma \) around axis \( y \) and \( U_{\gamma_x/2,001} \) is a rotation by an angle \( \gamma \) around axis \( x \) in pseudospin space (which is not the same as a rotation in the physical crystal space). Making use of these dualities means that we do not actually need to study the full parameter space of \( \tilde{J}_x, \tilde{J}_y, \tilde{J}_z \), it is enough to consider a subregion

\[
|\tilde{J}_x| \geq |\tilde{J}_y|, |\tilde{J}_y|, \tilde{J}_x > \tilde{J}_y
\]

from which we can then generate the rest of the phase diagram by applying the transformations from Eq. (4) to our results.

Taking \( \tilde{J}_z \) to be the strongest exchange parameter as in (5), if \( \tilde{J}_z < 0 \) it is clear that the ground state will simply order ferromagnetically with respect to the \( z \)-axis of pseudospin space. In terms of the physical magnetic moments this implies AIAO order. The more challenging problem is to discover what happens when \( \tilde{J}_z > 0 \).

To study this case we rewrite the Hamiltonian in terms of spin ladder operators \( \tilde{t}_i^\pm \):

\[
\mathcal{H} = \sum_{\langle ij \rangle} \left[ \tilde{J}_x \tilde{t}_i^+ \tilde{t}_j^- + \tilde{J}_x \left( \tilde{t}_i^+ \tilde{t}_j^- + \tilde{t}_i^- \tilde{t}_j^+ \right) + \tilde{J}_\pm \left( \tilde{t}_i^+ \tilde{t}_j^- + \tilde{t}_i^- \tilde{t}_j^+ \right) \right]
\]

where \( \tilde{J}_\pm = -\frac{1}{4} \left( \tilde{J}_x + \tilde{J}_y \right) \) and \( \tilde{J}_\pm = \frac{1}{4} \left( \tilde{J}_x - \tilde{J}_y \right) \). The subregion of parameter space given by (5) then becomes:

\[
|2(\tilde{J}_\pm - \tilde{J}_z)| < \tilde{J}_z, |2(\tilde{J}_\pm + \tilde{J}_z)| < \tilde{J}_z, \tilde{J}_\pm > 0. (7)
\]

To begin, we consider the phase diagram using a tetrahedral CMFT, as employed for the XXZ limit (\( \tilde{J}_\pm = 0 \)) in [52]. To construct the CMFT use the fact that the pyrochlore lattice can be divided into two sets of tetrahedra ‘A’ and ‘B’, with all neighbors of an ‘A’ tetrahedron being ‘B’ tetrahedra and vice versa. We then seek to optimize a product wave function over all ‘A’ tetrahedra:

\[
|\psi_{CMFT} \rangle = \prod_{t \in A} |\phi_t \rangle.
\]
The wave function $|\phi_i\rangle$ on each tetrahedron $t$ is defined to be the ground state of a single tetrahedron Hamiltonian

$$\mathcal{H}_i|\phi_i\rangle = \epsilon_{0,i}|\phi_i\rangle. \tag{9}$$

$\mathcal{H}_i$ contains the original exchange terms acting on the bonds of $t$ as well as auxiliary fields $h_i$ on each site

$$\mathcal{H}_i = \sum_{(ij)\in t} \left[ J_{\pm} \tilde{\tau}_i^{\alpha} \tilde{\tau}_j^{\bar{\alpha}} - J_{\pm} \left( \tilde{\tau}_i^+ \tilde{\tau}_j^- + \tilde{\tau}_i^- \tilde{\tau}_j^+ \right) \right] + \tilde{J}_{\pm} \left( \tilde{\tau}_i^+ \tilde{\tau}_j^- + \tilde{\tau}_i^- \tilde{\tau}_j^+ \right) - \sum_{t \alpha = \bar{\alpha}} h_i^{\alpha} \tilde{\tau}_i^{\alpha}. \tag{10}$$

The auxiliary fields $h_i$ then serve as variational parameters for optimizing $|\psi_{\text{CMFT}}\rangle$, and a CMFT wave function can be indexed by a configuration of $h_i$ on the lattice.

There are two regimes for the optimal configuration of $h_i$ in CMFT as shown in Fig. 2. For sufficiently large, positive values of $\tilde{J}_{\pm}$ or $J_{\pm}$ the optimal solutions have $h_i$ ordered ferromagnetically along the $y$-axis of pseudospin space. This implies $\langle \tilde{\tau}_i \rangle \neq 0$, and therefore octupole order since $\tilde{\tau}$ transforms like a magnetic octupole [45].

In the remainder of the phase diagram there is a large, ice-like, degeneracy of disordered CMFT solutions, with

$$h_i = \sigma_i \tilde{\mathbf{r}}_i,$$

where $h$ is a fixed, uniform, magnitude and $\sigma_i = \pm 1$, subject to the constraint that $\sigma_i$ sum to zero on every tetrahedron.

To resolve the CMFT degeneracy in the disordered regime, we follow the cluster variational (CVAR) method [52, 58]. Labelling CMFT ground states according to their configuration of signs $\{\sigma\}$ we write down a generalized superposition of CMFT solutions

$$|\varphi\rangle = \sum_{\{\sigma\}} a_{\{\sigma\}} |\psi_{\text{CMFT}}(\{\sigma\})\rangle \tag{11}$$

where $a_{\{\sigma\}}$ are unknown coefficients. We then seek to optimize the new variational energy

$$E_{\text{var}} = \frac{\langle \psi | \mathcal{H} | \psi \rangle}{\langle \psi | \psi \rangle}. \tag{12}$$

Eq. (12) can be expanded in terms of the overlap between distinct CMFT wavefunctions, in a similar spirit to the derivation of dimer models from an expansion in the overlap between singlet coverings of a lattice [59]. This generates an effective Hamiltonian in the space of CMFT solutions, where the leading term is a six-site ring exchange which flips the values of $\sigma_i$ on hexagonal plaquettes where $\sigma$ alternates in sign around the plaquette, with matrix element $g_{\text{eff}}$. 

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**FIG. 2.** CMFT and CVAR calculations of the ground state phase diagram of $\mathcal{H}$ [Eqs. (2), (6)] within the region of parameter space given by (7) with $J_z > 0$. CMFT calculations give two regimes for the optimal configuration of the auxiliary fields $h_i$, an ordered region where the $h_i$ point uniformly along the $y$ axis of pseudospin space (red) and a disordered region with a large degeneracy of CMFT solutions where $h_i = \sigma_i \tilde{\mathbf{r}}_i$, with signs $\sigma_i$ summing to zero on every tetrahedron (green). The CVAR calculation, which incorporates quantum tunnelling between CMFT solutions, breaks the degenerate region into two, based on the sign of the effective tunnelling matrix element $g_{\text{eff}}$. Positive (negative) values of $g_{\text{eff}}$ lead ultimately to a $\pi$-flux (0-flux) U(1) QSL ground state.

**FIG. 3.** ED calculations of the ground state phase diagram of $\mathcal{H}$ [Eqs. (2), (6)] within the region of parameter space given by (7) with $J_z > 0$. (a) Second derivative of the ground state energy in ED on a 16-site cubic cluster with respect to $J_z$ for various values of $J_{\pm}/J_z$. The peaks indicate a qualitative change in the ground state [57], associated to the transition to long range order. (b) Color plot of the gap to the $\pi$-rotation symmetry around the $z$-axis in the thermodynamic limit.
This Hamiltonian has already been studied using Quantum Monte Carlo \([47, 49]\). It can have two different QSL ground states depending on the sign of \(g_{eff}\). Both are \(U(1)\) QSLs with gapped, bosonic, charges and gapless photons. The two ground states are distinguished by the \(U(1)\) flux threading elementary plaquettes in the ground state. This background flux vanishes for \(g_{eff} < 0\) \((U(1)\_0)\) but is equal to \(\pi\) on every plaquette for \(g_{eff} > 0\) \((U(1)\_\pi)\). The value of \(g_{eff}\) can be extracted from the CMFT calculation for all values of exchange parameters \([58]\), and by this means the degenerate region within CMFT can be divided into ground ground state QSL phases \((U(1)\_0 \text{ and } U(1)\_\pi)\) depending on the sign of \(g_{eff}\). The boundary between regions with different signs of \(g_{eff}\) is shown in Fig. 2. This constitutes our estimate of the boundary between 0-flux and \(\pi\)-flux QSLs.

We now turn to ED calculations on a 16-site cubic cluster with periodic boundaries. Fig. 3(a) shows the second derivative of the ground state energy on this cluster with respect to \(\tilde{J}_z\), at various fixed values of \(\tilde{J}_{\pm}/\tilde{J}_z\). This second derivative exhibits a peak as \(\tilde{J}_z\) is swept, indicating a qualitative change in the ground state \([57]\).

Fig. 3(b) shows the position of these peaks as a function of \(\tilde{J}_{\pm}/\tilde{J}_z\) and \(\tilde{J}_{\pm}/\tilde{J}_z\), laid over a color plot of the gap to excitations with odd total \(\tilde{z}\). The parity \(p = (-1)^{\sum \tilde{r}_i^z}\) is conserved by \(H\), with the ground state always having \(p = 1\). The line of peaks in the second derivative of the ground state energy coincides with a rapid decrease of the gap to \(p = -1\) excitations. This suggests the formation of a twofold degenerate ground state in the thermodynamic limit, breaking \(\pi\) rotation symmetry around the \(\tilde{z}\) axis, consistent with the octupolar order identified in CMFT. We thus interpret the peaks in the second derivative of the ground state energy as indicative of a transition to octupolar order.

For \(\tilde{J}_z < 0\) the CMFT/CVAR and ED estimates of the octupolar phase boundary agree closely. For \(\tilde{J}_z > 0\) the ED estimates a larger region of octupolar order (and hence a smaller QSL region) than does the CMFT/CVAR approach. For \(\tilde{J}_\pm > 0\) the model has no sign problem from the perspective of QMC, and in this regime we can compare with a QMC study by Huang et al \([55]\). The ED calculation gives closer agreement with the QMC results from \([55]\) than CMFT/CVAR does, and therefore we will take the ED calculation as our estimate of the boundary of the octupolar phase. We did not find a signature of the boundary between the two QSL phases within ED on the 16-site cluster, and so take the CVAR calculation as our estimate of this boundary.

Combining the information from CMFT/CVAR and ED gives the phase diagram shown in Fig. 4. This phase diagram can then be extended to the full parameter space using the duality relations \([Eq. (4)]\).

In doing so, we must take into account how the duality transformations act on the ground states. For example, the octupolar ordered phase with \(\langle \tilde{r}_i^z \rangle \neq 0\) becomes an AIAO phase when acted on by a transformation which swaps the \(\tilde{y}\)-axis with the \(\tilde{x}\)-axis or \(\tilde{z}\)-axis. On the other hand, transformations which swap only the \(\tilde{x}\)-axis and \(\tilde{z}\)-axis, don’t change the classification of the ground state phase because \(\tilde{r}_i^x\) and \(\tilde{r}_i^z\) transform equivalently under point-group and time reversal symmetries.

Similar considerations allow us to distinguish four different kinds of \(U(1)\) QSL, generated from the two in the phase diagram of Fig. 4. In the 0-flux and \(\pi\)-flux QSLs in Fig. 4 the emergent electric field of the QSL \(E_i \sim \tilde{r}_i^z\) \([4, 50]\) and therefore transforms like a magnetic dipole. If we act a transformation that swaps the \(\tilde{z}\)-axis and \(\tilde{y}\)-axes, then \(E_i \sim \tilde{r}_i^\theta\) and transforms like an octupole. We should therefore not only distinguish \(U(1)\) QSLs by the flux but by the dipolar or octupolar character of the emergent electric field \([56]\), giving four distinct QSLs on the complete phase diagram.

Applying these arguments to the parameter space covered in Fig. 4, and to the case of \(\tilde{J}_z < 0\), allows us to generate the full phase diagram, shown using spherical coordinates \([Eq. (3)]\) in Fig. 1.

We have thus established a phase diagram for the generic, symmetry allowed, nearest neighbour exchange Hamiltonian describing dipolar-octupolar (DO) pyrochlores \(R_2M_2O_7\) (\(R=\text{Ce, Sm, Nd}\)). The picture we arrive at is an encouraging one for the realization of QSL states. There are four distinct \(U(1)\) QSLs on the phase diagram of the generic nearest neighbor model, and between them they occupy \(\sim 19\%\) of the available parameter space.

Amongst materials, \(\text{Ce}_2\text{Zr}_2\text{O}_7\) \([29, 30]\), \(\text{Ce}_2\text{Sn}_2\text{O}_7\) \([27, 28]\) and \(\text{Sm}_2\text{Zr}_2\text{O}_7\) \([35]\) stand out as lacking low temperature order. The Ce pyrochlores in particular seem promising with recent neutron scattering results on \(\text{Ce}_2\text{Zr}_2\text{O}_7\) bearing similarity to predictions for emergent photons \([30]\). Low energy correlations in \(\text{Ce}_2\text{Sn}_2\text{O}_7\) seem to be dominantly octupolar in nature \([28]\), which would be consistent with either of the two octupolar spin liquids.
on the phase diagram [Fig. 1].

It will be important to establish estimates of the exchange parameters of \( \text{Ce}_2\text{Zr}_2\text{O}_7 \) and \( \text{Ce}_2\text{Sn}_2\text{O}_7 \), combining information from inelastic neutron scattering with fits to thermodynamic data. If these parameterisations place \( \text{Ce}_2\text{Zr}_2\text{O}_7 \) and \( \text{Ce}_2\text{Sn}_2\text{O}_7 \) within the QSL regimes of Fig. 1, then this will be a strong indication that they are indeed U(1) QSLs, and the parameterized model will provide a platform for further theoretical study. Understanding the effects of disorder of the crystal structure is also likely to be crucial, particularly in regard to the possible substitution of magnetic \( \text{Ce}^{3+} \) with non-magnetic \( \text{Ce}^{4+} \) [30].

For those DO pyrochlores that are known to possess magnetic order at low temperature, the spin liquid phases may also manifest at finite temperature, as suggested recently in \( \text{Nd}_2\text{Zr}_2\text{O}_7 \) [60]. In such cases it may even be possible to tune into the \( T = 0 \) QSL phase using chemical or physical pressure, giving another avenue to realize these exotic states of matter.

Note: After completion of this work, the author became aware of a recent preprint by Patri et al [61] which also presents calculations of the ground state phase diagram of DO pyrochlores.

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SUPPLEMENTAL MATERIAL: GROUND STATE
PHASE DIAGRAM OF DIPOLAR-OCTUPOLAR
PYROCHLORES

Here we give details of the cluster variational (CVAR) calculation used to go beyond Cluster Mean Field Theory (CMFT) in the determination of the phase diagram shown in the main text. In particular, this approach enables to access quantum spin liquid phases which cannot be described using CMFT alone. This calculation is a straightforward extension of that described in Ref. [52], but we give the details here for completeness.

This calculation is applied in the parameter régime where the CMFT solutions are highly degenerate and ice-like. Below, we give some details of these degenerate CMFT solutions and then show how the CVAR calculation is applied.

CMFT SOLUTIONS IN THE ICE-LIKE RÉGIME

The CMFT proceeds by optimizing variational wavefunctions of the form:

$$|\psi_{\text{CMFT}}(\{h_i\})\rangle = \prod_{t \in A} |\phi_t(\{h_{ij}\})\rangle$$

(13)

where the product is over all ‘A’ tetrahedra [Fig. 5], \(\{h_i\}\) is the configuration of auxiliary fields defined on each site and the single tetrahedron wavefunctions \(|\phi_t\rangle\) depend only on the fields on sites belonging to tetrahedron \(t\). The auxiliary fields \(h_i\) are variational parameters for optimizing the CMFT energy

$$E_{\text{CMFT}} = \langle \psi_{\text{CMFT}} | \mathcal{H} | \psi_{\text{CMFT}} \rangle$$

(14)

The wave functions \(|\phi_t(\{h_{ij}\})\rangle\) are taken to be eigenstates of a single tetrahedron Hamiltonian \(\mathcal{H}_t^i\)

$$\mathcal{H}_t^i = \sum_{\langle ij \rangle} \sum_{\alpha=x,y,z} J_{ij}^\alpha \tau_i^\alpha \tau_j^\alpha - \sum_{i \in t} \sum_{\alpha=x,y,z} h_i^\alpha \tau_i^\alpha$$

(15)

$$\mathcal{H}_t^i|\phi_t(\{h_{ij}\})\rangle = \epsilon_{0,t} |\phi_t(\{h_{ij}\})\rangle$$

(16)

where the final term in Eq. (17) sums over bonds belonging to ‘B’ tetrahedra and accounts for the interactions on those tetrahedra.

There is a large region of the phase diagram [Fig. 2 of main text] in which the optimal solutions for \(h_i\) take the form:

$$h_i^x = h_i^y = 0, h_i^z = \sigma_i h$$

$$\sigma_i = \pm 1.$$  

(18)

Correspondingly, the expectation values of the spin components are:

$$\langle \tilde{\tau}_i^x \rangle = 0$$

$$\langle \tilde{\tau}_i^y \rangle = 0$$

$$\langle \tilde{\tau}_i^z \rangle = \sigma_i s$$

(19)

with \(h\) and \(s\) being uniform across the system, and fixed by the energy optimization for a given parameter set.

With this form for the auxiliary fields, the mean field energy [Eq. (17)] becomes

$$E_{\text{CMFT}} = \sum_{t \in A} \epsilon_{0,t} + N hs + \sum_{\langle ij \rangle} \sum_{\alpha} \sigma_i \sigma_j (de-$$

(20)

Any arrangement of signs \(\sigma_i\) such that

$$\sum_{i \in t} \sigma_i = 0 \quad \forall\ \text{tetrahedra } t$$

(21)

gives rise to the same value of \(\epsilon_{0,t}\), as can be inferred from the symmetries of the original Hamiltonian. The remaining terms in Eq. (20) are also the same for all configurations obeying Eq. (21). Thus we have a large degeneracy of mean field solutions in this regime.

Each arrangement of signs \(\sigma_i\) obeying Eq. (21) defines a CMFT wavefunction [via Eqs. (13), (16) and (18)] which we will denote with \(|\psi_{\text{CMFT}}(\{\sigma_i\})\rangle\). Explicitly, the form of single tetrahedron wave functions \(|\phi_t(\{\sigma_{ij}\})\rangle\) (denoted simply as \(|\sigma_0 \sigma_1 \sigma_2 \sigma_3\rangle\)) relates to the configuration of signs on \(t\) in the following way, written in the basis
diagonalizing $\tilde{\tau}_i^z$:

$$
|+ + - -\rangle = \sqrt{1 - \mu^2 - \nu^2 - \rho^2} \uparrow \uparrow \downarrow \downarrow \\
+ \frac{\mu}{2} (|\uparrow \uparrow \downarrow \uparrow + |\uparrow \downarrow \downarrow \uparrow + |\downarrow \uparrow \uparrow \downarrow + |\downarrow \downarrow \uparrow \downarrow) \\
+ \nu |\downarrow \uparrow \uparrow \downarrow + \frac{\rho}{\sqrt{2}} (|\uparrow \uparrow \uparrow \uparrow + |\downarrow \downarrow \downarrow \downarrow) \\
| + - + -\rangle = \sqrt{1 - \mu^2 - \nu^2 - \rho^2} \uparrow \downarrow \uparrow \downarrow \\
+ \frac{\mu}{2} (|\uparrow \uparrow \downarrow \downarrow + |\uparrow \downarrow \uparrow \downarrow + |\downarrow \uparrow \downarrow \uparrow + |\downarrow \downarrow \downarrow \uparrow) \\
+ \nu |\uparrow \downarrow \uparrow \downarrow + \frac{\rho}{\sqrt{2}} (|\uparrow \uparrow \uparrow \uparrow + |\downarrow \downarrow \downarrow \downarrow) \\
| - + - +\rangle = \sqrt{1 - \mu^2 - \nu^2 - \rho^2} \downarrow \uparrow \downarrow \uparrow \\
+ \frac{\mu}{2} (|\uparrow \downarrow \downarrow \uparrow + |\downarrow \uparrow \uparrow \downarrow + |\downarrow \downarrow \uparrow \uparrow + |\uparrow \downarrow \uparrow \downarrow) \\
+ \nu |\uparrow \uparrow \downarrow \downarrow + \frac{\rho}{\sqrt{2}} (|\uparrow \uparrow \uparrow \uparrow + |\downarrow \downarrow \downarrow \downarrow) \\
| - - + +\rangle = \sqrt{1 - \mu^2 - \nu^2 - \rho^2} \downarrow \downarrow \uparrow \uparrow \\
+ \frac{\mu}{2} (|\downarrow \uparrow \downarrow \uparrow + |\downarrow \uparrow \uparrow \downarrow + |\uparrow \downarrow \downarrow \uparrow + |\uparrow \downarrow \uparrow \downarrow) \\
+ \nu |\downarrow \uparrow \downarrow \downarrow + \frac{\rho}{\sqrt{2}} (|\uparrow \uparrow \uparrow \uparrow + |\downarrow \downarrow \downarrow \downarrow) \\
| - + + -\rangle = \sqrt{1 - \mu^2 - \nu^2 - \rho^2} \downarrow \uparrow \downarrow \downarrow \\
+ \frac{\mu}{2} (|\uparrow \downarrow \downarrow \downarrow + |\downarrow \uparrow \downarrow \uparrow + |\downarrow \uparrow \downarrow \downarrow + |\uparrow \downarrow \uparrow \downarrow) \\
+ \nu |\downarrow \uparrow \uparrow \downarrow + \frac{\rho}{\sqrt{2}} (|\uparrow \uparrow \uparrow \uparrow + |\downarrow \downarrow \downarrow \downarrow) \\
| - - - +\rangle = \sqrt{1 - \mu^2 - \nu^2 - \rho^2} \downarrow \downarrow \downarrow \uparrow \\
+ \frac{\mu}{2} (|\downarrow \uparrow \downarrow \downarrow + |\downarrow \uparrow \downarrow \uparrow + |\uparrow \downarrow \uparrow \downarrow + |\uparrow \downarrow \uparrow \downarrow) \\
+ \nu |\downarrow \uparrow \downarrow \downarrow + \frac{\rho}{\sqrt{2}} (|\uparrow \uparrow \uparrow \uparrow + |\downarrow \downarrow \downarrow \downarrow) \\
$$

The parameters $\mu, \nu$ and $\rho$ can always be chosen to be real. This choice, combined with the choice to define the first term on the right hand side of each line of (22) to be positive, removes any phase ambiguity in the CMFT wavefunctions. $\mu, \nu$ and $\rho$ vary as a function of the exchange parameters $\tilde{J}_\alpha$ and are plotted in Fig. 6.

**DETAILS OF CVAR CALCULATION**

The goal of the CVAR calculation is to resolve the degeneracy of the CMFT solutions by considering a new trial wavefunction which is a superposition of the CMFT solutions:

$$
|\varphi\rangle = \sum_{\{\sigma\}} a_{\{\sigma\}} |\psi_{\text{CMFT}}(\{\sigma\})\rangle. \quad (23)
$$

where $a_{\{\sigma\}}$ are, a priori unknown, complex coefficients.

We then seek to optimize the variational energy

$$
E_{\text{var}} = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} = \frac{\sum_{\{\sigma\}} \langle \varphi | a_{\{\sigma\}}^* a_{\{\sigma\}} X_{\{\sigma\}}(\{\sigma\}) \rangle}{\sum_{\{\sigma\}} a_{\{\sigma\}}^* a_{\{\sigma\}} O_{\{\sigma\}}(\{\sigma\})}
$$

$$
= \frac{a^\dagger \cdot X \cdot a}{a^\dagger \cdot O \cdot a} \quad (24)
$$

where $X$ is a matrix containing the Hamiltonian matrix elements between different CMFT wavefunctions and $O$ contains the overlaps (the CMFT wavefunctions are not generally orthogonal to one another)

$$
X_{\{\sigma\}}(\{\sigma\}) = \langle \psi_{\text{CMFT}}(\{\sigma\}) | H | \psi_{\text{CMFT}}(\{\sigma\}) \rangle \quad (25)
$$

$$
O_{\{\sigma\}}(\{\sigma\}) = \langle \psi_{\text{CMFT}}(\{\sigma\}) | \psi_{\text{CMFT}}(\{\sigma\}) \rangle. \quad (26)
$$

It is then useful to define a new matrix $X'$ with vanishing diagonal elements:

$$
X' = X - E_{\text{CMFT}} O \quad (27)
$$
FIG. 7. Magnitudes of the single tetrahedron overlap parameters $o_2$ and $o_4$. These function as the small parameters for the expansion of the CVAR energy.

FIG. 8. Processes which flip a six-site loop of alternating sign variables $\sigma_i$ provide the leading matrix elements in $X', O'$ and $H_{\text{eff}}$ [Eq. (32)], [52].

such that

$$E_{\text{var}} = E_{\text{CMFT}} + \frac{a^\dagger \cdot X' \cdot a}{a^\dagger \cdot O \cdot a}. \quad (28)$$

We then relate the vector of coefficients $a$, to a new normalized vector $b$ via:

$$a = O^{-1/2} \cdot b \quad (29)$$
$$b^\dagger \cdot b = 1 \quad (30)$$

The variational energy is then

$$E_{\text{var}} = E_{\text{CMFT}} + b^\dagger \cdot H_{\text{eff}} b \quad (31)$$

where

$$H_{\text{eff}} = O^{-1/2} \cdot X' \cdot O^{-1/2} \quad (32)$$

The optimal superposition of CMFT solitions is then given by the ground state of $H_{\text{eff}}$ and Eq. (29).

We then expand $H_{\text{eff}}$ in terms of two overlap parameters $o_2$ and $o_4$, which can be defined from the wavefunctions in Eqs. (22):

$$o_2 = \langle + + - | + + - \rangle = \mu^2 + \rho^2 + \mu(\nu + \sqrt{1 - \mu^2 - \nu^2 - \rho^2})$$
$$o_4 = \langle + + - | + - + \rangle = \mu^2 + \rho^2 + 2\nu\sqrt{1 - \mu^2 - \nu^2 - \rho^2}. \quad (33)$$

These two quantities are treated as small parameters for the purposes of the expansion and indeed they are small through most of the relevant parameter space, as shown in Fig. 7.

To expand Eq. (32) we note that all the diagonal elements of $O$ are unity, and the leading off diagonal elements $\sim (o_2)^3$ (coming from the process illustrated in Fig. 8) so we can write

$$O^{-1/2} = (1 + O')^{-1/2} \approx 1 - \frac{1}{2} O'. \quad (35)$$

The first two terms of the expansion of $H_{\text{eff}}$ are then:

$$H_{\text{eff}} \approx X' - \frac{1}{2}(O' \cdot X' + X' \cdot O'). \quad (36)$$

The leading elements in $X'$ are $\sim (o_2)^2$ (again, from the process in Fig. 8) and the leading elements in $O' \cdot X'$ are $\sim (o_2)^5$ and so we henceforth drop the second term.

We then need to evaluate the leading matrix elements in $X'$ which connect configurations of $\sigma_i$ which differ on a single hexagonal plaquette as shown in Fig. 8. The matrix element to a flip a hexagon is $g_{\text{eff}}$. The sign of $g_{\text{eff}}$ determines whether the ground state should be a 0
from $\mathcal{H}'$ in Eq. (15)) and

$$\epsilon_A = \langle + - - | \mathcal{H}_t | + - - \rangle$$

$$= J_z \left( -\frac{1}{2} + 2\rho^2 \right)$$

$$+ 2\sqrt{2}j_{\pm}\rho(2\mu + \nu + \sqrt{1 - \mu^2 - \nu^2 - \rho^2})$$

$$- 2j_{\pm}\mu(\mu + 2(\nu + \sqrt{1 - \mu^2 - \nu^2 - \rho^2})).$$  \hfill (40)

The contribution of any ‘A’ tetrahedron which does not change configurations between $\{\sigma'\}$ and $\{\sigma\}$ to Eq. (39) vanishes. Similarly, the contribution of any ‘B’ bond connecting two unchanged ‘A’ tetrahedra vanishes.

There are three kinds of non-vanishing contribution to the matrix element to flip a hexagon. Firstly, the three ‘A’ tetrahedra belonging to the flipped hexagon (highlighted in red in Fig. 9) contribute:

$$g_A = (o_2)^2(\eta_2 - o_2\epsilon_A)$$  \hfill (41)

where

$$\eta_2 = \langle + - - | \mathcal{H}_t | + - - \rangle$$

$$= -\frac{1}{4}J_z \left( \mu^2 - 6\rho^2 + 2\mu(\nu + \sqrt{1 - \mu^2 - \nu^2 - \rho^2}) \right)$$

$$+ 2\sqrt{2}j_{\pm}\rho(2\mu + \nu + \sqrt{1 - \mu^2 - \nu^2 - \rho^2})$$

$$- j_{\pm}(1 - \rho^2 + 2(\mu + \nu))(\mu + 2(\nu + \sqrt{1 - \mu^2 - \nu^2 - \rho^2})).$$  \hfill (42)

Secondly, there are contributions from ‘B’ bonds connecting to the interior of the flipped hexagon (highlighted in red in Fig. 9):

$$g_{B1,ij} = -J_z s^2 \sigma_i \sigma_j (o_2)^3.$$  \hfill (43)

Finally, there are contributions from ‘B’ bonds connecting to the exterior of the ‘A’ tetrahedra on the flipped hexagon (highlighted in green in Fig. 9):

$$g_{B2,ij} = J_z s(\zeta - s) \sigma_i \sigma_j (o_2)^3.$$  \hfill (44)

where

$$\zeta = \langle + - - | \tilde{\tilde{\tilde{\tilde{\tilde{\mathcal{H}}}}}} | + - - \rangle$$

$$= \frac{o_2}{\mu^2 + 2\rho^2 + 2\mu(\nu + \sqrt{1 - \mu^2 - \nu^2 - \rho^2})}.$$  \hfill (45)

Summing these contributions and accounting for the fact that $\sigma_i$ must alternate around the hexagon and must obey Eq. (21) everywhere, we arrive at the matrix element:

$$g_{eff} = 3(o_2)^2 \left( \eta_2 - \epsilon_A o_2 + J_z s^2 o_2 - 2J_z s(\zeta - s)o_2 \right)$$  \hfill (46)

From Eq. (46) and the numerically determined CMFT wavefunctions we can calculate $g_{eff}$ and thus predict the

or $\pi$ flux QSL, with

$$g_{eff} < 0 \implies U(1)\text{QSL}_0$$  \hfill (37)

$$g_{eff} > 0 \implies U(1)\text{QSL}_\pi$$  \hfill (38)

as may be inferred from prior quantum Monte Carlo studies of the six-site ring exchange Hamiltonian [49] and from a unitary transformation which relates the sign-problem free case ($g_{eff} < 0$) to the frustrated case ($g_{eff} > 0$) [4].

Quite generally the matrix element of $X'$ between two CMFT wavefunctions can be written as

$$X'_{\{\sigma'\}\{\sigma\}} =$$

$$\sum_{\tau \in A} \left( \langle \psi_{\text{CMFT}}(|\{\sigma'\}|) | \mathcal{H}_t | \psi_{\text{CMFT}}(|\{\sigma\}|) \rangle - \epsilon_A O_{\{\sigma'\}\{\sigma\}} \right)$$

$$+ \sum_{(ij) \in B} \left( \tilde{J}_z \langle \psi_{\text{CMFT}}(|\{\sigma'\}|) | \tilde{\tilde{\tilde{\tilde{\tilde{\mathcal{H}}}}} \rangle |\{\sigma|\} \rangle - s^2 \sigma_i \sigma_j O_{\{\sigma'\}\{\sigma\}} \right)$$  \hfill (39)

where the first sum is over ‘A’ tetrahedra and the second is over bonds belonging to ‘B’ tetrahedra. $\mathcal{H}_t$ is the original exchange Hamiltonian on tetrahedron $t$ (distinct

FIG. 9. Contributions to $g_{eff}$. The matrix element between two configurations which differ by flipping the central hexagon has three distinct non-vanishing contributions: from the ‘A’ tetrahedra highlighted in red, from the ‘B’ bonds in blue which connect to the interior of the hexagon and from the ‘B’ bonds in green which connect to the exterior of the ‘A’ tetrahedra on the flipped tetrahedra. The contribution from bonds drawn with narrow black lines vanishes.
FIG. 10. Tunnelling matrix element $g_{\text{eff}}$, calculated using Eq. (46), and the numerically determined CMFT wavefunctions, plotted over the region of parameter space where the CMFT solutions are highly degenerate. The sign of $g_{\text{eff}}$, shown in the second panel, determines whether a 0-flux or $\pi$-flux U(1) QSL phase is predicted.

The ground state in the degenerate region of CMFT from the sign of $g_{\text{eff}}$. The behavior of $g_{\text{eff}}$ and sign($g_{\text{eff}}$) over the relevant region of parameter space is shown in Fig. (10).