From quantum spin liquid to paramagnetic ground states in disordered non-Kramers pyrochlores

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Quantum spin liquids (QSLs) are exotic phases of matter exhibiting long-range entanglement and supporting emergent gauge fields. A vigorous search for experimental realizations of these states has turned up several materials with properties hinting at QSL physics. A key issue in understanding these QSL candidates is often the interplay of weak disorder of the crystal structure with the spin liquid state. It has recently been pointed out that in at least one important class of candidate QSLs - pyrochlore magnets based on non-Kramers ions such as Pr^{3+} or Tb^{3+} - structural disorder can actually promote a U(1) QSL ground state. Here we set this proposal on a quantitative footing by analyzing the stability regime of the QSL state against the condensation of spinons in the minimal model for these systems: a random transverse field Ising model. Having obtained stability bounds on the QSL state we apply our results directly to the disordered candidate QSL Pr2Zr2O7. Combining insights from Numerical Linked Cluster and Exact Diagonalization calculations we parameterize a Hamiltonian for this material and consider where it belongs on the phase diagram. We find that the available data for currently studied samples of Pr2Zr2O7 is most consistent with a ground state outside the spin liquid regime, in a paramagnetic phase with quadrupole moments near saturation due to the influence of structural disorder.

Experimental realizations of Quantum Spin Liquid (QSL) ground states are the goal of an enthusiastic and long-lasting research effort [1][2]. The interest in QSL states stems from their ability to support fractional spin excitations, emergent gauge fields and large-scale quantum entanglement [3][4]. Many candidate QSLs are now known and one key subset of these is found amongst the rare earth pyrochlore oxides R2M2O7 [5][6]. The geometrical frustration of the pyrochlore lattice famously gives rise to the spin ice state- a classical spin liquid with magnetic monopole excitations- in the Ho and Dy based pyrochlores [7][8]. The established theoretical result that a spin ice imbued with quantum fluctuations can host a U(1) quantum spin liquid state with gapless emergent photons [10][13] has fueled interest in pyrochlore magnets related to spin ice but with stronger quantum effects [19][33].

In understanding the low temperature physics of these materials, a recurrent issue is the role of quenched structural and chemical disorder [34][37]. In a recent work [38], Savary and Balents have demonstrated that for pyrochlore magnets based on non-Kramers ions weak structural disorder can actually act to promote the QSL ground state. This can occur since deviations from the local D_{3d} symmetry of the magnetic sites act as transverse fields on the low energy effective $S = 1/2$ degrees of freedom. These effective transverse field induce quantum tunneling between ground states of the classical spin ice problem, and by this means stabilize the U(1) QSL. This scenario has been given experimental support by a recent study [39] of the candidate quantum spin ice Pr2Zr2O7 which parameterized the distribution of effective transverse fields and suggested a disorder induced QSL ground state.

In this Letter we seek to answer two questions. Firstly, what is the extent of the QSL phase in the minimal model for non-Kramers pyrochlores with weak structural disorder? Secondly, do currently studied samples of Pr2Zr2O7 fall within this QSL phase?

We answer the first of these questions by using perturbation theory to calculate the energy of the gapped spinon excitations of the QSL phase. The closing of the gap to these excitations indicates a transition to a topologically trivial paramagnetic ground state. Fig. 1 shows the stability regime of the U(1) QSL estimated by this calculation.

Determining which phase Pr2Zr2O7 falls into requires parameterizing a model for this material. We do this using Numerical Linked Cluster (NLC) [40][42] calculations which are compared to available thermodynamic data for Pr2Zr2O7. The model we obtain for Pr2Zr2O7 suggests that this material falls quite deep within the paramagnetic phase, with 4f quadrupole moments nearly saturated by the effective transverse fields. Exact Diagonalization (ED) calculations based on our model parameterization suggest that this conclusion is consistent with available scattering data which shows a broad continuum of spin excitations and spin-ice like correlations at low energies, cut-off by a finite length scale [50][53].
Stability regime of the QSL. We consider a minimal model for non-Kramers pyrochlores where the degeneracy of a low energy crystal electric field (CEF) doublet is lifted by local devations from $D_{3d}$ site symmetry. We will suppose that the gap to higher energy CEF states is large such that the only relevant degrees of freedom are pseudospin-1/2 operators $\hat{\sigma}_i$, describing the two states of the low energy doublet. Due to the symmetry of non-Kramers doublets [44, 45] on the pyrochlore lattice, the magnetic moment on site $i$ points only along the local-axis $\hat{z}_i$ which joins the centers of the two pyrochlore tetrahedra sharing the site.

$$m_i = \mu_{\text{eff}} \sigma_i^z \hat{z}_i$$ \hspace{1cm} (1)

where $\mu_{\text{eff}}$ is the effective moment size. Nearest-neighbor Ising interactions

$$\mathcal{H}_{\text{SI}} = J \sum_{\langle ij \rangle} \sigma_i^x \sigma_j^x$$ \hspace{1cm} (2)

with $J > 0$ favour spin-ice like ground states in which the total value of $\sigma_i^z$ vanishes on every tetrahedron in the lattice

$$\sum_{t \in i} \sigma_i^z = 0 \hspace{1cm}\forall \hspace{0.1cm} \text{tetrahedra } t$$ \hspace{1cm} (3)

The transverse pseudospin operators $\sigma_i^{x,y}$ are invariant under time reversal symmetry and therefore cannot contribute to the magnetic moment. A finite value of these operators corresponds instead to a finite quadrupole moment on site $i$ [44, 45]. The invariance of $\sigma_i^{x,y}$ under time reversal symmetry allows them to couple linearly to lattice imperfections which lift the local $D_{3d}$ symmetry [33]. These imperfections thus act as an effective transverse field acting on $\sigma_i$

$$\mathcal{H}_{\text{TF}} = -\sum_i h_i \sigma_i^z$$ \hspace{1cm} (4)

where we have used local coordinate transformations on $\sigma_i^z$ such that the coupling is always to the $x$ component of the pseudospin [33]. The transverse fields $h_i$ are distributed on the interval $[0, \infty]$ and throughout this work we will assume them to be uncorrelated on different sites $h_i h_j = \overline{h_i h_j}$. We shall use $\overline{x}$ to denote the average of $x$ over disorder realizations, reserving $\langle x \rangle$ for quantum statistical averages at fixed disorder realization.

The minimal model for non-Kramers pyrochlores with weak structural disorder is thus a random transverse field Ising model [38]

$$\mathcal{H}_{\text{RTFIM}} = \mathcal{H}_{\text{SI}} + \mathcal{H}_{\text{TF}}.$$ \hspace{1cm} (5)

For weak transverse fields $h_i << J$ we expect $U(1)$ QSL phase with gapless photon excitations, while for strong transverse fields $h_i >> J$ a topologically trivial paramagnetic ground state is expected [33]. The transition between these two phases occurs via a condensation of the gapped spinon excitations of the $U(1)$ QSL [38, 46]. In the argument below we use perturbation theory to estimate the point at which such a condensation becomes energetically favourable.

In the limit $h_i = 0$ a spinon corresponds to a tetrahedron $t$ where the ground state condition [Eq. (3)] is locally violated, with $\sum_{t \in i} \sigma_i^z = \pm 2$ and a gap $\Delta_0 = 2J$. To calculate the closing of this spinon gap in the presence of disordered transverse fields we consider a state containing $M$ spinons. We take $1 << M << N_t$, where $N_t$ is the number of tetrahedra in the lattice, such that the spinon density is low and spinon interactions may be neglected. Using degenerate perturbation theory we can obtain an effective Hamiltonian which acts only amongst these $M$ spinon states

$$\mathcal{H}_{\text{eff}}^{(M)} = E_0^{\text{cl}} + M\Delta_0 + \mathcal{H}_1^{(M)} + \mathcal{H}_2^{(M)}$$ \hspace{1cm} (6)

$$\mathcal{H}_1^{(M)} = \mathcal{P}_M \mathcal{H}_{\text{TF}} \mathcal{P}_M$$ \hspace{1cm} (7)

$$\mathcal{H}_2^{(M)} = -\mathcal{P}_M \mathcal{H}_{\text{TF}} \sum\limits_{M} \mathcal{Q}_M \mathcal{H}_{\text{TF}} \mathcal{P}_M$$ \hspace{1cm} (8)

where $E_0^{\text{cl}}$ is the classical ground state energy, $\mathcal{P}_M$ projects onto the manifold of states with $M$ spinons and $\mathcal{Q}_M$ projects onto its orthogonal complement.

In order to find the energy of the lowest energy quantum state for $M$ spinons we use the fact that for $1 << M << N_t$ the column sum of $H_{\text{eff}}^{(M)}$ is approximately constant [47, 48]. To see this consider first $\mathcal{H}_1^{(M)}$, which allows each spinon to tunnel to three of its four neighboring tetrahedra. The column sum of $\mathcal{H}_1^{(M)}$ is

$$\sum_{\alpha} \left( \mathcal{H}_1^{(M)} \right)_{\alpha\beta} = -\sum_{i \text{flippable}} h_i$$ \hspace{1cm} (9)

For sparse spinons $M << N$ there are $3M$ flippable spins and we have

$$\sum_{\alpha} \left( \mathcal{H}_1^{(M)} \right)_{\alpha\beta} = -3M \frac{1}{3M} \sum_{i \text{flippable}} h_i = -3M \overline{h}$$ \hspace{1cm} (10)

where in the last step we have used the fact that $M >> 1$ and the assumption that the transverse field strengths are uncorrelated on different sites.

The second order part of the effective Hamiltonian $\mathcal{H}_2^{(M)}$, contains a diagonal contribution which is constant for $1 << M << N$

$$\left( \mathcal{H}_2^{(M)} \right)_{\alpha\alpha} = -\frac{N_t}{2J} \overline{h^2} + \frac{3M}{8J} \overline{h^2}$$ \hspace{1cm} (11)

coming from virtual processes in which the same spin is flipped and flipped back. The off diagonal part of $\left( \mathcal{H}_2^{(M)} \right)_{\alpha\beta}$ contains terms which enable spinons to hop to 6 out of their 12 second-nearest-neighbor tetrahedra by flipping two spins $k,l$ with matrix element $-\frac{h_k h_l}{4J}$. Since once again each $M$ spinon configuration can tunnel to the same number of other $M$ spinon configurations we find that the column sum of the second order Hamiltonian is also approximately constant and given by

$$\sum_{\alpha} \left( \mathcal{H}_2^{(M)} \right)_{\alpha\beta} = -\frac{N_t}{2J} \overline{h^2} + \frac{3M}{8J} \overline{h^2} - \frac{3}{2J} \overline{h^2}$$ \hspace{1cm} (12)
where we have defined $\delta h$ of the other phase which dominate certain properties [38]. The of the two phases (QSL or paramagnet) there are rare regions

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Since the effective Hamiltonian Eq. (6) has approximately
constant column sum, and has all negative off diagonal
matrix elements we may infer that its ground state is an equal
weight, Rokhsar-Kivelson like, superposition of all configurations containing $M$ spinons [47-49]

$$|\phi_M\rangle = \frac{1}{\sqrt{N_M}} \sum_{|\alpha\rangle \in \{|M\} } |\alpha\rangle$$

where $N_M$ is the number of such configurations.

Evaluating the energy of this wave function with respect to
the effective Hamiltonian [Eq. (6)] we obtain

$$E(M) = E_0 + N_M \frac{\hbar^2}{2J} + M \left(2J - 3\hbar + \frac{7\delta h^2 - 5\hbar^2}{8J}\right)$$

where we have defined $\delta h = \sqrt{\hbar^2 - \hbar^2}$.

When the coefficient of $M$ in Eq. (14) becomes negative it
becomes energetically favorable for spinons to be pulled out
of the vacuum and condense. Thus a stability criterion for the
QSL is

$$2J - 3\hbar + \frac{7}{8J} \delta h^2 - \frac{5\hbar^2}{8J} > 0$$

The gives rise to the phase diagram shown in Fig. 1.

Beyond the instability line given by Eq. (15) the system
gives way to a topologically trivial paramagnetic ground state.

Some portion of the phase diagram may also be occupied by
Griffiths phases in which while the bulk of the system is in one
of the two phases (QSL or paramagnet) there are rare regions
of the other phase which dominate certain properties [38]. The

The phase diagram in Fig. 1 gives the stability of the QSL as a bulk phase.

We can compare the result of Eq. (15) to that obtained for
the phase boundary of the uniform transverse field model
($\delta h = 0$) in Ref. [46]. Inserting $\delta h = 0$, $\hbar = h$ into Eq. (15) we find that the critical value for $h$ is $h_c \approx 0.598\bar{J}$, which is very close to the $h_c \approx 0.602\bar{J}$ obtained from high field expansion in [46].

Modeling $Pr_2Zr_2O_7$- We now come to try to determine
a specific model for the candidate quantum spin liquid
$Pr_2Zr_2O_7$, and to find where it belongs on the phase diagram.
In Ref. [39] the distribution of transverse fields $h_i$ arising in
a sample of $Pr_2Zr_2O_7$ was characterized by analyzing inelastic neutron scattering results in an applied magnetic field. The result was a Lorentzian distribution

$$p(h) = \frac{2\Gamma}{\pi} \frac{1}{h^2 + \Gamma^2}, \ h \in [0, \infty]$$

with $\Gamma = 0.27$meV.

Taking inspiration from this we have compared available
thermodynamic data from other samples of $Pr_2Zr_2O_7$
[43, 50, 51] to NLC calculations using the Hamiltonian in
Eq. (5), with a Lorentzian distribution of transverse fields. The
NLC expansion is a means of estimating quantities in
the thermodynamic limit from a series of exact diagonalizations
of small clusters [40-42], which has been successful in
describing the thermodynamics of other pyrochlore magnets
[33,36]. Disorder averages can be taken term by term in the
expansion [37,38]. Details of the NLC expansion are given in
the supplemental material. NLC results are shown for zeroth
(NLC0), first (NLC1) and second (NLC2) order expansions,
which incorporate clusters of 1 site, 1 tetrahedron and two

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FIG. 2: Establishing a model for $Pr_2Zr_2O_7$. Numerical Linked Cluster (NLC) calculations for the random transverse field Ising Hamiltonian [Eq. (1)] using $J = 0.02$ meV and a Lorentzian distribution of transverse fields with width $\Gamma = 0.19$ meV give a good description of the heat capacity [(a)] and inverse susceptibility [(b)]. We assume an effective magnetic moment per site $\mu_{\text{eff}} = 2.45\mu_B$ [43]. Experimental results for the heat capacity are extracted [39] from Ref. [43] and results for the susceptibility from Refs. [50, 51]. The inset of (a) shows the development of the temperature of the specific heat maximum under a magnetic field applied along the [110] direction, compared between the NLC calculations and the data from Ref. [43]. The heat capacity of isostructural $La_2Zr_2O_7$ [52] was subtracted from the data from [43] to remove the phonon contribution. (c) On-site correlation function $C_{ii}(\omega)$ calculated for three values of external magnetic field along the [100] direction ($h = 2T, 4T, 6T$). Calculations are made using exact diagonalization of the seven site cluster shown in the inset and the model parameters obtained from the thermodynamics in (a) and (b). $C_{ii}(\omega)$ is calculated for the central spin of the cluster. The dashed lines show a single site calculation (i.e. neglecting interactions $J$) and the calculations are compared with $q$ integrated data from Ref. [49], which are multiplied by an overall scale factor. All calculations are averaged over $2 \times 10^5$ disorder realizations. The calculation in (c) has been convoluted with a Gaussian of Full Width at Half Maximum (FWHM) $0.11$ meV to mimic finite experimental resolution.
tetrahedra respectively. We allow both the interaction strength $J$ and distribution width $\Gamma$ to be adjustable parameters in our comparison. We have focussed on obtaining agreement with the thermodynamic data from Refs. [43, 50], but the quantitatively similar heat capacity curves obtained in other studies [30, 51] suggest that variation between samples is not an essential issue, and that the model we obtain should be at least approximately valid for all the currently studied samples.

Good agreement with available thermodynamic data is obtained by setting $J = 0.02\text{meV}$ and $\Gamma = 0.19\text{meV}$, with an effective magnetic moment per site $\mu_{\text{eff}} = 2.45\mu_B$, as shown in Figure 2(a)-(b). Our fits capture the antiferromagnetic Curie-Weiss behavior in spite of having a spin-ice like $J > 0$. This is a consequence of the distribution of transverse fields. They also capture the broad maximum in the specific heat and its evolution as a function of external magnetic field [inset of Fig. 2(a)].

Despite obtaining a somewhat narrower distribution of transverse fields than quoted in [39], our fitted model nevertheless gives a reasonable description of the neutron scattering data from that study. This is shown in Fig. 2(c) where we compare the disorder averaged on-site correlation function

$$\overline{C}_{ii}(\omega) = \sum_{|\alpha]\langle 0|\sigma_i^z|\alpha\rangle^2\delta(\omega - E_\alpha)$$

(17)

for the central of a 2-tetrahedron cluster with the $q$-integrated neutron scattering data from Ref. [39]. The model somewhat overestimates the scattering close to the Zeeman energy at each value of field, but gives a good fit to the high energy scattering, and agrees qualitatively with the form of the lower energy scattering. Residual differences between the model and experimental data may be attributable to additional interactions not included in the simple model Eq. (5), to spatial correlations in the transverse field distribution [49] and to variation between samples.

What does this model parameterization suggest about Pr$_2$Zr$_2$O$_7$? A difficulty with the Lorentzian distribution [Eq. (16)] is that its moments $\overline{\mu^2}$, $\overline{\mu^2}$ are not well defined. This makes direct application of the stability criterion problematic. We can circumvent this issue by applying a finite cut-off $h_{\text{max}}$ to the distribution in Eq. (16) and observing the trajectory of $\overline{\mu}$ as the cut-off is increased, while keeping $J = 0.02\text{meV}$ and $\Gamma = 0.19\text{meV}$. Upon the increasing the cut-off from $h_{\text{max}} = 0$, the model crosses into the paramagnetic region of Fig. 1 for cut-offs as low as $h_{\text{max},c} = 0.025\text{meV}$. Since the distribution of transverse fields in Pr$_2$Zr$_2$O$_7$ certainly extends far beyond this point, we should expect Pr$_2$Zr$_2$O$_7$ to fall quite deep within the paramagnetic phase of the model.

This conclusion is in agreement with both NLC and 16-site ED calculations which predict a nearly saturated ground state expectation value of $\langle \sigma^z \rangle \approx 0.97$ with the model parameters $J = 0.02\text{meV}$ and $\Gamma = 0.19\text{meV}$. This suggests that the low temperature Pr quadrupole moments are nearly saturated in Pr$_2$Zr$_2$O$_7$, which is consistent with the observations of Petit et al. [43] who suggested a quadrupole-dominated ground state on the basis of neutron scattering measurements.

A natural question at this point is whether this conclusion can be reconciled with low-energy inelastic neutron scattering experiments. To address this we have calculated the disorder averaged correlation functions in real space up to third nearest neighbour in 16-site ED

$$\overline{C}_{ij}(\omega) = \sum_{|\alpha}\langle 0|\sigma_i^z|\alpha\rangle\langle \alpha|\sigma_j^z|0\rangle\delta(\omega - E_\alpha).$$

(18)

These can be combined into a calculation of the dynamical structure factor for neutron scattering

$$S(q, \omega) = \frac{1}{N} \sum_{i,j} \langle \tilde{z}_i \cdot \tilde{z}_j - \langle \tilde{z}_i \cdot \tilde{q} \rangle \langle \tilde{z}_j \cdot \tilde{q} \rangle \rangle$$

$$\overline{C}_{ij}(\omega)e^{iq(r_i - r_j)}.$$  

(19)

Using our model parameters to calculate this at finite energy $\omega = 0.2\text{meV}$, we obtain a similar pattern to that observed in Refs. [30, 43], namely broadened remnants of spin-ice like correlations. This suggests that neutron scattering observations on Pr$_2$Zr$_2$O$_7$ can be reconciled with the paramagnetic ground state predicted in this work.

**Conclusions**- In this work we have investigated the instability of the $U(1)$ QSL phase against the proliferation of spinons in a model describing non-Kramers pyrochlore magnets with weak structural disorder. We have parameterized this model for the current studied samples of the quantum spin ice candidate Pr$_2$Zr$_2$O$_7$ and found that it most likely falls in the paramagnetic regime, a result which is consistent with available experimental data. The search for $U(1)$ QSLs in pyrochlore magnets will continue, and it is worth noting that thermodynamic measurements on other Pr pyrochlores such as Pr$_2$Hf$_2$O$_7$ [31,32] and Pr$_2$Sn$_2$O$_7$ [28] are consistent with somewhat less extended transverse field distributions, perhaps
more favorable to the spin liquid phase. Recent experimental results indicating the possible existence of low energy emergent photons in Pr$_2$Hf$_2$O$_7$ [33] are of great interest, and further work is needed to determine whether this material may realize the $U(1)$ QSL.

Acknowledgments The author acknowledges useful discussions with Bella Lake, Kate Ross, Nic Shannon and Jiajia Wen.

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SUPPLEMENTAL MATERIAL: DETAILS OF NUMERICAL LINKED CLUSTER CALCULATIONS

FIG. 4: Series of clusters used in NLC calculations in the main text.

Here we give some details of the Numerical Linked Cluster (NLC) calculations presented in the main text. A pedagogical introduction to NLC expansions is given in [42].

In Numerical Linked Cluster expansions an extensive quantity $\mathcal{O}$ divided by the number of sites $N$, is calculated as a sum over contributions from all clusters $c$ that can be embedded in the lattice

$$\frac{1}{N} \langle \mathcal{O} \rangle = \sum_c M(c) W(c). \quad (20)$$

$M(c)$ is the multiplicity of the cluster per site- i.e. how many times that cluster can be embedded in a lattice of $N$ sites, divided by $N$. $W(c)$ is the cluster weight defined as

$$W(c) = \langle \mathcal{O} \rangle_c - \sum_{s \subset c} W(s) \quad (21)$$

where $\langle \mathcal{O} \rangle_c$ is the expectation value of $\mathcal{O}$ on the cluster $c$, which is calculated from exact diagonalization. The sum in the second term is a sum of the weights of all the subclusters of $c$. 

(a) Cluster $c_1$: One site (b) Cluster $c_4$: One tetrahedron (c) Cluster $c_7$: Two tetrahedra
In our calculations we have used the series of clusters shown in Fig. 4, calculating the series up to second order. We have used clusters of 1, 4 and 7 sites and we denote them as $c_1, c_4, c_7$. The multiplicities of these clusters per site are

$$M(c_1) = 1, \quad M(c_4) = \frac{1}{2}, \quad M(c_7) = 1$$

and the weights for calculation of quantity $O$ per site are

$$W(c_1) = \langle O \rangle_{c_1},$$
$$W(c_4) = \langle O \rangle_{c_4} - 4\langle O \rangle_{c_1},$$
$$W(c_7) = \langle O \rangle_{c_7} - 2(\langle O \rangle_{c_4} - 4\langle O \rangle_{c_1}) - 7\langle O \rangle_{c_1}. $$

In the presence of disorder, disorder averaged quantities can be calculated by taking the disorder average term by term \[58\], i.e.

$$\frac{1}{N} \langle O \rangle = \sum_c M(c)W(c)$$

$$W(c) = \langle O \rangle_c - \sum_{s \subset c} W(s)$$

For the calculations in the presence of an external [110] magnetic field [inset of Fig. 2(a) of main text], the reduction in point group symmetry due to the applied field means that the clusters $c_1$ and $c_7$ now have two inequivalent types which must be treated separately \[55\].