

Geometrically Frustrated Quadrupoles on the Pyrochlore Lattice and Generalized Spin Liquids

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As an instance of geometrical frustration with nonmagnetic degrees of freedom, we explore the physics of local spin $S \geq 1$ moments on the pyrochlore lattice that interact via pure quadrupolar couplings. In the presence of spin-orbit coupling, there are nine allowed couplings between nearest-neighbor quadrupoles. We determine the semiclassical phases and survey the phase diagram of the model. One may view the Hamiltonian as being composed of two copies of the well-studied dipolar model with couplings between the copies, and we find that each easy-plane dipolar phase has two quadrupolar counterparts. As geometrical frustration is important over broad swathes of the parameter space, there are many classical quadrupolar liquids and regions with order-by-disorder selection of discrete states. Order by disorder with quadrupoles admits cubic terms in the Landau theory whose effects appear in Monte Carlo simulations and flavor-wave calculations for fixed spin S . We showcase a number of examples of quadrupolar spin liquids, including one realizing a rank-3 symmetric tensor gauge theory exhibiting sixfold pinch point singularities. We discuss remarkable differences between the quadrupolar physics of different spin quantum number. We also discuss connections to the non-Kramers rare earth pyrochlore materials.

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I. INTRODUCTION

Geometrical frustration is the generation of unsatisfiable classical energetic constraints through a combination of suitable local couplings and lattice connectivity. Classic examples of geometrically frustrated models include Heisenberg antiferromagnets on kagome and pyrochlore lattices. In practice, geometrical frustration provides a route to generate a large low-lying density of strongly coupled states from which exotic phases may arise, especially in quantum many-body systems. Antiferromagnetism on suitable lattices used as a criterion for materials searches has been an extremely fruitful path to new and interesting physical phenomena [1].

The pyrochlore lattice is the most prominent of the three-dimensional crystal structures where geometrical magnetic frustration can be studied in the absence of disorder. The significance of this structure was recognized in the early

modern era of condensed matter physics [2], but a systematic exploration of the magnetism of pyrochlores in conjunction with experiment did not start until the 1990s. From then until now, the field has generated a steady stream of insights [3,4]. An early notable event that has played a considerable role in shaping the field was the discovery of the spin ice materials [5–8], which realize Ising classical spin liquids at finite temperature. However, geometrical frustration combined with spin-orbit coupling and quantum spins are responsible for an even richer spectrum of phenomena that has been explored extensively, especially among the family of rare earth pyrochlore materials. We refer the reader to various excellent reviews of the subject for further details [3,4].

A Maxwellian argument first applied to classical spin models in Ref. [9] seeks to maximize nontrivial ground state degeneracy by putting n -component degrees of freedom (with Heisenberg spins having $n = 3$) on a corner-sharing lattice of q site clusters. The origin of the constraint is the condition from the Heisenberg Hamiltonian that the lowest-energy states have total moment on each cluster equal to zero. The number of degrees of freedom minus the number of constraints may have an extensive contribution going like $q(n-1)/b - n$, where b is the number of clusters connected to each site with $b = 2$ on the

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pyrochlore lattice. From this point of view, it might seem attractive to consider local degrees of freedom with more components. Physics supplies them in the form of multipolar degrees of freedom originating from angular momenta $J \geq 1$.

The study of interacting multipoles has a long history in condensed matter. One classic model in this context is the bilinear-biquadratic model on some lattice [10–45]:

$$H = \sum_{(i,j)} \left(\cos \theta \mathbf{S}_i \cdot \mathbf{S}_j + \sin \theta (\mathbf{S}_i \cdot \mathbf{S}_j)^2 \right). \quad (1)$$

Implicitly, the second term couples local quadrupoles, and for some range of parameters this model leads to a nematic ground state where the quadrupoles acquire a nonzero expectation value while the spins have vanishing expectation value. This is a lattice model realization of the nematic phase of liquid crystals. Evidence has accumulated over the years that the isotropic bilinear-biquadratic model is the correct leading-order description of certain materials [19,46] including spin-one pyrochlore $\text{NaCaNi}_2\text{F}_7$ [45,47]. Nematic phases have long been sought in quantum materials, and the situation now is that such phases are well established in certain instances albeit often at high magnetic fields where the microscopic description is more naturally phrased in terms of a condensate of bound state excitations [48–58].

In parallel with these advances, investigations into heavy electron systems such as the actinides have revealed materials where multipolar order is known or at least strongly suspected in several materials [59]. In these systems, spin-orbit coupling is strong and interactions between multipoles have low symmetry. A schematic model that generalizes the bilinear-biquadratic model to such cases is

$$H = H_{\text{CEF}} + \sum_{(ij)} \sum_{L,L',M,M'} [O_L^M]_i [J_{LL'}^{MM'}]_{ij} [O_{L'}^{M'}]_j, \quad (2)$$

where O_L^M are Steven's operator equivalents and H_{CEF} is the single-ion crystal field Hamiltonian. Superexchange in actinides can generate L up to rank 7 [59].

Multipolar interactions in rare earth pyrochlores at the bare ion level are similarly anisotropic, and quantum chemistry calculations suggest that couplings between multipoles of all possible ranks are of comparable magnitude. This forbidding situation is simplified greatly by the crystal field spectrum that often leads to a single-ion ground state doublet that is separated from the first excited state on a scale much larger than the scale of interactions. In such cases, the low-energy physics is well described by an effective spin-1/2 model, albeit one perhaps of mixed character. Many years of intensive investigation of pyrochlore magnets have clarified our understanding of several materials and sharpened the problems. An all-too-brief summary of the current situation is that, of all pyrochlore

magnets, the most puzzling have mixed character crystal field ground states.

Of particular relevance to this work is the set of non-Kramers rare earths. Among the pyrochlores with rare earth ions R^{3+} (with, for example, $R = \text{Pr}, \text{Tb}$) where the crystal field ground state is a doublet, this is an effective spin one-half of mixed character that can be thought of as an Ising spin with component along z and with transverse components that are quadrupolar in nature. Among the non-Kramers pyrochlores, $\text{Tb}_2\text{Ti}_2\text{O}_7$ stands out. It exhibits no signs of magnetic order at low temperatures well below the Curie scale [60–68]. This material is complicated by the presence of low-lying crystal field levels and significant magnetoelastic coupling. Similarly puzzling are praseodymium pyrochlores with $M = \text{Hf}, \text{Sn}, \text{Zr}$ [69–73]. Accounting for the observed properties of these materials is among the central problems in the field of frustrated magnetism, and a significant literature has built up in this direction.

Given the mixed character of the local degrees of freedom, it is natural to consider the activity of quadrupoles and possible quadrupolar long-range order in these systems. But, while thermodynamic anomalies are expected at the transition temperature, the usual probes available to experimentalists present challenges in definitively demonstrating quadrupolar long-range order. In short, there is no way to measure the multipolar analog of magnetic Bragg peaks that both signal and characterize the type of dipolar order. Multipolar order has not been seen definitively in the rare earth pyrochlores, though quadrupolar order has been suggested as a possible explanation for features of the weakly site-mixed $\text{Tb}_{2-x}\text{Ti}_{2+x}\text{O}_7$ [64,65,68].

In this paper, we have two main motivations. One is to extend our understanding of magnetic frustration to a new domain of nonmagnetic degrees of freedom and, in particular, to quadrupoles that naturally have a larger local configuration space than spins one-half or vector spins. Our second motivation is to bring a new perspective to the set of non-Kramers pyrochlores which are extremely poorly understood. These materials are quadrupolar active, and our hope is that by mapping out the landscape of quadrupolar states we might be able to stimulate progress on these systems. Concretely, we take microscopic quadrupoles living on sites of the pyrochlore lattice with couplings between nearest neighbors (Sec. II). The couplings are strongly constrained by the symmetry of the crystal, and we explore all of them together. Although there are nine couplings, there are considerable simplifications, and we may benefit from known results for the dipoles. Among the semiclassical phases (Sec. III) are quadrupolar analogues of the ice states, the all-in–all-out states, splayed ferromagnet, Γ_5 , and Palmer-Chalker phases familiar from the magnetic case. In fact, we can show that the easy-plane states are in a sense doubled in passing from magnetism to quadrupoles (Sec. IV). This means that the order-by-disorder regime is doubled. This, along with the peculiar time-reversal

properties of quadrupoles, leads to rich and unusual order-by-disorder physics (Sec. VI). Much of the paper dwells on the range of semiclassical quadrupolar liquids that arise, which includes all of the types seen in the magnetic case and more besides (Sec. VII).

So far, we have said little about the underlying angular momentum degrees of freedom that are the precursors to the quadrupoles. It turns out that the physics very much depends on effective spin. Spin one, which is the usual choice for studies of spin nematic phases, is highly constrained such that the full space of quadrupolar states is not available. Increasing the total spin relaxes this constraint but introduces new features that we discuss at length in Sec. V.

II. THE ANISOTROPIC BILINEAR QUADRUPOLE MODEL

For spin $S \geq 1$, multipoles higher than the dipole moment may be active. In this paper, we consider the quadrupole moments, encoded in the tensor operator

$$Q^{\alpha\beta} = \frac{1}{2}(S^\alpha S^\beta + S^\beta S^\alpha) - \frac{1}{3}|S|^2 \delta^{\alpha\beta}, \quad \alpha, \beta \in \{x, y, z\}, \quad (3)$$

as the dominant terms in the Hamiltonian. These spin operators could arise either as physical angular momenta of electronic degrees of freedom in an ion or as effective pseudospin operators acting in a restricted Hilbert space of low-energy crystal field states. Many previous works have studied the effects of quadrupole interactions in combination with dipolar couplings on various lattices: the most well-known example being the rotationally symmetric bilinear-biquadratic model [Eq. (1)]. This model exhibits quadrupolar order for some range of the free parameter θ , as the biquadratic term is the isotropic quadrupole-quadrupole interaction:

$$\text{Tr}[Q_i Q_j] \equiv \sum_{\alpha, \beta} Q_i^{\alpha\beta} Q_j^{\beta\alpha} = (\mathbf{S}_i \cdot \mathbf{S}_j)^2 + \frac{1}{2}(\mathbf{S}_i \cdot \mathbf{S}_j) - \frac{1}{3}|S|^4. \quad (4)$$

For spins arising from light elements in the periodic table, it is often the case that quadrupolar couplings are very much a subleading contribution to the magnetic exchange. In general, when spin-orbit coupling is significant at the bare ion level, which is the case especially for magnetic materials with heavy elements, such a rotationally symmetric form of the Hamiltonian is fine-tuned. Also, especially in rare earth and actinide systems, multipolar operators may be the primary couplings between the local degrees of freedom. In the case of dipolar and quadrupole active spin-orbit-coupled systems, one should expect all symmetry-allowed anisotropic interactions between dipole operators S_i^α and quadrupole operators $Q_i^{\alpha\beta}$ to be present. The most general Hamiltonian of dipolar-quadrupolar character allowed by spatial and time-reversal symmetry has the form [74]

$$H = H_{\text{CEF}} + \sum_{ij} \sum_{\alpha\beta} \left(S_i^\alpha [\mathcal{J}_S]_{ij}^{\alpha\beta} S_j^\beta + Q_i^{\alpha\beta} [\mathcal{J}_Q]_{ij}^{\alpha\beta, \alpha'\beta'} Q_j^{\alpha'\beta'} \right). \quad (5)$$

Such anisotropies are well studied in the context of dipoles on the pyrochlore lattice, giving rise to a rich phase diagram featuring a plethora of phenomena such as order by disorder and exotic spin liquids [4,75–87]. As the dipolar sector is relatively well understood, here, we focus on the physics of the model with purely quadrupolar couplings. We expect that the intermediate regime in which dipolar and quadrupolar couplings are comparable can yield a variety of interesting behaviors (see Ref. [41] for the spin-1 maximally isotropic case). We discuss the mixed Hamiltonian in more detail in Sec. VIII.

A. Symmetry-allowed interactions: Global frame

The symmetric trace-free tensor operators $Q^{\alpha\beta}$ transform in a five-dimensional irreducible representation (hereafter *irrep*) of $O(3)$. In an anisotropic crystalline environment, the symmetry is lowered and this five-dimensional representation becomes reducible [88]. For a lattice with cubic point group O_h , such as the pyrochlore, it decomposes as $t_{2g} \oplus e_g$, corresponding to the symmetric off-diagonal (t_{2g}) and trace-free diagonal (e_g) components of $Q^{\alpha\beta}$. They can be organized into a five-component vector as

$$\begin{pmatrix} Q_{yz} \\ Q_{zx} \\ Q_{xy} \\ Q_{3z^2-r^2} \\ Q_{x^2-y^2} \end{pmatrix} \equiv \begin{pmatrix} Q_{t_{2g}}^x \\ Q_{t_{2g}}^y \\ Q_{t_{2g}}^z \\ Q_{e_g}^{w_2} \\ Q_{e_g}^{w_3} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}}(Q^{yz} + Q^{zy}) \\ \frac{1}{\sqrt{2}}(Q^{zx} + Q^{xz}) \\ \frac{1}{\sqrt{2}}(Q^{xy} + Q^{yx}) \\ \frac{1}{\sqrt{6}}(2Q^{zz} - Q^{xx} - Q^{yy}) \\ \frac{1}{\sqrt{2}}(Q^{xx} - Q^{yy}) \end{pmatrix}. \quad (6)$$

This corresponds to choosing a basis in the five-dimensional space of symmetric traceless 3×3 matrices, and each such basis matrix can be visualized by plotting its “orbital structure,” as shown in Fig. 1. The transformation of these five degrees of freedom under rotations is given by the Wigner D -matrix in the basis of real spherical harmonics (or, equivalently, by projecting the transformation $Q \rightarrow RQR^{-1}$ to the five-dimensional basis). The quadrupole-quadrupole interaction term in Eq. (5) can be written as

$$H = \frac{1}{2} \sum_{ij} \sum_{a,b=1}^5 Q_i^a \mathcal{J}_{ij}^{ab} Q_j^b, \quad (7)$$

where we suppress the subscript on the quadrupole interaction matrix, $\mathcal{J}_Q \equiv \mathcal{J}$, which must be symmetric, $\mathcal{J}_{ij}^{ab} = \mathcal{J}_{ji}^{ba}$. Single-site anisotropies $\mathcal{J}_{ii}^{ab}$ are allowed by symmetry and given in Appendix C, but for this work we set all such terms to be zero.

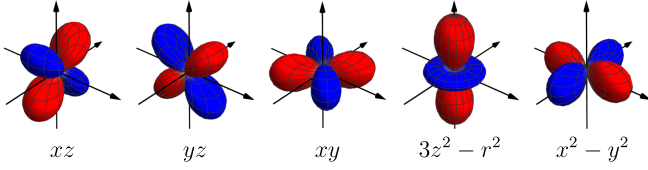


FIG. 1. (a) Shapes of the quadrupolar orbitals, corresponding to an orthonormal basis in the space of symmetric trace-free tensors $q^{\alpha\beta}$. Surfaces are plotted as a function of angular positions $\hat{r}$ on a unit sphere, with radius $\hat{r}^\alpha q^{\alpha\beta} \hat{r}^\beta$, and with positive radii colored red and negative ones colored blue.

From here on, we focus on studying the Hamiltonian Eq. (7) with all symmetry-allowed nearest-neighbor interactions on the pyrochlore lattice of corner-sharing tetrahedra. Restricting to nearest-neighbor interactions, the matrix $\mathcal{J}_{ij}^{ab}$ is the same on every tetrahedron; for each tetrahedron, it is a 20×20 matrix $\mathcal{J}_{\mu\nu}^{ab}$, where $\mu, \nu \in \{1 \dots 4\}$ label the four corners of a tetrahedron, and the Hamiltonian simplifies to

$$H = \frac{1}{2} \sum_t \sum_{\mu, \nu=1}^4 \sum_{a, b=1}^5 Q_{t, \mu}^a \mathcal{J}_{\mu\nu}^{ab} Q_{t, \nu}^b, \quad (8)$$

where t labels tetrahedra. The matrix elements are restricted by the T_d subgroup of the O_h point-group symmetries, which map a single tetrahedron back to itself. For a single tetrahedron, the four five-dimensional Q vectors, arranged as a single 20-component vector, transform collectively in a 20-dimensional representation of T_d , which we denote ρ_{20} . The matrix $\mathcal{J}$ transforms in the 400-dimensional tensor product representation $\rho_{20} \otimes \rho_{20}^T$, which reduces to a 150-dimensional representation when applying the constraint that $\mathcal{J} = \mathcal{J}^T$ and that $\mathcal{J}_{ii}^{ab} = 0$. Invariance of the Hamiltonian under T_d symmetry demands that the matrix elements of $\mathcal{J}$ are restricted such that it transforms in the trivial representation. Direct decomposition shows that the 150-dimensional representation contains nine copies of the trivial representation, indicating that there are nine symmetry-allowed couplings. Transforming in the trivial representation means that $\mathcal{J}$ commutes with the matrices $\rho_{20}(g)$ for every $g \in T_d$. Directly solving the equations $[\rho_{20}(g), \mathcal{J}] = 0$ for all $g \in T_d$ allows us to express the matrix elements coupling sublattices 1 and 2 in the global basis Eq. (6) as

$$g_{12}^{ab} = \underbrace{\begin{pmatrix} J_1 & J_3 & -J_4 \\ J_3 & J_1 & -J_4 \\ J_4 & J_4 & J_2 \end{pmatrix}}_{t_{2g}} \underbrace{\begin{pmatrix} -J'_6 & -J_7 \\ -J'_6 & J_7 \\ J'_5 & 0 \end{pmatrix}}_{e_g} \quad (9)$$

where we define $J'_5 \equiv -2J_5/\sqrt{3}$ and $J'_6 \equiv (2J_6 - J_7)/\sqrt{3}$ for convenience. Lines indicate the separation of the t_{2g} and e_g components of the five-component quadrupoles. The t_{2g} sector has the exact same structure as that of the dipolar Hamiltonian [4, 77, 89–91]. The two e_g -sector components are coupled to the three t_{2g} -sector components through the J_5 , J_6 , and J_7 couplings.

B. Local frame and mixed basis

The Hamiltonian may be expressed in a more symmetric manner by changing basis to a local symmetry-adapted frame. We define a local frame on the first sublattice:

$$\hat{x}_1 \propto [\bar{1} \bar{1} 2], \quad \hat{y}_1 \propto [1 \bar{1} 0], \quad \hat{z}_1 \propto [\bar{1} \bar{1} \bar{1}] \quad (10)$$

and similarly for the other four sublattices, where the $\hat{z}_i$ lie along the local threefold easy axis, the $\hat{y}_i$ lie along a local twofold axis, and the $\hat{x}_i$ lie in a mirror plane. We present first a “mixed” local-global frame which respects the separation of each quadrupole into a 3D t_{2g} component and a 2D e_g component [Eq. (6)]. We exploit the fact that the t_{2g} component transforms as a vector, while the e_g component (as we know from the dipolar case) transforms as an easy-plane XY spin, defining the following two vector multiplets:

$$\begin{aligned} Q_i^{(t_{2g})} &= (Q_{t_{2g}}^x)_i \hat{x}_i + (Q_{t_{2g}}^y)_i \hat{y}_i + (Q_{t_{2g}}^z)_i \hat{z}_i, \\ Q_i^{(e_g)} &= (Q_{e_g}^{\psi_2})_i \hat{x}_i + (Q_{e_g}^{\psi_3})_i \hat{y}_i, \end{aligned} \quad (11)$$

where for the t_{2g} components we utilize the global Cartesian frame basis vectors and for the e_g components we utilize the local easy-plane basis vectors. We then rotate the t_{2g} multiplet into the local frame, i.e., decompose it as

$$Q_i^{(t_{2g})} = Q_{t_{2g},i}^{x_{\text{loc}}} \hat{x}_i + Q_{t_{2g},i}^{y_{\text{loc}}} \hat{y}_i + Q_{t_{2g},i}^{z_{\text{loc}}} \hat{z}_i. \quad (12)$$

Lastly, we rotate into the eigenbasis of rotations in the local xy planes, creating complex linear combinations of the local x and y degrees of freedom on each site for both the t_{2g} and e_g components:

$$Q_{t_{2g}}^\pm = Q_{t_{2g}}^{x_{\text{loc}}} \pm i Q_{t_{2g}}^{y_{\text{loc}}} \quad \text{and} \quad Q_{e_g}^\pm = Q_{e_g}^{\psi_2} \pm i Q_{e_g}^{\psi_3}. \quad (13)$$

The end result is a remarkable simplification of the interaction matrix into a highly symmetric form:

$$g_{\mu\nu}^{\bar{a}\bar{b}} = \omega_{\mu\nu}^{\bar{a}\bar{b}} \left(\underbrace{\begin{pmatrix} -J_{\pm}^{t_{2g}} & J_{\pm\pm}^{t_{2g}} \\ J_{\pm\pm}^{t_{2g}} & -J_{\pm}^{t_{2g}} \end{pmatrix}}_{Q_{t_{2g}}^\pm} \underbrace{\begin{pmatrix} J_{z\pm}^{t_{2g}} & J_{\pm\pm}^{t_{2g}} \\ J_{z\pm}^{t_{2g}} & J_{\pm}^{t_{2g}} \end{pmatrix}}_{Q_{t_{2g}}^{z_{\text{loc}}}} \underbrace{\begin{pmatrix} J_{\pm}^{e_g} & J_{\pm\pm}^{e_g} \\ -J_{\pm}^{e_g} & J_{\pm\pm}^{e_g} \end{pmatrix}}_{Q_{e_g}^\pm} \right)^{\bar{a}\bar{b}} \quad (14)$$

where $\omega_{\mu\nu}^{\tilde{a}\tilde{b}}$ is a matrix of phase factors. We have used tildes to differentiate these indices from the global frame ones. For sublattices 1 and 2 they are all 1, while for sublattices 1 and 3 they have the banded matrix form

$$\omega_{13}^{\tilde{a}\tilde{b}} = \begin{pmatrix} 1 & -\omega & \omega^2 & 1 & -\omega \\ \omega^2 & 1 & -\omega & \omega^2 & 1 \\ -\omega & \omega^2 & 1 & -\omega & \omega^2 \\ 1 & -\omega & \omega^2 & 1 & -\omega \\ \omega^2 & 1 & -\omega & \omega^2 & 1 \end{pmatrix}^{\tilde{a}\tilde{b}} \quad \text{with} \quad \omega = e^{i\pi/3}. \quad (15)$$

In this basis, the Hamiltonian may be written in a form which directly parallels to the well-known dipolar Hamiltonian in the local frame, as $H = \sum_t \sum_{\langle ij \rangle \in t} H_{ij}$ with

$$\begin{aligned} H_{ij} = & \sum_{r \in \{e_g, t_{2g}\}} \left[-J_{\pm}^r (Q_{r,i}^+ Q_{r,j}^- + Q_{r,i}^- Q_{r,j}^+) \right. \\ & + J_{\pm\pm}^r (\gamma_{ij} Q_{r,i}^+ Q_{r,j}^+ + \gamma_{ij}^* Q_{r,i}^- Q_{r,j}^-) \\ & + J_{z\pm}^r \left(\zeta_{ij} (Q_{r,i}^+ Q_{t_{2g},j}^{z_{\text{loc}}} + Q_{t_{2g},i}^{z_{\text{loc}}} Q_{r,j}^+) + \text{H.c.} \right) \\ & + J_{zz}^r Q_{t_{2g},i}^{z_{\text{loc}}} Q_{t_{2g},j}^{z_{\text{loc}}} + J_{\pm}^r \left(Q_{t_{2g},i}^+ Q_{e_g,j}^- + Q_{e_g,i}^+ Q_{t_{2g},j}^- + \text{H.c.} \right) \\ & \left. + J_{\pm\pm}^r ((\gamma_{ij} Q_{t_{2g},i}^+ Q_{e_g,j}^+ + \gamma_{ij}^* Q_{e_g,i}^- Q_{t_{2g},j}^-) + \text{H.c.}) \right]. \quad (16) \end{aligned}$$

We can compare term by term to the dipolar Hamiltonian [4,91]: The first three terms are identical to terms involving S^+ and S^- in the dipolar Hamiltonian, but they each appear twice, once for each irrep. The local z - z term, of course, also appears in the dipolar Hamiltonian. The matrices γ_{ij} and ζ_{ij} contain the phase factors arising from Eq. (15), and they are identical to those in the standard presentation of the dipolar Hamiltonian. The last two terms are new—they couple the e_g and t_{2g} sectors explicitly (they are also coupled implicitly through their respective couplings to the Q_i^z via the two $J_{z\pm}^r$ terms). Notice that if we turn off all e_g components and the last two couplings, we recover precisely the form of the dipolar Hamiltonian.

In this form, it is clear that there is an effective doubling of the easy-plane degrees of freedom compared to the dipolar case. The technical reason for this is that in the pyrochlore lattice each quadrupole transforms locally under the site symmetry group $D_{3d} \subseteq O_h \subseteq O(3)$, which has only 1D and 2D irreps. The five-dimensional quadrupolar irrep of $O(3)$ reduces to $e_g \oplus t_{2g}$ when restricting to the O_h subgroup. Further restricting to D_{3d} , the three-dimensional t_{2g} representation reduces to $a_{1g} \oplus e_g$, such that the five-dimensional quadrupolar representation of $O(3)$ decomposes as $a_{1g} \oplus 2e_g \in \text{Rep}(D_{3d})$, corresponding to the easy-

axis Q^z components and the easy-plane $Q_{t_{2g}}^{\pm}$ and $Q_{e_g}^{\pm}$ components (whose subscripts refer to irreps of O_h).

C. Local frame spherical harmonics basis

Because of the doubling of the easy-plane degrees of freedom, there is a freedom to make a change of basis between them, albeit at the cost of changing the phase factors appearing in the Hamiltonian. There is another natural basis to consider: the basis of spherical harmonics in the local frame. We can write the quadrupole operator components in the local frame:

$$\begin{aligned} Q_{\text{loc}}^{\tilde{\alpha}\tilde{\beta}} &= [\hat{e}_{i,\tilde{\alpha}}^{\text{loc}}]^\alpha Q_{\text{glo}}^{\alpha\beta} [\hat{e}_{i,\tilde{\beta}}^{\text{loc}}]^\beta \\ &= \frac{1}{2} (S^{\tilde{\alpha}} S^{\tilde{\beta}} + S^{\tilde{\beta}} S^{\tilde{\alpha}}) - \frac{1}{3} |S|^2 \delta^{\tilde{\alpha}\tilde{\beta}}, \quad (17) \end{aligned}$$

where $\hat{e}_{i,\tilde{\alpha}}^{\text{loc}} = \{\hat{x}_i, \hat{y}_i, \hat{z}_i\}_{\tilde{\alpha}}$ are the local frame basis vectors such as given by Eq. (10) and we use a bar on the local frame indices. This is equivalent to performing a rotation— $[\hat{e}_{i,\tilde{\alpha}}^{\text{loc}}]^\alpha$ are the matrix elements of the SO(3) rotation which sends the global Cartesian axes to the local ones at site i . Equivalently, the five quadrupole operators Eq. (6) rotate as

$$Q_{\text{loc}}^{\tilde{a}} = D_i^{\tilde{a}b} Q_{\text{glo}}^b, \quad (18)$$

where D_i is the Wigner D -matrix corresponding to the SO(3) rotation. The operators $Q_{\text{loc}}^{\tilde{a}}$ are the same as those operators in Eq. (6) but with $Q^{\alpha\beta}$ replaced by the local frame components $Q_{\text{loc}}^{\tilde{\alpha}\tilde{\beta}}$ in Eq. (17). This is the basis of cubic harmonics in the local frame, explicitly given in Appendix D. In this basis, the interaction matrix takes a nice symmetric form:

$$\mathcal{J}_{12}^{\tilde{a}\tilde{b}} = \begin{pmatrix} K_1 - \sqrt{3}K_2 & 0 & 0 & 0 & K_3 + \sqrt{3}K_5 \\ 0 & K_1 + \frac{K_2}{\sqrt{3}} & -\frac{2K_4}{\sqrt{3}} & \frac{K_5}{\sqrt{3}} - K_3 & 0 \\ 0 & -\frac{2K_4}{\sqrt{3}} & K_9 & \frac{2K_7}{\sqrt{3}} & 0 \\ 0 & \frac{K_5}{\sqrt{3}} - K_3 & \frac{2K_7}{\sqrt{3}} & K_6 - \frac{K_8}{\sqrt{3}} & 0 \\ K_3 + \sqrt{3}K_5 & 0 & 0 & 0 & K_6 + \sqrt{3}K_8 \end{pmatrix} \begin{matrix} \tilde{y}\tilde{z} & \tilde{z}\tilde{x} & 3\tilde{z}^2 - r^2 & \tilde{x}^2 - \tilde{y}^2 & \tilde{x}\tilde{y} \end{matrix} \quad (19)$$

where for convenience of presentation we have changed the order of the quadrupole components. We can then make a complex rotation to the local frame spherical harmonic basis by defining the linear combinations

$$\begin{aligned} Q_{\text{loc}}^0 &= Q_{3\tilde{z}^2 - r^2}, \\ Q_{\text{loc}}^{\pm 1} &= Q_{\tilde{x}\tilde{z}} \pm iQ_{\tilde{y}\tilde{z}} = \frac{1}{\sqrt{2}} (S^{\pm} S^{\tilde{z}} + S^{\tilde{z}} S^{\pm}), \\ Q_{\text{loc}}^{\pm 2} &= Q_{\tilde{x}^2 - \tilde{y}^2} \pm iQ_{\tilde{x}\tilde{y}} = \frac{1}{\sqrt{2}} (S^{\pm})^2, \quad (20) \end{aligned}$$

where $S^\pm \equiv S^x \pm iS^y$. Then, the Hamiltonian can be written in this frame as

$$\begin{aligned}
 H_{ij} = & \sum_{m \in \{1,2\}} \left[-K_\pm^m (Q_i^{+m} Q_j^{-m} + Q_i^{-m} Q_j^{+m}) \right. \\
 & + K_{\pm\pm}^m (\gamma_{ij} Q_i^{+m} Q_j^{+m} + \gamma_{ij}^* Q_i^{-m} Q_j^{-m}) \\
 & + K_{z\pm}^m (\zeta_{ij} (Q_i^{+m} Q_j^0 + Q_i^0 Q_j^{+m}) + \text{H.c.}) \Big] \\
 & + K_{zz} Q_i^0 Q_j^0 + K'_\pm (Q_i^{+1} Q_j^{-2} + Q_i^{-2} Q_j^{-1} + \text{H.c.}) \\
 & + K'_{\pm\pm} \left((\gamma_{ij} Q_i^{+1} Q_j^{+2} + \gamma_{ij}^* Q_i^{-1} Q_j^{-2}) + \text{H.c.} \right), \quad (21)
 \end{aligned}$$

which closely parallels the form of Eq. (16). Each basis may be useful for identifying interesting symmetric combinations of parameters. In practice, we can always map back to the global basis Eq. (9) for computational purposes, where there are no complex phase factors appearing in the Hamiltonian. The mappings are given in Appendix B.

III. IRREPS, MULTIPOLES, AND SYMMETRY-BROKEN PHASES

In this section, we study the Hamiltonian Eq. (16) in more detail, by identifying linear combinations of quadrupole operators on each tetrahedron which transform irreducibly under the point-group symmetry of a tetrahedron, T_d . This is equivalent to identifying the set of possible translationally symmetric symmetry-breaking patterns and their order parameters. An alternative statement is that these irreducible multiplets define a set of symmetric normal modes for fluctuations on each tetrahedron. This method has been used to great success in the study of the dipolar Hamiltonian and its phase diagram [77–79,87]. Given the remarkable structure of the interaction matrix in the local frame [Eq. (16)], one may guess that the phase structure looks much like that of the dipolar case but with all phases involving the local-xy components “doubled.” Indeed, we see that this is the case.

A. Irreducible representation multiplets

For each tetrahedron, there are 20 linearly independent quadrupole operators, indexed as Q_μ^a . They transform in a 20-dimensional reducible representation of T_d . By decomposing this into its irreducible components, we can identify multiplets of operators which are equivalent under symmetry and whose eigenstates have the same energies. In other words, this decomposition block diagonalizes the interaction matrix, with each block labeled by an irrep. Each block may then be further diagonalized, and the multiplet with the lowest energy gives the zero-temperature semiclassical ground states on a single tetrahedron.

The 20-dimensional representation is a tensor product of the permutations of the sublattice index and the rotation

of the five quadrupole operators given by the Wigner D -matrix:

$$Q_\mu^a \mapsto \sum_{\nu,b} \pi_{\mu\nu} D^{ab} Q_\nu^b. \quad (22)$$

Direct calculation gives the reduction [92]

$$\begin{aligned}
 \pi \otimes (t_{2g} \oplus e_g) &= (A_1 \oplus E \oplus T_1 \oplus 2T_2)_{t_{2g}} \\
 &\quad \oplus (E \oplus T_1 \oplus T_2)_{e_g} \\
 &= A_1 \oplus 2E \oplus 2T_1 \oplus 3T_2, \quad (23)
 \end{aligned}$$

where π is a four-dimensional permutation representation. From this decomposition, we can already see the “doubling” of the easy-plane modes relative to the dipolar case. To see this, first note that the vectorlike component of a quadrupole transforms as t_{2g} , while a dipole transforms as t_{1g} . The irrep decomposition for dipoles is $\pi \otimes t_{1g} = A_2 \oplus E \oplus T_2 \oplus 2T_1$ [77,78,90]. To compare this to Eq. (23), we relate $A_1^{\text{quad}} \sim A_2^{\text{dip}}$, $T_1^{\text{quad}} \sim T_2^{\text{dip}}$, and $T_2^{\text{quad}} \sim T_1^{\text{dip}}$. In the dipolar case, the E , T_2 , and one of the T_1 irreps involve only the local-xy components [77,78,90], and in the quadrupole case there is one extra copy of each of these irreps.

B. Multipole decomposition

Following Ref. [78], we can explicitly construct the irreducible multiplets by decomposing the multipole moments of a single tetrahedron into irreducible pieces—multipoles are irreducible representations of $O(3)$ which become reducible when restricting to the T_d subgroup. Here, we show that the 20-dimensional representation cleanly separates into the five-component net quadrupole moment, the seven-dimensional octupole moment, and a residual eight-component “toroidal quadrupole moment.” These further break down under the point-group symmetries to yield the decomposition in Eq. (23).

1. Quadrupole moment

First, we construct the net quadrupole moment tensor

$$Q_i^{\alpha\beta} = \sum_{\mu} Q_{i\mu}^{\alpha\beta}. \quad (24)$$

This naturally decomposes as $E \oplus T_2$, since a single quadrupole decomposes as such using Eq. (6), corresponding to trace-free diagonal and symmetric off-diagonal components, respectively, accounting for five of 20 components.

2. Octupole moment

Next, we construct a rank-3 moment tensor, which will contain the remaining irrep components,

$$\mathcal{M}_i^{\alpha\beta\gamma} = \sum_{\mu} \hat{r}_i^\alpha Q_{i\mu}^{\beta\gamma} = \sum_{\mu} \hat{z}_i^\alpha Q_{i\mu}^{\beta\gamma}, \quad (25)$$

where $\mathbf{r}_i$ is the displacement of corner i from the center of the tetrahedron. This is symmetric trace-free in the second two indices and so contains $3 \times 5 = 15$ independent components. We can extract the remaining irreps by decomposing $\mathcal{M}$ into irreducible components. The decomposition of a general rank-3 tensor into irreducible representations of $O(3)$ is given in Ref. [93]. The obvious component is the octupole tensor, which is obtained by symmetrizing and trace-subtracting $\mathcal{M}$. We fully symmetrize all the indices, defining the tensor

$$S_i^{\alpha\beta\gamma} = \mathcal{M}_i^{(\alpha\beta\gamma)}, \quad (26)$$

where parentheses indicate averaging over all permutations of the contained indices. Next, we obtain its vector trace

$$\chi_i^\alpha = S_i^{\alpha\beta\beta}, \quad (27)$$

with summation of the repeated index, from which the octupole moment is [93]

$$\mathcal{O}_i^{\alpha\beta\gamma} = S_i^{\alpha\beta\gamma} - \frac{1}{5}(\chi_i^\alpha \delta^{\beta\gamma} + \chi_i^\beta \delta^{\gamma\alpha} + \chi_i^\gamma \delta^{\alpha\beta}), \quad (28)$$

where $\delta^{\alpha\beta}$ is the Kronecker delta. The octupole tensor transforms in a seven-dimensional irreducible representation of $O(3)$ and is further reducible when restricted to the subgroup $T_d \subseteq O(3)$. To obtain the irreducible components under T_d , we define the following rank-2 tensor:

$$\bar{\mathcal{O}}_i^{\alpha\beta} = |\epsilon_{\alpha\gamma\gamma}| \mathcal{O}_i^{\rho\gamma\beta}, \quad (29)$$

where ϵ is the fully antisymmetric Levi-Civita symbol, so that $|\epsilon|$ is fully symmetric and off diagonal [94]. One can check that all diagonal elements $\bar{\mathcal{O}}^{\alpha\alpha}$ are equal, so it has only seven independent degrees of freedom. Its trace transforms in the A_1 irrep, while its off-diagonal symmetric (antisymmetric) components transform in the T_2 (T_1) irrep. This accounts for all seven of the octupole moment components.

3. Toroidal quadrupolar moment

The remaining eight degrees of freedom are contained in the so-called residue tensor [95]

$$\mathcal{R}_i^{\alpha\beta} = \epsilon_{\alpha\gamma\gamma} \mathcal{M}_i^{\rho\gamma\beta}. \quad (30)$$

Physically, this tensor can be described as a *toroidal quadrupole moment*. The analogous tensor in the dipolar case is the toroidal dipole moment, $\sum_i \mathbf{r}_i \times \mathbf{S}_i$, which is saturated in the chiral Palmer-Chalker ground states [78]. The tensor $\mathcal{R}$ may be written schematically as $\mathcal{R} = \sum_i \mathbf{r}_i \times \mathbf{Q}_i$, where the cross product is taken with the first component of the quadrupole tensor $\mathbf{Q}$. This tensor has zero trace. Its two independent diagonal elements transform in the 2D E irrep. Its off-diagonal symmetric components

TABLE I. Irreducible symmetry multiplets of quadrupolar operators on a single tetrahedron obtained from the multipole construction. The first column lists the irreps from the decomposition Eq. (23). The second lists the (unnormalized) operator multiplets in terms of multipole tensors, and the third column lists the corresponding multipole moment of the tetrahedron from which this multiplet descended. The fourth and fifth list the decomposition in the t_{2g} and e_g sectors, respectively, using Eq. (11) in terms of the analogous modes found in the dipolar model [4,77,78]. Here, we use the shorthand AIAO for all-in-all-out; PC for Palmer-Chalker; col-FM for collinear ferromagnet (called $T_{1\parallel}$ in Ref. [78]); biax-AFM for biaxial antiferromagnet (called $T_{1\perp}$ in Refs. [78,87]); and SFM for easy-plane splayed ferromagnet (called $T_{1,\text{planar}}$ in Refs. [77,78]).

Irrep	Order parameter	Moment	t_{2g}	e_g
A_1	$\text{Tr}[\bar{\mathcal{O}}]$	Octupole	AIAO	...
E	$\mathcal{Q}^{\alpha\alpha}$	Quadrupole	...	ψ_2/ψ_3
E	$\mathcal{R}^{\alpha\alpha}$	Toroidal quadrupole	ψ_2/ψ_3	...
T_1	$\epsilon_{\alpha\beta\gamma} \bar{\mathcal{O}}^{\beta\gamma}$	Octupole	PC	-PC
T_1	$ \epsilon_{\alpha\beta\gamma} \mathcal{R}^{\beta\gamma}$	Toroidal quadrupole	PC	+PC
T_2	$ \epsilon_{\alpha\beta\gamma} \mathcal{Q}^{\beta\gamma}$	Quadrupole	col-FM	...
T_2	$ \epsilon_{\alpha\beta\gamma} \bar{\mathcal{O}}^{\beta\gamma}$	Octupole	biax-AFM	-SFM
T_2	$\epsilon_{\alpha\beta\gamma} \mathcal{R}^{\beta\gamma}$	Toroidal quadrupole	biax-AFM	+SFM

transform in the T_1 irrep and its antisymmetric components transform in the T_2 irrep [96], thus accounting for the remaining eight degrees of freedom.

This exhausts all of the irreps and provides a canonical global frame orthonormal basis for them, listed in Table I. Each irreducible multiplet derived this way is a linear combination of the 20 independent quadrupole operators on a single tetrahedron, of the form

$$[\mathcal{O}_{\Gamma,r}^\alpha]_i = \sum_{i \in \Gamma} \sum_{a=1}^5 [\psi_{\Gamma,r}^\alpha]_i^a \mathcal{Q}_i^a, \quad (31)$$

where Γ labels an irreducible representation of T_d , r labels the copies of each irrep, and $\alpha \in \{1 \dots d_\Gamma\}$ labels its components, where d_Γ is the dimension of the irrep. The coefficients $\psi_{\Gamma,r}^\alpha$ form a 20-component unit vector. Note that the redundant third component of each E irrep can be removed by taking the inner product of these three-component vector multiplets with $\hat{\mathbf{x}}_1$ and $\hat{\mathbf{y}}_1$ from Eq. (10) to extract the two nontrivial components, since the inner product with $[111]$ computes the trace of the corresponding tensor, which is zero. One can check that the 20 components from this decomposition indeed form an orthogonal basis.

In Table I, we have given a description of the projections of each $\psi_{\Gamma,r}^\alpha$ into the t_{2g} and e_g sectors in terms of normal modes of the dipolar case. The resulting configurations are described in the last two columns in Table I in terms of their equivalent configurations in the dipole case [78]. We know

TABLE II. Choice of orthonormal basis for the irreducible representations of T_d under which the four quadrupoles in a tetrahedron transform, where we have separated the t_{2g} and e_g components. The basis obtained in the multipole decomposition defined by the order parameters in Table I contains linear combinations of t_{2g} and e_g components. Here, we use the abbreviations for comparison with the corresponding degrees of freedom in the dipolar case [77,78]: AIAO = all-in–all-out; PC = Palmer-Chalker; SI = spin ice; SFM = splayed ferromagnet. Irreps from the t_{2g} sector reproduce those of the dipolar model, while ground states in the e_g sector duplicate the easy-plane irreps. These are mixed by the couplings $J'_\pm$ and $J'_{\pm\pm}$ in Eq. (14). The 20-component vectors are separated by sublattice, where each resulting five-component vector is given in the basis of Eq. (6), with the t_{2g} and e_g contributions separated by a vertical line. $\mathcal{N}$ is a normalization such that $\psi_{\Gamma,r}^\alpha$ is a unit vector. An analogous basis in the spherical harmonics local frame of Sec. II C is given in Appendix D.

Irrep	t_{2g}	e_g	$\mathcal{N}[\psi_{\Gamma,r}^\alpha]_1^a$	$\mathcal{N}[\psi_{\Gamma,r}^\alpha]_2^a$	$\mathcal{N}[\psi_{\Gamma,r}^\alpha]_3^a$	$\mathcal{N}[\psi_{\Gamma,r}^\alpha]_4^a$
$A_1^{(t_{2g})}$	AIAO	0	$(-1, -1, -1 0, 0)$	$(1, 1, -1 0, 0)$	$(1, -1, 1 0, 0)$	$(-1, 1, 1 0, 0)$
$E^{(t_{2g})}$	$\begin{pmatrix} \psi_2 \\ \psi_3 \end{pmatrix}$	0	$(-1, -1, 2 0, 0)$ $(-1, 1, 0 0, 0)$	$(1, 1, 2 0, 0)$ $(1, -1, 0 0, 0)$	$(1, -1, -2 0, 0)$ $(1, 1, 0 0, 0)$	$(-1, 1, -2 0, 0)$ $(-1, -1, 0 0, 0)$
$E^{(e_g)}$	0	$\begin{pmatrix} \psi_2 \\ \psi_3 \end{pmatrix}$	$(0, 0, 0 -1, 0)$ $(0, 0, 0 0, 1)$	$(0, 0, 0 -1, 0)$ $(0, 0, 0 0, 1)$	$(0, 0, 0 -1, 0)$ $(0, 0, 0 0, 1)$	$(0, 0, 0 -1, 0)$ $(0, 0, 0 0, 1)$
$T_1^{(t_{2g})}$	$\begin{pmatrix} \text{PC}_x \\ \text{PC}_y \\ \text{PC}_z \end{pmatrix}$	0	$(0, -1, 1 0, 0)$ $(1, 0, -1 0, 0)$ $(-1, 1, 0 0, 0)$	$(0, -1, -1 0, 0)$ $(1, 0, 1 0, 0)$ $(1, -1, 0 0, 0)$	$(0, 1, 1 0, 0)$ $(-1, 0, 1 0, 0)$ $(-1, -1, 0 0, 0)$	$(0, 1, -1 0, 0)$ $(-1, 0, -1 0, 0)$ $(1, 1, 0 0, 0)$
$T_1^{(e_g)}$	0	$\begin{pmatrix} \text{PC}_x \\ \text{PC}_y \\ \text{PC}_z \end{pmatrix}$	$(0, 0, 0 \sqrt{3}, 1)$ $(0, 0, 0 -\sqrt{3}, 1)$ $(0, 0, 0 0, -2)$	$(0, 0, 0 -\sqrt{3}, -1)$ $(0, 0, 0 \sqrt{3}, -1)$ $(0, 0, 0 0, -2)$	$(0, 0, 0 -\sqrt{3}, -1)$ $(0, 0, 0 -\sqrt{3}, 1)$ $(0, 0, 0 0, 2)$	$(0, 0, 0 \sqrt{3}, 1)$ $(0, 0, 0 \sqrt{3}, -1)$ $(0, 0, 0 0, 2)$
$T_{2,\text{ice}}^{(t_{2g})}$	$\begin{pmatrix} \text{SI}_x \\ \text{SI}_y \\ \text{SI}_z \end{pmatrix}$	0	$(1, 1, 1 0, 0)$ $(1, 1, 1 0, 0)$ $(1, 1, 1 0, 0)$	$(1, 1, -1 0, 0)$ $(-1, -1, 1 0, 0)$ $(2, -1, -1 0, 0)$	$(-1, 1, -1 0, 0)$ $(1, -1, 1 0, 0)$ $(2, 1, -1 0, 0)$	$(-1, 1, 1 0, 0)$ $(-1, 1, 1 0, 0)$ $(2, 1, 1 0, 0)$
$T_{2,\text{planar}}^{(t_{2g})}$	$\begin{pmatrix} \text{SFM}_x \\ \text{SFM}_y \\ \text{SFM}_z \end{pmatrix}$	0	$(-1, 2, -1 0, 0)$ $(-1, -1, 2 0, 0)$ $(0, 0, 0 -1, \sqrt{3})$	$(-1, 2, 1 0, 0)$ $(1, 1, 2 0, 0)$ $(0, 0, 0 1, -\sqrt{3})$	$(1, 2, 1 0, 0)$ $(-1, 1, 2 0, 0)$ $(0, 0, 0 1, -\sqrt{3})$	$(1, 2, -1 0, 0)$ $(1, -1, 2 0, 0)$ $(0, 0, 0 1, \sqrt{3})$
$T_{2,\text{planar}}^{(e_g)}$	0	$\begin{pmatrix} \text{SFM}_x \\ \text{SFM}_y \\ \text{SFM}_z \end{pmatrix}$	$(0, 0, 0 -1, -\sqrt{3})$ $(0, 0, 0 1, \sqrt{3})$ $(0, 0, 0 2, 0)$	$(0, 0, 0 1, \sqrt{3})$ $(0, 0, 0 2, 0)$ $(0, 0, 0 2, 0)$	$(0, 0, 0 1, -\sqrt{3})$ $(0, 0, 0 -1, -\sqrt{3})$ $(0, 0, 0 -2, 0)$	$(0, 0, 0 1, \sqrt{3})$ $(0, 0, 0 1, \sqrt{3})$ $(0, 0, 0 -2, 0)$

from the dipole case that a local symmetry-adapted frame is most well suited to understand the ways that the irreps mix. In Table II, we give a basis for the irreducible multiplets appropriate for the mixed local-global frame introduced in Sec. II C. This table makes clear that the e_g components of the quadrupoles duplicate all of the easy-plane components of the t_{2g} sector. These multiplets are illustrated in Fig. 2, in which the vectors $[\psi_{\Gamma,r}]_\mu$ are converted to symmetric trace-free tensors and plotted as spherical harmonics using

the same method as in Fig. 1. The t_{2g} and e_g components are mapped to vectors according to Eq. (6), which are shown in magenta and cyan, respectively, which can be compared directly to corresponding vector configurations in Ref. [78].

C. Decoupled multiplets and canting

Symmetry forbids linear couplings between multiplets in different irreps. However, multiple copies of a single irrep may couple, leading to a mixing of multiplets within each

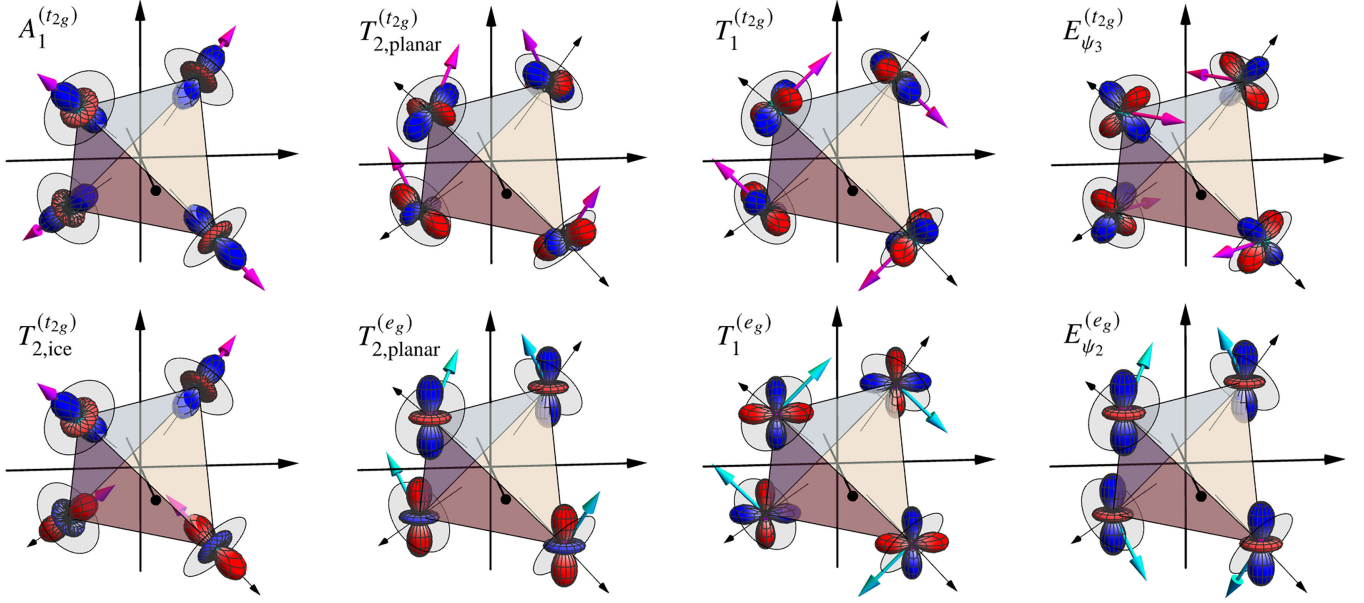


FIG. 2. Illustrations of irreducible symmetry multiplets in the basis defined in Table II. Quadrupole operators on each site of form $\sum_{a=1}^5 [\psi_{\Gamma,r}^a] Q_\mu^a$ are depicted by mapping the five coefficients to a symmetric trace-free tensor [using Eq. (53)] and plotting the corresponding orbitals as in Fig. 1. Magenta (cyan) arrows depict the corresponding decomposition of the coefficients into a t_{2g} and e_g vector using Eq. (11), illustrating how these correspond to analogous modes in the dipolar Hamiltonian (where dipoles are represented as vectors) [4,77,78].

irrep which varies continuously as the parameters in the Hamiltonian are varied. Given an orthonormal choice of irrep multiplets $\mathcal{O}_{\Gamma,r}$, the Hamiltonian can be put in a block-diagonalized form in terms of matrices $\mathcal{J}_\Gamma$:

$$H = \frac{1}{2} \sum_t \sum_\Gamma \sum_{r,r'} [\mathcal{J}_\Gamma]_{r,r'} \mathcal{O}_{\Gamma,r} \cdot \mathcal{O}_{\Gamma,r'}. \quad (32)$$

If there is more than one multiplet of a given irrep, symmetry allows for a coupling between them, i.e., between $r \neq r'$. This coupling is removed by a parameter-dependent orthogonal transform U which diagonalizes the symmetric real matrix $\mathcal{J}_\Gamma$, defining new multiplets

$$\tilde{\mathcal{O}}_{\Gamma,\tilde{r}} = \sum_r [U(J_1, \dots, J_9)]_{\tilde{r},r} \mathcal{O}_{\Gamma,r}. \quad (33)$$

In the dipolar case, there is only one repeated irrep, which appears twice. Its coupling is removed by a parameter-dependent $SO(2)$ rotation, causing the dipoles to cant continuously as the parameters are tuned [4,77,78]. In the quadrupolar case, the T_1 and E irreps both appear twice and require an $SO(2)$ rotation to decouple, while the T_2 irrep appears three times, requiring an $SO(3)$ rotation to decouple. Once we have rotated to the proper irreducible multiplets $\tilde{\mathcal{O}}_{\Gamma,\tilde{r}}$, the Hamiltonian can be expressed as a sum of decoupled quadratic multiplets:

$$H = \frac{1}{2} \sum_t \sum_{\Gamma,\tilde{r}} J_{\Gamma,\tilde{r}} |\tilde{\mathcal{O}}_{\Gamma,\tilde{r}}|^2. \quad (34)$$

This form of the Hamiltonian allows one to read off the ground states at the semiclassical level from the relative $J_{\Gamma,\tilde{r}}$ when the quadrupolar operators are normalized and when the quadrupoles are not overly constrained (discussed further in Sec. V). For the unique one-dimensional A_1 irrep, no decoupling is required, and we have simply

$$\mathcal{J}_{A_1} = 3J_{zz}. \quad (35)$$

For the remaining irreps, we work in the basis given in Table II and use the corresponding local frame defined in Sec. II B.

For the E irrep, we have, in terms of the local frame parameters given in Eq. (14),

$$[\mathcal{J}_E]_{r,r'} = -\frac{1}{6} \begin{pmatrix} J_\pm^{t_{2g}} & J'_\pm \\ J'_\pm & J_\pm^{e_g} \end{pmatrix}, \quad (36)$$

which can be diagonalized to give the energies of the two decoupled E irreps:

$$J_{E\pm} = -\frac{1}{3} (J_\pm^{t_{2g}} + J_\pm^{e_g}) \pm \frac{1}{3} \sqrt{(J_\pm^{t_{2g}} - J_\pm^{e_g})^2 + 4(J'_\pm)^2}, \quad (37)$$

where the $SO(2)$ canting angle is given by

$$\tan(2\theta_E) = \frac{2J'_\pm}{J_\pm^{e_g} - J_\pm^{t_{2g}}}. \quad (38)$$

For the T_1 irrep, the coupling is given by

$$[\mathcal{J}_{T_1}]_{r,r'} = \frac{1}{2} \begin{pmatrix} J_{\pm}^{t_{2g}} - 2J_{\pm\pm}^{t_{2g}} & -(J'_{\pm} + 2J'_{\pm\pm}) \\ -(J'_{\pm} + 2J'_{\pm\pm}) & J_{\pm}^{e_g} - 2J_{\pm\pm}^{e_g} \end{pmatrix}, \quad (39)$$

and the eigenvalues are

$$J_{T_1\pm} = (J_{\pm}^{t_{2g}} - 2J_{\pm\pm}^{t_{2g}}) + (J_{\pm}^{e_g} - 2J_{\pm\pm}^{e_g}) \pm \sqrt{[(J_{\pm}^{t_{2g}} - 2J_{\pm\pm}^{t_{2g}}) - (J_{\pm}^{e_g} - 2J_{\pm\pm}^{e_g})]^2 + 4(J'_{\pm} + 2J'_{\pm\pm})^2}. \quad (40)$$

The SO(2) canting angle which decouples them is

$$\tan(2\theta_{T_1}) = \frac{2(J'_{\pm} + 2J'_{\pm\pm})}{(J_{\pm}^{t_{2g}} - 2J_{\pm\pm}^{t_{2g}}) - (J_{\pm}^{e_g} - 2J_{\pm\pm}^{e_g})}. \quad (41)$$

For the triple T_2 irrep, we have

$$[\mathcal{J}_{T_2}]_{r,r'} = \begin{pmatrix} J_{\pm}^{t_{2g}} + 2J_{\pm\pm}^{t_{2g}} & 2J_{z\pm}^{t_{2g}} & 2J'_{\pm\pm} - J'_{\pm} \\ 2J_{z\pm}^{t_{2g}} & -J_{zz}/2 & 2J_{z\pm}^{e_g} \\ 2J'_{\pm\pm} - J'_{\pm} & 2J_{z\pm}^{e_g} & J_{\pm}^{e_g} + 2J_{\pm\pm}^{e_g} \end{pmatrix}. \quad (42)$$

Unfortunately there is no straightforward way to express analytically the eigenvalues of such a 3×3 matrix or to express the formula for the SO(3) rotation which diagonalizes it. This prevents us from performing the type of analysis done in Ref. [78] in which the parameters were reexpressed as functions of the eigenvalues, which greatly aided in parametrizing the phase diagram and all degenerate intersections of phases. Nevertheless, there is no issue in numerically diagonalizing the matrix. It is useful, however, to define a canting angle between the two easy-plane T_2 modes:

$$\tan(2\theta_{T_{2,\text{planar}}}) = \frac{2(2J'_{\pm\pm} - J'_{\pm})}{(J_{\pm}^{e_g} + 2J_{\pm\pm}^{e_g}) - (J_{\pm}^{t_{2g}} + 2J_{\pm\pm}^{t_{2g}})}, \quad (43)$$

which decouples them when both $J_{z\pm}$ couplings are zero. It makes sense, in general, to first determine each of the three above-defined canting angles between the easy-plane modes and rotate into the corresponding basis which decouples them. This produces new values for the two $z\pm$ couplings, and the remaining difficulty is diagonalizing the T_2 sector, which is, in general, not possible to do analytically unless one of the resulting $z\pm$ couplings is zero.

D. Symmetry-breaking phases and order parameters

At the level of irreps, we expect there to be nominally four phases, one for each unique irrep in the decomposition. The exception is the E irrep, where in the dipolar case it is known that a fluctuation-driven order-by-disorder mechanism splits this irrep into multiple symmetry-inequivalent phases. We find a similar situation for quadrupoles, discussed further in Sec. VI.

Since all interactions are within a single unit cell, and due to the corner-sharing nature of the pyrochlore lattice, it is possible to stabilize only zero-momentum ground states. To define order parameters for the symmetry-breaking patterns, let

$$\mathcal{Q}_{\mu}^a = \frac{1}{N_S} \sum_{t \in A} Q_{t,\mu}^a \quad (44)$$

be the net quadrupole moment of the entire system resolved by sublattice [written as a five-component vector via Eq. (6)], where each site is indexed by an A tetrahedron t and a sublattice μ . Summing over all A tetrahedra is equivalent to summing over all primitive fcc unit cells; thus, each site is included once. We have added a normalization factor N_S such that the maximum normalized quadrupole moment per site is unity, which depends on the spin quantum number S and is given later in Eq. (58) and discussed in more detail there.

For each irrep, we define a projector into the corresponding subspace of the 20-dimensional space of single-tetrahedron degrees of freedom:

$$P^{(\Gamma)} = \sum_r \sum_{\alpha} \psi_{\Gamma,r}^{\alpha} \otimes [\psi_{\Gamma,r}^{\alpha}]^{\dagger}, \quad (45)$$

in terms of an orthonormal basis such as the one given in Table II (the projector itself is independent of the basis). We extract the projections of the total quadrupole moment to each irrep:

$$[\phi_{\Gamma}]_{\mu}^a = \frac{1}{N} \sum_{\nu=1}^4 \sum_{b=1}^5 P_{\mu,a;\nu,b}^{(\Gamma)} \mathcal{Q}_{\nu}^b, \quad (46)$$

where N is the number of lattice sites, and define scalar order parameters for each irrep:

$$\Phi_{\Gamma} = |\langle \phi_{\Gamma} \rangle| \in [0, 1], \quad (47)$$

where the angle brackets indicate the quantum expectation value at fixed temperature.

IV. STRUCTURE OF THE SEMICLASSICAL PHASE DIAGRAM

We now turn to an exploration of the basic structure of the phase diagram. To do so, we investigate how the energies of the single-tetrahedron irreducible symmetry multiplets vary as functions of the nine couplings. The single-tetrahedron mean-field ground states are the maximal weight eigenstates of the lowest-energy multiplet operators. These then form zero-momentum ground states of the entire system by translating them to all A tetrahedra, which is a ground state on all of the B tetrahedra as well. This is analogous to the Luttinger-Tisza type of analysis applied to dipolar Hamiltonians [97,98], and we refer to it

as such. Later, in Sec. V, we discuss how constraints arising from the quantum spin Hilbert space and the behavior of semiclassical quadrupoles modify these pictures. In particular, while we do expect that the minimal irrep captures the correct symmetry breaking in the ground state, it may occur that additional irreps are also active. In Sec. VI, we discuss how the E irrep ground state is split into multiple distinct phases by quantum effects and fluctuations not captured by mean-field theory. While we do not present a complete picture of the entire phase diagram, we highlight (at the level of the minimal energy irreps) some of its important subspaces and intersection points.

With nine parameters to vary, the phase diagram is very difficult to visualize. Furthermore, due to the presence of three copies of the T_2 irrep, it is not possible to use the method of Ref. [78] to parametrize all of the intersections of phases. Nevertheless, we can gain significant intuition for the general structure by using the fact that the Hamiltonian can be put into a form which directly parallels the dipolar one, Eq. (16)(21). For example, if we turn off all couplings except those in the t_{2g} sector in Eq. (16), then it is clear that the phase diagram (again at the level of irrep energies) must be the same as that of the dipolar case, for which a comprehensive picture is available in Ref. [78]. It also must be the case that by turning off the easy-plane t_{2g} couplings, leaving only $Q_{t_{2g}}^{\text{loc}}$ and the two e_g degrees of freedom, the Hamiltonian again has the same form as the dipolar one, so this limit of the phase diagram is also the same at the level of irrep energies. On the other hand, we can do the same in Eq. (21) by turning off either the $m = \pm 1$ or the $m = \pm 2$ couplings, and again the Hamiltonian reduces to a form identical to the dipolar case and will again show the same phase diagram. This is illustrated in Fig. 3. We have plotted phase diagrams in which the coupling between easy-axis and easy-plane modes is set to zero and either the (a) t_{2g} , (b) e_g , (c) $|m| = 1$, or (d) $|m| = 2$ sectors are the ground states. This reproduces the analogous phase diagram found in the dipolar Hamiltonian [4,78], with phases labeled accordingly, but with different mixing of the easy-plane E , T_1 , and T_2 irreps as indicated by the varying colors.

We expect that, in fact, one can continuously rotate the parametrization in such a way that the Hamiltonian always reduces to the form of Eq. (16)(21) and the phase diagram looks the same but with a continuous rotation of the canting angles of the irreps. That is, rotating into the basis defined by the easy-plane canting angles given in Sec. III C, the Hamiltonian may, in general, be rewritten in the form of Eq. (16)(21) with new couplings $\tilde{J}_{\pm}^r$, $\tilde{J}_{\pm\pm}^r$, etc., but *without* any direct coupling between the two sets of easy-plane modes, i.e., with $\tilde{J}_{\pm}^r = \tilde{J}_{\pm\pm}^r = 0$. For example, if $J_{\pm}^r = J_{\pm\pm}^r = 0$ in Eq. (16), then $K'_{\pm}$ and $K'_{\pm\pm}$ are nonzero in Eq. (21).

To clearly exhibit the doubling of all easy-plane phases, we show in Fig. 4 a cut of the phase diagram which exhibits

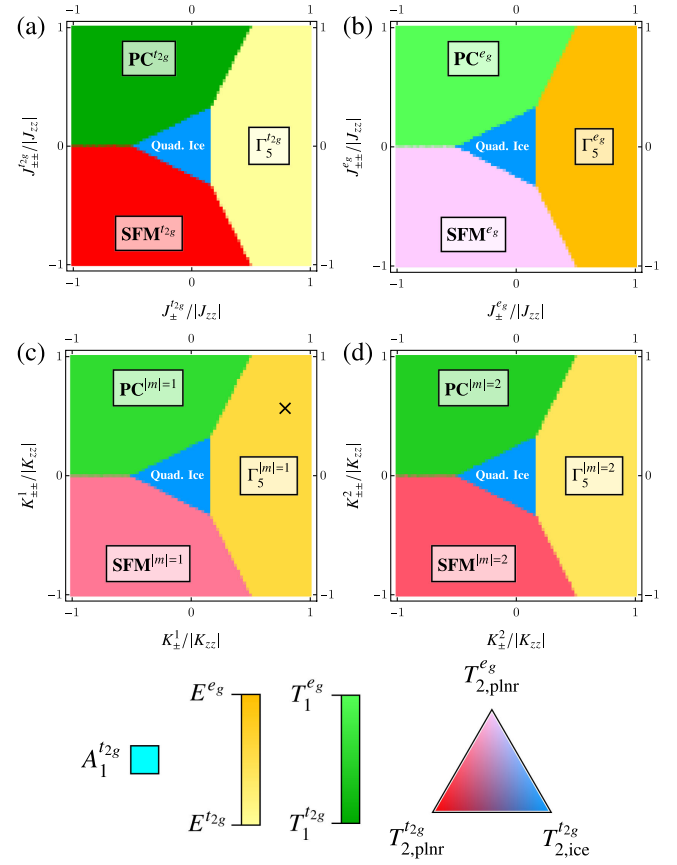


FIG. 3. Luttinger-Tisza phase diagrams with $z\pm$ couplings in either Eq. (16) or Eq. (21) set to zero and $J_{zz} > 0$, which reproduce the analogous ones of the dipolar model (unspecified parameters are zero). We have labeled the phases using the dipolar conventional names—Palmer-Chalker (PC, T_1), splayed ferromagnet (SFM, T_2), and Γ_5 (E). The analog of the spin ice phase is labeled as quadrupolar ice. (a) Phase diagram where the t_{2g} sector in Eq. (16) has minimal energy and (b) case where the e_g sector has minimal energy. (c) Phase diagram where the $|m| = 1$ sector in Eq. (21) has minimal energy and (d) case where the $|m| = 2$ sector has minimal energy. The phases are colored according to the canting angle of the ground state irrep as illustrated in the color legends below. The cross in (c) corresponds to the simulation parameters for Fig. 12.

all of the easy-plane phases bordering the all-in–all-out phase (an analogous phase diagram with quadrupolar spin ice in the middle is obtained by switching the sign of J_{zz}). This is achieved by setting $J_{\pm}^r$ to have opposite signs in the two sectors, and similarly for $J_{\pm\pm}^r$.

A. Dualities

In the dipolar Hamiltonian, it is known that there are two dualities—first, switching the sign of $J_{z\pm}$ is equivalent to a π pseudospin rotation about the easy axis, which maps each irrep to itself. Second, when $J_{z\pm} = 0$, switching the sign of $J_{\pm\pm}$ is equivalent to a $\pi/2$ rotation about the easy axis, which switches the Palmer-Chalker and splayed

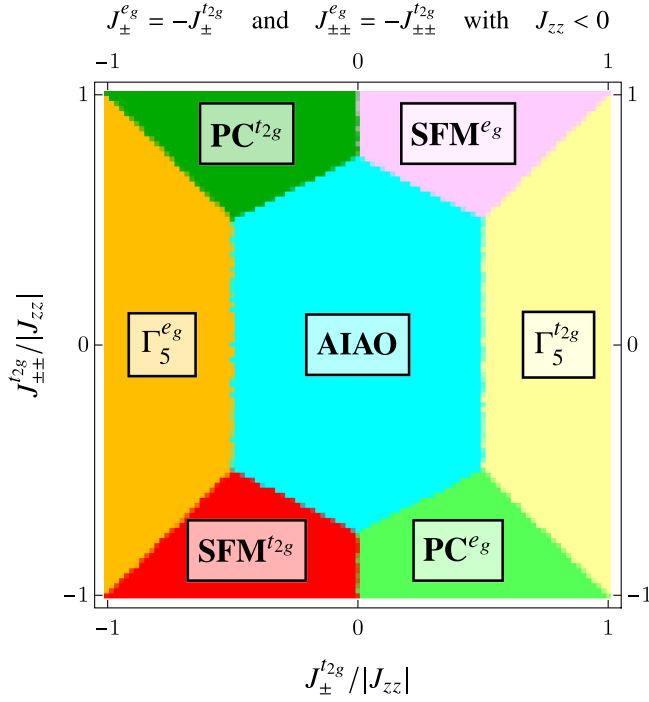


FIG. 4. A Luttinger-Tisza phase diagram cut which exhibits all easy-plane phases surrounding the quadrupolar all-in-all-out phase.

ferromagnetic phases (i.e., switches the easy-plane T_1 and T_2 irreps). Clearly, these dualities are also present in the Hamiltonian Eq. (16) when the coupling terms between the two easy-plane sectors, $J'_\pm$ and $J'_{\pm\pm}$, are zero. When they are nonzero, we can make a rotation between the two easy-plane sectors to remove them; then, both dualities are present with respect to the decoupled basis.

Additionally, Eq. (14) reveals a remarkable duality structure of the Hamiltonian, which *exchanges* the two

easy-plane sectors. We refer to this as antidiagonal duality, since it transposes the matrix Eq. (14) across the anti-diagonal. It is interesting to consider phase diagram cuts which are self-dual under this antidiagonal duality. We show examples of such cuts in Figs. 5(a) and 5(b). Figure 5(a) shows precisely such a cut with both $J'_{z\pm}$ couplings set to zero. This corresponds to making both easy-plane sectors from Figs. 3(a) and 3(b) degenerate, so all canting angles in each phase are degenerate.

Since both $J'_{z\pm}$ are zero in Fig. 5(a), we can also combine the antidiagonal duality with the two $J'_{\pm\pm}$ dualities, switching the sign of one of the $J'_{\pm\pm}$ couplings, in order to obtain an “anti-self-dual” phase diagram shown in Fig. 5(b). This phase diagram has the same form, but instead of having T_1 degenerate with T_1 and T_2 degenerate with T_2 in the two sectors, we have T_1 degenerate with T_2 and vice versa in the two sectors.

Lastly, Fig. 5(c) demonstrates the dualities under switching the signs of either $J'_{z\pm}$ coupling. Here, we take $J_{zz} > 0$ to put the quadrupolar ice phase in the center and vary $J_{z\pm}^{t2g}$ and $J_{z\pm}^{e_g}$, which continuously mixes the three T_2 irreps. This cut shows symmetry under flipping the sign of either of the $J_{z\pm}$ couplings.

B. Diabolical loci

Reference [78] demonstrated that in the phase diagram of the dipolar Hamiltonian there is a locus along which the doubly repeated irrep becomes degenerate with itself. Whereas a phase boundary occurs in codimension 1, meaning that a single parameter must be tuned to cross it, the locus on which an irrep can become degenerate with another copy of itself has codimension 2. This is a manifestation of level repulsion of matrix eigenvalues, due to the fact that symmetry does not forbid a coupling

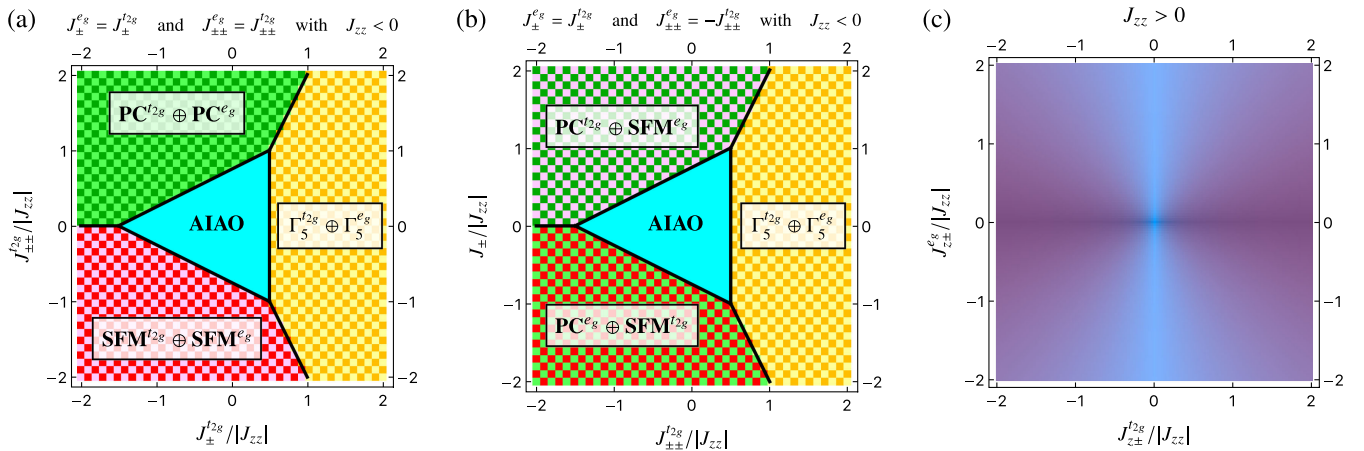


FIG. 5. Luttinger-Tisza phase diagram cuts illustrating different dualities of the Hamiltonian. (a) A phase diagram cut which is self-dual under the antidiagonal duality which exchanges the two easy-plane sectors. (b) An “anti-self-dual” cut which combines the antidiagonal duality with a duality switching the sign of one $J_{\pm\pm}$ coupling (when $J_{z\pm} = 0$). (c) A cut which demonstrates the duality under reversing the signs of either of the $J_{z\pm}$. The color legend is the same as in Fig. 3. Unspecified parameters are zero.

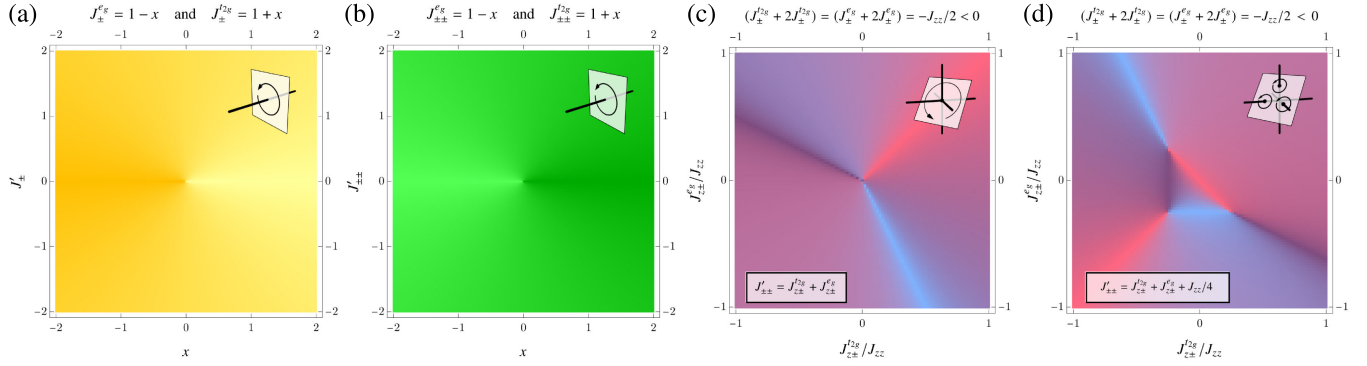


FIG. 6. Examples of Luttinger-Tisza phase diagram cuts which intersect the diabolical loci where multiplets in the same irrep become degenerate with each other. Insets illustrate the geometry of the cuts relative to the loci that they intersect. (a) Cutting the E locus. (b) Cutting the T_1 locus. (c) Cutting through the triply degenerate T_2 locus, where all three T_2 irreps are degenerate. (d) The triple T_2 locus sits at the intersection of three doubly T_2 loci, and here we make a cut of the phase diagram which intersects all three, showing three singular points. The color legend is the same used in Fig. 3. Unspecified couplings are zero.

between copies of the same irrep. For example, using Eq. (36)(39), in order to make the two E irreps or the two T_1 irreps degenerate, it is clear that we must set the two diagonal elements of the matrix to be the same and the off-diagonal matrix element to be zero, thus requiring two parameters to be tuned to find this locus. As such, these loci are analogs of diabolical points (conical intersections) in quantum mechanics or diabolical loci in quantum field theory [99]. They may be viewed as sources of Berry curvature in the space of couplings, in the sense that if the system is adiabatically transported around a path linking the locus, the corresponding ground state canting angle must wind nontrivially. Figures 6(a) and 6(b) show examples of phase diagram cuts which intersect the diabolical loci of the E and T_1 phases.

One particularly interesting aspect of the pyrochlore quadrupole Hamiltonian is that it contains three copies of the T_2 irrep. Making any two of them degenerate again requires tuning two parameters, but it is also possible for all three to be degenerate. This occurs in codimension 5, because we must set the three off-diagonal elements to be zero and set two pairs of diagonal entries to be the same. Clearly, all three of the double-degenerate T_2 loci must intersect at the triple T_2 locus. Figure 6(c) shows a cut through the triple-degenerate locus, showing a singularity at the center around which variation in all three T_2 irrep components can be seen. Figure 6(d) shows a cut where all three double-degenerate T_2 singularities are visible.

V. QUANTUM QUADRUPOLES

For a dipolar Hamiltonian, involving only bilinears of spin operators, the standard semiclassical approximation is to replace the spin operators by classical unit-length vectors. The situation for quadrupoles is much more subtle, and a semiclassical treatment requires a careful analysis.

For example, while it is true that the quadrupole operators are bilinears of spin operators, if we simply replace those spin operators with vectors, then we would be restricted to describe only uniaxial quadrupole configurations and would fail to capture the biaxial configurations which appear as ground states of the single-tetrahedron Hamiltonian illustrated in Fig. 2. In this section, we study the problem of the semiclassical treatment of quadrupoles in detail. We briefly review for juxtaposition the case of dipoles, where the semiclassical configuration space is the unit sphere in three dimensions.

A. Dipolar coherent states and unit vectors

We begin by briefly reviewing the standard approach for dipoles, in order to contrast it with what we find for quadrupoles. Consider the problem of identifying the mean-field ground state of a bilinear dipole Hamiltonian of the form Eq. (5) without the quadrupolar terms. At a single site, the mean-field Hamiltonian has the form

$$H_{S,j}^{\text{MF}} = \sum_j \langle S_i^\alpha \rangle [\mathcal{J}_S]_{ij}^{\alpha\beta} S_j^\beta \equiv -|\mathbf{h}_j| \hat{\mathbf{h}}_j \cdot \mathbf{S}_j, \quad (48)$$

where $\mathbf{h}_j$ is the local molecular field due to the neighboring spin configurations. The mean-field ground state, which neglects entanglement between different spins, must be the maximum weight eigenstate of the operator $\hat{\mathbf{h}} \cdot \mathbf{S}$. Such a state is a coherent state:

$$|\hat{\mathbf{n}}\rangle = \text{max positive weight eigenstate of } \hat{\mathbf{n}} \cdot \mathbf{S} \\ = R(\theta, \phi)|S\rangle, \quad (49)$$

where $\hat{\mathbf{n}}$ is the direction of the dipole moment and $R(\theta, \phi)$ the rotation operator from the global z axis to $\hat{\mathbf{n}}$. The states $|\hat{\mathbf{n}}\rangle$ maximize the dipole moment $|\langle \mathbf{S} \rangle|$, such that it remains to minimize the interaction energy by adjusting the angular

directions $\hat{n}$. Thus, the semiclassical description of a dipolar Hamiltonian is in terms of unit-length three-component vectors, whose configuration space is a two-sphere, regardless of the spin quantum number. Semiclassical finite-temperature Monte Carlo simulations can be performed with respect to the classical energy functional

$$\begin{aligned} H_S^{\text{MC}} &= \sum_{ij} \sum_{\alpha\beta} \langle \hat{n}_i | S_i^\alpha | \hat{n}_i \rangle [\mathcal{J}_S]_{ij}^{\alpha\beta} \langle \hat{n}_j | S_j^\beta | \hat{n}_j \rangle \\ &= S^2 \sum_{ij} \sum_{\alpha\beta} \hat{n}_i^\alpha [\mathcal{J}_S]_{ij}^{\alpha\beta} \hat{n}_j^\beta, \end{aligned} \quad (50)$$

where the unit vectors $\hat{n}_i$ are varied, interpreted as varying the angular direction of the local expectation value of the dipole moment. This is equivalent to using a variational product state ansatz for the many-body wave function, $|\psi\rangle = \otimes_i |\hat{n}_i\rangle$. This reproduces the mean-field zero-temperature ground states and agrees with the lowest order of a high-temperature series expansion of the partition function [46]. The weighting of angular configurations on the surface of the two-sphere are uniform, because all of the spin operators $\hat{n} \cdot \mathbf{S}$ are unitarily related.

B. Quadrupolar coherent states and biaxial nematics

Now consider the same problem for a quadrupolar Hamiltonian. The mean-field Hamiltonian can be written

$$\begin{aligned} H_{Qj}^{\text{MF}} &= \sum_j \langle Q_i^{\alpha'\beta'} \rangle [\mathcal{J}_Q]_{ij}^{\alpha'\beta',\alpha\beta} Q_j^{\alpha\beta} \\ &\equiv -\text{Tr}[q_j^2]^{1/2} \text{Tr}[\hat{q}_j Q_j], \end{aligned} \quad (51)$$

where q is a symmetric trace-free tensor, $\text{Tr}[q^2]^{1/2}$ is its Frobenius norm, and $\hat{q}$ is the normalized form of the tensor with unit norm, describing the “angular configuration” analogous to $\hat{n}$. The ground states of such a Hamiltonian are maximal weight eigenstates of quadrupolar operators $\text{Tr}[\hat{q}Q]$, which we refer to as “quadrupolar coherent states”:

$$|\hat{q}\rangle = \text{max positive weight eigenstate of } \text{Tr}[\hat{q}Q]. \quad (52)$$

Such states are not generally constructed by simple rotations of a fixed state as in the dipolar coherent states Eq. (49). Only uniaxial quadrupole states can be written in this way, but the space of quadrupolar configurations also contains biaxial states. Rather, the tensor $\hat{q}$ lives on the unit four-sphere in the five-dimensional space of symmetric trace-free matrices, which parametrizes the set of quadrupolar coherent states in the same way that the two-sphere parametrizes the set of dipolar coherent states. The map from five-component vectors to symmetric tensors is given by

$$\begin{pmatrix} q_x \\ q_y \\ q_z \\ q_{3z^2-r^2} \\ q_{x^2-y^2} \end{pmatrix} \mapsto \begin{pmatrix} -\frac{q_{3z^2-r^2}}{\sqrt{6}} + \frac{q_{x^2-y^2}}{\sqrt{2}} & \frac{q_x}{\sqrt{2}} & \frac{q_y}{\sqrt{2}} \\ \frac{q_x}{\sqrt{2}} & -\frac{q_{3z^2-r^2}}{\sqrt{6}} - \frac{q_{x^2-y^2}}{\sqrt{2}} & \frac{q_z}{\sqrt{2}} \\ \frac{q_y}{\sqrt{2}} & \frac{q_z}{\sqrt{2}} & \frac{2q_{3z^2-r^2}}{\sqrt{6}} \end{pmatrix}. \quad (53)$$

We can interpret this four-sphere as the configuration space of a biaxial nematic with fixed volume. This is naively the natural candidate for the semiclassical configuration space of quantum quadrupoles, akin to the unit vectors for dipoles. A given biaxial nematic configuration can be expressed in terms of an orthonormal frame $\hat{e}_\alpha$ as

$$q_{\text{diag}} = \frac{S}{\sqrt{6}} (3\hat{e}_z \otimes \hat{e}_z - \mathbb{1}) + \frac{T}{\sqrt{2}} (\hat{e}_x \otimes \hat{e}_x - \hat{e}_y \otimes \hat{e}_y), \quad (54)$$

where $T = 0$ is the pure uniaxial case and $S = 0$ is the pure biaxial case, normalized so that $\text{Tr}[q_{\text{diag}}^2] = S^2 + T^2$. A general biaxial nematic configuration can then be described by performing an SO(3) rotation of this tensor and varying the S and T parameters [100]:

$$q(\theta, \phi, \psi, S, T) = R(\theta, \phi, \psi) q_{\text{diag}}(S, T) R(\theta, \phi, \psi)^{-1}. \quad (55)$$

Any symmetric trace-free tensor, such as the expected quadrupole moment $\langle Q^{\alpha\beta} \rangle$, can be written in the form of Eq. (54) in its eigenframe. This provides an intuitive picture of semiclassical quadrupole configurations, analogous to the unit vectors for semiclassical dipole configurations, but it does not address the issue of how different classical quadrupole configurations ought to be weighted.

C. Dependence on spin quantum number

In fact, the answer to the question of how to appropriately weight the quadrupolar states is strongly dependent on the spin quantum number S . A key reason for this, which highlights the distinction of quadrupoles compared to dipoles, is that, while there are five linearly independent quadrupole operators transforming irreducibly under the action of SO(3), the operator $Q_{3z^2-r^2}$ is *not unitarily equivalent* to Q_{xy} , Q_{yz} , Q_{xz} , or $Q_{x^2-y^2}$, which are all unitarily equivalent to each other by a rotation. This is clearly seen in the corresponding orbital structures shown in Fig. 1—four of them are just rotated versions of each other, while the fifth is not related by a rotation but rather a change in the S and T parameters. In terms of Eq. (54), $Q_{3z^2-r^2}$ corresponds to a $T = 0$ uniaxial tensor, while the other four are all $S = 0$ biaxial tensors related by rotations. Indeed, the spectrum of $Q_{3z^2-r^2}$ is different from the others, as shown in Figs. 7(a) and 7(b). For $S > 2$, its maximal

eigenvalue is larger than the others', and it grows more quickly in the $S \rightarrow \infty$ limit. As a result, uniaxial states tend to dominate at large spin, and there is a trade-off between maximizing the total magnitude of the quadrupole moment, as measured by $\text{Tr}[\langle Q \rangle^2]$, and satisfying the interaction energy between neighboring quadrupoles. Meanwhile, the behavior for $S \leq 2$ is strongly constrained. This does not occur for dipoles, where all three operators are unitarily related and the semiclassical description is given by uniform weighting of the two-sphere for any spin quantum number.

There are two invariants for a symmetric trace-free tensor, $\text{Tr}[q^2]$ and $\text{Tr}[q^3]$. For uniaxial configurations, the sign of $\text{Tr}[q^3]$ indicates whether it is rodlike (positive) or disklike (negative) [101]. From them, we can define a parameter quantifying the degree of biaxiality:

$$\beta = 1 - 6 \frac{\text{Tr}[q^3]^2}{\text{Tr}[q^2]^3} \in [0, 1], \quad (56)$$

which is zero for purely uniaxial configurations and unity for purely biaxial configurations. For a given spin quantum number S , the maximum of $\text{Tr}[\langle Q \rangle^2]$ occurs for the states

$$|\psi_{\text{uni}}\rangle = \frac{1}{\sqrt{2}}(|S\rangle + |-S\rangle), \quad (57)$$

which has maximal uniaxial quadrupole moment. The maximum values are given by [102]

$$N_S^2 = \text{Tr}[\langle \psi_{\text{uni}} | Q | \psi_{\text{uni}} \rangle^2] = \begin{cases} S^2(1-2S)^2/6 & S > 1, \\ 2/3 & S = 1. \end{cases} \quad (58)$$

With these definitions, we are prepared to explore the variation of the behavior of quantum and semiclassical quadrupoles for different spin quantum number. Normalizing the quadrupole operator by the square root of this quantity, in Figs. 7(c) and 7(d), we plot the variation of $\text{Tr}[\langle Q/N_S \rangle^2]$ versus $\text{Tr}[\langle Q/N_S \rangle^3]$ and β for a uniform sampling of random states $|\psi\rangle$ in the spin- S Hilbert space and a uniform sampling of random quadrupole coherent states $|\hat{q}\rangle$ [Eq. (52)]. Figures 7(e) and 7(f) show the distributions of the uniaxial and biaxial components, respectively, of randomly generated quadrupolar coherent states. The results are strikingly different for $S = 1, 3/2, 2$, and $S > 2$.

1. $S = 1$

Referring to Figs. 7(c) and 7(d), for $S = 1$ there is a strong constraint on the possible values of the two invariants [103]:

$$\text{Tr}[\langle Q \rangle^3] + \frac{1}{2} \text{Tr}[\langle Q \rangle^2] = \frac{1}{9} \quad (S = 1) \quad (59)$$

and the moment is bounded: $\text{Tr}[\langle Q \rangle^2] \in [1/6, 2/3]$. This means that there are no states which have zero quadrupole

moment (i.e., $\text{Tr}[\langle Q \rangle^2] = 0$), and the biaxiality of a state is determined entirely by the magnitude of the quadrupole moment. The only states which saturate the quadrupole moment, i.e., with $\text{Tr}[\langle Q \rangle^2] = 2/3$, are disklike uniaxial ones, with $\beta = 0$ and $\text{Tr}[\langle Q \rangle^3] < 0$. All of the quadrupolar coherent states are such maximal quadrupole moment disklike uniaxial ones, seen as a red point in Figs. 7(c) and 7(d). For this case, an appropriate semiclassical description is, therefore, in terms of a uniaxial disklike nematic. This can explore only a subspace of the four-sphere isomorphic to the real projective plane $\mathbb{RP}^2$, i.e., a two-sphere with antipodal points identified. To see this more clearly, in Figs. 7(e) and 7(f), we have plotted the distribution of the biaxial and uniaxial components, respectively, of the five-component vectors [Eq. (11)] corresponding to the expected quadrupole tensor in a quadrupolar coherent state. This distribution exactly matches that of a disklike uniaxial tensor, i.e., one of the form

$$q_{\text{disk-uniaxial}} = -\frac{1}{\sqrt{6}}(3\hat{n}^\alpha \hat{n}^\beta - \delta^{\alpha\beta}) \quad (60)$$

for a random three-component unit vector $\hat{n}$.

2. $S = 3/2$ and $S = 2$

The case $S = 3/2$ is also highly constrained, in that every state has maximal magnitude of the quadrupole moment. In fact, $S = 3/2$ is the only case where all five quadrupole operators have the same spectrum, as seen in Figs. 7(a) and 7(b). In the case $S = 2$, the spectra of the quadrupole operators are not identical, but the maximum eigenvalues are. Indeed, one can check numerically that the quadrupole coherent states satisfy

$$\langle \hat{q} | Q^{\alpha\beta} | \hat{q} \rangle \propto \hat{q}^{\alpha\beta}, \quad (61)$$

for $S = 3/2$ and $S = 2$, directly parallel to the equivalent statement for dipolar coherent states (which holds for arbitrary spin quantum number), but not for other values of S . Thus, for both $S = 3/2$ and $S = 2$, we expect the semiclassical configuration space, corresponding to the space of expected coherent-state quadrupole moments $\langle \hat{q} | Q^{\alpha\beta} | \hat{q} \rangle$, to be the four-sphere of unit-norm symmetric trace-free tensors. For $S = 3/2$, the states are uniformly weighted on this sphere because all quadrupole operators are unitarily equivalent. This has the important implication that spin-3/2 quadrupoles behave like spins on the four-sphere (i.e., unit-length five-component vectors) with an effective orientation given by the sign of the quadrupole, and the bilinear quadrupolar model built from these has an effective time-reversal symmetry that is broken by ordered states. For $S = 2$, the quadrupolar expectation values $\langle Q^{\alpha\beta} \rangle$ can take arbitrary values within the unit sphere for a general (noncoherent) state, reflected in the ‘‘cloud’’ of black points in Figs. 7(c) and 7(d), and the coherent states indeed

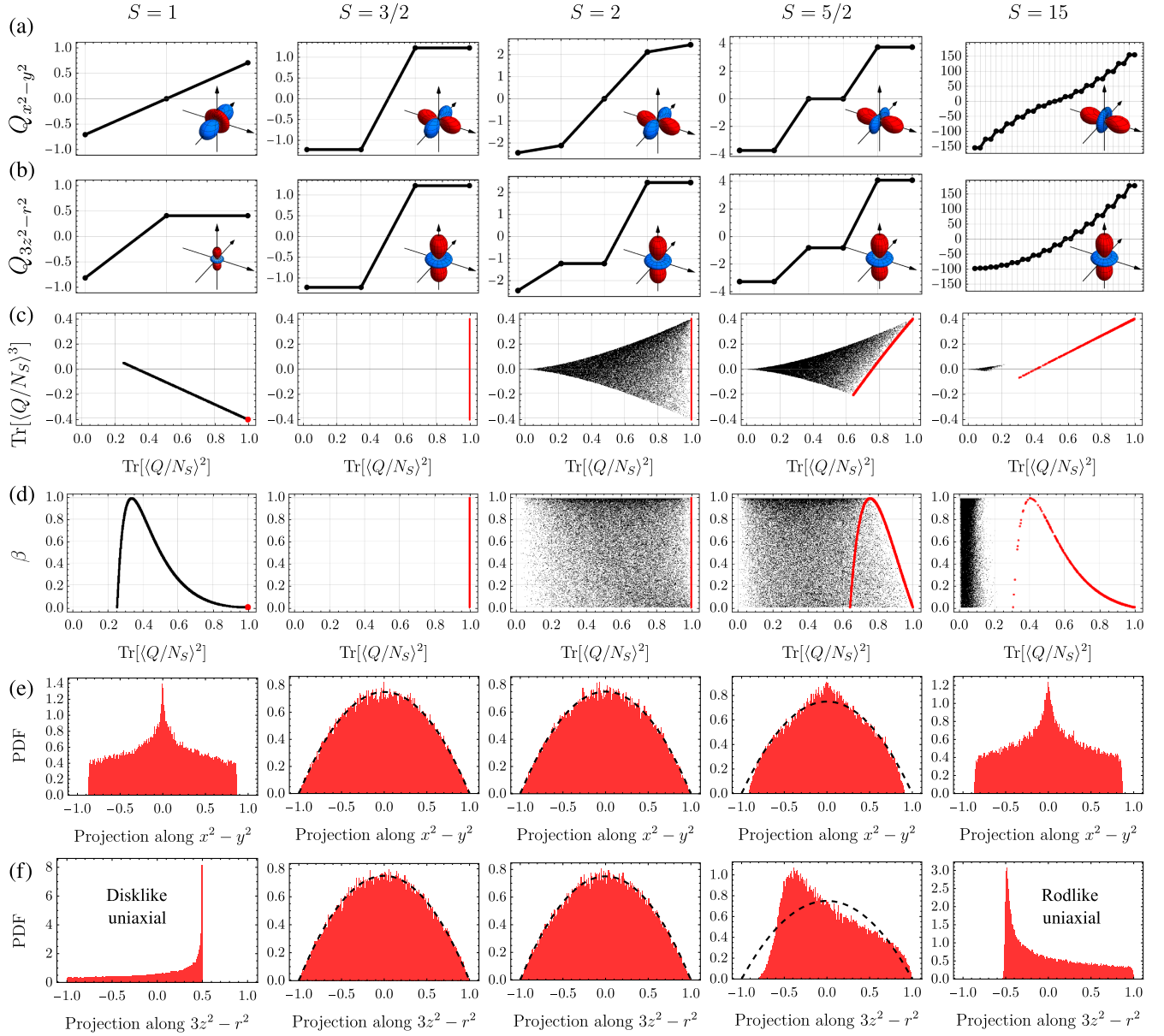


FIG. 7. Plots showing the S dependence of the expected quadrupole moment. (a) Spectrum of $Q_{x^2-y^2} = [(S^x)^2 - (S^y)^2]/\sqrt{2}$. The operators Q_{xy} , Q_{yz} , and Q_{xz} have the same spectrum. Inset: the shape of the expected quadrupole moment $\langle Q^{ab} \rangle$ evaluated in the maximal weight eigenstate of $Q_{x^2-y^2}$. For $S = 3/2$ and $S = 2$, the shape matches that of the corresponding orbital shown in Fig. 1; for $S = 1$, it is a disklike uniaxial with director along y ; for $S > 2$, it tends toward a rodlike uniaxial moment oriented along x . (b) Spectrum of $Q_{3z^2-r^2}$. The spectrum matches that of the other four operators only in the case $S = 3/2$. For $S = 2$ the maximum eigenvalues are the same, while for $S > 2$ the maximum eigenvalue of $Q_{3z^2-r^2}$ is larger. (c) Plots of $\text{Tr}[\langle Q/N_S \rangle^3]$ versus $\text{Tr}[\langle Q/N_S \rangle^2]$ for randomly sampled spin- S states (black dots) and randomly sampled quadrupolar coherent states (red). (d) Variation of biaxial parameter β versus $\text{Tr}[\langle Q/N_S \rangle^2]$. Note that the end points of the red curves at $\beta = 0$ correspond to the states $|S\rangle + | -S\rangle$ (with maximum value of $\text{Tr}[\langle Q^2 \rangle]$) and either $|0\rangle$ for integer spin or $|1/2\rangle + |-1/2\rangle$ for half-integer spin (with minimal value of $\text{Tr}[\langle Q^2 \rangle]$). In the large- S limit, the red curve approaches the same distribution as the $S = 1$ case. (e) Probability density function (PDF) of the $x^2 - y^2$ component of $\langle \hat{q} | Q^{ab} | \hat{q} \rangle$ evaluated for random coherent states with uniform distribution of $\hat{q}$ on the unit four-sphere in the space of symmetric trace-free tensors. Dashed lines show the corresponding distribution of uniformly distributed points on the four-sphere. (f) Distribution of $3z^2 - r^2$ components of coherent states. For $S = 3/2$ and $S = 2$, the distribution appears uniform on the four-sphere, but for other values of S , the $3z^2 - r^2$ components show significant anisotropy and cannot take all values in $[-1, 1]$.

explore all of the maximal quadrupolar moment configurations with arbitrary biaxiality. Furthermore, Figs. 7(e) and 7(f) demonstrate that the distributions are the same for the uniaxial and biaxial components of the coherent state quadrupole moments, as implied from Eq. (61).

3. $S > 2$

All spins $S > 2$ are qualitatively similar to each other, uniformly approaching the large- S limit. In all of these cases, the maximum eigenvalue of the uniaxial operator $Q_{3z^2-r^2}$ is larger than that of the four biaxial operators, approaching the limiting ratio

$$\lim_{S \rightarrow \infty} \frac{\max \text{eigenvalue of } Q_{\text{uniaxial}}}{\max \text{eigenvalue of } Q_{\text{biaxial}}} = \frac{\sqrt{3}}{2}. \quad (62)$$

They share the property that only rodlike uniaxial states ($\text{Tr}[\langle Q \rangle^3] > 0$) maximize the quadrupole moment. This is clearest in the allowed values of the biaxial parameter β —the only states which have maximum quadrupolar moment are uniaxial ones with $\beta = 0$, and biaxial states with large β necessarily have suppressed quadrupole moment. This effect becomes more pronounced for larger spin. Therefore, for $S > 2$, we expect a competition between maximizing the quadrupole moment and satisfying the interaction energy between quadrupoles, which may prefer biaxial configurations. Interestingly, the limiting curve traced by the coherent states in Figs. 7(c) and 7(d) appears to be the same as the curve for random $S = 1$ states but with the opposite sign of $\text{Tr}[\langle Q \rangle^3]$. This is further emphasized by Figs. 7(e) and 7(f), which show that the distribution tends toward that of a rodlike uniaxial tensor, i.e., one of the form Eq. (60) but with opposite sign. This partially justifies the replacement of spin operators with unit vectors in the definition of the quadrupole tensor, Eq. (3), resulting in only rodlike uniaxial states. Importantly, however, the quadrupolar coherent states are still able to explore the full range of biaxial configurations, despite being heavily weighted toward the uniaxial ones, so such an approximation is ultimately not fully appropriate as it cannot capture biaxial states, which are present in the quantum Hilbert space.

D. Semiclassical Monte Carlo simulation of quadrupoles

To perform classical Monte Carlo simulations for a quadrupolar Hamiltonian of the form of Eq. (7), one could evaluate it in the quadrupolar coherent state basis, directly analogous to Eq. (50):

$$\begin{aligned} H_Q^{\text{MC}} &= \sum_{ij} \sum_{a,b=1}^5 \langle \hat{q}_i | Q_i^a | \hat{q}_i \rangle \mathcal{J}_{ij}^{ab} \langle \hat{q}_j | Q_j^b | \hat{q}_j \rangle \\ &= N_S^2 \sum_{ij} \sum_{a,b=1}^5 \tilde{q}_i^a \mathcal{J}_{ij}^{ab} \tilde{q}_j^b, \end{aligned} \quad (63)$$

where $\tilde{q}_i$ are classical five-component vectors with $|\tilde{q}_i| \leq 1$ defined by the sequence of maps

$$\hat{q} \in S^4 \mapsto |\hat{q}\rangle \in \mathbb{CP}^{2S} \mapsto \tilde{q} = \sum_{a=1}^5 \langle \hat{q} | Q^a | \hat{q} \rangle \tilde{e}_a \in \mathbb{R}^5. \quad (64)$$

In the first map, we take a point on the four-sphere (the space of quadrupole operators up to scale) and obtain the corresponding quadrupolar coherent state in the complex projective space of quantum states via Eq. (52). In the second, we compute the quadrupole moment expectation value, mapped to a five-component vector via Eq. (11), where $\tilde{e}_a$ are orthonormal basis vectors in the space of symmetric trace-free matrices. This is a well-defined Monte Carlo protocol, which correctly captures the number of degrees of freedom of a classical quadrupole, but involves diagonalizing the operator $\hat{q}_i^a Q^a$ for each update and so is quite inefficient. It would be preferable if we could directly identify the classical configuration space, which depends on S and is the image of the mapping $S^4 \rightarrow \mathbb{R}^5$ given in Eq. (64), and sample it directly. However, it is unclear how to analytically identify it or the corresponding distribution. For $S = 3/2$ and $S = 2$, the image is apparently just the four-sphere again [e.g., due to Eq. (61)], but the distribution on the four-sphere may not be uniform [though numerically, according to Figs. 7(e) and 7(f), it does appear to be].

To sidestep these concerns, we take a somewhat simpler approach to semiclassical simulation. We treat the quantum problem exactly at the level of a single site, by taking the internal configuration space to be that of unit-length $(2S + 1)$ -component complex vectors representing a general spin- S product state

$$|\psi_{\text{sc}}\rangle = \bigotimes_i |\psi\rangle_i, \quad |\psi\rangle_i = \sum_{m=-S}^S \psi_i^m |m\rangle_i, \quad (65)$$

where $|m\rangle_i$ are the local eigenstates of S_i^z . This method was introduced in Ref. [46] for $S = 1$, where it was called “semiclassical SU(3)” since it simulates three-component complex unit vectors. Its direct generalization may naturally be referred to as semiclassical SU($2S + 1$). We then perform finite-temperature classical Monte Carlo simulations wherein the product state is varied according to a Metropolis update with respect to the variational energy given by

$$\begin{aligned} E_{\text{sc}}(\psi) &= \langle \psi_{\text{sc}} | H | \psi_{\text{sc}} \rangle \\ &= \sum_{ij} \sum_{\alpha\beta, \alpha'\beta'} \langle \psi_i | Q_i^{\alpha\beta} | \psi_i \rangle \mathcal{J}_{ij}^{\alpha\beta, \alpha'\beta'} \langle \psi_j | Q_j^{\alpha'\beta'} | \psi_j \rangle. \end{aligned} \quad (66)$$

As argued in Ref. [46], this agrees at zero temperature with the mean-field ground state and corresponds to the first-order term in a high-temperature series expansion of the

partition function. It allows us to capture single-site quantum fluctuations and the correct distribution of quadrupole moments without the need for identifying the precise semiclassical configuration space.

The downside to this method is that it does not correctly capture the number of independent degrees of freedom, because the number of fluctuating modes increases linearly with the dimension of the Hilbert space, $2S + 1$. For example, ferroquadrupolar order corresponds to the ordering of the five-component quadrupolar order parameter, leading to four quadratic modes and a low-temperature specific heat of $2k_B$ per spin, while this method would predict $4S$ quadratic modes, arising from fluctuations of a $(2S + 1)$ -component complex unit vector minus one ordered real component and one real gauge degree of freedom in the overall phase of the wave function. Notably, this gives the correct count for $S = 1/2$ dipolar order and $S = 1$ quadrupolar order but not for $S > 1$ in either case. Nevertheless, for the purposes of obtaining symmetry-broken ground states and order parameters, identifying phase transitions, and studying order-by-disorder effects, it should be a reliable method which sidesteps the issue of identifying the semiclassical configuration space and is much more efficient to implement than having to compute the quadrupolar coherent state in Eq. (63) with each update.

E. Spin dependence of mean-field ground states

The foregoing discussion demonstrated that $S = 3/2$ and $S = 2$ are relatively isotropic in the space of quadrupoles, while all other spins host uniaxial quadrupoles when the quadrupolar moment is saturated. In general, this fact has ramifications for the mean-field ground state phase diagram. Figure 8 gives one example showing spin dependence of the phase diagram. It shows the analogous phase diagram cut to Fig. 4 but in the local spherical harmonics frame defined in Sec. II C. Figure 8(a) shows the $S = 3/2$ phase diagram. In accordance with the isotropy of the configuration space, the ground states are pure irreps and the phases and phase boundaries agree with the results obtained from the Luttinger-Tisza analysis. The labeling of the irreps refers to the local frame given in Appendix D, where a subscript A (B) refers to $|m| = 2$ ($|m| = 1$).

For spin one, however, the constraints on the quadrupolar length and biaxiality alter the nature of the phases and the phase boundaries, as seen in the bottom panel. Although the ground state irrep observed from Luttinger-Tisza appears in the corresponding region of the $S = 1$ phase diagram, a nonvanishing A_1 component is switched on simultaneously. In addition, for three of the seven regions we find, in addition, that an additional E irrep is switched on. Furthermore, the left and right regions composed of $A_1 \oplus E_A$ and $A_1 \oplus E_A \oplus E_B$, respectively,

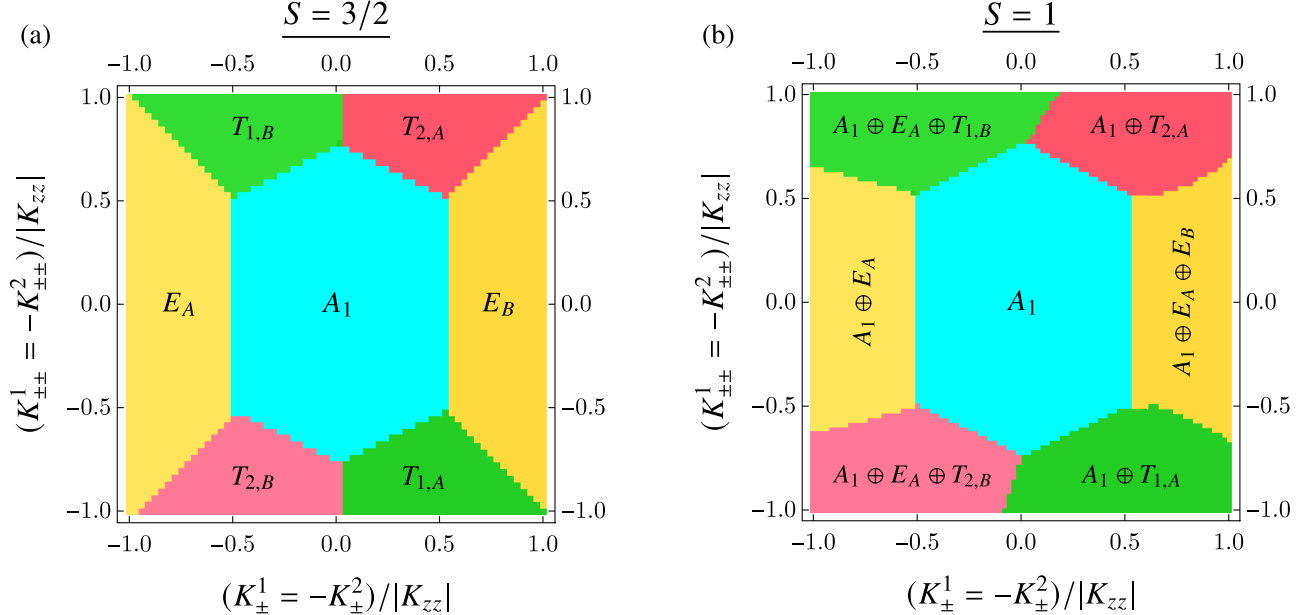


FIG. 8. Mean-field phase diagrams equivalent to Fig. 4 but in the spherical harmonics basis of Eq. (21), for (a) $S = 3/2$ and (b) $S = 1$, showing the spin dependence of the ground states and phase boundaries. The $S = 3/2$ phase boundaries agree with Luttinger-Tisza, while for $S = 1$ the strong constraints force uniaxial A_1 order to coexist with the biaxial orders. An E irrep is also switched on, since one the E irreps include global uniaxial ferroquadrupolar order (cf. Fig. 2, bottom right panel labeled $E_{\psi_2}^{(e_g)}$). The labeling of the irreps refers to the local frame states listed in Appendix D, where a subscript A (B) refers to $|m| = 2$ (1). For these phase diagrams, $K_{zz} < 0$ and $K'_{\pm} = K'_{\pm\pm} = 0$. The color scheme of (a) is the same as in Fig. 3, while in (b) we keep the same color scheme for the phases without adding additional colors for the extra switched on irreps.

are suppressed compared to the corresponding regions in the $S = 3/2$ phase diagram.

In general, we expect the Luttinger-Tisza calculation to be captured well for spins $3/2$ and 2 and for ground states to have mixed irreps for all other spins.

VI. ORDER-BY-DISORDER SELECTION

In the dipolar case, it is well known that the E irrep ground state has an accidental semiclassical $U(1)$ symmetry in the ground state manifold which is lifted by thermal or quantum fluctuations to sixfold degenerate discrete states of two possible types denoted ψ_2 (the $n\pi/3$ states in the local easy plane as measured from the $+\hat{x}_i$ axis) and ψ_3 (the $n\pi/3 + \pi/6$ states). This physics is directly relevant to the material $\text{Er}_2\text{Ti}_2\text{O}_7$ (ψ_2) [104,105] and, most likely, also $\text{Yb}_2\text{Ge}_2\text{O}_7$ (ψ_3) [106].

In the quadrupolar case, the two- and three-dimensional irreps are potentially continuously degenerate. However, in the T_1 and T_2 cases, only a discrete set of states can satisfy the constant quadrupolar length constraint. This leaves the E sector. Unlike the dipolar case, the quadrupolar problem has two E irreps. In each, the quadrupolar length constraint is satisfied by a continuous set of states implying a $U(1)$ degeneracy that may be broken by fluctuations as in the dipolar case. In this section, we study the fate of these states in the two E irreps finding a rich set of order-by-disorder phenomena involving a complex interplay between the two E irreps and the size of the spin. In general, sixfold selection is possible but fine-tuned, with threefold selection being the typical outcome.

A. Time-reversal symmetry, Landau theory, and threefold selection

To set the scene, we discuss Landau theory within the E sector where we see threefold selection arising by symmetry. For this discussion, it is most convenient to use the spherical harmonics basis from Sec. II C, whose behavior under rotations is straightforward and for which the E irreps can be separated into the simple forms

$$\begin{aligned}\Phi_{E_A} &= \begin{pmatrix} \Phi_{E_A}^{\psi_2} \\ \Phi_{E_A}^{\psi_3} \end{pmatrix} = \sum_{\mu} \begin{pmatrix} Q_{\mu}^{\bar{x}^2 - \bar{y}^2} \\ Q_{\mu}^{\bar{x}\bar{y}} \end{pmatrix} \quad (|m| = 2), \\ \Phi_{E_B} &= \begin{pmatrix} \Phi_{E_B}^{\psi_2} \\ \Phi_{E_B}^{\psi_3} \end{pmatrix} = \sum_{\mu} \begin{pmatrix} Q_{\mu}^{\bar{x}\bar{z}} \\ Q_{\mu}^{\bar{y}\bar{z}} \end{pmatrix} \quad (|m| = 1).\end{aligned}\quad (67)$$

We have observed that these appear at the quadratic level through

$$\eta_1 |\Phi_{E_A}|^2 + \eta_2 |\Phi_{E_B}|^2 + \eta_3 \Phi_{E_A} \cdot \Phi_{E_B}. \quad (68)$$

We then introduce

$$\begin{aligned}\Phi_{E_A}^{\pm} &\equiv \Phi_{E_A}^{\psi_2} \pm i\Phi_{E_A}^{\psi_3}, \\ \Phi_{E_B}^{\pm} &\equiv \Phi_{E_B}^{\psi_2} \pm i\Phi_{E_B}^{\psi_3}.\end{aligned}\quad (69)$$

In this basis, transformations under the point group O_h are as simple as possible. In summary, the twofold rotations about the cubic axes act as the identity in this frame. The eight C_3 rotations ($n = 1, 2, 3$) act as local frame rotations such as

$$\begin{aligned}\Phi_{E_A}^+ &\rightarrow e^{4\pi i n/3} \Phi_{E_A}^+, \\ \Phi_{E_B}^+ &\rightarrow e^{2\pi i n/3} \Phi_{E_B}^+.\end{aligned}\quad (70)$$

The remaining elements are twofold rotations about axes in the local easy plane ($m = -1, 0, 1$):

$$\begin{aligned}\Phi_{E_A}^+ &\rightarrow e^{2\pi i m/3} \Phi_{E_A}^-, \\ \Phi_{E_B}^+ &\rightarrow e^{4\pi i m/3} \Phi_{E_B}^-.\end{aligned}\quad (71)$$

Time-reversal symmetry does not forbid terms cubic in the quadrupoles as it does for dipoles. Symmetry allows

$$\begin{aligned}(\Phi_{E_A}^+)^3 + (\Phi_{E_A}^-)^3, \\ (\Phi_{E_B}^+)^3 + (\Phi_{E_B}^-)^3.\end{aligned}\quad (72)$$

It also allows for cubic terms that combine irreps A and B :

$$(\Phi_{E_A}^+)^2 \Phi_{E_B}^- + \text{c.c.} \quad (73)$$

The presence of cubic terms in the Landau theory implies that the $U(1)$ degeneracy present at the quadratic order in E_A and E_B is generally broken by fluctuations. This order by disorder takes place in such a way that three states at either angles $2n\pi/3$ or $\pi/3 + 2n\pi/3$ are selected. This is in contrast to the dipolar case, where sixfold selection into angles $n\pi/3$ (ψ_2) or $\pi/6 + n\pi/3$ (ψ_3) is typical and threefold selection is forbidden by time-reversal symmetry [4,75,76].

The cubic term coupling the two irreps *locks* the angles in the two E sectors. A short calculation reveals that $\phi_B = -\phi_A$ or $\phi_B = \pi - \phi_A$. It follows that four distinct cubic selection sectors are possible.

We further note that sixfold selection terms are also allowed by symmetry as they are in the dipolar case. Some degree of fine-tuning is necessary to bring the threefold selection terms to zero so that sixfold selection becomes the primary degeneracy-breaking mechanism.

In the dipolar case, it is possible to show that ψ_2 states and not ψ_3 states are susceptible to uniform canting in the local frame. More precisely, there is a coupling between the A_2 irrep and the E irrep of the form $m_z \cos 3\phi$ [75]. For the quadrupole, the A irrep couples to quadrupoles through $|\Psi_E|^2 \Psi_{A_2}$. In other words, an A irrep component tends to be

present whenever there is ordering in either of the E irreps or a mixture of the two. It is also straightforward to show that there are couplings living within the product $E \otimes T \otimes T$.

B. Flavor-wave selection and order by disorder

In this section, we begin our exploration of the semiclassical dynamics of the quadrupoles. We do this through a multiboson expansion (otherwise known as flavor waves) of the quadrupolar model for underlying spin S . Our starting point is the following Hamiltonian:

$$H = \frac{1}{2} \sum_{i,j} J_{ij}^{\alpha\beta} \hat{O}_i^\alpha \hat{O}_j^\beta - \sum_{i,\alpha} B_i^\alpha \hat{O}_i^\alpha, \quad (74)$$

where the $\hat{O}_i^\alpha$ are some kind of on-site operators—later assumed to be quadrupolar operators.

We carry out local mean-field theory on this model to obtain the spectrum on each magnetically distinct site $|i, \mu\rangle$, and we introduce boson operators that create these states on top of the vacuum $|i, \mu\rangle \equiv A_{i,\mu}^\dagger |\text{VAC}\rangle$ for $\mu = 0, \dots, 2S$. There is a constraint that the boson number is equal to one per site $\sum_\mu A_{i,\mu}^\dagger A_{i,\mu} = 1$. For the purposes of formulating a spin wave expansion, we take

$$\sum_\mu A_{i,\mu}^\dagger A_{i,\mu} = M \quad (75)$$

for fixed M . The ground state is a condensate of bosons so that

$$A_{i0} = A_{i0}^\dagger = \sqrt{M - \sum_{\mu=1}^{2S} A_{i,\mu}^\dagger A_{i,\mu}}. \quad (76)$$

We now write the operators in the Hamiltonian in the on-site basis:

$$\hat{O}_i^\alpha = \sum_{\mu,\nu} |i\mu\rangle \langle i\mu| \hat{O}_i^\alpha |i\nu\rangle \langle i\nu| \rightarrow \sum_{\mu,\nu} \langle i\mu| \hat{O}_i^\alpha |i\nu\rangle A_{i,\mu}^\dagger A_{i,\nu}. \quad (77)$$

We expand the Hamiltonian around the mean-field ground state and redefine $B_i^\alpha = M \tilde{B}_i^\alpha$. We find

$$H = M^2 H^{(0)} + M^{3/2} H^{(1)} + M H^{(2)} + \dots, \quad (78)$$

where

$$H^{(0)} = \frac{1}{2} \sum_{i,j} J_{ij}^{\alpha\beta} [\hat{O}_i^\alpha]_{00} [\hat{O}_j^\beta]_{00} - \sum_{i,\alpha} B_i^\alpha [\hat{O}_i^\alpha]_{00} \quad (79)$$

using notation $\langle i\mu| \hat{O}_i^\alpha |i\nu\rangle \equiv [\hat{O}_i^\alpha]_{\mu\nu}$.

The terms linear in the bosonic operators should vanish in any mean-field local minimum. About such a minimum, we compute the quadratic Hamiltonian

$$H^{(2)} = \frac{1}{2} \sum_{\mathbf{k}} \Upsilon_{\mathbf{k}}^\dagger \begin{pmatrix} \mathbf{A}(\mathbf{k}) & \mathbf{B}(\mathbf{k}) \\ \mathbf{B}^*(-\mathbf{k}) & \mathbf{A}^*(-\mathbf{k}) \end{pmatrix} \Upsilon_{\mathbf{k}} \quad (80)$$

with $\Upsilon_{\mathbf{k}} = (A_{\mathbf{k}1}, \dots, A_{\mathbf{k}2S}, A_{-\mathbf{k}1}^\dagger, \dots, A_{-\mathbf{k}2S}^\dagger)^T$. We find

$$\begin{aligned} A_{ab}^{\mu\nu}(\mathbf{k}) &= \sum_{\alpha\beta} J_{ab}^{\alpha\beta}(\mathbf{k}) [O_a^\alpha]_{\mu 0} [O_b^\beta]_{0\nu} + \delta_{ab} \sum_c J_{ac}^{\alpha\beta}(\mathbf{k}=0) \\ &\times \left[[O_a^\alpha]_{\mu\nu} [O_c^\beta]_{00} - \delta_{\mu\nu} [O_a^\alpha]_{00} [O_c^\beta]_{00} \right] \\ &- \sum_\alpha \tilde{B}_a^\alpha ([O_a^\alpha]_{\mu\nu} - \delta_{\mu\nu} [O_a^\alpha]_{00}) \end{aligned} \quad (81)$$

and

$$B_{ab}^{\mu\nu}(\mathbf{k}) = \sum_{\alpha\beta} J_{ab}^{\alpha\beta}(\mathbf{k}) [O_a^\alpha]_{\mu 0} [O_b^\beta]_{\nu 0}. \quad (82)$$

We carry out a bosonic Bogoliubov transformation on Eq. (80) to obtain the spectrum of states with energies $\omega_{\mathbf{k}m}$ for $m = 1, \dots, 8S$.

We are mainly interested in cases where there is an accidental U(1) degeneracy in the ground state as happens under certain circumstances within the E irrep. In these cases, the fluctuations computed from spin wave theory will tend to lift the degeneracy. This so-called *order-by-disorder* mechanism [107,108] can often be captured through the leading quantum correction to the energy

$$\delta E = \frac{1}{4N} \frac{1}{2S} \sum_{\mathbf{k},n} \omega_{\mathbf{k}n}. \quad (83)$$

In the dipolar model, when the single E irrep is the lowest-energy mean-field state, there is always an accidental degeneracy and this linear spin wave correction to the energy leads to one of two classes of sixfold degenerate states denoted ψ_2 and ψ_3 . For the quadrupolar model, one might expect greater complexity coming from the appearance of a pair of E irreps. This is indeed the case, yet the results are also highly dependent on the choice of spin S .

We begin by discussing the case where only one of the irreps E_A or E_B , defined in Eq. (67), is coupled. We see that this turns out to be a special basis. Concretely, we couple only components of E_B , $Q^{\bar{x}\bar{z}}$, and $Q^{\bar{y}\bar{z}}$, by switching on K_1 and K_2 . With only K_1 , for any spin, there is a U(1) degeneracy that is not lifted once corrections from Eq. (83) are included. Including K_2 leads to order by disorder as shown in Fig. 9. For all spins, the irrep that is directly coupled orders into a discrete set of states with sixfold degeneracy. The angles match those of ψ_2 order familiar from the dipolar case. Spins 3/2 and 2 exhibit this selection alone with expectation values of the other components vanishing. However, other values of S have constraints that switch on

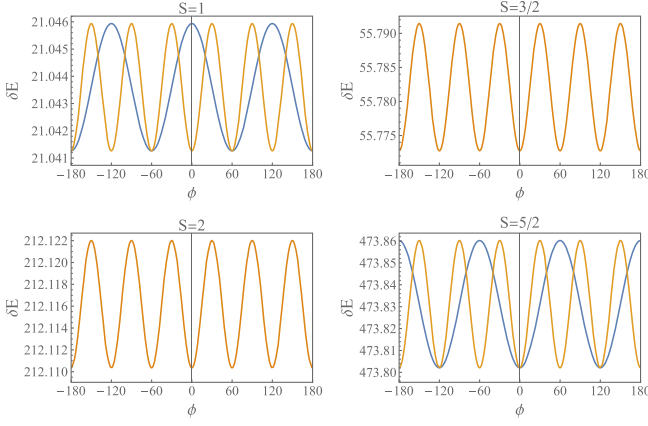


FIG. 9. Zero-point energy computed from flavor-wave theory for model with $K_1 = -K_2 = -1$ coupling only the E_B sector. Each panel has the energy on the vertical axis, and the horizontal axis is an angle ϕ that parametrizes the states. While there is, in principle, a separate angle for each sector, we overlay both on the same axes with blue for E_A and orange for E_B . The four panels are for spins 1, 3/2, 2, and 5/2 from left to right. There is sixfold selection in the E_B sector for all spins. For $S = 1$ and 5/2, the constraints on the quadrupoles are such that the E_A acquires a nonzero expectation value with threefold selection—the E_A angle being doubled relative to the E_B angle.

expectation values for all components. We discuss these constraints in some detail in Sec. V. In summary, spin 1 and $S \geq 5/2$ are biased toward uniaxial nematic states. We find that, for spin 1 and 5/2, E_A expectation values are nonvanishing and the U(1) angle parametrizing this irrep is locked to double the E_B angle resulting in threefold selection in E_A . From a Landau theory perspective, all cubic terms vanish in the $S = 3/2$ and 2 cases, reflecting the fine-tuning of microscopic parameters.

The generic case where both irreps E_A and E_B are coupled also exhibits a clear dependence on the spin length. The most strongly constrained cases— $S = 1$ and $S \geq 5/2$ —cease to exhibit order by disorder altogether. Instead, there is threefold selection of states within both E_A and E_B at the mean-field level. Two states appear depending on the couplings $\phi_A = -\phi_B$ and $\phi_A = \pi - \phi_B$. Spins 3/2 and 2 do generally have a U(1) degeneracy at the mean-field level, and there is fluctuation selection. The configuration space of spin 3/2 is remarkably isotropic such that the selection for this spin is mimicked by Monte Carlo on the four-sphere with an effective time-reversal symmetry. For this reason, in general, $S = 3/2$ has sixfold selection. In contrast, $S = 2$ with coupled E_A and E_B sectors orders into states with a threefold degeneracy. Figure 10 shows generic features of the order-by-disorder selection for $S = 2$.

Finally, we revisit the mean-field phase diagram in Fig. 3(c) obtained using Luttinger-Tisza. The $\Gamma_5^{|m|=1}$ phase—belonging to the E_B irrep in the local frame

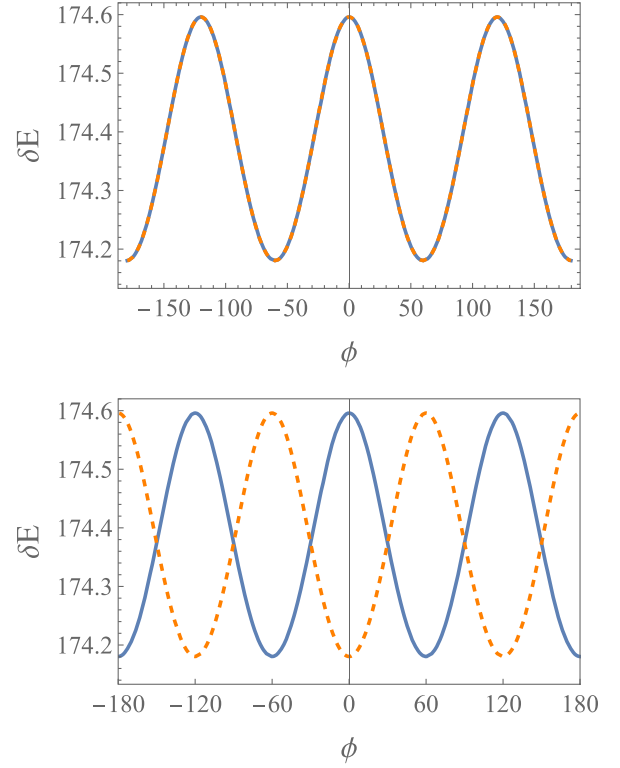


FIG. 10. Zero-point energy computed from flavor-wave theory for models coupling irreps E_A and E_B : $K_1 = -1$, $K_2 = \pm 0.5$, and $K_3 = \pm 0.1$ for $S = 2$. Each plot shows the ordering in the E_A (solid lines) and E_B (dashed lines) sectors. The E_A sector orders always into configurations with $\phi = 60^\circ, 180^\circ, 300^\circ$. The E_B sector orders with the same angles as E_A for $K_2 = \pm 0.5$ (with $\phi_A = -\phi_B$ locking) and $K_3 = +0.1$ and with angles 0, 120, and 240 (with $\phi_A = \pi - \phi_B$ locking) for $K_3 = -0.1$.

$Q^{\bar{x}\bar{z}}, Q^{\bar{y}\bar{z}}$ components—is subject to order by disorder. The resulting phase boundary (at least for $S = 1, 3/2, 2, 5/2$) between the fluctuation selected phases is shown in Fig. 11(a) obtained using a flavor-wave calculation of the zero-point energy. For spins $S = 3/2$ and 2, for which the mean-field theory produces ground states entirely within the E_B irrep, we use a quadrupolar pinning field to fix the order parameter orientation in the mean-field theory. For spins $S = 1$ and 5/2, we use random initial configurations in the mean-field theory to sample the landscape of zero-point energies, as the mean-field ground states mix three irreps including both E irreps.

C. Finite-temperature Monte Carlo

We now turn to exploring the selection due to thermal fluctuations, using the Monte Carlo method described in Sec. V D for various spin quantum numbers. To do so, we perform simulations at finite temperature for parameters in the E phase, with parameters $-K_1 = K_2 = K_9 = K > 0$ and other $K_n = 0$ in terms of Eq. (19), corresponding to the point marked $\times$ in Fig. 3(c). This choice keeps the

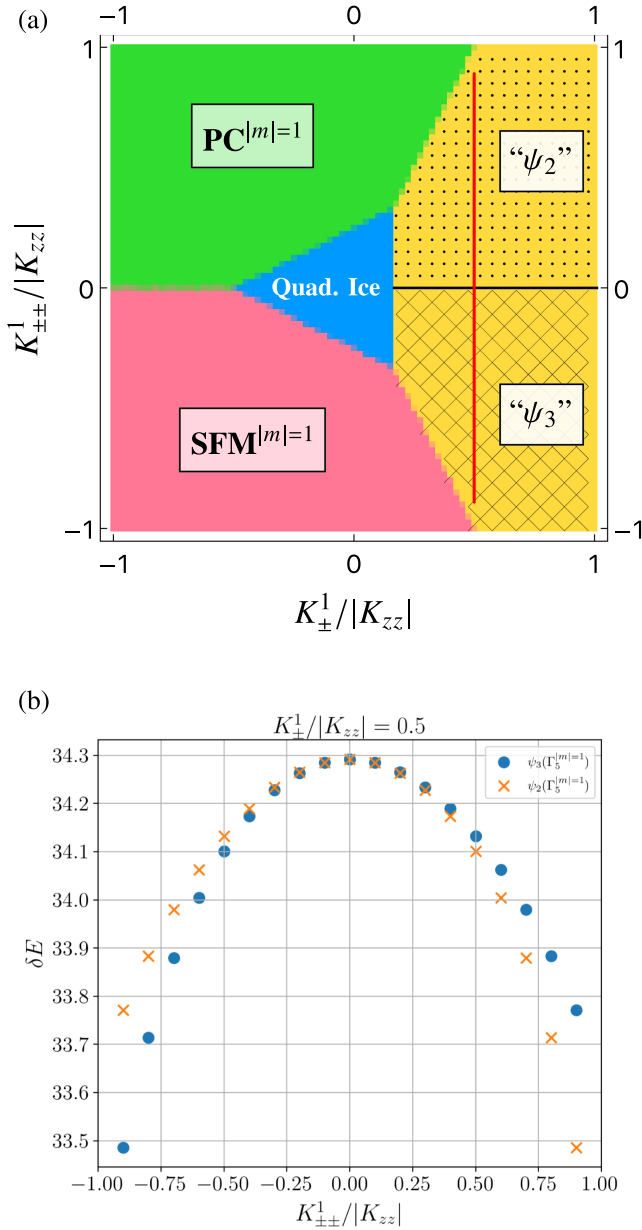


FIG. 11. (a) The same phase diagram as in Fig. 3(c), now showing that the region where the E irrep is the ground state (yellow) is split into two phases due to order by disorder. We have labeled these “ ψ_2 ” and “ ψ_3 ” so that this phase diagram may be compared directly to the analogous one in the dipolar model; see, e.g., Fig. 2(a) in Ref. [4]. (b) The correction to the zero-point energy of the two states, which are degenerate at the mean-field level, as $K_{\pm\pm}^1$ is varied along the red line shown in (a). The two states are degenerate at $K_{\pm\pm}^1 = 0$ but differ in energy away from this point.

E irreps decoupled in the spherical harmonics basis ($K'_{\pm} = K'_{\pm\pm} = 0$), and the ground state irrep is E_B ($|m| = 1$). To visualize the order-by-disorder selection, we measure the quadrupole configuration on each tetrahedron, project it into the 4D $E \oplus E$ space, and further

separate this into two 2D orthogonal E subspaces. We choose two different separations—as $E_{t_{2g}} \oplus E_{e_g}$ (defined in Table II) and the local frame $E_A \oplus E_B$ [defined in Eq. (67)]. We then produce density histograms within each 2D subspace, the results of which are shown in Fig. 12.

First, as a control to differentiate the effects of the spin quantum number, we take high-temperature data in the paramagnetic phase at $T/K = 100$, shown in Figs. 12(a)–12(d). At this temperature, each spin is practically independent and assumes nearly random states in its local Hilbert space, such as represented by the clouds of black points in Figs. 7(c) and 7(d). The strong constraints on $S = 1$ spins are starkly visible in Fig. 12(a), particularly in the e_g subspace, where the allowed quadrupolar configurations all lie inside of the blue triangle. The $S = 3/2$ case appears completely isotropic, with no difference between the two different cuts of the $E \oplus E$ space. The $S = 2$ and $S = 5/2$ cases exhibit a threefold triangular anisotropy in the distributions in the e_g and t_{2g} subspaces. These threefold anisotropies for $S \neq 3/2$ are not visible in the $|m| = 1$ and $|m| = 2$ subspaces.

Next, we thermally anneal the system down to a low temperature well in the ordered phase, at $T/K = 0.03$, shown in Figs. 12(e)–12(h). Focusing first on the isotropic $S = 3/2$ case, we can clearly see a sixfold selection of states out of a continuous $U(1)$ manifold of E_B ground states. The same appears to be the case for $S = 2$, despite the high-temperature data showing a threefold anisotropy. This is likely because at low temperatures the system prefers to maximize the quadrupole moment, selecting locally quadrupolar coherent states, which from Figs. 7(e) and 7(f) have a uniform distribution. This is consistent with the fact that the uniaxial and biaxial operators do not have the same spectrum for $S = 2$, but they do have the same maximum eigenvalue. The cases $S = 1$ and $S = 5/2$ are different: The E_A components are switched on despite costing more energy, with the E_B components no longer saturating. This is a manifestation of the previously mentioned competition between maximizing the local quadrupole moment, which is possible only for uniaxial configurations, and minimizing the exchange energy, which may prefer biaxial ground states (Sec. V C 3). The E_A components exhibit threefold selection, while the E_B components exhibit sixfold selection, which is consistent with the flavor-wave calculations. This effect becomes far more pronounced when looking at the $t_{2g} \oplus e_g$ cross sections—while $S = 2$ and $S = 3/2$ show sixfold selection out of an isotropic distribution, $S = 1$ and $S = 5/2$ show that states at the corners of the triangular distributions seen in Figs. 12(a) and 12(d) are selected, which are maximally uniaxial ones (for example, $E_{\psi_2}^{(e_g)}$ in Fig. 2). This implies that for $S \neq 3/2$ or 2 there is a direct selection of three discrete ground states rather than

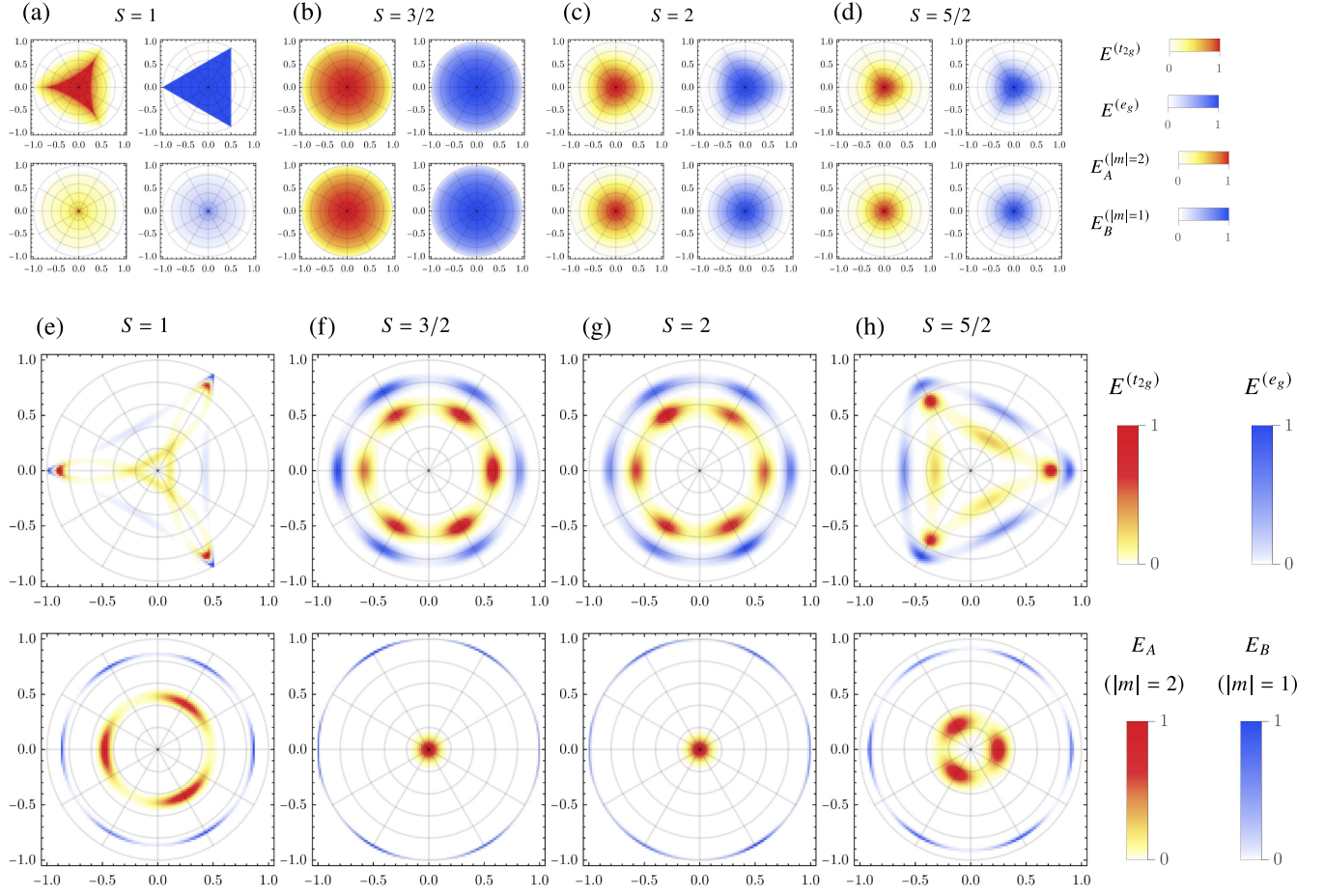


FIG. 12. Monte Carlo results demonstrating the order-by-disorder selection in the two E irreps for parameters $(K_1, K_2, K_9) = K(-1, 1, 1)$ and all other $K_n = 0$, which corresponds to the point marked “ $\times$ ” in Fig. 3(c). Plots show histograms of the projection of the 20-component quadrupolar configuration on each tetrahedron $Q_{i,\mu}^a$ into two orthogonal E subspaces, decomposed as either $E^{(t_{2g})} \oplus E^{(e_g)}$ (cf. Table II) or $E_A \oplus E_B$ [Eq. (67)]. The ground state irrep is E_B . (a)–(d) High-temperature $T/K = 100$ deep in the paramagnetic phase, demonstrating how the spin quantum number affects the distribution of quadrupolar configurations in the E sector. This is clear in the $t_{2g} \oplus e_g$ decomposition: for $S = 1$, not all possible E configurations are accessible; for $S = 3/2$, all configurations are accessible and exhibit a uniform distribution; for $S \geq 2$, all configurations are accessible, but a threefold anisotropy is clearly visible in the distribution. (e)–(h) Low-temperature $T/K = 0.03$ deep in the ordered phase, where E_A is the ground state irrep, showing threefold and sixfold selection patterns. Data are taken for an $L = 8$ system ($4L^3$ sites), thermalized over 10^7 sweeps starting from a random state and annealed by continuously lowering the temperature incrementally to the target temperature, averaged over 10^7 sweeps, and further averaged over 64 independent runs. Results are consistent with quantum flavor-wave calculations.

a fluctuation-driven selection from a continuous ground state manifold.

VII. QUADRUPOLEAR SPIN LIQUIDS

We now turn to consider generalized spin liquids in the quadrupolar model. First, there is obviously the quadrupolar ice spin liquid, which occurs when the ground state irrep is $T_{2,\text{ice}}^{(t_{2g})}$. Its physics is identical at the semiclassical level to that of ordinary classical spin ice; i.e., it has the usual set of two-in-two-out ground states, where “in” means rodlike uniaxial configurations along the easy axes and “out” means disklike uniaxial. More interesting for our purposes are the quadrupolar spin liquids which occur

when multiple irrep multiplets are degenerate in the ground state.

In dipolar spin liquids, a basic classification for bilinear Hamiltonians is given by examining the band structure of the interaction matrix, with classical spin liquids corresponding to a set of flat bands at the base of the spectrum [109–112]. The flat bands provide an extensive set of degenerate zero-energy modes (i.e., an extensive number of Luttinger-Tisza ground states), and topologically nontrivial touching between the flat bands and higher-energy dispersive bands encodes Gauss law constraints of a coarse-grained gauge field theory. In dipolar models, it is common to use the so-called self-consistent Gaussian approximation as a starting point for analysis, wherein the semiclassical spin length

constraint is replaced by a Lagrange multiplier and in which the zero-temperature two-point correlation function is proportional to the projector to the flat bands [78,112].

For a Hamiltonian containing dipolar and quadrupolar bilinears in the form of Eq. (5), this general approach remains a viable starting point for identifying potential spin liquids with quadrupolar degrees of freedom. In particular, the Hamiltonian can be put in the form

$$H = \frac{1}{2} \sum_{ij} \sum_{\alpha, \beta, a, b} \begin{pmatrix} S_i^\alpha \\ Q_i^a \end{pmatrix} \begin{pmatrix} [\mathcal{J}_S]_{ij}^{\alpha\beta} & 0 \\ 0 & [\mathcal{J}_Q]_{ij}^{ab} \end{pmatrix} \begin{pmatrix} S_j^\beta \\ Q_j^b \end{pmatrix}, \quad (84)$$

and this block-diagonal interaction matrix can be Fourier transformed and its band structure analyzed. The dipolar interaction matrix $\mathcal{J}_S$ has been extensively studied and all of its degenerate irrep combinations cataloged for nearest-neighbor interactions [78] and the stability of the corresponding classical spin liquids in the semiclassical limit analyzed [79]. Unfortunately, a complete classification and parametrization of all degenerate combinations of irreps as was done in Ref. [78] is not possible for the quadrupolar interaction matrix due to the triply degenerate T_2 irrep, which cannot be diagonalized analytically. A detailed analysis could be carried out in the case that two of the off-diagonal terms in Eq. (42) are turned off, but we do not pursue it here. Instead, we highlight a number of readily identifiable interesting cases.

One can, in principle, apply a Gaussian-type approximation to the bilinear quadrupolar Hamiltonian, by treating the quadrupoles as five-component vectors with Gaussian length constraint. Based on our discussions in Sec. V, this is likely not a very accurate characterization except possibly in the cases $S = 3/2$ and $S = 2$. Nevertheless, the low-energy band structure of the interaction matrix—its flat bands and band touchings—should accurately reflect the emergent gauge structure of these semiclassical quadrupolar spin liquids. The projector to the flat bands also provides a useful baseline point of comparison for low-temperature correlation functions derived from Monte Carlo, i.e.,

$$\langle Q_\mu^a(-\mathbf{q}) Q_\nu^b(\mathbf{q}) \rangle_{\text{Gauss } T=0} \propto [P_{\text{flat}}]_{\mu\nu}^{ab}(\mathbf{q}), \quad (85)$$

where $\mathbf{q}$ is the wave vector and μ and ν index fcc sublattices. For our purposes, we show only the isotropic quadrupole-quadrupole correlator:

$$S_Q(\mathbf{q}) = \frac{1}{4L^3} \sum_{i,j} \langle \text{Tr}[Q_i Q_j] \rangle e^{-i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_i)}, \quad (86)$$

where we use the four-site basis fcc primitive unit cell with L^3 unit cells and periodic boundaries.

A. Dipolarlike liquids and evidence for fragmentation

As discussed in Sec. III C, we can, in general, make a change of basis to remove the couplings $J'_\pm$ and $J'_{\pm\pm}$

which couple the two easy-plane sectors from the Hamiltonian; then, if we further turn off one of the resulting $J_{z\pm}$ couplings, the decoupled irrep multiplets behave like those of the dipolar model. It follows then that all of the flat band cases of the dipolar model, categorized in Ref. [78], are reproduced in the phase diagram of the quadrupolar model, once in each easy-plane sector, and as an extended manifold as the $J'_\pm$ and $J'_{\pm\pm}$ couplings are varied (along with the $J_{z\pm}$ couplings to keep one of them zero in the rotated basis). The actual ground state behavior, however, depends on the parameters and the spin quantum number, even if the flat band content is the same.

Here, we demonstrate with an example. The dipolar model has a continuous one-dimensional family of spin liquids at the intersection of the Palmer-Chalker, splayed ferromagnet, and Γ_5 phases which is a rank-2 tensor spin liquid with pinch line singularities along the high-symmetry (hhh) directions of reciprocal space [79,84,113]. Reference [78] gives a parametrization of the family in terms of a parameter $x \in [-1, 1]$. By taking those couplings and using them for the t_{2g} couplings in Eq. (14) with all other couplings zero, we reproduce the same form of the Hamiltonian, obtain the same set of flat bands and band touchings in the interaction matrix spectrum, and find the ground state irreps are $E \oplus T_1 \oplus T_2$ as expected from the dipolar model. In particular, this family of Hamiltonians has one-dimensional lines in reciprocal space where a quadratically dispersing band touches the flat bands, giving rise to pinch line features in the structure factors.

Fig. 13(a) shows the corresponding quadrupolar structure factor computed from the projector to the flat bands as well as from semiclassical Monte Carlo simulations for spin quantum numbers ranging from $S = 1$ to $S = 5/2$. The $S = 3/2$ simulations agree closely with the projector calculation reflecting the isotropic behavior of the quadrupole operators, while other spin quantum numbers show some deviations. In particular, $S = 1$ shows a relatively strong peak at some zone centers compared to the other cases, although the background intensity is qualitatively consistent and at the same intensity scale as the Luttinger-Tisza. We have seen that in the $S = 1$ case it may occur that multiple irreps become active simultaneously when Luttinger-Tisza predicts only a single irrep ground state, such as illustrated in Fig. 8, raising the possibility that the peak may indicate the activation of another irrep and coexistence of a spin liquid with long-range quadrupolar order; i.e., the spin liquid may be fragmented [114–116], somewhat like the case reported in Refs. [113,117], where a spin liquid coexists with a very weak partially saturated long-range order. To investigate this, we check the finite system size scaling of the peak height, shown in Fig. 14. These data are consistent with a finite Bragg peak consisting of only a small finite fraction of the total

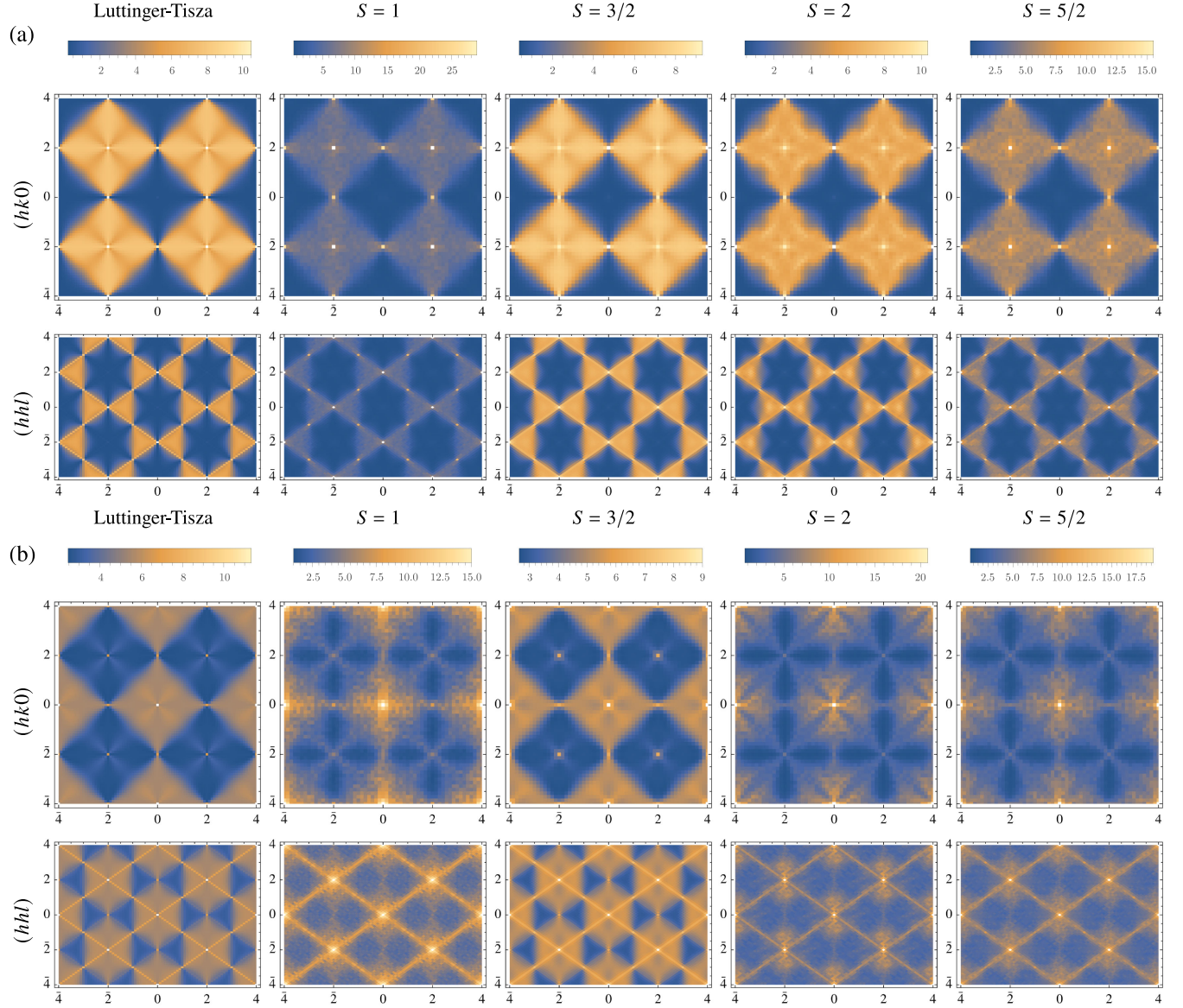


FIG. 13. (a) Example of a spin liquid which arises from setting the e_g couplings to zero and tuning the t_{2g} couplings to those of a rank-2 tensor spin liquid in the dipolar Hamiltonian, corresponding to a point on the triple intersection of the Palmer-Chalker, ferromagnetic, and Γ_5 phases in the t_{2g} sector. The ground state irreps are $E \oplus T_1 \oplus T_2$. Here, we show the quadrupolar structure factor [Eq. (86)] computed from the projector to the flat bands [Eq. (85)]. (b) The antidiagonal dual of the spin liquid from (a), with switched easy-plane sectors. Simulations are performed for a system with $4L^3$ spins at $L = 14$, thermalized for 10^5 sweeps and averaged over 10^6 sample configurations and further averaged over 64 independent simulations.

spectral weight. This situation is commonly referred to as spin liquid fragmentation [114–116].

We can obtain another family of spin liquids by applying the antidiagonal duality, switching the easy-plane t_{2g} and e_g components. Figure 13(b) shows the resulting structure factors, again from the projector to the flat bands and from semiclassical Monte Carlo. Again, we see good agreement for $S = 3/2$ and some deviations for other spin quantum number. The qualitative features in this case remain consistent, and, in particular, the fourfold pinch points at (220) points remain well resolved for all spin quantum numbers.

B. Liquids connected to the biquadratic point—Planar band touchings

In the dipolar Hamiltonian, there is a special point in the phase diagram at which all four phases meet—the isotropic Heisenberg antiferromagnet [9,78]. Correspondingly, at this point, four of the five irreps are degenerate in the ground state, six of 12 bands are flat, and the system is described three decoupled copies of a U(1) gauge theory [79,112,118–120]. By lifting the degeneracy of any one of the irreps, it is possible to move along a

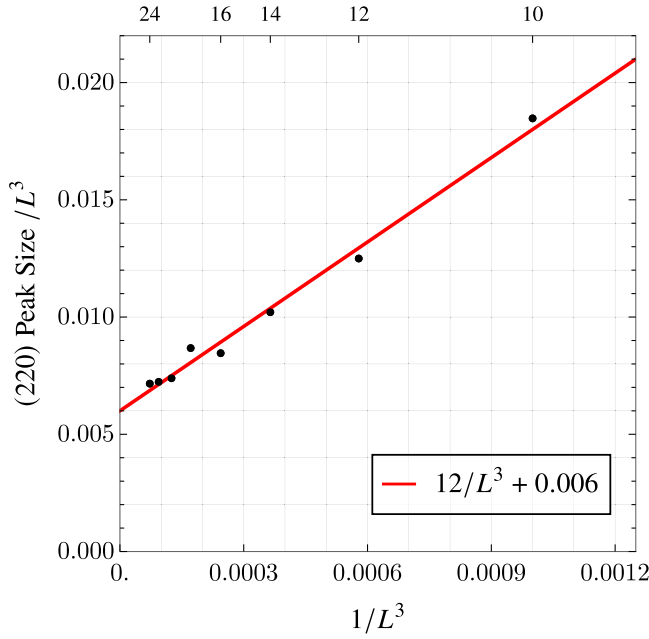


FIG. 14. Finite-size scaling of the (220) peak in the dipolarlike spin liquid from Fig. 13(a) for $S = 1$. The peak height increases with system size, but per unit cell it approaches a nonzero constant in the thermodynamic limit. This suggests that this classical quadrupolar spin liquid is fragmented for $S = 1$.

line where three irreps remain degenerate, which gives families of flat band models [78,79,82].

The most symmetric point is the pure biquadratic point, where the Hamiltonian can be written in the global frame as

$$H_{\text{BQ}} = J \sum_t \sum_{\langle ij \rangle} \text{Tr}[Q_i Q_j] \\ \propto \text{const} + \frac{J}{2} \sum_t \text{Tr} \left[\left(\sum_{i \in t} Q_i \right)^2 \right]. \quad (87)$$

Ground states, therefore, have zero quadrupole moment on each tetrahedron. In terms of the global frame parameters Eq. (9), it has $J_1 = J_2 = J_8 = J_9 > 1$ and all off-diagonal couplings zero. This is the analog of the Heisenberg AFM (HAFM) point in the dipolar case, where every tetrahedron has zero dipole moment in the ground state. It has ten flat bands (out of 20) and, in a naive coarse-graining, is described by five decoupled copies of U(1) spin liquids (whereas the dipolar case is described by three [79,119,120]). Monte Carlo simulation (cf. Sec. V D) shows that it is stable for all spin quantum numbers and exhibits ordinary twofold pinch points in the quadrupolar structure factor identical to those seen in the dipolar HAFM.

Figure 15(a) shows a cut of the phase diagram in terms of global frame parameters in Eq. (9) which intersects the

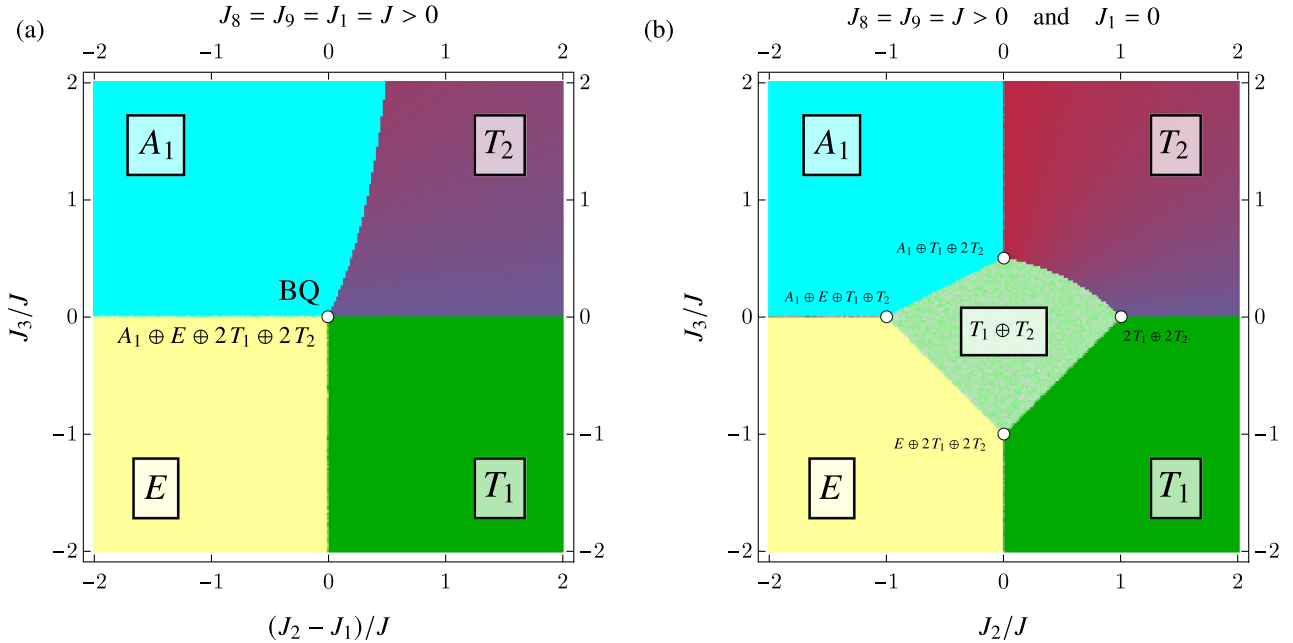


FIG. 15. (a) Phase diagram cutting through the biquadratic (BQ) point, which has maximal degeneracy of irreps in the ground state, with ten flat bands. Perturbing it to lift the degeneracy of some of the irreps, one can move along loci in parameter space where many remain degenerate, giving many flat band models. (b) Another cut where one parameter has been perturbed, showing that the BQ point splits into multiple degenerate combinations, each of which has a number of flat bands. The color legend is the same as in Fig. 3. The four points labeled with white dots belong to families of Hamiltonians emerging from the BQ point containing flat bands with various flat line touchings. The two points with $J_3 = 0$ have flat plane touchings, which do not occur in the dipolar case. Their structure factors are shown in Fig. 16.

BQ point, showing the meeting of all four phases. This point is zero-dimensional in the phase diagram (up to overall energy scale) and has six minimal energy irreps $A_1 \oplus E \oplus 2T_1 \oplus 2T_2$, with gapped irreps $E^{(e_g)}$ and $T_2^{(t_{2g})}$ corresponding to the net quadrupole moment of a single tetrahedron [Eq. (24)]. Perturbing it, there will be one-dimensional lines of parameters emerging from this point where multiple irreps remain degenerate. The precise number of irreps depends on how the irreps are split, since the number of parameters required to be tuned to make multiple copies of the same irrep degenerate is two, while the number of parameters to be tuned to make different irreps degenerate is one. An example is illustrated in Fig. 15(b), where J_1 has been set to zero, showing in the middle a diamond-shaped region where T_1 and T_2 irreps are degenerate and at the corners of this region points where either four or five irreps are degenerate. Each of these high-degeneracy points lies along a line where the irreps remain degenerate in the ground state, giving rise to a family of Hamiltonians which potentially host spin liquids.

Indeed, all of these have four flat bands, meaning that Luttinger-Tisza predicts that they are spin liquids. Similar to spin liquids found in the dipolar model, these all host flat lines—there is at least one quadratically dispersing band which touches the flat bands along either the (hhh) or $(00l)$ high-symmetry lines of reciprocal space (or both). Moreover, the two corner points in Fig. 15(b) with $J_3 = 0$ host *flat planes*—a quadratically dispersing band touches the flat bands everywhere on the 2D (hhl) plane of reciprocal space. To our knowledge, these are the first examples of flat plane touchings in classical spin liquids. The possibility was raised in Ref. [110] but no examples were given. Additionally, two more quadratically dispersing bands touch the flat bands along the 1D (hhh) and $(h00)$ lines.

In Fig. 16, we show quadrupolar structure factors computed from Luttinger-Tisza and Monte Carlo for different spin quantum numbers for these two points. Since we are taking 2D cuts of reciprocal space, the flat planes are intersected along 1D lines, which are clearly visible as lines along which the intensity is higher than the background. Note that Fig. 16(b) is the antidiagonal dual of the HAFM in the t_{2g} sector. It is unclear what types of pinch singularities can be associated to flat planes in a three-dimensional system, as they cannot be linked by a closed manifold on which the dispersing band's eigenvectors can wind. It is also unclear what type of tensor gauge theory they can correspond to. We leave the detailed study of these curious band touchings for future research.

C. Rank-3 symmetric tensor spin liquid

The spin liquids arising from degenerate irreps discussed thus far, such as those in Fig. 13, have complex pinch structures such as fourfold pinch points, which reflect a Gauss law of a tensor gauge theory [83,84,121,122], which

themselves arise in the description of fractonic phases of matter [122–132]. For the dipolar Hamiltonian, all of the tensor spin liquids found in the nearest-neighbor phase diagram carry nodal lines, which give rise to their multifold pinch points [78]. It is, however, possible to construct a “clean” rank-2 symmetric trace-free tensor spin liquid, which exhibits fourfold pinch points without pinch lines, if one allows for breathing anisotropy [83]. The key is to recognize that the various irreps correspond to components of the multipole moments of a single tetrahedron. To obtain a theory whose low-energy limit is described by a symmetric rank-2 tensor field, the most natural place to consider is to suppress all multipole components except the net quadrupole moment on each tetrahedron. In the dipolar Hamiltonian, this can be achieved by adding a Dzyaloshinskii-Moriya interaction to the Heisenberg anti-ferromagnet, which places the ground state on the phase boundary between the Γ_5 phase and the splayed ferromagnet phase, with the splay angle precisely tuned so that the allowed ground state configurations are quadrupole configurations. This is insufficient degeneracy to stabilize a spin liquid, but one can exploit the bipartiteness of the tetrahedra and relax some constraints on one set, by setting the Dzyaloshinskii-Moriya interaction to zero on the “B” tetrahedra [83]. This leads to two flat bands with a quadratic band touching at the zone center which realizes the trace-free symmetric rank-2 U(1) spin liquid in the coarse-grained limit at the level of Luttinger-Tisza [83].

Since the fundamental objects of the theory are already rank 2, it is natural to wonder whether we can construct a rank-3 spin liquid. Indeed, for a system of quadrupolar degrees of freedom, we naturally have higher multipoles on each tetrahedron, as laid out in Table I. Following the intuition just described for the dipolar rank-2 spin liquid, such a spin liquid ought to occur when we tune the Hamiltonian parameters so that the seven components of the octupole moment are the ground state modes. We can work out the required fine-tuning by obtaining the equivalent of the matrices in Eqs. (36), (39), and (42) in the basis defined by Table I. We then require that the T_1 and T_2 components of the octupole moment do not cant; i.e., we restrict the off-diagonal couplings between them and the other copies of the same irreps to be zero, giving three constraints. We then further require that the energies of the A_1 , T_1 , and T_2 components of the octupole moment be degenerate, giving another two constraints. In the global basis Eq. (9), these constraints are satisfied if

$$\begin{aligned} J_5 &= J_1 - J_2 + 2J_3, \\ J_6 &= -J_1 + J_2 - J_3 - 2J_4, \\ J_7 &= J_3 - J_4, \\ 3J_8 &= -4J_1 + 7J_2 - 8J_3, \\ J_9 &= J_2. \end{aligned} \tag{88}$$

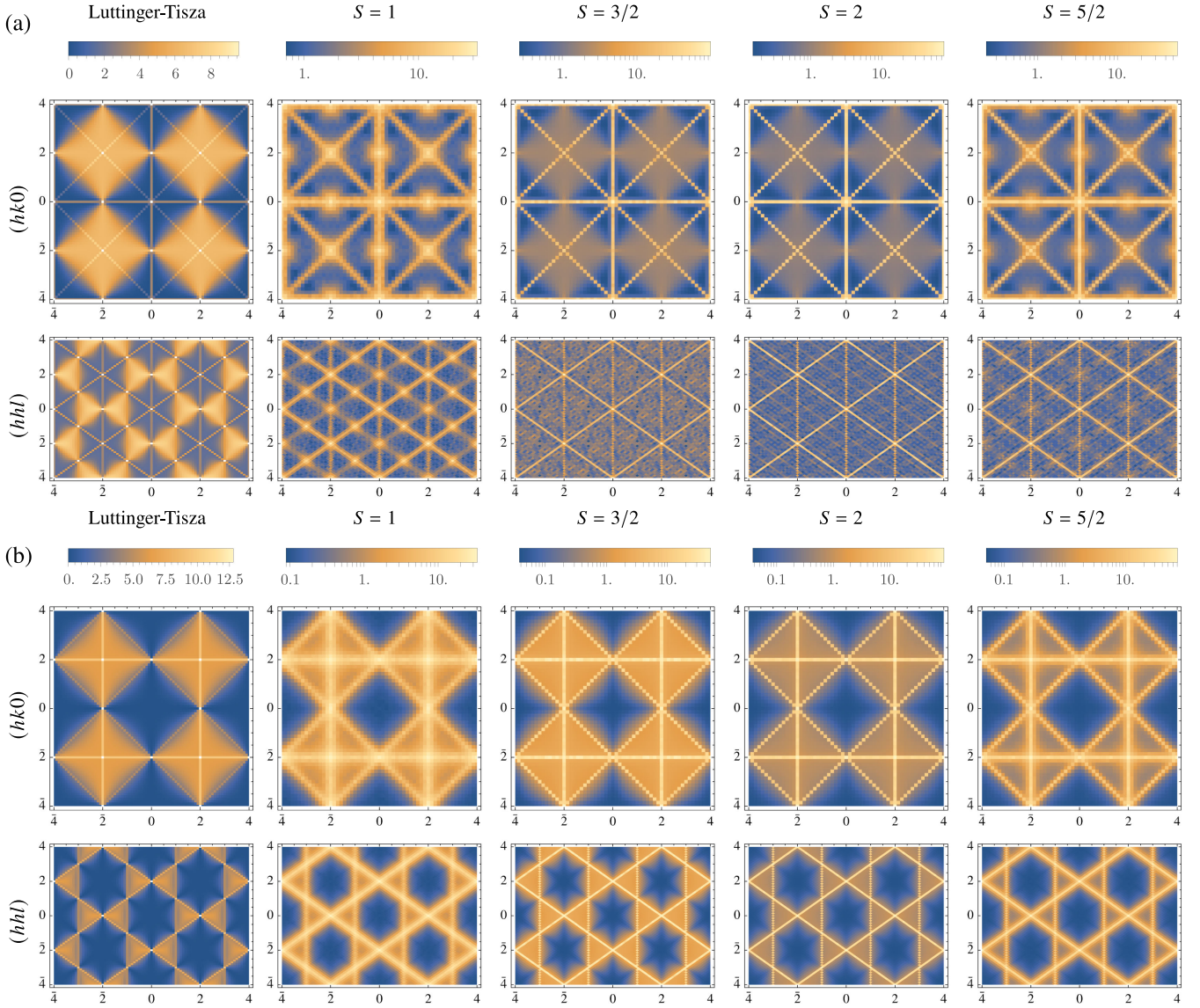


FIG. 16. Examples of quadrupolar structure factors of semiclassical spin liquids emerging from perturbing the biquadratic model, corresponding to points in Fig. 15. (a) The $A_1 \oplus E \oplus T_1 \oplus T_2$ point ($J_2 < 0$). (b) The $2T_1 \oplus 2T_2$ point ($J_2 > 0$). The first column shows the zero-temperature Luttinger-Tisza result, where the two-body correlation matrix is given by the projector to the flat bands. The remaining columns show Monte Carlo results for different spin quantum numbers. Both of these models have four flat bands and one *flat plane* where a quadratically dispersing band touches the flat bands, along with two flat line band touchings along $(00h)$ and (hhh) and three quadratic band touchings at the zone center.

We then can choose J_1 – J_4 such that the octupole moment irreps have the lowest energies. For example, $J_1 = J_2 = J > 0$, $J_3 = 0$, and $J_4 = 0.1J$ will do.

While this gives the right ground state irreps, it does not yield a spin liquid—the interaction matrix has flat lines but no flat bands. In other words, the system is overconstrained, which is also what happened in the dipolar case. In order to relax some of the constraints, we can change the couplings on the B tetrahedra to be those of the biquadratic model (the analog of the HAFM) [Eq. (87)], which contains many more irreps in its ground state and does not cant the octupole ones. Doing so, the resulting model yields two flat

bands, with five quadratic bands touching the flat band at zero center. Because the low-energy degrees of freedom on the A tetrahedra are given by the octupole moment—a rank-3 symmetric trace-free tensor—we expect the long-wavelength coarse-grained theory to be a rank-3 $U(1)$ gauge theory with a single-derivative Gauss law (as the dispersion is quadratic):

$$\partial_\alpha O^{\alpha\beta\gamma} = \rho^{\beta\gamma} = 0, \quad (89)$$

where O is the coarse-grained equivalent of the local octupole moment on a single octahedron. Excitations of

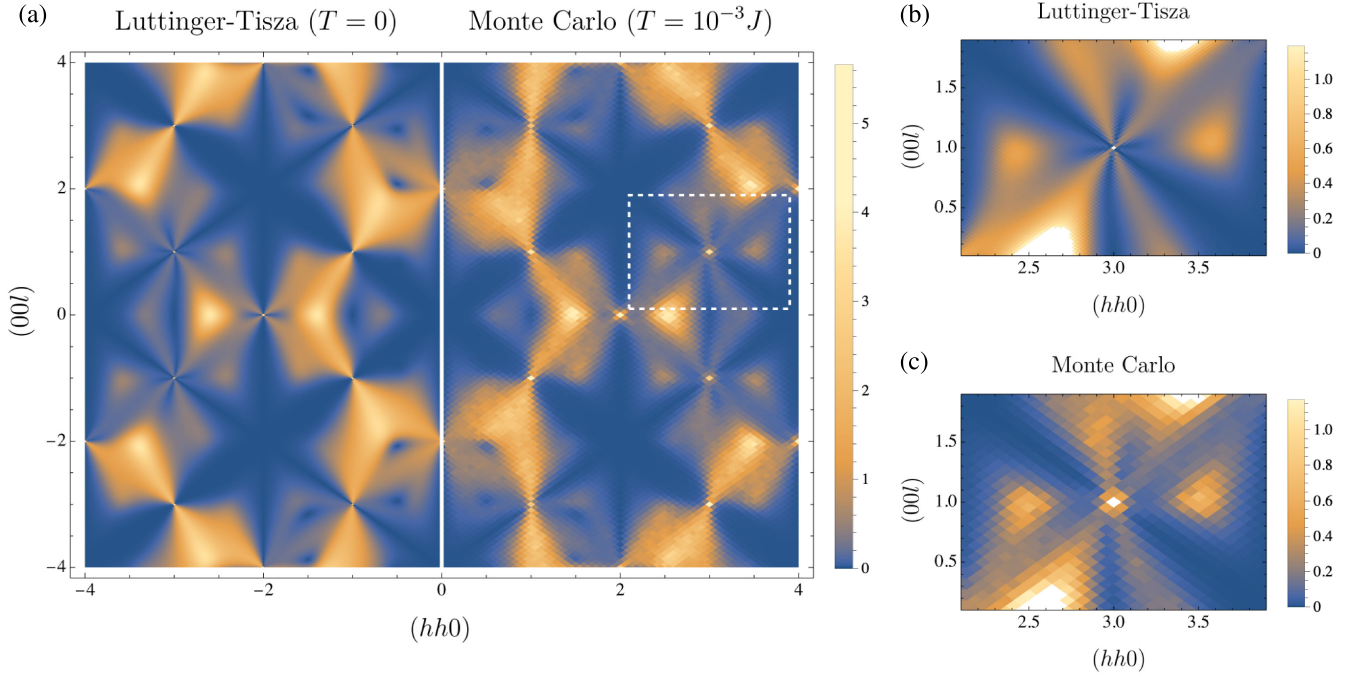


FIG. 17. (a) Longitudinal structure factor in the t_{2g} channel [Eq. (90)] in the (hhl) plane for the rank-3 symmetric tensor spin liquid with $S = 3/2$. The spin liquid is obtained by restricting the low-energy degrees of freedom to be those of the octupole moment on the A tetrahedra, with isotropic biquadratic interactions on the B tetrahedra. Left half: structure factor computed from the projector to the flat bands; right half: structure factor computed in Monte Carlo. (b),(c) Enlarged section [indicated by dashed lines in (a)] showing the sixfold pinch point at the (331) point, confirming the rank-3 structure. Simulations are performed for a system with $4L^3$ spins at $L = 22$, thermalized for 5×10^5 sweeps and averaged over 5×10^5 sample configurations, and further averaged over 192 independent simulations.

this tensor gauge theory are naturally quadrupoles, since violations of the Gauss law take the form of a symmetric trace-free rank-2 tensor charge density $\rho^{\beta\gamma}$. Note that this agrees with the band counting: For a long-wavelength expansion of the form $(q_\alpha O^{\alpha\beta\gamma})^2$, since the octupole tensor O has seven degrees of freedom and the charge density $\rho^{\beta\gamma}$ has five degrees of freedom, the band structure should have five quadratically dispersing bands and two nondispersing bands. Such a theory is expected to have a combination of fracton (immobile) and lineon (mobile along lines) excitations [132].

The rank-3 theory is expected to exhibit sixfold pinch points in correlation functions [121]. This is because in the coarse-grained theory the zero-temperature two-point correlator of the rank-3 tensor field (carrying six total indices) must be zero when any index is contracted with the wave vector, due to the Gauss law [Eq. (89)]. As in the dipolar rank-2 spin liquid [83], the multifold pinch points do not appear in the isotropic quadrupolar structure factor. Instead, it is necessary to study a structure factor in which the quadrupole moment indices are contracted with a wave-vector-dependent form factor. We define the following structure factor from the longitudinal projection of the t_{2g} components of the quadrupole-quadrupole correlator:

$$S_{t_{2g}}^{\text{long}}(\mathbf{q}) = \sum_{\mu\nu} \sum_{a=1}^3 \hat{q}^a \langle Q_\mu^a(-\mathbf{q}) Q_\nu^b(\mathbf{q}) \rangle \hat{q}^b, \quad (90)$$

where the wave vector is contracted with the t_{2g} components of the quadrupole (treated as a three-component vector). The left half in Fig. 17 shows the structure factor computed via the Luttinger-Tisza method, i.e., from the projector to the flat bands. The right half shows the same computed from $S = 3/2$ Monte Carlo simulations using the parameters given just below Eq. (88) at low temperature $T/J = 10^{-3}$. The low-temperature Monte Carlo result agrees to excellent precision with the zero-temperature Luttinger-Tisza calculation [133]. The structure factor exhibits a complex pattern with clearly visible twofold and fourfold pinch points. More importantly, however, is the sixfold pinch point faintly visible at the (331) point. In Figs. 17(b) and 17(c), we have enlarged and changed the color scale in order to highlight the sixfold singularity. This confirms this to be a rank-3 symmetric tensor spin liquid, to the best of our knowledge the first such identified in an anisotropic spin model.

It is worth noting that the analogous rank-2 symmetric-tensor spin liquid found in the dipolar model, introduced in

Ref. [83], is stable only at finite temperature. At low enough temperature (just below $T/J \sim 10^{-3}$), the system eventually orders via an order-by-disorder mechanism into a complex symmetry-breaking pattern which was identified by Ref. [134] using a specially tailored machine learning approach. It is possible that the rank-3 spin liquid in the quadrupolar model is unstable at lower temperatures, but we have not observed any ordering tendency; the spin liquid appears to be stable within the semiclassical treatment.

This rank-3 spin liquid demonstrates the general principle that increasing the rank of the microscopic degrees of freedom by one increases the rank of the resulting spin liquids by one. In the dipolar model, essentially all of the spin liquids one finds are rank-2 [79,81–84], the only exceptions being spin ice, where only the local- z components of the dipoles participate in the spin liquid, and isotropic Heisenberg points, where one obtains three decoupled copies of a rank-1 spin liquid [78,79,85]. All other spin liquids in the dipolar phase diagram are rank 2 [79]. This is because they mix all of the dipole components together and so involve all of the single-tetrahedron multipole modes in the ground state, the highest rank of which are the rank-2 quadrupole and toroidal dipole moments [78]. By this logic, we expect that most of the spin liquids in the quadrupolar model which such as those whose structure factors are shown in Fig. 16 should also be described by rank-3 tensor gauge theories, albeit ones characterized by much more complicated Gauss laws than Eq. (89). This is because a general spin liquid will mix all quadrupole components and activate all single-tetrahedron multipole modes, the highest rank of which are the rank-3 octupole and toroidal quadrupole moments.

VIII. PUTTING BACK THE DIPOLES

So far in this paper, we have considered only quadrupolar degrees of freedom. But in materials, whether quadrupoles are important or not, there are certainly dipolar moments. Here, we consider the possible couplings between the quadrupolar order parameters and their dipolar counterparts.

As a general rule, the minimal coupling between quadrupolar Φ_Q^A and dipolar Φ_D^a order parameters takes the schematic form $\Phi_Q^A \Phi_D^a \Phi_D^b$ to respect time-reversal symmetry. These order parameters may belong to different irreps. In such cases, one refers to Φ_Q as primary and Φ_D as secondary. In situations where there is a phase transition into a quadrupolar ordered phase, this may drive the onset of dipolar order.

We take a simple example specializing now to the pyrochlore lattice. We know that all-in–all-out order corresponds to the A_{2g} irrep and the analog quadrupolar order transforms trivially (as A_{1g}). These may couple through $Q_{A_{1g}} D_{A_{2g}}^2$. Thus, all-in–all-out dipolar order may

naturally accompany the A_{1g} quadrupolar order although they transform differently—the dipolar order breaking time-reversal symmetry and switching sign under transformations that map “up” to “down” tetrahedra, whereas the quadrupolar order breaks no lattice symmetries and preserves time reversal.

A more interesting example is connected to the mixed dipolar-quadrupolar character of non-Kramers doublets at the single-ion level. The dipolar matrix elements of such doublets may be interpreted as belonging to an Ising spin (transverse components being zero). This fixes possible dipolar long-range order to irreps A_{2g} for AIAO order and T_{1g} for spin ice states. If the dipolar irrep is A_{2g} , then cubic terms pin the multipolar order to A_{1g} .

However, if the dipolar sector condenses in the ice manifold, then, since $T_{1g} \otimes T_{1g} = A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$, all quadrupolar phases may couple to these states. The A_{1g} quadrupolar phase simply couples to the uniform $\Phi_D^{T_{1g}} \cdot \Phi_D^{T_{1g}}$. Considering next the E_g quadrupoles, a calculation of the components gives

$$F_{E-\text{Ice}} = \frac{1}{2} \left(-\Phi_Q^{E1} - \sqrt{3}\Phi_Q^{E2} \right) \left(\Phi_D^{T_{11}} \right)^2 + \Phi_Q^{E1} \left(\Phi_D^{T_{12}} \right)^2 + \frac{1}{2} \left(-\Phi_Q^{E1} + \sqrt{3}\Phi_Q^{E2} \right) \left(\Phi_D^{T_{13}} \right)^2, \quad (91)$$

which correlates one of three discrete quadrupolar E states to the ice configuration on a single tetrahedron. Here, the three components in the dipolar T_{1g} basis correspond to three orthogonal ice states on a tetrahedron.

Although a cubic coupling between T_{1g} quadrupolar states and dipolar ice states is allowed by symmetry, the precise form of the term is antisymmetric in the dipolar terms and, therefore, vanishes. Finally, the coupling between T_{2g} quadrupolar states and the ice states takes the following form:

$$F_{T_{2g}-\text{Ice}} = \Phi_Q^{T_{2g}1} \Phi_D^{T_{12}} \Phi_D^{T_{13}} + \Phi_Q^{T_{2g}2} \Phi_D^{T_{11}} \Phi_D^{T_{12}} - \Phi_Q^{T_{2g}3} \Phi_D^{T_{11}} \Phi_D^{T_{13}}. \quad (92)$$

This also vanishes within a uniform dipolar T_{1g} state.

The interpretation of these terms is subtle within a quasidegenerate spin ice regime. But long-range quadrupolar order in any of the A_{1g} , E_g , and T_{2g} irreps couples to the ice states, and at least A_{1g} long-range quadrupolar order may apparently emerge from a disordered ice background.

IX. MATERIALS

The rare earth pyrochlores $R_2M_2O_7$ with rare earth magnetic ion R^{3+} and nonmagnetic M^{4+} exhibit a very wide range of magnetic phenomena. It is helpful to divide these materials into three classes depending on the nature of the single-ion ground state: (i) the dipolar Kramers ions

including those with crystal field ground state doublets whose effective spin one-half description has all three effective spin components transforming as dipoles, (ii) the non-Kramers ions with ground state doublets where one effective spin component is dipolar and the transverse components are quadrupolar, and (iii) the Kramers ions whose crystal field ground state doublets have mixed dipolar-octupolar character. As examples, class (i) includes the Yb^{3+} and Er^{3+} pyrochlores that are relatively well understood, and class (ii) includes Pr^{3+} and Tb^{3+} , while class (iii) includes Ce^{3+} and Nd^{3+} . Broadly, the least understood of the pyrochlore materials are those with mixed character crystal field ground state doublets. We focus on the non-Kramers case (ii), as these are quadrupolar active.

$\text{Tb}_2\text{Ti}_2\text{O}_7$ is one of the most remarkable of the rare earth pyrochlore magnets. Upon cooling through the Curie scale, there is a Schottky anomaly. At lower temperatures, the thermodynamic properties depend sensitively on the degree to which titanium and terbium ions mix on the two pyrochlore sublattices. In the materials closest to stoichiometric, there is no clear sign of a phase transition from susceptibility and heat capacity. Above some small degree of stuffing $\text{Tb}_{2-x}\text{Ti}_{2+x}\text{O}_7$ for $x > 0.0025$, there is a relatively sharp thermodynamic anomaly that has been attributed to the onset of quadrupolar long-range order [64,65]. This picture is supported by experiments revealing the presence of a dispersive mode significantly below the energy of the lowest-lying crystal field excitations [135]. The latter feature is also shared by relatives $\text{Tb}_2\text{Sn}_2\text{O}_7$ [136] and $\text{Tb}_2\text{Hf}_2\text{O}_7$ [137] of $\text{Tb}_2\text{Ti}_2\text{O}_7$. In this context, we mention also $\text{Tb}_2\text{Ir}_2\text{O}_7$ in which the iridium sublattice is magnetic and long-range ordered at low temperatures. Again, there is an unusual inelastic signal in this material.

The magnetic Tb^{3+} has $J = 6$ and is, therefore, non-Kramers. The crystal field spectrum is separated from the first excited doublet by a gap of about 15 K, which is atypically small among this class of materials though still significantly larger than the exchange and dipolar scales of approximately 1 K. We consider the action of dipolar and quadrupolar operators on the two lowest-energy doublets. There are several works exploring the crystal field of $\text{Tb}_2\text{Ti}_2\text{O}_7$ both from first principles and by fitting the experimentally measured levels. To be concrete, we consider the set of parameters from Zhang *et al.* [138]:

$$\begin{aligned} B_2^0 &= -8.41835, \\ B_4^0 &= 0.0476754, \\ B_4^3 &= 0.681092, \\ B_6^0 &= -0.000139008, \\ B_6^3 &= -0.00581111, \\ B_6^6 &= -0.00987507 \end{aligned} \quad (93)$$

in Kelvin with crystal field Hamiltonian

$$H_{\text{CEF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_6^0 O_6^0 + B_6^3 O_6^3 + B_6^6 O_6^6, \quad (94)$$

where O_l^m are the Steven's operators. The spectrum has two low-lying doublets separated by an energy of about 16 K. The eigenstates of the four low-lying levels $n = 1, \dots, 4$

$$|\psi_n\rangle = \sum_{m=-6}^6 \alpha_n^m |m\rangle \quad (95)$$

have nonzero amplitude in the states $|m\rangle$ for $m = \pm 5, \pm 4, \pm 2, \pm 1$. The ground state doublet is principally $|G, \pm\rangle = |\pm 5\rangle$, and the first excited doublet is $|E, \pm\rangle = |\pm 4\rangle$. As $|G, \pm\rangle$ and $|E, \pm\rangle$ are non-Kramers doublets, they are Ising-like, meaning that there are non-vanishing J^z matrix elements $\langle p, \pm | J^z | p, \pm \rangle = \pm \alpha_p$ with all other dipolar matrix elements equal to zero. There are dipolar matrix elements connecting the two doublets: in particular, $\langle G, \pm | J^z | E, \mp \rangle$ and $\langle G, \pm | J^{x/y} | E, \pm \rangle$. So, if we wish to consider the lowest four states as belonging to an effective spin three-half S^a , then there has to be a term that both splits the spectra that do not commute with effective S^z .

Matrix elements of the quadrupolar operators can introduce dynamics even into the ground states as all of O_2^{2s}, O_2^{2c} and O_2^{1s}, O_2^{1c} have off-diagonal matrix elements between $|p, \pm\rangle$ for fixed p , while O_2^0 is diagonal in this basis. In an effective spin one-half description, the effective transverse spin components encode quadrupolar components while the effective z components are dipolar and, hence, Ising-like. When directly projected onto the non-Kramers ground state doublet, the nine quadrupolar couplings are folded onto three exchange couplings.

Magnetic interactions introduce a weak admixture of the two lowest-lying doublets. In addition to the aforementioned dipolar matrix elements connecting the doublets, all quadrupolar operators couple them [139].

The pyrochlore magnets based on praseodymium include $\text{Pr}_2\text{M}_2\text{O}_7$ with $M = \text{Hf}, \text{Sn}$, and Zr . Pr^{3+} is non-Kramers with $J = 4$. In these materials, the excited crystal field levels are well separated from the ground state doublet [70,72,140], so an effective spin one-half model is fully justified at low energies. In this case also, matrix elements of the quadrupolar operators can introduce dynamics even into the ground doublet [141].

Structural disorder is of particular significance in the non-Kramers cases, as doublets are not protected by time-reversal symmetry and are, therefore, sensitive to time-reversal-invariant perturbations including all varieties of structural disorder. The zirconates and hafnates are instances of such effects where static and dynamic disorder appear to play a crucial role in the low-energy physics

although interactions between the moments are significant [137,141,142]. A simple picture within the doublet is of disorder modifying the quadrupolar terms at the single-ion level which amounts to the appearance of transverse fields in an effective spin one-half model. The correct description of these systems, therefore, most likely involves the interplay of magnetic interactions with disordered transverse fields. The quadrupolar activity of these praseodymium-containing pyrochlore is borne out again by the appearance of low-energy spectral weight in inelastic neutron scattering studies.

X. DISCUSSION AND CONCLUSION

This work combines two central ingredients in modern frustrated magnetism—anisotropic couplings induced by spin-orbit coupling and lattices with geometrical frustration—but instead of magnetic moments we couple quadrupoles. In particular, we studied a model with pure quadrupolar degrees of freedom on a pyrochlore lattices: the symmetry-allowed couplings, the semiclassical ground states including order-by-disorder selection and classical quadrupolar liquids, and their finite-temperature stability. We highlight some findings.

Among our main results—going beyond our investigation of the pyrochlore lattice problem—is a characterization of the nature of quadrupoles for different spins. Although quadrupolar degrees of freedom are present for all $S \geq 1$, different spins have different constraints on the possible expectation values. A naive counting tells us that $S \geq 1$ has the full number of quadrupolar degrees of freedom (four continuous parameters) albeit these may be tied to other multipolar components. However, the local spins may not be able to span the full space of quadrupolar states. $S = 1$ is particularly constrained such that the purely biaxial configurations are forbidden. This profoundly affects the semiclassical phase diagram for this spin by mixing irreps. One might imagine that large values of the spin would have more freedom to explore the states. However, it is spin $3/2$ that is the most isotropic and, therefore, has the greatest freedom to explore the quadrupolar states. $S = 2$ ground states are also free to explore the semiclassical states. Higher spins are biased toward uniaxial nematic states.

In the pyrochlore model, although there are nine couplings—a forbiddingly large parameter space—there are great simplifications as (i) the dipolar easy-plane phases are in some sense doubled and (ii) this feature carries over to the model which can be thought of as two (generically coupled) dipolar copies. For this reason, we can find semiclassical phase diagrams much like those of the dipolar model.

Aside from the semiclassical spin dependence of the ground states and the increased number of ground states, one major difference between the dipolar and quadrupolar models is the nature of order by disorder. First, there are two E irreps instead of one for the dipolar case. Second, the

crystalline symmetries and the time-reversal symmetry of the quadrupoles allows threefold selection in the E irreps. This is the generic behavior observed in both flavor-wave calculations (quantum fluctuations) and Monte Carlo (thermal fluctuations). The differing spin lengths enter the story again here. For example, $S = 1$ generally does not exhibit the semiclassical accidental degeneracy that is a prerequisite for order by disorder. Instead, there is direct energetic selection at the mean-field level for this spin. The same is typically the case for $S \geq 5/2$. $S = 3/2$ is, once again, special by having typical sixfold selection similar to the dipolar case.

The dipolar model has a varied set of classical spin liquids. These include the Ising ice regime, the Heisenberg and pseudo-Heisenberg points, and higher-rank spin liquids. The quadrupolar model has quadrupolar liquid analogs of all of these states and more, and, in particular, we have demonstrated the presence of new physics in the form of a rank-3 quadrupolar liquid phase.

We have addressed some of the possible couplings between the quadrupolar order phases and the better-known dipolar phases on the pyrochlore lattice. We have brought the analysis to the point where a natural next step is to bring the connection to materials closer. The principal target is to understand $\text{Tb}_2\text{Ti}_2\text{O}_7$ in which quadrupolar order has been suggested when there is small terbium-titanium site mixing. If this is true, the nature of the order must fit into the scheme developed here. Indeed, the whole family of terbium pyrochlores exhibits somewhat similar physics where the quadrupolar degrees of freedom are active and the crystal field gap is quite small. We expect this work to connect directly to these materials.

In this connection, it would be interesting to combine dipolar and quadrupolar couplings. We have partially considered this problem at the level of symmetry. The isotropic spin one bilinear-biquadratic model on the pyrochlore lattice has been considered in Ref. [45], revealing the presence of many liquid phases. This work on the isotropic case highlights the possibility of dipolar long-range order even in the disordered and purely quadrupolar coupled regime as well as hinting at considerable additional richness in passing over to the spin-orbit coupled case.

More broadly, our work is one of few examples where the effects of geometrical frustration and spin-orbit coupling have been explored with nonmagnetic local degrees of freedom. As we have seen, the space of possibilities compared to traditional frustrated magnetism is considerably enlarged.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX A: CONVENTIONS

The primitive unit cell is an fcc lattice with four-site basis, with primitive Bravais lattice vectors

$$\mathbf{a}_1 = \frac{a_0}{2} [110], \quad \mathbf{a}_2 = \frac{a_0}{2} [101], \quad \mathbf{a}_3 = \frac{a_0}{2} [011], \quad (\text{A1})$$

where a_0 is the edge length of the cubic conventional cell. Each tetrahedron has six corners whose easy-axis directions are labeled as

$$\hat{\mathbf{z}}_1 = [\bar{1}\bar{1}\bar{1}], \quad \hat{\mathbf{z}}_2 = [11\bar{1}], \quad \hat{\mathbf{z}}_3 = [\bar{1}11], \quad \hat{\mathbf{z}}_4 = [1\bar{1}1]. \quad (\text{A2})$$

The sublattice basis positions (tetrahedron corners) are given by the vectors

$$\mathbf{c}_\mu = \frac{\mathbf{a}_{\mu-1}}{2} \quad (\mu = 1 \dots 4) \quad (\mathbf{a}_0 \equiv [000]). \quad (\text{A3})$$

APPENDIX B: MAPPING BETWEEN PARAMETRIZATIONS

We have provided three different parametrizations of the quadrupole-quadrupole interactions, Eq. (9) in the global frame and Eq. (19)(19) in the local frame. We define the following nine-component vectors of parameters:

$$\vec{J} = \begin{pmatrix} J_1 \\ J_2 \\ J_3 \\ J_4 \\ J_5 \\ J_6 \\ J_7 \\ J_8 \\ J_9 \end{pmatrix}, \quad \vec{J}_\pm = \begin{pmatrix} J_\pm^{t_{2g}} \\ J_{\pm\pm}^{t_{2g}} \\ J_{zz} \\ J_{z\pm}^{t_{2g}} \\ J_\pm^{e_g} \\ J_{\pm\pm}^{e_g} \\ J_{z\pm}^{e_g} \\ J'_\pm \\ J'_{\pm\pm} \end{pmatrix}, \quad \vec{K} = \begin{pmatrix} K_1 \\ K_2 \\ K_3 \\ K_4 \\ K_5 \\ K_6 \\ K_7 \\ K_8 \\ K_9 \end{pmatrix}, \quad \vec{K}_\pm = \begin{pmatrix} K_\pm^1 \\ K_{\pm\pm}^1 \\ K_{zz} \\ K_{z\pm}^1 \\ K_\pm^2 \\ K_{\pm\pm}^2 \\ K_{z\pm}^2 \\ K'_\pm \\ K'_{\pm\pm} \end{pmatrix}. \quad (\text{B1})$$

These are related by invertible linear transformations such as

$$J_n = \sum_{m=1}^9 [M_{J \leftarrow J_\pm}]_{nm} [J_\pm]_m, \quad (\text{B2})$$

with

$$M_{J \leftarrow J_\pm} = \begin{pmatrix} \frac{4}{3} & \frac{2}{3} & -\frac{1}{3} & \frac{2\sqrt{2}}{3} & 0 & 0 & 0 & 0 & 0 \\ -\frac{4}{3} & \frac{4}{3} & \frac{1}{3} & \frac{4\sqrt{2}}{3} & 0 & 0 & 0 & 0 & 0 \\ -\frac{2}{3} & -\frac{4}{3} & -\frac{1}{3} & \frac{2\sqrt{2}}{3} & 0 & 0 & 0 & 0 & 0 \\ -\frac{2}{3} & \frac{2}{3} & -\frac{1}{3} & -\frac{\sqrt{2}}{3} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & -\sqrt{2} & -\sqrt{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & \sqrt{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\sqrt{2} & \sqrt{2} \\ 0 & 0 & 0 & 0 & -2 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2 & -2 & 0 & 0 & 0 \end{pmatrix}, \quad (\text{B3})$$

$$M_{J \leftarrow K} = \begin{pmatrix} -\frac{2}{9} & \frac{4}{9\sqrt{3}} & -\frac{4\sqrt{2}}{9} & \frac{2\sqrt{2}}{9} & -\frac{8\sqrt{\frac{2}{3}}}{9} & -\frac{4}{9} & \frac{4}{9} & -\frac{8}{9\sqrt{3}} & -\frac{1}{3} \\ \frac{2}{9} & \frac{2}{9\sqrt{3}} & \frac{4\sqrt{2}}{9} & \frac{4\sqrt{2}}{9} & -\frac{4\sqrt{\frac{2}{3}}}{9} & \frac{4}{9} & \frac{8}{9} & -\frac{4}{9\sqrt{3}} & \frac{1}{3} \\ \frac{1}{9} & -\frac{5}{9\sqrt{3}} & \frac{2\sqrt{2}}{9} & \frac{2\sqrt{2}}{9} & \frac{10\sqrt{\frac{2}{3}}}{9} & \frac{2}{9} & \frac{4}{9} & \frac{10}{9\sqrt{3}} & -\frac{1}{3} \\ \frac{1}{9} & \frac{1}{9\sqrt{3}} & \frac{2\sqrt{2}}{9} & -\frac{\sqrt{2}}{9} & -\frac{2\sqrt{\frac{2}{3}}}{9} & \frac{2}{9} & -\frac{2}{9} & -\frac{2}{9\sqrt{3}} & -\frac{1}{3} \\ \frac{1}{3} & \frac{1}{3\sqrt{3}} & \frac{1}{3\sqrt{2}} & \frac{\sqrt{2}}{3} & -\frac{1}{3\sqrt{6}} & -\frac{1}{3} & -\frac{1}{3} & \frac{1}{3\sqrt{3}} & 0 \\ 0 & -\frac{2}{3\sqrt{3}} & 0 & \frac{\sqrt{2}}{3} & \frac{\sqrt{\frac{2}{3}}}{3} & 0 & -\frac{1}{3} & -\frac{2}{3\sqrt{3}} & 0 \\ \frac{1}{3} & -\frac{1}{\sqrt{3}} & \frac{1}{3\sqrt{2}} & 0 & \frac{1}{\sqrt{6}} & -\frac{1}{3} & 0 & -\frac{1}{\sqrt{3}} & 0 \\ \frac{2}{3} & \frac{2}{3\sqrt{3}} & -\frac{2\sqrt{2}}{3} & 0 & \frac{2\sqrt{\frac{2}{3}}}{3} & \frac{1}{3} & 0 & -\frac{1}{3\sqrt{3}} & 0 \\ \frac{2}{3} & -\frac{2}{\sqrt{3}} & -\frac{2\sqrt{2}}{3} & 0 & -2\sqrt{\frac{2}{3}} & \frac{1}{3} & 0 & \frac{1}{\sqrt{3}} & 0 \end{pmatrix}, \quad (\text{B4})$$

$$M_{J \leftarrow K_{\pm}} = \begin{pmatrix} \frac{4}{9} & \frac{2}{9} & -\frac{1}{3} & -\frac{2\sqrt{\frac{2}{3}}}{3} & \frac{8}{9} & \frac{4}{9} & \frac{4}{3\sqrt{3}} & \frac{8\sqrt{2}}{9} & -\frac{4\sqrt{2}}{9} \\ -\frac{4}{9} & \frac{4}{9} & \frac{1}{3} & -\frac{4\sqrt{\frac{2}{3}}}{3} & -\frac{8}{9} & \frac{8}{9} & \frac{8}{3\sqrt{3}} & -\frac{8\sqrt{2}}{9} & -\frac{8\sqrt{2}}{9} \\ -\frac{2}{9} & -\frac{4}{9} & -\frac{1}{3} & -\frac{2\sqrt{\frac{2}{3}}}{3} & -\frac{4}{9} & -\frac{8}{9} & \frac{4}{3\sqrt{3}} & -\frac{4\sqrt{2}}{9} & \frac{8\sqrt{2}}{9} \\ -\frac{2}{9} & \frac{2}{9} & -\frac{1}{3} & \frac{\sqrt{\frac{2}{3}}}{3} & -\frac{4}{9} & \frac{4}{9} & -\frac{2}{3\sqrt{3}} & -\frac{4\sqrt{2}}{9} & -\frac{4\sqrt{2}}{9} \\ -\frac{2}{3} & \frac{2}{3} & 0 & -\sqrt{\frac{2}{3}} & \frac{2}{3} & -\frac{2}{3} & -\frac{1}{\sqrt{3}} & -\frac{\sqrt{2}}{3} & -\frac{\sqrt{2}}{3} \\ 0 & -\frac{2}{3} & 0 & -\sqrt{\frac{2}{3}} & 0 & \frac{2}{3} & -\frac{1}{\sqrt{3}} & 0 & \frac{\sqrt{2}}{3} \\ -\frac{2}{3} & -\frac{2}{3} & 0 & 0 & \frac{2}{3} & \frac{2}{3} & 0 & -\frac{\sqrt{2}}{3} & \frac{\sqrt{2}}{3} \\ -\frac{4}{3} & \frac{4}{3} & 0 & 0 & -\frac{2}{3} & \frac{2}{3} & 0 & \frac{4\sqrt{2}}{3} & \frac{4\sqrt{2}}{3} \\ -\frac{4}{3} & -\frac{4}{3} & 0 & 0 & -\frac{2}{3} & -\frac{2}{3} & 0 & \frac{4\sqrt{2}}{3} & -\frac{4\sqrt{2}}{3} \end{pmatrix}. \quad (\text{B5})$$

The remaining transformations can all be obtained by, for example,

$$M_{K \leftarrow J_{\pm}} = M_{K \leftarrow J} M_{J \leftarrow J_{\pm}} \quad \text{with} \quad M_{K \leftarrow J} = M_{J \leftarrow K}^{-1}. \quad (\text{B6})$$

APPENDIX C: SINGLE-ION ANISOTROPIES

For $S = 1/2$, all quadrupole operators are zero. Similarly, the symmetry-allowed single-ion dipole anisotropy term $(S_i^z)^2$ is a constant. For $S \geq 1$, quadrupoles can become active along with the dipolar single-ion anisotropy. In addition, there are single-ion quadrupole anisotropies allowed by the site symmetry group which

may be nonzero. These appear in Eq. (7) as diagonal elements $\mathcal{J}_{ii}^{ab}$. For the pyrochlore lattice with site symmetry D_{3d} , these have the form in the local frame

$$\begin{aligned} H_{\text{SIA}} = & J_{zz}^{\text{SIA}} (Q^z)^2 + J_{t_{2g}, \pm}^{\text{SIA}} (Q_{t_{2g}}^+ Q_{t_{2g}}^- + Q_{t_{2g}}^- Q_{t_{2g}}^+) \\ & + J_{e_g, \pm}^{\text{SIA}} (Q_{e_g}^+ Q_{e_g}^- + Q_{e_g}^- Q_{e_g}^+) \\ & + J_{\text{off-diag}, \pm}^{\text{SIA}} (Q_{t_{2g}}^+ Q_{e_g}^- + Q_{t_{2g}}^- Q_{e_g}^+), \end{aligned} \quad (\text{C1})$$

where all operators are on a single site. One of the three diagonal terms may be freely set to zero thanks to the operator identity $\text{Tr}[Q^2] = \text{const}$. The quantum quadrupole moment operator satisfies

$$\begin{aligned}
& 4\text{Tr}[Q^2] \\
&= \left([S^\alpha S^\beta + S^\beta S^\alpha] - \frac{2}{3} |S|^2 \delta^{\alpha\beta} \right) \left([S^\beta S^\alpha + S^\alpha S^\beta] - \frac{2}{3} |S|^2 \delta^{\beta\alpha} \right) \\
&= (S^\alpha S^\beta + S^\beta S^\alpha)^2 + \frac{4}{9} \text{Tr}[1] |S|^4 - 2 \cdot \frac{2}{3} |S|^2 (|S|^2 + |S|^2) \\
&= 2|S|^4 + \frac{4}{3} |S|^4 - \frac{8}{3} |S|^4 + 2(S^\alpha S^\beta S^\alpha S^\beta) \\
&= \frac{2}{3} |S|^4 + 2(|S|^4 - \hbar |S|^2) \\
&= \frac{8}{3} |S|^4 - 2\hbar |S|^2 \\
&= \left(\frac{8}{3} [S(S+1)]^2 - 2[S(S+1)] \right) \hbar^2, \tag{C2}
\end{aligned}$$

where

$$\begin{aligned}
S^\alpha S^\beta S^\alpha S^\beta &= S^\alpha S^\beta (S^\beta S^\alpha + i\hbar \epsilon_{\alpha\beta\gamma} S^\gamma) \\
&= |S|^4 + i\hbar \epsilon_{\alpha\beta\gamma} S^\alpha S^\beta S^\gamma = |S|^4 - \hbar^2 |S|^2, \tag{C3}
\end{aligned}$$

using the relation

$$\begin{aligned}
\epsilon_{\alpha\beta\gamma} S^\alpha S^\beta S^\gamma &= S^x [S^y, S^z] + S^y [S^z, S^x] + S^z [S^x, S^y] \\
&= i\hbar |S|^2. \tag{C4}
\end{aligned}$$

APPENDIX D: LOCAL FRAME IRREP BASIS

Here, we provide a local frame basis for the irreducible representations which separates the $|m| = 1$ and $|m| = 2$ sectors, similar to how the basis provided in Table II separated instead the t_{2g} and e_g sectors. In terms of the local frame spin operators (where bars indicate local components), we use the notation

$$\begin{aligned}
(|m| = 2) \quad Q^1 &\equiv ((S^{\bar{x}})^2 - (S^{\bar{y}})^2), \\
(|m| = 0) \quad Q^2 &\equiv \frac{1}{\sqrt{3}} (2(S^{\bar{z}})^2 - (S^{\bar{x}})^2 - (S^{\bar{y}})^2), \\
(|m| = 2) \quad Q^3 &\equiv (S^{\bar{x}} S^{\bar{y}} + S^{\bar{y}} S^{\bar{x}}), \\
(|m| = 1) \quad Q^4 &\equiv (S^{\bar{x}} S^{\bar{z}} + S^{\bar{z}} S^{\bar{x}}), \\
(|m| = 1) \quad Q^5 &\equiv (S^{\bar{y}} S^{\bar{z}} + S^{\bar{z}} S^{\bar{y}}), \tag{D1}
\end{aligned}$$

which are the cubic harmonic equivalents (real and imaginary parts) of the spherical harmonic basis defined in Eq. (20). We begin with the A_1 irrep, for which the sole operator is given by

$$O_{A_1} = Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2, \tag{D2}$$

where the lower index is the sublattice index. The E irrep multiplet can be nicely separated into two components which we label A ($|m| = 2$) and B ($|m| = 1$):

$$\begin{aligned}
O_{E_A}^1 &= Q_1^1 + Q_2^1 + Q_3^1 + Q_4^1, \\
O_{E_A}^2 &= Q_1^3 + Q_2^3 + Q_3^3 + Q_4^3, \\
O_{E_B}^1 &= Q_1^4 + Q_2^4 + Q_3^4 + Q_4^4, \\
O_{E_B}^2 &= Q_1^5 + Q_2^5 + Q_3^5 + Q_4^5, \tag{D3}
\end{aligned}$$

which is equivalent to Eq. (67). A similar local basis for the T_1 multiplets separating the $m = \pm$ and $m = \pm 2$ components is given by

$$\begin{aligned}
O_{T_1,A}^1 &= Q_1^3 - Q_2^3 - Q_3^3 + Q_4^3, \\
O_{T_1,A}^2 &= \frac{\sqrt{3}}{2} Q_1^1 + \frac{1}{2} Q_1^3 + \frac{\sqrt{3}}{2} Q_2^1 + \frac{1}{2} Q_2^3 \\
&\quad - \frac{\sqrt{3}}{2} Q_3^1 - \frac{1}{2} Q_3^3 - \frac{\sqrt{3}}{2} Q_4^1 - \frac{1}{2} Q_4^3, \\
O_{T_1,A}^3 &= \frac{\sqrt{3}}{2} Q_1^1 - \frac{1}{2} Q_1^3 - \frac{\sqrt{3}}{2} Q_2^1 + \frac{1}{2} Q_2^3 \\
&\quad + \frac{\sqrt{3}}{2} Q_3^1 - \frac{1}{2} Q_3^3 - \frac{\sqrt{3}}{2} Q_4^1 + \frac{1}{2} Q_4^3, \tag{D4}
\end{aligned}$$

$$\begin{aligned}
O_{T_1,B}^1 &= -Q_1^5 + Q_2^5 + Q_3^5 - Q_4^5, \\
O_{T_1,B}^2 &= \frac{\sqrt{3}}{2} Q_1^4 - \frac{1}{2} Q_1^5 + \frac{\sqrt{3}}{2} Q_2^4 - \frac{1}{2} Q_2^5 \\
&\quad - \frac{\sqrt{3}}{2} Q_3^4 + \frac{1}{2} Q_3^5 - \frac{\sqrt{3}}{2} Q_4^4 + \frac{1}{2} Q_4^5, \\
O_{T_1,B}^3 &= \frac{\sqrt{3}}{2} Q_1^4 + \frac{1}{2} Q_1^5 - \frac{\sqrt{3}}{2} Q_2^4 - \frac{1}{2} Q_2^5 \\
&\quad + \frac{\sqrt{3}}{2} Q_3^4 + \frac{1}{2} Q_3^5 - \frac{\sqrt{3}}{2} Q_4^4 - \frac{1}{2} Q_4^5. \tag{D5}
\end{aligned}$$

Similarly, a local basis for the three T_2 multiplets is

$$\begin{aligned}
O_{T_2,A}^1 &= \frac{1}{2} Q_1^1 - \frac{\sqrt{3}}{2} Q_1^3 + \frac{1}{2} Q_2^1 - \frac{\sqrt{3}}{2} Q_2^3 \\
&\quad - \frac{1}{2} Q_3^1 + \frac{\sqrt{3}}{2} Q_3^3 - \frac{1}{2} Q_4^1 + \frac{\sqrt{3}}{2} Q_4^3, \\
O_{T_2,A}^2 &= -\frac{1}{2} Q_1^1 - \frac{\sqrt{3}}{2} Q_1^3 + \frac{1}{2} Q_2^1 + \frac{\sqrt{3}}{2} Q_2^3 \\
&\quad - \frac{1}{2} Q_3^1 - \frac{\sqrt{3}}{2} Q_3^3 + \frac{1}{2} Q_4^1 + \frac{\sqrt{3}}{2} Q_4^3, \\
O_{T_2,A}^3 &= Q_1^1 - Q_2^1 - Q_3^1 + Q_4^1, \tag{D6}
\end{aligned}$$

$$\begin{aligned}
O_{T_2,B}^1 &= -\frac{1}{2}Q_1^4 - \frac{\sqrt{3}}{2}Q_1^5 - \frac{1}{2}Q_2^4 - \frac{\sqrt{3}}{2}Q_2^5 \\
&\quad + \frac{1}{2}Q_3^4 + \frac{\sqrt{3}}{2}Q_3^5 + \frac{1}{2}Q_4^4 + \frac{\sqrt{3}}{2}Q_4^5, \\
O_{T_2,B}^2 &= \frac{1}{2}Q_1^4 - \frac{\sqrt{3}}{2}Q_1^5 - \frac{1}{2}Q_2^4 + \frac{\sqrt{3}}{2}Q_2^5 \\
&\quad + \frac{1}{2}Q_3^4 - \frac{\sqrt{3}}{2}Q_3^5 - \frac{1}{2}Q_4^4 + \frac{\sqrt{3}}{2}Q_4^5, \\
O_{T_2,B}^3 &= Q_1^4 + Q_2^4 + Q_3^4 - Q_4^4,
\end{aligned} \tag{D7}$$

$$\begin{aligned}
O_{T_2,\text{ice}}^1 &= -Q_1^2 - Q_2^2 + Q_3^2 + Q_4^2, \\
O_{T_2,\text{ice}}^2 &= Q_1^2 - Q_2^2 + Q_3^2 - Q_4^2, \\
O_{T_2,\text{ice}}^3 &= Q_1^2 - Q_2^2 - Q_3^2 + Q_4^2.
\end{aligned} \tag{D8}$$

These bases are used for labeling the mean-field phase diagrams in Fig. 8.

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- $$|\epsilon_{\alpha\beta\gamma}| = |\epsilon_{\rho\delta\sigma}| R(g)_{\rho\alpha} R(g)_{\delta\beta} R(g)_{\sigma\gamma}$$
- for all $g \in T_d$, where $R(g)$ is the corresponding $O(3)$ rotation.
- [95] The tensor $\mathcal{R}$ is one of three rank-2 “residue tensors” defined by pairwise contraction of the antisymmetric Levi-Civita symbol with a general rank-3 tensor [93]. In our case, two are identical and the third is zero, because $\mathcal{M}^{\alpha\beta\gamma} = \mathcal{M}^{\alpha\beta}$ following from the symmetry of the quadrupole tensors Q .
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- [100] This description is redundant and covers the four-sphere multiple times, for example, $q(0, \pi/2, 0, S, -T) = q(0, 0, 0, S, T)$. In practice, one can simply work with a unit five-component vector and reconstruct the symmetric trace-free matrix without any redundancy.
- [101] Note that, for uniaxial tensors with $T = 0$ in Eq. (54), $\text{Tr}[q^3] = S^3/\sqrt{6}$, so the sign of $\text{Tr}[q^3]$ is equivalent to the sign of S .
- [102] For $S > 1$ it is sufficient to evaluate $\langle S|Q^{\alpha\beta}|S \rangle$, but for $S = 1$ there is also a nontrivial cross term coming from $\langle -1|Q^{\alpha\beta}|+1 \rangle$.
- [103] We thank Karlo Penc for pointing out that such a constraint exists for $S = 1$.
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