Order by virtual crystal field fluctuations in pyrochlore XY antiferromagnets

Jeffrey G. Rau,1 Sylvain Petit,2 and Michel J. P. Gingras1,3,4,5,6

1Department of Physics and Astronomy, University of Waterloo, Ontario, N2L 3G1, Canada
2CEA, Centre de Saclay, DSM/IRAMIS/ Laboratoire Leon Brillouin, F-91191 Gif-sur-Yvette, France
3Perimeter Institute for Theoretical Physics, Waterloo, Ontario, N2L 2Y5, Canada
4Canadian Institute for Advanced Research, 180 Dundas Street West, Suite 1400, Toronto, ON, M5G 1Z8, Canada
5Quantum Matter Institute, University of British Columbia, Vancouver, BC, V6T 1Z4, Canada
6TRIUMF, Theory Group, 4004 Wesbrook Mall, Vancouver, BC V6T 2A3, Canada

(Dated: October 16, 2015)

Conclusive evidence of order by disorder is scarce in real materials. Perhaps one of the strongest cases presented has been for the pyrochlore XY antiferromagnet Er2Ti2O7, with the ground state selection proceeding by order by disorder induced through the effects of quantum fluctuations. This identification assumes the smallness of the effect of virtual crystal field fluctuations that could provide an alternative route to picking the ground state. Here we show that this order by virtual crystal field fluctuations is not only significant, but competitive with the effects of quantum fluctuations. Further, we argue that higher-multipolar interactions that are generically present in rare-earth magnets can dramatically enhance this effect. From a simplified bilinear-biquadratic model of these multipolar interactions, we show how the virtual crystal field fluctuations manifest in Er2Ti2O7 using a combination of strong coupling perturbation theory and the random phase approximation. We find that the experimentally observed ψ2 state is indeed selected and the experimentally measured excitation gap can be reproduced when the bilinear and biquadratic couplings are comparable while maintaining agreement with the entire experimental spin-wave excitation spectrum. Finally, we comment on possible tests of this scenario and discuss implications for other order-by-disorder candidates in rare-earth magnets.

I. INTRODUCTION

The study of frustrated magnetism has led to the discovery of several new and exotic phenomena [1]. Much of this physics can be traced back to frustration inducing a large number of degenerate or nearly degenerate low energy states, with the ultimate ground state and low energy physics being sensitive to subtle effects that act within this manifold. Due to this degeneracy, the relevant energy scales are much smaller than in conventional unfrustrated systems and thus may arise from a wider variety of sources. The competition between the small interactions can lead to a rich set of phases, from unconventional magnetically ordered states or even novel non-magnetic phases such as classical or quantum spin liquids [1–3].

A particularly interesting class of degeneracy lifting mechanisms is order by disorder. In the seminal incarnations of Villain et al. [4] and Shender [5], thermal or quantum fluctuations respectively select the states from the degenerate manifold that have the largest space to fluctuate. This perspective naturally leads to a generalization of the idea of order by disorder, i.e. the selection from a degenerate manifold via any set of fluctuation corrections to the energy. This mechanism of fluctuation induced order is not only a concept within the purview of frustrated magnetism, or even condensed matter physics taken more broadly, but even appears in high-energy physics in the guise of the Coleman-Weinberg mechanism [6]. This stabilization of order by quantum fluctuations, or order by quantum disorder [5, 7, 8], has an even longer history. While largely unnoticed, one of the earliest examples was put forth by Tessman [9] where quantum zero-point fluctuations select the magnetization direction in a dipolar ferromagnet [10, 11].

More formally, we consider a system whose ordering is described by some order parameter m. The natural low-energy description can then be framed in terms of the effective action Γ[m]. In each order by disorder scenario, one starts from an artificial limit where there is an accidental degeneracy; that is the effective action at this point, Γ0[m], has an accidental symmetry. For order by thermal disorder this limit is T → 0, while for order by quantum-disorder this is the classical limit where the spin becomes large, or 1/S → 0. Adding such perturbations moves the theory away from this artificial limit, adding a term δΓ[m] to the effective action as Γ[m] = Γ0[m] + δΓ[m]. A distinction is usually drawn between energetic and fluctuation-driven contributions to selection, i.e. between zeroth order and higher order perturbative
corrections to $\delta \Gamma [m]$, though this can be somewhat ambiguous. Generically, $\delta \Gamma [m]$ breaks the accidental symmetry, lifting the degeneracy present in $\Gamma_0 [m]$. In real systems such a $\delta \Gamma [m]$ correction should always be present, so long as the symmetry is not exact, with each order by disorder mechanism providing its own contribution to $\delta \Gamma [m]$. The identification of an order by disorder mechanism then relies not only on a proximity to the idealized $\Gamma [m]$ limit, but also on the contribution of that mechanism to $\delta \Gamma [m]$ being dominant over all other sources of $\delta \Gamma [m]$ corrections. Beyond having just a single dominant order by disorder channel, these fluctuation selection mechanisms could thus cooperate and select the same state, or perhaps compete and prefer different states [4, 7]. Competing order by disorder can lead to exotic multiple-step phase transitions, an unusual sensitivity to perturbations or a host of other interesting properties.

While it is easy for deviations from the initial idealized limit to spoil an order by disorder selection mechanism, there are many systems where the simplest energetic selection mechanisms can be forbidden on fairly general grounds. Indeed, some of the early examples [5, 9] focus on selection of the moment direction in simple ferromagnets and antiferromagnets with high symmetry. Classically, the presence of three-, four- or six-fold rotations axes can forbid the selection of a moment orientation purely from exchange anisotropy. In low-spin systems without sufficient single-ion anisotropy, the leading anisotropy then must come from effective multi-spin interactions. These can be generated at the level of a Landau-Ginzburg theory through the order by disorder mechanisms discussed above, be it thermal, quantum or otherwise. To find a clear demonstration of this physics the challenge is then to find a material that is sufficiently close to such a limit with accidental ground state degeneracy. Theoretical and experimental control are essential: one must be able to characterize and quantify deviations from the idealized theoretical limit with the degeneracy while experimentally, one must be able to validate the theoretical model and approach the limiting regime closely, removing any extrinsic complications.

The class of rare-earth pyrochlore magnets $R_2 M_2 O_7$ are promising toward this goal [3, 12]. Aside from having the requisite high-symmetry, many are well described by an effective spin-1/2 model [13–15] and thus lack any on-site anisotropy. At the nearest-neighbor level, there are four symmetry allowed exchanges [16] leading to a diverse phase diagram that includes a variety of magnetic and non-magnetic phases [17, 18]. Included in this phase diagram is a large region where the effective spins order uniformly within their local XY planes [19]. This so-called $\Gamma_5$ manifold (see Fig. 1) can be thought of as a local ferromagnet and enjoys the degeneracy protection [15] discussed above. Of these rare-earth pyrochlores, we will focus on the titanate $Er_2 Ti_2 O_7$ which is close to ideal in each of these regards, having long been proposed as a prime example of order by disorder [20]. Experimentally, the thermodynamic properties of this material are uncontroversial and have been well-characterized. The $Er^{3+}$ free ion hosts a $J = 15/2$ manifold that is quenched by the crystal field into an effective spin-1/2 degree of freedom with a strong planar (XY) anisotropy [20]. The low-lying crystal field energy levels have been measured to fair precision [20] and match well with theoretical models [21, 22]. Ordering occurs near $T_N \sim 1.2$ K into the so-called $\psi_2$ state (see Fig. 1), a non-coplanar antiferromagnet [20, 23]. The magnetic excitations above this state are sharp and have been measured across many cuts in reciprocal space via inelastic neutron scattering [15, 24, 25]. A nearly gapless mode is observed [24–26], suggesting a quasi-degenerate set of ground states, as needed for order by disorder. Further, crystals of $Er_2 Ti_2 O_7$ can be made very clean, and disorder can be re-introduced in a controlled manner via depletion or stuffing [27]. The appropriate theoretical model of the effective spin-1/2 degrees of freedom has been tightly constrained by matching to the experimental data, through fitting of the inelastic neutron scattering spectrum in both zero and finite magnetic fields [15, 25]. Altogether, this model can reproduce nearly all of the current experimental data at a qualitative, and sometimes even a quantitative level [28].

Classically, this effective spin-1/2 model has an accidental degeneracy, the $\Gamma_5$ manifold mentioned above, consistent with the soft-mode seen experimentally. Similarly, conventional mean-field theory shows the same accidental degeneracy in the Landau-Ginzburg theory near $T_N$ [29]. This classical degeneracy remains unbroken for any symmetry allowed, two-spin interactions between the spins, to arbitrary distance [15]. Several proposals on how to lift this degeneracy have been put forth; these include order by thermal disorder (for $T \rightarrow 0^+$ or $T \rightarrow T_\Gamma^-$) [20, 29–32], order by quantum disorder [15, 19, 30, 31] or order by structural disorder [33, 34]. A case has been made for order by quantum disorder [15, 31] as the operant mechanism in lifting the degeneracy of the classical ground state manifold in $Er_2 Ti_2 O_7$, with order by thermal disorder [28] cooperating at the ordering temperature $T_N$. A key prediction of the order by quantum disorder proposal is a gap in the excitation spectrum of order $\sim 20 \mu$eV, comparable to the $\sim 40 – 45 \mu$eV gap that was later observed experimentally [25, 26]. One implicit limit that has been taken in all these studies is to assume that an effective spin-1/2 model with only two-spin interactions is itself sufficient. This can justified if one can take the crystal field energy scale $\eta$ to be much larger than the exchange scale. Taking $\eta$ to be finite then allows for corrections to the effective spin-1/2 model through virtual crystal field excitations, yet another channel contributing to $\delta \Gamma [m]$ as defined above. While these terms [25, 35] have been argued to be extremely small [15], the complexity of the multiparticle interactions between rare-earth ions [36–39] and the subleties arising from the combinatorics of high-order perturbation theory demand a more careful accounting of these effects.

In this article, we aim to carefully address the effects of virtual crystal field fluctuations [25, 35] on the ground state selection in $Er_2 Ti_2 O_7$. We find that such an order by virtual crystal field fluctuations is not only significant, but is naturally comparable with the effects from order by quantum disorder. When mapped into the effective spin-1/2 description via strong coupling perturbation theory, these fluctuations manifest as multi-spin interactions, with a complementary interpretation as classical energetic selection. We argue...
that the complex multipolar interactions that exist in the full $J = 15/2$ manifold further enhance these fluctuations, compared to the case of only bilinear interactions between the angular momenta $\mathbf{J}$, and render them very relevant in describing $\text{Er}_2\text{T}_{12}\text{O}_{7}$. For definiteness, we consider a bilinear-biquadratic exchange model of the $J = 15/2$ moments as a minimal model of this physics. We analyze the effects of virtual crystal field fluctuations using a combination of mean-field theory (MFT) and random-phase approximation (RPA) calculations. We show that these MFT+RPA calculations are qualitatively consistent with a treatment of the multi-spin interactionally, we find that this mechanism is cooperative with thermal exchange model of the $\text{Er}^{3+}$ over the effective (MFT) and random-phase approximation (RPA) calculations. We show that these MFT+RPA calculations are qualitatively consistent with a treatment of the multi-spin interactions via strong-coupling perturbation theory, and thus capture the effects of the virtual crystal field excitations. Generically, we find that this mechanism is cooperative with thermal and quantum selection, selecting the $\psi_2$ state as is seen experimentally. From these calculations we find that when the bilinear and biquadratic couplings are comparable, this selection mechanism can be of similar magnitude or even dominate over the effects of order by quantum disorder [15, 31]. We thus conclude that $\text{Er}_2\text{T}_{12}\text{O}_{7}$ may not ultimately be the long sought definite case for order by quantum disorder control by virtual crystal field fluctuations. In Sec. III A, we show how this selection proceeds and how it is related to the gap in the coarsest approximation, one simply projects the $J = 15/2$ moment $\mathbf{J}_r$ at site $\mathbf{r}_i$ into this manifold

$$P|\text{I}|P = \lambda_+ (S_i^+ \hat{x} + S_i^y \hat{y}) + \lambda_- S_i^z \hat{z} \equiv A_\mathbf{S}_i,$$

where $\mathbf{S}_i$ is the effective spin-1/2 operator and $\lambda = \text{diag}(\lambda_+, \lambda_-, \lambda_c)$ with $\lambda_+ \sim 6$ and $\lambda_- \sim 2$ depends on the details of the crystal field parameters through the spectral composition of the ground doublet. These $\lambda$-factors are related to the $g$-factors which characterize the response to an applied magnetic field via $\lambda_\mu = g_\mu / g_J$ where $\mu = x, y, z$ and $g_J = 6/5$ is the Landé factor for $\text{Er}^{3+}$. Both the $\mathbf{J}_r$ and $\mathbf{S}_i$ operators are defined in the local basis $(\hat{x}, \hat{y}, \hat{z})$ defined with respect to the high-symmetry directions at each site, as defined in Appendix A. In this local picture, the $\Gamma_3$ manifold corresponds to ferromagnetic ordering in the local XY plane, with $\psi_2$ defined as the moments ordered in the local $\hat{x}$ direction (see Fig. 1). The remaining states can be obtained from $\psi_2$ by a rotation of of all the spins about their local [111] direction.

As discussed in the Introduction, the most detailed information on the interactions with the $\text{Er}^{3+}$ ions comes from fitting such an effective spin-1/2 model to the results of inelastic neutron scattering experiments [15, 25]. It was found that a model with only nearest-neighbor anisotropic exchange between the effective spin-1/2 moments provides a fairly good description of the observed spectrum. By symmetry, the effective spin-1/2 Hamiltonian takes the form [15, 16]

$$H_{\text{eff}} = \sum_{\langle ij \rangle} \mathbf{J}_{ij} \mathbf{S}_i \mathbf{S}_j \equiv \sum_{\langle ij \rangle} \left[ \mathbf{J}_{zz} S_i^z S_j^z - \mathbf{J}_{\pm} \left( S_i^+ S_j^- + S_i^- S_j^+ \right) \right] + \mathbf{J}_{zx} \left( \gamma_{ij} S_i^+ S_j^+ + \text{h.c.} \right) + \mathbf{J}_{\pm} \left( \zeta_{ij} \left( S_i^+ S_j^- + S_i^- S_j^+ \right) + \text{h.c.} \right).$$

Details of the complex form factors $\gamma_{ij}$ and $\zeta_{ij}$ are given in Appendix A. From experimental fitting [15, 25], the $\mathbf{J}_{ij}$ couplings are of order $10^{-2}$ meV with $\mathbf{J}_{xx}$ and $\mathbf{J}_{zz}$ being the largest. A representative example, from Ref. [15], is

$$\mathbf{J}_{zz} = -2.5 \times 10^{-2} \text{ meV}, \quad \mathbf{J}_{xx} = +6.5 \times 10^{-2} \text{ meV},$$

$$\mathbf{J}_{\pm} = +4.2 \times 10^{-2} \text{ meV}, \quad \mathbf{J}_{zx} = -0.88 \times 10^{-2} \text{ meV.}$$

II. EFFECTIVE MODELS

Before delving into the detailed modeling of $\text{Er}_2\text{T}_{12}\text{O}_{7}$, we first summarize the arguments that lead to the effective spin-1/2 model that has been used in prior works [15, 28]. The ground state of the free $\text{Er}^{3+}$ ion consists of the $4f^{11}$ electronic configuration which carries a $J = 15/2$ moment. In the pyrochlore structure of $\text{Er}_2\text{T}_{12}\text{O}_{7}$ (space group $Fd\bar{3}m$), the $\text{Er}^{3+}$ ion lies at a site with $D_{3d}$ symmetry. The crystal field lifts the degeneracy of the $4f^{11}$ manifold, splitting it into a set of effective spin-1/2 $\Gamma_4$ doublets and dipolar-octupolar $\Gamma_5 \oplus \Gamma_6 \equiv \Gamma_{56}$ doublets [40]. The ground doublet is an effective spin-1/2 degree of freedom of type $\Gamma_4$, with a gap of $\Delta \sim 6 \text{ meV} \sim 70 \text{ K}$ to the first excited state [20]. Since this energy scale is large relative to the exchanges, which are expected to be $\sim 0.1 \text{ K} \sim 1 \text{ K}$ [15, 25], it is justified to consider an effective spin-1/2 model, down-folding the full set of crystal field levels into the ground doublet defined as $|\pm\rangle$. In the coarsest approximation, one simply projects the $J = 15/2$ moment $\mathbf{J}_r$ at site $\mathbf{r}_i$ into this manifold

$$P|\text{I}|P = \lambda_+ (S_i^+ \hat{x} + S_i^y \hat{y}) + \lambda_- S_i^z \hat{z} \equiv A_\mathbf{S}_i,$$

where $\mathbf{S}_i$ is the effective spin-1/2 operator and $\lambda = \text{diag}(\lambda_+, \lambda_-, \lambda_c)$ with $\lambda_+ \sim 6$ and $\lambda_- \sim 2$ depends on the details of the crystal field parameters through the spectral composition of the ground doublet. These $\lambda$-factors are related to the $g$-factors which characterize the response to an applied magnetic field via $\lambda_\mu = g_\mu / g_J$ where $\mu = x, y, z$ and $g_J = 6/5$ is the Landé factor for $\text{Er}^{3+}$. Both the $\mathbf{J}_r$ and $\mathbf{S}_i$ operators are defined in the local basis $(\hat{x}, \hat{y}, \hat{z})$ defined with respect to the high-symmetry directions at each site, as defined in Appendix A. In this local picture, the $\Gamma_3$ manifold corresponds to ferromagnetic ordering in the local XY plane, with $\psi_2$ defined as the moments ordered in the local $\hat{x}$ direction (see Fig. 1). The remaining states can be obtained from $\psi_2$ by a rotation of of all the spins about their local [111] direction.

As discussed in the Introduction, the most detailed information on the interactions with the $\text{Er}^{3+}$ ions comes from fitting such an effective spin-1/2 model to the results of inelastic neutron scattering experiments [15, 25]. It was found that a model with only nearest-neighbor anisotropic exchange between the effective spin-1/2 moments provides a fairly good description of the observed spectrum. By symmetry, the effective spin-1/2 Hamiltonian takes the form [15, 16]

$$H_{\text{eff}} = \sum_{\langle ij \rangle} \mathbf{J}_{ij} \mathbf{S}_i \mathbf{S}_j \equiv \sum_{\langle ij \rangle} \left[ \mathbf{J}_{zz} S_i^z S_j^z - \mathbf{J}_{\pm} \left( S_i^+ S_j^- + S_i^- S_j^+ \right) \right] + \mathbf{J}_{zx} \left( \gamma_{ij} S_i^+ S_j^+ + \text{h.c.} \right) + \mathbf{J}_{\pm} \left( \zeta_{ij} \left( S_i^+ S_j^- + S_i^- S_j^+ \right) + \text{h.c.} \right).$$

Details of the complex form factors $\gamma_{ij}$ and $\zeta_{ij}$ are given in Appendix A. From experimental fitting [15, 25], the $\mathbf{J}_{ij}$ couplings are of order $10^{-2}$ meV with $\mathbf{J}_{xx}$ and $\mathbf{J}_{zz}$ being the largest. A representative example, from Ref. [15], is

$$\mathbf{J}_{zz} = -2.5 \times 10^{-2} \text{ meV}, \quad \mathbf{J}_{xx} = +6.5 \times 10^{-2} \text{ meV},$$

$$\mathbf{J}_{\pm} = +4.2 \times 10^{-2} \text{ meV}, \quad \mathbf{J}_{zx} = -0.88 \times 10^{-2} \text{ meV.}$$
Further details on other proposed sets of effective spin-1/2 exchanges are found in Appendix B 2. Longer range couplings, such as second or third neighbor exchanges or dipolar interactions are generally expected to be present, but have not been found to be necessary to reproduce the features that are theoretically accessible within current experimental uncertainties. While this model has been found to be fairly successful, we show, as outlined in the Introduction, that higher corrections that go beyond the coarse approximation encapsulated in Eq. (2) will prove to be significant. To include such corrections, we must build a model for Er$_2$Ti$_2$O$_7$ starting from the atomic physics and progressing towards the low-energy effective Hamiltonian.

A. Multipolar interactions

The structure of the model (2) was essentially fixed by symmetry and the restriction to only two-spin (bilinear) interactions between the effective spin-1/2 degrees of freedom. Information on the microscopic interactions between the $J_i$ moments or the 4$f$ electrons themselves is essentially lost through the projection into the ground doublets; compressed into the four exchange parameters $J_{z^2}, J_{z^2}, J_{zz}$ and $J_{zz}$. To go beyond this projection into the ground doublets, we move up in energy and consider a model of the multipolar interactions between the $J = 15/2$ moments. As above, we consider only interactions between nearest-neighbor sites. This can be partially justified as, aside from the long-range dipolar interactions, one expects multipolar couplings to arise from short-range super-exchange type processes [36, 37].

In contrast to the effective spin-1/2 model of Eq. (2), we do not expect these more microscopic interactions to have only a bilinear form. Unlike the effective spin-1/2 moments, the $J = 15/2$ manifolds of the Er$^{3+}$ ions can support many higher-order multipoles. These multipoles can be classified into ranks; the familiar dipole operators $\sim J^0$ are rank-1, quadrupole operators $\sim J^2J^0$ are rank-2 and so forth. As $J = 15/2$, such multipoles can be constructed up to including rank-15. To proceed in a systematic fashion we introduce a basis for these multipole operators that transforms in the same way as the spherical harmonics. As for the spherical harmonics, for a rank-$K$ multipole we have 2$K$ + 1 operators indexed by $Q = -K, -K+1, \ldots +K-1, +K$. More explicitly, we define the set of rank-$K$ multipoles $O_{KQ}(J)$

$$
(J, M) | O_{KQ}(J)|J, M'\rangle \equiv \sqrt{\frac{2K + 1}{2J + 1}} | J, M; K, -Q | J, M'\rangle,
$$

where $| J, M; K, -Q | J, M'\rangle$ is a Clebsch-Gordan coefficient and $| J, M \rangle$ are eigenstates of $J^2 - J^z$. These operators have been normalized so that $\mathrm{tr}(O_{KQ}(J)\dagger O_{KQ}(J)) = 1$, so the different ranks can be compared on equal footing without worrying about large matrix element factors that arise when acting on the $| J, M \rangle$ states. The rank-1 vector operators are then simply a reformulation of the dipole moment $J$,

$$
O_{1,0}(J) = \frac{1}{2\sqrt{85}} J^0, \quad O_{1,\pm 1}(J) = \pm \frac{1}{2\sqrt{85}} \left( J^\pm \mp iJ^y \right),
$$

where the factor of $1/(2\sqrt{85})$ enforces the trace normalization. We note that these operators are similar to, but not identical to the Stevens’ operator equivalents [41] used to define the crystal field potential.

With these degrees of freedom in hand, we can write down a model of their interactions. Aside from the crystal field potential, because of the weakness of super-exchange processes in 4$f$ insulators [37] we expect them to be predominantly pairwise, generically giving the model

$$
\sum (ij) \sum_{K, K', Q} O_{KQ}(J_i) M_{ij}^{KQ, K'Q'} O_{K'Q'}(J_j) + \sum_i \mathcal{V}(J_i), \quad (6)
$$

where $\mathcal{V}(J)$ is the crystal field potential, $O_{KQ}(J_i)$ is a multipole of rank-$K$ and $M$ are the multipolar coupling constants. The form and parameters we use for $\mathcal{V}(J)$ are discussed in Appendix B 1. Processes such as super-exchange can only generate interactions up to including rank-7 multipoles [36–39]. Given that the anisotropy in the fitted exchanges in Er$_2$Ti$_2$O$_7$ deviates strongly from that expected from magnetostatic dipolar interactions, we expect the super-exchange scale to be significant, and thus a wide range of multipolar ranks to be present in the interactions of the $J = 15/2$ model given by Eq. (6). There are an enormous number of independent couplings embedded in the matrix $M$, given that $K, K' \leq 7$ and $|Q| \leq K$. Even accounting for symmetry leaves hundreds of possible couplings. Thankfully, we have some semblance of a separation of scales via the crystal field potential, which at $\lambda \sim 6$ meV is roughly two orders of magnitude larger than the expected scale for $M$.

We now have all the pieces to improve on the effective model of Eq. (2), which can, in principle, be obtained for a given $M$ by a bare projection of Eq. (6) into the ground doublets. In the following section we sketch a derivation of the low energy effective model that goes beyond simply the bilinear interactions defined in Eq. (2). We do this leaving the multipolar interactions somewhat arbitrary, relegating the detailed discussion of their form to Sec. IV.

B. Strong coupling perturbation theory

To derive the low-energy effective model, we carry out strong coupling perturbation theory in the crystal field potential, perturbing with the multipolar interactions. Aside from the simple model of Eq. (2), we also consider the higher order corrections that have been ignored in previous studies. More concretely, we use the Rayleigh-Schrödinger perturbation theory as presented in Lindgren [42]. We decompose the full Hamiltonian, $H$, as $H = H_0 + V$ where

$$
H_0 = \sum_i \mathcal{V}(J_i), \quad (7a)
$$

$$
V = \sum (ij) \sum_{K, K', Q} O_{KQ}(J_i) M_{ij}^{KQ, K'Q'} O_{K'Q'}(J_j). \quad (7b)
$$

To control the passage from the $J = 15/2$ model to the effective spin-1/2, we have added a dimensionless rescaling parameter $\eta$ to the crystal field. The choice $\eta = 1$ corresponds to the
physical, experimentally fitted crystal field Hamiltonian [22], with larger values suppressing the effects (i.e. admixing) of the higher lying crystal field doublets in the low-energy sector composed of the ground doublets. The bare Hamiltonian \( H_0 \) is diagonalized using single-ion crystal field states at each site. To proceed with the perturbation theory, we define a projector into the ground state manifold, \( P = \sum_{E_n} |n\rangle \langle n| \), along with a resolvent operator

\[
R = \sum_{E_n=E_0} \frac{|n\rangle \langle n|}{E_0 - E_n},
\]

(8)

where \( E_n \) and \( |n\rangle \) are the eigenvalues and eigenstates of \( H_0 \). This perturbation theory becomes formally exact in the limit \( \eta \to \infty \). The expansion of the effective Hamiltonian is given in Lindgren [42] as \( H_{\text{eff}} = \sum_n \eta^{n+1} H_{\text{eff},n} \). Here one considers a wave-operator, \( \Omega \), related to the effective Hamiltonian as \( H_{\text{eff}} = PV\Omega \) with the analogous expansion \( \Omega = \sum_n \eta^{n+1} \Omega_n \). These are defined via the relation

\[
\Omega_n = RV\Omega_{n-1} - R \sum_{m=1}^{n-1} \Omega_{n-m} V\Omega_{m-1}.
\]

(9)

Starting with \( \Omega_1 = P \), the higher order \( \Omega_n \), and thus \( H_{\text{eff},n} \), can be computed recursively. The first three orders are given by

\[
\begin{align*}
H_{\text{eff},1} &= PV\Omega, \quad (10a) \\
H_{\text{eff},2} &= PV\Omega V\Omega, \quad (10b) \\
H_{\text{eff},3} &= PV\Omega V\Omega V\Omega - \frac{1}{2} \{PV\Omega V\Omega, PV\Omega\}, \quad (10c)
\end{align*}
\]

where \( \{,\} \) is the anti-commutator [43]. Due to their complexity, we will not give the expressions for \( H_{\text{eff},4} \) and \( H_{\text{eff},5} \), but they can be straightforwardly computed from Eq. (9).

The leading term, \( H_{\text{eff},1} \), is simply the projection of the multipolar interactions, \( V \), into the ground doublets. This can be accomplished by projecting the multipoles individually

\[
PO_{KQ}(J_i)P = \begin{cases} 
V_{KQ} \cdot S_i & \text{if } K \text{ odd} \\
\text{const.} & \text{if } K \text{ even}
\end{cases}
\]

(11)

then substituting them back into \( V \) in Eq. (6). The vectors \( V_{KQ} \) are in general complex and define the mapping into the effective spin-1/2, depending only on the spectral composition of the ground doublet. At first order in perturbation theory, the even rank terms lead only to a constant shift of the energy and can be ignored. As such, we see that the even-rank multipolar interactions are completely unconstrained by the fitted effective-spin-1/2 exchanges, \( J_{ij} \). Combined together, the odd terms give the interactions between the effective spin-1/2 operators \( S_i \) as

\[
H_{\text{eff},1} = \sum_{i,j} S_i^z \left( \sum_{KQ,K'Q'} v_{KQ} V_{K'Q'}^{KQ} M_{ij}^{KQ,K'Q'} S_j \right), \quad (12)
\]

This leads to the symmetry allowed nearest-neighbor model as given in Eq. (2), with only two-spin interactions, where the tremendous complexity of \( M \) is embedded in the four symmetry allowed exchanges \( J_{zz}, \ J_{zz}, \ J_{zz} \), and \( J_{zz} \).

At higher order, further corrections will be generated through virtual crystal field fluctuations [44] involving the excited single-ion states through the resolvent operators that appear in Eq. (10). The leading corrections that do not simply renormalize the bilinear couplings are four- and six-spin interactions [19, 29] which appear at third and fifth order in \( \mathcal{M} \). We thus write the effective Hamiltonian at fifth order in three pieces, \( H_{\text{eff}} = H_2 + H_4 + H_6 \) containing the two-, four- and six-spin interactions. Explicitly, we have

\[
\begin{align*}
H_2 &= \sum_{i_1,\ldots,i_4} J_{i_1\cdots i_4} S_{i_1} S_{i_2} S_{i_3} S_{i_4}, \quad (13a) \\
H_4 &= \sum_{i_1,\ldots,i_4} K_{i_1\cdots i_4} S_{i_1} S_{i_2} S_{i_3} S_{i_4}, \quad (13b) \\
H_6 &= \sum_{i_1,\ldots,i_6} \sum_{\alpha} \Omega_{i_1\cdots i_6}^{\alpha} S_{i_1} S_{i_2} S_{i_3} S_{i_4} S_{i_5} S_{i_6}. \quad (13c)
\end{align*}
\]

The lowest order part of the bilinear couplings \( J \) in Eq. (13) are the nearest neighbor projection of the multipolar interactions at order \( \mathcal{M} \), as given in Eq. (12). Higher corrections at orders \( \mathcal{M}^2/(\eta\Lambda) \) up to \( \mathcal{M}^5/(\eta\Lambda)^5 \) renormalize bilinear couplings between the effective spin-1/2 operators, as well as inducing second, third and further neighbor exchanges where \( \Lambda \) defines the scale of crystal field when \( \eta = 1 \). The nearest-neighbor part will be taken to match the experimentally determined values of Eq. (3). The subleading further neighbor exchanges do not lift the \( \Gamma_5 \) degeneracy on their own [15] and serve only to renormalize the bilinear exchange scale. While this will modify the spin-wave dispersion and other features of model, it will not affect the ground state selection or excitation gap. Since this is our focus and the question of foremost interest, we ignore these terms.

The four-spin interactions, \( K \), appear first at order \( \mathcal{M}^4/(\eta\Lambda)^2 \) and receive subleading corrections from fourth- and fifth-order as \( \mathcal{M}^4/(\eta\Lambda)^3 \) and \( \mathcal{M}^6/(\eta\Lambda)^5 \). We keep only the leading terms, at order \( \mathcal{M}^4/(\eta\Lambda)^2 \), where the four sites \( i_1,\ldots,i_4 \) take the form of trees built from three nearest-neighbor bonds of the lattice. For example, a tree for three bonds can involve four distinct sites and thus contribute to the four-spin operators at order \( \mathcal{M}^4/(\eta\Lambda)^2 \). Contributions with three bonds that have a loop involve at most two or three spins and can not contribute to a four-spin term. Similarly, for the six-spin interactions, \( L \), the leading contribution comes at order \( \mathcal{M}^6/(\eta\Lambda)^4 \) with the sites \( i_1,\ldots,i_6 \) forming trees built from five nearest-neighbor bonds. A large number of possible anisotropic couplings are allowed through the dependence on the spin indices in both the four- and six-spin interaction terms.

### III. ORDER BY VIRTUAL CRYSTAL FIELD FLUCTUATIONS

Having understood how higher spin interactions are induced by virtual crystal field excitations, we next need to understand how the four- and six-spin interactions affect the ground state selection and the energy gap. To do this, we construct a variational product state for each local ferromagnetic
ordering direction $|\mathbf{n}\rangle$ as

$$\langle \mathbf{n} \mid S_i \mid \mathbf{n} \rangle = \frac{1}{2} \left[ \sin \theta (\cos \phi \hat{x} + \sin \phi \hat{y}) + \cos \theta \hat{z} \right] = \frac{1}{2} \mathbf{n},$$

(15)

where $|\uparrow\rangle_i$, $|\downarrow\rangle_i$ are effective spin-1/2 states of the low-energy effective model and $(\theta, \phi)$ are the spherical angles for the direction $\mathbf{n}$. By construction, the expectation value of the effective spin-1/2 is oriented in the direction specified by $\theta$ and $\phi$.

$$\langle \mathbf{n} \mid S_i \mid \mathbf{n} \rangle = \frac{1}{2} \left[ \sin \theta (\cos \phi \hat{x} + \sin \phi \hat{y}) + \cos \theta \hat{z} \right] = \frac{1}{2} \mathbf{n}. \quad (15)$$

The $\Gamma_3$ manifold is then the set of states with $\theta = \pi/2$; $\psi_2$ corresponding to $\phi = n\pi/3$ and $\psi_3$ to $\phi = n\pi/3 + \pi/6$ with $n = 0, 1, 2, \ldots, 5$.

When phrased in terms of the states in the low-energy effective model, the state $|\mathbf{n}\rangle$ contains no inter-site correlations. Thus when viewed through the lens of the low-energy effective model, the selection via multi-spin interactions could be regarded as a purely classical energetic effect. While intuitive, such a perspective obscures some of the key aspects of the physics. A more complete viewpoint requires consideration of what $|\mathbf{n}\rangle$ corresponds to in terms of the physical $|\pm\rangle_i$ crystal field ground doublets. At zeroth order one would simply map the effective spin-1/2 states into the ground doublets directly, replacing $|\uparrow\rangle_i \rightarrow |+\rangle_i$ and $|\downarrow\rangle_i \rightarrow |-\rangle_i$ in Eq. (14). At higher orders in perturbation theory the relationship between the states of the low-energy effective theory and the underlying $J = 15/2$ manifold becomes non-trivial. Following Lindgren [42], the $|\mathbf{n}\rangle$ state maps to

$$|\mathbf{n}\rangle_{\Omega} \equiv \Omega |\mathbf{n}\rangle,$$

(16)

where $\Omega$ is the wave-operator whose expansion was given in Eq. (9). The physical state $|\mathbf{n}\rangle_{\Omega}$ is not a product state in the ground doublets $|\pm\rangle_i$. The wave-operator $\Omega$ has much of the same structure as the effective Hamiltonian and is non-local in the moment operators $\mathbf{J}_i$. This mapping encodes non-trivial correlations between the sites, as well as virtual fluctuations into the higher crystal field levels.

These contributions to degeneracy lifting are thus induced through virtual fluctuations into the higher crystal field levels of the $J = 15/2$ manifold that are built into the state itself. We therefore refrain from referring to this ground state selection as “energetic”, and thus call this mechanism order by virtual crystal field fluctuations. Most importantly, this is distinct from the correlations built into the state in the order by quantum disorder scenario [15]; the correlations induced here vanish as the crystal field energy scale becomes large, i.e. as $\eta \rightarrow \infty$.

Given this mapping, one may ask how the direction $\mathbf{n}$ relates to direction of the physical moments $\mathbf{J}_i$. For the $\psi_2$ ($\phi = n\pi/3$) and $\psi_3$ ($\phi = n\pi/3 + \pi/6$) states of interest, this is partially constrained by their remnant symmetry. Each $\psi_3$ state is preserved (locally) by the $C_2$ rotation along the moment direction, while each $\psi_2$ state is preserved by a combination of a $C_2$ axis perpendicular to the moment, combined with time-reversal. As the mapping $\Omega$ preserves the underlying space-group symmetries of the model, these remnant symmetries are also reflected in the expectations of the moments $\mathbf{J}_i$. This then implies that the local in-plane angle is preserved by $\Omega$ for the $\psi_2$ and $\psi_3$ states. We note that for $\psi_3$ the vanishing of the component out of the local [111] plane is also preserved with the expectation $\mathbf{J}$, remaining fixed in the local XY planes. For $\psi_2$, a finite canting out of the XY plane [29] is generically induced by this mapping, in addition to an intrinsic generation that will be discussed in the following section.

### A. Selection and excitation gap

We can now look at the selection of the $\psi_2$ or $\psi_3$ state and the excitation gap that follows generically. Using the effective spin-1/2 language, we compute the energy per spin as

$$E(\mathbf{n}) = \langle \mathbf{n} \mid H_{\text{eff}} \mid \mathbf{n} \rangle / N.$$

(17)

Practically, one simply replaces each effective spin-1/2 operator in $H_{\text{eff}}$ with the classical spin vector in Eq. (15), dividing by the total number of sites. The energy per spin is then given by

$$E(\mathbf{n}) = C_2 \cos^2 \theta + C_4 \cos \theta \sin^3 \theta \cos 3\phi - C_6 \cos 6\phi,$$

(18)

where the overall form is dictated by symmetry constraints, as has been discussed in Refs. [19, 29]. The $C_n$ coefficients are determined by the exchanges in Eq. (13) and are given by

$$C_2 = \frac{1}{2} \sum_{i \neq j} \sum_{\alpha \beta} J_{ij}^{\alpha \beta}, \quad (19a)$$

$$C_4 = \frac{1}{2} \sum_{i \neq j} \sum_{\kappa \lambda \mu \nu} K_{ij}^{\kappa \lambda \mu \nu}, \quad (19b)$$

$$C_6 = \frac{1}{26} \sum_{i \neq j} \sum_{\alpha \beta \gamma \delta} L_{ij}^{\alpha \beta \gamma \delta}. \quad (19c)$$

At zeroth order in $1/\eta$, the $C_2$ coefficient can be worked out from the bare projected couplings with

$$C_2 \approx 3(\mathcal{J}_{xx} + 2\mathcal{J}_{+z}).$$

(20)

The value of this coefficient does not depend too much on the choice of the exchange parameters; using the parameters of Ref. [15] one has $C_2 \approx 0.3 \pm 0.1$ meV, while from Ref. [25] one has $C_2 \approx 0.3 \pm 0.05$ meV. The contributions from the $\mathcal{J}_{xx}$ and $\mathcal{J}_{zz}$ terms cancel for local ferromagnetic states due to their complex form factors $\gamma_{ij}$ and $\zeta_{ij}$ in Eq. (2). Such a cancellation is generic [15], as a by-product of lattice symmetries further guaranteeing that further bilinear interactions of arbitrary range do not lift the degeneracy of the $\Gamma_3$ manifold.

To see which state is selected, we minimize the total energy per spin, $E(\mathbf{n})$, as a function of $\theta$ and $\phi$. Given that the coefficient $C_2$ is positive and leading for the parameters relevant to Er$_2$Ti$_2$O$_7$, we expect predominantly in-plane order ($\theta \sim \pi/2$). We thus can expand about $\theta = \pi/2$ as

$$E(\mathbf{n}) \sim C_2 \left( \theta - \frac{\pi}{2} \right)^2 - C_4 \left( \theta - \frac{\pi}{2} \right) \cos(3\phi) + \cdots$$

(21)
where the omitted terms do not depend on $\theta$. This gives a minimum at

$$\theta_0 = \frac{\pi}{2} + \left(\frac{C_4}{2C_2}\right) \cos(3\phi). \quad (22)$$

Fixing $\theta = \theta_0$ and using Eq. (18), the energy difference [45] between the $\psi_2$ and $\psi_3$ states is then

$$\delta E \equiv E(\psi_3) - E(\psi_2) = 2\left(\frac{C_4^2}{8C_2} + C_6\right). \quad (23)$$

If $C_4^2 + 8C_2C_6 > 0$, then the $\psi_2$ states are selected and otherwise $\psi_3$ is selected. The $\psi_2$ ($\phi = n\pi/3$) states are modified by a small canting out of the local XY plane as indicated by $\theta_0 \neq \pi/2$ [29] in Eq. (22). One sees then that a non-zero $C_4$ always favors the selection of $\psi_2$ while a finite $C_6$ can select $\psi_2$ or $\psi_3$ depending on its sign. This can be seen in by the absence of canting in the $\psi_3$ state where $\theta_0 = \pi/2$ for $\phi = n\pi/3 + \pi/6$ in Eq. (22). Thus $\psi_3$ cannot gain any energy from the $C_4$ term and must be stabilized solely by $C_6$.

Having identified how $\psi_2$ or $\psi_3$ are selected within the $\Gamma_3$ manifold, we estimate the size of the spin-wave gap in the $\psi_2$ state. Solving the classical equations of motion for a finite energy $k = 0$ mode, the gap is given by [46]

$$\Delta = 2\sqrt{A_{\phi\phi}A_{\theta\theta} - A_{\phi\theta}^2}, \quad (24)$$

The $A_{\phi\phi}$, $A_{\theta\theta}$ and $A_{\phi\theta}$ are the curvatures of the classical energy, defined as

$$E(\mathbf{\hat{n}}) \sim \frac{1}{2}A_{\theta\theta}(\theta - \theta_0)^2 + \frac{1}{2}A_{\phi\phi}(\phi - \phi_0)^2 + A_{\phi\theta}(\theta - \theta_0)(\phi - \phi_0) + \cdots, \quad (25)$$

where $\phi_0$ is taken to be zero for the $\psi_2$ state. The cross-term $A_{\phi\theta}$ vanishes, so the classical gap $\Delta$ is given by the geometric mean of the curvatures divided by the moment size [25, 46] as in Eq. (24). Explicitly,

$$\Delta = 3\sqrt{C_4^2 + 8C_2C_6}. \quad (26)$$

In this form, we see from Eq. (23) that the energy difference, $\delta E$, between the $\psi_3$ and $\psi_2$ states and the gap size are related as

$$\Delta^2 = 36C_2\delta E. \quad (27)$$

We note that in the quantum order by disorder scenario [15], a similar relation is given for the order by quantum disorder gap as found in linear spin-wave theory, albeit with a different numerical prefactor. With the relationship of the multi-spin interactions to the energy difference and excitation gap in hand, we move on to derive some estimates of the size of the four- and six-spin interactions $C_4$ and $C_6$.

### B. Scaling arguments

While we have assumed that $|C_4|, |C_6| \ll C_2$, to understand if these terms are competitive with other effects, such as order by quantum disorder, we need a more explicit estimate of their magnitude. First, we consider simple scaling arguments [15, 25] for the size of these terms from the strong coupling expansion sketched in Sec. II B. One has

$$C_2 \sim \mathcal{J}, \quad C_4 \sim \mathcal{J}^3/(\eta\Lambda)^2, \quad C_6 \sim \mathcal{J}^5/(\eta\Lambda)^4, \quad (28)$$

where $\mathcal{J} = \lambda^{-1}M_{\chi^{-1}}$. The $\lambda$-factors of size $\lambda_c \sim 2$ and $\lambda_s \sim 6$ provide an accounting for the size of the matrix elements of the $J = 15/2$ operators. From Eq. (26), the gap should then scale as $\Delta \sim \mathcal{J}^3/(\eta\Lambda)^2$ when a $\psi_2$ state has been stabilized. From the fitted exchanges [15, 25], one has $\mathcal{J} \sim 0.01 - 0.1$ meV and $\Lambda \sim 6$ meV, so even optimistically it would seem that one would estimate a very small gap $\Delta \sim 0.001 - 0.01$ meV via Eq. (26) and Eq. (28). This value is roughly in agreement with that argued in Ref. [15], and suggests that the virtual crystal field excitations are irrelevant to the ground state selection.

However, this is somewhat naïve, as it excludes significant combinatoric factors. To see this, consider the multipolar interactions in $V$ on each nearest-neighbor bond as being independent perturbations to $\eta H_0$, with $V = \sum_{ij} V_{ij}$. We then define a contribution to $H_{\text{all}}$, as some string of $n - 1$ resolvent operators $R$ and $n$ perturbations $V_{ij}$. These bonds must be connected and, for the leading contributions to $C_4$ and $C_6$, must form trees, i.e. have no loops. Any contribution to $H_{\text{all}}$, with loops will involve less than $n$ distinct sites and thus will not be the leading parts of the coefficient, as mentioned in Sec. II B. The number of contributions from these connected nearest-neighbor bonds of the pyrochlore lattice is of order $10^6$ and from five connected nearest-neighbors is of order $10^3 - 10^4$. Since each of these contributions is of order $\mathcal{J}$, the estimates given above should include these large prefactors. This is in some sense conservative, as each bond alone has many different multipolar ranks interacting. We note that the scale $\mathcal{M}$ is determined from the fitted constants $\mathcal{J}$ and thus is, in some sense, an overall scale for all the odd-rank multipolar interactions, not just those of rank-1. We thus see that assuming a classical $\psi_2$ selection, when the combinatoric factors are included, the rough estimate of the excitation gap increases by a factor of 100 to ~ 0.1 – 1 µeV.

Furthermore, this result is sensitive to the scale of multipolar interactions between the $J = 15/2$ moments; if the scale $\mathcal{M}$ is increased by some factor the induced gap increases by its cube, as shown in Eqs. (26, 28). Moreover, the above estimate does not include the role played by even-rank multipolar interactions that do not contribute at first order to the scale $\mathcal{J}$ obtained from the experimental fitting. As we saw in Eq. (11), these simply give irrelevant constants when projected into the ground doublets. Given that there is no reason to expect the even-rank interactions to be smaller than the odd-rank [36, 37], this could be a significant underestimate of the size of the virtual crystal field fluctuations. Beyond this, it is not a priori excluded that the multitude of higher odd-rank interactions could also have an effect in the virtual crystal field fluctuations that is disproportionate to their effects in the bare projection. Since our very rough estimate above is within an order of magnitude or so of the ~ 20 µeV gap estimated from quantum zero-point fluctuations [15] and the ~ 40 – 45 µeV gap measured experimentally [25, 26], the importance of vir-
tual crystal fluctuations must be re-evaluated. These heuristic arguments are one of the main results of this work, forming the backbone of the detailed calculations we present next. In sections to follow, we flesh out these statements with quantitative calculations of the energetic selection and excitation gap due to the effects of virtual crystal field fluctuations.

IV. BILINEAR-BIQUADRATIC MODEL

As argued in the previous section, simple scaling arguments suggest that the effects of virtual crystal field fluctuations may be significant in Er$_2$Ti$_2$O$_7$. To address the magnitude of these effects in a quantitative fashion, we first need an explicit model of the multipolar interactions within the $J = 15/2$ manifold, rather than the schematic form of the previous section. Determination of these multipolar interactions from experiments is a difficult endeavor; as most of the experimental data on Er$_2$Ti$_2$O$_7$ can be described almost quantitatively using the effective spin-1/2 model of Ref. [15], there is little data left to constrain the model of Eq. (6). Indeed, the odd-rank interactions are only constrained through their projection into the effective spin-1/2 model of Eq. (2), while no constraints at all are placed on the even-rank interactions. Estimating the multipolar couplings by purely theoretical means is also similarly challenging. Given this daunting state of affairs, we will not attempt to study the full $J = 15/2$ multipolar interactions, but will restrict to some simpler caricature that captures the essential physics of having both time-reversal even and odd multipolar interactions.

The most straightforward approach [25, 35] is to consider only bilinear interactions between the $J = 15/2$ moments. This takes the form

$$H_J \equiv \sum_{\langle ij \rangle} J_{ij}^{-1} f_{ij} J_{ij}^{-1} + \eta \sum_i V(J_i). \tag{29}$$

The exchanges $J_{ij}^{-1} f_{ij} J_{ij}^{-1}$ have been chosen to reproduce Eq. (2) after one projects into the ground doublet, with $P(J^{-1}J_i)P = S_i$. While appealing in its simplicity, the lack of even-rank interactions or higher odd-rank interactions eliminates a possibly potent source of virtual crystal field fluctuations. To capture some aspects of these even-rank multipolar interactions that must be present in the microscopic model, we supplement this bilinear model with biquadratic interactions between $J = 15/2$ moments. These are couplings between rank-2 multipoles as defined in Eq. (4) with

$$H_Q \equiv \sum_{\langle ij \rangle} \sum_{QQ'} M_{ij}^{Q2Q'2} O_{2Q}(J_i)O_{2Q'}(J_j). \tag{30}$$

where $Q, Q' = 0, \pm 1, \pm 2$. The interaction matrix needs only be specified on a single bond while the rest can be determined by symmetry. While in principle unconstrained, we expect the scale of these interactions to be comparable to that of the bilinear terms. We thus consider the bilinear-biquadratic model

$$H \equiv H_J + \kappa H_Q + \eta H_{CEF},$$

$$= \sum_{\langle ij \rangle} J_{ij}^{-1} f_{ij} J_{ij}^{-1} J_j + \eta \sum_i V(J_i) + \kappa \sum_{\langle ij \rangle} \sum_{QQ'} M_{ij}^{Q2Q'2} O_{2Q}(J_i)O_{2Q'}(J_j) \tag{31}$$

We have added a single tuning parameter $\kappa$, in analogy to the parameter $\eta$, to control the scale of the biquadratic interactions. To ensure we are treating the rank-1 and rank-2 interactions on equal footing, we normalize the matrix $M_{ij}^{Q_1Q_2}$ so that

$$\frac{1}{2^2} \sum_{QQ'} |M_{ij}^{Q2Q'2}| = \frac{1}{2^2} \sum_{QQ'} |M_{ij}^{Q1Q'1}|, \tag{32}$$

where $M_{ij}^{Q_1Q_2}$ are the spherical tensor components of the rank-1 interactions, as normalized in Eq. (4). In this way, the average matrix elements for the rank-1 and rank-2 interactions are equal when $\kappa = 1$.

In this model, the bilinear terms serve as a proxy for all the odd-rank interactions, while the biquadratic terms do the same for all the even-rank interactions. Even with this simplification, there are a large number of free parameters. For nearest-neighbor bonds we find that there are 10 symmetry allowed independent biquadratic couplings. We will fix the ratios of these couplings using models motivated from two microscopic schemes, leaving the overall scale $\kappa$ as a tuning parameter. These schemes are complementary and motivated by super-exchange [14] and the microscopic electric quadrupole-quadrupole interaction [47]. We do not intend to imply that these different schemes are strictly realistic models for biquadratic exchange in Er$_2$Ti$_2$O$_7$, though both would be present in the material; they simply serve as useful parametrizations of the biquadratic couplings. Furthermore, the similarity of the results for the different biquadratic coupling schemes that we find below is a strong indication that the order by virtual crystal field fluctuation mechanism is enhanced when including biquadratic couplings, independently of the details of even-rank interactions.

A. Super-exchange model

One natural source of higher-multipole interactions [48] in rare-earths comes from super-exchange [37]. Due to the large separation of the Er$^{3+}$ ion relative to the extent of the 4$f$ orbitals, we expect this proceeds largely through the neighboring oxygen atoms. For a detailed treatment we refer the reader to Refs. [14 and 39]. Here, we simply quote the form of the interaction in the so-called charging approximation [49]:

$$\sum_{\langle ij \rangle} \sum_{\alpha \beta \mu \nu} (P f_{i\alpha}^4 f_{j\beta}^4) I_{ij}^{|\alpha \beta \mu \nu|} (P f_{j\mu}^4 f_{i\nu}^4 P), \tag{33}$$

where we have used a combined spin-orbital index $\alpha \equiv (m, \sigma)$ and $f_{i\alpha}^4$ creates a 4$f$ electron with spin $\sigma$ and orbital $m$ at site
The local operators can be expressed in terms of multipoles of rank-$K$ with $K \leq 7$

$$P f_{ij}^{\alpha} P \equiv \sum_{KQ} A_{KQ}^{\alpha\beta} O_{KQ}(J),$$

(34)

for some set of coefficients $A_{KQ}^{\alpha\beta}$. The interaction matrix $I$ is defined as

$$I_{ij}^{\alpha\beta\mu\nu} \equiv \frac{2}{(U_j^t + \Delta_{fp})^2} \left[ -\frac{2}{2U_j^t + U_p + 2\Delta_{fp}} \right] [t_i f_j^{\mu\nu} [t_i f_j^{\alpha\beta}],$$

(35)

where $U_j^t \sim E(4f^{11+\pm}) - E(4f^{11})$ gives the energy differences between adjacent charge configurations of the $E^{2+}$ ion. $\Delta_{fp}$ is the charge gap between the $4f$ and $2p$ levels. The $t_i$ matrices define the $4f$-$2p$ overlap. In the Slater-Koster approximation [50], these are expressed as $t_i \equiv R_i' t_0$ where $R_i$ is a rotation of the $f$ and $p$ orbitals that takes a set of axes aligned to the local axes at site $r_i$ into the global frame. The matrices $t_0$ define the $4f$-$2p$ overlap. In the Slater-Koster parameters to the canonical ratio [51] $t_{fj\sigma} / t_{p\sigma} \sim -0.3$, one finds that a very complex set of multipolar interactions are generated. As illustrated in Fig. 2, these include significant odd and even-rank interactions up to and including rank-$7$ [38, 39]. To fit this within our biquadratic framework, we simply truncate all multipolar interactions with rank $> 2$ and replace the rank-1 interactions with those of Eq. (31) to reproduce the experimentally fitted model of Eq. (2) when projected into the ground doublet. We again emphasize that this is not expected to be a quantitative model of the microscopic super-exchange interactions due to the neglect of the higher multipoles as well as the charging approximation used to arrive at Eq. (35). However, we do expect this form to capture the essential features of even-rank interactions and thus will serve as a useful tool for exploring how these multipolar interactions affect the virtual crystal field fluctuations.

B. Electric quadrupole-quadrupole model

Another simple interaction between the quadrupolar degrees of freedom arises simply due to electrostatics [47, 52, 53]. To present this compactly, it will be useful to consider a more conventional definition of the quadrupolar operators, rather than the spherical tensor basis we have been using so far. We consider the Cartesian tensors $Q_{ij}$ defined with respect to the global axes as

$$Q_{ij} \equiv R_i^T (3 \hat{J}_i^2 \hat{J}_j - J(J + 1)) R_j,$$

(36)

where $R_i^T R_j \equiv \delta_{ij}$ is the moment at site $r_i$ in the global axes and the product is symmetrized, i.e. $\tilde{J} \tilde{J} \equiv (J^\mu J^\nu + J^\nu J^\mu)/2$. This is a symmetric traceless matrix with five independent components. The explicit relationship between spherical tensors defined in Eq. (4) and the Cartesian form of Eq. (36) is given Appendix D. These electric quadrupole-quadrupole (EQQ) interactions decay as $\sim 1/r^6$ so we consider only the nearest-neighbor contribution

$$\mathcal{D} \sum_{(ij)} \frac{\hat{r}_{ij}}{r_{nm}^6} \left[ \frac{1}{3} \text{tr} [Q_i Q_j] - \frac{10}{3} Q_i Q_j + \frac{35}{6} Q_i \hat{r}_{ij} Q_j \hat{r}_{ij} Q_j \right] \hat{r}_{ij},$$

(37)

where $r_{ij} \equiv r_i - r_j$. The microscopic quadrupolar coupling constant $\mathcal{D}$ is given by [47]

$$\mathcal{D} \equiv \frac{\alpha J (e^2)^2}{r_{nm}^6} \left( \frac{e^2}{4\pi \epsilon} \right) \sim 6.664 \times 10^{-6} \text{ meV}.$$

(38)

Shielding effects likely reduce this further by a factor of $\sim 0.25$ or so [47]. The smallness of this numerical value is highly misleading: given the large matrix elements $\sim J^4$ the true scale of these interactions is closer to $10^{-3}$ meV to $10^{-4}$ meV. As for the super-exchange model, this interaction is used as a convenient parametric form of the biquadratic couplings and is not intended to be realistic. We thus do not use the bare microscopic interaction strength, but normalize the biquadratic couplings as given in Eq. (32), allowing the overall scale to vary via $\kappa$. 

![FIG. 2. Representation of the multipolar interaction matrix $M$ generated by the super-exchange interaction given in Eq. (35). The overall scale is arbitrary. For each pair of ranks $K, K' = 1, 2, \ldots, 7$ the matrix elements $M_{KQ}^{K'Q'}$ can be arranged into a $2K + 1$ by $2K + 1$ matrix with the $Q, Q'$ indices running along the column and row respectively. These blocks are shown arranged in a table by their $K, K'$ indices, with the dashed lines showing the boundaries of each block where $Q = \pm K$ or $Q' = \pm K'$. Significant interactions beyond purely bilinear, i.e. with $K, K' > 1$, are present.](image)
C. Mean-field and random-phase approximation

With these concrete models defined, we can now analyze the effects of the biquadratic interactions within an approach that uses mean-field theory (MFT) and the random-phase approximation (RPA) [46]. For the case of purely bilinear interactions, such an analysis has been presented in Ref. [25] (differences from the present study are discussed in Appendix C). This provides a route to estimating the gap, and thus the condensation energy, without the heavy machinery of the high-order perturbative expansion presented in Sec. II B. We lose however, the quantitative mapping to the effective spin-1/2 degrees of freedom. Still, as we shall see, the MFT and RPA results are entirely consistent with the scaling expected from the strong coupling expansion, and even include effects that go beyond the leading order results given in Sec. II B. We formulate these methods for general multipoles, then apply the results to the specific bilinear-biquadratic models discussed in Secs. IV A and IV B.

In the mean-field approximation we simply decouple the multipolar interactions as

\[ O_{kQ,j}O_{K'Q'}(j_j) \approx \delta_{j,j}^{K'}O_{kQ}(j_j) + \delta_{j,j}^{K}O_{K'Q'}(j_j) - \delta_{j,j}^{K}O_{K'Q'}^{\dagger}(j_j), \]

where \( \delta_{j,j}^{K} \equiv \langle O_{kQ}(j_j) \rangle \) are expectation values of the multipole operators. The full multipolar exchange Hamiltonian then reduces to single-site terms

\[ H = \sum_{i} \eta_{i}V_{i}(\mathbf{J}_{i}) + \sum_{kQ} h_{kQ,i}O_{kQ}(\mathbf{J}_{i}) \equiv \sum_{i} \mathcal{H}_{i}(\mathbf{J}_{i}), \]

where we have defined the effective multipole mean fields

\[ h_{kQ,i} = \sum_{j} \sum_{k'Q'} (M_{ij}^{kQ,k'Q'} + M_{ji}^{k'Q'kQ}) \cdot \delta_{j,j}^{k'Q'}. \]

This defines a set of effective single-site Hamiltonians \( \mathcal{H}_{i} \) that can be solved self-consistently for the multipole expectation values \( \delta_{j,j}^{K} \). This is equivalent to performing variational minimization on an ansatz that is an arbitrary product state in the \( J = 15/2 \) site basis.

To access the spin-wave excitation gap, \( \Delta \), we compute the low-energy susceptibility \( \chi(\mathbf{k}, \omega) \) within the RPA. The imaginary part of \( \chi(\mathbf{k}, \omega) \) is directly related to the intensity observed in inelastic neutron scattering experiments. With only bilinear interactions between the \( J_{i} \) moments, one can use the standard RPA equation [46]

\[ \left[ 1 - \chi^{0}(\omega)\mathcal{J}(\mathbf{k}) \right] \chi(\mathbf{k}, \omega) = \chi^{0}(\omega), \]

where \( \mathcal{J}(\mathbf{k}) \) is the Fourier transform of the bilinear exchange matrix and \( \chi^{0}(\omega) \) is the on-site susceptibility

\[ \chi^{0} = \sum_{n} \frac{\langle \Psi | O_{n}^{\dagger}(\mathbf{J}) | O_{n}(\mathbf{J}) \rangle}{E_{n}} \]

where \( E_{n} \) and \( | n \rangle \) denote the energies and eigenstates of the single-site mean-field Hamiltonian defined in Eq. (40) and \( \rho_{n} \equiv e^{-\beta E_{n}}/Z \) are the associated Boltzmann weights.

V. RESULTS

The MFT is formulated in terms of the order parameters for rank-1 and rank-2 multipoles, defined as

\[ m_{i} = \langle J_{i} \rangle, \quad q_{0,i} = \langle O_{2Q}(\mathbf{J}) \rangle. \]

The five expectation values \( q_{0,i} \) can be organized as a vector \( \mathbf{q}_{i} = (q_{0,i}, q_{1,i}, q_{2,i}, q_{-1,i}, q_{-2,i}) \). We note that the \( q_{0,i} \) component is non-zero even without any ordering as \( O_{2Q}(\mathbf{J}) \) breaks no symmetries of the model. Concretely, this is due to the

![FIG. 3. (a) Dependence of the canted moment \( m_{i} \) on the biquadratic coupling strength \( \kappa \) in the super-exchange and EQQ cases. Note that throughout the range \( |m_{i}| \) is at most \( -0.1 \) while the in-plane components \( m_{\perp} \) take on a value \( \sim 3 \) expected from the effective-spin picture. (b) Dependence of \( |m_{i}| \) on the crystal field rescaling \( \eta \), showing the \( \eta^{2} \) scaling for several values of \( \kappa \) for the super-exchange model.](image-url)
presence of the crystalline electric field. Solving the self-consistent equations on a single tetrahedron for both \( \mathbf{m} \) and \( \mathbf{q} \), we generically find a \( \psi \) state with uniform mean fields \( \mathbf{m}_0 \equiv \mathbf{m} \) and \( \mathbf{q}_0 \equiv \mathbf{q} \). In contrast to the effective spin-1/2 model of Eq. (2), the degeneracy of the \( \Gamma_5 \) manifold is already lifted at the mean-field level through the inclusion of the higher crystal field levels, as previously found in Refs. [35, 25]. In this local basis, the \( \psi \) states are characterized by the expectation value \( \mathbf{m} \), taking one of the six symmetry-related solutions

\[
\mathbf{m} = \pm m_1 \hat{\mathbf{x}} \mp m_2 \hat{\mathbf{z}}, \quad (46a)
\]

\[
= \pm m_1 \left( -\frac{1}{2} \hat{\mathbf{x}} \mp \frac{\sqrt{3}}{2} \hat{\mathbf{y}} \right) \mp m_2 \hat{\mathbf{z}}, \quad (46b)
\]

\[
= \pm m_1 \left( -\frac{1}{2} \hat{\mathbf{x}} \mp \frac{\sqrt{3}}{2} \hat{\mathbf{y}} \right) \pm m_2 \hat{\mathbf{z}}, \quad (46c)
\]

with \( m_1 \sim O(1) \) and \( |m_2| \ll m_1 \) at low temperature. One can think of these as planar \( \psi \) states with a small amount of canting into the local \( \hat{\mathbf{z}} \) direction, as expected from the analysis of Sec. III A. The small component \( m_2 \) is a secondary order parameter and is pinned as \( m_2 \propto m_1^3 \) as temperature is varied. This can be understood at the level of Landau-Ginzburg theory where allowed terms such as \( m_2 m_1^3 \) cause \( m_1^3 \) to act as a conjugate field to \( m_2 \) in the ordered phase [29]. As \( m_2 \) is induced by the four-spin term \( C_6 \), it gives some indication of the magnitudes of energetic selection and excitation gap. However, as we saw in Sec. III A, both these effects depend on not only \( C_6 \) but on the six-spin term \( C_8 \) as well. Since the small \( m_2 \sim 10^2 \) moment is independent of \( C_6 \) (see Eq. (22)), the magnitude of \( |m_2| \) gives only a partial picture of the selection mechanism. This is particularly true in regions where \( m_2 \), and thus \( C_4 \), change sign relative to \( m_1 \).

The exact values of \( m_1 \) and \( m_2 \) depend on the crystal field and exchange parameter sets used as well as the strength of the biquadratic coupling. For definiteness, we focus on the crystal field parameterization of Bertin et al. [22] with the bilinear exchange parameters of Savary et al. [15] (see Appendix B) mapped to bilinear interactions as in Eq. (29). Results using other parameter sets (see Appendix B) from the literature give qualitatively similar values. We then gain some insight into the effects of the biquadratic interactions by looking at the dependence of \( |m_2| \) on the tuning parameter \( \kappa \) at \( T = 0 \). We present these results for the super-exchange and EQQ model interactions in Fig. 3. For \( \kappa = 0 \) one finds that \( |m_2| \) is small but finite, of order \( \sim 10^{-2} \). This is purely a consequence of the high-lying crystal field states, as can be seen by looking at the dependence of \( m_2 \) on the crystal field rescaling \( \eta \). As shown in Fig. 3, it scales as \( \sim \eta^{-2} \) as expected from Sec. III A. Turning to the effect of finite \( \kappa \), we see that the magnitude of \( m_2 \) increases dramatically from the bare value \( |m_2| \sim 10^{-2} \) present at \( \kappa = 0 \). This indicates generation of four-spin term and thus that the selection of the \( \psi \) state can be significantly enhanced by including biquadratic interactions, or more generally, high-rank multipolar interactions.

Experimentally, while the selection itself can be observed [20, 23], there is no good way to probe the condensation energy, \( \delta E \), directly. Instead, we look to the gap in the excitation spectrum via the RPA. As to more closely compare with the experimental results, we present dynamic structure factor as would be seen in inelastic neutron scattering experiments [46]

\[
S(\mathbf{k}, \omega) \propto \sum_{\mu \nu} \left( \frac{\delta_{\mu \nu} - \frac{k^\mu k^\nu}{|k|^2}}{1 - e^{-\beta \omega}} \right) \text{Im}
\]

\[
\propto \sum_{\mu \nu} \left( \frac{\delta_{\mu \nu} - \frac{k^\mu k^\nu}{|k|^2}}{1 - e^{-\beta \omega}} \right) \text{Im}
\]

which is directly related to the results of inelastic neutron scattering experiments [15, 31]. We average over the six domains of the \( \psi \) ordering, as given in Eq. (46), to compare directly with experimental results. For simplicity, we do not include the magnetic form factor of \( \text{Er}^{3+} \). The gap size as a function of \( \kappa \) is shown in Fig. 4. As in the case of \( m_2 \), the scaling of the gap with the crystal field is also consistent with the order by virtual-crystal field fluctuations scenario; the gap closes as \( \eta^{-2} \), as expected from Sec. III A. The minima as a function of \( \kappa \) are those points where \( m_2 \), and thus \( C_4 \), change sign relative to \( m_1 \), and selection is purely from \( C_6 \). As shown in Fig. 4, the excitation gap is strongly dependent on the strength of the biquadratic coupling; for moderate, but reasonable values of \( \kappa \), one can find a gap that is comparable or larger than that found in the order by quantum-disorder scenario [15]. In fact, when the biquadratic coupling is comparable to the bilinear, this gap can easily be made consistent with experimental estimates. For the super-exchange model, this occurs near \( \kappa \sim 1.5 \), while for the EQQ model this is at the larger value \( \kappa \sim 3.5 \). Note that the gross features of the excitation spectrum are preserved when a finite biquadratic coupling is introduced. For concreteness, we compare the \( \eta \to \infty \) limit where our model reduces to an effective spin-1/2 model as shown in Fig. 5 to the result with finite super-exchange type biquadratic interactions shown in Fig. 6. The biquadratic coupling has been chosen to be \( \kappa = -1.5 \) to reproduce the experimental gap size. Aside from the gap at \( [111] \) and small upward shift in energy, the features of the two spectra are nearly indistinguishable. Comparing to the experimental results of Ref. [15] or Ref. [25] we find that, aside from the gap, the model with the biquadratic coupling fits the data as well as the effective spin-1/2 model within theoretical and experimental uncertain-
ties. This agreement should be further improved by renormalizing the bare $J$-couplings to remove the second-order shifts from virtual crystal field fluctuations. This qualitative similarity persists past the point $\kappa = 1$, where we consider the bilinear and biquadratic interactions to be of comparable magnitude. Indeed, we can extend the EQQ model to the larger value $\kappa \sim 3.5$ and still obtain a spectrum nearly identical to that shown in Fig. 6. This indicates that there is a wide range of biquadratic coupling strengths that induce a significant gap and remain consistent with the overall features of the excitation spectrum as reported in Ref. [15].

These two consequences of the biquadratic interactions, the large induced gap and the invariance of the broad features of the spectrum form the main result of this work. Together, they imply that significant biquadratic coupling can not only produce a gap large enough to account for the observed results but, crucially, can do so without spoiling the agreement between the excitation spectrum and experiments. More generally, this tells us that the higher multipolar interactions, that are expected to be not only present but significant [37], can have observable effects at low energies. With this proof of principle, we see that virtual crystal field effects can not necessarily be ignored. Next we discuss how this scenario could be tested in Er$_2$Ti$_2$O$_7$.

VI. DISCUSSION

The question of the role of order by disorder type mechanism in Er$_2$Ti$_2$O$_7$ is a quantitative, not a qualitative question. Given any mechanism that selects the $\psi_2$ state from the $\Gamma_5$ manifold, one expects a soft-mode in the spin-wave spectrum with a small gap [30]. Thus the observed excitation gap is a consequence of the $\psi_2$ selection and does not provide a signature for any given selection mechanism. The identification of the mechanism thus lies in the details, for example through the absolute magnitude of the gap or dependence on other effects such as random disorder or magnetic field. In the order by quantum disorder order scenario of Ref. [15], this final identification rested on the effects of virtual crystal field fluctuations being taken to be entirely negligible. As established in Secs. III, IV and V, the assumptions unpinning this conclusion are unwarranted. Not only are the effects of virtual crystal field fluctuations non-negligible, they can be comparable to or even larger than the corresponding quantum fluctuations when multipolar interactions are taken into account. We are thus left with the difficult task of disentangling these two fluctuation effects, as both will be present generically.

We first should focus on the magnitude of the gap seen experimentally. In Ref. [26] and Ref. [25] a gap of $\sim 40-45 \mu$eV is observed. In the order by quantum disorder scenario, the excitation gap is fully determined from the fitted exchanges of the effective spin-1/2 model. However, this model is not analytically or numerically tractable; given these theoretical limitations we must resort to approximate methods to estimate the gap. In Ref. [15], the large-$S$ result from linear spin-wave theory (LSWT) is extrapolated to $S = 1/2$ giving a gap of $\Delta \sim 20 \mu$eV, about 50% of the observed gap size. A complementary perturbative approach undertaken in Ref. [33] suggests that effects beyond LSWT could further reduce this value. Using real-space perturbation theory, Ref. [33] finds that the $U(1)$ breaking term obtained from LSWT is exactly canceled at higher-order in perturbation theory when evaluated for $S = 1/2$. A more careful calculation [33] gives a degeneracy lifting $\delta E$ that is reduced by $\sim 40\%$ from the value reported in Ref. [15]. Since we expect $\Delta^2 \sim C_2 \delta E$ (see Eq. (27)), this would reduce the gap size and move us significantly further away from the experimental result. If taken at face value, these estimates suggest that the order by quantum-disorder contribution to the condensation energy of the $\psi_2$ state could be as little as 25% of the value inferred from the experimental gap. This raises some doubt to whether order by quantum-disorder is the leading origin of $\psi_2$ selection in Er$_2$Ti$_2$O$_7$. 

FIG. 5. Excitation spectrum of the effective spin-1/2 model ($\eta \rightarrow \infty$) in the RPA, cut along the $[11L]$ direction. Intensity scale is arbitrary. The gapless mode is visible near $[111]$.

FIG. 6. Excitation spectrum of the bilinear-biquadratic model ($\eta = 1$) in the RPA, shown for super-exchange interactions with $\kappa = -1.5$ along the $[11L]$ direction. Intensity scale is arbitrary. Aside from the $\sim 50 \mu$eV gap near $[111]$, the bands show a very strong similarity to the spin-1/2 case ($\eta \rightarrow \infty$) in Fig. 5.
Another indirect probe into the selection mechanism is provided by the effects of disorder. It has been argued [33, 34] that diluting Er$^{3+}$ in Er$_2$Ti$_2$O$_7$ with non-magnetic Y$^{3+}$ ions could provide another mechanism to break the degeneracy of the $\Gamma_5$ manifold. Such dilution favors the $\psi_2$ state, not the $\psi_2$ state found in the clean limit. This presents the intriguing possibility that by a controlled introduction of vacancies at the Er$^{3+}$ sites, one could tune from the $\psi_2$ state into the $\psi_3$ state. The critical dilution would provide some indication of condensation energy that stabilizes the $\psi_2$ state. Estimating this critical dilution, $\rho_c$, suffers from many of the theoretical limitations such as estimating the gap in the pure effective spin-1/2 model. In Ref. [33], this is estimated to be as low as $\rho_c \sim 7\%$, taking the degeneracy lifting term $\delta E$ to be $\sim 40\%$ of the LSWT result, as described above. If instead of relying on the theoretical stabilization energy, we extract $\delta E$ from the experimental gap using Eq. (27), one obtains a $\delta E$ that is four times larger. An equivalent enhancement of $\rho_c$ follows, raising the critical dilution to 25% or so. This could provide further evidence towards a stronger selection effect than predicted by the order by quantum disorder proposals.

The question then remains: what is responsible for the remaining stabilization of the $\psi_2$ state? The results presented here suggest that this quantitative difference could be resolved through the effects of virtual crystal field fluctuations. Further, we have shown that the full experimental gap can be accounted for with reasonable values of the biquadratic coupling. Accounting for only the fraction remaining after order by quantum disorder requires even less biquadratic coupling. We caution that a definitive experimental signature of this order by virtual crystal field fluctuations mechanism is difficult to formulate. These questions are highly quantitative and, given the small scale of these effects, are thus muddled by the combination of theoretical and experimental uncertainties. In principle, the presence of higher-rank multipolar couplings could be probed by looking at the dispersion of the higher crystal field levels in the ordered state. For example, a rough estimate of the magnitude of the higher multipolar interactions could be inferred by comparing with predictions assuming only the bilinear interactions of Eq. (29). However, given the large number of independent parameters defining the multipolar couplings, extracting a definite scale for the higher-rank parts is likely to be an ill-posed challenge. Another possible signature could be the finite $m_1$ moment. Indeed, this is zero at leading order in the LSWT of Ref. [15] and in the real space perturbation theory of Ref. [33]. There are several difficulties with this: it is generically expected to be finite for the $\psi_2$ state, as it is allowed by symmetry [29], and thus should appear at higher order in both such theories. Further, the relationship between the size of $m_1$ and the condensation energy is indirect, and even when enhanced it may be too small to be observed experimentally.

VII. CONCLUSION

The concept of order by disorder is a cornerstone of the theory of highly frustrated magnetism [3, 4, 7], representing a middle ground between ordering in an unfrustrated system and a fully magnetically disordered state. However, due to the need for a nearly accidental symmetry and the difficulty in distinguishing it from more conventional ordering scenario, clear material examples are scarce. Even in a compelling material such as Er$_2$Ti$_2$O$_7$, we have shown here that it is difficult to distinguish between possible selection mechanisms. But not all interesting physics is lost; we have proposed a novel order by disorder mechanism that proceeds through the virtual crystal field excitations of the Er$^{3+}$ ion. Despite the naively large crystal field energy scale, this order by virtual crystal field fluctuations can be quite effective in selecting the ordered ground state. While the selection induced solely by bilinear interactions is to some extent weaker than that seen experimentally (e.g. the gap, $\Delta$, is roughly five times too small), once multipolar interactions are taken into account, we find this mechanism to be competitive with order by quantum disorder and is able to account for the experimentally observed excitation gap, maintaining agreement with the rest of the excitation spectrum. While determining the relative size of the contributions of each of these mechanism is difficult, the availability of high-quality single crystals of Er$_2$Ti$_2$O$_7$ provides some hope that these effects could ultimately be disentangled.

To obtain a clearer signal for order by quantum- or thermal-order, one should then look for materials with a larger crystal field scale. A good candidate may be provided by Yb$_2$Ge$_2$O$_7$ [54] which should be described using the same effective spin-1/2 model as Er$_2$Ti$_2$O$_7$ at low energies [55, 56]. As the related material Yb$_2$Ge$_2$O$_7$ appears to be proximate to the $\Gamma_3$ phase [55, 56], it is plausible that the ground state of Yb$_2$Ge$_2$O$_7$ is drawn from this manifold. All of the considerations for Er$_2$Ti$_2$O$_7$ are then applicable, with the significant difference that the crystal field energy scale in Yb$_2$Ge$_2$O$_7$, as in Yb$_2$Ti$_2$O$_7$ [22], is likely an order of magnitude larger. This renders the order by virtual-crystal-field-fluctuations mechanism described in the present work negligible, leaving for all practical purposes only quantum fluctuations to select the ground state.

ACKNOWLEDGMENTS

This work was supported by the NSERC of Canada, the Canada Research Chair program (M.G., Tier 1), the Canadian Foundation for Advanced Research and the Perimeter Institute (PI) for Theoretical Physics. Research at PI is supported by the Government of Canada through Industry Canada and by the Province of Ontario through the Ministry of Economic Development & Innovation. M.G. acknowledges the hospitality and generous support of the Quantum Matter Institute at the University of British Columbia and TRIUMF where part of this work was completed.
Appendix A: Local basis

We follow the conventions of Savary et al. [15] and work in the basis local to each pyrochlore site. From the global basis, these local axes are defined as

\[ \hat{z}_1 = \frac{1}{\sqrt{3}} (\hat{x} + \hat{y} + \hat{z}), \quad \hat{x}_1 = \frac{1}{\sqrt{6}} (-2\hat{x} + \hat{y} + \hat{z}), \]

\[ \hat{z}_2 = \frac{1}{\sqrt{3}} (\hat{x} - \hat{y} - \hat{z}), \quad \hat{x}_2 = \frac{1}{\sqrt{6}} (-2\hat{x} - \hat{y} - \hat{z}), \]

\[ \hat{z}_3 = \frac{1}{\sqrt{3}} (-\hat{x} + \hat{y} - \hat{z}), \quad \hat{x}_3 = \frac{1}{\sqrt{6}} (+2\hat{x} + \hat{y} - \hat{z}), \]

\[ \hat{z}_4 = \frac{1}{\sqrt{3}} (-\hat{x} - \hat{y} + \hat{z}), \quad \hat{x}_4 = \frac{1}{\sqrt{6}} (+2\hat{x} - \hat{y} + \hat{z}), \quad \text{(A1)} \]

where \( \gamma_i \) and \( \zeta_{ij} = -\gamma^*_{ij} \) depend only on the basis sites they connect and thus can be expressed as a matrix

\[ \gamma = \begin{pmatrix} 0 & +1 & \omega & \omega^2 \\ +1 & 0 & \omega & \omega^2 \\ \omega & \omega^2 & 0 & +1 \\ \omega^2 & \omega & +1 & 0 \end{pmatrix}, \quad \text{(A2)} \]

where \( \omega = e^{2\pi i/3} \).

Appendix B: Model parameters

1. Crystal fields

Several parametrizations of the crystal field potential for the Er\(^{3+}\) ion in Er\(_2\)Ti\(_2\)O\(_7\) exist. We consider two of these parameter sets: those of Petit et al. [25] and Bertin et al. [22]. Both provide a good description of the crystal field levels observed experimentally. Considering the results for these two parameter sets serve as a benchmark to the sensitivity of our conclusions to the precise details of the crystal field potential. We write the crystal field potential \( V(J) \) as

\[ V(J) = \sum_{KQ} B_{KQ} \hat{O}_{KQ}(J), \quad \text{(B1)} \]

where the \( \hat{O}_{KQ}(J) \) are Stevens’ operators [41] defined using the conventions listed in Jensen and Mackintosh [46]. Converted into the Stevens’ convention, the non-zero parameters of Petit et al. [25] are

\[ B_{20} = +6.741 \cdot 10^{-2} \text{ meV}, \quad B_{40} = +1.363 \cdot 10^{-3} \text{ meV}, \]

\[ B_{43} = -8.998 \cdot 10^{-3} \text{ meV}, \quad B_{50} = +9.565 \cdot 10^{-6} \text{ meV}, \]

\[ B_{63} = +1.113 \cdot 10^{-4} \text{ meV}, \quad B_{66} = +1.661 \cdot 10^{-4} \text{ meV}. \quad \text{(B2)} \]

The ground state \( \lambda \)-factors are given by \( \lambda_\pm = 5.706 \) and \( \lambda_z = 2.136 \) and the first excited doublet lies at 7.51 meV. The parameters of Bertin et al. [22] are given by

\[ B_{20} = +7.50 \cdot 10^{-2} \text{ meV}, \quad B_{40} = +1.41 \cdot 10^{-3} \text{ meV}, \]

\[ B_{43} = +1.25 \cdot 10^{-2} \text{ meV}, \quad B_{60} = +1.09 \cdot 10^{-5} \text{ meV}, \]

\[ B_{63} = -1.80 \cdot 10^{-4} \text{ meV}, \quad B_{66} = +1.50 \cdot 10^{-4} \text{ meV}. \quad \text{(B3)} \]

The ground state \( \lambda \)-factors are given by \( \lambda_\pm = 6.434 \) and \( \lambda_z = 1.758 \) and the first excited doublet lies at 6.15 meV.

2. Exchanges

Estimates for the exchanges in the effective spin-1/2 model have been extracted from fitting the excitation spectrum seen inelastic neutron neutron scattering experiments [15, 25]. The fitting of Savary et al. [15] was done in a magnetic field and yields the parameters

\[ J_{zz} = -2.50 \pm 1.80 \cdot 10^{-2} \text{ meV}, \]

\[ J_\pm = +6.50 \pm 0.75 \cdot 10^{-2} \text{ meV}, \]

\[ J_{zz} = +4.20 \pm 0.50 \cdot 10^{-2} \text{ meV}, \]

\[ J_{zz} = -0.88 \pm 1.50 \cdot 10^{-2} \text{ meV}. \quad \text{(B4)} \]

The fitting of Petit et al. [25] was done in zero-field and yields (Model B)

\[ J_{zz} = -2.2 \pm 0.1 \cdot 10^{-2} \text{ meV}, \]

\[ J_\pm = +6.0 \pm 0.1 \cdot 10^{-2} \text{ meV}, \]

\[ J_{zz} = +4.3 \pm 0.1 \cdot 10^{-2} \text{ meV}, \]

\[ J_{zz} = -1.5 \pm 0.1 \cdot 10^{-2} \text{ meV}. \quad \text{(B5)} \]

Petit et al. [25] also did a fit directly using an RPA calculation within the full \( J = 15/2 \) manifold. Projected into the effective spin-1/2 model this yields (Model A)

\[ J_{zz} = -0.84 \pm 0.1 \cdot 10^{-2} \text{ meV}, \]

\[ J_\pm = +5.93 \pm 0.1 \cdot 10^{-2} \text{ meV}, \]

\[ J_{zz} = +4.61 \pm 0.1 \cdot 10^{-2} \text{ meV}, \]

\[ J_{zz} = +0.91 \pm 0.1 \cdot 10^{-2} \text{ meV}. \quad \text{(B6)} \]

These three parameter sets are qualitatively compatible: each has large positive in-plane exchanges \( J_\pm \) and \( J_{zz} \) with smaller \( J_{zz} \) and \( J_{zz} \) couplings.

Appendix C: Differences with Petit et al. [25]

In Petit et al. [25], a theoretical gap size of \( \sim 15 \mu \text{eV} \) was reported, with an \( \eta^{-1/2} \) dependence under crystal field rescaling. This was computed through the same RPA approximation discussed in Sec. IV C, but using a model that has only bilinear interactions between the \( J \) moments. These results were computed using a cutoff in the computation of the RPA excitation spectrum; some of the highest lying crystal field states were omitted from the calculation. This has significant effects
on the $\eta \to \infty$ limit, effectively removing the $U(1)$ degeneracy that should appear in the effective spin-1/2 model. This causes the erroneously large gap size and the incorrect $\eta^{-1/2}$ scaling reported in Petit et al. [25].

**Appendix D: Spherical vs Cartesian quadrupoles**

Here we give the relationship between the Cartesian quadrupoles of Eq. (36) and the spherical tensors defined in Eq. (4)

$$O_{2,0}(\mathbf{J}) = \frac{1}{12} \sqrt{357} \mathbf{Q}^{zz}, \quad (D1a)$$

$$O_{2,\pm 1}(\mathbf{J}) = \pm \frac{1}{12} \sqrt{357} \left[ \frac{\sqrt{2}}{3} (\mathbf{Q}^{zz} \pm i\mathbf{Q}^{xy}) \right], \quad (D1b)$$

$$O_{2,\pm 2}(\mathbf{J}) = \frac{1}{12} \sqrt{357} \left[ \sqrt{\frac{1}{6}} (\mathbf{Q}^{xx} \mp Q^{yy} \mp 2i\mathbf{Q}^{xy}) \right]. \quad (D1c)$$

---

[1] Claudine Lacroix, Philippe Mendels, and Frédéric Mila, eds., *Introduction to Frustrated Magnetism* (Springer Berlin Heidelberg, 2011).

[2] L. Balents, “Spin liquids in frustrated magnets,” *Nature* 464, 199–208 (2010).

[3] M. J. P. Gingras and P. A. McClarty, “Quantum spin ice: a search for gapless quantum spin liquids in pyrochlore magnets,” *Rep. Prog. Phys.* 77, 056501 (2014).

[4] J. Villain, R. Bidaux, J.-P. Carton, and R. Conte, “Order as an effect of disorder,” *Journal de Physique* 41, 1263–1272 (1980).

[5] E.F. Shender, “Antiferromagnetic garnets with fluctuationally interacting sublattices,” *Sov. Phys. JETP* 56, 178–184 (1982).

[6] J. H. van Vleck, “On the anisotropy of cubic ferromagnetic crystals,” *Physical Review* 77, 1888–1910 (1950).

[7] S. Coleman and E. Weinberg, “Radiative corrections as the origin of spontaneous symmetry breaking,” *Physical Review D* 7, 1888–1910 (1973).

[8] C. L. Henley, “Ordering due to disorder in a frustrated vector antiferromagnet,” *Phys. Rev. Lett.* 62, 2056–2059 (1989).

[9] A. Chubukov, “Order from disorder in a kagomé antiferromagnet,” *Phys. Rev. Lett.* 69, 832–835 (1992).

[10] J. R. Tessman, “Magnetic anisotropy at 0° K,” *Physical Review* 96, 1192–1195 (1954).

[11] J. H. van Vleck, “On the anisotropy of cubic ferromagnetic crystals,” *Physical Review* 52, 1178–1188 (1937).

[12] C. Kittel, “Dipolar domains in paramagnetic crystals at low temperatures,” *Physical Review* 82, 965–966 (1951).

[13] J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, “Magnetic pyrochlore oxides,” *Reviews of Modern Physics* 82, 53–107 (2010).

[14] K. A. Ross, L. Savary, B. D. Gaulin, and L. Balents, “Quantum excitations in quantum spin ice,” *Phys. Rev. X* 1, 021002 (2011).

[15] S. Onoda and Y. Tanaka, “Quantum fluctuations in the effective pseudospin-1/2 model for magnetic pyrochlore oxides,” *Physical Review B* 83, 094411 (2011).

[16] S. H. Curnoe, “Quantum spin configurations in Tb$_2$Ti$_2$O$_7$,” *Phys. Rev. B* 75, 212404 (2007).

[17] Han Yan, Owen Benton, Ludovic D. C. Jaubert, and Nic Shannor, “Living on the edge: ground-state selection in quantum spin-ice pyrochlores,” (2013), arXiv:1311.3501 [cond-mat.str-el].

[18] Lucile Savary and Leon Balents, “Spin liquid regimes at nonzero temperature in quantum spin ice,” *Phys. Rev. B* 87, 205130 (2013).

[19] A. W. C. Wong, Z. Hao, and M. J. P. Gingras, “Ground state phase diagram of generic XY pyrochlore magnets with quantum fluctuations,” *Physical Review B* 88, 144402 (2013).

[20] J. D. M. Champion, M. J. Harris, P. C. W. Holdsworth, A. S. Wills, G. Balakrishnan, S. T. Bramwell, E. Čičmár, T. Fennell, J. S. Gardner, J. Lago, D. F. McMorrow, M. Orendač, A. Orendačová, D. McK. Paul, R. I. Smith, M. T. F. Telling, and A. Willes, “Er$_2$Ti$_2$O$_7$ : Evidence of quantum order by disorder in a frustrated antiferromagnet,” *Physical Review B* 68, 202401 (2003).

[21] B. Z. Malkin, T. T. A. Lummen, P. H. M. van Loosdrecht, G. Dhalenne, and A. R. Zakirov, “Static magnetic susceptibility, crystal field and exchange interactions in rare earth titanate pyrochlores,” *Journal of Physics: Condensed Matter* 22, 276003 (2010).

[22] A. Bertin, Y. Chapuis, P. Dalmas de Réotier, and A. Yaouanc, “Crystal electric field in the R$^2$Ti$_2$O$_7$ pyrochlore compounds,” *Journal of Physics: Condensed Matter* 24, 256003 (2012).

[23] A. Poole, A. S. Wills, and E. Lelièvre-Berna, “Magnetic ordering in the XY pyrochlore antiferromagnet Er$_2$Ti$_2$O$_7$ : a spherical neutron polarimetry study,” *Journal of Physics: Condensed Matter* 19, 452201 (2007).

[24] J. P. C. Ruff, J. P. Clancy, A. Bourque, M. A. White, M. Ramazanoglu, J. S. Gardner, Y. Qiu, J. R. D. Copley, M. B. Johnson, H. A. Dabkowski, and B. D. Gaulin, “Spin waves and quantum criticality in the frustrated XY pyrochlore antiferromagnet Er$_2$Ti$_2$O$_7$,” *Phys. Rev. Lett.* 101, 147205 (2008).

[25] S. Petit, J. Robert, S. Guitteny, P. Bonville, C. Decorse, J. Olivier, H. Mutka, M. J. P. Gingras, and I. Mirebeau, “Order by
disorder or energetic selection of the ground state in the XY pyrochlore antiferromagnet $\text{Er}_2\text{Ti}_2\text{O}_7$ : An inelastic neutron scattering study,” Physical Review B 90, 060410 (2014).

[26] K. A. Ross, Y. Qiu, J. R. D. Copley, H. A. Dabkowska, and B. D. Gaulin, “Order by disorder spin wave gap in the XY pyrochlore magnet $\text{Er}_2\text{Ti}_2\text{O}_7$,” Phys. Rev. Lett. 112, 057201 (2014).

[27] K. Baroudi, B. D. Gaulin, S. H. Lapidus, J. Gaudet, and R. J. Cava, “Symmetry and light stuffng of $\text{Ho}_2\text{Ti}_2\text{O}_7$, $\text{Er}_2\text{Ti}_2\text{O}_7$, and $\text{Yb}_2\text{Ti}_2\text{O}_7$ characterized by synchrotron X-ray diffraction,” Phys. Rev. B 92, 024110 (2015).

[28] J. Oitmaa, R. R. P. Singh, B. Javanparast, A. G. R. Day, B. V. Bagheri, and M. J. P. Gingras, “Phase transition and thermal order-by-disorder in the pyrochlore antiferromagnet $\text{Er}_2\text{Ti}_2\text{O}_7$ : A high-temperature series expansion study,” Physical Review B 88, 220404 (2013).

[29] B. Javanparast, A. G. R. Day, Z. Hao, and M. J. P. Gingras, “Order-by-disorder near criticality in XY pyrochlore magnets,” Physical Review B 91, 174424 (2015).

[30] P. A. McClarty, P. Stasiak, and M. J. P. Gingras, “Order-by-disorder in the XY pyrochlore antiferromagnet,” Phys. Rev. B 89, 024425 (2014).

[31] M. E. Zhitomirsky, M. V. Gvozdikova, P. C. W. Holdsworth, and R. Moessner, “Quantum order by disorder and accidental soft mode in $\text{Er}_2\text{Ti}_2\text{O}_7$,” Phys. Rev. Lett. 109, 077204 (2012).

[32] M. E. Zhitomirsky, P. C. W. Holdsworth, and R. Moessner, “Nature of finite-temperature transition in anisotropic pyrochlore $\text{Er}_2\text{Ti}_2\text{O}_7$,” Phys. Rev. B 89, 140403 (2014).

[33] V. S. Maryasin and M. E. Zhitomirsky, “Order from structural disorder in the XY pyrochlore antiferromagnet $\text{Er}_2\text{Ti}_2\text{O}_7$,” Physical Review B 90, 094412 (2014).

[34] A. Andreanov and P. A. McClarty, “Order induced by dilution in pyrochlore XY antiferromagnets,” Phys. Rev. B 91, 064401 (2015).

[35] P. A. McClarty, S. H. Curnoe, and M. J. P. Gingras, “Energetic selection of ordered states in a model of the $\text{Er}_7\text{Ti}_7$ frustrated pyrochlore XY antiferromagnet,” J. Phys.: Conf. Ser. 145, 012032 (2009).

[36] R. J. Elliott, “Orbital effects on exchange interactions,” J. Appl. Phys. 39, 802 (1968).

[37] P. Santini, S. Carretta, G. Amoretti, R. Caciuffo, N. Magnani, and G. H. Lander, “Multipolar interactions in f-electron systems: The paradigm of actinide dioxides,” Reviews of Modern Physics 81, 807–863 (2009).

[38] N. Iwahara and L. F. Chibotaru, “Exchange interaction between $J$ multipoles,” Phys. Rev. B 91, 074438 (2015).

[39] J. G. Rau and M. J. P. Gingras, “How quantum are classical spin ices?” (2015), to appear in Phys. Rev. B, arXiv:1503.04808 [cond-mat.str-el].

[40] Y.-P. Huang, G. Chen, and M. Hermee, “Quantum spin ices and topological phases from dipolar-oc-tupolar doublets on the pyrochlore lattice,” Phys. Rev. Lett. 112, 167203 (2014).

[41] K. W. H. Stevens, “Matrix elements and operator equivalents connected with the magnetic properties of rare earth ions,” Proc. Phys. Soc. A 65, 209–215 (1952).

[42] I. Lindgren, “The Rayleigh-Schrödinger perturbation and the linked-diagram theorem for a multi-configurational model space,” Journal of Physics B: Atomic and Molecular Physics 7, 2441–2470 (1974).

[43] The higher order terms $H_{\text{eff},3}$ and $H_{\text{eff},5}$ have been symmetrized via $H_{\text{eff},n} \rightarrow (H_{\text{eff},n} + H_{\text{eff},-n})/2$ to render the effective Hamiltonian Hermitian. This procedure can be justified in that there exists a transformation that maps the unsymmetrized form into the symmetrized form, as described by des Cloizeaux [57].

[44] H. R. Molavian, M. J. P. Gingras, and B. Canals, “Dynamically induced frustration as a route to a quantum spin ice state in $\text{Yb}_2\text{Ti}_2\text{O}_7$ via virtual crystal field excitations and quantum many-body effects,” Phys. Rev. Lett. 98, 107204 (2012).

[45] We note that contributions to the energy such as $\cos(6\varphi)$ are also allowed. Since each of these terms carries a factor $S^m$, so for $S = 1/2$ we will neglect all but the $n = 1$ case which has been considered.

[46] J. Jensen and A. R. Mackintosh, Rare earth magnetism (Clarendon Oxford, 1991).

[47] W. P. Wolf and R. J. Birgeneau, “Electric multipole interactions between rare-earth ions,” Physical Review 166, 376–382 (1968).

[48] Note that due to the large orbital moments in the Er$^{3+}$ ground doublets, super-exchange generates multipolar interactions at leading order. This is in contrast to spin-only moments where they appear only at higher order in perturbation theory.

[49] In this approximation, only the energy differences between atomic states with different charge configurations are retained. The splittings of the atomic manifold within each $4f^n$ configuration are ignored.

[50] J. C. Slater and G. F. Koster, “Simplified LCAO method for the periodic potential problem,” Physical Review 94, 1498–1524 (1954).

[51] K. Takegahara, Y. Aoki, and A. Yanase, “Slater-Koster tables for $f$ electrons,” J. Phys. C: Solid State Phys. 13, 583–588 (1980).

[52] R. Finkelstein and A. Mencher, “Interatomic electric quadrupole-quadrupole coupling in salts of cerium,” J. Chem. Phys. 21, 472 (1953).

[53] B. Bleaney, “Quadrupole-quadrupole interaction in the rare earths,” Proc. Phys. Soc. 77, 113–115 (1961).

[54] Z. L. Dun, M. Lee, E. S. Choi, A. M. Hallas, C. R. Wiebe, J. S. Gardner, E. Arrighi, R. S. Freitas, A. M. Arevalo-Lopez, J. P. Attfield, H. D. Zhou, and J. G. Cheng, “Chemical pressure effects on magnetism in the quantum spin liquid candidates $\text{Yb}_2\text{X}_2\text{O}_7$ (X = Sn, Ti, Ge),” Phys. Rev. B 89, 064401 (2014).

[55] L. D. C. Jaubert, O. Benton, J. G. Rau, J. Oitmaa, R. R. P. Singh, N. Shannon, and M. J. P. Gingras, “Are multiphase competitions between rare-earth ions,” Proc. Phys. Soc. A 65, 209–215 (1952).

[56] I. Lindgren, “The Rayleigh-Schrödinger perturbation and the linked-diagram theorem for a multi-configurational model space,” Journal of Physics B: Atomic and Molecular Physics 7, 2441–2470 (1974).

[57] J. des Cloizeaux, “Extension d’une formule de Lagrange à des problèmes de valeurs propres,” Nuclear Physics 20, 321–346 (1960).