Degenerate perturbation theory of quantum fluctuations in a pyrochlore antiferromagnet

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We study the effect of quantum fluctuations on the half-polarized magnetization plateau of a pyrochlore antiferromagnet. We argue that an expansion around the easy axis limit is appropriate for discussing the ground state selection amongst the classically degenerate manifold of collinear states with a 3:1 ratio of spins parallel/anti-parallel to the magnetization axis. A general approach to the necessary degenerate perturbation theory is presented, and an effective quantum dimer model within this degenerate manifold is derived for arbitrary spin $s$. We also generalize the existing semiclassical analysis of Hizi and Henley [Phys. Rev. B 73, 054403 (2006)] to the easy axis limit, and show that both approaches agree at large $s$. We show that under rather general conditions, the first non-constant terms in the effective Hamiltonian for $s \geq 1$ occur only at sixth order in the transverse exchange coupling. For $s \geq 3/2$, the effective Hamiltonian predicts a magnetically ordered state. For $s \leq 1$ more exotic possibilities may be realized, though an analytical solution of the resulting quantum dimer model is not possible.

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I. INTRODUCTION

Magnetism is an inherently quantum mechanical effect that ultimately arises from the exchange processes in an interacting many-particle quantum system. Thus, magnetic systems can reveal much about the richness of quantum mechanics itself, especially when cooperative effects are operational and emergent effective low-energy theories describe the relevant physics. A few notable theoretical examples are the spin liquid phases obtained in frustrated magnets,\textsuperscript{1,2,3,4,5} Quantum effects may play a central role in other types of order as well. Recent experiments on a number of insulating chromate compounds, namely CdCr$_2$O$_4$ and HgCr$_2$O$_4$, have shown peculiar features in the low-temperature magnetization as a function of applied magnetic field. At low temperatures the magnetization grows linearly with magnetic field up to some critical value at which point there is a sharp jump in magnetization onto a rather wide plateau with half the full saturation magnetization.\textsuperscript{6,7,8} With sufficiently large fields it is possible to observe a smooth transition off the half-magnetization plateau and a gradual increase in magnetization up to what may be a fully polarized plateau.\textsuperscript{9} As described in Ref.\textsuperscript{1} it is expected that the magnetism in these compounds is well described by the Heisenberg antiferromagnet (AFM) of spin $s = 1/2$ on the pyrochlore lattice.

Motivated by these experimental examples of a half polarization plateau in the pyrochlore Heisenberg AFM, we conduct a theoretical study of the quantum pyrochlore Heisenberg AFM for any spin value $s$, in a strong magnetic field, focusing on a half polarization plateau. While the physics of HgCr$_2$O$_4$ is probably determined to a large degree by the classical physics of spin-lattice interactions,\textsuperscript{10,11,12,13,14} it may be that in other similar compounds where coupling to phonons is weak, quantum effects could play a significant role.

In any case, the general problem of determining the spin state on plateaus of non-zero magnetization in frustrated magnets occurs in a large number of materials.\textsuperscript{15,16,17,18,19,20,21,22} At fields large enough to induce substantial magnetization, the ground state is expected to be very different from the zero field state and one would ideally pursue a theoretical approach that takes advantage of the large external field. The methods developed indeed use this explicitly, and the particular application to the half-polarized pyrochlore magnetization plateau provides a rather non-trivial test bed. We make use of the large field to justify an easy-axis approximation to a nearest-neighbor XXZ antiferromagnetic in an external field. Physically, at large fields the spin is oriented on average more along the field axis than transverse to it. Furthermore, specifically on a magnetization plateau, general arguments imply that the static transverse moment vanishes on every site, $\langle S_i^\tau \rangle = 0$. Thus we expect that Degenerate Perturbation Theory (DPT) about the easy-axis (Ising) limit should be justified on the plateau, and one may thereby derive an effective Hamiltonian. This effective Hamiltonian acts in the constrained “3:1” space of states with 3 majority spins with $S_i^z = +s$ and 1 minority spin with $S_i^z = -s$ on each tetrahedron. This space is macroscopically degenerate, and all its members have half the saturation magnetization.

The reader may well wonder whether there is any need for an approach of this sort, given the successes of the large $s$ semiclassical spin-wave method in many other contexts. Indeed, for unfrustrated antiferromagnets, it is known that the $1/s$ expansion gives reasonably convergent results even down to $s = 1/2$. However, this convergence is strongly dependent upon the lattice – large corrections to the spin-wave dispersion have recently been obtained even for the rather weakly-frustrated triangu-
lar lattice.\textsuperscript{23,24} In highly frustrated magnets such as the pyrochlore, another approach is warranted. Particularly worrisome in the $1/s$ expansion is the difficulty of treating tunneling, which is non-perturbative in this method.\textsuperscript{25,26,27} By contrast, in the easy-axis expansion, tunneling and virtual exchange are treated on the same footing. Of course, for large $s$ both approaches must agree, and we will indeed check that this is the case in our specific application.

The effective Hamiltonian describing splittings within the degenerate manifold of Ising ground states will generally take the form of a constrained quantum Ising model. As explained in a previous publication\textsuperscript{2} for the case of the pyrochlore half-magnetization plateau in the easy-axis limit, it can be cast in the form of a “Quantum Dimer Model” (QDM) on the bipartite diamond lattice. Such QDMs are known to display both ordered and disordered (spin-liquid) ground states in different regions of their phase diagrams.\textsuperscript{2,4,28,29,30,31} We derive the parameters of this QDM for general $s$, and discuss several limits and the expectations for the plateau ground state. For simplicity of presentation we perform this calculation here for the simplest XXZ spin model with no additional anisotropy or other spin interaction terms. However, the method is straightforwardly generalized to include other on-site (e.g. uniaxial anisotropy)\textsuperscript{22} or nearest-neighbor (e.g. bi-quadratic) interactions without substantial increase in computational complexity. More generally, the flexibility to include such effects allows one to consider the quantum effects upon the ground state selection within a magnetization plateau even when the dominant mechanism of plateau stabilization is a classical one.

A remarkable feature of the DPT is that all diagonal terms describing splitting of the low energy manifold vanish below sixth order! For $s \geq 1$, off-diagonal tunneling terms also vanish up to this order, so that the entire effective Hamiltonian is determined by terms of sixth order and higher. This behavior is similar to a result of Henley\textsuperscript{28} that in the large-$s$ limit, the effective Hamiltonian is expressed entirely in terms of a “spin flux” variable involving a product of 6 spins around an elementary loop of the lattice. We show here that our result is rather general, and originates from two basic features: the absence of non-trivial loops of length less than 6 links on the pyrochlore lattice, and the fact that all low-energy spin states on a single tetrahedron are permutations of one another. From our proof of this result, it can readily be seen that similar behavior holds for any lattice of corner sharing simplexes with only on-site and nearest-neighbor interactions and permutation-related ground states on a single simplex. We will apply the methods of this paper to other such problems of interest in future work.

For the pyrochlore magnetization plateau and QDM studied here, the conclusions are as follows. For $s > 3/2$, we find that diagonal terms in the QDM are much larger than off-diagonal ones. In this case, the latter are negligible, and because the diagonal QDM is effectively classical, it is soluble and the ground state is ordered. We discuss the preferred spin ordered states as a function of $s$. For $s \leq 3/2$, the off-diagonal terms are non-negligible, and a simple solution is no longer availed. For $s = 3/2$, various arguments lead us to still expect an ordered state. After correction of an error in Ref\textsuperscript{2}, we find two candidate states for this case. One of these is the $\mathbf{R}$ state discussed previously in Ref\textsuperscript{2}, which is the state containing the maximal number of hexagonal loops with alternating spins (flippable plaquettes in the QDM language). Another candidate is a $\sqrt{3} \times \sqrt{3}$ state with a planar structure. In fact, the diagonal terms in the effective Hamiltonian do not entirely fix the relation between adjacent planes in the latter state, so there is additional degeneracy whose breaking we cannot resolve at the present time. Because the off-diagonal and diagonal terms are comparable in this case, however, some other states may also be possible, and a definite conclusion must await more serious computational (e.g. quantum Monte Carlo) analysis. For $s \leq 1$, the off-diagonal term in the QDM is dominant. In this case, either the $\mathbf{R}$ state or $U(1)$ spin liquid is the most likely candidate ground state. Indeed, as argued in Ref\textsuperscript{53}, it is quite possible that the simplest QDM displays a direct quantum phase transition between these two states.

The ground state of the QDM just discussed is determined only by the dimensionless ratios of coupling constants. However, the DPT calculation also gives the overall scale of the effective interaction in terms of the microscopic exchange $J$. For $s = 3/2$, the largest interaction energy (extrapolated from the easy axis perturbation theory to the Heisenberg limit) generated by quantum fluctuations is only $\approx 0.02J$. Were this the true scale for ground state selection in the degenerate 3:1 manifold in $\text{HgCr}_2\text{O}_4$, the magnetic ordering would occur at a temperature of this order, i.e. $\approx 0.2K$. Experimentally, however, magnetic ordering is observed at a substantial fraction of the temperature of onset of the plateau formation, which is around $6K$. The closeness of the ordering and plateau scales in experiment suggests that both are determined by the same physical mechanism, and argues against the importance of quantum fluctuations in the ground state selection in $\text{HgCr}_2\text{O}_4$. Indeed, we have recently shown\textsuperscript{10} that the same spin-lattice coupling which leads to plateau formation can also account for the state selection. Curiously, the $\mathbf{R}$ state is also stabilized by the lattice mechanism. This is symptomatic of the very strong constraints defining the 3:1 QDM states, which lead rather different microscopic interactions to favor the same ground state. For $s = 1$ and $s = 1/2$, the DPT gives much larger characteristic scales for the QDM, the off-diagonal term being of order $0.16J$ and $1.5J$ in the two cases. Thus such $s \leq 1$ antiferromagnets, if realized experimentally, would be promising systems to observe quantum fluctuation effects.

This manuscript is organized as follows. In Section II, we describe our theoretical model, the nearest-neighbor quantum Heisenberg antiferromagnet on a pyrochlore lattice in an external field. An easy-axis limit is taken un-
under the assumption of the suppression of transverse spin fluctuations in large magnetic fields. After applying degenerate perturbation theory (DPT) in the transverse spin fluctuations, an effective dimer model emerges in Section III that can be used to obtain an approximate ground state of the original model. In Section IV we carry out a large $s$ analysis of the XXZ model, deriving a different effective Hamiltonian splitting the 3:1 manifold of degenerate states. This new effective Hamiltonian turns out to coincide with the $s \to \infty$ limit of the effective Hamiltonian from the DPT analysis. In Section V we explore the ground state of the diagonal part of the effective Hamiltonian from DPT. In Section V we explore the ground state of the diagonal part of the effective Hamiltonian from DPT. In Section VI we analyze how the half polarization plateau is modified by quantum fluctuations. An alternative method of performing DPT is presented in Appendix B, and shows perfect agreement with the result of Section III. Finally, in Appendix C we explore the states degenerate with the $\sqrt{3} \times \sqrt{3}$ states, found for $s = \frac{1}{2}$.

II. MODELS

A. Hamiltonians and Limits

We begin with the simple spin-$s$ Heisenberg antiferromagnet (AFM) residing on the sites of the pyrochlore lattice in the presence of a magnetic field $\mathbf{H}$,

$$
\mathcal{H} = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - \mathbf{H} \cdot \sum_j \mathbf{S}_j .
$$

(1)

On the pyrochlore lattice one may recast the nearest-neighbor exchange in terms of the total spin on tetrahedra using the identity

$$
2 \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j = \sum_i (\mathbf{S}_i)^2 - \sum_{j \in t} \sum_j (\mathbf{S}_j)^2 ,
$$

(2)

where $\mathbf{S}_t = \sum_{j \in t} \mathbf{S}_j$ is the sum of spins on a tetrahedron labeled by $t$, and $(\mathbf{S}_j)^2|j\rangle = S(S+1)|j\rangle$. This gives the more convenient form

$$
\mathcal{H} = \frac{J}{2} \sum_t (|\mathbf{S}_t - \mathbf{h}|^2 - \mathbf{h}^2) ,
$$

(3)

where we have introduced the dimensionless magnetic field $\mathbf{h} = \mathbf{H}/2J = \mathbf{h} \hat{z}$, and ignored a trivial constant term in the Hamiltonian.

1. Classical limit

The form in Eq. (3) makes the behavior in the large $s$ limit apparent. In this limit the spins behave classically, and one may replace $\mathbf{S}_t \to s \hat{n}_t$, where $\hat{n}_t$ is a unit vector. The ground states then consist simply of all states for which $\mathbf{S}_t = s \sum_{i \in t} \hat{n}_i = \mathbf{h}$ on every tetrahedron. This set has a large continuous degeneracy. Furthermore, since the magnetization is simply half the sum of the $\mathbf{S}_t$ (because each spin is contained in two tetrahedra), this implies a continuous linear behavior of the magnetization with field. Thus, in this model magnetization plateaus can emerge only from quantum corrections to the classical limit.

2. Easy axis limit

An alternative approach exploits the fact that, with the application of the magnetic field, the global $SU(2)$ symmetry of the bare Heisenberg model is broken down to a $U(1)$ symmetry (rotations about the magnetic field direction). Moreover, when the magnetization per spin is substantial, on average the transverse components $S^\perp$ are smaller in magnitude than the longitudinal ones. It is therefore natural to treat transverse and longitudinal exchange couplings on a different footing, with the latter taking the dominant role. Formally, this is accomplished by replacing the isotropic Heisenberg Hamiltonian by an XXZ model:

$$
\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 ,
$$

(4)

where

$$
\mathcal{H}_0 = \frac{J}{2} \sum_i [(\mathbf{S}_i^z - \mathbf{h})^2 - \mathbf{h}^2] - J_\perp \sum_i (\mathbf{S}_i^\perp)^2 ,
$$

(5)

and

$$
\mathcal{H}_1 = \frac{J}{2} \sum_{\langle ij \rangle} (\mathbf{S}_i^x \mathbf{S}_j^x + h.c.) .
$$

(6)

We use the notation $\mathbf{S}_i^z = \sum_{j \in t} \mathbf{S}_i^z$, and we have made use of the identity

$$
\sum_{\langle ij \rangle} \mathbf{S}_i^z \mathbf{S}_j^x = \frac{1}{2} \sum_t (\mathbf{S}_t^z)^2 - \sum_i (\mathbf{S}_i^z)^2 .
$$

(7)

In the equations above, and elsewhere in this manuscript, $\langle ij \rangle$ denotes a sum over nearest neighbor sites on the pyrochlore lattice, and $\mathbf{S}_i^\perp$ are the spin ladder operators. Note that in the Heisenberg model $J_\perp = J_z = J$, but the more general XXZ model has all the same symmetries as the former even when this condition is not obeyed. From the above reasoning, we expect that the transverse terms involving $J_\perp$ may be treated as “small” perturbations in the strong-field regime of interest. We note that this is expected to be a particularly good approximation when the system exhibits a magnetization plateau. This is because, as described in the introduction, $(\mathbf{S}_i^\perp)$ must vanish in such a state. Formally, this “easy axis” limit consists of taking $J_\perp \ll J_z$ and doing degenerate perturbation...
theory in $\alpha = \frac{1}{T}$. We will assess the validity of this approximation later by considering the magnitude the perturbative corrections extrapolated to $\alpha = 1$. Finally, we note that several other effects can stabilize a collinear state. One is the addition of easy axis anisotropy,

$$H_0' = -K \sum_i (S_i^z)^2 ,$$

with $K \gg J_\perp > 0$. A second mechanism is biquadratic exchange,

$$H_0'' = -bJ \sum_{ij} (S_i \cdot S_j)^2 ,$$

with $b > 0$. A term of this form can be generated dynamically from spin-lattice interactions, known to be strong in HgCr$_2$O$_4$. The DPT treatment discussed below can readily be generalized to include either or both of the terms in Eqs. (8,9). For simplicity of presentation we do not do so here. While easy-axis terms similar to Eq. (5) are allowed for $s > 1/2$, this particular simple form, with the same spatial direction for the local easy axis of all spins, is not physically appropriate for the cubic pyrochlore spinels, and the proper anisotropy terms allowed by symmetry in these materials are likely to be very small in any case.

B. Magnetization process in the Ising model

The evolution of the ground state with field in the extreme easy-axis limit $\alpha = 0$ is less trivial than in the classical limit. The system is then described by the Ising Hamiltonian, Eq. (5). We shall focus on the $h \geq 0$ case, as the case $h \leq 0$ is equivalent. The expression Eq. (5) can be written as a sum over tetrahedra $H_0 = \sum_\ell H_\ell$ with

$$H_\ell = \frac{J_z}{2} \left[ (S_\ell^z - h)^2 - h^2 - \sum_{j \neq \ell} (S_j^z)^2 \right] ,$$

and therefore if one can minimize this energy on each single tetrahedron, one will have attained the minimum energy of the many-body system.

The magnetization $S_\ell^z$ of any individual tetrahedron is quantized to the values $S_\ell^z = 0, \pm 1, \pm 2, \ldots, \pm 4s$. The 1st term in (10) favors the magnetization of the tetrahedron to take on a value close to the integer part of the 2nd term in (10) favors larger $z$-components of the spin values $S_\ell^z = \pm s$. This 2nd term is trivial only in the spin-1/2 case where the spin-1/2 Pauli matrices square to the identity.

A state with the magnetization $S_\ell^z = m = [h]$ (the integer part of $h$) clearly minimizes the energy of the first term in (10). However, given the magnetization, there is some freedom for the values of the spins on each tetrahedron. The 2nd term in (10) reduces this freedom by adding an energy cost for small $S^z$ components.

Consider 4 spins on a tetrahedron with total magnetization $m$, and individual values of $S_1^z, S_2^z, S_3^z, S_4^z$. Now compare the energy of this state with that of $S_1^z - 1, S_2^z + 1, S_3^z, S_4^z$. The only energy difference comes from the second term in (10)

$$\Delta E = - (S_1^z + 1)^2 - (S_2^z - 1)^2 + (S_1^z)^2 + (S_2^z)^2 = -2 (1 - S_1^z + S_2^z) .$$

From this expression one deduces that if one begins with $S_2^z > S_1^z$, then it is energetically favorable to increase $S_2^z$ even more at the expense of $S_1^z$. This increase in $S_2^z$ can only be halted by one of $S_1^z, S_2^z$ reaching an extreme spin value of $\pm s$. From this reasoning we conclude that the lowest energy state on a single tetrahedron with a fixed total magnetization $m$ has a spin configuration with the largest possible number of extreme valued spins. This also makes intuitive sense, since ideally all the spins should take on extreme values if possible. In three particular choices of $m$, all the spins take on extreme values. Zero magnetization $m = 0$ with $s, s, -s, -s$, half polarization of $m = 2s$ with $s, -s, -s, s$ and full polarization $m = 4s$ with $s, s, s, s$. For $m < 2s$ we find the lowest energy configuration for the spins $s, s, -s, -s$, and for $m > 2s$, we find $s, s, s, m - 3s$. Finally, we can find the minimal energy for given magnetization $m$ by using the spin configurations described above for every value of $m$, and plugging them into (10). For $m < 2s$ we find

$$E_m = \frac{J_z}{2} \left[ 2m(s - h) - 4s^2 \right] ,$$

and for $m > 2s$ we find

$$E_m = \frac{J_z}{2} \left[ 2(m - 2s)(3s - h) - 4hs \right] .$$

From the above expressions it is easy to see that at $h = s$ all $m < 2s$ yield the same energy - all these states are degenerate at this field value. Similarly, for $h = 3s$ all $m > 2s$ yield the same energy. For other values of the magnetic field, we find for $h < s$ the lowest energy state is the $m = 0$ zero magnetization state, for $h < s < 3s$ the lowest energy state is the $m = 2s$ half polarized state, and for $h > 3s$ the lowest energy state is the $m = 4s$ fully polarized state.

The three lowest energy states in the various magnetic field ranges have all spins at extreme values $\pm s$, and can be realized on every tetrahedron in the pyrochlore lattice. The $m = 0$ state induces a degenerate manifold of states with every tetrahedron having $s, s, -s, -s$ on it. This 2:2 proportionality is well known as the “ice rules” encountered in a particular phase of water ices as well as spin ice compounds. The half polarization states are also massively degenerate, with every tetrahedron in a 3:1 proportionality of $S_\ell^z = + s$ to $S_\ell^z = - s$ spins (or 3 up one down). This particular degenerate manifold will be the focus of the remainder of our discussion. To summarize, the magnetization curve for (3) exhibits 3 plateaus at zero, half and full polarization, for all values of $s$. 
III. EASY AXIS DEGENERATE PERTURBATION THEORY

A. Structure of perturbation theory

1. Basic formulation

In the previous section, we observed that the extreme easy axis limit of the Heisenberg model exhibits a broad magnetization plateau at half polarization. However, the ground states on this plateau are macroscopically degenerate, consisting of all states with a 3:1 ratio of majority and minority spins on each tetrahedron. In this section, we study the splitting of this degeneracy by perturbation theory in $J_\perp$. We employ the following formulation of Degenerate Perturbation Theory (DPT). Define the projection operator, $\mathcal{P}$, onto any degenerate manifold of states $M$. Consider any exact eigenstate $|\Psi\rangle$. Its projection $|\Psi_0\rangle = \mathcal{P}|\Psi\rangle$ satisfies the “effective Schrödinger equation”

$$\left[ E_0 + \mathcal{P} \mathcal{H}_1 \sum_{n=0}^{\infty} G^n \mathcal{P} \right] |\Psi_0\rangle = E|\Psi_0\rangle = \mathcal{H}_{\text{eff}}|\Psi_0\rangle, \quad (14)$$

where the operator $\mathcal{G} = \frac{1}{E - E_0} (1 - \mathcal{P}) \mathcal{H}_1$. Because the resolvent contains the exact energy $E$, Eq. (14) is actually a non-linear eigenvalue problem. However, to any given order of DPT, $E$ may be expanded in a series in $J_\perp$ to obtain an equation with a true Hamiltonian form within the degenerate manifold. Each factor of $\mathcal{G}$ is at least of order $O(J_\perp)$ due to the explicit factor in $\mathcal{H}_1$, with higher order corrections coming from the expansion of $E$. Once $|\Psi_0\rangle$ and $E$ are known, the full wavefunction can be reconstructed as $|\Psi\rangle = (1 - G)^{-1}|\Psi_0\rangle = \sum_{n=0}^{\infty} G^n |\Psi_0\rangle$.

Considering the lowest order term in DPT that breaks the degeneracy, the precise energy $E = E_0 + O(\alpha)$ in the resolvent can be replaced by $E_0$, where $O(\alpha)$ represents possible energy shifts from lower order terms that do not break the degeneracy, and $E_0$ is the 0-th order energy of the degenerate manifold of states.

2. Order of off-diagonal terms

Every order in DPT can in principle have diagonal (in the $S_z^i$ basis) as well as off-diagonal terms in which the degeneracy is removed. Any off-diagonal term in the effective Hamiltonian must flip spins in such a way as to preserve the 3:1 constraint on each tetrahedron. This can only be accomplished by flipping spins around a non-trivial closed loop on the pyrochlore lattice (see, e.g., Ref.2). The smallest such loop involves flipping spins on 3 different bonds, and flipping a spin from $S^z = \pm s$ to $S^z = \mp s$ requires $\mathcal{H}_1$ to act 2$s$ times, so off-diagonal processes occur first at order $O(J_\perp^{6s})$. Therefore, below this order of DPT, one may consider only diagonal terms. In subsection III.B we will demonstrate that the lowest order diagonal energy splitting term for any $s$ can occur only at 6th order. For spin $s = \frac{1}{2}$ an off-diagonal term appears at 3rd order in DPT, and no diagonal energy splitting occurs at this order, resulting in a purely off-diagonal effective Hamiltonian. For spin $s = 1$ the lowest order diagonal and off-diagonal terms simultaneously appear at 6th order. For any higher value of $s$, the diagonal energy splitting appears at a lower order than any off-diagonal term can occur, and therefore the leading order effective Hamiltonian is purely diagonal in the 3:1 states. We will nevertheless compute the first non-vanishing off-diagonal term for various values of $s$ in Section V.B to use its magnitude for an assessment of the validity of the truncation of the DPT expansion.

3. Unitarily transformed formalism for diagonal terms

We next develop a scheme to compute the diagonal terms, by unitarily transforming the expression in Eq. (14) to obtain a formula for the diagonal effective Hamiltonian with all dependence upon the spin state explicit. The 3:1 manifold can be described using Ising variables to indicate which spins are minority sites. That is, in the 3:1 states, we denote $S_z^j = \sigma_j s$ with $\sigma_j = \pm 1$ the Ising variable. At $n$th order, assuming that all lower order terms are constants, the diagonal terms in the effective Hamiltonian constitute the function of the set $\{\sigma_i\}$ given by

$$\mathcal{H}_n[\{\sigma_i\}] = (-1)^{n+1} \langle \psi[\{\sigma_i\}] | (\mathcal{H}_1 \mathcal{R} \mathcal{Q})^{n-1} \mathcal{H}_1 | \psi[\{\sigma_i\}] \rangle, \quad (15)$$

where the resolvent $\mathcal{R} = (\mathcal{H}_0 - E_0)^{-1}$, $\mathcal{Q} = 1 - \mathcal{P}$, and

$$|\psi[\{\sigma_i\}]\rangle = \otimes_i |S_z^i = \sigma_i s\rangle. \quad (16)$$

The assumption that all lower order terms are constant allows us to replace $E$ by $E_0$ in the denominators in Eq. (14), since the constant corrections to $E$ lead to higher order terms in the effective Hamiltonian.

The dependence upon the $\sigma_i$ in Eq. (15), is not explicit, but, following Hizj et al., it can be made so by a unitary transformation. The operator

$$\hat{U} = e^{i\pi \sum_j \frac{1-\sigma_j}{2} S_z^j} \quad (17)$$

effects a rotation about the $x$-axis in spin space only for the minority spins. This interchanges raising and lowering operators, and reverses the orientation of $S_z^i$ for these sites. We may therefore write

$$|\psi[\{\sigma_i\}]\rangle = \hat{U} |\psi_0\rangle, \quad (18)$$

where

$$|\psi_0\rangle = \otimes_i |S_z^i = s\rangle. \quad (19)$$

is the fully polarized state, which is now independent of $\sigma_i$. Then we have

$$\mathcal{H}_n[\{\sigma_i\}] = (-1)^{n+1} \langle \psi_0 | (\mathcal{H}_1 \mathcal{R} \mathcal{Q})^{n-1} \mathcal{H}_1 | \psi_0 \rangle, \quad (20)$$
where

$$\tilde{\mathcal{Q}} = U^\dagger O U,$$

(21)

for any operator $O$. In what follows, all the operators appearing in Eq. (20) above, will be simplified so that their dependence upon $\sigma_i$ becomes explicit.

First consider $\mathcal{H}_1$. It consists, from Eq. (14), of a sum of operators transferring spin 1 between two nearest neighbor sites, i.e. a bond of the pyrochlore lattice. We define the nearest-neighbor connectivity matrix of the lattice

$$\Gamma_{ij} = \Gamma_{ji} = 1 \text{ when } i \text{ and } j \text{ are nearest neighbors, and } \Gamma_{ij} = 0 \text{ otherwise.}$$

With this terminology we write $\mathcal{H}_1$ as

$$\mathcal{H}_1 = J_z \frac{\alpha}{4} \sum_{ij} \Gamma_{ij} (S_i^+ S_j^- + h.c.) .$$

(22)

After the unitary transformation, one obtains

$$\tilde{\mathcal{H}}_1 = U^\dagger \mathcal{H}_1 U = J_z \frac{\alpha}{4} \sum_{ij} \Gamma_{ij} \left[ (1 + \sigma_i \sigma_j) \left( S_i^+ S_j^- + h.c. \right) \right.
+ \left. \frac{1 - \sigma_i \sigma_j}{2} \left( S_i^+ S_j^- + h.c. \right) \right].$$

(23)

Here the expressions $\frac{1 + \sigma_i \sigma_j}{2}$ denote “Ising delta functions” that select the cases in which the two $\sigma_{i,j}$ have the same or opposite sign.

Assuming the lowest order term in DPT that splits the 3:1 configurations is a diagonal term of order $n_0$, the only 3:1 configuration which can be reached as an intermediate state in Eq. (15), for any $n \leq n_0$ is the starting state $|\psi(\{\sigma_i\})\rangle$. Under the unitary transformation, this state maps to $|\psi_0\rangle$, and therefore the projection operator $\mathcal{Q}$ may be replaced by

$$\tilde{\mathcal{Q}} \rightarrow 1 - |\psi_0\rangle \langle \psi_0|$$

(24)

in Eq. (24).

Finally, we consider the resolvent. Using $U^\dagger S_i^z U = \sigma_i S_i^z$, one finds

$$\tilde{\mathcal{R}}^{-1} = \frac{J_z}{2} \sum_{ij} \Gamma_{ij} \sigma_i \sigma_j (S_i^z S_j^-) - 2J_z h \sum_j \sigma_j S_j^z - E_0.$$

(25)

First we note that because both $\mathcal{H}_0$ and $\mathcal{H}_1$ conserve the total magnetization of the lattice (this is just the conserved quantity arising from the global $U(1)$ symmetry), the term $\sum_j \sigma_j S_j^z$ remains unchanged at every stage in a DPT process, and we can therefore absorb this term into the constant energy $E_0$. Clearly, the inverse resolvent should vanish when acting upon the fully polarized state $|\psi_0\rangle$. Hence we may absorb the constant energy $E_0$ into the sum as

$$\tilde{\mathcal{R}}^{-1} = \frac{J_z}{2} \sum_{ij} \Gamma_{ij} \sigma_i \sigma_j (S_i^z S_j^- - s^2).$$

(26)

We can simplify the resolvent in the restricted space of virtual states which will be accessed in evaluating Eq. (20). In particular, the $\sigma_i$ configurations are restricted to the 3:1 manifold. Furthermore we note that all intermediate states will have only some small finite set of spins whose $S_i^z$ quantum numbers are different from $s$, due to the action of $\mathcal{H}_1$. Let us consider then the action of the resolvent on a state for which this set of sites is denoted by $F$. In this case, only terms in Eq. (26) for which at least one of $i$ or $j$ is in $F$ can contribute. Thus

$$\tilde{\mathcal{R}}^{-1} = \frac{J_z}{2} \sum_{ij \in F} \Gamma_{ij} \sigma_i \sigma_j (S_i^z S_j^- - s^2) + J_z s \sum_{i \in F} \sum_{j \notin F} \Gamma_{ij} \sigma_i \sigma_j (S_i^z - s).$$

(27)

One may replace the sum over $j$ by $\sum_{j \notin F} = \sum_j - \sum_{j \in F}$ to obtain

$$\tilde{\mathcal{R}}^{-1} = \frac{J_z}{2} \sum_{ij \in F} \Gamma_{ij} \sigma_i \sigma_j (S_i^z - s)(S_j^z - s) + J_z s \sum_{i \in F} \sigma_i \left( \sum_{j \notin F} \Gamma_{ij} \sigma_j \right) (S_i^z - s).$$

(28)

The crucial observation is that the 3:1 constraint implies

$$\sum_j \Gamma_{ij} \sigma_j = 4 - 2\sigma_i.$$ 

(29)

This is because once $\sigma_i$ is specified, the set of its neighbors is also specified (see also Fig. 3). Eq. (29) allows one to eliminate the latter sum and obtain

$$\tilde{\mathcal{R}}^{-1} = \frac{J_z}{2} \sum_{ij \in F} \Gamma_{ij} \sigma_i \sigma_j (S_i^z - s)(S_j^z - s) + 2J_z s \sum_{i \in F} \left( 2\sigma_i - 1 \right) (S_i^z - s).$$

(30)

Using again the observation that $\sum_j \sigma_j S_j^z$ remains unchanged throughout the stages of any DPT process, it is equal to the constant $\sum_j \sigma_j S_j^z = \sum_j \sigma_j s$. Using this fact, we finally obtain

$$\tilde{\mathcal{R}}^{-1} = \frac{J_z}{2} \sum_{ij \in F} \Gamma_{ij} \sigma_i \sigma_j (S_i^z - s)(S_j^z - s) - 2J_z s \sum_{i \in F} (S_i^z - s).$$

(31)

By successive action of $\mathcal{H}_1$, $\tilde{\mathcal{Q}}$, and $\tilde{\mathcal{R}}$ using Eqs. (23, 24, 31), one can obtain explicit expressions for any intermediate state in the DPT expression of Eq. (20), with $n \leq n_0$. For example, one action of each of these operators gives

$$\tilde{\mathcal{R}} \tilde{\mathcal{Q}} \mathcal{H}_1 |\psi_0\rangle = \frac{\alpha s}{4(4s - 1)} \sum_{a_1 a_2} \Gamma_{a_1 a_2} (1 - \sigma_{a_1} \sigma_{a_2}) |a_1, a_2\rangle.$$
where we have introduced the compact notation

\[
| (m_1)_{a_1} \cdots (m_n)_{a_n} \rangle = | S^z_{a_1} = s - m_1 \cdots | S^z_{a_n} = s - m_n \rangle
\]

\[
\otimes_{i \neq a_1 \cdots a_n} | S^z_i = s \rangle.
\]  

(33)

Acting twice with the same sequence of operators gives

\[
\left( \hat{R} \hat{Q} \hat{H}_1 \right)^2 | \psi_0 \rangle = \frac{\alpha^2 s^2}{16(4s - 1)} \sum_{a_1,a_2} \Gamma_{a_1a_2} (1 - \sigma_{a_1} \sigma_{a_2}) |2a_1,2a_2\rangle
\]

\[
+ \frac{\alpha^2 s^2}{4(4s - 1)} \sum_{a_1,a_2,a_3} \Gamma_{a_1a_2a_3} \eta_{a_1a_2} \left[ (\sigma_{a_1} + \sigma_{a_2}) \sigma_{a_2} - \sigma_{a_1} \sigma_{a_3} - 1 \right] |1a_1,1a_2\rangle
\]

\[
+ \frac{\alpha^2 s^{3/2}}{4(4s - 1)} \sum_{a_1,a_2,a_3,a_4} \Gamma_{a_1a_2a_3a_4} \eta_{a_1a_2} \eta_{a_2a_3} \eta_{a_3a_4} \left[ 1 + \sigma_{a_2} \sigma_{a_3} - \sigma_{a_1} (\sigma_{a_2} + \sigma_{a_3}) \right] |2a_1,2a_2,1a_3\rangle
\]

\[
+ \frac{\alpha^2 s^2}{16(4s - 1)} \sum_{a_1,a_2,a_3,a_4} \Gamma_{a_1a_2a_3a_4} \eta_{a_1a_2} \eta_{a_2a_3} \eta_{a_3a_4} (1 - \sigma_{a_1} \sigma_{a_2})(1 - \sigma_{a_3} \sigma_{a_4}) |1a_1,1a_2,1a_3,1a_4\rangle,
\]  

(34)

where we have introduced the “non-coincident” symbol

\[
\eta_{ab} = 1 - \delta_{ab}.
\]  

(35)

The corresponding expressions for more successive actions of these operators upon \(| \psi_0 \rangle\) can also be obtained, but are too unwieldy to present here.

Using such expressions, one may readily evaluate the terms \(\mathcal{H}_n[\{\sigma_i\}]\) in the diagonal effective Hamiltonian, Eq. (30). For \(n_0\) an even number, a convenient way to calculate the \(n_0\)-th order term is to consider the state

\[
| \Psi \rangle = \hat{R}^{1/2} \hat{Q} \hat{H}_1 \left( \hat{R} \hat{Q} \hat{H}_1 \right)^{n_0-1} | \psi_0 \rangle
\]  

(36)

and then find the magnitude of this wavefunction:

\[
\mathcal{H}_{n_0}[\{\sigma_i\}] = -\langle \Psi | \Psi \rangle.
\]  

(37)

Note that the square-root of \(\hat{R}\) in Eq. (36) is easily evaluated by just taking the square-root of Eq. (31), since it is diagonal in the basis of 3:1 configurations. Other terms can be obtained similarly.

B. Restricting the Hilbert space to the 3:1 manifold

Calculating each such magnitude as defined in the previous subsection leads to an explicit expression for the corresponding term in DPT. These expressions appear to be extremely complex and formidable functions of the Ising spin variables \(\{\sigma_i\}\). In this subsection, we show that the projection of these functions to the 3:1 manifold of allowed \(\{\sigma_i\}\) configurations affords a tremendous simplification. In fact, we will demonstrate that all terms in DPT below 6th order can give only constant functions – i.e. no splitting – within the 3:1 states. At 6th order, the full functional dependence can be characterized by only 3 independent numbers which may be defined on plaquettes of the pyrochlore lattice. We show how these numbers can be extracted from the expressions obtained by the analysis of the previous subsection.

1. Functional form of diagonal DPT terms

From the analysis of the previous subsection, the \(n^{th}\) order effective diagonal Hamiltonian in DPT must take the form of a multiple sum of \(n\) site indices \(a_1 \cdots a_n\), where each site index is summed over all lattice sites. The summand is a function only of \(\sigma_i\), \(i, j\) must belong to the set of the site indices. The general form can be somewhat simplified by noting first that the dependence upon the \(\eta_{ij}\) can be eliminating by rewriting them in terms of \(\delta_{ij}\) using Eq. (25), and then eliminating all \(\delta_{ij}\) by collapsing the sums containing these factors. Finally, we note that any factors of \(\Gamma_{ij}\) in the denominators in these expressions can be moved to the numerator using the identity

\[
g(\Gamma_{ij}) = g(0) + \Gamma_{ij} \left[ g(1) - g(0) \right],
\]  

(38)

for any function \(g\) (which may also depend upon any other set of variables), since \(\Gamma_{ij} = 0, 1\).

By these manipulations, one may write the effective Hamiltonian \(\mathcal{H}_{\text{eff}}[\{\sigma_i\}]\) as

\[
\mathcal{H}_{\text{eff}}[\{\sigma_i\}] = \sum_n \mathcal{H}_n[\{\sigma_i\}]
\]  

(39)

Here we have divided the effective Hamiltonian into terms involving \(n\) independent sites variables, \(a_1 \cdots a_n\) that are
summed over the lattice sites. A given order \( N \) in DPT contributes terms with \( n \leq N \). For a given \( n \), all possible products of \( \Gamma_{a_i} \) can appear. The different such products are specified by \( G_n \), which may be considered as a “diagram” in the following fashion. Each \( G_n \) can be represented by drawing \( n \) points, corresponding to \( i = 1 \ldots n \), and connecting some arbitrary set of pairs of these points by lines. For each (unordered) pair of points \((ij)\) which is connected in \( G_n \), we include one factor of \( \Gamma_{a_i,a_j} \). Since there are \( n(n - 1)/2 \) pairs of points, and each pair may or may not be connected, there are \( 2^{n(n-1)/2} \) distinct diagrams \( G_n \). For example, in our conventions, \( \Gamma_{a_1a_2}\Gamma_{a_2a_3}\Gamma_{a_3a_4} \) and \( \Gamma_{a_1a_2}\Gamma_{a_2a_3}\Gamma_{a_3a_5} \) are represented by different diagrams (see Fig. 1); which means that \( f_{G_n}(\sigma_{a_1},\ldots,\sigma_{a_n}) \) is not necessarily symmetric with respect to swapping \( \sigma_{a_k} \) and \( \sigma_{a_l} \). We will refer to the number \( n \) as the order of the given term, even though it can come from a term of that order or higher in DPT.

2. Contractible diagrams

First we would like to show that any such term represented by a diagram containing a point \( i \) with less than two connections to other points can be reduced to a term of one lower order. These diagrams are “contractible” (see Fig. 2 for examples). We prove this by showing that the sum over \( a_i \) can be carried out explicitly to obtain an expression of the same form of Eq. (39) in terms of the \( n-1 \) remaining sum variables. There are two cases. Suppose in \( G_n \), the point \( i \) in question has no lines connected to it. Taking \( i = n \) without loss of generality, we note that the sum on \( a_n \) is unconstrained, i.e. it runs over all lattice sites. Thus we may write

\[
2 \sum_{a_n} f_{G_n}(\sigma_{a_1},\ldots,\sigma_{a_n}) = \sum_{\ell} \sum_{a \in \ell} f_{G_{\ell}}(\sigma_{a_1},\ldots,\sigma_{a}) \quad (40)
\]

\[
= N_{\ell} [3 f_{G_{\ell}}(\sigma_{a_1},\ldots,\sigma_{a_{n-1}},+) + f_{G_{\ell}}(\sigma_{a_1},\ldots,\sigma_{a_{n-1}},-)] .
\]

The second line applies because on every tetrahedron there is the same set of four single-spin states. By inserting Eq. (40) into Eq. (39), one reduces the order of this term, as asserted above.

Consider the second case, in which there is one connection to the point \( i = n \). We may suppose this connection is to the point \( j < n \). The sum over \( a_n \) is then constrained only by the requirement that \( a_n \) be a nearest-neighbor of \( a_j \). For fixed \( a_j \), this includes just 6 sites on the pyrochlore lattice. Moreover, the set of spins on these six sites is entirely determined by the spin at site \( a_j \). In particular, if \( \sigma_{a_j} = +1 \), the sum contains 4 terms with \( \sigma_{a_n} = +1 \) and 2 terms with \( \sigma_{a_n} = -1 \); if \( \sigma_{a_j} = -1 \), the sum contains 6 spins with \( \sigma_{a_n} = +1 \). This can easily be understood from Fig. 3. Therefore the sum can again
be carried out explicitly:

\[
\sum_{\sigma_n} \Gamma_{a_n a_j} f_{G_n}(\sigma_1, \ldots, \sigma_n) = \\
\frac{1 + \sigma_{a_2}}{2} [4 f_{G_n}(\sigma_1, \ldots, +) + 2 f_{G_n}(\sigma_1, \ldots, -)] \\
+ \frac{1 - \sigma_{a_2}}{2} 6 f_{G_n}(\sigma_2, \ldots, \sigma_{n-1}, +). \tag{41}
\]

Once again, Eq. (41) can be inserted into Eq. (40) to reduce the order by one.

3. Non-contractible diagrams

Since all contractible diagrams can be reduced using the above rules until they become either non-contractible or constant, we therefore need to consider only non-contractible diagrams. In these diagrams, each point in $G_n$ is connected to at least two other points. Let us first make a few general observations about these diagrams. One can readily see that for these diagrams at order $n \leq 5$, all points must be connected, i.e., it is possible to pass from one point to any other by a sequence of links. It is useful to consider the notion of a loop, or sequence of points, each connected to the next by a link, which visits no point twice and returns to the first point of the sequence. For $n \leq 4$, there is always at least one loop which includes all $n$ points. For $n = 5$, all but three non-contractible diagrams contain a loop of length 5. The three remaining diagrams at $n = 5$ contain smaller loops (see part (c) of Fig. 4). All the non-contractible single loop diagrams for $n \leq 5$ are shown in Fig. 4. For $n = 6$, there is one possible disconnected diagram, which contains two disjoint loops of length 3. Apart from this last diagram, all others are fully connected.

Let us consider the physical pyrochlore sites which are summed over in a given term. They comprise a set $S(G_n) = \{(a_1^{(1)}, \ldots, a_n^{(1)}), (a_1^{(2)}, \ldots, a_n^{(2)}), \ldots\}$ of solutions, $(a_1^{(i)}, \ldots, a_n^{(i)})$, to the conditions

\[
\Gamma_{a_i a_j} = 1 \quad \text{for} \quad (ij) \in G_n. \tag{42}
\]

We will call these solutions “clusters”. In an infinite system, $S$ is of course infinite because of translational symmetry, but this is immaterial. A given term may then be written simply as

\[
\sum_{(a_1, \ldots, a_n) \in S(G_n)} f(\sigma_1, \ldots, \sigma_n). \tag{43}
\]

We note that all the clusters for $n \leq 5$ are confined to one or two adjacent tetrahedra. This can be seen by considering the constraints imposed on clusters by the non-contractibility of the diagram. For instance, all but three diagrams at order $n = 5$ contain a loop of length 5, and this allows only three topologies of clusters, which are illustrated in Fig. 5. The remaining three diagrams only allow clusters that are confined to two or less adjacent tetrahedra. We will show more generally that any term containing only clusters confined to three or fewer adjacent tetrahedra is a constant.

The set $S$ can therefore be broken up into three components, comprising clusters which contain 1, 2, or only 3 multiply-occupied tetrahedra,

\[
S(G_n) = S_1(G_n) + S_2(G_n) + S_3(G_n). \tag{44}
\]

The sum in Eq. (44) can be carried out separately over these three sets. Let us consider first the sum over $S_1$. The clusters in $S_1$ can be divided into subsets of those residing on a specific tetrahedron $S_1^t$.

An arbitrary permutation $P$ of the 4 sites on tetrahedron $t$ leaves the set $S_1^t(G_n)$ invariant. This is because each solution obeys Eq. (42), and $\Gamma_{a_i a_j} = \Gamma_{P(a_i) P(a_j)}$ for $a_i, a_j \in t$ (this is a set of permutations that leaves nearest neighbor pairs invariant).

The contribution of all clusters on $t$ to the term in question can only be a function of the 4 Ising variables of the 4 sites $q = 1, 2, 3, 4 \in t$

\[
\sum_{(a_1, \ldots, a_n) \in S_1^t} f_{G_n}(\sigma_1, \ldots, \sigma_n) = F(\sigma_1, \sigma_2, \sigma_3, \sigma_4). \tag{45}
\]

Now we can use the fact that the spin configurations on one tetrahedron are always constrained to be of the 3:1 form, i.e., they are a permutation $P$ of the specific configuration $+++-$:

\[
\sigma_q = \sigma_{P(q)}^0, \tag{46}
\]
with $(\sigma_1^0, \sigma_2^0, \sigma_3^0, \sigma_4^0) = (+, +, +, -)$. Here $q \rightarrow P(q)$ is a permutation of the 4 sites. The specific (cyclic) permutation $P$ now encodes the spin state on this tetrahedron

$$F(\sigma_{P(1)}^0, \sigma_{P(2)}^0, \sigma_{P(3)}^0, \sigma_{P(4)}^0) = \sum_{(a_1, \ldots, a_6) \in S_1^T} f_{G_n}(\sigma_{P(a_1)}^0, \ldots, \sigma_{P(a_6)}^0) \quad (47)$$

Since the set $S_1^T(G_n)$ is invariant under these permutations, we find from the last expression, that $F(\sigma_1, \sigma_2, \sigma_3, \sigma_4)$ is also invariant under the permutations. Hence this contribution is identical for all spin configurations, and is a constant within the 3:1 manifold.

Let us next consider the clusters in $S_2$. For each cluster, there are two neighboring tetrahedra $t, t'$ which each contain two or more sites $a_i$. These tetrahedra share one specific site, which we call $A$. The pair of tetrahedra in question are determined by $A$ (the tetrahedra $t$ and $t'$ are determined by the choice of $A$). For one such cluster, the sites $a_i$ with $i = 1 \ldots n$ may be partitioned into three groups: the site $A$, and those which are on $t$ or $t'$ but are not $A$:

$$t = \{a_i | a_i \in t, a_i \neq A\}, \quad t' = \{a_i | a_i \in t', a_i \neq A\}. \quad (48, 49)$$

Similarly to $S_1$, we can divide $S_2$ into subsets $S_2^A$ based on tetrahedron pairs defined by the site $A$. We can then rewrite the sum by summing $A$ over all lattice sites, and summing the set of sites $a_1 \ldots a_n$ over $S_2^A$

$$\sum_{(a_1, \ldots, a_6) \in S_2^A} f_{G_n}(\sigma_{a_1}, \ldots, \sigma_{a_6}) = \sum_A \sum_{(a_1, \ldots, a_6) \in S_2^A} f_{G_n}(\sigma_{a_1}, \ldots, \sigma_{a_6}) \quad (50)$$

We now observe that the set of solutions $S_2^A$ is invariant under any permutation $P_t$ ($P_{t'}$) of the 3 sites in $t$ ($t'$). Exactly as for $S_1$, this is because each solution in $S_2^A$ obeys Eq. (12), and $\Gamma_{a_i,a_j} = \Gamma_{P_t(a_i),P_t(a_j)}$ for $a_i, a_j \in A \cup t$. (the same holds if $P_t$ is replaced by $P_{t'}$).

The sum

$$\sum_{(a_1, \ldots, a_6) \in S_2^A} f_{G_n}(\sigma_{a_1}, \ldots, \sigma_{a_6}) \quad (51)$$

can only be a function of the 7 Ising variables of the sites in $A \cup t \cup t'$. Due to the 3:1 constraint, if $\sigma_A = +$, then the Ising variables $\sigma_q$ for $q \in t$ must be a permutation $P_t$ of $\sigma_t^0 = (+, +, +, -)$. If $\sigma_A = -$, then all the $\sigma_q = +$. Hence we may write

$$\sigma_q = \begin{cases} \frac{1 + \sigma_A}{2} \sigma_{P_t(q)} + \frac{1 - \sigma_A}{2} (+ + +) & \text{for } q \in t \\ \frac{1 + \sigma_A}{2} \sigma_{P_t(q)} + \frac{1 - \sigma_A}{2} (+ + +) & \text{for } q \in t'. \end{cases} \quad (52)$$

Using these expressions, and the fact that $S_2^A$ is invariant under these two permutations, the sum in Eq. (51) is found to depend only on $\sigma_A$.

This leaves finally

$$\sum_{(a_1, \ldots, a_6) \in S_2^A} = \sum_A \hat{f}(\sigma_A), \quad (53)$$

where $\hat{f}(\sigma_A)$ is a complicated function obtained from the above manipulations – which however does not depend upon $A$ itself. The sum is clearly then constant, as the number of $+$ and $-$ spins are fixed for the lattice. Thus all terms in $S_2$ are also constants.

Finally, consider $S_3$. In these clusters there are three adjoining tetrahedra, and one may identify a “central” tetrahedron $t$ which shares a site with each of the other two tetrahedra $t', t''$. Here one may divide the sum variables into five groups: two corresponding to the site shared by $t, t'$ and the site shared by $t, t''$, and three others corresponding to the sites on $t, t', t''$ but not shared. One can again sum over the unshared sites on $t'$ and $t''$, and obtain an expression for the cluster sum which involves sites only on $t$. By manipulations of the type used to analyze $S_1$, one finds that this remaining single-tetrahedron sum must also be constant.

We conclude that any term for which the corresponding clusters are confined to three or fewer adjacent tetrahedra must be constant. Therefore all terms up to and including 5th order are constant. At sixth order, amongst the non-contractible diagrams there are a few exceptions. First, there is one disconnected diagram containing two loops of length three. In this term, the sum over variables in the first and second groups is independent, and therefore each can be carried out separately as for a third order term. This gives immediately a constant contribution. The remaining diagrams are connected. All but one of these diagrams contains a loop of length 5 or less (possibly in addition to other larger loops). Such terms are confined to three or fewer tetrahedra, and are constant by the above arguments. What remains is the single diagram consisting of only a single loop of length six, shown in Fig. 6.

This “large loop” diagram is thus the sole non-trivial contribution. It can be written in the form

$$\mathcal{H}_L(\{\sigma_i\}) = \sum_{a_1 \ldots a_6} \left( \prod_{i=1}^6 \Gamma_{a_i,a_i+1} \right) \hat{f}_L(\sigma_{a_1}, \ldots, \sigma_{a_6}) \quad (54)$$

where we identify $a_6 = a_1$. To analyze each term (given a particular set $a_1 \ldots a_6$), we employ a trick: multiplying it by a carefully chosen representation of the identity

$$1 = \prod_{i,j} \left( \delta_{a_i,a_j} + \eta_{a_i,a_j} \right) \quad (55)$$

with $\eta_{ab} = 1 - \delta_{ab}$. Here the product is over distinct pairs $i, j$ which are not connected in the loop diagram. We multiply the loop term by this expression and expand
the product fully. All but one term involves at least one Kronecker δ-function. In each of these summand terms, at least one sum can be collapsed, leading to a lower-order term, which we have already shown is necessarily a constant. The remaining non-vanishing part is the original summand term multiplied by the product,

$$
\prod_{\langle\langle ij\rangle\rangle} \eta_{a_i a_j}.
$$

This factor is non-zero if and only if all $n = 6$ sites $a_i$ are distinct. Thus the sites $a_i$ must comprise a closed walk on the lattice in which each site on the walk is visited only once. On the pyrochlore lattice, this is exactly the set of hexagonal plaquettes. A specific plaquette on the lattice containing sites $i_1 \ldots i_6$ in sequence around the plaquette appears 12 times in the sum in Eq. (54), with $a_1 \ldots a_6$ taking the six cyclic permutations of $i_1 \ldots i_6$ and the six cyclic permutations of these sites in reverse order. Hence the non-constant contribution to the diagonal energy at 6th order in DPT can be written:

$$
\mathcal{H}_6 = \sum_{\mathcal{P}} \mathcal{E}_\mathcal{P}(i_1, \ldots, i_6),
$$

where $i_1, \ldots, i_6$ are the six sites moving clockwise around plaquette $\mathcal{P}$, and

$$
\mathcal{E}_\mathcal{P}(\sigma_{i_1}, \ldots, \sigma_{i_6}) =
\sum_{k=1}^{6} \left[ f_L(\sigma_{i_k}, \ldots, \sigma_{i_{k+5}}) + f_L(\sigma_{i_{k+5}}, \ldots, \sigma_{i_k}) \right],
$$

where $i_{k+6} \equiv i_k$.

\section{C. Results}

We have carried out the calculations detailed in the previous subsections. Specifically, by explicitly constructing $|\Psi\rangle$ in Eq. (36), we obtained $\mathcal{H}_6[|\sigma_j\rangle]$ in Eq. (37). From this, we extracted the function $f_L$ in Eq. (34) and thereby determined the plaquette energies $\mathcal{E}_\mathcal{P}$ using Eq. (38). Using the 3:1 constraint, there are 5 configurations possible on any plaquette, which we denote “type 0” to “type 4”. These are enumerated in Table I. The DPT calculation gives a specific energy (proportional to $J_z \alpha^6$) for each type.

| Type | Configuration | Fraction of minority spins |
|------|---------------|---------------------------|
| 0    | ↑↑↑↑↑         | 0                         |
| 1    | ↑↑↑↑↑↑        | 1/3                       |
| 2    | ↑↑↑↑↑         | 1/3                       |
| 3    | ↑↑↑↑↑         | 1/3                       |
| 4    | ↑↑↑↑↑         | 1/3                       |

There is some freedom in the choice of these 5 energies. That is, certain changes of the plaquette energies leave the differences of total energy amongst distinct 3:1 states unchanged. One obvious such “gauge” change is a global shift of all 5 energies by the same amount. Another less obvious constraint comes directly from the 3:1 rule. If one denotes the fraction of plaquettes in the lattice in configuration $a$ by $x_a$, the total fraction of minority sites must always be 1/4. Each plaquette configuration has a fixed fraction of minority sites $M_a$, given in Table I.

Thus

$$
\frac{1}{4} = \sum_{a=0}^{4} M_a x_a.
$$

The energy per plaquette is then

$$
\mathcal{H}_6 = \sum_{a=0}^{4} \mathcal{E}_a x_a
$$

Using (59), one sees that a shift $\Delta \mathcal{E}_a = c M_a$, with arbitrary constant $c$ shifts the energy by a constant. The obvious global energy shift remarked on above derives similarly from the normalization condition $\sum_a x_a = 1$. Using these two constraints, we see there are only 3 independent plaquette fractions. We (arbitrarily) choose to keep $x_{1,2,4}$ as our independent variables. Substituting the solutions for the other fractions ($x_{0,3}$ into (60), we find

$$
\mathcal{H}_6 = x_1 V_1 + x_2 V_2 + x_4 V_4,
$$

with the 3 “gauge invariant” physical energy parameters

$$
V_1 = \frac{1}{2} (\mathcal{E}_0 + 2 \mathcal{E}_1 - 3 \mathcal{E}_3),
$$

$$
V_2 = \frac{1}{2} (-\mathcal{E}_0 + 2 \mathcal{E}_2 - \mathcal{E}_3),
$$

$$
V_4 = (\mathcal{E}_4 - \mathcal{E}_3).
$$
Our DPT results are:

\[
V_1 = -J_z \alpha^6 \frac{3s^4(98304s^5 - 139648s^4 + 79136s^3 - 22040s^2 + 3006s - 165)}{32(2s - 1)(4s - 1)^5(8s - 3)^2(12s - 5)},
\]

\[
V_2 = J_z \alpha^6 \frac{3s^3(256s^3 - 51s + 9)}{32(4s - 1)^3(8s - 3)^2},
\]

\[
V_4 = J_z \alpha^6 \frac{3s^3(272s^2 - 136s + 15)}{16(4s - 1)^3(8s - 3)^2}.
\]  

We have made several checks on the above calculation. First, we have carried out a more direct scheme which sums the terms in DPT in a completely different manner from the methods described in this section. We leave the vast details of this calculation to Appendix B. The results of this alternative method agree perfectly with those quoted above. Second, in the following section we will compare the \( s \to \infty \) limit of the above result with the result of a large \( s \) calculation for the XXZ model. The large \( s \) limit of the energies we find in DPT becomes

\[
\lim_{s \to \infty} \frac{V_1}{s} = 0,
\]

\[
\lim_{s \to \infty} \frac{V_2}{s} = \frac{512}{512},
\]

\[
\lim_{s \to \infty} \frac{V_4}{s} = 0.
\]  

(64)

We shall see that this result indeed agrees exactly with the corresponding limit of the large \( s \) expansion.

### D. Off diagonal term

In this section we describe how the lowest order off diagonal term in the DPT effective Hamiltonian is calculated. As explained in Section IIIA, this appears at order \( O(\alpha^{6s}) \).

The lowest order off diagonal term acts only on a hexagonal plaquette in the flippable configuration (type 1 plaquette, as in Table I). It changes the plaquette configuration from one flippable configuration to the other flippable configuration. Therefore the off diagonal term has the following general form

\[
\mathcal{H}_{\text{off diagonal}} = (-1)^{6s+1} \alpha^{6s} J_z K \sum_P \left( \hat{z} \hat{x} \hat{y} + \text{h.c.} \right),
\]

\[
= (-1)^{6s+1} \alpha^{6s} J_z K \sum_P \left( |↓↑↑↑↓⟩⟨↑↓↑↓↑| + \text{h.c.} \right),
\]

(65)

where we denote the two flippable configurations of the plaquette by \( \hat{z} \hat{x} \hat{y} \) for the sake of brevity. Note that we can change the \((-1)^{6s+1}\) factor into a \((-1)\) by a unitary transformation similar to that employed in Ref. [4]. We shall now describe how the coefficient \( K \) is calculated.

Each one of the DPT processes contributing to the off-diagonal term consists of 2s spin transfer operations along each one of 3 links of a hexagonal plaquette of the pyrochlore lattice (see Fig. 7), acting in some particular order.

We can calculate \( K \) by adding the contributions from all the DPT processes occurring on a single plaquette, starting in the state \( |↓↓↑↑↑⟩\) and ending in the state \( |↑↓↑↑↓⟩\).

In every such process 3 spins go from an initial state of \(+s\) to \(-s\), and 3 start with \(-s\) and end up as \(+s\). The spins change via ladder operators \( S^\pm \), and therefore we get “angular momentum factors” from the action of these operators. The same set of operators \( S^\pm \) act in every process, and so these factors are always the same. For the \( S^+ \) operators taking a single site from \(-s\) to \(+s\) we find

\[
\prod_{m=-s}^{s-1} \sqrt{s(s+1) - m(m+1)} = (2s)!,
\]

(66)

and for the \( S^- \) operators taking a single site from \(+s\) to \(-s\) we find

\[
\prod_{m=-s+1}^{s} \sqrt{s(s+1) - m(m-1)} = (2s)!.
\]

(67)

In total from all the ladder operators, we find a common factor \(((2s)!)^6\). From the 6 spin transfer operators we have another common factor of \(1/2^{6s}\).

All that remains to be calculated for a single DPT process is the product of resolvents of each stage in the spin transfer process. First let us classify the different processes on a single plaquette. We can choose one of two sets of three links on which spin transfer will occur (one such choice is shown in Fig. 7). The contribution from each one of these two cases is identical, so we shall calculate the contributions for one set of three links, and multiply the final result by 2. The processes we will sum over only differ by the order in which the spin transfer operators act on the 3 predetermined links. We call the three links \( A,B, \) and \( C \), and then each process is described by a string of 6s letters \( q_1 \ldots q_{6s} \) which contain 2s instances of each one of the three letters \( A,B,C \). For example, a possible string for \( s = 1 \) is \( AABBC \). From this classification, it is evident that in total there are \((2s)!/(2s)!(2s)!(2s)!\).
different processes. At this point we can write a formal expression for the coefficient $K$

$$K = 2 \left( \frac{(2s)!}{2^{6s}} \right) \sum_{\{q_n\}} \prod_{\ell=1}^{6s-1} \tilde{R}_\ell(\{q_n\}),$$

(68)

where $\tilde{R}_\ell(\{q_n\})$ denotes the resolvent at step $\ell$ of the DPT process described by the string $\{q_n\}$.

Now we turn to formulating the resolvent in a convenient manner that will facilitate the summation over all processes. Starting from Eq. (61), in this case the set $\mathcal{F}$ consists only of the 6 sites surrounding the hexagonal plaquette. We shall denote these 6 sites 1 through 6, as in Fig. 7 so that $A$ denotes the link (1,2), $B$ denotes the link (3,4), and $C$ denotes the link (5,6). Since the 6 sites have alternating initial states ±s, any pair of nearest neighbor sites has $\sigma_\ell \sigma_j = -1$. We can therefore rewrite the inverse resolvent operator as

$$\tilde{R}^{-1} = -J_z \sum_{j=1}^{6} (S_j^z - s) (S_{j+1}^z - s) - 2J_z s \sum_{j=1}^{6} (S_j^z - s),$$

(69)

where the indices are defined modulo 6, so that $S_{j+1} = S_j$. From this point on, all index arithmetic is defined modulo 6 as well, for ease of presentation.

To further simplify the resolvent, we introduce $n_A(\ell, \{q_n\})$ as the number of times the link A has had spin transfer occur on it up to stage $\ell$ in the process described by the string $\{q_n\}$. The same numbers can be also introduced for $B$ and $C$. Then, by definition, the total number of spin transfer operations is $n_A(\ell, \{q_n\}) + n_B(\ell, \{q_n\}) + n_C(\ell, \{q_n\}) = \ell$. In what follows we will show that the resolvent can be described only by these 3 numbers. To see this, notice first that, regardless of the order of spin transfer operations, a spin transfer operator on the link $(j, j+1)$ changes $(S_j^z - s) \rightarrow (S_j^z - s - 1)$ and $(S_{j+1}^z - s - 1) \rightarrow (S_{j+1}^z - s - 1)$. Note also that, in the initial state, all $(S_j^z - s) = 0$. Thus, at every stage of any process, $(S_i^z - s) = (S_n^z - s) = -n_A(\ell, \{q_n\})$ Similarly $(S_i^z - s) = (S_n^z - s) = -n_B(\ell, \{q_n\})$, and $(S_i^z - s) = (S_n^z - s) = -n_C(\ell, \{q_n\})$. Using these variables, one can then rewrite the resolvent as

$$\tilde{R}_\ell(\{q_n\}) = 4J_z s \ell - \frac{J_z}{2} \left[ (n_A + n_B)^2 + (n_B + n_C)^2 + (n_C + n_A)^2 \right],$$

(70)

where we have suppressed the explicit dependence of the $n_{A,B,C}$ numbers on $\ell, \{q_n\}$ for clarity. It is more convenient to derive a recursion relation for the resolvent at stage $\ell$

$$\tilde{R}_{\ell+1}(\{q_n\}) = \tilde{R}_\ell(\{q_n\}) + J_z \left( 4s - 1 - \ell - n_{q_{\ell+1}}(\ell, \{q_n\}) \right).$$

(71)

The initial condition for this recursive series is $\tilde{R}_0^{-1} = 0$. Using Eq. (71), we can calculate the product $\prod_{\ell=1}^{\ell=6} \tilde{R}_\ell(\{q_n\})$ for a given process. For every process, we need to track only of the 3 numbers $n_{A,B,C}$ in the various steps of the the process.

We have calculated the coefficient $K$ explicitly for a number of interesting values of $s$. The results are summarized in Table II.

| $s$ | $K$  |
|-----|-----|
| $\frac{1}{2}$ | 0.166 |
| 1   | 0.00839536 |
| $\frac{3}{2}$ | 0.000304464 |
| $\frac{5}{2}$ | 9.1747 $\times 10^{-4}$ |

TABLE II: Values $K$ of the coefficient for the lowest order off-diagonal term, for various values of $s$.

IV. LARGE $s$ EXPANSION

A large $s$ analysis has recently been employed in Ref. 27 to explore the magnetic order for the general spin $s$ Heisenberg AFM on the pyrochlore lattice. Restricting the Hilbert space to collinear spin configurations, the authors of Ref. 27 derived an effective Hamiltonian out of the harmonic spin wave energy contribution, to order $O(s)$. The effective Hamiltonian prefers spin products around hexagonal plaquettes to be $-s^6$ in the zero magnetic field, and $+s^6$ in the half-polarized plateau region. Following a terminology inspired by Ising gauge theory, these are denoted “π flux” configurations and “zero flux” configurations, respectively. In order to compare this approach, which is justified in the large $s$ limit, with the DPT analysis of Section III I we have repeated the same type of effective Hamiltonian calculation for the the XXZ model. Our derivation follows closely that of Ref. 27.

The large $s$ expansion consists of expressing the spin degrees of freedom in terms of Holstein-Primakoff bosons and expanding in decreasing powers of $s$. The lowest order term in the large $s$ expansion is of order $s^2$, and corresponds to the classical spin version of the quantum
where  as before $\alpha < 1$ a half polarization plateau exists.

**XXZ Hamiltonian**

$$\mathcal{H}_{cl} = J_z \sum_{(ij)} [\alpha (S_i \cdot S_j) + (1 - \alpha) (S_i \cdot \hat{z}) (S_j \cdot \hat{z})] - 2J_z \hbar \sum_j S_j^z,$$  

where as before $\alpha = J_\perp / J_z$.

In order to analyze the ground state of this anisotropic classical model (72), we first calculate the minimum energy configuration for a single tetrahedron. For the single tetrahedron we obtain the magnetization curve shown in Fig. 8. We find that for $\alpha < 1$ a half polarization plateau opens up, and the plateau becomes wider as $\alpha$ decreases from 1. In this plateau, the classical spins on the single tetrahedron being analyzed are in a collinear configuration, with three $S_j = s \hat{z}$ and one $S_j = -s \hat{z}$ spins. This is just the classical analog of the 3:1 configuration on a single tetrahedron found in Section II A 3:1 spin configuration can be realized on each and every tetrahedron of the lattice simultaneously. We therefore conclude that in the range of magnetic fields where the single tetrahedron is in a half polarized state, the ground state of the many body system is the manifold of 3:1 configurations. This means that the plateaus in the classical XXZ model on the complete pyrochlore lattice are at least as wide as in Fig. 8.

In the following we will discuss only this half magnetization plateau. We then assume the collinear 3:1 state, which allows us to describe the magnetic configuration in terms of the same Ising variables $\sigma_j = \pm 1$ as in Section II.

As in Ref. 26, we use the unitary transformation so that we can define the Holstein-Primakoff bosons, which amounts to replacing the rotated spin operators as follows

$$S_j^z = s - \hat{m}_j,$$
$$S_j^+ = \sqrt{2s - \hat{m}_j} \hat{b}_j \approx \sqrt{2s} b_j,$$

where $\hat{b}_j$ are canonical bosonic operators, and $\hat{m}_j = \hat{b}_j^{\dagger} \hat{b}_j$ is the boson number operator. We plug these into the Hamiltonian (11), and keep only the quadratic terms in the bosonic operators.

Since the spin configurations are now restricted to the 3:1 manifold, the magnetic field term is the same for every 3:1 configuration as the magnetization is constant on the plateau. In terms of the rotated spin variables $S_j^z$, this amounts to $\sum_j S_j^z = \frac{s}{2} N$ where $N$ is the number of sites in the pyrochlore lattice. Varying the magnetic field in the plateau region causes an overall shift in the spin wave energies of all the 3:1 states, and thus will not alter the energy differences between different 3:1 states. Similarly the Ising variables have a sum of $\sum_j \sigma_j = \frac{1}{2} N$, and we can use these two identities to derive $\sum_j \sigma_j \hat{m}_j = 0$, which is useful in simplifying other terms. Therefore, we can ignore the magnetic field term, since we are searching for an effective Hamiltonian splitting the energies of different 3:1 states. The effect of the magnetic field is to determine the energy gap for spin wave excitations. The vanishing of the spin wave gap signifies an instability of the 3:1 manifold, corresponding to the edges of the half polarization plateau.

From Eqs. (13), (23), the resulting harmonic spin wave term reads

$$\mathcal{H}_{harm}^{\pm} = J_z s \sum_{i,j} [\frac{1 + \sigma_i \sigma_j}{2} (\hat{b}_i^{\dagger} \hat{b}_i + h.c.) + \frac{1 - \sigma_i \sigma_j}{2} (\hat{b}_i^{\dagger} \hat{b}_i + h.c.)] + J_z s \sum \hat{m}_j.$$

Following the derivation Ref. 26, the zero point energy of this harmonic term for given 3:1 spin configuration (described by $\{\sigma_j\}_{N=1}$) is

$$E_{harm} = J_z s \sum_{k=1}^N \frac{\lambda_k}{2},$$

where $\lambda_k$ are the solutions of the eigenvalue equation

$$\left( \frac{A}{2} \right)^2 \mathbf{v} = \left[ 1 - \frac{A}{2} \left( \hat{\sigma} \hat{\Gamma} \hat{\sigma} + \hat{\Gamma} \right) + \frac{A^2}{4} \left( \hat{\sigma} \hat{\Gamma} \right)^2 \right] \cdot \mathbf{v}.$$

In the right hand side $\hat{\Gamma}$ denotes the same $N \times N$ connectivity matrix introduced in Section II and $\hat{\sigma}$ is a diagonal $N \times N$ matrix with $\sigma_j$ as its diagonal elements. Without specifying the 3:1 configuration, we can write an expression for the harmonic energy in terms of $\sigma_j$

$$E_{harm} = J_z s \text{Tr} \left[ \sqrt{1 + \frac{A}{2} \left( \hat{\sigma} \hat{\Gamma} \hat{\sigma} + \hat{\Gamma} \right) + \frac{A^2}{4} \left( \hat{\sigma} \hat{\Gamma} \right)^2} \right].$$

One can calculate the spin wave energies by assuming a particular spin configuration and computing the trace exactly. However, as in Ref. 26 if one does not know which candidate spin configurations to consider, one can derive an effective Hamiltonian to determine which spin
configuration gives the lowest harmonic energy, and find a favorable spin configuration.

The square root in (63) can be expanded in powers of matrix operators. We first observe that $\alpha$ only appears as a multiplier of the matrix $\Gamma$. Therefore, an expansion in powers of matrix operators is equivalent to expansion in the parameter $\alpha$. In the present context, this expansion is justified due to the easy axis anisotropy $\alpha < 1$.

The terms in the expansion can be organized as a sum of traces over products of $\Gamma$ matrices and Ising variables $\sigma_j$. The order of $\alpha$ for each term also specifies the number of connectivity matrices $\Gamma$ appearing in that term.

Due to the trace operation, the product of $\Gamma$ matrices represents closed loops on the lattice. The Ising variables appearing in each such term can only involve the sites on the loops defined by the product of $\Gamma$ matrices. Using the results of Section III B 2, which discuss functions of Ising variables appearing in each such term can only involve the sites on the loops. The Ising variables $\sigma$ and $\sigma_j$ are the Ising variables and $\Gamma$ matrices precisely of the form appearing in this expansion; it is evident that all terms involving less than six $\Gamma$ matrices will result in constants, which will not split energies of the 3:1 states. As in Section III, the lowest order term in the expansion in $\alpha$ causing energy splitting in the 3:1 manifold involves loops around hexagonal plaquettes of the pyrochlore lattice. For simplicity, we consider only these terms, and ignore any higher order term in the expansion in $\alpha$. After extensive simplification, the 6-th order term reads

$$H_{\text{harm}} = J s \left(\frac{\alpha}{2}\right)^6 \frac{1}{512} \left[ 14 \text{Tr} (\sigma \Gamma \sigma \Gamma) + 14 \text{Tr} (\sigma \Gamma^2 \sigma \Gamma^4) + 7 \text{Tr} (\sigma \Gamma^3 \sigma \Gamma^3) - 6 \text{Tr} (\sigma \Gamma \sigma \Gamma \sigma \Gamma \sigma \Gamma) - 3 \text{Tr} (\sigma \Gamma^2 \sigma \Gamma \sigma \Gamma^2 \sigma \Gamma) - 6 \text{Tr} (\sigma \Gamma^2 \sigma \Gamma^3 \sigma \Gamma^3) + \text{Tr}(\sigma \Gamma \sigma \Gamma \sigma \Gamma \sigma \Gamma \sigma \Gamma) \right] + O(\alpha^8).$$

(78)

From the expression one extracts only those terms corresponding to loops around hexagonal plaquettes. Eq. (78) takes the form of the function in Eq. (39), with $n = 6$ and the “loop” diagram $G_n = \{ (12), (23), (34), (45), (56), (61) \}$. The corresponding function $f(\sigma_a, \ldots, \sigma_a)$ reads

$$f(\sigma_1, \ldots, \sigma_a) = 14 \sigma_1 \sigma_2 + 14 \sigma_3 \sigma_4 + 7 \sigma_1 \sigma_4$$

$$- 6 \sigma_1 \sigma_2 \sigma_3 \sigma_4 - 3 \sigma_1 \sigma_3 \sigma_4 \sigma_6 - 6 \sigma_1 \sigma_3 \sigma_5 \sigma_6 + \sigma_1 \sigma_2 \sigma_3 \sigma_4 \sigma_5 \sigma_6.$$

(79)

The effective Hamiltonian therefore describes all possible spin interactions on the hexagonal plaquette of the pyrochlore lattice – 2, 4, and 6 spin interactions. It is far more convenient to express this complicated Hamiltonian in terms of energies of plaquette configurations, in the same way we formulated the results of the DPT in Section III as $H_{\text{harm}} = \sum_{p} E_p$ (using the same 5 plaquettes in Table III).

As in Section III C there are only 3 independent plaquette configuration energies, $V_1, V_2, V_4$ which to $O(\alpha^8)$ are

$$V_1 = 0,$$

$$V_2 = \frac{J_2 \alpha^6 s}{512},$$

$$V_4 = 0.$$

Comparing (80) with (64), we find complete agreement between the DPT of Section III and the large $s$ expansion of this section, in the limit of both $\alpha \to 0$ and $s \to \infty$, where both approaches are justified (see Fig. 9). This serves an excellent check on the correctness as well as validity of our calculations, in the parameter regime where the approximations overlap.

V. LOW ENERGY STATES OF THE EFFECTIVE HAMILTONIAN

A. Strict easy axis limit for $s \geq 3/2$

In this subsection, we consider the $\alpha = J_1 / J_2 \ll 1$ limit, for which the lowest-order non-vanishing terms in the effective Hamiltonian are dominant. For any $s \geq 3/2$, this is just the sixth order diagonal contribution.

1. Large-$s$ case

We first consider the large $s$ limit. As is clear from Eq. (77), at order $s$ only the type 2 plaquette suffers from a positive energy correction, while $V_1$ and $V_4$ are only nonzero at order $s^0$ or lower. Hence the type 2 plaquette is strongly disfavored for large $s$. This in combination with the 3:1 constraint allows us to restrict ourselves to the “0-flux manifold” in the large $s$ region (See Section IV for the definition of a 0-flux manifold.)

To see this, let us first introduce a “cell” comprised by 4 link-sharing plaquettes. Choose 4 hexagonal plaquettes

![Figure 9: This figure shows the regions of parameter space where the DPT and large S expansions are justified, and their region of overlapping validity.](image-url)
such that any pair of two plaquettes out of these 4 plaquettes always share a link. Then these four plaquettes form a single polyhedron (a truncated tetrahedron), with 4 hexagonal faces, and 4 triangular faces (see Fig. 10). We will refer to this polyhedron as a cell. In the pyrochlore lattice, one may distinguish two kinds of cells – when one completes the tetrahedra enclosing a cell, we can identify up-headed and down-headed cells, according to the direction at which the tetrahedra are pointing (see Fig. 10 for examples of both kinds). Each up/down-headed cell shares its faces (hexagonal plaquettes) with 4 nearest neighboring down/up-headed cells. Thus, centers of cells constitute a diamond lattice, where those of up-headed cells take part of one FCC lattice and those of down-headed cells form the other FCC lattice. It suffices to determine the spin configuration on only the up-headed (down-headed) cells in order to specify the spin configuration on all sites of the lattice.

Observing the local constraint, one can readily enumerate the various minority spin configurations of a cell. In Table. III all possible cell configurations allowed in the 3:1 manifold are listed. Each cell type is described by the configurations of its 4 hexagonal plaquettes.

To see that the ground state manifold in the large-$s$ region is composed only of type 0, 3 and 4 plaquettes (i.e. 0-flux states), notice from Table. III that any cell type which contains a type 1 plaquette always contains at least one type 2 hexagonal plaquette. This implies

$$0 \leq x_1 \leq x_2 \quad (81)$$

where $x_a$ are the plaquette type fractions, as introduced in Section III-C. Disallowing the type 2 plaquette inevitably leads to excluding the type 1 plaquette, and therefore, the positive $V_2$ in leading order of $s^{-1}$ expansion allows us to conclude that the classical ground state spin configurations in the large-$s$ limit consist of only the 0-flux states.

This ground state, however, is massively degenerate. Higher order quantum corrections in $s^{-1}$ can select a particular classical state out of this 0-flux manifold. To see this, let us expand the plaquette energies in $s^{-1}$

$$V_1 = -\frac{3}{512} + O(s^{-1}),$$

$$V_2 = \frac{s}{512} + \frac{3}{1024} + O(s^{-1}), \quad (82)$$

$$V_4 = \frac{17}{65536s} + O(s^{-2}).$$

Notice first that the $O(1)$ negative energy correction to $V_1$ plays no role in lifting the degeneracy of the 0-flux manifold, since this manifold does not contain any type 1 hexagonal plaquettes. Thus, provided that $V_2$ dominates the other two, the most relevant correction in the large $s$ limit is $V_4$, which always disfavors the type 4 hexagonal plaquette, since it is positive.

Since the type 4 plaquette is disfavored, observing the 0-flux condition on all plaquettes, we have only to minimize $x_4$ to obtain the ground state in the large $s$ region.

However, in the 3:1 manifold, the 0-flux condition becomes so strong that $x_4$ is in fact bounded by $\frac{3}{28}$ from below ($x_4 \geq \frac{3}{28}$). To see this, notice first that only the type 9, 10, 11 and 12 cells are allowed in the 0-flux manifold. Next, we denote by $y_{9,10,11,12}$ the fraction of cell types 9...12 in the entire pyrochlore lattice (we use these instead of plaquette type fractions $(x_3, x_4, x_0)$ for later convenience). In the 0-flux manifold, only these cell types may occur, and therefore $\sum_{j=9}^{12} y_j = 1$. Together with the “global” 3:1 constraint, i.e. Eq. (31) one finds

$$3y_{12} = y_0, \quad (83)$$

or alternatively,

$$y_{12} = \frac{1}{4}(1 - y_{10} - y_{11}), \quad (84)$$

An important step to identify the lower bound on $x_4$ is to note that packing these four cell types into a pyrochlore lattice is highly constrained by the local 3:1 rule.
imposed on each tetrahedron. For example, a type 12 cell can only have cell types 10, 11 and 12 as neighboring cells. Each type 10 and 11 cell can neighbor at most one type 12 cell, as they both have only one type 0 plaquette, and the type 12 cell consists only of type 0 plaquettes.

One can also show that a type 12 cell can have at most one neighboring type 12 cell. the remaining neighboring cells must be of type 10 or 11. These observations are already sufficient to conclude that

\[ 3y_{12} \leq y_{10} + y_{11}. \]  

Now using Eq. (84), we obtain the lower bound on the fraction of type 10 and type 11 cells: \( y_{10} + y_{11} \geq \frac{y}{7} \).

Since these two types of cell are the only cells allowed in the 0-flux manifold which have type 4 hexagonal plaquettes, this lower bound immediately gives us that for the fraction of type 4 hexagonal plaquette:

\[ x_4 = \frac{1}{4} y_{10} + \frac{3}{4} y_{11} \geq \frac{1}{4} y_{10} + \frac{1}{4} y_{11} \geq \frac{3}{28}. \]  

From the derivation above, one can easily see that the equal sign is realized if and only if \( y_{11} = 0 \). Excluding type 11 cell configurations, one can show that a type 12 cell always neighbors three type 10 cells, and one type 12 cell. As a consequence, the condition \( 3y_{12} = y_{10} \) is satisfied only when any type 10 cell has a type 12 cell as its nearest neighboring cell, through its single type 0 plaquette. Since the fraction of type 9 cells is uniquely determined by the fraction of type 12 cells, and we have already excluded any type 11 cells from a state saturating the bound on \( x_4 \), if a state saturating this bound exists, since it minimizes the fraction \( x_4 \) it must be configuration with a maximum number of type 12 cells on the lattice. Without any type 12 cells, we cannot have any type 9 cells either, and are limited to type 10 and 11 cells. A state comprised only of type 10 and type 11 cell, has fraction of type 4 plaquettes that is always greater than \( \frac{1}{7} \).

In what follows, we will show that this lower bound for \( x_4 \) is uniquely (up to a finite degeneracy) realized by the periodic minority spin configuration depicted in Fig. 12

This collinear magnetic ordered state, which we shall refer to as the “trigonal” state, contains 7 pyrochlore unit cells. It has a magnetic unit cell with primitive vectors \( E_1 = 2a_1 - a_3 \), \( E_2 = 2a_2 - a_1 \), and \( E_3 = 2a_3 - a_2 \), where \( a_{1,2,3} \) are the primitive unit vectors of the pyrochlore lattice (FCC lattice vectors \( a_1 = \frac{1}{2}(0,1,1) \) and cyclic permutations). From the unit cell vectors, we can find the volume of the magnetic unit cell

\[ (E_1 \times E_2) \cdot E_3 = 7(a_1 \times a_2) \cdot a_3 \]  

These 3 primitive vectors are of equal length, and are not mutually perpendicular. Therefore, the magnetic Bravais lattice is in the trigonal crystal system – whence the name trigonal state.

From the planar view in Fig. 12 it is clear that this magnetic state has a three-fold rotation symmetry about the \( a_1 + a_2 + a_3 = a(1,1,1) \) axis perpendicular to the page. In the direction of the pyrochlore lattice directions, there is a periodicity of 7, giving rise to a seven fold degeneracy due to FCC lattice translations alone. The trigonal state
breaks a reflection symmetry about a plane perpendicular to the Kagome plane, parallel to $a_2$ and passing through the point where the three vectors $E_{1,2,3}$ originate in the figure (see Fig. 13 for another view of this symmetry operation). Together with the 4-fold choice of the set of Kagome planes, it is evident that the degeneracy of this magnetic state is $4 \times 7 = 28$.

As is clear from Fig. 12, the spin configuration satisfies both the local zero flux condition and the local 3:1 constraint. To see that this trigonal state saturates the lower bound for $x_4$, one has only to count the fraction of type 9, 10, 11 and 12 cells: $y_9 : y_{10} : y_{11} : y_{12} = 3 : 3 : 0 : 1$. From Table V we find the trigonal state realizes the lower bound $x_4 = \frac{3}{28}$. We conclude the trigonal state is at least one of the ground states in large-$s$ region.

As argued above, any state saturating the bound must have every type 0 plaquette connecting between a type 12 cell and a type 10 cell. Starting with a type 12 cell, and using this rule together with the 3:1 constraint and the zero flux condition, successively construct the trigonal state, up to the finite degeneracy described in above. Starting from the initial type 12 cell, the plaquette connecting this cell to another type 12 cell defines the Kagome plane in Fig. 12. Next, pick one of the two mirror image choices in Fig. 13 of the type 10 cell configurations neighboring the first type 12 cell. From this point on, the three rules mentioned above uniquely determine the rest of the magnetic configuration in the entire lattice.

Finally, the energy per plaquette of the trigonal state is

$$\frac{1}{N} E_{\text{trigonal}} = \frac{3}{28} V_4.$$  \hspace{1cm} (88)

2. Spin $s \geq 2$

We expect that the trigonal state described above is the ground state for sufficiently large $s$. In the following, we shall argue that this is indeed the case for $s \geq 2$. For $s = 5/2, 2, 3/2, 1$, the energy parameters in the effective Hamiltonian are given in Table V.

For all the cases in Table V, $V_1$ is the largest and most negative energy. This would suggest that the lowest energy 3:1 state is one with a maximum number of plaquettes of type 1. However, the geometry of the lattice as well as the 3:1 constraint pose stringent restrictions. By enumerating all possible types of cells in Table III one finds that every type 1 plaquette must be accompanied by at least one type 2 plaquette on the same cell. The configuration of the entire lattice can be determined by considering only up-headed cells, and therefore, the existence of $M$ type 1 plaquettes demands that at least $M$ type 2 plaquettes are present as well. We deduce the following inequality $x_1 \leq x_2$, in any 3:1 configuration. From this we see that the energy of a type 1 plaquette is offset by the energy cost of a type 2 plaquette which is the highest energy cost for all the $s$ values in Table V. Therefore, the number of type 1 plaquettes is not necessarily maximized in the ground state even with small $s$.

One observes that the magnitude of the energy $V_1$ is comparable to $V_2$ already at $s = 5/2$, and this trend continues to higher $s$ - $V_2$ becomes more dominant. Given the restriction $x_1 \leq x_2$, and the large energy cost of type 2 plaquettes, the analytic arguments in the above subsection suggest the trigonal state may be the lowest energy state for $s \geq 5/2$. The case $s = 2$ is close to the boundary for a change in behavior.

In order to search for other candidate ground states, we have enumerated all 3:1 states on a variety of periodic finite clusters, and determined the exact lowest energy state for each one, for $s = 1, 3/2, 2, 5/2, \ldots, 6$. For $s \geq 2$ we find no states with lower energy than that of the trigonal state. This strongly suggests that the trigonal state is the ground state for all $s \geq 2$, though of course this limited numerical investigation does not constitute a proof that this is the case. Moreover, states with large numbers of type 1 plaquettes, are among the highest energy states we have found, which does give credence to our assessment that when the $V_2$ and $V_4$ are comparable energy scales (with opposite sign), because of the condition $x_1 \leq x_2$, the energy $V_2$ is still dominant. One can conclude that if there is a state with lower energy for $s \geq 2$, it must have a large unit cell which is incompatible with all the clusters considered in Table V.

3. Spin $s = 3/2$

Spin $s = 3/2$ is the smallest spin value for which in the extreme easy-axis limit $\alpha \ll 1$ the off-diagonal term in the effective Hamiltonian may be ignored. The cor-
responding plaquette energies are given in column 4 of Table IV. The energy for type 1 plaquettes is approximately 50% larger (more negative) than for \( s = 2 \). In the extreme limit of very large and negative \( V_0 \), the ground state has been determined previously in Ref.9. The state, referred to as the \( R \) state in Ref.9, as well as in the remainder of this manuscript, maximizes the fraction of type 1 plaquettes, and is unique (up to lattice symmetries).

The numerical investigation mentioned in the previous subsection, shows that the \( R \) state is not the lowest energy state for the diagonal effective Hamiltonian at \( s = 3/2 \). Instead, we find a massively degenerate set of classical ground states. One example of these states has all the minority sites contained in a set of parallel Kagome layers of the pyrochlore lattice. Every Kagome plane will be have the same spin configuration shown in Fig. 14. This example, and many other states in this degenerate manifold all have a \( \sqrt{3} \times \sqrt{3} \) structure in the Kagome planes, and therefore we shall refer to a large subset of this manifold of states as the \( \sqrt{3} \times \sqrt{3} \) states.

The analysis of this degenerate manifold of states is somewhat involved. We therefore leave the details to Appendix C and only mention a number of facts here. All the states we have found numerically have plaquette type fractions of \( x_0 = \frac{1}{6}, x_1 = \frac{1}{3}, x_2 = \frac{2}{3}, x_3 = \frac{1}{3}, \) and \( x_4 = \frac{1}{6} \). As a consequence, the energy per plaquette of these states is

\[
\frac{1}{N} E_{\sqrt{3} \times \sqrt{3}} = \frac{1}{6} (V_1 + 2V_2 + V_4). \tag{89}
\]

| Energy | \( s = \frac{1}{2} \) | \( s = 2 \) | \( s = 3 \) | \( s = 1 \) |
|--------|----------------|----------------|----------------|----------------|
| \( V_1 \) | -0.0113 | -0.0135 | -0.0188 | -0.0410 |
| \( V_2 \) | 0.0009 | 0.0084 | 0.0083 | 0.0099 |
| \( V_3 \) | 0.0002 | 0.0003 | 0.0005 | 0.0015 |

TABLE IV: Energies \( V_{1,2,3} \) of the plaquette configurations type 1, 2, 3, 4 for \( s = 2, \frac{1}{2}, 3, 1 \)

In appendix C we show by explicit construction that the degeneracy is at least

\[
18 \times 2^{\frac{N}{3}} + 4 \times 3^L - 36, \tag{90}
\]

which grows exponentially with system size. We have not shown that the above states exhaust the possibilities with energy given by Eq. (89), so the above formula is only a lower bound for the degeneracy.

### B. Effect of off-diagonal term

In this subsection we add to the effective Hamiltonian the off-diagonal term where it is likely to be important (low values of \( s \)). For \( s = 1/2 \), the off-diagonal term is parametrically larger than the diagonal terms in the \( \alpha < 1 \) limit. For \( s = 1 \), it is of the same order as the diagonal terms. However, our explicit calculations demonstrate that even in this case, the off-diagonal term is numerically more than four times larger than the largest diagonal plaquette energy.

For \( s = 3/2 \), the off-diagonal term is negligible in the \( \alpha < 1 \) limit, but extrapolating the DPT results to the isotropic case \( \alpha = 1 \) indicates that while it is not larger than the diagonal terms, it is likely not negligible either.

To gauge the importance of the off-diagonal plaquette term, it is instructive to compare the diagonal energy of the various candidate ground states studied above. Their energies per plaquette are shown for small values of \( s \) in Table V. We see that the energy differences amongst these competing states are rather small on the scale of the off-diagonal amplitude \( K \). For instance, for \( s = 3/2 \), the energy difference between the “worst” of these three states (the \( R \) state) and the “best” (the \( \sqrt{3} \times \sqrt{3} \) state) is only 0.0018 per plaquette, approximately four times smaller than the diagonal coupling \( K = 0.008 \). Thus we
can expect that adding the $K$ term can introduce sufficient quantum fluctuations to alter the balance between these states, either destabilizing one in favor of the other, or perhaps stabilizing a superposition of these orders in some form.

We cannot hope to establish the result of such subtle energetics here, particularly given the non-trivial nature of the effective QDM Hamiltonian including the off-diagonal term. However, we will discuss several natural candidate ground states from the perspective of order-by-disorder and the general theoretical framework of QDM-type models.

1. Purely off-diagonal QDM — $s = 1/2$ case —

Let us consider first the simple case of $s = 1/2$, for which the Hamiltonian is well-approximated by including the off-diagonal only. Clearly low-energy ground states of this Hamiltonian must have significant amplitude for type 1 plaquettes, as other plaquettes are annihilated by the off-diagonal term. We note that the trigonal state has no type 1 plaquettes. This implies that it is an exact zero energy eigenstate of the purely kinetic Hamiltonian. Since it is straightforward to construct states with significantly negative energy per plaquette, the classical trigonal state is clearly an excited state in this case. It seems difficult to imagine any way that the ground state could be adiabatically connected to the trigonal state (or any other zero energy state with no type 1 plaquettes).

Let us instead consider what sorts of states might naturally minimize the energy of the kinetic term. This sort of pure QDM problem has been considered in numerous places in the literature. Specifically for the QDM on the diamond lattice, the question has been discussed in Ref. 2 (see references therein for a guide to QDMs). Roughly speaking, the energy is minimized by delocalizing the wavefunction as much as possible amongst different dimer configurations. However, the non-trivial connectivity in the constrained space of dimer coverings makes the nature of this delocalization subtle.

One possibility in such a 3d QDM is that the ground state is a $U(1)$ spin liquid, in which the delocalization is sufficiently complete as to prevent any symmetry breaking (the meaning of the $U(1)$ is discussed in-depth in e.g. Ref. 2). Roughly speaking, the wavefunction has support for all possible dimer coverings, with equal amplitude for all topologically equivalent configurations. The existence and stability of such a state can be established in a QDM with a particular form of diagonal interaction, in the neighborhood of the so-called “Rokhsar-Kivelson” (RK) point. While this point (corresponding to $V_1 = K > 0$, $V_2 = V_4 = 0$) is not physically relevant to the pyrochlore antiferromagnets, it is possible that such a $U(1)$ spin liquid state remains the ground state for the purely off-diagonal QDM.

A second possibility is that the delocalization is incomplete, due to “order-by-disorder” physics. In particular, it may be favorable to delocalize only over a limited set of classical states, amongst which the connections are greater than those amongst generic classical configurations. In this case there is generally some symmetry-breaking induced by the selection of the states involved. Two sorts of such ordering have been proposed and observed in other similar QDM models. The first type of order-by-disorder state is one in which the set of classical states for which the ground state wavefunction has the largest amplitude are “centered” about a single classical state having the maximal number of type 1 plaquettes. Such a wavefunction may be “selected” by the kinetic energy, since under the action of the kinetic term of the QDM, this is the classical state is connected to the largest number of other classical states. In our problem, this classical state is just the $R$ state mentioned above and discussed at length in Refs. 9, 10. A simple form for such a wavefunction is

$$|R, \{\gamma_P\} \rangle = \exp \left[ \sum_P \gamma_P \left( \hat{S}^+ \hat{S}^- + h.c. \right) \right] |R\rangle,$$

where $|R\rangle$ is the classical $R$ state (with definite $S_i^z = S_0$), and $\gamma_P$ are variational parameters which can be used to optimize the quantum state $|R, \{\gamma_P\}\rangle$.

The second type of order-by-disorder state is one in which there are a maximal number of independently resonating plaquettes. This is based on the observation that the exact ground state for the kinetic term on a single plaquette is simply an equal amplitude superposition of the two type 1 states. However, neighboring plaquettes share sites, and therefore it is not possible to form a direct product of such resonances on all plaquettes. Instead, the best one can naively do along these lines is to find the classical state with the largest number of type 1 plaquettes which can be independently flipped, and on these type 1 plaquettes form an equal amplitude superposition of these two states. A state with the maximal number of independently flippable plaquettes can be described, starting from the $\sqrt{3} \times \sqrt{3}$ states introduced in Sec. V.A:

| Spin | R state | Trigonal $7\times 3$ state | $\sqrt{3} \times \sqrt{3}$ state |
|------|---------|--------------------------|-------------------------------|
| $s = 1$ | $-2.8 \times 10^{-3}$ | $1.7 \times 10^{-4}$ | $-3.3 \times 10^{-3}$ |
| $s = \frac{1}{2}$ | $1.5 \times 10^{-3}$ | $5.7 \times 10^{-5}$ | $-2.9 \times 10^{-4}$ |
| $s = 2$ | $2.9 \times 10^{-3}$ | $3.1 \times 10^{-5}$ | $6.0 \times 10^{-4}$ |
| $s = \infty$ | $1.5 \times 10^{-3} s$ | $0.0$ | $6.5 \times 10^{-4} s$ |

TABLE VI: Diagonal energy per plaquette in various classical ground states. Energies are given in units of $J_s$.\(^b\)
resonating. The degeneracy of these states therefore is $2^L \times 3^L \times 4 = 6^L \times 4$. Other states realizing this maximum number of independently resonating plaquettes may be possible, but we have not pursued this further. We refer to these states as “Resonating Plaquette States” (RPS). A precise wavefunction describing the RPSs we have derived from the $\sqrt{3} \times \sqrt{3}$ states is

$$|RPS\rangle = \prod_{p \in G} \frac{1}{\sqrt{2}} \left(1 + (|A\rangle\langle B| + h.c.)\right)|\Psi\rangle,$$  \hspace{1cm} (92)

where $G$ denotes the set of non-overlapping resonating plaquettes, and $|\Psi\rangle$ denotes one of the $\sqrt{3} \times \sqrt{3}$ states. There are $4 \times 3^L$ choices for $|\Psi\rangle$, and $2^L$ choices for $G$ given $|\Psi\rangle$. We note that the symmetry of the RPS is distinct and lower than that of the $\sqrt{3} \times \sqrt{3}$ state – even in a single layer. Thus there is a precise distinction between these two states independent of the detailed form of their wavefunctions, for which the above explicit forms are of course only crude approximations.

While potentially there might be some other state we have not anticipated, we think that most likely one of the three above states obtains in the purely kinetic QDM valid for $s = 1/2$. We will, however, refrain from making any definite statement as to which of these is the true ground state. One may imagine comparing the energies of the wavefunctions in Eqs. (91,92) to gauge the relative favorability of the $R$ and RPS states. Unfortunately, even evaluating the variational energy of the $|R\rangle$ state in Eq. (91) is rather challenging. Another difficulty is the considerable freedom in choosing the RPS wavefunctions. Furthermore, a good variational wavefunction for the spin liquid is also needed for a more complete comparison. As always, there is much arbitrariness in defining each variational wavefunction, making the predictive power of such an approach unclear. We believe this issue is more likely to reliably resolved in the future thorough numerically exact methods such as quantum Monte Carlo or exact diagonalization.

2. $s > 1/2$ QDMs

For $s = 1$ and $s = 3/2$, significant diagonal terms enter the QDM Hamiltonian. These act to alter the balance between the three candidate states discussed above, and also potentially to introduce the possibility of other states disfavored in the purely kinetic Hamiltonian. For both $s = 1$ and $s = 3/2$, the ground state of the classical diagonal term alone is actually a massively degenerate set of states discussed briefly in Section $\sqrt{A \times 3}$ and in more detail in Appendix. From all the $\sqrt{3} \times \sqrt{3}$ states, we can construct RPSs. For $s = 3/2$, as we have shown, however, the $R$ state is also quite low in diagonal energy and indeed only slightly worse than the $\sqrt{3} \times \sqrt{3}$ states, as far as the diagonal term is concerned. Thus we expect that introducing the diagonal terms tends to favor both the RPS and the “renormalized” $R$ state over the $U(1)$ spin liquid. If their effects are strong enough, they could also stabilize the “non-resonating” $\sqrt{3} \times \sqrt{3}$ states (or any one of the other states with the same energy). We speculate that a spin liquid is unlikely to be realized in these cases, but that the RPS, $R$, and $\sqrt{3} \times \sqrt{3}$ states (or more precisely all the states degenerate with the $\sqrt{3} \times \sqrt{3}$ states) remain very reasonable candidate ground states for these values of $s$ in the isotropic limit.

VI. DISCUSSION

Since the development of the DPT and its analysis in this paper is rather involved, we begin in the first subsection by recapitulating the central points. In the second subsection we will then turn to a brief discussion of the implications on experiments and future directions of this work.

A. Summary

As a prototypical model of a magnetization plateau in a strongly frustrated quantum antiferromagnet, we considered in this paper a nearest-neighbor spin-$s$ model on the pyrochlore lattice at half the saturation magnetization. Such plateaus have been observed in the spinel materials $\text{HgCr}_2\text{O}_4$, and $\text{CdCr}_2\text{O}_4$. We argued that a useful starting model is the easy-axis XXZ Heisenberg model in an external field, Eq. (4). This model possesses all same symmetries as the isotropic Heisenberg model in an external field, and indeed we were able to extrapolate our results to this limit. This model has the advantage that the transverse spin fluctuations can be treated systematically as a perturbation to the underlying Ising model. The resulting Ising model can be written as a sum over the elementary tetrahedra of the pyrochlore lattice. In this Ising limit on the plateau, the spins on each
tetrahedron satisfy a 3:1 constraint, comprising a set of 3 majority spins fully polarized parallel to the field, and 1 minority spin antiparallel to the field. The half-polarized state has a macroscopic degeneracy corresponding to the number of possible positions for all the down pointing spins in the lattice. It is expected that the transverse spin fluctuations will play a role in selecting a ground state or set of ground states from the massively degenerate 3:1 manifold. In this way, we are lead to a theoretical model involving a “constrained” degenerate perturbation theory in the 3:1 manifold. Our paper is devoted to a detailed analysis of such a theory and many parts are couched in sufficiently general language to be applicable to a broad class of systems.

We began our discussion of the constrained easy-axis degenerate perturbation theory by deriving the general structure of the effective Hamiltonian that occurs at each order of dimensionless coupling \( \alpha = J_z/J_x \), Eq. (14). We found that the effective Hamiltonian could be cast into a convenient form by performing a unitary transformation that rotates all down pointing (minority) spins to up pointing spins and also by introducing a connectivity matrix (whose elements are one for nearest neighbor spins and zero otherwise). The latter makes it possible to convert the sums over nearest-neighbor lattice sites to sums over the entire lattice \( \sum_{\alpha} \). These transformations cast the terms of the effective Hamiltonian coming from each order of perturbation theory into a form rather convenient for analysis. The resulting terms are expressed explicitly in terms of the Ising variables on the lattice sites, the spin \( s \), and the connectivity matrix. These terms were studied order-by-order in perturbation theory. We found that diagrams representing these terms naturally fell into two categories: contractible and non-contractible. Contractible diagrams are those whose dependence on some of the Ising variables is eliminated by summing with respect to their site index over all lattice points. Thus, a function of \( N \) Ising variables can be reduced to a function of less than \( N \) Ising variables after this “contraction” process. The allowed contractions depend on the lattice geometry, the 3:1 constraint, and the Ising nature of the spin variables. Diagrams for which it is not possible to perform a contraction (equivalently, a reduction in the number of relevant Ising variables) we termed non-contractible.

The central result of the analysis of contractible and non-contractible diagrams is that all terms in the constrained degenerate perturbation theory up to and including 5th order are constant within the 3:1 manifold. Individual terms are shown to be constant by first contracting the diagrams as much as possible and then noting that the value of the diagram is unchanged under permutation among site indices associated with the Ising variables. The latter statement implies that the value of the diagram is independent of spin configurations allowed in the 3:1 manifold and hence a constant. In a similar manner, most terms at 6th order are also shown to be constant. However, we also observe that, at 6th order, there appears a “single large loop” diagram which cannot be contracted, and also defies the permutation arguments mentioned above. In fact, this loop diagram brings about non-constant contributions to the effective Hamiltonian in the 3:1 manifold. Therefore, this is the lowest order term which lifts the degeneracy of the 3:1 manifold (at least for \( s > 1 \)). The non-constant 6th order term includes effective interactions among spins on each hexagonal plaquette of the pyrochlore lattice. Depending on the arrangement of minority sites, there are five distinct kinds of plaquettes that may appear and we label them 0,1,4 (See Table 1). Using the results of our degenerate perturbation theory, we evaluate the energy of each of these plaquettes as a function of \( \alpha \) and \( s \), and correct a mistake in Ref. \( 1 \). The 3:1 condition constrains the allowed ratios of the various plaquettes in the lattice and allows us to express the total energy of the system (up to an overall constant), Eq. (60), in terms of only 3 energies \( \varepsilon_0 \).

As a check on the results immediately above and as a further test of the robustness of those results, we also performed a large-\( s \) expansion in the easy-axis limit. As with the fully quantum theory, we expanded the harmonic spin wave energy in powers of \( \alpha \) up to the 6th order, applied the diagrammatic analysis above involving contractible and non-contractible diagrams, and studied the resulting energy of the non-constant 6th order terms. The result \( \varepsilon_0 \) agrees exactly with the \( O(\alpha) \) term obtained from the quantum degenerate perturbation theory, \( \varepsilon_0 \). This satisfying consistency tells us that the large-\( s \) limit and small-\( \alpha \) limit commute, and thus our analysis is likely well controlled.

In the final section of the paper we used the results of the degenerate perturbation theory to determine the low energy states on the plateau as a function of \( s \). Our result that the first non-constant diagonal term in perturbation theory comes at 6th order is independent of the spin value \( s \). However, terms that allow plaquettes (such as type 1) to resonate occur at order 6\( s \), which can be either larger or smaller than 6 depending on \( s \). In the strict easy-axis limit, therefore, for \( s \geq 3/2 \), the low energy states are therefore determined only by a diagonal effective Hamiltonian, which can be analyzed classically. In the large but finite \( s \) limit, we are able to resolve the degeneracy of the “zero flux” manifold found in the large-\( s \) analysis (extended from that of Hizi and Henley to the XXZ model). We predict a “trigonal state” (see Fig. 12) to be the exact ground state in this easy-axis limit and for large \( s \), and numerical analysis suggests this obtains for \( s \geq 2 \). For \( s = 3/2 \), the lowest energy configuration we have found in the Ising limit is a massively degenerate set of states (for example the \( \sqrt{3} \times \sqrt{3} \) states, see Fig. 14). For \( s \leq 1 \), and for \( s = 3/2 \) extrapolated to the isotropic limit, we find that the off-diagonal term in the effective Hamiltonian becomes significant, and we suggest several likely candidates for the ground states in these cases. This includes a possible \( U(1) \) spin liquid state, which would be quite remarkable if realized.
B. Implications and future directions

First let us comment briefly upon the relevance to the spinel chromites. For HgCr$_2$O$_4$, it is known that
the temperature at which the plateau forms ($\approx 7^\circ$K) is comparable to the highest temperature at which magnetic
order is observed. The theoretical estimate of the magnitude of the couplings in the effective Hamiltonian
due to quantum fluctuations for $s = 3/2$ is however small, e.g. $V_1 \approx 0.02 J$ from Eq. (20). Thus the
temperature at which quantum fluctuations are expected to induce magnetic ordering would be very low. A crude
estimate based on the measured Curie-Weiss temperature in HgCr$_2$O$_4\approx$ would predict an ordering temperature
$\approx 0.2 K$. This strong quantitative disagreement with experiment indicates that a stronger classical mechanism
– i.e. physics outside the Heisenberg model – must be behind the plateau formation. Indeed, a recent study of
a simple model of spin-lattice coupling gives a reasonable explanation of the plateau and its order, predicting sta-
bilization of the $R$ state. It would be quite interesting to see whether quantum fluctuations might however play
a role in the other chromite spinels, e.g. CdCr$_2$O$_4$.

We now move away from the experiments on HgCr$_2$O$_4$, where the pure nearest-neighbor Heisenberg antiferro-
magnet neglecting spin-lattice interactions is clearly inadequate. Instead, we would like to address a basic question
that may be in the mind of the reader. In the pure spin-$s$ isotropic Heisenberg model (i.e. $J_\perp = J_\parallel = J$),
is there a plateau at half-magnetization? At $s = \infty$, i.e. the strict classical limit, the answer is no, and indeed the
magnetization is a simple linear function of field in this case. In principle this question can be addressed by the
$1/s$ expansion. However, to the order studied, the situation remains unclear: the leading-order spin-wave spec-
trum remains gapless even in a field. Higher-order calculations in $1/s$ are required to resolve this question via
that approach. Within the XXZ model, for any amount of anisotropy ($\alpha < 1$), a plateau is expected even in the
classical limit, so by continuity it is likely to persist at smaller $s$. However, the extrapolation to $\alpha = 1$ is not clear.
In Appendix A we present some simple calculations aimed at addressing the plateau width. In particular,
we show that the plateau narrows both from above and below upon perturbing away from the Ising limit,
where it is maximal. The plateau edges are determined by the points at which the gap to excitations with non-
zero $S^z$ vanishes. Unfortunately, unlike the calculation of the splitting within the plateau states (the main focus
of this paper), the energy difference between the plateau ground state and excited states with higher/lower $S^z$
is non-vanishing already at quadratic-linear order in $\alpha$. Hence, a high-order calculation of this gap becomes much
more involved than those in the bulk of this paper, and an extrapolation to the isotropic limit is probably not reliable.
The existence of a plateau in the isotropic limit is a subject worthy of study by other methods.

Next we turn to future applications of the formalism developed here to other problems. From our exposition,
it should be evident that our methods generalize rather straightforwardly to other models of quantum antiferro-
magnets with Ising anisotropy, provided a few conditions hold. First, the lattices should be composed of site-
sharing simplexes. A simplex is a collection of sites in which every pair of sites is connected by a bond; examples
include triangle, crossed square, and tetrahedron. Second, the ground states of the Ising part of the Hamil-
tonian on a single simplex should all be permutations of one another. This allows Ising exchange, single-site anisotropies, biquadratic and other interactions. Third, the interactions should be the same on each bond, but
could include quite arbitrary combinations of exchange, biquadratic couplings etc. There are quite a number of
interesting models of frustrated magnetism which share these features. For instance, the XXZ models on the
Kagome and checkerboard lattices can be studied this way at several values of the magnetization. The XXZ model
on the pyrochlore lattice at zero field is also such a system. It will be interesting to explore the behavior of
these models at various values of $s$ using the methods of this paper.

More generally, the methods of this paper are possible because of a key simplification: in a strong magnetic field,
the symmetry of the spin Hamiltonian is $U(1)$ rather than $SU(2)$. Many more theoretical methods are available to
treat systems with abelian conserved charges than for $SU(2)$-invariant spin models. Furthermore, in the interest-
ing search for spin-liquid states of quantum antiferromagnets, much theoretical success has been achieved in
recent years in realizing such states in $U(1)$-symmetric models, while examples of $SU(2)$-invariant spin liquids,
even in models, are much more limited. Therefore it seems likely that quantized magnetization plateaus may
be an excellent hunting ground for such exotic states of matter, and moreover there is hope for theory and exper-
iment to meet on this plain.

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APPENDIX A: EDGES OF THE MAGNETIZATION PLATEAU

In this appendix we analyze the gap to spin excitations above the 3:1 plateau. To lowest order in the trans-
vise spin fluctuations, in the field range corresponding to the plateau in the Ising model, excitations carrying
$\Delta S^z = \pm 1$ are are separated by an energy gap of order $J_z$ from the manifold of half-polarized states. As
the magnetic field is varied this gap decreases. At zero temperature, the magnetization plateau ends when the
energy gap to one of these spinful excitations vanishes.
We shall consider the spin $\Delta S = \pm 1$ “single particle”
excitations above the 3:1 manifold only, and find a rough
perturbative estimate for the limits of the half magnetization
plateau region. Clearly, the plateau region cannot extend beyond the magnetic field values at which the gap
to these excitations vanishes, and so can only be more
narrow than the extent we shall find here.

Consider $\Delta S = +1$ excitations above the ground state.
These excitations are more favorable in higher magnetic
fields. The simplest way to insert such an excitation is by raising one minority spin by one unit, i.e. obtained
by acting with $S_{ij}^z$ on a minority site to change $S_{ij}^z = -s$
to $S_{ij}^z = 1 - s$. This creates two “defective” tetrahedra
(shared by this site), which no longer have the optimal
3:1 spin configuration. We will call the space of such
states “manifold A”. For $s > 1/2$, manifold A comprises
all the lowest energy $\Delta S = +1$ excitations in the Ising
Hamiltonian. Other $\Delta S = +1$ states which involve more
spin raising/lowering operators, e.g. those created by
$S_{ij}^z S_{jk}^z S_{kl}^-$, have higher energy because they either create
more defect tetrahedra or make the two defect tetrahedra
more energetically costly. The exception is $s = 1/2$, for
which manifold A is actually incomplete, and there are
other $\Delta S = +1$ excitations outside it with the same 0th
order energy. We will henceforth assume $s > 1/2$ in the
remainder of this appendix to avoid this complication.

The 0th order energy difference from the ground state
manifold is

$$E_A^0 - E_{3:1}^0 = 2J_z(3s - h). \quad (A1)$$

The gap shrinks as $h$ increases, and vanishes at a magnetic
field $h_A = 3s$. This corresponds to the high field
element of the half polarized plateau in the $s = 0$ limit. The
single site excitation is however highly degenerate. The
excitation can reside on any one of $N$ minority sites ($N$
is the number of pyrochlore sites). We expect breaking
this massive degeneracy (i.e. having this magnon “flat
band” acquire some dispersion) will lower the energy of
this excitation (closing the gap at lower magnetic field).
One therefore needs to take into account corrections from
higher orders in DPT.

To first order in $s$, only spin $\Delta S^z = \pm 1$ can be transferred from one site to a nearest neighbor. In any 3:1
configuration, the nearest minority spins reside on next nearest
neighboring sites in the lattice sense, which means these sites are a distance of two links apart. Therefore
this process always leaves manifold A, and the first order
term has no contribution.

To 2nd order in $s$ there are various viable processes. Apart from hopping spin $1$ between neighboring sites,
and then back, there is also a non-trivial process in which
the defect site (the $-s + 1$ spin) swaps with one of the
(next-) nearest neighbor minority spins. This is also a
legitimate member of the A manifold. Processes not in-
volving the defect directly are affected by the presence
of the defect only when involving the nearest neighbors
of the defect site. All other sites have the same contri-
bution to the 2nd order correction as in the ground state
manifold.

We immediately conclude the form of the effective
“magnon Hamiltonian” to 2nd order is

$$\mathcal{H}_A^2 - \mathcal{H}_{3:1}^2 = - \left[ c_1 + c_2 \sum_{\langle ij \rangle} \left( e_{ij}^z e_j + h.c. \right) \right], \quad (A2)$$

where $\langle \langle ij \rangle \rangle$ denotes next nearest neighbor sites on the
pyrochlore lattice that are both minority sites, $c_1, 2 > 0$
are coefficients depending on the physical couplings, and
the operator $e_{ij}^z$ creates a local excitation – it replaces a
spin $S_{ij}^z = -s$ with a spin $S_{ij}^z = 1 - s$ on site $j$:\n
$$e_{ij}^z = | - s \rangle_j \langle 1 - s |. \quad (A3)$$

An arduous yet straightforward calculation for the A
manifold results in

$$\mathcal{H}_A^2 - \mathcal{H}_{3:1}^2 =$$

$$- \frac{J_z \alpha^2}{2s - 1} \left\{ \frac{3s (4s^2 - 3s + 1)}{4s - 1} + \frac{s^2}{2} \sum_{\langle \langle ij \rangle \rangle} \left( e_{ij}^z e_j + h.c. \right) \right\} \right\}.$$ \hspace{1cm} (A4)

Note the singularity in Eq. (A4) for $s = 1/2$, which re-
fects the incompleteness of manifold A in this case.

In a hopping Hamiltonian of the form of Eq. (A3),
the magnon eigenstates are delocalized Bloch states. The
spectrum of these states in general depends in detail upon
the structure of the lattice of minority sites. However, if
we are interested in the minimum energy state only, there
is an amusing simplification. Since the hopping above is
everywhere negative, the lowest energy state is expected
to be nodeless, Thus the minimum energy state is simply
a constant amplitude (i.e. zero quasimomentum) Bloch state.
For any configuration of the minority spins $|\Psi_0\rangle$
in the ground state manifold, the corresponding state in the
A manifold is

$$|\Psi\rangle = \sum_j e_{ij}^z |\Psi_0\rangle. \quad (A5)$$

Direct calculation yields

$$\sum_{\langle \langle ij \rangle \rangle} \left( e_{ij}^z e_j + h.c. \right) |\Psi\rangle = 6|\Psi\rangle \equiv 6\langle \Psi | \Psi \rangle.$$ \hspace{1cm} (A6)

where 6 comes about as the number of next nearest neigh-
bors with spin $S_{ij}^z = -s$ the excitation can hop over to. Because in any 3:1 configuration there are always pre-
cisely 6 minority spins two links away, we are therefore
able to obtain the lowest-energy $\Delta S^z = +1$ magnon en-
ergy irrespective of the particular arrangement of the mini-
ortality sites!

The minimum energy of (A3) is therefore

$$E_{A,\text{min}}^2 - E_{3:1}^2 = - \frac{J_z \alpha^2 3s (8s^2 - 4s + 1)}{(2s - 1)(4s - 1)}. \quad (A7)$$
The combined gap to manifold A is now

$$\Delta E_A = J_z 2(3s - h) - J_z \alpha^2 3s \frac{(8s^2 - 4s + 1)}{(2s - 1)(4s - 1)}.$$  \hspace{1cm} (A8)

The gap vanishes at a magnetic field of

$$h_A = 3s - \alpha^2 3s \frac{(8s^2 - 4s + 1)}{2(2s - 1)(4s - 1)}.$$  \hspace{1cm} (A9)

Note that for $s \gg 1$, the $O(\alpha^2)$ correction is well-behaved, i.e. it scales in the same way as the zeroth order threshold field.

Excitations with $\Delta S = -1$ (manifold B) can be realized by replacing a spin $S^z_j = +s$ with a spin $S^z_j = s - 1$. The 6th order energy difference from the ground state manifold is calculated in an identical manner as in the $\Delta S = +1$ case, and yields

$$E^{\alpha}_{B} - E^{\alpha}_{B+1} = 2J_z(h - s).$$  \hspace{1cm} (A10)

At this order, the $\Delta S = \pm 1$ excitation spectra are symmetric about $h = 2s$.

Oppositely from the behavior at the high field edge of the plateau, the gap shrinks as $h$ decreases, and vanishes at a magnetic field $h_B = s$. Once again, due to a huge degeneracy (the defect can reside on any one of $2^N$ majority sites) we must resort to DPT in order to break the massive degeneracy of manifold B, expecting to lower the excitation energy.

In contrast to the $\Delta S^z = +1$ excitations above, it is already possible at first order to hop the spin $S^z = s - 1$ onto other sites and stay within the B manifold. This is because the majority sites are not isolated (4 of the 6 neighboring sites of a majority site are also majority sites). Therefore, for any given 3:1 state, one can immediately obtain the effective Hamiltonian to $O(\alpha)$:

$$H^1_{B} = J_z s \alpha \sum_{ij} W_{ij} \hat{h}^\dagger_i \hat{h}_j.$$  \hspace{1cm} (A11)

Here $W_{ij}$ is the connectivity matrix of the lattice of majority sites for the particular 3:1 state in consideration, and the operator $\hat{h}^\dagger_i$ creates a local excitation – it replaces a spin $S^z_i = s$ with spin $S^z_i = s - 1$ on site $j$:

$$\hat{h}_j = |s-1\rangle_j \langle s|.$$  \hspace{1cm} (A12)

Since $\alpha > 0$, the hopping amplitudes in this case are positive, rather than negative as above. Thus, unfortunately, the lowest-energy eigenstate is a non-trivial Bloch state, whose energy depends upon the precise form of $W_{ij}$, i.e. it is different for each of the 3:1 states. Therefore it is difficult to say anything specific about the $O(\alpha)$ correction to the minimum $\Delta S^z = -1$ magnon energy. Because one can easily construct variational states with negative hopping energy (e.g. an antibonding state with support only on two sites), the $O(\alpha)$ correction must be negative, and clearly from Eq. (A11) is of the form $E^{\alpha}_B = -J_z s \alpha c$, with $c > 0$ a dimensionless constant (the largest eigenvalue of $W_{ij}$). This gives

$$h_B = s(1 + \alpha c) > s.$$  \hspace{1cm} (A13)

Thus the upper edge of the plateau decreases and the lower edge of the plateau increases as $\alpha$ is increased, narrowing the plateau with increasing quantum fluctuations. It is plausible that for sufficiently large $\alpha$ the plateau is obliterated entirely, the upper and lower edge meeting. Unfortunately, this is beyond the realm of this perturbative analysis. Even a naïve extrapolation of the above lowest-order results is non-trivial, since the lower plateau edge depends upon the non-trivial constant $c$. It can in principle be computed for the various states obtained in Section III but we do not do so here.

**APPENDIX B: ALTERNATIVE CALCULATION OF THE DEGENERATE PERTURBATION THEORY**

In this appendix we present an alternative way of calculating the DPT 6th order diagonal term, providing a check on the calculation described in Section III.

The perturbation (6) can be viewed as a sum over spin transfer operators

$$H_1 = \frac{\alpha}{2} J_z \sum_{\langle i,j \rangle} \left( \hat{S}^+_i \hat{S}^-_j + h.c. \right) = \frac{\alpha}{2} J_z \sum_{\ell = \langle i,j \rangle} \left( \hat{h}_\ell + h.c. \right),$$  \hspace{1cm} (B1)

where $\hat{h}_\ell$ transfers one quantum of spin angular momentum from site $i$ to site $j$ if these are on adjacent sites, $i, j$. As a result, the $n$-th order virtual processes can be classified by choosing $n$ links to act on with spin transfer operators, in a particular order. In order to return to the initial 3:1 configuration, the links must form closed loops of spin transfer. These include self retracting loops, defined as loops where after following some path in the lattice, we turn back and travel the same path in the reverse order back to the origin. The chosen links can be represented by a graph on the lattice, by coloring these links. Apart from the graph, we must also specify the order by which the links operate.

The virtual states in a DPT process will have a number of sites in a different spin state relative to the initial 3:1 state. We denote $S^z_j = \sigma_j(s - m_j)$, where the variables $m_j$ are non-negative, and take on any integer value between 0 and 2$s$. Let us denote the set of modified sites by $M$. Thus $m_j \neq 0$ only if $j \in M$. Using the fact that $\sum_j \sigma_j = \frac{1}{2} \sum_j 1$ and $\sum_{\langle i,j \rangle} \sigma_i \sigma_j = 0$, both due to the 3:1 constraint, we find the inverse resolvent can be rewritten
where we have absorbed all constant energies into \( E \). Therefore conclude that the energy difference to a state in the 3:1 manifold and 

\[
H_0 - E_0 = J_z \sum_{(ij)} S_i^z S_j^z - E'_0
\]

\[
= J_z \sum_{(ij)} \sigma_i \sigma_j (s - m_i) (s - m_j) - E''_0
\]

\[
= J_z \left( \sum_{(ij) \in M} \sigma_i \sigma_j m_i m_j + 2 s \sum_{j \in M} m_j \right) - E''_0 ,
\]  

(B2)

where we have absorbed all constant energies into \( E'_0 \). With all \( m_j = 0 \), this resulting energy should vanish (energy difference to a state in the 3:1 manifold) and therefore conclude that the energy \( E''_0 = 0 \) in the final expression above. Finally, our virtual state energy is

\[
H_0 - E_0 = J_z \left( \sum_{(ij) \in M} \sigma_i \sigma_j m_i m_j + 2 s \sum_{j \in M} m_j \right). \quad (B3)
\]

At 1st order, the perturbation takes any initial state out of the 3:1 manifold, and therefore gives no contribution (equivalently no loop can be closed with only one link).

In 2nd order, we must act on the same link twice to undo the spin transfer, and return to the 3:1 manifold. Therefore all non-vanishing processes are confined to one tetrahedron. The same process can act on any one of the links of this tetrahedron, with the same resolvents for a given order of the link operators. Therefore, by summing up these diagrams, we will get a function of the spins on this tetrahedron which is invariant under any permutation of the 4 sites (the sum is represented in a diagrammatic way drawn in Fig. 17). Therefore the 3:1 configuration on any single tetrahedron has the same energy at this order in DPT, no matter which corner is chosen to be the minority site. For this reason, the 2nd order contribution gives a constant shift in energy to all the 3:1 states.

In 3rd order, the only way one can return to the 3:1 manifold is by forming a single closed loop of spin transfer, around a triangular side of a single tetrahedron. As in the 2nd order processes, we can sum over all such processes occurring on the single tetrahedron. One again we end up with a function that is invariant under any permutation of the 4 sites of the single tetrahedron (the sum is represented in a diagrammatic way drawn in Fig. 17). Once again, we cannot distinguish energetically between the different 3:1 states defined on this single tetrahedron. As a result, the 3rd order term must produce a constant shift in energy.

As exemplified in the 2nd and 3rd order terms, all DPT processes (of any order) that are confined to one tetrahedron (meaning all the spin transfer operators act on links in the same tetrahedron) all add up to constant shifts in energy. In every such case the argument is the same as above. Starting with a given process defined on a single tetrahedron, sum over all the processes of the same structure on the same tetrahedron. Then one always arrives at a function that is invariant under any permutation of the 4 corners. Within the 3:1 manifold, these processes cannot favor one configuration over the other, and must produce a mere shift in the overall energy. More explicitly, every process results in a function of the four Ising variables on a tetrahedron, as defined in Section III. The sum of all diagrams with same structure then takes on the generic form

\[
f(\sigma_1, \sigma_2, \sigma_3, \sigma_4) + (\text{all permutations of } 1...4) = a_0 + a_1 (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) + a_2 (\sigma_1 \sigma_2 + \sigma_1 \sigma_3 + \sigma_2 \sigma_3 + \sigma_2 \sigma_4 + \sigma_3 \sigma_4) + a_3 \sigma_1 \sigma_2 \sigma_3 \sigma_4 (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) + a_4 \sigma_1 \sigma_2 \sigma_3 \sigma_4 . \quad (B4)
\]

The 3:1 constraint gives \( \sigma_1 \sigma_2 \sigma_3 \sigma_4 = -1 \) as well as \( (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) = 2 \). The generic 4 spin function then reduces to

\[
f(\sigma_1, \sigma_2, \sigma_3, \sigma_4) = \text{const} + a_2 \sum_{i<j=1}^{4} \sigma_i \sigma_j
\]

\[
= \text{const} + \frac{a_2}{2} \left( \sum_{j=1}^{4} \sigma_j \right)^2 = \text{const} . \quad (B5)
\]

Given this result, we can always ignore virtual processes confined to one tetrahedron for the remainder of our discussion.

Similar arguments can be applied to processes confined to 2 adjacent tetrahedra. Summing over all possible processes confined to pairs of adjacent tetrahedra, one always ends up with a constant energy shift in the 3:1 manifold. A pair of adjacent tetrahedra can only be in one
of 3 configurations in the 3:1 manifold (see Fig. 13). The adjacent tetrahedron pairs can be enumerated by the site connecting them. Therefore the number of distinct pairs is equal to the number of pyrochlore sites. In the 3:1 manifold, the number of configurations where the shared site is a minority site (see Fig. 13(a)) is fixed to be $\frac{1}{4}$ of the sites. In the remaining $\frac{3}{4}$ of the sites, the shared site is a majority site. The two configurations in Fig. 13(a) with a majority site connecting the pair of tetrahedra are distinguishable physically because of the different directions of the links, but in terms of the diagrams defining DPT processes Fig. 13(b) and Fig. 13(c) are indistinguishable (they are identical in the graph sense - the link structure is the same). Therefore, the summation over all possible processes confined to these two adjacent tetrahedra always results in a function of the Ising variable defined on the shared site

$$f(\sigma_i) = a_0 + a_1 \sigma_i.$$  \hfill (B6)

For each pair of adjacent tetrahedra, we have the same function (B6) of the shared site Ising variable. Summing over all pairs of adjacent tetrahedra, is equivalent to summing over the sites of the pyrochlore lattice. Therefore, the sum of all the DPT processes of this sort results in

$$\sum_i f(\sigma_i) = N a_0 + a_1 \sum_i \sigma_i = N a_0 + \frac{N}{2} a_1,$$

where $N$ denotes the total number of pyrochlore lattice points. Once again, we are led to the conclusion that all such processes can only give a constant shift in energy, and we shall ignore all such instances in the remainder of our discussion.

At 4th order we have a number of possible processes. The only spin transfer processes comprising a single loop will be confined to 2 adjacent tetrahedra. According to the arguments above, this single loop process will give a constant shift in energy, within the 3:1 manifold. Apart from single closed loop, we can only also have processes with 2 separate closed loops, comprising two non-overlapping links which get acted on twice. Each chosen link occupies its own tetrahedron (if the two links are on the same tetrahedron, one must act on a bond with two majority spins, and automatically produces zero). The case in which these 2 tetrahedra are adjacent, will result in a constant, by our arguments above. Otherwise, there are only two possibility. In one case these two tetrahedra share a neighboring tetrahedron. In the 2nd case, they are separated by more than one tetrahedra. This classification is necessary because, in the former case, different resolvents may show up through the interaction term of the virtual state energy (B3). If the two links are separable by more than one tetrahedron, this does not occur.

In the case where the two tetrahedra are sufficiently well separated, with no mutual interaction in the virtual state energy, we can once again invoke the trick of summing over all such processes on each single tetrahedron containing a link, and the DPT term cannot distinguish between the four 3:1 configurations on each tetrahedron. Once again we end up with a constant shift in the overall energy for all the 3:1 configurations.

Now we consider the processes where the two tetrahedra share a neighboring tetrahedron. One such diagram is pictured in Fig. 18. The structure spans a chain of three tetrahedra. In the present case, when summing over diagrams one must be cautious to sum over diagrams with the same resolvents. Summing over equivalent diagrams on the chain of three tetrahedra, such as those found by permuting site 2 with 3 and 4, yields a function that treats the 3 sites at the outer side of each edge tetrahedron on equal footing. We graphically indicate the sum of diagrams, by coloring all the links that appeared in one of the diagrams we summed over (see Fig. 19).

Formally, the sum of processes gives rise to a function of the 8 Ising variables on the two edge tetrahedra

$$f(\sigma_1, \ldots, \sigma_8).$$  \hfill (B8)

Because of the above arguments, this function has to be invariant under permutations of the 3 outer edge spins. Considering all possible expressions we can form out of the 3 edge spins in a “symmetric” way

$$f(\sigma_1, \ldots, \sigma_8) = a_0 + a_1 (\sigma_2 + \sigma_3 + \sigma_4) + a_2 (\sigma_2 \sigma_3 + \sigma_2 \sigma_4 + \sigma_3 \sigma_4) + a_3 \sigma_2 \sigma_3 \sigma_4,$$

where the dependences of $a_0, a_1, a_2$ on $\sigma_1, \sigma_2, \sigma_3, \sigma_4$ are implicit. Using the 3:1 constraint on this tetrahedron $(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) = 2$, as well as the identities it implies $\sigma_1 \sigma_2 \sigma_3 \sigma_4 = -1$ (or $\sigma_2 \sigma_3 \sigma_4 = -\sigma_1$) and $(\sigma_2 \sigma_3 + \sigma_2 \sigma_4 + \sigma_3 \sigma_4) = 1-2\sigma_1$, we find that $f(\sigma_1, \ldots, \sigma_8)$ can be rewritten as a function of $\sigma_1, \sigma_2, \sigma_3, \sigma_4$ alone;

$$f(\sigma_1, \ldots, \sigma_8) = a_0 + a_1 (2 - \sigma_1) + a_2 (1 - 2\sigma_1) - a_3 \sigma_1 = \tilde{a}_0 + \tilde{a}_1 \sigma_1.$$  \hfill (B9)
Repeating the same simplification for the three Ising variables of the other edge, \( \sigma_{6,7,8} \), one finds that the sum of diagrams above can only produce a function depending on the 2 spins connecting the edge tetrahedra to the third tetrahedron in the middle of the chain (sites 1 and 5 in Fig. 19). This function is therefore a function of 2 neighboring spins on a single tetrahedron \( f(\sigma_1, \sigma_5) \). Each three tetrahedron chain process can be represented by the pyrochlore link between the two sites shared between the tetrahedra (sites 1 and 5 in Fig. 19). Summing over all the processes represented by the 6 links in the central tetrahedron which contains sites 1 and 5, one ends up with a function which is symmetric under an permutation of the 4 sites on this tetrahedron. Repeating the steps outlined in Eqs. (B4) and (B5), we find the resulting function is constant.

The particular case analyzed above is only an example of a vastly more general case, which we now describe. Given a set of diagrams that reside on chains of tetrahedra, with the two edge tetrahedra not sharing a neighboring tetrahedron between them in any one of the diagrams (except through the chain itself), one can sum over sites at the edge that we are free to permute (see examples in Fig. 20 and Fig. 21). The summation in both examples will result in a function of the spins at site 1. This procedure of contractng the diagram can be continued from both edges, and we will always end up with a function of 2 sites residing on one tetrahedron. We then sum over all the different choices of the last 2 remaining sites on this tetrahedron. We then end up with a symmetric function of the 4 sites on a single tetrahedron, which is always a constant, from Eqs. (B4) and (B5). Therefore, we conclude that all such diagrams can be summed over to give constant shifts in energy. We shall refer to these sets of diagrams as “retractable chains”.

Bearing the above arguments in mind, we now turn to 5th order in DPT. Any diagram which consists of only one closed loop of spin transfer, is confined to two adjacent tetrahedra. As elaborated above, the different configurations on the pair of adjacent tetrahedra are indistinguishable in the graph sense. These diagrams can therefore contribute only a constant shift in energy. Other than these diagrams, the only possibility is to have two separate closed loops of spin transfer. One must involve a single link being acted on twice, and the other must be a 3–link loop. Both loops reside on two different tetrahedra. If the two tetrahedra are adjacent, or share a neighboring tetrahedron (as in in Fig. 22), the tetrahedra are part of a retractable chain. Our general analysis for retractable chains then applies here as well. Therefore, these diagrams must also sum up to a constant in the 3:1 manifold. Otherwise the two tetrahedra are sufficiently well separated, and we can sum over the various diagrams on each tetrahedron separately. The summation gives an expression in which each of the 4 tetrahedron corners are on equal footing, and cannot distinguish between different 3:1 states, resulting in a constant energy shift.

In agreement with the results of Section II, DPT terms of order less than 6 will not split the energy of the 3:1 states. Finally, we turn to 6th order in DPT

\[
\mathcal{H}_6 = -\mathcal{P} \left( \mathcal{H}_1 \mathcal{R} \right)^5 \mathcal{H}_1 \mathcal{P}
\]

where \( \mathcal{R} = \frac{1-\mathcal{P}}{\mathcal{R}_0 - \mathcal{P}} \) is the resolvent. At this order we have a new class of single closed loops - loops around hexagonal plaquettes of the pyrochlore lattice (see Fig. 23), which will split the energy of different 3:1 configurations. These processes can be enumerated by the hexagonal plaquettes they act on. So we can write the contribution from these processes \( \sum \mathcal{P} \tilde{g}(\sigma_1 \ldots \sigma_6) \) where the spins around the hexagonal plaquette are denoted 1 \ldots 6.

All other single closed loop diagrams are confined to 1, 2 or 3 adjacent tetrahedra, the first two we already know will sum up to constant shifts in energy. The self-retracting loop residing on a chain of 3 tetrahedra is depicted in Fig. 24 and is also summed over to produce a constant, since this is a retractable chain.

Next we consider the diagrams which comprise 2 closed loops. There must be two of length 3, or one of length 4 and one of length 2. In the case of 2 loops of length 3, each loop must reside on a single tetrahedron. If the two tetrahedra are adjacent, or even share a neighboring tetrahedron (as in Fig. 25), they form a retractable chain, and result in a constant. Otherwise the tetrahedra are sufficiently well separated so that we can sum over diagrams on the two tetrahedra separately, and end up with a constant.
We now turn our attention to the case of one loop of length 4 and one of length 2. The loop of length 2 must be one link appearing twice, and is therefore confined to a single tetrahedron. The loop of length 4 must be confined to 2 adjacent tetrahedra (or even just 1). If the two loops are sufficiently well separated (by more than one tetrahedra), we can sum over all 2-loop diagrams in the tetrahedron where the loop of length 2 resides, resulting in a constant. We can then sum over diagrams on the tetrahedron cluster containing the 4-loop to produce another constant. If the two clusters are adjacent, or separated by just one tetrahedron, we have a retractable chain, which we have already shown must result in a constant.

The last set of 6th order diagrams are those of 3 closed loops, each comprising a single link, acted on twice. Each loop is therefore confined to a single tetrahedron. Using the same arguments as before, if all three tetrahedra are separated by more than one tetrahedra from one another, we can sum over all such diagrams contained in the same tetrahedra. In particular, sum over diagrams related by permuting over sites on each single tetrahedron separately results in a constant. Even if only one tetrahedron is well separated from the other two, we can first sum over diagrams on the isolated tetrahedron to produce a constant, and then deal with the other two tetrahedra. The remaining two will reside on a retractable chain of tetrahedra, again resulting in a constant.

The only cases which we must deal with more carefully are those diagrams where each pair of tetrahedra either shares a neighboring tetrahedron, or the two are adjacent. When at least one pair of loops resides on adjacent tetrahedra, the cluster of tetrahedra will always be a retractable chain, with either 4 or 3 tetrahedra. We are left only with diagrams where all three tetrahedra containing the loops are not adjacent, but rather have shared neighboring tetrahedra. There are 3 tetrahedron clusters possible, where this occurs. Fig. 26 shows a diagram residing on a closed chain of 6 tetrahedra, enclosing a hexagonal plaquette. This is not a retractable chain. In Fig. 27 the three tetrahedra containing the loops all share one single neighboring tetrahedron. Finally, in Fig. 28 the three loops reside on a linear chain of 5 tetrahedra. However, it is important to note at this point that the tetrahedra at the two edges of this chain (1 and 7) can be identified to give the cluster shown in Fig. 26.

The processes on the cluster shown in Fig. 26 cannot be contracted, and will split the energy of the different
In fact already been taken into account in tetrahedra 1 and 6 may now interact. These 2 terms have been subtracted from the other 79 diagrams in this sum, since the sites on 1 and 7 at the edges of the chain are permutations of sites. However, two of these diagrams give constant energy shifts requires that the diagrams give constant energy shifts requires that the terms we need to subtract are enumerated by the choice of central tetrahedron in the chain in Fig. 26 (tetrahedron number 4), which we can identify with the tetrahedron containing sites 3 and 4 in Fig. 26. Given a choice of the central tetrahedron, each term of this sort is a function of the 6 spins $r(\sigma_1 \ldots \sigma_6)$ as defined in Fig. 26. Given a hexagonal plaquette there are 6 choices of the central tetrahedron, and correspondingly 6 terms and we must take into account all of these. Choosing a different central tetrahedron is equivalent to cyclically permuting the spins 1...6, and so the total contribution of all these process is

$$- \sum_p \left( r(\sigma_1 \ldots \sigma_6) + r(\sigma_6 \ldots \sigma_5) + r(\sigma_5 \ldots \sigma_4) + r(\sigma_4 \ldots \sigma_3) + r(\sigma_3 \ldots \sigma_2) + r(\sigma_2 \ldots \sigma_1) \right).$$

The processes on the cluster shown in Fig. 27 can be contracted from the “loose ends” of the diagram, similar to the contraction we have implemented for the retractable chains. For the particular example in Fig. 27 we sum over the corresponding diagrams with 2 permuted with 3 and 4. The resulting sum can only be a function of site 1, 5, 7, 9, and 12. We then sum over the corresponding diagrams with 7 permuted with 6 and 8, and then sum over 12 permuted with 10 and 11. After these summations, the resulting function can only be a function of the sites 1, 5, 9. Finally, we sum over all choices of three such sites on the central tetrahedron, which must result in a constant (a symmetric function of the 4 sites of a single tetrahedron).

Next, we turn to the processes on the chain in Fig. 28. At first glance, it would seem that these are retractable diagrams, that will amount to a constant. Such a summation would include 81 different diagrams (we retract the tetrahedra 2,3,5, and 6, each time summing over three permutations of sites). However, two of these diagrams are of the form of Fig. 26 in which case the tetrahedra 1 and 7 at the edges of the chain are identified. As a result, these two diagrams may have different resolvents from the other 79 diagrams in this sum, since the sites on tetrahedra 1 and 6 may now interact. These 2 terms have in fact already been taken into account in $f(\sigma_1 \ldots \sigma_6)$, and therefore should not be added again to the effective Hamiltonian. The summation that makes contractible diagrams give constant energy shifts requires that the resolvents be identical for the entire set of diagrams.

Rather than explicitly calculating the remaining 79 diagrams, we employ the following trick. In order to produce a constant, we add to the 79 diagrams two terms having the same resolvent, but replacing the spin variables $\sigma_j$ with those at the positions 1 through 6 in Fig. 26. All these 81 terms have the same resolvent as that of the process in Fig. 28 and therefore will result in a constant. The two additional terms do not represent actual DPT processes, and therefore must be subtracted from the effective Hamiltonian. The terms we need to subtract are enumerated by the choice of central tetrahedron in the chain in Fig. 28 (tetrahedron number 4), which we can identify with the tetrahedron containing sites 3 and 4 in Fig. 26. Given a choice of the central tetrahedron, each term of this sort is a function of the 6 spins $r(\sigma_1 \ldots \sigma_6)$ as defined in Fig. 26. Given a hexagonal plaquette there are 6 choices of the central tetrahedron, and correspondingly 6 terms and we must take into account all of these. Choosing a different central tetrahedron is equivalent to cyclically permuting the spins 1...6, and so the total contribution of all these process is

$$- \sum_p \left( r(\sigma_1 \ldots \sigma_6) + r(\sigma_6 \ldots \sigma_5) + r(\sigma_5 \ldots \sigma_4) + r(\sigma_4 \ldots \sigma_3) + r(\sigma_3 \ldots \sigma_2) + r(\sigma_2 \ldots \sigma_1) \right).$$

The 6th order term in the effective Hamiltonian finally reads

$$\mathcal{H}_6 = \sum_p y(\sigma_1 \ldots \sigma_6) + \sum_p \left( f(\sigma_1 \ldots \sigma_6) + f(\sigma_6, \sigma_1 \ldots \sigma_5) \right) - \sum_p \left( r(\sigma_1 \ldots \sigma_6) + r(\sigma_6 \ldots \sigma_5) + r(\sigma_5 \ldots \sigma_4) + r(\sigma_4 \ldots \sigma_3) + r(\sigma_3 \ldots \sigma_2) + r(\sigma_2 \ldots \sigma_1) \right).$$

Calculating these functions explicitly, we find the exact same results as in Section 11.

**APPENDIX C: SPIN $s = \frac{3}{2}$ DIAGONAL TERM GROUND STATE DEGENERACY.**

In this appendix we analyze the lowest energy states found for the diagonal term in the effective Hamiltonian for spin $s = \frac{3}{2}$ discussed briefly in Section V A 3. The lowest energy states turn out to be massively degenerate. We have found what is at the very least a subset of this manifold, which already exhibits a degeneracy that grows with the system size, diverging in the thermodynamic limit.

First we consider all the possible states we can construct with all the Kagome layers in the pyrochlore taking
on the $\sqrt{3} \times \sqrt{3}$ configuration in Fig. 14. Given a plane in this $\sqrt{3} \times \sqrt{3}$ configuration, there are 3 different ways to place the following layer (also in the $\sqrt{3} \times \sqrt{3}$ configuration) above it, as described in Fig. 29. This freedom in the way the planar configurations are stacked is the source of a massive degeneracy – there are $3^L$ possible stacking choices, where $L$ is the linear dimension of the system. Also, there are 4 plaquette directions in which to choose the direction of the stacking, resulting in an overall number of such states $4 \times 3^L$. For now, we shall work with this subset of the entire degenerate manifold, since these states are rather easy to handle. We shall refer to his set of states as the $\sqrt{3} \times \sqrt{3}$ states.

Now we turn to calculate the energy of these states, proving these are degenerate states. Each plaquette in the $\sqrt{3} \times \sqrt{3}$ planes shares links with three plaquettes above it. These 4 plaquettes enclose an up-headed cell, as defined in Section 8.1. For any one of the 3 $\sqrt{3} \times \sqrt{3}$ spin configurations of the next Kagome plane, we always get the same up-headed cell types above the type 1 and type 0 plaquettes in the $\sqrt{3} \times \sqrt{3}$ plane. The clusters enclosing these up-headed cells above the type 1 and type 0 plaquettes are depicted in Fig. 29(a) and Fig. 29(b) respectively. Since we are only considering up-headed cells, every one of the plaquettes appears in only one cell.

Inspection of Fig. 29(a) shows that it includes one plaquette of type 1, one of type 2, one of type 3, and one of type 4 (This is just the type 1 cell in Table III). For the cluster in Fig. 29(b) we find it includes two type 0 plaquettes, and two type 2 (type 8 cell in Table III). Of the plaquettes in the planes, which comprise $1/3$ of the plaquettes in the lattice, $2/3$ are in a type 1 configuration, and $1/3$ are in a type 0 configuration. Since each planar plaquette determines the configuration of the unique up-headed cell it is a part of, we find therefore, that $2/3$ of the up-headed cells are type 1 cells ($y_1 = 2/3$) and the remaining $1/3$ are type 8 cells ($y_8 = 1/3$). The corresponding plaquette type fractions are $x_0 = 1/6$, $x_1 = 1/6$, $x_2 = 1/3$, $x_3 = 1/6$, and $x_4 = 1/6$. Finally, the energy per plaquette of the $\sqrt{3} \times \sqrt{3}$ states is

$$E_{\sqrt{3} \times \sqrt{3}} = \frac{1}{N} \left( V_1 + 2V_2 + V_4 \right).$$

(C1)

We expect the fractions of plaquettes in all the states in this degenerate manifold to be the same as in this subset, since otherwise, it is rather unlikely (though not impossible) that a different combination of fractions will yield the same energy.

Having analyzed this set of states, we turn to an additional set of states, with the same energy. Consider a particular subset of $\sqrt{3} \times \sqrt{3}$ states, with every two Kagome planes stacked in the same manner. This subset of the $\sqrt{3} \times \sqrt{3}$ states has a total of $4 \times 3^2 = 36$ states - factor 4 for choosing the direction of the layering, a factor 3 for the choice of how to position the planar configuration on one plane, and another factor of 3 from the freedom to choose how to stack the next planar layer. We shall refer to these as the uniformly stacked states.

Starting from any one of these uniformly stacked states we note that the type 1 cell can swap its type 1 and type 3 plaquettes by changing the position of only one minority site. In Fig. 29(a) this can be accomplished by moving the minority site at site 4 to site 5. In addition, site 5 is part of a type 8 cell, and it is denoted also in Fig. 29(b) where it is evident that in order to maintain the 3:1 constraint, we must also shift the minority site at site 1 in Fig. 29(b) to site 6. Because the stacking of the next layer is exactly the same, the same shifting of minority sites must occur along the entire straight line passing through site 4 in the direction from site 4 to site 5. Closing this chain at infinity makes this chain into an infinite length loop of alternating minority and majority sites, that are flipped, and therefore this maintains the 3:1 constraint. One can convince one self from Fig. 29(b) that the type 8 cell will remain a type 8 cell under these minority site shifts. Since all the cells remain in the same configuration type, the plaquette type fractions remain the same as in the $\sqrt{3} \times \sqrt{3}$ states, have the same energy, and are therefore degenerate.

We now turn to calculate the degeneracy of this new set of states. Each type 8 cell has exactly one site it can shift in this manner, but since the chains are not shared between different type 0 plaquettes in the plane, one can convince oneself that these straight line chains of sites can be flipped independently. Therefore, starting from a particular uniformly stacked state, since there are $\frac{3}{12}$ plaquettes in every plane (where $N$ is the number of pyrochlore sites, and the number of hexagonal plaquettes), there are $\frac{N}{12}$ chains we can independently flip between two configurations, resulting in a degeneracy of $36 \times 2^N$. However, an additional subtlety must be addressed.

Every $\sqrt{3} \times \sqrt{3}$ state has all the up pointing tetrahedra in one of three 3:1 configurations. Flipping any chain in a uniformly stacked state will introduce some number of up pointing tetrahedra in the 4th possible 3:1 configuration of a single tetrahedron. Starting from one uniformly stacked state, flipping all possible chains, we will change all the tetrahedra of one of the three 3:1 configurations into the 4th tetrahedron configuration type, which was absent in the initial uniformly stacked state. Once again we will find ourselves with all tetrahedra in only three possible different 3:1 configurations. This suggests, that perhaps this final state we have reached is also a uniformly stacked state. From inspection we find this indeed is the case, so that from one uniformly stacked state we can reach one other such state by flipping all possible chains in the manner described above. We must therefore correct the degeneracy to $18 \times 2^{\frac{N}{12}}$ to account for this double counting.

In total we have found the degeneracy of these two sets of states to be

$$18 \times 2^{\frac{N}{12}} + 4 \times 3^L - 36,$$

(C2)

where we have subtracted 36 since this is the number of
states that appear in both sets of states we have analyzed (these are simply the uniformly stacked states). We shall refer to the combined set of states as the $1-8$ manifold of states, since it involves only type 1 and type 8 cells. The degeneracy we have calculated matches precisely the degeneracies in Table V for all the clusters where we have found the lowest energy state for $s = \frac{3}{2}$, namely the $3 \times 3 \times 1, 6 \times 3 \times 1, 3 \times 3 \times 2$ and $3 \times 3 \times 3$ clusters. Our analysis clearly shows that this set of states is massively degenerate, and despite exhausting all the states we have found numerically with this energy, we cannot be certain that these exhaust all possible states with this energy.

In a previous publication analyzing the same 3:1 degenerate manifold of states, the authors ascertained the maximum fraction of type 1 plaquettes that can be placed on a pyrochlore lattice is $\frac{1}{3}$. The 1–8 states do not realize this limit, but come fairly close to it with $\frac{5}{8}$ of the plaquettes in the type 1 configuration. Therefore, the $\sqrt{3} \times \sqrt{3}$ states are a “compromise” between the energy gain of $V_1$ (which favors the type 1 plaquettes) and the energy loss of $V_2$ (which disfavors the type 2 plaquettes), taking into account the constraint $x_1 < x_2$. This becomes evident when calculating the energy of the various cell types. The state realizing the maximum fraction of type 1 plaquettes found in Ref. 18 is comprised of only type 2 cells. For $s = \frac{3}{2}$, type 1 cells are far more favorable in energy than type 2 cells, and type 1 cells are abundant in the $1-8$ states.

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