Spin-orbit effects in Na$_4$Ir$_3$O$_8$, a hyper-kagomé lattice antiferromagnet

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We consider spin-orbit coupling effects in Na$_4$Ir$_3$O$_8$, a material in which Ir$^{4+}$ spins form an hyper-kagomé lattice, a three-dimensional network of corner-sharing triangles. In ideal classical models, these lattices support highly degenerate ground states which prevent order down to very low temperature. Instead, the spins continue to fluctuate strongly despite significant quantum effects and many non-ideal features of the materials must be taken into account. The answer to this question is quite subtle, due to many competing effects that can come into play. Quantum and thermal fluctuations may break the ground state degeneracy and actually induce magnetic order, an effect known as order-by-disorder. This effect, however, is understood theoretically only in the large spin, $S \gg 1$ limit, in which spins behave semi-classically. Nevertheless, some models even with the smallest possible spins, $S = 1/2$, seem at least qualitatively to follow the order-by-disorder scenario. Conversely, in other models with small spin, quantum spin liquids have been shown to occur. No general theory to predict which of these two tendencies obtains exists at present.

Despite this lack of theoretical discrimination, experimentalists have forged onward in recent years, uncovering a number of promising candidate quantum spin liquid materials with small spin $S = 1/2$ on geometrically frustrated lattices. These include an organic magnet, $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$, containing spin-1/2 moments on a slightly spatially anisotropic triangular lattice, ZnCu$_3$(OH)$_6$Cl$_2$, an inorganic realization of a spatially isotropic spin-1/2 kagome antiferromagnet, and very recently the cubic material Na$_4$Ir$_3$O$_8$ which realizes an hyper-kagomé antiferromagnet, in which spin-1/2 moments reside on a three-dimensional network of corner-sharing triangles -- see Fig. 1. None of these compounds exhibit indications of magnetic ordering. The interpretation of the first two materials, however, is complicated by the appearance of inhomogeneous magnetic moments at low temperature in $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$, and by fairly high levels of substitutional disorder (Zn for Cu) in ZnCu$_3$(OH)$_6$Cl$_2$. By contrast, the Ir$^{4+}$ moments are expected to be well ordered in Na$_4$Ir$_3$O$_8$, due to the much larger ionic radius of Ir compared to Na and O.

Recent two works\textsuperscript{9,10} assumed the nearest neighbor antiferromagnetic Heisenberg model for Na$_4$Ir$_3$O$_8$. In Ref.\textsuperscript{2} the authors treated the spin as a classical $O(N)$ spin. By a large-$N$ mean field theory and classical Monte Carlo simulation, they found that the classical ground states are highly degenerate and a nematic order emerges at low temperatures in the Heisenberg model ($N = 3$).
via “order by disorder”, representing the dominance of coplanar spin configuration. In Ref. 10, the authors presented a large-$N$ $Sp(N)$ method and studied both the semi-classical spin and quantum spin regimes. In the semi-classical limit, they predicted that an unusual $\vec{k} = (0,0,0)$ coplanar magnetically ordered ground state is stabilized with no local “weather vane” modes. While in the quantum limit, a gapped topological $Z_2$ spin liquid emerges.

Due to the large atomic number ($Z = 77$) of Ir, however, we should carefully consider the role of spin-orbit coupling, whose leading effect in localized $S = 1/2$ electron systems is the Dzyaloshinskii-Moriya (DM) interaction in the weak spin-orbit coupling limit. In fact, DM interactions have been argued to play an important role even in ZnCu$_3$(OH)$_2$Cl$_2$, with much less relativistic Cu ($Z = 29$) moments. The DM interaction reduces the full SU(2) spin-rotational invariance of the Heisenberg Hamiltonian to the $Z_2$ discrete time-reversal symmetry (in addition to coupling spin transformations to the discrete point group operations of the lattice). On general grounds, this is expected to lower the degeneracy of the classical ground state manifold. However, depending upon the detailed form of the DM coupling, varying degrees of degeneracy remain, indicative of different amounts of frustration. The tendency of the system to retain the order of the classical ground state is certainly also variable, and warrants investigation. This is one of the motivations of the present study.

Another motivation comes directly from the experiments in Ref.11, several aspects of which are suggestive of the presence of spin-orbit coupling. First, the “Wilson ratio” $R = T_\chi / c_v$, is observed to grow with cooling at low temperature, following a power-law $R \sim 1/T^\alpha - 1$, with $2 < \alpha < 3$. Here $\chi \sim$ const. is the magnetic susceptibility and $c_v \sim T^\alpha$ is the specific heat. As will be discussed in Sec. III such a low temperature behavior is incompatible with any spin-rotationally invariant phase of matter supporting well-defined quasi-particle excitations. To our knowledge, it is at odds with all known theoretical models of quantum spin liquids, and seems highly unlikely on general grounds. Taking into account the observed field-independence (up to 12 Tesla) of the specific heat $c_v$ brings the behavior even further into disagreement with spin-rotationally invariant theories. Second, samples in which a fraction $x$ of Ir atoms are substituted by Ti (which are in a non-magnetic Ti$^{4+}$ state) display a Curie component in the susceptibility linearly proportional to $x$ with a strongly suppressed amplitude, of approximately $1/3$ of a spin-1/2 moment per Ti. As we also show in Sec. III A such behavior is also at odds with any simple spin-rotationally invariant low-temperature phase (assuming no clustering of the Ti atoms), though some more exotic. All these observations, however, are readily reconciled by assuming the presence of spin-rotational symmetry breaking. Given the lack of any observed magnetic ordering, explicit and substantial spin-orbit interactions would appear to be a likely candidate.

In Sec. III we consider an explicit semi-microscopic calculation of the exchange Hamiltonian in the presence of spin-orbit coupling. We consider both super-exchange through the intermediate O atoms, and direct exchange between closest pairs of Ir spins. The results depend crucially upon the relative magnitude of the spin orbit coupling constant $\lambda$ and the non-cubic splittings of the $t_{2g}$ multiplet. This is quantified by two dimensionless ratios of $\lambda$ to the two energy splittings $\epsilon_2 - \epsilon_1$ and $\epsilon_3 - \epsilon_1$ of the orbital levels in the absence of spin-orbit. When $\lambda$ is the largest energy scale – the “strong spin orbit limit” – the “spin” has a substantial orbital angular momentum component, while in the opposite “weak spin orbit limit”, it is predominantly microscopic spin angular momentum. Indeed, the $g$-factor has opposite sign in the two limits. Which if either limit applies is the most fundamental physical question to be understood concerning the nature of magnetism in Na$_4$Ir$_3$O$_8$. We are not aware of any calculations or direct experimental measurements that indicate whether Na$_4$Ir$_3$O$_8$ is in the weak or strong spin-orbit limits, or intermediate between these situations. Instead we will address this question by comparing the expected phenomenology for the two cases to experimental observations.

In the strong spin-orbit limit, when the dominant mechanism is Ir-O-Ir superexchange, we find an highly anisotropic effective spin Hamiltonian, in which two spin components on each bond interact antiferromagnetically while the third interacts ferromagnetically. Specifically,

$$\mathcal{H} = \sum_{\langle ij \rangle} J_{ij} \epsilon_{ij}^\mu S_i^\mu S_j^\mu ,$$

where $(\epsilon_{ij}^x, \epsilon_{ij}^y, \epsilon_{ij}^z)$ is a permutation of $(+1, +1, -1)$ chosen appropriately for each bond (see Sec. III A) to specify the two antiferromagnetic and one ferromagnetic direction. We call Eq. 1 the “strong anisotropy” Hamiltonian.

Somewhat surprisingly, the remaining three cases: strong spin orbit and direct exchange, and weak spin-orbit and superexchange or direct exchange, all lead to approximately isotropic Heisenberg interactions. For the weak spin-orbit limit, this is guaranteed, but it is certainly not in the strong spin-orbit case. The dominant spin-rotational symmetry breaking effect, which is perturbative in all three regimes, is the DM interaction. The effective Hamiltonian has the form

$$\mathcal{H} = \sum_{\langle ij \rangle} [JS_i \cdot S_j + D_{ij} \cdot (S_i \times S_j)] .$$

Here $J$ is the same for all bonds, and estimated as $J \approx 400 K$ from the measured Curie-Weiss temperature $\Theta_{CW} \approx -650 K$. Symmetry strongly restricts the structure of this effective magnetic Hamiltonian for hyper-kagomé. The full set of DM vectors $D_{ij}$ may be fixed by just three parameters. That is, $D_{ij}$ on any one bond is arbitrary (by symmetry), but that choice determines all remaining $D_{ij}$ in the system. It is convenient to choose
disagreement of these expectations with the experimen-
dering temperature relative to the Curie-W eiss scale. The
little reason to suppose a significant suppression of the or-
symmetry as the classical one is rather likely, and there is
but one would expect that an ordered phase of the same
the physical
 prevents ordering in a classical system. The behavior in
hether, this degeneracy is presumably insufficient to
which do not protect any continuous degeneracies. Nev-
only discrete (space-group and time-reversal) symmetries
(small) accidental degeneracy , since the system has itself
states, in which any one spin can be specified arbitrar-
We find a continuous
system in this limit has an almost unique ground state.
parameters proportional to the number of spins), the
ground states are specified by a number of continuous
classical approximation. Remarkably , unlike the Heisen-
ered the strong anisotropy Hamiltonian, Eq. (1) in the
hemperature of Na
above, are consistent with the observed spin liquid behav-
iw corresponds to the ordering temperature relative to the Curie-Weiss scale. The disagreement of these expectations with the experimen-
tal observations suggests that it is the weakly-anisotropic
DM Hamiltonian rather than this one which is most ap-
propriate. We however return to this question in more
detail in Sec. VII

In Sec. V we turn to the weak anisotropy limit, and
first explore the classical phase diagram of Eq. (2). In
general, even this optimization problem is highly non-
trivial, given the large unit cell of the hyper-kagomé lat-
tice, and the possibility that the magnetic unit cell of
the ground states may be yet larger. In the special case

$D_1 = D_3 = 0$ and $D_2 < 0$, however, it is possible to
solve this problem exactly. The degeneracy is broken
completely to a single Kramer’s pair of coplanar ground
states, for which the magnetic unit cell is equal to the
crystallographic one. These may in this sense be con-
sidered $k = (0,0,0)$ states. One is drawn in Fig. 2. We
call this the “windmill” state. By several approximate
methods, we establish the form of the phase diagram in
the general $D_1-D_2-D_3$ parameter space. Generically the
windmill state distorts to a “canted windmill” state (still
with $k = (0,0,0)$), occupying a finite region of the phase
diagram. In addition, one finds a wide range of incom-
mensurate phase, in which the ordering wavevector $k$ is
non-zero and generically irrational in reciprocal lattice
coordinates. Owing to the breaking of space group sym-
metries, the incommensurate phase retains more of the
frustration-induced degeneracy.

A key question is whether the DM interactions, ex-
pected on physical grounds and invoked phenomenolog-
ically to explain the experimental properties discussed
above, are consistent with the observed spin liquid behav-
ior of Na$_4$Ir$_3$O$_8$, i.e. the lack of any ordering down to the
very low temperatures of $T \approx 1.8K = \Theta_{CW}/360$. The
breaking of degeneracy by DM might be expected to re-

FIG. 1: The hyper-kagomé lattice of Ir$^{4+}$ spins, with one
classical ground state of the strong anisotropy Hamiltonian
shown. Though this particular ground state is collinear, other
ground states are not.

FIG. 2: (Color online) The “windmill” state, which is the
classical ground state in the weak anisotropy limit when $D_2 < 0$. It is also the basis vector $\psi_1$ (Table. V) of one dimensional
representation $\Gamma_1^{(1)}$ (see Eq. (22)). In the generic system with
non-zero $D_1, D_3$, the spins are slightly canted out of the plane of
each triangle.
duce quantum fluctuations and thereby lead to ordering, in conflict with experiment. To study this possibility, we carried out spin wave calculations of the excitation gap and the quantum correction to the classical ordered moment. Indeed, we find that deep inside the $k = (0,0,0)$ phases, the quantum correction is not too large, which leads us to expect that the spin-1/2 system exhibits the classical order. However, we find very large quantum corrections elsewhere in the phase diagram, even for fairly substantial $|D_i|$. In our results, small excitation gap will lead to a large quantum correction to classical ordered moment. Decreasing the excitation gap by changing the DM vector will eventually destroy the classical ordered moment completely. In this regime, the large quantum effects invalidate the spin-wave treatment and indeed leave open the possibility of a quantum spin liquid, consistent with experiment. To further confirm the results and treatment of spin wave theory, we implemented exact diagonalization on a small cluster (six triangles with 13 spins). The excitation gap obtained from numerical data of specific heat qualitatively agrees with the prediction of spin wave theory.

The remainder of this paper is organized as follows. In Sec. III we discuss the symmetry allowed DM vector components and calculate the exchange spin Hamiltonian with a microscopic theory for both strong and weak spin-orbit coupling. In Sec. IV we discuss the classical ground states of the strong anisotropic exchange Hamiltonian obtained from Ir-O-Ir superexchange in the strong spin-orbit coupling limit. In Sec. V we will turn to look at the weak anisotropy Hamiltonian, namely, the nearest-neighbor Heisenberg model with small DM interactions. We first present the magnetic ordered state when $D_2 < 0$ then discuss the more general case when nonvanishing $D_3$ and $D_3$ components are present in the system. In Sec. VI we present a linear spin wave theory to find the zero temperature quantum correction to the magnetically ordered phase and compare with exact diagonalization. Finally, a discussion of our main results and their relevance to Na$_4$Ir$_3$O$_8$ is given in Sec. VII.

II. THERMODYNAMICS OF SPIN-ROTATIONALLY INVARIANT MAGNETIC PHASES

In this section, we discuss some apparent constraints on the low temperature susceptibility and specific heat in spin-rotationally invariant phases of matter. As described in the introduction, these constraints appear to be violated in Na$_4$Ir$_3$O$_8$, which we take as an indication of the presence of substantial spin-orbit interactions.

A. Clean system

We take spin-rotational invariance to mean the existence of global SU(2) spin symmetry. According to standard quantum mechanics, this implies that all states may be chosen as eigenstates of $S_\text{TOT}^2$ and $S_\text{TOT}^z$, where $\vec S_\text{TOT}$ is the operator for total spin. The choice of $z$ axis being arbitrary, we take it along the axis of any applied field. The effect of the field on the system is then entirely described by the term

$$\mathcal{H}_H = -H \sum_i S_i^z = -HS_\text{TOT}^z,$$

where we have absorbed the (presumed known) $g$-factor, Bohr magneton, etc. into the definition of $H$. One observes from Eq. (3) that $\mathcal{H}_H$ is diagonal in the $S_\text{TOT}^z$ basis, and thus the Hamiltonian eigenstates themselves are independent of field, and only the eigenvalues change. Focusing on the states rather than their energies, we may say that the only effect of the field upon the system in equilibrium is to modify the occupation probabilities of states. In this sense, the magnetic field is a thermodynamic perturbation, and the susceptibility is a thermodynamic quantity, determined only by the density of states. The specific heat is of course also such a thermodynamic quantity, determined from the same density of states. Thus they are connected.

Specifically, the specific heat is a measure of the full density of states for all excitations above the ground state, irrespective of their spin quantum numbers. The susceptibility, however, only counts those excitations which carry non-zero spin $S^z$ along the field. The possibility of spin-less excitations allows some independence of the two: by introducing more $S^z = 0$ states, one can increase $c_v$ arbitrarily while leaving $\chi$ unchanged. However, the converse is not true. It would seem difficult to increase $\chi$ without also contributing to $c_v$. The only way in which this can be done is to introduce states with very large $S^z$ (which then contribute a large amount to $\chi$) but very low energy (and hence do not contribute much to $c_v$). This case corresponds to a system on the verge of a ferromagnetic instability.

Without fine-tuning to such a point, we are led to expect that, in the presence of SU(2) symmetry, the Wilson ratio,

$$R = \frac{T\chi}{c_v} \quad (4)$$

should have an upper bound, corresponding to all excitations contributing both to $\chi$ and $c_v$. This can indeed be shown provided we assume the system can be described by a non-magnetic ground state and non-interacting quasiparticles characterized by a spin $S^z$ quantum number. We define the density of state $g_m^b(\epsilon)$ and $g_m^f(\epsilon)$ for boson or fermion excitations carrying spin $S^z = m$, respectively. The specific heat is

$$c_v = \partial_T \sum_m \int_0^\infty d\epsilon \left[g_m^b(\epsilon)n_b(\epsilon) + g_m^f(\epsilon)n_f(\epsilon)\right], \quad (5)$$

where

$$n_{b/f}(\epsilon) = \frac{1}{e^{\beta\epsilon} + 1}. \quad (6)$$
One finds 
\[ \frac{k_B T}{4} \sum_m \int_0^\infty dx x^2 \left[ \frac{g_m^b (k_B T x)}{\sinh^2 (x/2)} + \frac{g_m^f (k_B T x)}{\cosh^2 (x/2)} \right]. \] (7)

Now consider the susceptibility
\[ \chi = \partial_H \sum_m \int_0^\infty d\epsilon m \left[ g_m^b (\epsilon) n_b (\epsilon - H m) + g_m^f (\epsilon) n_f (\epsilon - H m) \right] \bigg|_{H=0}. \] (8)

One finds
\[ \chi = \frac{1}{4} \sum_m m^2 \int_0^\infty dx \left[ \frac{g_m^b (k_B T x)}{\sinh^2 (x/2)} + \frac{g_m^f (k_B T x)}{\cosh^2 (x/2)} \right]. \] (9)

In the low temperature limit, we may approximate \( g_m^{b/f} (k_B T x) \) by its small argument behavior, which is usually a power-law form:
\[ g_m^{b/f} (\epsilon) \sim A_m^{b/f} \epsilon^{\gamma_m^{b/f}}. \] (10)

One needs obviously \( \gamma_m^{b/f} > -1 \) for the density of states to be integrable (and hence the cumulative distribution well defined). We will encounter problems with Eq. (9) if \( \gamma_m^b \leq 1 \) for any \( m \neq 0 \). This could be fixed by the inclusion of a chemical potential, whose temperature dependence we have ignored, and as usual is necessary to avoid Bose condensation of free bosons at low \( T \) when their energy is close to zero. This effect, however, does not change any of the results, so we have excluded it for simplicity here.

Given Eq. (10), the specific heat will be controlled at low \( T \) by the minimum exponent over all \( \gamma_m^{b/f} \):
\[ \gamma_0 = \min \left\{ \gamma_m^{b/f} \right\}. \] (11)

One has
\[ c_v \sim A_0 k_B^{2+\gamma_0} T^{1+\gamma_0}, \] (12)
with some constant \( A_0 \). The susceptibility is controlled by the minimum exponent for \( m \neq 0 \):
\[ \gamma_1 = \min \left\{ \gamma_m^{b/f}; \quad m \neq 0 \right\}. \] (13)

Note that by definition, \( \gamma_0 \leq \gamma_1 \). Then
\[ \chi \sim A_1 T^{\gamma_1}. \] (14)

Then the Wilson ratio becomes
\[ R \sim R_0 T^T, \] (15)
where \( R_0 = \frac{A_1}{A_0 k_B} \) and
\[ \Upsilon = \gamma_1 - \gamma_0 \geq 0. \] (16)

Because \( \Upsilon \geq 0 \), the Wilson ratio cannot diverge on lowering \( T \), and unless \( \Upsilon = 0 \), actually vanishes as \( T \to 0 \). In defining the Wilson ratio, we have considered only the zero field specific heat. In a field, contributions from all excitations with \( m \neq 0 \) will be field dependent. So unless the \( m = 0 \) mode is dominant in \( c_v \), the specific heat should be expected to be field dependent. Conversely, field independence of the specific heat requires that the \( m = 0 \) excitations dominate \( c_v \). In this case, we have \( \Upsilon > 0 \), and the equality is not satisfied. Thus a field-independent low-temperature specific heat would be expected to correspond to a vanishing Wilson ratio as \( T \to 0 \). This makes the observed divergence of \( R \) on lowering \( T \) in Na\textsubscript{3}Ir\textsubscript{4}O\textsubscript{8} even more at odds with the theoretical expectation for an SU(2) invariant system.

A few comments are in order. First, while we have assumed power-law forms for the low energy density of states, this is not essential. We believe the lack of low temperature divergence in \( R(T) \) is very robust within the quasiparticle picture. Beyond the quasiparticle approximation, the situation is less clear, and we do not have a definitive proof of this behavior of \( R(T) \). However, we do not know of any single theoretical counter-examples in the literature for SU(2) invariant low temperature phases.

If SU(2) symmetry (or more specifically, invariance under spin rotations about the measurement axis) is broken, however, one readily and indeed almost generically observes this behavior. This is quite familiar from the case of ordered antiferromagnets in two or three dimensions. These are well-known to display a non-vanishing constant zero temperature uniform susceptibility \( \chi_0 \) and a power-law specific heat \( c_v \sim AT^d \) due to spin wave excitations, hence a Wilson ratio obeying Eq. (15) with however \( \Upsilon = 1 - d < 0 \). This arises because the ground state itself is modified continuously by the introduction of a magnetic field. Semi-classically, the magnetic field leads to a smooth canting of the antiferromagnetic moments in the field direction, linearly proportional to the applied field.

This phenomena is, however, not limited to systems with spontaneous symmetry breaking. It occurs whenever the effective Hamiltonian for the low temperature phase does not conserve the spin component along the magnetic field. As an extreme example, one may consider the case of two spin-1/2 spins coupled together by antiferromagnetic exchange and DM interaction:
\[ \mathcal{H}_2 = J \mathbf{S}_1 \cdot \mathbf{S}_2 - D \mathbf{z} \cdot \mathbf{S}_1 \times \mathbf{S}_2 - H (S_1^z + S_2^z), \] (17)
where we have chosen the DM vector along the \( z \) axis, and therefore oriented the field along \( x \) so that it couples to a non-conserved magnetization. One can readily diagonalize the Hamiltonian, and find that in zero field has a unique ground state with a gap \( \Delta = (J + \sqrt{J^2 + D^2})/2 \). Nevertheless, the susceptibility is non-zero when \( D \neq 0 \):
\[ \chi = \frac{\partial S^g_z}{\partial H} \bigg|_{H=0} = \frac{\sqrt{J^2 + D^2} - J}{J (\sqrt{J^2 + D^2} + J)}. \] (18)
Because of the gap, the specific heat of the dimer is activated at low temperature, and hence the dimer’s Wilson ratio diverges exponentially at low temperature. In general, a non-zero limit for the low temperature susceptibility is always to be expected once SU(2) symmetry breaking perturbations are taken into account. The specific heat, however, is insensitive to symmetry, and remains a true probe of low energy modes.

B. Impurity susceptibility

In Na$_4$Ir$_3$O$_8$, the introduction of non-magnetic impurities (substitution of Ti$^{4+}$ for Ir$^{4+}$) was observed to give rise to a Curie component with a reduced effective moment of $\mu_{\text{eff}} \approx (2\mu_B)/3$ per Ti. We would like to argue that a spin liquid state with such a large reduction from the moment of a free spin, $2\mu_B$, is unlikely in the absence of spin-orbit interactions, but quite likely when they are invoked.

Suppose the Hamiltonian has global SU(2) spin-rotational symmetry in the absence of an applied magnetic field. Then a spin-liquid ground state, which, by definition, does not break SU(2) symmetry, must be a spin singlet, i.e. a state of total spin $S = 0$. Its excitations can therefore be characterized by spin quantum numbers. Representations of SU(2) always have integer or half-integer spin, and in particular for all these the projection of the total spin along any field axis is a multiple of 1/2.

Now consider a single impurity. It may be a strong perturbation locally, but does not perturb the Hamiltonian far from itself. Again presuming spin-orbit can be neglected, the ground state of this system should be a spin eigenstate, though not necessarily non-zero. Nevertheless, it can be classified by a total spin which is a multiple of 1

$$\mu_B \approx \frac{2\mu_B}{3}$$

per impurity.

The caveat in this argument is the possibility of a Kondo-like effect. If the spin liquid state is gapless, then there is a possibility for an impurity moment to be “screened” by the bulk degrees of freedom. Still, the possibility of a fractional impurity moment is delicate. Most Kondo effects either completely screen the moment (as in the single channel case, leading to $\mu_{\text{eff}} = 0$) or to weaker temperature dependence of the impurity susceptibility (e.g. $\chi_{\text{imp}} \sim |\ln T|$ in the two-channel model, which has a non-trivial Kondo fixed point). Thus most types of Kondo effect do not allow for such behavior. Recently, it has been suggested that some spin liquids might sustain a critical fixed line of Kondo fixed points, connected to the free impurity fixed point. This situation can in fact lead to a renormalized Curie constant $\mu_B$. It would indeed be appealing should such an exotic possibility be realized in Na$_4$Ir$_3$O$_8$, but we should allow for simpler explanations.

As is well-known, the effective moment of ions in solids varies widely from the quantized values expected from SU(2) symmetric considerations. This is of course due to spin-orbit coupling. In general, with spin-orbit interactions present, the ground state of an impurity can be expected to be a Kramer’s singlet or a Kramer’s doublet. In the latter case, it will behave energetically (i.e. in specific heat) as a spin-1/2 spin, but will have in general a non-trivial g-tensor describing its coupling to a field. This reflects a change in the effective moment. Thus there is no “quantization” of the effective moment once spin-orbit coupling is substantial. The observed fractional effective moment in Na$_4$Ir$_3$O$_8$ is perhaps another indication in this direction.

III. SPIN-ORBIT COUPLING IN THE HYPER-KAGOMÉ LATTICE

In this section, we discuss the form of the spin-orbit modifications to the isotropic Heisenberg Hamiltonian. This is not directly calculable from semi-microscopic considerations without some assumptions about the local energetics due to crystal field splittings. Therefore we consider below a number of cases.

A. Symmetry allowed DM vector components

In several cases, we will find that the dominant effect of spin-orbit coupling is to induce Dzyaloshinskii-Moriya (DM) interactions between the nearest-neighbor spins. Therefore before attempting any calculations, it is instructive to first consider the symmetry constraints upon them. Generally, DM interactions are rather highly constrained. For instance, they are absent if there is an inversion center between the two spins in question (this is not the case in Na$_4$Ir$_3$O$_8$). The compound Na$_4$Ir$_3$O$_8$ has cubic symmetry, described by the space group P4$_3$32, and consequently has a number of point group symmetries. For our purposes, it is useful to consider a unconventional set of generators of these symmetries. Specifically, the full point group can be generated from the set of 180° rotations around a local $C_2$ axis at each site. Due to this symmetry, all the hyper-kagomé sites and bonds are equivalent. In Table 1, we list the directions of the $C_2$ axes ($\psi_1$) for every site in the unit cell (see Fig. 3 for the labeling). The $C_2$ rotational symmetries relate the DM vectors of any two bonds. That is, given the DM vector on any one hyper-kagomé bond, all others are determined. This one DM vector, however, is itself entirely unconstrained by the P4$_3$32 symmetry.

Since any single bond of the hyper-kagomé is uniquely
associated with one triangle, it is natural to adopt a local coordinate system based on this triangle to describe the DM vector’s components. We denote the component aligned with the bond $D_1$, the component normal to the triangle plane $D_2$ and the component normal to the bond but localized in the triangle plane $D_3$. Three components have been illustrated in Fig.

If we select the direction of $D_1$ component axis by assigning a direction to one bond (arrows in Fig.

C$_2$ rotation symmetry can generate the equivalent $D_1$ axis for other bonds (see Fig.

In every triangle, there is a chirality of the $D_1$ axis of three edges, which can be considered as the direction of $D_2$ axis. The cross product of $D_1$ and $D_2$ directional vector generates the direction of $D_3$ axis.

Such a parametrization may be applied not only for the hyper-kagomé lattice, but for any lattice consisting of corner-sharing triangles, such as the slightly distorted kagomé lattice of Fe/Cr-jarosites.$^{13,14,15}$ In that example, the $D_1$ component is forbidden by a mirror plane symmetry. In Na$_2$Ir$_3$O$_8$, there are as we said no constraints on the $D_1$, and we might naively expect all three components to be non-vanishing and comparable. We will investigate this by microscopic calculations below.

![Figure 3](image1.png)

**FIG. 3:** (Color online) Left: One unit cell of the hyper-kagomé lattice. The pink balls are occupied by magnetic ions, which are connected by dark black bonds. There are 12 sites in one primitive unit cell. The arrow from site $i$ to site $j$ corresponds to $D_{ij} \cdot (S_i \times S_j)$ in the Hamiltonian. We will call these arrows DM interaction path. Right: DM vector components illustrated on one triangle. $D_1$ is the component which is aligned with the DM interaction path (Left). $D_2$ is the component normal to triangle plane. The direction is decided by the chirality of bond direction. $D_3$ is the component perpendicular to the bond but in the triangle plane.

**B. Local electron energetics of Ir ion**

Before moving to the microscopic theory of spin-orbit interactions, we need to understand the electron energy levels of the Ir$^{4+}$ ions. With coordinates taken from Table. I in Ref.$^7$, two Ir$^{4+}$ and their surrounding O$^{2-}$ are drawn in Fig.$^4$. For A ion, the C$_2$ axis orients along $\frac{1}{\sqrt{2}}(1,-1,0)$. Under this symmetry operation, $x \rightarrow -y$, $y \rightarrow -x$ and $z \rightarrow -z$. Accordingly, we can group the 5$d$ orbitals into even and odd parity sectors, as shown in Table. I

![Figure 4](image2.png)

**FIG. 4:** (Color online) Ir$^{4+}$ and octahedron O$^{2-}$ environment (Thin black line). Two neighboring Ir$^{4+}$ are denoted by A and B (In orange). A/B’s six O$^{2-}$ are labelled as 1/1’, 2/2’, 3/3’, 4/4’, 5/5’ and 6/6’ (In pink), in which, 2 and 3’, 5 and 6’ label the same points. The distances between Ir$^{4+}$ and O$^{2-}$ order this way: $|A5|=|A6|=|B5’|=|B6’|>|A3|=|A4|=|B3’|=|B4’|>|A1|=|A2|=|B1’|=|B2’|$. The C$_2$ axis (thick dash line) orients along $\frac{1}{\sqrt{2}}(1,-1,0)$ at Ir$^{4+}$ A and $\frac{1}{\sqrt{2}}(0,1,1)$ at Ir$^{4+}$ B. Mapped to the ideal hyper-kagomé lattice, A and B correspond to point 4 and 8 in Fig.

| state | 5$d$ orbitals at A | 5$d$ orbitals at B | parity |
|-------|------------------|------------------|-------|
| 1)    | $xy$             | $yz$             | even  |
| 2)    | $\frac{1}{\sqrt{2}}(xz-yz)$ | $\frac{1}{\sqrt{2}}(yx+zx)$ | odd   |
| 3)    | $\frac{1}{2}(xz+yz)$           | $\frac{1}{2}(yx-zx)$           | even  |
| 4)    | $x^2-y^2$           | $y^2-z^2$           | odd   |
| 5)    | $3z^2-r^2$           | $3x^2-r^2$           | even  |

**TABLE I:** The parity sectors of 5$d$ electron orbitals by C$_2$ rotation

A large cubic crystal field splits the $e_g$ and $t_{2g}$ states. The surrounding O$^{2-}$ octahedron is slightly distorted to further split all the three $t_{2g}$ states. Ultimately no degeneracy is protected because the C$_2$ symmetry has only one dimensional irreducible representations. The energetic ordering of orbitals shown in Fig.$^4$ was determined by looking at Coulomb interaction from surrounding O$^{2-}$ and ignoring the spin-orbit interaction.
where, \( \epsilon_p \) is the creation operator of an electron on the \( 2p \) orbital with spin \( \sigma \). The energies are measured from the lowest energy level of the Ir \( 5d \) orbitals, and \( U_d \) and \( U_p \) are the Coulomb interaction constants between holes on the \( 4^{+} \) site and \( O^{2-} \) site, respectively. We assume that \( U_d \) and \( U_p \) are orbital-independent and ignore other “Kanamori parameters” in the inter-orbital exchange coupling and the pair-hopping amplitude, which should be small compared with Coulomb interaction. We also ignore the Coulomb interaction between two electrons on different intermediate \( O^{2-} \) ions. Here \( t_{jm,kn} \) denotes the transfer of an electron between the \( m \)th orbital of \( 4^{+} \) ion \( j \) and one of the \( p_n \) orbitals of the neighboring \( O^{2-} \) ions \( k \). Similarly, \( t^{\dagger}_{jm,j'm} \) is the matrix element for electron transfer between \( m \) and \( m' \) orbitals on two nearest-neighbor (in the hyper-kagomé sense) Ir atoms. \( \ell_j \) and \( s_j \) denote the orbital and spin angular momenta at the \( j \)th \( 4^{+} \) ion, respectively, and \( \lambda \) is the spin-orbit coupling constant of the \( 4^{+} \) ion.

In order to understand the electron occupation on each site, we collect the quadratic terms for each site in Eq. (22) and write down the onsite Hamiltonian as

\[
\mathcal{H}^{(i)} = \sum_{m'm'\sigma'\sigma} d^\dagger_{im\sigma} \mathcal{M}^{(i)}_{m'm\sigma'\sigma} d_{im'\sigma'}
\]

with

\[
\mathcal{M}^{(i)}_{m'm\sigma'\sigma} = \epsilon_m \delta_{\sigma\sigma'} \delta_{mm'} + \mathcal{E}_{m'm} \cdot \sigma \sigma',
\]

where \( \sigma \) is the Pauli matrix and \( \mathcal{L}_{m'm} \) is the matrix element of \( \mathbf{L} \) between the \( m \)th and \( m' \)th orbital of the \( i \)th \( 4^{+} \) ion. It is useful to note that the vector of three-dimensional matrix orbital angular momentum operators projected into the \( 2p \) manifold is actually proportional to the vector of orbital angular momentum operators for the 3 ordinary \( (p_x, p_y, p_z) \) states, but with a proportionality constant of \(-1!\). That is, suppressing the \( m, m' \) indices,

\[
\ell_i = -\mathbf{L}_i,
\]

where \( \mathbf{L} \) is a canonical angular momentum operator with \( \ell^2 = \ell (\ell + 1) = 2 \). This effectively makes the spin-orbit coupling term directly analogous to the familiar one from an isolated atom with spherical symmetry in a \( p \) shell, but with the sign of the spin-orbit coupling reversed.

### D. Strong and weak spin orbit limits

Obviously the nature of the “spin” itself (i.e. the Kramer’s doublet ground state of the single whole in this multiplet) is crucially dependent upon the strength of the spin-orbit interaction, relative to the non-cubic splittings \( \epsilon_3 - \epsilon_2, \epsilon_3 - \epsilon_1 \). This determines the nature of the wavefunctions of the Kramer’s pair, for instance the degree to which the “spin” carries true electron spin angular
moment or instead orbital angular momentum. This is more fundamental than the exchange interaction, so we consider it first.

1. Strong spin orbit

In the strong spin-orbit limit, we can to a first approximation ignore the non-cubic splittings, and we have simply

\[ \mathcal{M}^{(i)} = \lambda L_i \cdot s_i = -\lambda L_i \cdot s_i. \]  

(26)

This is of course diagonalized by constructing eigenstates of the “total angular momentum”

\[ J_i = L_i + s_i. \]  

(27)

Because of the minus sign in Eq. (26), the highest energy doublet is simply the \( j = 1/2 \) Kramer’s pair. This describes the wavefunction of the half-filled orbital. It is natural to define the effective spin operator in this case as

\[ S_i = J_i. \]  

(28)

Clearly it is a strong mix of orbital and spin components. According to the Wigner-Eckart theorem, the matrix elements of \( s_i \), \( L_i \), and \( J_i \) are all proportional. This enables one, with a little Clebsch-Gordan algebra, to arrive at an expression for the magnetic moment operator (in the \( j = 1/2 \) manifold)

\[ M_i = -\mu_B (L_i + 2s_i) = +2\mu_B S_i, \]  

(29)

where \( \mu_B \) is the Bohr magneton. Interestingly, this is the same magnitude but opposite sign as for a free electron! It will of course suffer corrections perturbative in \( (\epsilon_i - \epsilon_j)/\lambda \), as one moves away from the strong spin orbit limit.

2. Weak spin orbit

Now consider the weak spin orbit limit. In this case, for \( \lambda = 0 \), the half-filled doublet is simply the \( m = 3 \) orbital, with two possible “true” spin orientations. Thus we approximately have

\[ S_i \approx s_i + \mathcal{O}(\lambda/(\epsilon_i - \epsilon_j)). \]  

(30)

Now there is essentially no orbital angular momentum component to the spin (\( L_i \approx 0 \)), and one obtains

\[ M_i = -2\mu_B S_i (1 + \mathcal{O}(\lambda/|\epsilon_{1,2} - \epsilon_3|)). \]  

(31)

Note the important sign difference from Eq. (29). This is the most fundamental physical distinction between the weak and strong spin-orbit limits. However, the magnitude of the proportionality between the magnetization and spin – the \( g \)-factor – is the same in both cases. This means that the simplest experimental measure, the Curie susceptibility, cannot distinguish the two possibilities. We will consider both cases below.

E. General exchange formulation

We now turn to the exchange calculations. Let us consider the general case first. We must deal with \( \mathcal{M}^{(i)} \), which is a \( 6 \times 6 \) matrix. Diagonalize \( \mathcal{M}^{(i)} \) so that \( \mathcal{M}^{(i)} = T^{(i)} \mathcal{E} T^{(i)} \). Here, \( \mathcal{E} \) is a site-independent eigenvalue matrix, and \( T^{(i)} \) is a unitary eigenvector matrix. \( \mathcal{M}^{(i)} \) has three different eigenvalues \( \mathcal{E}_1 \), \( \mathcal{E}_2 \), and \( \mathcal{E}_3 \), each has a two-fold degeneracy due to Kramers’ degenerancy theorem. The effective spin operator \( S_i \) will be defined to act in this doublet. In the strong and weak spin-orbit limits, we have explicitly Eq. (28) and Eq. (30), respectively. Furthermore, we define a new set of electron creation and annihilation operators

\[ a_{i m \sigma} = T^{(i)}_{m \sigma, m' \sigma'} d_{i m' \sigma'}. \]  

(32)

with \( a_{i m \sigma} \) annihilates an electron on the \( \mathcal{E}_m \) state with spin \( \sigma \) at site \( i \).

Without losing any generality, we assume that \( \mathcal{E}_3 > \mathcal{E}_{1,2} \), then \( \mathcal{E}_{1,2} \) states are fully occupied and \( \mathcal{E}_3 \) state is half-occupied, leading to a total spin-1/2 at every site. Accordingly, the magnetic momentum operator \( (M_i = -\mu_B (L_i + 2s_i) \) at each site should be projected onto the Kramers’ doublet ground states:

\[ \frac{M_i}{\mu_B} = -P_i \sum_{m \sigma \alpha \beta} d^\dagger_{im \sigma} (\epsilon_{im} \delta_{m \alpha \beta} + \delta_{im} \sigma_{\alpha \beta}) d_{im \sigma} P_i \]

\[ = -G^{(i)}_{3, \sigma, \beta} \sigma_{\beta \alpha} \cdot S_i \]

(33)

with \( \sigma \) the vector of Pauli matrices. Also, \( G^{(i)}_{\sigma, \alpha, \beta} \) and the effective spin operator \( S_i \) are defined as

\[ G^{(i)}_{\sigma, \alpha, \beta} = \sum_{m \sigma \alpha \beta} T^{(i)}_{\sigma, m \sigma} (\epsilon_{im} \delta_{m \alpha \beta} + \delta_{im} \sigma_{\alpha \beta}) T^{(i)*}_{\beta, m \beta}, \]

\[ S_i = \sum_{\alpha, \beta} \frac{1}{2} a_{i 3 \alpha}^\dagger \sigma_{\alpha \beta} a_{i 3 \beta}, \]

(34)

and \( P_i \) is the ground state projection operator:

\[ P_i = a_{i 3 \uparrow} | \phi \rangle \langle \phi | a_{i 3 \uparrow}^\dagger + a_{i 3 \downarrow} | \phi \rangle \langle \phi | a_{i 3 \downarrow}^\dagger. \]  

(35)

Here \( | \phi \rangle \) is the \( \mathcal{E}_{1,2,3} \) fully-occupied state. In the last step Eq. (33), \( \sum_{\sigma} a_{i 3 \sigma}^\dagger a_{i 3 \sigma} = 1 \) has been used.

Let’s go back to Eq. (22), and express the microscopic Hamiltonian in terms of \( a_{j m \sigma} \) and \( a_{j m \sigma}^\dagger \). Given the Hamiltonian in Eq. (19), which includes the largest Coulomb energy \( U \) but neglects the smaller Hunds-rule exchange coupling between electrons in different orbitals on the same atom (and other similar interactions), only hopping through the half-filled orbital contributes to the super-exchange interaction. This is in accord with the “Goodenough-Kanamori” rules, which state that the exchange coupling contributed from a half-occupied orbital and a fully-occupied orbitals is much weaker than the one from two half-occupied orbitals. Thus, we only need
to focus on the hopping between the $E_3$ orbitals, as half-occupied orbital. The microscopic Hamiltonian is written as

\begin{align}
\mathcal{H} &= \sum_{kn\sigma} \epsilon_{p_k} p_{kn\sigma}^\dagger p_{kn\sigma} + \frac{U_p}{2} \sum_{kn'\sigma'} \bar{p}_{kn\sigma}^\dagger p_{kn'\sigma'}^\dagger p_{kn'\sigma'} p_{kn\sigma} + \sum_{jm\sigma} \epsilon_{m} a_{jm\sigma}^\dagger a_{jm\sigma} + \frac{U_d}{2} \sum_{jm'\sigma'\alpha} a_{jm\sigma}^\dagger a_{jm'\sigma'\alpha}^\dagger a_{jm'\sigma'\alpha} a_{jm\sigma} \\
&\quad + \sum_{jk(j)\alpha\beta} \left[ (\hat{t}_{j3,kn} \delta_{\alpha\beta} + C_{j,kn} \cdot \sigma_{\alpha\beta}) a_{j3a}^\dagger p_{kn\beta} + H.c. \right] + \sum_{(jj')\alpha\beta} \left[ (\hat{t}_{j3,j'3} \delta_{\alpha\beta} + C_{j,j'3}^d \cdot \sigma_{\alpha\beta}) a_{j3a}^\dagger a_{j'3\beta} + H.c. \right],
\end{align}

with

\begin{align}
\hat{t}_{j3,kn} &= \sum_{m\sigma} \frac{1}{2} \hat{t}_{jm,kn} T^{(j)}_{3\sigma,m\sigma}, \\
C_{j,kn} &= \sum_{m,\alpha \beta} \frac{1}{2} \hat{t}_{jm,kn} T^{(j)}_{3\sigma,m\beta} \sigma_{\beta \alpha},
\end{align}

and

\begin{align}
\hat{t}_{j3,j'3}^d &= \sum_{mm',\alpha \beta} \frac{1}{2} \hat{t}_{jm,j'm} T^{(j)}_{3\sigma,m\sigma} T^{(j')}_{m'\sigma,3\alpha} \sigma_{\beta \alpha}, \\
C_{j,j'3}^d &= \sum_{mm',\alpha \beta} \frac{1}{2} \hat{t}_{jm,j'm} T^{(j)}_{3\sigma,m\beta} T^{(j')}_{m'\sigma,3\alpha} \sigma_{\beta \alpha}.
\end{align}

where $\sigma$ is vector of the three Pauli matrices. Now we may follow the standard perturbative treatment of superexchange. We consider separately the superexchange through the intermediate $O^{2-}$ ions, and the direct exchange contributions.

1. Superexchange through oxygen ions

In this case the leading contribution is fourth order in hopping, i.e. a result of fourth order degenerate perturbation theory. We must include four “hops” between Ir$^{4+}$ and $O^{2-}$ ions, which consist of “hops” described by spin-isotropic $\hat{t}$ matrix elements, and “hops” given by anisotropic $C$ matrix elements. One thereby obtains the exchange Hamiltonian as

\begin{align}
\mathcal{H}_{ex} &= \sum_{\langle ij \rangle} [ J S_i \cdot S_j + D_{ij} \cdot (S_i \times S_j) + S_i \cdot \overrightarrow{T}_{ij} \cdot S_j ]
\end{align}

with the first two terms the Heisenberg and DM interactions precisely as in Eq. (2), and the third term the anisotropic exchange. The explicit formulae for the coupling constants are:

\begin{align}
J &= 4 \sum_{kn,k'n'} s_{ij,kn,k'n'} s_{ji,k'n'} \\
D_{ij} &= -4 \hat{t} \sum_{kn,k'n'} (\mathbf{v}_{ij,kn,k'n'} - s_{ij,kn,k'n'} \mathbf{v}_{ji,k'n'}) \\
\overrightarrow{T}_{ij} &= 4 \sum_{kn,k'n'} [(\mathbf{v}_{ij,kn,k'n'} - s_{ij,kn,k'n'} \mathbf{v}_{ji,k'n'}) - \overrightarrow{T} (s_{ij,kn,k'n'} \mathbf{v}_{ji,k'n'})].
\end{align}

The vector with arrow $\leftarrow$ or $\rightarrow$ indicates that inner product is taken with the spin operator put in the direction of the arrow. $\overrightarrow{T}$ is a $3 \times 3$ unit matrix. $s_{ij,kn}$, $\mathbf{v}_{ij,kn}$ and $g_{kn,k'n'}$ are given by

\begin{align}
s_{ij,kn} &= \hat{t}_{i3,kn} \hat{t}_{kn,i3} + C_{i,kn} \cdot C_{kn,j} \\
\mathbf{v}_{ij,kn} &= C_{i,kn} \hat{t}_{kn,i3} + \hat{t}_{i3,kn} C_{kn,j} + \hat{t} (C_{i,kn} \times C_{kn,j}) \\
g_{kn,k'n'} &= \frac{(1 - \frac{1}{2} \delta_{kk'} \delta_{nn'}) (\hat{t}_{pn} - \hat{t}_{pn'})^2}{\hat{t}_{pn} + \hat{t}_{pn'} + U_p \delta_{kk'}} + (\hat{t}_{pn} \hat{t}_{pn'} U_d)^{-1}
\end{align}

with $\hat{t}_{pn} = E_3 - \epsilon_{pn} + 5(U_d - U_p)$. In the following subsections, we will try to estimate these exchange couplings in both the strong and weak spin-orbit interaction cases.
2. Direct exchange

Here we require only second order perturbation theory in the direct matrix elements. One obtains the results: \( J = \frac{2|t_{ij}|^2}{U_d} \), \( D_{ij} = \frac{4i}{U_d} (C_{ij}^{d\dagger} j_{ji} - j_{ij} C_{ji}^{d\dagger}) \), \( \Gamma_{ij} = \frac{4}{U_d} (\overline{C}_{ij}^d C_{ji}^d + \overline{C}_{ij}^d C_{ji}^d - \overline{1}(C_{ij}^d \cdot C_{ji}^d)) \).

F. Strong spin-orbit interaction

As discussed above in Sec. III D 1, in the strong spin-orbit limit, \( \lambda \gg |\epsilon_{1,2} - \epsilon_3| \), one can obtain effective total angular momentum eigenstates with \( j = 1/2 \). Choosing Eq. (28), and rewriting the corresponding eigenstates in the canonical \( t_{2g} \) basis, Eq. (32) becomes

\[
a_{i31} = \frac{1}{\sqrt{3}} \left( \langle (-i) d_{i,xz} + d_{i,yz} + d_{i,xy} \rangle \right) \quad (49)
\]

\[
a_{i31} = \frac{1}{\sqrt{3}} \left( \langle i d_{i,xz} + d_{i,yz} - d_{i,xy} \rangle \right), \quad (50)
\]
in which, we have expressed \( a_{i31}/a_{i31} \) in terms of the \( t_{2g} \) annihilation operator to avoid the position dependence of the coefficients.

1. Supercoupling through oxygen ions

The complicated expression of Eq. (42) requires simplification if we want to have a quantitative understanding of the exchange coupling. However, some information can be immediately obtained from Eq. (40), in particular that all \( t_{ik,j,kn} = 0 \), which makes \( J, D_{ij} \) and \( \Gamma_{ij} \) only remain terms with \( C_{i,kn} \). To simplify further, we need some explicit form for the transfer integrals \( t_{jm,kn} \). Hence, we will make further approximation that the surrounding octahedra of Ir\(^{4+}\) are perfect so that we can apply the cubic symmetry to find out the nonvanishing transfer integrals and also the relation between them, which is listed in Table II for Ir\(^{4+}\) A and B in Fig. 3. Deviations from these forms should presumably be small, since the non-cubic distortion is.

*Based on the transfer integrals listed in Table III we evaluate the exchange coupling constant \( J \) and \( \Gamma_{AB} \). For bond AB, collecting non-zero coupling constants (actually \( J = 0 \), \( D_{AB} = 0 \)), we obtain

\[
\mathcal{H}_{AB} = -JS_A^x S_B^x + JS_A^y S_B^y + JS_A^z S_B^z \quad (51)
\]

with

\[
J = \frac{4}{9}|t|^4 (2g_{2p_x,5p_x} - 2g_{2p_x,2p_x} - g_{5p_x,5p_x}) \quad (52)
\]

Since from Eq. (40) \( g_{2p_x,5p_x} > g_{2p_x,2p_x}, g_{5p_x,5p_x} \), then \( J > 0 \). Thus we find ferromagnetic interaction between the \( x \) components and antiferromagnetic interactions between \( y \) and \( z \) components along this link. This corresponds to the form in Eq. (1) of the Introduction, with \( \epsilon_{ij} = \epsilon_{ij} = \epsilon_{ij} = -\epsilon_{ij} = 1 \) for this link.

Because all links are equivalent by point group operations, we can deduce the exchange interactions of all other bonds by symmetry. The sites A and B correspond to point 4 and 8 in our notation in Fig. 3. The result is that the exchange interactions on each bond are ferromagnetic between one component, and antiferromagnetic between the other two. These principle components are always along \( x, y, \) or \( z \). We will call a bond in which the \( x \) component is ferromagnetic a “type \( x \) bond”, and similarly for \( y, z \). The type of each bond is listed in Table III. This Hamiltonian breaks spin-rotational symmetry strongly. A simple rule can be used to characterize the Hamiltonian of a given bond: if bond \((ij)\) is located in the \( y-z \) plane, then the bond is type \( x \) bond and has type \( x \) exchange Hamiltonian; if it is located in the \( x-z \) plane, then the bond is type \( y \) bond and has type \( y \) exchange Hamiltonian. As a result, the three bonds in every triangle (See Fig. 3) have different exchange Hamiltonian. The ground states of this
Hamiltonian will be studied in Sec. \[\text{LV}\]

2. Direct exchange

We consider two Ir atoms A and B, connected by a line along the (0, 1, -1) direction. There are two principle overlaps. The largest, whose magnitude we denote \(t_1^d\), is between the \(yz\) orbitals at each atom – this is a \(\sigma\)-bond. A secondary overlap, of magnitude \(t_2^d\), occurs between orbitals of the form \(xy - xz\) at each site, which corresponds to \(\pi\) bonding. All other overlaps are expected to be negligible or zero. This leads remarkably to

\[
t_{j,j'}^d = (t_1^d + t_2^d)/3, \quad C_{jj'} = 0. \tag{53}
\]

The result appears isotropic, despite the strong spin-orbit interactions! As a consequence, one obtains only Heisenberg exchange, and \(D_{ij} = \mathbf{T} = 0\). It is remarkable that one finds apparent isotropy even though the spin itself contains a substantial orbital component. As seen from the superexchange calculation above, this is by no means guaranteed.

The first corrections to the strong spin orbit limit are linear in the non-cubic splittings, and produce corrections to the Heisenberg model. This occurs by a contribution to \(C_{jj'}\) of \(\mathcal{O}(|\epsilon_3 - \epsilon_{1,2}|/\lambda)\). The leading spin-orbit corrections to the exchange Hamiltonian are then of the DM form, and constrained by symmetry according to considerations of Sec. \[\text{III A}\]

G. Weak spin-orbit interaction

In this part, we are going to look at the weak spin-orbit interaction limit, \(\lambda \ll |\epsilon_1 - \epsilon_2|, |\epsilon_2 - \epsilon_3|\). This is the regime which was often studied in literature. Standard perturbation treatment can be applied, which yields

\[
a_{jms} = d_{jms} + \frac{\lambda}{2} \sum_{m's'} \frac{\ell_{jmm'}}{\epsilon_m - \epsilon_{m'}} d_{jm's'} \tag{54}
\]

with \(\ell_{jmm'}\) introduced previously in Eq. \[\text{23}\]. Using this in Eq. \[\text{33}\] reproduces Eq. \[\text{31}\].

Keeping the exchange coupling constant to the linear order of \(\lambda/|\epsilon_{1,2}-\epsilon_3|\) we can ignore \(\mathbf{T}_{ij}\), as it is of \(\mathcal{O}((\lambda/|\epsilon_{1,2}-\epsilon_3|)^2)\) compared with \(J\), thus we only need to evaluate \(J\) and \(D_{ij}\).

1. Supercexchange through oxygen ions

Since all the bonds and sites are equivalent, we can take \(ij\) as bond BA in Fig. 4. Denote the unit directional vectors for \(D_1\), \(D_2\) and \(D_3\) as \(\mathbf{e}_1\), \(\mathbf{e}_2\) and \(\mathbf{e}_3\). Ignoring the small effect of lattice distortion on these vectors and taking the corresponding values for an ideal hyper-kagomé lattice, we will get \(\mathbf{e}_1 = \frac{1}{\sqrt{2}}(0, -1, 1), \mathbf{e}_2 = \frac{1}{\sqrt{3}}(-1, 1, 1)\) and \(\mathbf{e}_3 = -\frac{1}{\sqrt{6}}(2, 1, 1)\). Making the same approximation as in previous section, we can evaluate the exchange coupling constants:

\[
J = |t| \frac{1}{2} g_{2p_x, 2p_z} \tag{55}
\]

\[
D_1 = D_{BA} \cdot \mathbf{e}_1 = \frac{\lambda}{\sqrt{2}} |t| \left( g_{2p_x, 2p_z} \frac{e_2 - e_3}{e_1 - e_3} - g_{2p_z, 2p_x} \frac{e_1 - e_3}{e_1 - e_3} \right) \tag{56}
\]

\[
D_2 = D_{BA} \cdot \mathbf{e}_2 = \frac{2\lambda}{\sqrt{3}} |t| \left( g_{2p_x, 2p_z} \frac{e_1 - e_3}{e_1 - e_3} - g_{2p_0, 2p_x} \frac{e_2 - e_3}{e_1 - e_3} \right) \tag{57}
\]

\[
D_3 = D_{BA} \cdot \mathbf{e}_3 = \frac{\lambda}{\sqrt{6}} |t| \left( 3 g_{2p_x, 2p_z} \frac{e_2 - e_3}{e_1 - e_3} - g_{2p_0, 2p_x} \frac{e_1 - e_3}{e_1 - e_3} \right) \tag{58}
\]

The three DM components we obtained in Eq. \[\text{55}\] are not independent from each other. That’s because we render some symmetry to the system by the transfer integrals. Hence, we will still consider all three components to be independent. As discussed in Sec. \[\text{III B}\] \(\epsilon_3 > \epsilon_2 > \epsilon_1\), additionally, we have \(g_{nm, n'm'} > 0\), then we can confer from Eq. \[\text{55}\] that \(J > 0, D_2 < 0, D_3\) is probably positive due to a factor of 3 in front of \(g_{2p_x, 2p_z}\) and the smaller denominator of the positive term than the negative term, and \(|D_1|\) is probably small compared to \(|D_2|\) due to the cancellation of positive and negative terms.

Using Eqs. \[\text{55}\] and ignoring its specific expression, we may estimate the strength of DM interactions crudely. Then, we estimate crudely

\[
|D_i|/J \approx \lambda/|\epsilon_{1,2} - \epsilon_3|. \tag{56}
\]

Since we assume \(\lambda \ll |\epsilon_{1,2} - \epsilon_3|\) otherwise the perturbative treatment doesn’t hold. We estimate the spin-orbit coupling \(\lambda \approx 0.4eV\), taken from Refs.20,21 (although the reference is not directly relevant to Na$_4$Ir$_3$O$_8$, we can use their spin-orbit coupling as an approximation). The splitting of the \(t_{2g}\) states due to the non-cubic environment which determines \(\epsilon_{1,2} - \epsilon_3\) is difficult to estimate. As mentioned in Refs.22, the \(\epsilon_{g} - t_{2g}\) splitting for [Ir(NH$_3$)$_6$]$^{3+}$ is about 5eV. However, if we seek a lower bound on \(|D_1|\) we can make due with what is probably an over-estimate of this splitting. Taking \(|\epsilon_{1,2} - \epsilon_3| \sim 5 - 10eV\) is surely in that category, and we therefore find \(|D_1|/J \gtrsim 0.04 - 0.1\).
2. Direct exchange

One can similarly evaluate the induced DM terms at first order in the spin-orbit coupling in the case of direct exchange. One again obtains a $\mathbf{D}$-vector consistent with the symmetry considerations in Sec. IIIA.

IV. CLASSICAL GROUND STATES OF THE STRONG EXCHANGE ANISOTROPY HAMILTONIAN

In this Section, we will consider the ground states of the strongly anisotropic Hamiltonian, Eq. (1), obtained in the strong spin-orbit limit from the Ir-O-Ir superexchange mechanism.

Take the triangle $\Delta 123$ in Fig. 3 for example. Bond (1, 2) is of bond type $x$; bond (1, 3) is of bond type $y$; bond (2, 3) is of bond type $z$. Then for bond (2, 3), the Hamiltonian is

$$\mathcal{H}_{(2,3)} = J(S_2^z S_3^z + S_2^y S_3^y - S_2^z S_3^z). \quad (57)$$

Clearly $\mathcal{H}_{2,3}$ is minimized if

$$S_2^z = S_3^z \quad (58)$$

$$S_2^y = -S_3^y. \quad (59)$$

In general, for each bond, the energy is minimized if the ferromagnetically interacting components of the two spins involved are parallel, and the antiferromagnetically interacting components are antiparallel. We can search for unfrustrated ground states by demanding this on every bond. Fixing one spin, its neighbors are therefore determined, and from them further neighbors, etc. It is straightforward to verify that in this procedure no contradictions are encountered despite the presence of loops on the lattice. In this way all classical ground states are determined from the choice of a single initial spin. Thus the Hamiltonian is unfrustrated, and we have found its full set of classical ground states. Mathematically, we can write the full spin configuration as

$$S_i = s^x V_{1,i} + s^y V_{2,i} + s^z V_{3,i}, \quad (60)$$

where $s = (s^x, s^y, s^z)$ is a unit vector, and $V_{a,i}$ is the vector $V_a$ corresponding to the $i$th spin in Table. IV. We see that the ground states are parametrized by two continuous parameters – the angles specifying the orientation of the initial spin, or of $s$. This is actually an accidental degeneracy, since the system has only discrete space-group symmetries, but it is very small. Still, it should be reduced to a discrete degeneracy by perturbations such as quantum or thermal fluctuations, or additional interactions, which will select a subset of these states.

| $V_1$ | $V_2$ | $V_3$ |
|-------|-------|-------|
| 1     | $-1$  | 0     |
| 2     | -1    | 0 0 1 |
| 3     | 1 0   | 0 -1 0|
| 4     | -1    | 0 0 1 |
| 5     | 1 0   | 0 1 0 |
| 6     | -1    | 0 1 0 |
| 7     | 1 0   | 0 0 1 |
| 8     | -1    | 0 0 1 |
| 9     | 1 0   | 0 1 0 |
| 10    | 1 0   | 0 0 1 |
| 11    | -1    | 0 0 1 |
| 12    | 1 0   | 0 0 1 |

TABLE IV: The basis vectors for the ground state spin configurations of the strong spin-orbit Hamiltonian.

V. CLASSICAL GROUND STATES INDUCED BY DZYALOSHINSKII-MORIYA INTERACTIONS

A. Order due to second component only

In Sec. III we found that the direction of the DM vector for a single bond is arbitrary, i.e. not determined from symmetry considerations, and not calculable from microscopic theory without a more detailed understanding of matrix elements than we have at present. A general solution for the ground state with such an arbitrary DM vector is quite difficult, because different triangles in the hyper-kagomé lattice are located in different planes. In this subsection, we will consider the special case in which the DM vector is normal to the triangular plane, i.e. $D_1 = D_3 = 0$ (see Fig. 3). This is a helpful starting point for the more general case which we will address thereafter.

As in the case of the nearest-neighbor kagomé antiferromagnet, a nonvanishing $D_2$ (here, by $D_2$ we mean the component of DM vector which is normal to the kagomé plane) selects coplanar ground states with $120^\circ$ spin orientations on each triangle. These are the only configurations in which the Heisenberg interactions on a triangle are minimized (i.e. the total sum of spins on a triangle is zero) and the DM interaction is minimized at the same time. In the kagome lattice, however, the coplanar ground state manifold is highly degenerate, since rotating the spins in a single hexagon about the normal axis of the kagomé plane by arbitrary angle generates a new ground state from any other one. In contrast, for the hyper-kagomé lattice, the non-coplanar nature of different triangles reduces the degeneracy to just a pair of Kramer’s degenerate (reversed) states. One of them is drawn in Fig. 2 (the other one is generated by reversing all the spin directions. The chirality of the hyper-kagomé
lattice makes this state a ground state only for \( D_2 < 0 \). With the other sign of \( D_2 \), the DM and Heisenberg interactions cannot be simultaneously satisfied. We will call these states uncanted “windmill” states – see Fig. 6.

To see that the uncanted windmill states are the only classical ground states, see Fig. 6. Starting from triangle ABS – denoted \( \Delta ABC \) – a nonvanishing \( D_2 \) component prefers a coplanar spin configuration, which requires that spin A, B, C should lie in the \( \Delta ABC \) plane and at 120 angles as dictated by the Heisenberg interaction. The same applies to \( \Delta CDE \). However, \( \Delta ABC \) and \( \Delta CDE \) are not in the same plane, which confines the spin orientation of site C to be aligned with the intersection line of \( \Delta ABC \) and \( \Delta CDE \). We apply this result to all spins, and the Heisenberg interaction will select two states, which simultaneously minimize the DM interaction with \( D_2 < 0 \). The magnetic unit cell of the windmill state is the same as the chemical cell.

The result that \( D_2 < 0 \) completely removes the massive but accidental ground state degeneracy of the hyperkagomé is quite dramatic. A classical antiferromagnet with this interaction will clearly order at low temperature, and the drastic reduction in degeneracy suggests that even for a quantum system, the suppression of quantum fluctuations by \( D_2 \) may be large. Before turning to this, we continue with the analysis of classical ordering in the remainder of this section.

### B. Magnetic representational analysis of space group

Representational analysis of the magnetic space group has proven to be a useful tool to extract information about low temperature ordered phases using lattice symmetry.\(^{23,24,25,26}\). The idea is to consider those types of magnetic order which can be reached by a continuous transition from the paramagnetic state, which has the full space group symmetry. Though there is no a priori reason why the ground state configuration need be of this type, this is a convenient way to generate candidate magnetically ordered states. In principle, one may iterate this procedure to generate lower temperature ordered states, generating all possible ordered phases.

The operators of the space group act on both the position of the magnetic ion and on the components of the spin vectors. The combination of these two results are described by the magnetic representation \( \Gamma \). The magnetic representation for a particular site can be decomposed into contributions from the irreducible representations of the little group

\[
\Gamma = \sum_\mu n_\mu \Gamma_\mu .
\]  

For Na\(_2\)Ir\(_3\)O\(_8\), the space group is \( P4_132 \) (although it can also be \( P4_332 \), the results should be equivalent),\(^2\) and the Ir\(^{4+}\) ions sit on the 12d. Here, we only focus the simplest case when the propagation vector \( \vec{k} = (0, 0, 0) \). A program called “SARAh”\(^24\) is used to do the decomposition of magnetic representation

\[
\Gamma = 1\Gamma_1^{(1)} + 2\Gamma_2^{(1)} + 3\Gamma_3^{(2)} + 3\Gamma_4^{(3)} + 3\Gamma_5^{(3)} ,
\]  

in which, the superindex represents the dimension of the irreducible representations, and the subindex counts the irreducible representation.

Landau theory requires that only one representation can be involved in a critical transition, and so with this constraint there are only five possible magnetic structure for \( \vec{k} = (0, 0, 0) \). Even within this decomposition and Landau theory constraints, for certain representations \((\Gamma_3, \Gamma_4, \Gamma_5)\), there still remain a lot of degrees of freedom because of the multiple basis elements in these 3-dimensional representations. For simplicity, we only discuss the one dimensional representation \( \Gamma_1, \Gamma_2 \). The basis vectors for these two representations calculated are given in Table.\(^V\)

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**TABLE V: The basis vectors of one dimensional irreducible group representations of the space group \( P4_132 \) appearing in the magnetic representation with \( \vec{k} = (0, 0, 0) \).**

| Basis vector | \( \psi_1 \) | \( \psi_2 \) | \( \psi_3 \) |
|--------------|-------------|-------------|-------------|
| \( \Gamma_1^{(1)} \) | \( S_x \) | \( S_y \) | \( S_z \) |
| \( \Gamma_2^{(1)} \) | \( 0 \) | \( 0 \) | \(-1 \) |
| \( \Gamma_3^{(2)} \) | \( 1 \) | \( 1 \) | \( 0 \) |
| \( \Gamma_4^{(3)} \) | \( -1 \) | \( 0 \) | \( 0 \) |
| \( \Gamma_5^{(3)} \) | \( 0 \) | \( 1 \) | \( 0 \) |

---

**FIG. 6:** (Color online) Illustration of spin direction at shared corner of two neighboring triangles. Black arrows indicate the DM interaction path. B, C and E are in the same line.
The physical interpretation of these representations is as follows. The basis vector \( \psi_1 \) is nothing but the \( C_2 \) rotation axis at every magnetic ion. The basis vector \( \psi_2 \) gives the spin directions of classical uncanted windmill state discussed above (see Fig. 2). The third basis vector \( \psi_3 \) may be obtained as the axis which is normal to both \( C_2 \) axis and the spin direction in \( \psi_2 \) (see Fig. 2). Note that these three basis vectors at each site form an orthonormal basis for the spin coordinates.

Evidently \( \Gamma_2 \) is related to the DM interaction, at least to the \( D_2 \) component. But what about \( D_1 \) and \( D_3 \)? Let us consider following situation. Starting from an ordered ground state of classical uncanted windmill state discussed above (see Fig. 2). The third basis vector \( \psi_3 \) is nothing but the \( C_2 \) rotation axis at every magnetic ion. The basis vector \( \psi_2 \) gives the spin directions of classical uncanted windmill state. Regardless, it is also interesting to note that because \( D_1 \), \( D_3 \) are all present in the system, is a linear superposition of basis vectors \( \psi_2 \) and \( \psi_3 \):

\[
\mathbf{S}_i = \sqrt{1 - (a^1_i)^2} \epsilon^1_i + (a^2_i)^3 e^2_i + (a^3_i)^3 e^3_i ,
\]

where \( \epsilon_1 \), \( \epsilon_2 \) and \( \epsilon_3 \) are simply the three orthogonal unit vectors given by basis \( \psi_1 \), \( \psi_2 \) and \( \psi_3 \), and \( a^1_i \) and \( a^3_i \) are small corrections to the ordered ground state due to the introduction of an infinitesimal \( D_1 \) (or \( D_3 \)) component. We plug Eq. (63) into the Hamiltonian, and expand to the 2\( nd \) order in \( a^1_i \), \( a^3_i \) and \( D_1 \) (or \( D_3 \)). To linear order \( a^3_i \) vanishes. Thus the ground state spin configuration with negative \( D_2 \) and an infinitesimal \( D_1 \) or \( D_3 \) component is related to \( \psi_2 \) and \( \psi_3 \). The irreducible representation \( \Gamma_2^{(1)} \) is relevant to the magnetic structure when the DM interaction is present.

Now, we proceed by assuming that the ground state configuration \( \psi \) of the more general case, when \( D_1 \), \( D_2 \) and \( D_3 \) are all present in the system, is a linear superposition of basis vectors \( \psi_2 \) and \( \psi_3 \):

\[
\mathbf{S}_i = \cos x \psi_{2,i} + \sin x \psi_{3,i} ,
\]

where \( \psi_{a,i} \) is the vector \( \psi_a \) corresponding to the \( i^{th} \) spin in Table III. Evaluating Eq. (2) for spin configurations of this form gives

\[
\mathcal{H}/N = 2(-3\sqrt{2}D_1 + 5\sqrt{3}D_2 - \sqrt{6}D_3 - 3J) + 2\sqrt{3}[(\sqrt{6}D_1 + D_2 + \sqrt{2}D_3 - \sqrt{3}J) \cos (2x) - (\sqrt{3}D_1 - 3D_3) \sin (2x)] ,
\]

where \( N \) is the number of unit cells in the lattice, not the number of spins (which is equal to 12\( N \)). Minimizing the Hamiltonian with respect to \( x \), we can find the canting angle \( x \) is given by

\[
\cos (2x) = -\frac{\sqrt{3}J + \sqrt{6}D_1 + D_2 + \sqrt{2}D_3}{W} \]

\[
\sin (2x) = \frac{\sqrt{3}D_1 - 3D_3}{W} ,
\]

where we have defined

\[
W = \sqrt{(\sqrt{6}D_1 + D_2 + \sqrt{2}D_3 - \sqrt{3}J)^2 + 3(D_1 - \sqrt{3}D_3)^2} \]

for convenience.

Fig. 3 is an example of this canted state when \( D_1 = 0.1J \), \( D_2 = -0.04J \) and \( D_3 = 0 \). We only plotted the spin configuration of \( \Delta 123 \) and \( \Delta 345 \) in Fig. 3. Because these states are obtained by smoothly introducing a \( \psi_3 \) component into the uncanted windmill states found in Sec. V, we will call this state a canting windmill state. The canting moment disappears not only when \( D_1 = D_3 = 0 \), but also for \( D_1 = \sqrt{3}D_3 \), at which point it degenerates into the uncanted windmill state. Regardless, it is also interesting to note that because \( D_1, D_3 \ll J \), from Eq. (67) the canting moment is much smaller than the coplanar component, which indicates the dominance of the coplanar spin configurations. Similar features have been found in other studies.

In the above treatment, we have assumed the ansatz in Eq. (64), which is not guaranteed to find the global minimum energy state, and gives no guidance as to where this
form of the ground state breaks down. In next section, we will consider this question from a different point of view.

C. Mean field spherical model

In this subsection we approach the general problem of finding classical ground states of the Hamiltonian from a different point of view. The problem is difficult because in addition to minimizing $\mathcal{H}$, which is quadratic in spins, we must also satisfy constraints that each spin have fixed magnitude $|S_i| = 1$. The large number (equal to the number of spins) of these constraints makes what otherwise would be a simple quadratic minimization problem difficult. Here we replace these many constraints by a single one,

$$\sum_i |S_i|^2 = 12N,$$  \hspace{1cm} (69)

where, as elsewhere in the text, we define $N$ as the number of unit cells for convenience. This is the “spherical model”, and is exactly soluble at both zero and non-zero temperature. At zero temperature, the spherical approximation must give a lower bound to the true ground state energy, since minimization is conducted with less constraints than in the physical spin model. Because of this observation, this approach can indeed often be used to construct physical ground states. This “Luttinger-Tisza” method consists of finding a subset of ground states of the spherical model which respect the spin normalization constraints of the physical problem. Any such states must be ground states of the full Hamiltonian. Moreover, when such states exist, they exhaust the full set of physical ground states. However, it is not always possible to find any ground states of the spherical model which satisfy the normalization constraint. If not, it simply means that ground state energy of the physical problem is strictly larger than that of the spherical model, and the Luttinger-Tisza method fails. Generally, the Luttinger-Tisza construction is less effective on lattices with a large number of sites in their basis. For the hyper-kagomé lattice with a 12 site basis, our expectations should not too high! Nevertheless, in some range of phase space, we will indeed find physical ground states from this approach. More generally, at non-zero temperature, the spherical model may be a useful approximation even when it fails to produce exact ground states at zero temperature.

Minimizing the quadratic Hamilton in Eq. (2) with the single global constraint in Eq. (69) is a standard problem, which is solved by finding the eigenvectors of the Hamiltonian matrix (coefficients of the quadratic form of spin components) with minimum eigenvalues. By translational invariance, the eigenfunctions have the Bloch form, i.e. are quasimomentum eigenstates. Hence it is useful to Fourier transform Eq. (2):

$$\mathcal{H} = N \sum_{\mathbf{k}} \sum_{i,j} \sum_{\nu,\mu} L^{ij}_{\nu\mu}(\mathbf{k}) Q_i^\nu(\mathbf{k}) Q_j^\mu(\mathbf{k}).$$  \hspace{1cm} (70)

Here

$$S_i^\nu(\mathbf{R}_n) = \sum_{\mathbf{k}} Q_i^\nu(\mathbf{k}) \exp (i\mathbf{k} \cdot \mathbf{R}_n)$$  \hspace{1cm} (71)

with $\nu, \mu$ index of spin vector components, $\mathbf{R}_n$ is the position of unit cell, $i$ and $j$ are the sublattice index and $L^{ij}_{\nu\mu}$ is the Fourier transformed Hamiltonian matrix in the Bloch representation (which is $12 \times 3 = 36$ dimensional because of the multiple basis sites and spin components). We need to minimize Eq. (70) subject to the soft constraint Eq. (72), which can be expressed as

$$\sum_{i=1}^{12} \sum_{\mathbf{k}} Q_i^\nu(\mathbf{k}) \cdot Q_i(\mathbf{k}) = 12.$$  \hspace{1cm} (72)

Minimization is equivalent to find the minimum eigenvalues (and corresponding eigenvectors) of $L^{ij}_{\nu\mu}(\mathbf{k})$. We did this numerically for every $\mathbf{k}$, and found the global minimum for every $(D_1, D_2), (D_2, D_3)$ and $(D_1, D_3)$ pairs. With this approach, phase diagrams in $D_1-D_2$, $D_2-D_3$, $D_1-D_3$ parameter spaces have been plotted in Fig. 3. In a wide region of the phase diagrams, the minimum eigenvalue is realized for $\mathbf{k} = (0,0,0)$. In this case, the corresponding eigenfunction can be chosen to satisfy the normalization constraint on every site, and so an exact ground state is found. This ordered state is in fact precisely the canted/uncanted windmill states we proposed in previous section. Thus in the regions for which $\mathbf{k} = (0,0,0)$ is indicated in the figures, this analysis proves that these windmill states are the exact global ground states. In a considerable large regions of the parameter spaces, we get canted/uncanted “windmill” states.

In other broad regions of the phase diagram, the spherical model predicts ordered states with incommensurate wavevectors, i.e. in which $\mathbf{k}$ has irrational projection onto reciprocal lattice vectors. This is indicated simply as “incommensurate phase” in the figures. In most cases we have studied, the incommensurate wavevectors are located around $0.85(\pi,\pi,\pi)$ and its eight equivalent momenta $0.85(\pm\pi,\pm\pi,\pm\pi)$. However, in this region of the phase diagram, we are unable to construct a linear combination of eigenfunctions which satisfies the local constraint on the spin magnitudes. Thus the incommensurate ground state of the spherical model does not immediately imply a corresponding ground state of the physical model. It is possible that the region of phase space occupied by the windmill states is actually expanded beyond what is shown here by this effect. Most likely, ground states with large unit cells or incommensurate order do exist in the physical model, but are more complex than those of the spherical approximation, and with somewhat higher energy. Even in the spherical model, we
VI. QUANTUM EFFECTS

A. Numerically constructed Bogoliubov transformation

In previous sections, the spins were treated classically and classical ground states were obtained. In this section, we discuss the quantum effect in the formalism of linear spin wave theory. In certain regions of \( D_1-D_2 \), \( D_2-D_3 \) and \( D_1-D_3 \) parameter spaces, we have an ordered ground state. We will use the Holstein-Primakoff Boson approach to explore the quantum effects.\(^{30}\) Now express the spin operator as follows,

\[
\mathbf{S}_i(R_n) \cdot \hat{S}_i^{ord} \approx S - a_i^\dagger(R_n)a_i(R_n) \quad (73)
\]

\[
\mathbf{S}_i(R_n) \cdot \mathbf{e}_i^1 \approx \frac{\sqrt{2S}}{2I} (a_i(R_n) - a_i^\dagger(R_n)) \quad (74)
\]

\[
\mathbf{S}_i(R_n) \cdot (\hat{S}_i^{ord} \times \mathbf{e}_i^1) \approx \frac{\sqrt{2S}}{2} (a_i(R_n) + a_i^\dagger(R_n)) \quad (75)
\]

where \( \hat{S}_i^{ord} \) is the unit vector along the spin order, \( \mathbf{e}_i^1 \) is the \( C_2 \) rotational axis at site \( i \) introduced in Sec. VI B and \( a_i \) and \( a_i^\dagger \) are the creation and annihilation operators of Holstein-Primakoff bosons at \( i \)th sublattice of unit cell at position \( R_n \), and we only keep the lowest order of \( a_i^\dagger \) and \( a_i \). Under this transformation, the Hamiltonian can be written as

\[
\mathcal{H} = -\frac{S}{2} \sum_{i,j,k} A_{ij}(k) a_i^\dagger(k) a_j(k) + B_{ij}(k) a_i^\dagger(k) a_j^\dagger(-k) + H.c., \quad (76)
\]

where \( A_{ij}(k) \) and \( B_{ij}(k) \) are the coefficient matrix we end up with after doing Fourier’s transform on the creation and annihilation operators. The Fourier’s transform we used is

\[
a_i^\dagger(R_n) = \frac{1}{\sqrt{N}} \sum_k a_k^\dagger \exp(i k \cdot R_n) \quad (77)
\]

\[
a_i(R_n) = \frac{1}{\sqrt{N}} \sum_k a_k \exp(-i k \cdot R_n) \quad (78)
\]

Since there are 12 sublattices, using the analytical Bogoliubov transformation is hopeless to diagonalize the Hamiltonian. Here, we will use a numerically constructed Bogoliubov transformation (NCBT) introduced and discussed in detail by Ref. 31,32 to diagonalize Eq. (76), find the spin wave energy gap and calculate the quantum corrections to the classical order. Write Eq. (76) as

\[
\mathcal{H} = \sum_k \mathbf{X}(k)^\dagger \mathbf{H}(k) \mathbf{X}(k), \quad (79)
\]

where

\[
\mathbf{X}(k) = (a_1(k) \ldots a_{12}(k),a_1^\dagger(-k) \ldots a_{12}^\dagger(-k))^T \quad (80)
\]

\[
\mathbf{H}(k) = -\frac{S}{2} \begin{pmatrix} A(k) & B(k) \\ B^*(k) & A^*(k) \end{pmatrix} \quad (81)
\]

see that in the incommensurate region, while the DM interaction removes much of the frustration-induced degeneracy, the enlargement of the unit cell implies a larger residual ground state degeneracy, and hence less effective removal of frustration than in the \( k = (0,0,0) \) regions.
spin polarization can be written as
\[ A_{ij}(k) = A^*_{ij}(k) \]  \hspace{1cm} (82)
\[ B_{ij}(k) = B_{ji}(k) . \]  \hspace{1cm} (83)
We now introduce the canonical transformation
\[ X(k) = Q(k)Y(k) , \]  \hspace{1cm} (84)
where, \( Y(k) \) is given by
\[ Y(k) = (b_1(k)\ldots b_{12}(k), b^*_1(-k)\ldots b^*_{12}(-k))^T , \]  \hspace{1cm} (85)
and satisfies
\[ [b_i(k), b^*_j(k')] = \delta_{ij}\delta_{k,k'} . \]  \hspace{1cm} (86)
The transformation \( Q \) is required to diagonalize the Hamiltonian as
\[ Q^\dagger(k)H(k)Q(k) = \Lambda(k) , \]  \hspace{1cm} (87)
where \( \Lambda(k) \) is the diagonal eigenvalue matrix whose diagonal matrix elements are given by
\( (\epsilon_1(k),\ldots,\epsilon_{12}(k),\epsilon_1(-k),\ldots,\epsilon_{12}(-k)) \). Using this transformation, the quantum correction to the classical spin polarization can be written as
\[ dS = \frac{1}{12N} \sum_{n,i} \langle a_i^\dagger(R_n)a_i(R_n) \rangle \]
\[ = \frac{1}{12N} \sum_{k,i} \langle a_i^\dagger(k)a_i(k) \rangle \]
\[ = \frac{1}{24N} \sum_{k} \langle X^\dagger X \rangle - \frac{1}{2} , \]  \hspace{1cm} (88)
At zero temperature, further making use of Eq. (84), Eq. (88) can be expressed as
\[ dS = \frac{1}{2} \left\{ \frac{1}{12N} \sum_{k} \sum_{i=1}^{12} |Q^\dagger Q|_{ii} - 1 \right\} . \]  \hspace{1cm} (89)
If we find the canonical transformation \( Q(k) \), the energy spectrum can also be obtained. With the energy spectrum, we can find the spin wave energy gap, \( \Delta \). Some care must be taken as the numerical construction of the Bogoliubov transformation is effective only when there is an energy gap.

B. Quantum corrections and spin wave gaps

By the method described in last section, we carried out the numerical procedure described in Ref. 31,32. Taking spin \( S = 1/2 \), we numerically construct the Bogoliubov transformation for every \( k \), and find its contribution to zero temperature quantum correction, \( dS \), and energy levels at every \( k \) to extract the spin wave gaps. The numerical results are plotted in Fig. 10. Fig. 11. Fig. 12 and Fig. 13. Corrections \( dS \) larger than 1/2 have been truncated to 1/2. In these figures, two components of the DM vector are kept constant while the third is varied. The ordered regions (the third varying DM vector component) of these figures can be found in the Fig. 9.

In these figures, spin wave gap is non-vanishing, so our calculation is valid. It is easy to find the quantum behavior also resembles the classical one: the different DM vector components have different effects in quantum corrections, which is similar to the effect of DM vector components in favoring canted “windmill” state in Sec. V B. Correction to DM magnitude studied in these figures, the quantum corrections decrease steadily as one goes deeper into the \( \mathbf{k} = 0 \) classically ordered region. If we crudely suppose that \( dS > 1/2 \) is indicative of the destruction of order by quantum fluctuations, we may expect broad regions of quantum spin liquid states occurring in and near the incommensurate regions of the classical phase diagram. This range of DM vectors then may be possible candi-
FIG. 11: (Color online) The dependence of quantum corrections and spin-wave gaps on the DM vector components. In the two figures, we set $D_3 = 0$ and vary $D_1$ with two fixed $D_2$ values ($D_2 = -0.08 J$ (in blue) and $D_2 = -0.05 J$ (in red)). 16 x 16 x 16 momentum points have been used to generated the data. No change has been found in quantum corrections and gaps within 1% compared with 10 x 10 x 10 momentum points (Same for Fig. 12 and Fig. 13).

FIG. 12: (Color online) The dependence of quantum corrections and spin-wave gaps on the DM vector components. In the two figures, we set $D_3 = 0$, $D_2 = 0$ and vary $D_1$. We also did the same thing with $D_2 = 0$, $D_3 = 1$ and varying $D_1$, and the quantum corrections always break the classical order completely.

larger than the previous cases. In Fig. 14 we see that both curves of $D_3 = \pm 0.10 J$ and $D_3 = \pm 0.25 J$ nearly overlap at low temperatures, and their sequence agrees with the magnitudes of the spin-wave gaps.

C. Comparison with exact diagonalization

In order to partially confirm our results in last section, we performed numerical exact diagonalization for $S = 1/2$ spins. We took six triangles with thirteen sites and used a Heisenberg model plus DM interaction with only $D_2 \neq 0$. We plot the resulting specific heat in Fig. 14. The gap in each case can be inferred from the plot by the temperature below which the specific heat becomes negligible. As we found in previous section, the more negative $D_2$ is, the greater the gap will be. At low temperatures in Fig. 14 the sequence of the curves agrees with what they should behave according to spin wave gaps in Fig. 14

Similarly, we also look at the case when only $D_3$ component is present by taking $D_3 = \pm 0.10 J$, $\pm 0.25 J$. According to Fig. 15, the spin wave gaps of $D_3 = \pm 0.10 J$ are close to each other, and the spin wave gaps of $D_3 = \pm 0.25 J$ are also close to each other, but much larger than the previous cases. In Fig. 15 we see that both curves of $D_3 = \pm 0.10 J$ and $D_3 = \pm 0.25 J$ nearly overlap at low temperatures, and their sequence agrees with the magnitudes of the spin-wave gaps.

VII. DISCUSSION

In this paper we have studied the effect of spin-orbit interactions in the hyper-kagomé lattice of Na$_4$Ir$_3$O$_8$. A crucial physical parameter is the strength of atomic spin-orbit coupling relative to non-cubic crystal field splittings. In the strong spin-orbit limit, Ir-O-Ir superexchange produces highly anisotropic effective spin interactions, with 2/3 antiferromagnetic and 1/3 ferromagnetic couplings between spin components. This Hamiltonian turns out to be unfrustrated, and has a small set of classical ground states. We speculated this even the $S = 1/2$ quantum model is likely ordered with a substantial critical temperature, inconsistent with experiments on Na$_4$Ir$_3$O$_8$.

By contrast, strong spin-orbit interactions and direct Ir-Ir exchange, or weak spin orbit interactions, all induce an Heisenberg-like Hamiltonian with a small correction
FIG. 13: (Color online) The dependence of quantum corrections and spin-wave gaps on the DM vector components. In the two figures, we set $D_1 = 0$ and vary $D_3$ with two $D_2$ values ($D_2 = 0$(in blue) and $D_2 = -0.04J$(in red)). We also did the same thing with $D_2 = 0$, $D_3 = 0$, and varying $D_1$, and the quantum corrections always break the classical order completely.

FIG. 14: (Color online) The specific heat of six triangle with negative $D_2$ component DM interaction. Along the thin vertical line, from top to bottom $D_2$ value of each curve increases from $-0.09J$ to $-0.01J$ with a step $0.01J$.

FIG. 15: (Color online) The specific heat of six triangle with $D_3$ component DM interaction. Along the thin vertical line, the upper curves have $|D_3| = 0.25J$, the down curves have $|D_3| = 0.10J$.

A. Zero temperature susceptibility in quantum spin liquids

Part of the motivation of the present study was the observation in Na$_4$Ir$_3$O$_8$ that the susceptibility $\chi$ tends to a constant at low temperature, despite the approximately quadratic decrease of specific heat. We argued that this combination, which implies a diverging Wilson ratio as $T \rightarrow 0$, is likely indication of spin-orbit interactions. Indeed, on general grounds, a constant zero temperature susceptibility is expected when SU(2) spin-rotation symmetry is broken. The situation of weak DM interaction is quite common in frustrated magnets, and may allow this behavior quite broadly. Therefore it is interesting to consider more generally how this occurs in the presence of weak DM coupling. We have not so far addressed the magnitude of this zero temperature susceptibility.

Presuming the DM interaction to be relatively weak, the magnitude of $\chi$ should be understood in terms of the correlations the spins would have in the underlying system without DM. Various SU(2) invariant phases lead to

of the form of a Dzyaloshinskii-Moriya (DM) term. The orientation of the DM vector, which is not determined by symmetry or our microscopic considerations, determines the extent to which the frustration of the Heisenberg model is relieved. In one region of phase space, frustration is fully relieved, and the DM interaction stabilizes a magnetically ordered “windmill” state, with nearly but generically not quite coplanar moments. Quantum fluctuations, which we assessed by spin wave theory, are sufficiently suppressed that we may expect this order to persist even for spin-$1/2$ spins (as in Na$_4$Ir$_3$O$_8$) in part of this region. In the remainder of phase space, the frustration is not fully removed, and the classical ground states break the lattice periodicity and may be incommensurate. We argued that in this regime, the classical ordering is fragile and may be destroyed by quantum fluctuations for $S = 1/2$ spins.
rather different behaviors. Generally speaking, one expects the most suppressed $\chi$ for systems with the least low-energy spin fluctuations in the absence of DM. Probably the most extreme example is a Valence Bond Solid (VBS) or dimer state, in which the eigenstates can be approximated by those of a single partition of the sites into pairs of spins which are coupled to each other only within the pairs. Such a VBS phase has a gap of order $J$ to all excitations, including the elementary triplets. A simple calculation by second order perturbation theory of the susceptibility shows that it is indeed non-zero, and of order

$$\chi_{VBS}(T = 0) \sim \frac{D^2}{J^3}. \quad (90)$$

One may also estimate the magnitude of $\chi$ for various phenomenological gapless spin liquid ground states perturbed by DM. The general arguments follow scaling theory. We presume the gapless spin liquid is a critical phase in the renormalization group sense, described by a scale invariant field theory. Introduction of DM interactions breaks SU(2) symmetry, and allows operators $O_\Delta$ breaking SU(2) to be added to the effective action/Hamiltonian. Generically, these appear with coefficients proportional to $D$. In the simplest situation, there is a single such operator $O_\Delta$ with the smallest scaling dimension $\Delta$. In most cases of interest, we expect $\Delta < d + z$, where $d$ is the spatial dimension and $z$ is the dynamical critical exponent ($z = 1$ is common). In this case, the presence of this operator in the Hamiltonian constitutes a relevant perturbation. Then, if the susceptibility at $D = 0$ behaves as $\chi \sim T^\beta$, we expect

$$\chi(\mu, \nu)(D, T) \sim T^\beta f_{\mu\nu}(D/T^{\frac{d+z-\Delta}{\Delta}}), \quad (91)$$

where $\mu, \nu$ are spin components $x, y, z$. The operator $O_\Delta$ is expected to break SU(2) down to some subgroup. This may contain either one or zero residual U(1) spin rotation axes. The susceptibility normal to this axis, if it exists, is expected to be constant at low temperature. If no such axis exists, then the susceptibility will be constant in all directions. In either case, we must have

$$f_{\mu\nu}(X) \sim A_{\mu\nu} X^{\frac{d+z-\Delta}{\Delta}}, \quad \text{for } |X| \gg 1. \quad (92)$$

Here $A_{\mu\nu}$ is a symmetric tensor with either 2 or 3 non-zero eigenvalues, in the cases with one or zero residual U(1) symmetries, respectively. One thereby obtains

$$\chi_{\mu\nu}(T = 0) \sim |D|^{\frac{d+z}{\Delta}} A_{\mu\nu}. \quad (93)$$

As an example, consider the 2d “Dirac” spin liquid with point nodes on the kagome lattice studied by Hermele et al. There, the dominant operator indeed preserves a single residual U(1) symmetry. Its scaling dimension is estimated as $\Delta \approx 2 - 3/(8\pi^2) \approx 1.6$ (based on a calculation for a generalized model with large number, $N_f$, of flavors of fermions, evaluated for the physical case $N_f = 4$). Taking $d = 2, z = 1, \beta = 1$ as appropriate for this case, we find, restoring units

$$\chi_\perp(T = 0) \sim \frac{\mu_B^2 D}{J} \left| \frac{D}{J} \right|^{0.7}. \quad (94)$$

Here $\chi_\perp$ is the susceptibility in the x-y plane perpendicular to the conserved U(1) spin axis. We see that the dependence on $D$ is sub-linear, making for a very large susceptibility even for rather small $D/J$.

It is noteworthy that the scaling prediction above should obtain regardless of the other properties of the system in the presence of DM interaction. The relevance of $O_\Delta$ at the spin liquid fixed point indeed implies that it drives the system into a different phase, which may not be a spin liquid at all. This is believed to be the case for the above Dirac spin liquid, for which the resulting state is expected to be magnetically ordered.

### B. Other possibilities

One may wonder whether the weak and strong spin orbit limits are the only possibilities for Na$_4$Ir$_3$O$_8$, and whether they might be distinguished more directly. Probably the principal difference in the two cases is the sign of the g-factor. In the weak spin orbit limit, one has approximately $M \approx -2\mu_B S$, while in the strong case, we found $M \approx +2\mu_B S$. While these lead to identical Curie laws, they are physically distinct (note that one cannot reverse the sign of $S$ and maintain its canonical commutation relations). It should be measurable in other experiments such as nuclear magnetic resonance. Microscopic reasoning gives no reason why the Ir$^{4+}$ spins might not be in an intermediate situation between the two extreme limits. However, in this case one would expect a $g$-factor in between these two values, i.e. with substantially reduced magnitude. A large deviation would seem to be inconsistent with the measured spin susceptibility.

This tends to support the notion that Na$_4$Ir$_3$O$_8$ is either in the strong or weak spin orbit limit, and not in between. Given the incompatibility of the strongly anisotropic Ir-O-Ir superexchange Hamiltonian in the strong spin-orbit case with experiment, we are led to believe the weakly anisotropic Hamiltonian with DM interactions is most appropriate (we note that “weak anisotropy” still allows for $|D|/J \approx 0.1$ which would have strong effects on the low energy physics). This, however, still leaves open the issue of weak versus strong spin-orbit interactions. Though susceptibility experiments do not distinguish the two cases, they are physically distinct, and could be discriminated by magnetic resonance methods, for instance. So far as we are aware, all prior measurements of Ir$^{4+}$ ions capable of this distinction have been interpreted in terms of the strong spin-orbit scenario (see for example, Ref[26]). This fundamental physical question in Na$_4$Ir$_3$O$_8$ warrants further investigation.

Could there be another scenario? We cannot rule out the possibility that other interactions might play a role.
Perhaps further neighbor exchange or spin-lattice coupling might be significant. These are important subjects for future theoretical studies.

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1 R. Moessner, Can. J. Phys. 79, 1283 (2001).
2 A. P. Ramirez, Ann. Rev. Mater. Sci. 24, 453 (1994).
3 M. Gvozdikova and M. Zhitomirsky, JETP Letters 81, 236 (2005).
4 C. Henley, J. Appl. Phys. 61, 3962 (1987).
5 J. Villain, R. Bidaux, J. Carton, and R. Conte, J. de Phys. 41, 1263 (1980).
6 D. Bergman, J. Alicea, E. Gull, S. Trebst, and L. Balents, Nature Physics 3, 487 (2007).
7 Y. Okamoto, M. Nohara, H. Aruga-Katori, and H. Takagi, Phys. Rev. Lett. 99, 137207 (2007).
8 Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Phys. Rev. B 73, 140407(R) (2006).
9 J. Hopkinson, S. Isakov, H.-Y. Kee, and Y. Kim, Phys. Rev. Lett. 99, 037201 (2007).
10 M. J. Lawler, H.-Y. Kee, Y. Kim, and A. Vishwanath, Unpublished, cond-mat/0705.0990.
11 M. Rigol and R.R.P. Singh, Phys. Rev. B 76, 184403 (2007).
12 A. Kolezhuk, S. Sachdev, R.R. Biswas, and P. Chen, Phys. Rev. B 74, 165114 (2006).
13 M. Elhajal, B. Canals, and C. Lacroix, Phys. Rev. B 66, 014422 (2002).
14 R. Ballou, B. Canals, M. Elhajal, C. Lacroix, and A. S. Wills, Phys. Stat. Sol.(b) 236, 240 (2003).
15 M. Elhajal, B. Canals, and C. Lacroix, Physica B 312, 716 (2002).
16 T. Moriya, Phys. Rev. 120, 91 (1960).
17 W. Koshibae, Y. Ohta, and S. Maekawa, Phys. Rev. B 47, 3391 (1993).
18 J. Kanamori, Prog. Theor. Phys. 30, 275 (1963).
19 J. Goodenough, Phys. Rev. 171, 466 (1967).
20 N. Vugman and S. Nogueira, Revista Brasileira de Fisica 19, 606 (1989).
21 S. Morov, I. Carmichael, and G. Hug, handbook of photochemistry (Marcel Dekker, New York, 1993).
22 R. Murugavel, Unpublished, Private communication.
23 A.S. Wills, Phys. Rev. B 63, 064430 (2001).
24 A. Wills, Physica B 276, 680 (2000).
25 J. Dimmock, Phys. Rev. 130, 1337 (1963).
26 E. Bertaut, Acta Cryst. A24, 217 (1968).
27 D. Lyons, T. Kaplan, K. Dwight, and N. Menyuk, Phys. Rev. 126, 540 (1962).
28 J. Luttinger and L. Tisza, Phys. Rev. 70, 954 (1946).
29 J. Luttinger, Phys. Rev. 81, 1015 (1951).
30 T. Holstein and H. Primakoff, Phys. Rev. 58, 1048 (1940).
31 A. D. Maestro and M. Gingras, J. Phys. Cond. Matt. 16, 3399 (2004).
32 A. D. Maestro, Master thesis.
33 F. A. et al. (ALPS collaboration), J. Phys. Soc. Jpn. Suppl. 74, 30 (2005).
34 F. A. et al. (ALPS collaboration), J. Mag. Mag. Mater. 310, 1187 (2007).
35 M. Hermelé, Y. Ran, P. Lee, and X.-G. Wen, Unpublished, cond-mat/0803.1150.
36 A. Raizman and J.T. Suss, prb 22, 1141 (1980).