A decorated Kagome spin model for 2D Metal Organic Framework

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A spin model on a decorated Kagome lattice, motivated by a recently synthesized 2D Metal Oranic Framework (MOF) was studied using Luttinger Tisza method. The model was shown to show an extensive degeneracy and is a candidate for exotic phenomena such as quantum spin liquid. At certain critical coupling, this degeneracy gets enhanced by threefold, suggesting the presence of an interesting phase transition.

I. INTRODUCTION

Spin systems on a Kagome lattice has attracted theoretical interest in the past decades due to its high degree of frustration. This geometric frustration is believed to give rise to such novel phenomena as order by disorder or quantum spin liquid. Experimental studies, on the other hand, started taking up recently, motivated by synthesis of various inorganic Kagome materials. However, there is another class of materials that are synthesized that has a Kagome structure that has gone largely unnoticed. Metal Organic Frameworks (MOFs) consist of organic ligands and metal ions that form a crystalline lattice. Recently, a series of two-dimensional MOFs with a kagome lattice has been synthesized, which has the potential to host a Kagome spin lattice.

Moreover, due to additional degrees of freedom vested on them by the presence of metal ions and organic ligands, MOFs have the capability of realizing many different variants of kagome lattice. However, these decorated Kagome lattices have not been studied quite as intensively, due in part to lack of experimental motivation. Here, we propose a simple decorated Kagome lattice for a 2D MOF and study its properties using Luttinger-Tisza method. We find the lattice hosts an extensive degenerate ground states, and undergoes ferromagnetic-antiferromagnetic transition as coupling constants are varied.

II. METAL ORGANIC FRAMEWORKS AND THEIR SPIN DEGREES OF FREEDOM

Metal Organic Frameworks are crystalline frameworks that consist of metal ions and organic linkers. The variety of structures of metal ions and of ligands give rise to a large number of distinct crystalline structures. Among them, we focus on two-dimensional MOFs with honeycomb structure. Even though MOfs are conventionally insulating due to insulating coordination bonds and covalent bonds, recent advances in MOF synthesis brought us highly conductive and/or magnetic materials. Of particular interest to us are copper hexahydroxytriphenylene (CuHHTP; Figure.1 (a)) and copper hexathiobenzene (Cu-HTB; Figure.1 (b)) and their derivatives. These MOFs have threefold rotation symmetric organic ligands

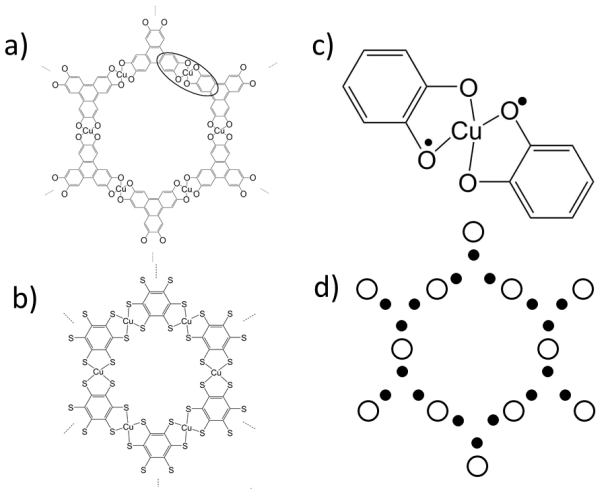

FIG. 1: Different Metal Organic Frameworks and a corresponding spin model. a) Copper hexahydroxytriphenylene (CuHHTP) b)Copper hexathiobenzene (Cu-HTB) c) A building block of CuHHTP. d) Proposed spin model for MOF. White sites (Kagome sites) correspond to copper and black sites (inner triangle sites) live adjacent to it.

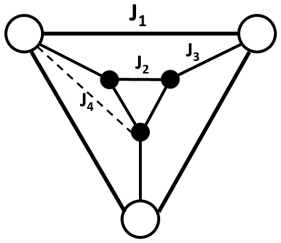

FIG. 2: Antiferromagnetic interactions of the model. Only one of J_4 interactions are shown.

at honeycomb sites, and Cu(II) ions at the kagome site. Due to its redox activity, the ligand is believed to host two spins adjacent to copper ions (Figure.1 (c)). Therefore, the spin model to be considered can be described as Figure.1 (d) where a unit cell contains 9 spin sites.

Interactions considered in this paper are summarized in Figure.2. For chemical reasons, all interactions are assumed to be anti-ferromagnetic, either through superexchange interaction, or due to electron electron repulsion on the same molecule.

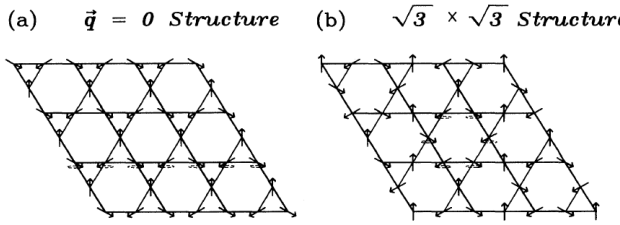

FIG. 3: Different ordering modes of Kagome Heisenberg model. Recreated from [1].

III. KAGOME LATTICE, EXTENSIVE DEGENERACY, ORDER BY DISORDER

Since our model is a decorated Kagome lattice model, we review the ground state configurations of Kagome lattice. Up to a constant, Kagome Heisenberg Hamiltonian can be written as

$$\mathcal{H} = -J \sum_{i=\triangle} (\mathbf{S}_{1i} + \mathbf{S}_{2i} + \mathbf{S}_{3i})^2 \tag{1}$$

where the sum is over all different triangle in the lattice. This can be minimized when the sum of three spins in each triangle is zero. There are an extensive number of configurations that satisfy this constraint, and this gives rise to various different patterns (Figure.3).

In real systems, fluctuation should lift this degeneracy, since some modes are more easily fluctuating than others. This mechanism of fluctuation induced ordering is termed "order by disorder" and has been studied in both thermal[1][2][3] and quantum context[4][5]. For classical system, there is a strong evidence that $\sqrt{3} \times \sqrt{3}$ mode is chosen in the classical limit. On the other hand, in the quantum case, the ground state is believed to be a quantum spin liquid without any order. In this case, we can view it as quantum fluctuation mixing different classically degenerate states to generate a quantum ground state.

IV. ISING LIMIT

First, we consider the Ising limit of this system. Though there is no chemical or physical reason to believe the MOF can be described by this limit, it can still give us an idea on the degree of frustration it has.

For this case, we can simply sum over the internal triangleto reduce it to a Kagome lattice with a coupling J given by

$$e^{4J} = e^{4J_1} \frac{e^{3J_2} \cosh 3J_3 + 3e^{-J2} \cosh (J_3 - J_2)}{e^{-3J_2} \cosh J_3 + e^{-J_2} (\cosh 3J_3 + 2 \cosh J_3)} \tag{2}$$

In the low temperature limit, this reduces to $J = J_1 - \frac{1}{2} \min \{J_2, J_3\}$. Therefore, even in the absence of J_4, the Ising model can be in an ordered phase provided J_2 and J_3 are sufficiently large. This is because the internal triangle gives rise to an effective ferromagnetic coupling between kagome sites.

V. HEISENBERG MODEL: SPHERICAL MODEL CALCULATION

Next, we consider the Heisenberg Hamiltonian, which is of more physical interest.

A. Luttinger-Tisza model calculation

For Heisenberg model, the simple summation procedure of Ising model does not work, So instead we will try to find the ground state Hamiltonian by using Luttinger-Tisza (LT) method [6][7], also known as spherical model. In LT method, we weaken the constraint of the spin length being zero to *the average* of spin length being unit length, i.e.

$$\sum |\vec{s}_i|^2 = N_s \tag{3}$$

where N_s is the number of spins. Then, we can perform a Fourier transform of the Heisenberg Hamiltonian and write

$$\mathcal{H} = \sum_{\mathbf{q}} \sum_{\alpha,\beta} \tilde{J}^{\alpha\beta}(\mathbf{q}) \tilde{\mathbf{S}}_\alpha(\mathbf{q}) \tilde{\mathbf{S}}_\beta(\mathbf{q}) \tag{4}$$

where α, β labels different basis in the unit cell, $\mathbf{q}$ levels momentum, $\tilde{\mathbf{S}}$ is the Fourier transform of spin vectors, and $\tilde{J}^{\alpha\beta}(\mathbf{q})$ is the Fourier transform of interaction Hamiltonian, which has the same form as the hopping matrix for a tight-binding model with same hopping parameters as the spin interaction. Thus, $\tilde{J}^{\alpha\beta}(\mathbf{q})$ can be diagonalized at different momenta to give "LT band structure". The ground state within Luttinger-Tisza method can then be found by finding $\mathbf{q}$ that minimizes the lowest eigenvalue of $\tilde{J}^{\alpha\beta}(\mathbf{q})$ We call this momentum $\mathbf{q_{LT}}$.

First, note that this procedure gives exact ground state for Bravais lattice in the form of coplaner rotating spins by taking a superposition of $\mathbf{q_{LT}}$ and $-\mathbf{q_{LT}}$ i.e.

$$\mathbf{S}(\mathbf{x}) = \hat{\mathbf{S}}_x \cos (\mathbf{q_{LT}} \cdot \mathbf{x}) + \hat{\mathbf{S}}_y \sin (\mathbf{q_{LT}} \cdot \mathbf{x}) \tag{5}$$

Even for non-Bravais lattices, exact ground states can be found when the problem has certain symmetries. For example, in the case of antiferromagnetic Kagome lattice, there are two states at $\mathbf{q} = 0$ that together correspond to E representation of the C_3V point group. Because of this degeneracy, a suitable superposition can be taken to create $\mathbf{q} = 0$ configuration in Figure.3.

However, for non-Bravais lattices, there is no guarantee that the eigenvector of the interaction matrix $\tilde{\mathbf{J}}$ has the same value in different sublattices, so the LT method can fail. For the classical Hamiltonian, this means we need to add more wave vectors in order to minimize the

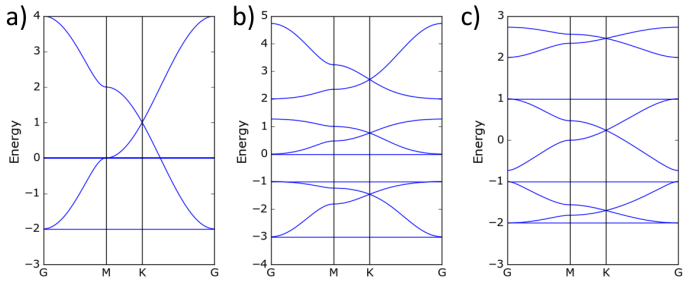

FIG. 4: Luttinger-Tisza band structure at different coupling constants. a) $J_1 = 1$, all else zero b)$J_1 = J_2 = J_3 = 1, J_4 = 0$ c)$J_2 = J_3 = 1, J_1 = J_4 = 0$

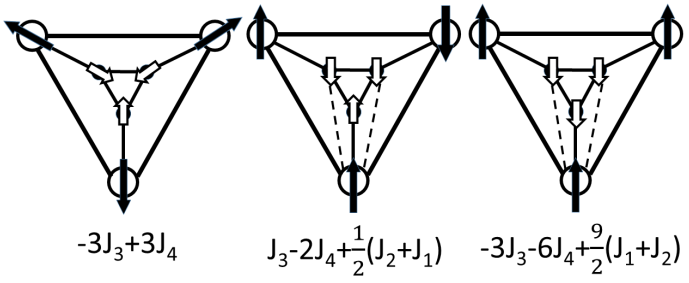

FIG. 5: Different spin configurations and their energies. These energies are shifted by a constant to make them look simpler.

energy, but as long as the $\mathbf{q_{LT}}$ mode is decently close to being normalized, we can expect the q_{LT} mode to be a dominant component. Similarly in quantum scenario, different length at different sites suggest the reduction of spin length due to quantum fluctuation, but as long as this length reduction is not too big, we can expect the ordering to be robust. In this case, LT method can be thought of as a "semiclassical" method that incorporates quantum fluctuation into account. On the other hand, in some highly frustrated systems, it has been observed that the LT method gives a mode with *zero* amplitude on a sublattice [8], in which case LT ground state is not to be trusted at all, and quantum fluctuation should dominate.

B. $J_4 = 0$ case

First, we calculate the LT band structure for zero J_4 coupling, anticipating to see a phase transition caused by competing antiferro and effective ferromagnetic interaction, as seen in Ising limit.

The LT band structure for different coupling constants are shown in Figure.4. First, in the limit where J_2 and J_3 are zero (Figure.4 (a)), we see a flatband at the bottom and six flatbands for internal triangle degrees of freedom. The bottom flatband corresponds to the extensive degeneracy present in the Kagome lattic and is an expected result. However, rather surprisingly, this flatband survives even after introducing J_2 and J_3 as can be seen in (Figure.4 (b)(c)). Unlike Ising case, the introduction of J_2 and J_3 does not make a ferromagnetic phase transition to happen.

This is because the minimum energy configuration for this Hamiltonian turns out to take the form in Figure.5. This ordering structure minimizes all J_1, J_2 and J_3 and therefore is a classical ground state. The constraint imposed on Kagome spins in this model is exactly the same as pure Kagome model, so we should expect a similar extensive degeneracy at any interaction strength. In this parameter region, the ratio between kagome sites and inner-triangle sites are at most two, so the effect of fluctuation is not dominant.

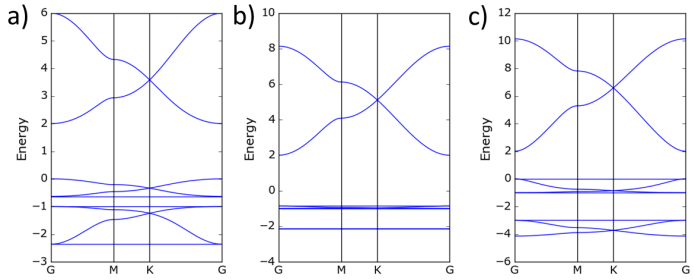

FIG. 6: Luttinger-Tisza band structure with J_4 coupling. a)$J_1 = J_2 = J_3 = 1, J_4 = 0$ b) $J_1 = J_2 = J_3 = 1, J_4 = 1.2826$ c)$J_1 = J_2 = J_3 = 1, J_4 = 2$

C. $J_4 \neq 0$ case

Different ordering patterns are expected to appear when J_4 interaction is added. Some of possible ordering patterns are enumerated in Figure.5. For these three configurations, sets of parameters can be found to minimize any given one of them. Thus, we expect a phase transition to happen between these different ordering patterns.

LT band structure was investigated at different J_4 coupling (Figure,6. For a small J_4, the band structure retains the extensive degeneracy ((a)). In this region, the eigenvectors at Gamma point belongs to the same E irreducible representation as before, and therefore appears to have the same ordering pattern as Figure.5 (a). However, at certain critical coupling strength, the three bands at the bottom become degenerate ((b)). Further increase of J_4 will make the gamma point a unique ground state of the LT calculation with the expected ordering pattern of Figure.5 (c). Therefore, while the ordering pattern in Figure.5 (b) is reduced in importance and does not show up, the transition into a ferromagnetically ordered state was observed.

This transition mirrors that of pure Kagome lattice. However, in the case of pure Kagome lattice, the threefold flatband that appears at the transition corresponds to J = 0, i.e. the degeneracy is a trivial consequence of non-interacting spins. However, in the present case case, Kagome sites and triangle sites are still coupled strongly, so the extensive degeneracy is among various strongly

coupled spin configurations.

In fact, we can see hat the degeneracy corresponds to a continuous family of normalized configurations [9]. For a system with N_f lowest flat bands, we can have $3N_f$ degrees of freedom per unit cell due to x, y, and z components of spin. On the other hand, unit cell containing N_s sites imposes N_s constraints on spin length. Therefore, $3N_f - N_s$ gives us the overall degrees of freedom left in the system, and when this is positive, we expect an extensive degeneracy. In fact, even when this number is zero, we can have an extensive degeneracy, such as in Kagome case ($N_f = 1, N_s = 3$), and due to similarity of structure, we expect the lattice to have a similar pattern of degeneracy.

VI. CONCLUSION

We investigated a Kagome lattice with inner triangle using its Ising limit and Luttinger Tisza method. While Ising model predicted a phase transition owing to J_2 and J_3 parameters, Heisenberg model required J_4 coupling to observe a ferromagnetic phase transition. In the antiferromagnetic region, the ordering pattern is that of interlocked triangle regardless of coupling constant.

Exactly at the phase transition, the bottom three bands become degenerate, and causes a massive degeneracy, which we believe will give rise to interesting physics. It should be of interest for us to ask what happens if this transition were to be implemented experimentally, since at this transition point, the system needs to pick a particular configuration out of massively entangled states, presumably by some kind of order by disorder mechanism.

In fact, the mere presence of threefold degenerate flatband is interesting, even if we ignore the spin degrees of freedom and treat it purely as electronic band structure. Most models with flatband contain a band touching due to real space topology[9], and for some applications the vanishing band gap proves problematic for some applications (e.g. a proposal for room temperature quantum Hall effect[10]). However, there is no band touching at the critical point of this model because all three flatbands are collapsed into one flat band altogether. If an appropriate spin-orbit coupling term can make these three bands to have net topological invariant, it might give us a different way to realize a topologically nontrivial almost flat band.

This short survey based on Ising and LT method points to an interesting competition between different interactions, and should justify future more rigorous studies of this model both in classical regime and quantum regime.

VII. ACKNOWLEDGEMENT

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