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Ground-state properties, excitation spectra, and phase transitions in the  $S=1/2$  and  $S=3/2$  bilayer Heisenberg models on the honeycomb lattice

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# Ground state properties, excitation spectra and phase transitions in the $S = 1/2$ and $S = 3/2$ bilayer Heisenberg models on the honeycomb Lattice

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Motivated by the observation of a disordered spin ground state in the  $S = 3/2$  material  $\text{Bi}_3\text{Mn}_4\text{O}_{12}\text{NO}_3$ , we study the ground state properties and excitation spectra of the  $S = 3/2$  (and for comparison  $S = 1/2$ ) bilayer Heisenberg model on the honeycomb lattice, with and without frustrating further neighbor interactions. We use series expansions around the Néel state to calculate properties of the magnetically order phase. Furthermore, series expansions in  $1/\lambda = J_1/J_\perp$ , where  $J_1$  is an in-plane exchange constant and  $J_\perp$  is the exchange constant between the layers are used to study properties of the spin singlet phase. For the unfrustrated case, our results for the phase transitions are in very good agreement with recent Quantum Monte Carlo studies. We also obtain the excitation spectra in the disordered phase and study the change in the critical  $\lambda$  when frustrating exchange interactions are added to the  $S = 3/2$  system and find a rapid suppression of the ordered phase with frustration. Implications for the material  $\text{Bi}_3\text{Mn}_4\text{O}_{12}\text{NO}_3$  are discussed.

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## INTRODUCTION

The honeycomb lattice is a bipartite but low-coordination number two-dimensional lattice. Thus collinear antiferromagnetism is unfrustrated on the lattice. However, it is more susceptible to disorder due to its low coordination number. Recent interest in antiferromagnetism on the honeycomb lattice comes from many directions. First, theoretical studies of quantum spin models on the lattice find a rich phase diagram, with several collinear, spiral and spin-disordered phases.[1–14] Second, a recent Quantum Monte Carlo finding that the Hubbard model on the honeycomb lattice shows strong evidence for a quantum spin-liquid phase sandwiched between the semi-metal phase at small  $U/t$  and an ordered antiferromagnetic phase at large  $U/t$ , has led to much follow-up activity.[15–20] Third, the discovery of graphene and the search for correlated topological insulator phases have also led to interest in strongly correlated electron models on the honeycomb lattice, including spin-orbit coupling.[21, 22]

In this paper, our primary motivation comes from the bismuth manganese oxynitrate material  $\text{Bi}_3\text{Mn}_4\text{O}_{12}\text{NO}_3$ , an  $S = 3/2$  antiferromagnet, with a Curie-Weiss constant of order  $250\text{K}$ , which does not show any long range order down to  $0.4\text{K}$ . [23] The material consists of honeycomb lattices of  $S = 3/2$   $Mn$  spins which are separated by bismuth and nitrate layers. Two such layers are separated by bismuth atoms, forming a bilayer, and these bilayers are then separated by significantly larger separations. Thus an appropriate model for such a system is a spin-3/2 Heisenberg model on the bilayer honeycomb lattice, with an in-plane nearest-neighbor exchange  $J_1$

and an exchange between the bilayers of  $J_\perp$ . [24] The bilayer exchange  $J_\perp$  has been estimated by an electronic structure calculation to be between  $J_1$  and  $2J_1$ , whereas further neighbor in-plane exchanges, which frustrate the system are down compared to  $J_1$  by an order of magnitude (less than  $0.2J_1$ ). [24] This system has also been studied recently by Quantum Monte Carlo (QMC) simulations and bond-operator based mean-field and variational theory [25, 26], which our results are compared to below.

We use series expansion methods to study the properties of the bilayer honeycomb Heisenberg model. [27, 28] Ising series expansions are used to calculate the ground state energy and antiferromagnetic order parameters in the Néel phase. Dimer series expansions are used to calculate the ground state energy, triplet energy gap and the excitation spectra in the disordered singlet phase. The phase transition in this model is known to be in the universality class of the  $3d$  classical Heisenberg model. [25] We use this in our series analysis to make our analysis more accurate. For the nearest neighbor model, we find the phase transition to be located at  $J_\perp/J_1$  value of  $1.66 \pm 0.01$  for  $S = 1/2$  and  $9.34 \pm .20$  for  $S = 3/2$ . These results are in very good agreement with the values reported in the QMC study of  $1.645(1)$  and  $9.194(3)$  for the two cases respectively. The bond-operator theory [26] is significantly less accurate.

Since the material  $\text{Bi}_3\text{Mn}_4\text{O}_{12}\text{NO}_3$  is unlikely to have  $J_\perp/J_1 \approx 9$ , frustration in the plane must play a role in disordering the system. Thus, we also study the model with frustration and discuss its possible relevance to the materials. We also present results for the excitation spectra in the disordered phase, which could be helpful in

further quantifying the experimental system.

### SERIES EXPANSIONS FOR THE HONEYCOMB BILAYER MODELS

We consider the Heisenberg model on the bilayer honeycomb lattice with Hamiltonian

$$\mathcal{H} = J_1 \sum_{\langle i,j \rangle, a} \vec{S}_i^a \cdot \vec{S}_j^a + J_2 \sum_{\langle i,k \rangle, a} \vec{S}_i^a \cdot \vec{S}_k^a + J_\perp \sum_i \vec{S}_i^1 \cdot \vec{S}_i^2. \quad (1)$$

Here  $a = 1, 2$  denotes the spins in the two layers. The first sum runs over nearest-neighbors in the honeycomb planes and the second sum is over the second neighbors in the honeycomb planes. The third sum is over the neighboring spins between the two bilayers.

For the unfrustrated models ( $J_2 = 0$ ), we have calculated Ising expansions for the ground state energy and sublattice magnetization to 14-th order for  $S = 1/2$  and to 12-th order for  $S = 3/2$ . The dimer expansions in  $1/\lambda = J_1/J_\perp$  are calculated for the ground state energy to order 12 for  $S = 1/2$  and to order 9 for  $S = 3/2$ . The energy gap series is calculated to order 10 for  $S = 1/2$  and to order 6 for  $S = 3/2$ . For  $J_2/J_1$  non-zero, the energy gap series is calculated in powers of  $1/\lambda$  to order 6 for  $S = 3/2$ . The series can be made available upon request.

In Fig. 1 (a) and (b), we show plots of the ground state energy for  $J_2 = 0$ . For both  $S = 1/2$  and  $S = 3/2$ , the results from Ising and dimer expansions join smoothly as expected for a second order phase transition. However, the energy is not the best quantity to determine the location of the phase transition.

In Fig. 2 (a) and (b), we show the Néel order parameters for the  $S = 1/2$  and  $S = 3/2$  cases. We use a square-root transformation[29] to remove the singularity before analyzing the series by Padé approximants. Our analysis is not accurate close to the transition where the magnetization vanishes. The uncertainties clearly become large for the shorter  $S = 3/2$  series for  $\lambda > 8$  as the transition is approached. Beyond  $\lambda = 9$ , the rapid decrease is sketched in the plot by a dashed line. The order parameter is also not the best way to get a precise estimate of the transition point, because the series are not directly in the variable  $1/\lambda$ , in which a power-law singularity, with an exponent  $\beta$  is expected. Rather, for every  $\lambda$  the series is analyzed in the anisotropy variable to calculate the order parameter for the Heisenberg model. It is difficult to enforce the correct power-law singularity in such an analysis.

The triplet excitation spectra for  $S = 1/2$  and  $S = 3/2$  along symmetry lines of the Brillouin zone ( $\Gamma(0,0)$ ,  $K(\frac{2\pi}{3a}, 0)$ ,  $M(\frac{2\pi}{3a}, \frac{2\pi}{\sqrt{3}a})$ ,  $\Gamma(0,0)$ ) are shown in Fig. 3 and Fig. 4 respectively. In the dimerized phase, there are two branches of the triplet spectrum at every  $k$

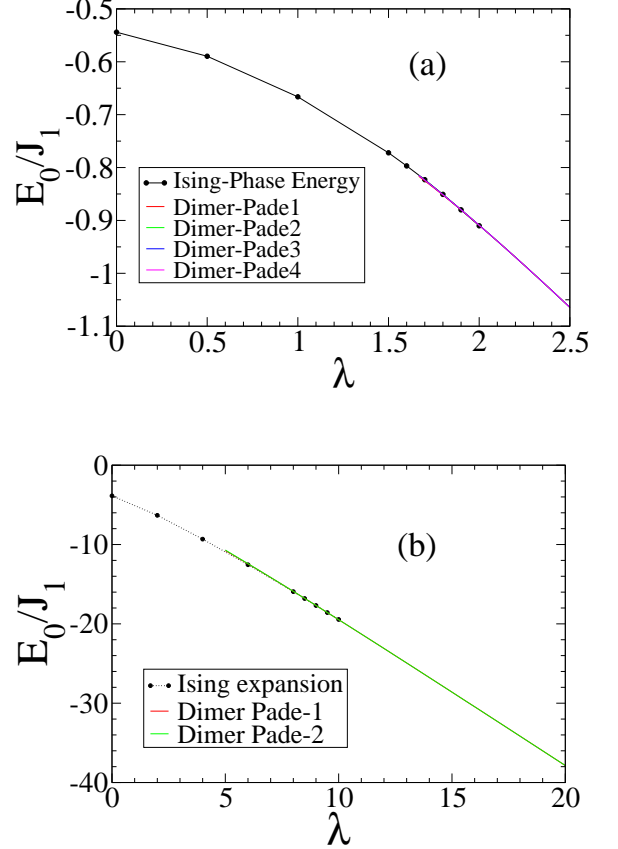


FIG. 1: Ground state energy as a function of  $\lambda = J_\perp/J_1$  for (a)  $S = 1/2$  and (b)  $S = 3/2$  models.

corresponding to the two atoms per unit cell in the honeycomb lattice. They become degenerate at the M point. The spectral gap approaches zero as the transition to the Néel phase is approached.

The most accurate way to determine the critical  $\lambda$  in our study is by analyzing the energy gap series. Here, we use the knowledge that this series has a singularity at the critical  $\lambda$  with a critical exponent  $\nu$  given by the  $3d$  Heisenberg universal value  $\nu = 0.71$ [30]. Thus, we first raise the series to a power  $1/\nu \approx 1.408$ , and then study it by Padé approximants to see where it goes to zero. The Padé approximants show excellent internal consistency for the longer  $S = 1/2$  series. Three different approximants are shown in Fig. 5a and they are almost indistinguishable from each other. Thus the uncertainty comes primarily from varying the value of  $\nu$ . We estimate  $1/\lambda_c = 0.6014 \pm 0.002$ , which translates to  $J_\perp/J_1 = 1.66 \pm 0.02$ . For  $S = 3/2$ , the shorter series though less accurate than for  $s = 1/2$  is still very accurate. Two different approximants are shown in Fig. 5b, and one can see that they begin to deviate a little close to the transition. In this case, we estimate  $1/\lambda_c = 0.107 \pm 0.002$ ,

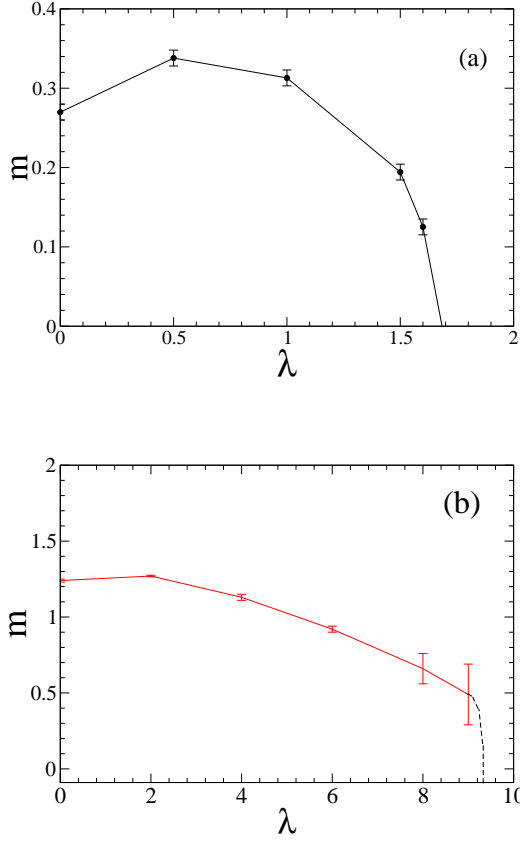


FIG. 2: Néel order parameter as a function of  $\lambda = J_{\perp}/J_1$  for (a)  $S = 1/2$  and (b)  $S = 3/2$  models.

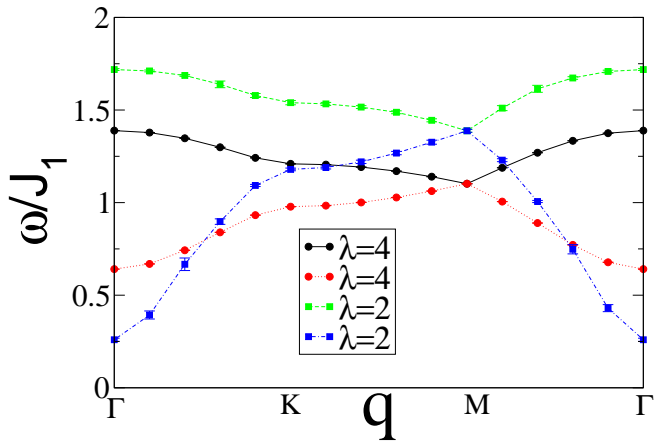


FIG. 3: Triplon spectra for the for  $S = 1/2$  models along the contour  $\Gamma(0,0), K(\frac{2\pi}{3a}, 0), M(\frac{2\pi}{3a}, \frac{2\pi}{\sqrt{3}a}), \Gamma(0,0)$  in the Brillouin zone for two different values of  $\lambda = J_{\perp}/J_1$ .

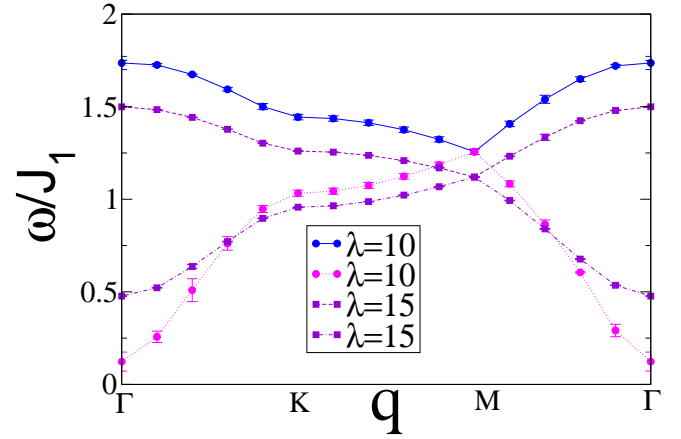


FIG. 4: Triplon spectra for the for  $S = 3/2$  models along the contour  $\Gamma(0,0), K(\frac{2\pi}{3a}, 0), M(\frac{2\pi}{3a}, \frac{2\pi}{\sqrt{3}a}), \Gamma(0,0)$  in the Brillouin zone for two different values of  $\lambda = J_{\perp}/J_1$ .

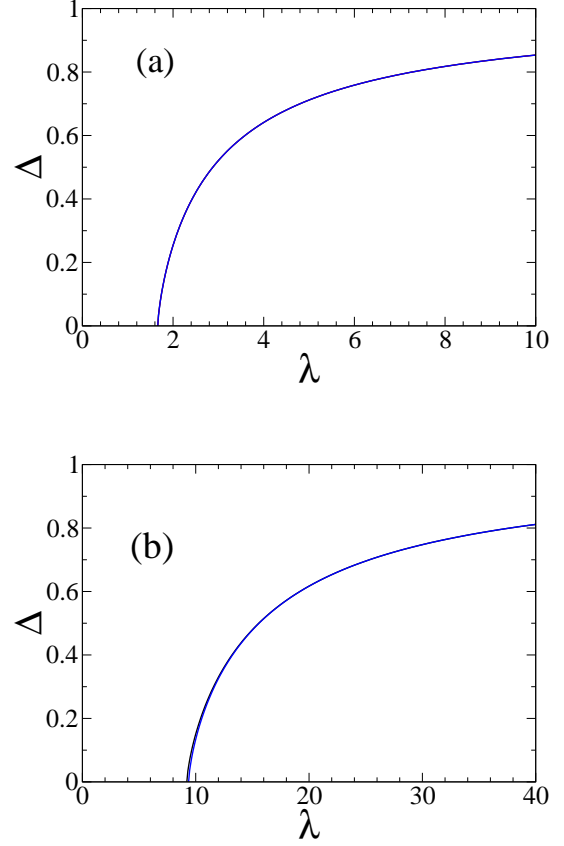


FIG. 5: Energy gap as a function of  $\lambda = J_{\perp}/J_1$  for  $J_2 = 0$  for (a)  $S = 1/2$  and (b)  $S = 3/2$  models.

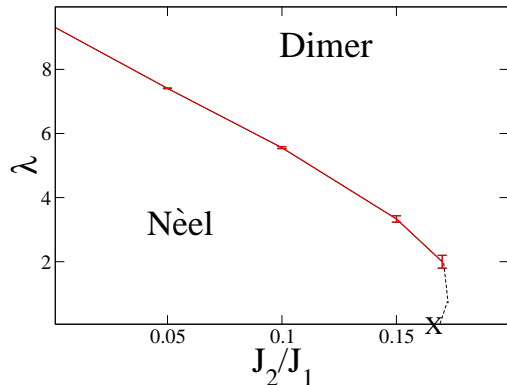


FIG. 6: Phase Diagram for the  $S = 3/2$  model with frustration in the honeycomb layers. The symbol X denotes the critical coupling where Néel order goes away for  $\lambda = 0$  in the classical limit.

which translates to  $J_{\perp}/J_1 = 9.3 \pm 0.2$ . Both these results are in very good agreement with the QMC study, which gives  $J_{\perp}/J_1 = 1.645(1)$  for  $S = 1/2$  and  $9.194(3)$  for  $S = 3/2$  respectively.[25]

### IN-PLANE FRUSTRATION AND THE BISMUTH MANGANESE OXYNITRATE MATERIALS

Since the spin-3/2 material  $\text{Bi}_3\text{Mn}_4\text{O}_{12}\text{NO}_3$  is unlikely to have  $J_{\perp}$  values an order of magnitude larger than in plane couplings, it is clear that frustration must be present to explain the absence of Néel order. To study this we add a frustrating second neighbor interaction  $J_2$  to our study of the  $S = 3/2$  model. We find that the addition of frustration rapidly decreases the critical value of  $J_{\perp}/J_1$ . The estimated phase boundary is shown in Fig. 6. For  $J_2/J_1 = 0.1$  this value is reduced to  $5.5 \pm 1$ , which is still significantly larger than the estimated ratio between 1 and 2 for the material in the electronic structure calculation. We find that a value of  $J_2/J_1$  larger than 0.15 can lead to a disorder with  $J_{\perp}/J_1$  less than 2. These numbers are within the range of values estimated for the material from electronic structure calculations.[24]

At the classical level, a single layer Heisenberg model loses Néel order at  $J_2/J_1 = 1/6$ . [7] This is indicated by X in Fig. 6. However, this ratio is somewhat enhanced in the presence of quantum fluctuations. Since, this enhancement in the critical  $J_2/J_1$  is roughly 0.03 for the  $S = 1/2$  case,[13] it should be much smaller for the  $S = 3/2$  case. The critical  $J_2/J_1$  should be further enhanced by the addition of a small  $J_{\perp}$  in the bilayer, since a small bilayer coupling makes the system more ordered. Thus, the phase diagram in the  $J_2/J_1$  and  $J_{\perp}/J_1$  plane has a slightly reentrant character for small  $J_{\perp}/J_1$ .

This has the effect that beyond  $J_2/J_1 = 0.17$ , the phase boundary becomes close to vertical and our series analysis is no longer accurate to locate it precisely. We sketch this phase boundary in Fig. 5 by dashed lines. We have analyzed the series at  $J_2/J_1 = 0.2$  and it shows no consistent point where the gap vanishes.

If the material  $\text{Bi}_3\text{Mn}_4\text{O}_{12}\text{NO}_3$  has  $J_2/J_1 < 0.17$ , then the singlet phase must arise from strong bilayer coupling and the material is almost certainly in the spin-disordered phase that is adiabatically related to the product singlet phase at large  $J_{\perp}$ . In this phase our calculation of the excitation spectra should be accurate. Neutron scattering on the material can help determine more precise exchange parameters.

However, it is possible that the material has  $J_2/J_1 > 0.17$  and in this case depending on how large  $J_{\perp}/J_1$  is, a magnetically disordered phase may or may not be adiabatically related to the product singlet phase found at large  $J_{\perp}$ . At  $J_{\perp}/J_1 < 2$ , there maybe a phase transition from one singlet phase to another. Whether a new spin-liquid phases arises in the spin-3/2 model at small  $J_{\perp}/J_1$  with frustration, and how far down in  $J_{\perp}/J_1$  the product singlet phase continues remains an open question, which deserves further study. If there is a frustration dominated spin-liquid phase for  $S = 3/2$  at small  $J_{\perp}$  values, and that is the appropriate phase for the material, that would make the material much more interesting. In this case, neutron scattering may show an absence of triplon-like excitations. Further experimental study is needed before more conclusions can be drawn.

In considering the material parameters, one should note that the third neighbor exchange interactions in the honeycomb planes  $J_3$  may be comparable to second neighbor interactions.[24] However,  $J_3$  is unfrustrating and hence enhances Néel order. If  $J_2$  and  $J_3$  become substantial, they lead to a complex phase diagram even for a single honeycomb plane.[12, 13] But, for  $J_2$  and  $J_3$  less than  $0.2J_1$  as expected for these materials, the main role of  $J_3$  is to slightly enhance the region of Néel order. It effectively reduces the value of  $J_2/J_1$ . Finally, quenched disorder and/or lattice distortions may also play a role in the materials.

### CONCLUSIONS

In conclusion, in this paper we have used series expansion methods to study the ground state properties of  $S = 1/2$  and  $S = 3/2$  bilayer honeycomb lattice Heisenberg models. We find that an explanation for the material  $\text{Bi}_3\text{Mn}_4\text{O}_{12}\text{NO}_3$  requires significant frustration in the honeycomb planes. We also present results for the evolution of the spectra with  $\lambda = J_{\perp}/J_1$  in the spin-disordered phase that is adiabatically related to the product singlet phase at large  $J_{\perp}$ . Further study of the experimental system, especially its triplet excitation spectra is necessary

before further conclusions can be drawn as to whether the material is in the product singlet phase or in a novel spin-liquid phase.

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