A new paradigm for two-dimensional spin-liquids

R. R. P. Singh\textsuperscript{1}, O. A. Starykh\textsuperscript{2} and P. J. Freitas\textsuperscript{1}

\textsuperscript{1} Department of Physics, University of California, Davis, California 95616
\textsuperscript{2} Department of Physics, University of Florida, Gainesville, FL 32611

(March 24, 2022)

Motivated by the geometry of the materials Na\textsubscript{2}Ti\textsubscript{2}As\textsubscript{2}O and Na\textsubscript{2}Ti\textsubscript{2}Sb\textsubscript{2}O, we study a square-lattice Heisenberg antiferromagnet with spins located at the bond-centers. The largest exchange constant $J$ couples neighboring spins in a given row or column. This leads to a mesh of isolated spin-chains running along the $X$ and $Y$ axes. A weaker exchange constant $J'$ couples the nearest-neighbor spins on the lattice. Classically, $J'$ fails to fix the relative spin orientation for different chains and hence the ground state is highly degenerate. Quantum order by disorder effect is studied by spin-wave theory and numerical methods. It is shown that a 4-sublattice order is favored by quantum fluctuations. However, several arguments are presented that suggest that the ground state of the system remains disordered, thus providing us with a paradigm for a two-dimensional spin-liquid.

PACS numbers: 75.10.Jm, 75.40.Cx, 75.40.Gb, 75.50.Ee

In recent years many new materials have been discovered which exhibit novel magnetic behavior. Various aspects of quantum magnetism, including quantum critical phenomena and existence of spin-disordered ground states with spin-gaps have been observed in a variety of Cuprates, Germanates, Vanadates and other low-dimensional materials. One interesting fact that has come to light in these studies is that the geometrical arrangement of the transition metal and Oxygen ions can have a dramatic impact on the underlying microscopic spin-Hamiltonian and hence on the macroscopic magnetic properties of the system. For example in various Cuprates, the Cu-O-Cu bond angle is crucial for determining the effective exchange constant between Copper spins. Thus, Strontium Cuprates with certain stoichiometry behave as virtually decoupled spin-ladders \cite{1}, even though the separation of the Copper spins between neighboring ladders maybe smaller than their separation within a given ladder. In the CuGeO\textsubscript{3} \cite{2} and CaV\textsubscript{2}O\textsubscript{2n+1} \cite{3} it is also believed that superexchange between the transition metal ions is mediated by Oxygen and because of the geometry of various bond angles and occupied orbitals the second neighbor interactions are substantial compared to nearest neighbor ones. This leads to various interesting quantum phase transitions and spin-gap behavior in these materials.

Here, we consider a Heisenberg model with spins at the bond-centers of a square lattice:

$$\mathcal{H} = J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j + J' \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j,$$

with $J' \ll J$. The interactions are shown in Fig. 1. The exchange $J$ couples neighboring spins in a given row or column, whereas $J'$ is the nearest neighbor coupling between rows and columns. In the absence of $J'$ the system consists of a square mesh of decoupled spin-chains running along the $X$ and $Y$ axes. The motivation for studying such a model comes from the materials Na\textsubscript{2}Ti\textsubscript{2}Sb\textsubscript{2}O (and also Na\textsubscript{2}Ti\textsubscript{2}As\textsubscript{2}O) \cite{4}. These layered Titanates consist of planes of (Ti\textsubscript{2}Sb\textsubscript{2}O\textsubscript{2})\textsuperscript{2-}, where the Oxygen atoms form a square-lattice and the Titanium atoms sit at the bond centers of the lattice. The Antimony atoms sit above and below the centers of the elementary squares. The Titanium atoms carry spin-half. It is evident from the geometry that if the dominant exchange interaction is provided by a direct overlap between the Titanium orbitals, this material would behave as a nearest-neighbor Heisenberg model. If on the other hand the dominant interaction is mediated by Oxygen orbitals it would result in the largest interaction between neighboring spins in a given row or column, thus leading to our Eq. \textsuperscript{1}. Finally, if the dominant exchange is mediated by the p-orbitals of Antimony, the Hamiltonian in Eq. \textsuperscript{1} could still be appropriate, the lattice being dual to the one shown. The magnetic properties of this material are currently under investigation \cite{5}. The rest of the paper will be devoted to a study of this model Hamiltonian.

FIG. 1. The exchange interactions $J$ and $J'$ in our model, shown by solid lines and broken lines respectively.
We begin by studying this model in the linear spin-wave approximation. As finding the correct local spin configuration is based on energetic considerations, we expect the spin-wave theory to be at least qualitatively correct. Notice that the problem at hand has ‘double’ degeneracy in the classical limit: it is evidently degenerate with respect to relative angle \(\phi\) between quantization axes on vertical and horizontal chains, as well as with respect to relative orientation \(\phi\) of quantization axes on the neighboring parallel chains. Based on the fact that Hamiltonian \(H_{\text{bare}}\) classically has no spiral ordering, and on insight from a somewhat analogous problem of coupled planes \(\{\text{2}\}\), we restrict ourselves to the strongest interaction, decay of the induced inter-chain interaction with the ground state energy due to this coupling we next treat between remaining parallel chains.

Notice that classically the system remains degenerate between \(\tau_{i,i+1} = 1(\phi = 0)\) or \(\tau_{i,i+1} = 0(\phi = \pi)\), defined for each pair of chains \((i,i+1)\). The calculations are simplified greatly by choosing quantization axes on all sites such that the ordering is ferromagnetic. This is achieved by a unitary transformation parametrized by an angle \(\theta\) and a set of \((\tau_{i,i+1})\).

We now integrate out spins on the horizontal chains to find an effective Hamiltonian for the remaining spins. This is achieved by representing spins on vertical (horizontal) chains in terms of Holstein-Primakoff bosons \(a(b)\), and doing perturbation expansion in \(J'/J\). First nonzero contribution is of the type \(J^2 \sum_{e,e'} S^e_{i+e'}(a) S^{e'}_{j+e'}(a) < S^e_i(b) S^{e'}_j(b) >_{b}\), where averaging is with respect to the bare Hamiltonian of horizontal chains and \(S_{i+e}\) spins belong to vertical chains, i.e. \(J'\) acts along the \(<i,i+e>\) links. The average is nonzero when \(i\) and \(j\) belong to the same horizontal chain and \(\alpha = \beta\). It is seen that effective interaction between spins on vertical chains is time-dependent, but strongest contribution comes from static \((\omega_n = 0)\) part of the average. Denoting \(J_{\perp}^\dagger(i-j) = J^2 < S^e_i(b) S^{e'}_j(b) >_{b}\) and \(J_{\parallel}(r) = J^2(r-1) + J_{\perp}^\dagger(r)\) we find that geometry dictates the following coupling between remaining parallel chains \(n\) and \(m\),

\[
H_{\text{nm}}^\perp = \sum_{\alpha} J_{\perp}^\dagger(n-m) S^\alpha_{n,i} \left( 2 S^\alpha_{m,i} + S^\alpha_{m,i+1} + S^\alpha_{m,i-1} \right).
\]

(2)

Notice that long-range-ordered part of \(< S^e_i(b) S^{e'}_j(b) >_{b}\), if any, cancels out due to AFM correlations along the chains, and the effective interaction decays at least as \((n-m)^{-2}\). It is also important to realize that \(J_{\perp}^\dagger\) is anisotropic in spin space, in particular \(J_{\perp}^\dagger(2) \sim \cos^2 \theta\).

Notice that classically the system remains degenerate because \(< 2 S^\alpha_{m,i} + S^\alpha_{m,i+1} + S^\alpha_{m,i-1} >= 0\). Given the fast decay of the induced inter-chain interaction with the distance we restrict ourselves to the strongest interaction, \(J_{\perp}^\dagger(1)\), between nearest chains. To find corrections to ground state energy due to this coupling we next treat \(\hat{J}_{\perp}\) as a perturbation (see Ref. \{10\} for description of the procedure). After long algebra one finds quantum correction to the ground state energy (per chain) of \(M\) parallel chains of length \(N\):

\[
\delta E_{\text{G.S.}} = -\frac{1}{M} \sum_{q_y} \epsilon(q_y) C(J'/J)^4 \cos^2 \theta \sum_{i=1}^{M} (1 - 2\tau_{i,i+1}),
\]

(3)

where \(\epsilon(q) = 2JS \sin q\) is the single AFM chain dispersion in spin-wave theory, \(C = (\langle S^x_0 S^x_0 \rangle + \langle S^y_0 S^y_0 \rangle)^2/64\), and explicit form of \(\hat{J}_{\perp}\) was used. Note that correction is down by \(1/S\) factor, showing its quantum origin. Thus the energy is minimized by choosing all \(\tau_{i,i+1} = 0\) (AFM configuration) and \(\cos^2 \theta = 1\). This result agrees with well-known tendency of quantum fluctuations to favor colinear structures \{4,11\}.

Having found the ground state configuration of spins, we can determine the spin-wave dispersion and calculate the reduction in sublattice magnetization due to quantum fluctuations. This reduction turns out to be divergent due to a remaining artificial degeneracy of the spin-wave spectra. Similar divergency arises in a quantum order by disorder calculations on other systems and is known to be removed by the higher-order quantum corrections to the spin-wave spectra \{13\}. This technically difficult calculation has not been done. We would like to stress that the ground state structure found in \{3\} is determined by short-range spin correlations (i.e. by the correlations within the correlation length range) for which spin-wave approximation should work even if the sublattice magnetization vanishes.

Let us now take a closer look at the elementary excitations of the single chain. It is convenient to perform “staggering” of the spin configuration so that Néel ordering along the chain corresponds to the ferromagnetic one in the new representation. In this representation an elementary excitation of the chain is a domain wall (spinon) separating ferromagnetic domains of different orientation. The energy of a single domain wall is \(J_{\perp}\). Consider now unfrustrated coupling \(J_{\perp}\) between nearest spins on neighboring parallel chains: however small \(J_{\perp}\) is, it immediately leads to the suppression of spinons because the energy costs is proportional to \(J_{\perp} \times (\text{length of the domain})\) and diverges in the thermodynamic limit. This is an intuitive reason for the stabilization of LRO in the system of unfrustrated coupled chains \{8\}. But this is not true for our Hamiltonian \{3\}, where each spin is coupled to the zero-spin combination of spins on the neighboring chains. Thus domain wall excitations of the single chain seems to survive in the presence of nonzero \(J'\), hinting the possibility of the absence of LRO.

The effect of the “mixing” interchain coupling \(J'\) can also be taken into account in the disordered phase, where the interspin interaction is isotropic. We write
the partition function of the Hamiltonian (1) in the interaction representation, where independent chains are considered as unperturbed system and interchain coupling $J'$ as a perturbation \([12]\). Performing trace over the horizontal chains first one finds effective interaction between spins on the vertical chains proportional to $(J'(k))^2 G(0)(k_x, \omega_n) S^x(k, \omega_n) S^x(k, \omega_n)$, similar to our previous spin-wave calculations. Here $G(0)(k_x, \omega_n)$ is the rotationally-invariant one-dimensional spin Green’s function in Matsubara representation, and $J'(k) = J' \cos \frac{k_x}{2} \cos \frac{k_y}{2}$. Decoupling spins on different chains via a Hubbard-Stratonovich transformation \([14]\), the 2D Green’s function of the spins on vertical chains becomes,

$$G(k_x, k_y, \omega_n) = \frac{G(0)(k_y, \omega_n)}{1 - (J'(k))^2 G(0)(k_x, \omega_n) G(0)(k_y, \omega_n)}.$$  

(4)

The known form of $G(0)(k_x, \omega_n)$ \([13]\) implies that (i) the singularity at $k_0 = (\pi, \pi)$ remains unchanged because $J'(k_0) = 0$, (ii) the uniform susceptibility is $\chi = \chi_0/[1 - (\chi_0 J')^2]$, where $\chi_0 = 1/(\pi^2 J)$ is susceptibility of single chain, and (iii) interchain coupling comes into play below $T' \sim J'$. Within this approximation, the two-dimensional system remains in the disordered critical state at $T = 0$, and in the quantum-critical one at finite temperatures. This result should also be viewed with some caution due to the large degeneracies in the underlying problem which we do not know yet how to take into account completely.

We now turn to numerical studies. Because of multiple energy scales, the development of short-range order at high temperatures is not necessarily indicative of the order for $T \sim J' \ll J$. Thus we need to study the ordering tendency directly at low temperatures. As $J'/J \ll 1$, the coupling between the local order parameters on the neighboring parallel chains can be gotten by perturbation theory. We study the following correlation function between neighboring vertical chains:

$$c_{12} = \langle \sum_i (-1)^i S^x_{1,i} \cdot \sum_j (-1)^j S^x_{2,j} \rangle,$$  

(5)

here $S_{1,i}$ represents spins on first vertical chain and $S_{2,j}$ represents spins on second vertical chain. A value of $c_{12} > 0$ would imply ferromagnetic ordering whereas $c_{12} < 0$ would imply antiferromagnetic ordering. The leading order contribution to $c_{12}$ requires the interactions to be mediated by at least two horizontal chains. To make the perturbation theory numerically tractable, we confine ourselves to finite chains along vertical and horizontal directions (with periodic boundary conditions). For four spins in each of the chains, we can carry out perturbation theory using series expansion methods \([13]\). We find that $c_{12} \approx -9 \times 10^{-6}(J'/J)^6$, which is negative confirming the tendency of the parallel chains to align antiferromagnetically. We have also used Lanczos methods to calculate this correlation function with up to 6-spins in each chain for $|J'/J| \leq 0.3$. In all cases the coupling remains antiferromagnetic and very weak. For the 6-spin system $c_{12}$ appears to scale as $(J'/J)^4$ as expected from general arguments and spin-wave theory presented earlier. Complete diagonalization of a 32-site system is currently in progress.

Assuming the local ordering pattern obtained in spin-wave theory, we can now investigate the question of long-range order by an Ising expansion for our original Hamiltonian. We write the Hamiltonian as $\mathcal{H}(\lambda) = H_0 + \lambda H_1$, where, $H_0$ consists of an Ising Hamiltonian, whose two ground states are ordered in the four-sublattice pattern and $H_1 \equiv \mathcal{H} - H_0$, with $\mathcal{H}$ being the full Hamiltonian in Eq. \((1)\). We develop expansions for the sublattice magnetization in terms of the expansion parameter $\lambda$. If the system has long-range order, the expansion should converge up to $\lambda = 1$, whereas if it is disordered there should be a critical point at $\lambda < 1$. Without explicit calculations, we can make the following observation: because of the cancellation of the effective field from one chain to another, the purely one-dimensional graphs remain unaffected by the coupling between the chains. We know that these add up to zero sublattice magnetization at the Heisenberg point. The effects of the other graphs is to further reduce order, thus moving the Heisenberg system into a quantum disordered phase. We have carried out these expansions to order $\lambda^8$ for a range of $J'/J$ values. The analysis suggests critical values less than unity, implying a disordered ground state for the Heisenberg limit.

Additional insight can be gained by studying the $J' \gg J$ limit of the model, where the Néel state on 45-degrees rotated lattice is stabilized by the $J'$ interaction. As $J$ increases from zero, quantum fluctuations grow stronger and at $(J'/J)_{\text{crit}} = 0.76$ (within linear spin-wave approximation) finally destroy long range order, analogous to $J_1 - J_2$ model \([6]\). That these two systems are very similar is also supported by the fact that the critical value of frustrating interaction $J$ quoted above is exactly twice the corresponding critical value of $J_1 - J_2$ model. Given this analogy, it is tempting to speculate that disordered phase at $J'/J \geq 0.76$ is a spontaneously dimerized one \([16,17]\), with vertical and horizontal chains formed by the exchange $J$ being in the valence-bond-type state. However, extensions of these results to $J'/J > 1$ is problematic as at $J = J'$ this system classically has a finite ground state entropy \([17]\) and may change character at that point. Clearly more work is needed to understand the nature of the disordered phase. It is very interesting to ask what will happen upon introducing of a mobile charge carriers into the chains. We would like to point out apparent similarities of this problem with a very recent study of a square mesh of conducting horizontal and vertical stripes \([18]\).

In conclusion, we have identified a new frustrated
layered Heisenberg model, which could have a two-
dimensional spin-liquid ground state. The magnetic
properties of the materials Na$_2$Ti$_2$As$_2$O and Na$_2$Ti$_2$Sb$_2$O
maybe represented by such a model.

We would like to thank S. Kauzlarich and A. Axtell for
bringing these materials to our attention, and I. Affleck,
A. Chubukov, S. Sachdev and M. Zhitomirsky for discus-
sions and suggestions. This work is supported in part by
the National Science Foundation Grant DMR-9616574,
the Campus Laboratory Collaboration of the University
of California, and NHMFL.

[1] E. Dagotto and T. M. Rice, Science 271, 618 (1996).
[2] G. Castilla, et. al. Phys. Rev. Lett. 75 1823 (1995);
W. Geertsma and D. Khomskii, Phys. Rev. B54, 3011
(1996).
[3] K. Ueda, et. al. Phys. Rev. Lett. 76, 1932 (1996).
[4] A. Adam and H. U. Schuster, Z. Anorg. Allg. Chem.,
584, 150 (1990).
[5] S. Kauzlarich and A. Axtell, unpublished.
[6] J. B. Goodenough, *Magnetism and the Chemical Bond*,
Interscience Publishers, New York-London (1963).
[7] E. F. Shender, Sov. Phys. JETP 56, 178 (1982)
[8] H. J. Schulz, Phys. Rev. Lett. 77 2790 (1996)
[9] A. Moreo, et. al. Phys. Rev. B 42, 6283 (1990).
[10] T. Yildirim, et. al. Phys. Rev. B 53, 6455 (1996).
[11] P. Chandra, et al. Phys. Rev. Lett. 64, 88 (1990).
[12] M. P. Gelfand, et. al. J. Stat. Phys. 59, 1093 (1990); H.
X. He, et. al. J. Phys. A 23, 1775 (1990).
[13] A. V. Chubukov, Phys. Rev. B 44, 392 (1991)
[14] D. Boies, et. al. Phys. Rev. Lett. 74 968 (1995).
[15] S. Sachdev, Phys. Rev. B 50 13006 (1994).
[16] I. Affleck and J. B. Marston, Phys. Rev. B 37, 3774
(1988); N. Read and S. Sachdev, Phys. Rev. Lett. 62,
1694 (1989); S. Sachdev and N. Read, Phys. Rev. Lett.
77, 4800 (1996).
[17] C. L. Henley, private communication.
[18] A. H. Castro Neto and F. Guinea. cond-mat/9709324