Possibility of \( S = 1 \) spin liquids with fermionic spinons on triangular lattices

Zheng-Xin Liu\textsuperscript{1}, Yi Zhou\textsuperscript{2} and Tai-Kai Ng\textsuperscript{1}

\textsuperscript{1}Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay Road, Kowloon, Hong Kong
\textsuperscript{2}Department of Physics, Zhejiang University, Hangzhou 310027, P. R. China

In this paper we generalize the fermionic representation for \( S = 1/2 \) spins to arbitrary spins. Within a mean field theory we obtain several spin liquid states for spin \( S = 1 \) antiferromagnets on triangular lattices, including gapless f-wave spin liquid and topologically nontrivial \( p_x + ip_y \) spin liquid. After considering different competing orders, we construct a phase diagram for the \( J_1-J_3-K \) model. The application to recently discovered material \( \text{NiGa}_2\text{S}_4 \) is discussed.

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I. INTRODUCTION

Spin liquids are novel quantum magnetic states where long ranged magnetic order is absent at zero temperature due to strong quantum fluctuations\textsuperscript{15}. Instead of spin wave excitations in spin ordered systems, spinons are proposed to be the elementary spin excitations in spin liquids. It is believed that spin liquid states can be found in spin \( S = 1/2 \) antiferromagnets(AMFs) on geometric frustrated lattices and several promising candidate materials have been experimentally discovered\textsuperscript{15}. A natural question is whether spin liquid states with fermionic spinons can also exist in \( S > 1/2 \) systems as is proposed for \( S = 1/2 \) systems.

To address this issue, we formulate a fully quantum mechanical fermionic mean field theory for \( S = 1 \) system. We study the Heisenberg AFM, and obtain spin-liquid type solutions which have not been proposed previously. We focus our interest on the \( J_1-J_3-K \) model, which is proposed to be the microscopic Hamiltonian for the interesting material \( \text{NiGa}_2\text{S}_4 \), an frustrated AFM on triangular lattice. We argue that a gapless spin liquid state obtained in our mean-field theory is a candidate for the ground state when compared with experimental results.

II. FERMIONIC REPRESENTATION OF SPIN

To begin with, we introduce the fermionic representation for spins. In the \( S = 1/2 \) case, two species of fermionic spinons representing up and down spins are introduced to construct the spin operators. This fermionic representation can be generalized to arbitrary spin\textsuperscript{15}, in the present paper, we only consider the case \( S = 1 \). We introduce 3 species of spinon operators \( c_1, c_0, c_- \) satisfying anti-commutation relations \( \{c_m, c_n^\dagger\} = \delta_{mn} \), where \( m, n = 1, 0, -1 \). It is easy to show that spin operators can be expressed in terms of \( c_m \) and \( c_m^\dagger \)’s, \( \mathbf{S} = C^\dagger \mathbf{I} C \), where \( C = (c_1, c_0, c_-)^T \) and \( \mathbf{I}^\alpha(\alpha = x, y, z) = 3 \times 3 \) matrix whose matrix elements are given by \( I^\alpha_{mn} = \langle m | S^\alpha | n \rangle \).

In this fermionic spinon representation, a constraint has to be imposed on the Hilbert space to ensure that there is only one fermion per site (particle representation, \( N_f = 1 \)). Alternatively, a spin can equally be represented in a Hilbert space with 2 fermions per site (hole representation, \( N_f = 2 \)). The two representations are identical for \( S = 1/2 \), reflecting a particle-hole symmetry of the Hilbert space which is absent for \( S = 1 \). For \( S = 1 \) the two representations are related by a symmetry group of the spin operators as we shall explain in the following.

Following Affleck et al\textsuperscript{16}, we introduce the “hole” operators \( \bar{C} = (c_1^-, c_0^-, c_-^\dagger)^T \). It is easy to check that \( \bar{C} \) and \( C \) behave in the same manner under spin rotation and the spin operators can also be written in terms of \( C: \mathbf{S} = C^\dagger \mathbf{I} C \). Combining \( C \) and \( \bar{C} \) into a \( 3 \times 2 \) matrix \( \psi = (C, \bar{C}) \), we can reexpress the spin operator as

\[ \hat{\mathbf{S}} = \frac{1}{2} \text{Tr}(\psi^\dagger \mathbf{I} \psi), \]

and the constraints can be represented as

\[ \text{Tr}(\psi \sigma_z \psi^\dagger) = 3 - 2N_f = \pm 1, \]  

where + sign for “particle” and − sign for “hole” representations, respectively.

The spin operator \( \mathbf{S} \) is invariant under certain transformation of the spinon operators \( \psi \rightarrow \psi W \). These transformations \( W \) form a \( U(1) \oplus \mathbb{Z}_2 \) group (we note that for half-integer spins the symmetry group is \( SU(2) \)). For \( S = 1/2 \), the constraint is invariant under the \( SU(2) \) group because of particle-hole symmetry mentioned above. However, for \( S = 1 \) the particle-hole symmetry is absent and the two constraints in Eq. 2 are not invariant under the symmetry group. In fact, the two constraints can be transformed from one to the other by the particle-hole transformation. We shall adopt the “particle” representation \( N_f = 1 \) in the following discussion.

III. THE EXTENDED HEISENBERG MODEL

We now apply the fermionic representation to frustrated 2D \( S = 1 \) spin models. We focus on the \( J_1-J_3-K \) model on triangular lattices,

\[ H = \sum_{\langle i,j \rangle} [J_1 \mathbf{S}_i \cdot \mathbf{S}_j + K(\mathbf{S}_i \cdot \mathbf{S}_j)^2] + J_3 \sum_{[i,j]} \mathbf{S}_i \cdot \mathbf{S}_j, \]

where \( \langle i,j \rangle \) denotes nearest neighbor (NN) and \( [i,j] \) the third nearest neighbors (NNNN). Several semi-classical...
mean field studies of this Hamiltonian have appeared in literature[12] where most of the trial ground states are unentangled states (or direct product of local states). Here we consider a fully quantum mechanical mean field theory based on the fermion representation which admits resonant valence bond (RVB) type spin liquid ground states. We first consider the case $K = 0, J_1, J_3 > 0$.

### A. Spin liquid solutions at $K = 0$

Similar to the spin-1/2 systems, the following expression also holds for $S = 1$,

$$\mathbf{S}_i \cdot \mathbf{S}_j = -\frac{1}{2} Tr : (\psi_j^\dagger \psi_i \psi_j \psi_i^\dagger) :$$

$$= - : (\chi_{ij} \chi_{ij} + \Delta_{ij}) :$$

where $\chi$ denotes normal ordering, $\chi_{ij} = C_i^\dagger C_j = c_i^\dagger c_j + c_{1i}^\dagger c_{1j} + c_{0i}^\dagger c_{0j} + c_{-1i}^\dagger c_{-1j}$ is an effective (spin singlet) hopping and $\Delta_{ij} = C_i^\dagger C_j - c_{-1i} c_{-1j} - c_{0i} c_{0j} + c_{1i} c_{1j}$ represents $(S = 1)$ spin-singlet pairing. A mean field theory can be formulated by replacing one of the operators by its expectation value, $\mathbf{S}_i \cdot \mathbf{S}_j \sim -\langle \chi_{ij}^\dagger \chi_{ij} + \Delta_{ij}^\dagger \Delta_{ij} + h.c. \rangle + \langle \chi_{ij} \rangle^2 + \langle \Delta_{ij} \rangle^2$. Notice that $\langle \Delta_{ij} \rangle = -\langle \Delta_{ji} \rangle$ and the pairing has odd parity which is different from the corresponding $S = 1/2$ RVB states. We shall first consider solutions which respect both translational and rotational symmetries. Two such solutions with $f$-wave and $p_x + i p_y$-wave symmetries respectively, are obtained[16]. The mean field Hamiltonian of the two states has the form

$$H_{MF} = \sum_k \chi_k (c_{1k}^\dagger c_{1k} + c_{0k}^\dagger c_{0k} + c_{-1k}^\dagger c_{-1k})$$

$$- \sum_k [\Delta_k (c_{-1k}^\dagger c_{1k} - c_{0k}^\dagger c_{0k}) + h.c.],$$

with $\chi_k = \lambda - Z(J_1 \chi_{1k} + J_3 \chi_{3k})$, $\Delta_k = iZ(J_1 \Delta_{1k} \psi_k + J_3 \Delta_{3k} \bar{\psi}_k)$. Here $Z = 6$ is the coordination number, $\lambda$ is the lagrangian multiplier determined by $\langle C_i^\dagger C_i \rangle = 1$, and $\gamma_k = \frac{1}{2} [\cos k_x + \cos (\frac{k_y + \sqrt{3} k_z}{2}) + \cos (\frac{k_y - \sqrt{3} k_z}{2})].$

The mean field Hamiltonian can be diagonalized with appropriate Bogoliubov transformations, and the parameters $\chi$, $\Delta$ and $\lambda$ are determined by the self-consistent equations,

$$\chi_1 = \langle C_i^\dagger C_{i+x} \rangle, \ \chi_3 = \langle C_i^\dagger C_{i+2x} \rangle,$$

$$\Delta_1 = \langle C_i^\dagger C_{i+y} \rangle, \ \Delta_3 = \langle C_i^\dagger C_{i+2y} \rangle,$$

$$1 = \langle C_i^\dagger C_i \rangle,$$

where $i + x$ denotes a NN site of $i$ and $i + 2x$ a NNN site along the $x$ direction, $\chi_{1(3)}$ and $\Delta_{1(3)}$ are parameters on NN(NNNN) bonds. Similar to the spin-1/2 mean field theory, a physical spin liquid state can be formed by Gutzwiller projection of the mean field ground state to the state with single occupancy.

The mean field Hamiltonian describes three branches of fermionic spinon excitations with $S_z = 0, \pm 1$ and identical dispersion $E_k = \sqrt{x_k^2 + y_k^2}$. For the $f$-wave pairing, the excitation is gapless with several Dirac cones in the Brillouin zone (the number of cones is given in Fig. 2). For the $p_x + i p_y$-wave pairing, the bulk excitation is fully gapped. Since $\chi_k < 0$ at the $\Gamma$ point, the $p_x + i p_y$ ansatz belongs to the weak pairing region, and there should exist gapless (chiral) Majorana edge modes on the open boundaries. Thus the state describes a time-reversal symmetry breaking topological spin liquid. The $p_x + i p_y$ state has slightly lower energy in mean-field level.

Our mean field theory predicts two different spin liquid states (for any fixed pairing symmetry) as a function of $J_1/J_3$. The $p_x + i p_y$ state remains lower in energy in both cases. A first order phase transition occurs at $J_1/J_3 \sim 1$. When $J_1$ dominates, the spin liquid state is characterized by $\chi_{1(3)} \neq 0$ and $\Delta_{1(3)} \neq 0$ (consequently $\langle \mathbf{S}_i \cdot \mathbf{S}_{i+1} \rangle < 0$ and $\langle \mathbf{S}_i \cdot \mathbf{S}_{i+2} \rangle < 0$); while when $J_3$ dominates, $\chi_1 = \chi_3 = 0$ and $\Delta_1 = \Delta_3$.
\(\Delta_1 = 0 \quad \text{and} \quad \chi_3 \neq 0, \Delta_3 \neq 0\) (consequently \(\langle S_i \cdot S_{i+1} \rangle = 0\), \(\langle S_i \cdot S_{i+2} \rangle < 0\)).

**B. Competing orders and the phase diagram**

It is known that the AFM Heisenberg model on triangular lattice with \(J_1 > 0, J_3 = K = 0\) has a 120° ordered ground state (with wave vector \((\frac{1}{3}, \frac{1}{3}, 0)\)). When \(J_1, J_3 > 0\), the classical ground state is still ordered, but with an incommensurate wave vector. The K term gives rise to spin nematic order through the identity:

\[(S_i \cdot S_j)^2 = Q_{ij}^{ab} Q_{ij}^{ab}, \quad (6)\]

where \(Q_{ij}^{ab} = \frac{1}{4}(S_i^a S_j^b + S_i^b S_j^a)\) is the spin quadrupole tensor. To incorporate these possibilities in our theory, we introduce additional decouplings in our mean field decomposition.

To reduce the number of trial parameters in our calculation we assume that the long-ranged magnetic order, if exist, is always 120° ordered in \(H_{MF}\). To introduce the AFM order, we divide the triangular lattice into three sublattices \(u, v\) and \(w\) as shown in Fig. 1(b). We assume without loss of generality that the direction of long-ranged magnetic order \((S_a)\) (here \(a \in \{u, v, w\}\)) is pointing along the new basis axis \(x_a\) of the \(a\)-sublattice (see Fig. 1(b)), i.e. \(M_a = \langle S_a \rangle = \langle \tilde{S}_a \rangle x_a = M x_a\) in the new reference frame and becomes an effective ferromagnetic order. The operators \(C(x)\) (in the old frame) and \(\tilde{C}(\tilde{x})\) (in the new frame) obey the relations \(C_u = \tilde{C}_u, C_v = e^{-iS_i^a \theta} \tilde{C}_v\) and \(C_w = e^{iS_i^a \theta} \tilde{C}_w\), where \(\theta = 2\pi/3\). Then Eq. (4) becomes \(S_{ai} \cdot S_{bj} = -(\chi_{ai,bj} \tilde{x}_{ai,bj} + \tilde{\Delta}_{ai,bj} \tilde{\Delta}_{ai,bj})\), where \((i, j)\) and \((a, b)\) are the site and sublattice indices respectively and

\[\tilde{x}_{ai,bj} = e^{-i\theta} \tilde{c}_{1ai+bj} + e^{i\theta} \tilde{c}_{-1ai-bj}, \quad \tilde{\Delta}_{ai,bj} = e^{-i\theta} \tilde{c}_{-1ai+bj} - e^{i\theta} \tilde{c}_{1ai-bj}, \quad (7)\]

for \((a, b) \in \{(u, v), (v, w), (w, u)\}\). Including the mean field decoupling \(S_i \cdot S_j \sim \langle S_i \rangle \cdot S_j + S_i \cdot \langle S_j \rangle - \langle S_i \rangle \cdot \langle S_j \rangle\)

where \(\langle S \rangle = M \tilde{x}\), we obtain

\[S_{ai} \cdot S_{bj} \sim -[(\chi_{ai,bj} + \Delta \tilde{\Delta}_{ai,bj} - M \cos \theta \tilde{S}_{bj}) + h.c.] + \chi^2 + \Delta^2 - M^2 \cos \theta, \quad (8)\]

where \(\chi = (\chi_{ai,bj})\) and \(\Delta = (\Delta_{ai,bj})\).

We next consider the K term. First we observe that the K term can be decoupled as \(K(S_i \cdot S_j)^2 \sim K' S_i \cdot S_j\), where \(K' = K(S_i \cdot S_j)\), and \(S_i \cdot S_j\) can be further decoupled as in [3]. This decoupling renormalizes \(J_1\). On the other hand, the K term may give rise to nematic order according to equation (6) and a corresponding mean field decoupling can be introduced in our calculation with

\[(S_i \cdot S_j)^2 \sim \langle Q_{ij}^{ab} \rangle Q_{ij}^{ab} + Q_{ij}^{ab} \langle Q_{ij}^{ab} \rangle - \langle Q_{ij}^{ab} \rangle (Q_{ij}^{ab})^2. \quad (9)\]

We shall assume that \(\langle Q_{ij}^{ab} \rangle\) is diagonalized in the new frame (hence the trial wave function has a 120° nematic order). So we have \(Q_{ij}^{ab} \rightarrow \cos \theta \tilde{Q}_{ij}^{xx} + \sin \theta \tilde{Q}_{ij}^{xy} + \sin \theta \tilde{Q}_{ij}^{yx} + \cos \theta \tilde{Q}_{ij}^{yy} + \langle Q_{ij}^{zz} \rangle\). It is easy to show that \(\tilde{Q}_{xx} = \tilde{S}_{xx}^2 = \frac{1}{2} \left[1 + \tilde{c}_{0\hat{x}}^2 \tilde{c}_{0\hat{y}}^2 + \tilde{c}_{1\hat{x}} + \tilde{c}_{1\hat{y}}^2 \right]\), \(\tilde{Q}_{yy} = \tilde{S}_{yy}^2 = \frac{1}{2} \left[1 + \tilde{c}_{0\hat{x}}^2 \tilde{c}_{0\hat{y}}^2 - \tilde{c}_{1\hat{x}}^2 - \tilde{c}_{1\hat{y}}^2 \right]\) and \(\tilde{Q}_{zz} = \tilde{S}_{zz}^2 = 1 - \tilde{c}_{0\hat{x}}^2 \tilde{c}_{0\hat{y}}^2\). Putting together, we obtain our mean field decoupling

\[K(S_i \cdot S_j)^2 \sim K' S_i \cdot S_j + 2K [\langle \tilde{S}_{0\hat{x}}^2 \rangle - \frac{1}{4} W(\tilde{c}_{0\hat{x}}^2 \tilde{c}_{0\hat{y}}^2 + \tilde{c}_{1\hat{x}}^2 + \tilde{c}_{1\hat{y}}^2) + h.c.], \quad (10)\]

where \(N_0 = 1 - \langle \tilde{Q}_{zz} \rangle = \langle \tilde{c}_{0\hat{x}}^2 \rangle \tilde{c}_{0\hat{y}}^2\) and \(W = \langle \tilde{Q}_{xx} - \tilde{Q}_{yy} \rangle = \langle \tilde{c}_{1\hat{x}}^2 + \tilde{c}_{1\hat{y}}^2 \rangle\) are two mean field parameters representing nematic order. Notice that \(N_0 > 1/3\) implies easy \(\tilde{x}\tilde{y}\)-plane anisotropy and nonzero \(W\) indicates anisotropy of the quadrupole in \(\tilde{x}\tilde{y}\)-plane. The total mean field Hamiltonian is thus

\[H_{MF} = \sum_{\langle ij \rangle} (-J_1 + K') \left[ \chi_{ij} \tilde{x}_{ij} + \Delta_1 \tilde{\Delta}_{ij} - M \cos \theta \tilde{S}_{ij}^x \right] + h.c.] - J_3 \sum_{\langle ij \rangle} \left[ \chi_{ij} \tilde{x}_{ij} + \Delta_3 \tilde{\Delta}_{ij} - M \cos \theta \tilde{S}_{ij}^x \right] + h.c.\]

\[+ KZ \sum_i \left[ \frac{3}{2} N_0 - \frac{1}{2} \tilde{c}_{0i}^2 \tilde{c}_{0i}^2 - \frac{1}{4} W(\tilde{c}_{1i} \tilde{c}_{-1i} + \tilde{c}_{-1i}^2 \tilde{c}_{1i}) \right] + \lambda \sum_i (\tilde{c}_{1i} \tilde{c}_{1i} + \tilde{c}_{0i}^2 \tilde{c}_{0i}^2 + \tilde{c}_{1i}^2 \tilde{c}_{-1i}^2) \quad (11)\]

The mean field Hamiltonian can be diagonalized straightforwardly and the self-consistent equations for the mean field parameters are similar to Eq. (4) except the presence of three more order parameters \(M = \langle \tilde{S}_i^z \rangle\), \(N_0 = \langle \tilde{c}_{0i}^2 \rangle\) and \(W = \langle \tilde{c}_{1i}^2 \tilde{c}_{-1i}^2 \rangle\). We find more than one solutions to above equations, and the one with lowest energy is chosen to be the ground state. The phase diagram(Fig. [3]) is constructed by finding the mean field ground states with different parameters \(K' / J_3\) and \(J_1 / J_3\).

Transitions between different phases are found to be all first order. The phase in the bottom of the phase diagram with negative \(K\) is an easy-plane ferro-nematic phase. In this phase, \(N_0 = 0\) and \(\chi_{13} = \Delta_{13} = M = W = 0\). All spin correlations \(\langle S_i \cdot S_j \rangle = 0\) vanish and \(\langle S_i \cdot S_{i+1} \rangle^2 = 2\).
FIG. 3: (Color online) Phase diagram based on the mean field theory. All the phase transitions are first order. The two spin liquid phases are coexisting with 120° anti-ferro nematic order. Insets (A), (B) and (C) show the parameters change along the lines of $J_1/J_3 = 1, 2$ and $K = 9$ respectively.

The ground state is a direct product state $\prod_i |\psi_i\rangle$, with $S_i^z|\psi_i\rangle = 0$. When $|K|$ becomes smaller, it goes into the 120° ordered phase, where $M \sim 1$, $W \sim 0.5$, $\Delta_{1,3} = \chi_{1,3} = 0$ and $(S_i \cdot S_j) \sim -0.5$ for NN and NNNN. When $K$ increases further, there appear two nematic phases. These are anisotropic spin phases with fermionic excitation similar to the two classes of spin liquids we found when $K = 0$ except that the spectrum is split into three separate branches with two branches gapped. The new feature here is that $W \neq 0$, meaning that a 120° AF nematic order is built in. Here a 120° AF nematic order means that the in-plane easy-axis of $Q^{\alpha\beta}$ form 120° angle between any two neighboring sites, and the fermionic spinon spectrum is modified. The ground state is no longer a spin singlet.

It should be noted that our mean field ansatz (11) is not able to include several plausible states, like the magnetic ordering at angles $\neq 120°$, or the 90° AFN phase proposed in refs. [1, 4]. Therefore, our mean field phase diagram should be considered as suggestive only. A more accurate phase diagram can be obtained only when the above plausible states are taken into account and the energies are calculated more accurately from, e.g., the Gutzwiller projected ground state wave function. Nevertheless, our calculation shows the possible existence of spin liquid states for spin systems with $S > 1/2$. The spin liquid state can be stabilized (at small $K$, without AF nematic ordering) by the ring exchange interactions, which are not included in our present study.

IV. DISCUSSION AND CONCLUSION

Before concluding this paper, we compare our theory with the experiment on the recently discovered magnetic insulator NiGa$_3$S$_4$ [14, 15]. In this compound, $S = 1$ Ni$^{2+}$ ions form a layered triangular lattice with antiferromagnetic (AFM) interaction. The system was found to be in a spin disordered state at temperatures down to 0.35K despite a Weiss temperature $\theta_W \sim -80K$. The $T^2$ temperature dependence of specific heat at low temperature (below 10K) indicates that spin excitation is gapless while magnetic susceptibility approaches a constant below 10K [12]. Several possible ground state have been proposed and studied [4, 5, 9, 11]. Here we propose that the $f$-wave spin liquid state we obtained is a plausible ground state. In this case, nodal points appear in the spectrum of low lying spin excitations, resulting in $T^2$ temperature dependence of specific heat which is consistent with the experiment [13]. The $f$-wave state also predicts linear temperature dependence of spin susceptibility at low temperature. However it should be noted that the existing sample NiGa$_3$S$_4$ is strongly disordered and is presumably in a spin-glass state at low temperature. A clean sample is desired for better characterization of the material.

Summarizing, in this paper we have generalized the fermionic representation of $S = 1/2$ spins to spins with arbitrary magnitude. A mean field theory is developed for a $S = 1$ spin model where several spin liquid solutions are obtained. We have also obtained a AF-nematic state with fermionic spinon excitations. Our approach opens the possibility of constructing new classes of spin states for systems with spin magnitude $S > 1/2$.

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We have also investigated $p$-wave states and found that they break the rotation symmetry and are energetically higher than the $p_x + ip_y$-state.

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