Weak Mott insulators on the triangular lattice: possibility of a gapless nematic quantum spin liquid

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We study the energetics of Gutzwiller projected BCS states of various symmetries for the triangular lattice antiferromagnet with a four particle ring exchange using variational Monte Carlo methods. In a range of parameters the energetically favored state is found to be a projected $d_{x^2−y^2}$ paired state which breaks lattice rotational symmetry. We show that the properties of this nematic or orientationally ordered paired spin liquid state as a function of temperature and pressure can account for many of the experiments on organic materials.

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In the last few years the quasi-two dimensional organic salts $\kappa − (ET)_2Cu_2( CN)_3$ and $EtMe_3Sb[Pd(dmit)]_2$ (abbreviated respectively as $\kappa CN$ and $DMIT$ in the paper) have emerged as possible realizations of Mott insulators in the long sought ‘quantum spin liquid’ state $\{1, 2, 3, 4, 5, 6, 7, 8\}$. These layered materials are believed to be well described by the single band Hubbard model on a nearly isotropic triangular lattice. At ambient pressure they are Mott insulators which do not order magnetically down to temperatures $\sim 30 mK$ (much lower than the exchange $J \sim 250 K$ inferred from high temperature susceptibility $\{1, 8\}$). The low temperature phase is characterized by a linear $T$ dependent heat capacity, and a finite spin susceptibility just like in a metal (even though the material is insulating) $\{1, 4, 6\}$ indicating the presence of low lying spin excitations. There is a sharp crossover or possibly a phase transition at a low temperature $\approx 5 K$ signalled by a peak in the heat capacity, and the onset of a susceptibility $\{1, 4\}$. Further an external magnetic field induces inhomogeneity that is evidenced by a broadening of the NMR line $\{3\}$. Application of moderate pressure ($\approx 0.5 GPa$) induces a transition to a superconductor ($\kappa CN$) or metal ($DMIT$) $\{2\}$.

At this point several questions arise: What is a good description of the spin liquid Mott state? What is the connection between the superconducting state and the underlying spin liquid state that becomes unstable upon applying pressure? What is the nature of the finite temperature transitions/crossovers? We find, using a variational Monte Carlo analysis of the energetics of several possible wave functions for a spin Hamiltonian with Heisenberg and ring exchange interactions, that the nodal d-wave projected BCS state is the best candidate for the spin liquid. This state has gapless spin excitations and can naturally explain many of the experiments in $\kappa CN$ though a number of open questions remain.

Our results are based on the model Hamiltonian $\{9\}$

$$H = 2J_2 \sum_{<rr'>} \vec{S}_r \cdot \vec{S}_{r'} + J_4 \sum_{\square} (P_{1234} + h.c) \quad (1)$$

Here $\vec{S}_r$ are spin-$1/2$ operators at the sites of a triangular lattice. The second term sums over all elementary parallelograms, and $P_{1234}$ performs a cyclic exchange of the four spins at the sites of the parallelogram. The multiple ring exchange is expected to be significant due to the proximity to the Mott transition in the organics. It is known that the 3 sublattice Neel order vanishes beyond a critical $J_4/J_2 \approx 0.1$ $\{10\}$ that can lead to novel spin liquid phases with no long range spin order.

Previous studies on the above model, used a Gutzwiller projected filled Fermi sea to interpret the experimental $\{1\}$. The low energy theory of this state is described by a gapless Fermi surface of neutral spin-$1/2$ fermionic spinons coupled to a massless $U(1)$ gauge field (also obtained $\{11\}$ within a Hubbard model description). The sharp crossover at $T \sim 5 K$ was associated with ‘pairing’ of spinons $\{12\}$. The condensation of the spinon pair field gaps out the $U(1)$ gauge field, and the resulting state is described as a $Z_2$ spin liquid. Ref. $\{12\}$ suggested an exotic paired state that retains a finite gapless portion of the spinon Fermi surface. The possibility of a more conventional triplet paired $Z_2$ state induced by Kohn-Luttinger effects $\{12\}$ of the spinons has also been pointed out.

Here we study various paired spin liquid states for the $J_2 − J_4$ model using variational Monte Carlo calculations. In terms of wavefunctions, paired states may be described by Gutzwiller projected BCS states. Two natural states (which retain the full symmetry of the triangular lattice) are projected singlet $d_{x^2−y^2} + id_{xy}$ and nodal triplet $f_{x^2−3xy}$ wave states. Remarkably in a range of $J_4/J_2$ we find that a projected singlet $d_{x^2−y^2}$ state has better energy than either of these states. The $d_{x^2−y^2}$ state is a gapless $Z_2$ spin liquid state with nodal fermionic spinons and gapped $Z_2$ vortices (visons). In addition it spontaneously breaks the discrete rotational symmetry of
the triangular lattice but preserves lattice translational symmetry. Thus it is a gapless $Z_2$ spin liquid coexisting with a ‘nematic’ or orientational order parameter. The pairing structure of the spinons determines the pairing structure of the superconductor that forms under pressure. Thus we propose a nodal $d$-wave state for the pressure induced superconductor as well. Due to the discrete broken rotational symmetry both the insulator and the superconductor will have non-trivial finite temperature phase transitions in an ideal sample. We describe these and comment on their implications for the experiments.

Various variational states may be constructed by starting with a system of spin-1/2 fermionic spinons $f_{\sigma}$ hopping on a finite triangular lattice of size $L1 \times L2$ at half-filling with a “mean field” Hamiltonian:

$$H_{MF} = \sum_{\sigma} \left[ -t_{rr'} f_{\sigma}^\dagger f_{\sigma'} + \left( \Delta_{rr'} f_{\sigma}^\dagger f_{\sigma'}^\dagger + h.c. \right) \right] $$ (2)

The variational spin wave-function $|\Psi\rangle_{var} = P_G|\Psi\rangle_{MF}$ where the Gutzwiller projector $P_G = \prod_i \left( 1 - n_i \right)$ ensures exactly one spinon per site. Unknown parameters in $|\Psi\rangle_{var}$ are fixed by minimizing the energy $E_{var} = \langle \Psi_{var} | H | \Psi_{var} \rangle / \langle \Psi_{var} | \Psi_{var} \rangle$ (with $H$ given by Eq. [4] with only nearest neighbor $t_{rr'} = t$). The simplest $|\Psi\rangle_{MF}$ corresponds to $\Delta_{rr'} = 0$ i.e. a filled Fermi sea. The corresponding $|\Psi\rangle_{var} = |\Psi\rangle_{PFL}$ is the ground state of the single-spinon level $\delta E \equiv |\langle \Psi_{MF} | H | \Psi_{MF} \rangle |$ with no variational parameters. The prime on the product implies restriction to $\vec{k}$ such that the single-spinon level $\epsilon_{\vec{k}} \leq E_F$, the Fermi energy. More complex variational wave-functions are obtained with different patterns of non-zero $\Delta_{rr'}$ which correspond to various projected BCS wavefunctions $|\Psi\rangle_{PBCS} = P_G|\Psi\rangle_{BCS} = P_G \left( \sum_{\vec{k}} \phi_{\vec{k}} f_{\vec{k}}^\dagger f_{\vec{k}} \right)^{N/2} |0\rangle$. Here $\phi_{\vec{k}} = \Delta_{\vec{k}} / \left( \xi_{\vec{k}}^2 + \epsilon_{\vec{k}}^2 + |\Delta_{\vec{k}}|^2 \right)$ with $\epsilon_{\vec{k}} = \epsilon_{\vec{k}} - \mu$. Further we write $\Delta_{\vec{k}}^2$, the Fourier transform of $\Delta_{rr'}$, as $\Delta_{\vec{k}} = \Delta_0 F(\vec{k})$ where the form of $F(\vec{k})$ is fully determined from a particular pattern of $\Delta_{rr'}$ (or equivalently, a particular Cooper pair channel). The two variational parameters: gap parameter $\Delta_0$ and the ‘chiral potential’ $\mu$, are both determined by minimizing the energy.

The properties of the three superconducting gap functions are as follows: The $d_{x^2-y^2} + id_{xy}$ state is invariant under spin rotation, lattice rotation and translation symmetries, but breaks both time-reversal and parity. After projection it corresponds to the ‘chiral spin-liquid’ state [12]. The $d_{x^2-y^2}$ state is a spin-singlet with a $cos(2\theta)$ angular dependence ($\theta$ is the angle subtended by a bond). It breaks lattice rotational symmetry while preserving translations and time-reversal. Finally, the triplet $f_{x^2-3xy^2}$-wave state has orbital part varying as $cos(3\theta)$ while in spin-space it has zero projection along a quantization axis. This breaks spin rotation but preserves all the lattice symmetries and time reversal. Both $d_{x^2-y^2}$ and $f_{x^2-3xy^2}$ possess nodes along the Fermi surface in $k$-space while $d_{x^2-y^2} + id_{xy}$ is fully gapped.

Figure 1(a) shows the the difference $\delta E = E_{PBCS} - E_{PFL}$ for the three paired states, namely projected $d_{x^2-y^2} + id_{xy}$, $f_{x^2-3xy^2}$ and $d_{x^2-y^2}$. Clearly for $J_1/J_2 \gtrsim 0.25$ the projected Fermi liquid is the best variational state. Interestingly, for a wide range of parameters $0.10 \lesssim J_1/J_2 \lesssim 0.23$ the projected $d_{x^2-y^2}$ wins over all projected Fermi liquid as well other two paired states. In this regime $0.23 \lesssim J_1/J_2 \lesssim 0.25$, the error bars preclude any conclusion. Figure 1(b) shows the optimal value of the gap parameter $\Delta_0$ for these three states. Consistent with the results for optimal energy, $\Delta_0 \approx 0$ for $J_1/J_2 \gtrsim 0.25$ while for $0.10 \lesssim J_1/J_2 \lesssim 0.23$ the state $d_{x^2-y^2}$ has a non-zero and largest value of $\Delta_0$ among all paired states. For smaller values of $J_1/J_2(\lesssim 0.10)$ it is expected that the spin-rotation symmetry breaking spiral state would be the ground state of $H_{MF}$. In addition, we also studied a projected Fermi liquid with staggered flux $\Phi$ through alternate triangular plaquettes. We found that the energy has minima at $\Phi = 0$ and that the $\pi$ flux state is always higher in energy than the zero flux state $|\Psi\rangle_{PFL}$ for all values of $J_1/J_2$.

Heuristically, large values of $J_1/J_2$ favors delocalization of electrons. Thus it is not surprising that $PFL$ is the ground state for large $J_1/J_2$. Since $J_2 > 0$, the triplet paired $f$-wave state is expected to be unfavorable, consistent with our results. Further, the electrons are more delocalized in the nodal-$d_{x^2-y^2}$ compared to $d_{x^2-y^2} + id_{xy}$ since the latter is fully gapped. Thus for values of $J_1/J_2$ not so small as to induce spiral order for spins but small enough that $PFL$ is destabilized, our result that a projected nodal paired state is favored seems reasonable. Our results connect well with earlier variational Monte Carlo [13, 14] and other numerical studies [17] of superconducting states in anisotropic triangular lattice Hubbard models which also found good evidence for a nodal $d$-wave state.
We now describe various properties of the state described by the nodal d-wave paired wavefunction. A mean field Hamiltonian that describes the excitations of this state is simply the $H_{MF}$ of Eqn. 2. Fluctuations about the mean field state are described by coupling the spinons to a $Z_2$ gauge field. This state is thus an example of a $Z_2$ spin liquid. The excitations of the $Z_2$ gauge field are $Z_2$ flux configurations (known as visons) which are gapped in this spin liquid phase. The low energy physics is then correctly described by the BCS Hamiltonian $H_{MF}$. Many properties of the nodal d-wave spin liquid at low temperature are thus similar to the familiar spin physics of a nodal d-wave superconductor. We now describe some of these in relation to the experiments.

Specific heat and spin susceptibility: In the absence of impurities, the density of states for a nodal superfluid vanishes linearly with energy and consequently the specific heat $C = aT^2$ where the coefficient $a$ is, in principle, determined by the velocities that characterize the nodal dispersion of the spinons. Impurity scattering generates a non-zero density of states leading to a specific heat $C \sim \gamma T$, and a constant spin susceptibility $\chi_0$ as $T \to 0$. Further the low-T Wilson ratio $\chi/T$ is constant of order one. All of these are in agreement with the experiments on the organic spin liquid materials.

The impurity scattering rate can be roughly estimated by equating the entropies of the paired nodal spin liquid and ‘normal’ states at $T^*$, where $T^*$ is a mean field or crossover scale below which the pairing sets in (Fig. 2). Above $T^*$ spinons may be described as having a gapless Fermi surface with a specific heat $C = \gamma_{\text{spinon}} T$. Here $\gamma_{\text{spinon}} = (\pi^2/3)k_B^2 n_{\text{spinon}}(E_F)$ and $n_{\text{spinon}}(E_F) = 0.28/t_{\text{spinon}}$ is the spinon density of states at the Fermi energy. Equating the entropies of the paired and normal states at $T^*$, we estimate $a = 2\gamma_{\text{spinon}}/T^*$. Impurities will cut-off the $T^2$ specific heat of the nodal spin liquid at a scale $\Gamma$ and lead to a low-$T$ gamma coefficient given by $\gamma = a\Gamma/k_B = 2\gamma_{\text{spinon}} \Gamma/(k_B T^*)$. Now $\Gamma_{\text{spinon}} \approx 2J_2 \approx 250$ K and from the measured low-$T$ specific heat with $\gamma \approx 15mJK^{-2}mol^{-1}$, we estimate an impurity scattering rate $\Gamma \lesssim 0.25k_B T^* \approx 1.5K$. While $\Gamma$ is reasonably small compared to superconducting gap it is appreciable enough to generate a constant density of states at low energy and lead to an apparent Fermi-liquid like behavior in the specific heat at the lowest temperatures accessible, consistent with the experiments. The experiments also apparently show that the low temperature linear specific heat is insensitive to magnetic fields upto about 8 T. This poses a difficulty for the present theory as the Zeeman coupling to the field is expected to increase the low energy density of states. Indeed the prior proposal of an ‘Amperean’ paired state was partly motivated by the insensitivity of the specific heat to a magnetic field. However as discussed below the Amperean pairing has some difficulty with describing the superconducting state that develops under pressure.

Theoretical conductivity: Nodal spinons (as also dirty d-wave superconductors) lead to a finite ‘universal’ metallic thermal conductivity $\kappa \sim T \to 0$. In practice however observation of this effect requires low temperatures to eliminate the phonon contribution. In thermal transport measurements on $\kappa CN$, a plot of $\kappa/T$ as a function of $T^2$ of data above 1 K indeed extrapolates to a constant in the zero temperature limit. However, data for $T \lesssim 0.5$ K rapidly extrapolates to zero and has been interpreted as evidence for a gap. We do not have an explanation of this phenomenon.

Field induced inhomogeneity: At ambient pressure NMR studies of $\kappa CN$ show the development of a magnetic-field induced inhomogeneity. Within our theory this may be rationalized as follows. Due to the effect proposed by Motrunich, the external magnetic field induces an internal magnetic field for the spinons which can lead to vortices (visons) of the spinon pair condensate. The resulting ‘mixed state’ is inhomogeneous that occurs below the pairing scale and increases in proportion to the field.

* $T = 0$ phase diagram under pressure and superconductivity: In general pressure increases the ratio $t/U$ which implies an increase of $J_1/J_2$ leading to suppression of the pair amplitude. Thus increasing pressure suppresses the pairing transition. Increasing pressure also leads to an insulator-to-metal transition. Clearly two situations are possible depending on whether the pair order is killed before or after this metal-insulator transition. In the latter case superconductivity will be obtained in the metal close to the Mott phase boundary. We propose that this is realized in $\kappa CN$. On the other hand superconductivity has not been found in $DMIT$ under pressure. We suggest that in this material the pair order is killed under pressure before the metal-insulator transition. An interesting experimental test of this suggestion is to study the Mott insulating phase of $DMIT$ at pressures just below the metal-insulator phase boundary. Here the spinon Fermi surface state, with its
characteristic signatures such as, for instance, the $T^{2/3}$ heat capacity (produced by gauge fluctuations) will then survive to low-$T$ without any pairing transition.

If the pairing extends into the metallic phase the superconductor that results will also have $d_{x^2-y^2}$ symmetry, and will (for an ideal isotropic triangular lattice) break lattice rotational symmetry. The spinons of the insulator now become the nodal Bogoliubov quasiparticles of this $d$-wave superconductor. Thus the low temperature specific heat and spin susceptibilities of the superconductor will behave similarly to that of the spin liquid insulator. Further the NMR relaxation rate $1/T_1T \sim T^2$ for $T > \Gamma$ (the impurity scattering rate) and will saturate to a constant at the lowest temperatures. The former is in agreement with existing data on $\kappa CN$ for $T$ close to $T_c$ [1]. Such a relaxation rate is not expected within the alternate Amperean paired state [12], making it difficult to connect the pairing transition in the spin liquid with that in the metal. The NMR data [5] also shows that the Knight shift is only weakly suppressed on entering the superconducting state. However this may be due to complications associated with sample heating [2].

**Finite-$T$ phase diagram:** The $d_{x^2-y^2}$ paired spin liquid breaks a discrete orientational symmetry. As the temperature is increased, it undergoes a phase transition in the three-state Potts universality class at a certain temperature. The nematic order also leads to a richer finite-$T$ phase diagram in the superconductor. A straightforward analysis shows that at any non-zero $T$, the superconducting order becomes power law while the discrete broken orientational symmetry is preserved up to a certain temperature, say $T_1$ after which the system enters a ‘floating’ phase where both superfluid and orientational orders have power law correlations. Finally at an even higher temperature, say, $T_2$ there is a further phase transition to the normal state with exponentially falling correlations for both orders. Both the phase transitions at $T_1$ and $T_2$ are of the Kosterlitz-Thouless type with very weak signatures in the specific heat. However in both the insulator and the superconductor for the initial pairing transition, $\lambda (T)$ will behave similarly to that of the spin liquid insulator.

To summarize we studied the energetics of various Gutzwiller projected BCS states for the triangular lattice antiferromagnet with a four particle ring exchange. In a range of parameters the best state is a projected $d_{x^2-y^2}$ paired state which breaks lattice rotational symmetry. We described many properties of this state in light of experiments on the candidate organic spin liquid materials. Future experiments will hopefully shed light on whether such a paired nematic spin liquid really exists in these materials.

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