Half-Filled Layered Organic Superconductors and the Resonating-Valence-Bond Theory of the Hubbard-Heisenberg Model

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We present a resonating-valence-bond theory of superconductivity for the Hubbard-Heisenberg model on an anisotropic triangular lattice. Our calculations are consistent with the observed phase diagram of the half-filled layered organic superconductors, such as the β , β' , κ , and λ phases of (BEDT-TTF)₂X [bis(ethylenedithio)tetrathiafulvalene] and (BETS)₂X [bis(ethylenedithio)tetraselenafulvalene]. We find a first order transition from a Mott insulator to a $d_{x^2-y^2}$ superconductor with a small superfluid stiffness and a pseudogap with $d_{x^2-y^2}$ symmetry.

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Describing strongly correlated electronic systems is one of the outstanding challenges of theoretical physics. In particular, one would like to understand if different model materials embody the same underlying physics. The similarities between the cuprates and the layered organics superconductors [1,2] suggest that similar physics may be realized in both classes of materials. A powerful approach to chemically complex materials is to define minimal models [3], which can then be treated at various levels of approximation [4,5]. In this Letter we take such an approach. We argue that the observed phase diagram of the half-filled layered organic superconductors ($\frac{1}{2}$ LOS) is well described by the resonating-valence-bond (RVB) theory of the Hubbard-Heisenberg model. Our theory reproduces the first order Mott transition and predicts $d_{x^2-y^2}$ superconductivity [6], a small superfluid stiffness [7], and a pseudogap [8].

Layered organic superconductors form several crystal structures, some of which, such as the β , β' , κ , and λ phases, are strongly dimerized, others, e.g., the α , β'' , and θ phases, are not. The chemical composition of these materials is D_2X where D is an organic donor molecule, for example, BEDT-TTF (ET) or BETS, and X is an anion. Crystals consist of alternating layers of donor molecules and anions [9]. In both the dimerized and undimerized salts the anion accepts one electron from a pair of donor molecules which leads, at the level of band structure, to an insulating anionic layer and a metallic donor layer. Quantum chemistry suggests that the band structure of the undimerized materials is well described by treating each donor molecule as a site in a (quarter-filled) tightbinding model [10]. In the dimerized materials the intradimer hopping integral is large enough that the band structure can be described by a half-filled tight-binding model with each site representing a dimer [3,7].

 $\frac{1}{2}$ LOS display insulating, metallic, superconducting, "bad metallic," and (possibly) pseudogap [8] phases. The nature of the superconducting state in $\frac{1}{2}$ LOS is controversial [6]: the pairing is thought to be singlet [6], but experiments have lead to both *s*-wave and *d*-wave scenarios being proposed. Both phononic and nonphononic pairing mechanisms have previously been considered [4,5,7]. The superfluid stiffness [11] is much smaller than is predicted by BCS theory but is too large for fluctuations in the phase of the order parameter to be important [7].

Figure 1 shows the phase diagram of κ -(ET)₂X as a function of pressure (both hydrostatic and "chemical") and temperature. Other $\frac{1}{2}$ LOS have similar phase diagrams [9]. A simple explanation of this phase diagram is as follows [1,3]: there is a strong on-site Coulomb repulsion, U, which causes the ambient pressure (Mott) insulating state. The application of hydrostatic pressure or varying the anion (often thought of as applying "chemical pressure") reduces U/W, where W is the bandwidth, and leads to a superconducting state caused by strong electronic correlations. The bad metal phase is due to nearly localized electrons as one crosses over from the Fermi liquid to the Mott insulator.

It has been argued that the Hubbard model on an anisotropic triangular lattice is a minimal model for the layered organic superconductors [3]. A dynamical mean-field theory (DMFT) of the Hubbard model on a hypercubic lattice gives a good quantitative description of the competition between the Mott insulator, the bad metal, and the Fermi liquid [12,13]. However, a mean-field treatment of the positive U Hubbard model will not correctly describe the materials as it neglects important spin correlations that arise from superexchange. We therefore consider the Hubbard-Heisenberg model, which can be derived [14] from the Hubbard model in the limit of large, but finite, U. The Hamiltonian is

$$\mathcal{H} = \mu \sum_{i\sigma} \hat{n}_{i\sigma} - t \sum_{\{ij\}\sigma} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma} - t' \sum_{\langle ij\rangle\sigma} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma} + J \sum_{\{ij\}} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + J' \sum_{\langle ij\rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + U \sum_i \hat{n}_{i\dagger} \hat{n}_{i\downarrow} \quad (1)$$

where $\hat{c}_{i\sigma}^{(\dagger)}$ annihilates (creates) an electron on-site i with



FIG. 1 (color online). The pressure-temperature phase diagram of κ -(ET)₂X. Top: data from ¹H NMR and ac susceptibility (dark blue diamonds show the transition from a nonmagnetic state to an antiferromagnetically ordered state, light blue diamonds show the metal-insulator transition [24]), magnetization (pink pluses [25]), thermal expansion (filled purple circles [26]), and resistivity [red squares (filled indicates a first order Mott transition, empty indicates a crossover from insulating to metallic behaviors [23]), filled green triangles [12], gray stars [27], and open purple diamond [28]]. We have offset the data to allow for the effect of "chemical pressure." P = 0 corresponds to ambient pressure for $X = Cu[N(CN)_2]Cl$ [12,23–26]. The chemical pressure is indicated by the arrows on the abscissa. H_8 -NCS $\Rightarrow X =$ $Cu(NCS)_2$ [26,28] and H_8 -Br $\Rightarrow X = Cu[N(CN)_2]Br$ [26,27]. D_8 -Br indicates the effective chemical pressure of X = $Cu[N(CN)_2]Br$ with the ET molecule fully deuterated [27]. Bottom: a schematic version of the same diagram is shown. The glassy transition between the ethylene liquid and frozen in disorder phases results from conformational disorder in the organic molecule [6,26].

spin σ , $\hat{\mathbf{S}}_i$ is the Heisenberg spin operator, $\hat{n}_{i\sigma}$ is the number operator, and $\{ij\}$ and $\langle ij\rangle$ indicate sums over nearest neighbors and next nearest neighbors across one diagonal only [3], respectively. In principle $J \simeq 4t^2/U$ and

 $J' \simeq 4t'^2/U$ due to superexchange. However, our meanfield treatment will not correctly describe the renormalization of the bare parameters. Therefore, we treat t, t', J, J', and U as independent parameters. To reduce our parameter space we choose J = t/3 and $J' = t'^2/3t$ [15], which correspond roughly to the values of J and J' extracted from experiments on the insulating phase of the layered organics [3,16]. Thus in the calculations presented below we only vary two parameters: t'/t and U/t.

Our treatment of the Hubbard-Heisenberg Hamiltonian (1) is based on Anderson's RVB theory [17]. Although the RVB wave function is a poor approximation for the Heisenberg model on a square lattice, it was recently shown that it is a good trial wave function for some frustrated Heisenberg models [18]. These models are closely related to ours as many of the $\frac{1}{2}$ LOS are expected [3,16] to have $J'/J = (t'/t)^2$ in the relevant range. Further evidence that the RVB theory is a much better theory for the triangular lattice than it is for the square lattice comes from the critical value of the on-site Coulomb repulsion, U_c , at which the Mott transition occurs. The square lattice is insulating for arbitrarily small values of U, whereas we find that the RVB theory gives $U_c \simeq 10.3t$. On the isotropic triangular lattice exact diagonalization of finite lattices gives $U_c = 12t$ [19] and we find that $U_c \simeq 12.4t$ in the RVB theory.

Anderson's RVB state, $|\text{RVB}\rangle$, is given by performing a Gutzwiller projection, $\hat{P}_G = \sum_i (1 - \alpha \hat{n}_{i\uparrow} \hat{n}_{i\downarrow})$, on the BCS wave function, $|\text{BCS}\rangle$, i.e., $|\text{RVB}\rangle = \hat{P}_G |\text{BCS}\rangle$. Here α is a variational parameter which controls the fraction of doubly occupied sites, *d*. A detailed analysis of the RVB theory of the Hubbard-Heisenberg model on the square lattice was reported by Gan *et al.* [20].

Following the spirit of Ref. [21], we make the Gutzwiller approximation [22], *viz.*, $\langle \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} \rangle_{\text{RVB}} = g_t \langle \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} \rangle_{\text{BCS}}$ and $\langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \rangle_{\text{RVB}} = g_s \langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \rangle_{\text{BCS}}$ where $\langle \mathcal{O} \rangle_{\psi} \equiv \langle \psi | \mathcal{O} | \psi \rangle$. Counting arguments show that [20,22] at half-filling $g_t =$ 8(1-2d)d and $g_s = 4(1-2d)^2$. The Gutzwiller approximation has several advantages: its simplicity allows some analytic progress to be made and allows one to consider infinite systems. However, the Gutzwiller approximation suppresses spin and charge fluctuations in the Hubbard model [22]. We have already sidestepped this problem somewhat by explicitly including the spin exchange terms in the Hubbard-Heisenberg model. Our theory produces a Mott insulating state that is a spin liquid rather than the antiferromagnetic insulating state observed in most (but not all [16]) $\frac{1}{2}$ LOS; however, generalization of $|\text{RVB}\rangle$ to allow for antiferromagnetism should not significantly alter the phase diagram. Clearly an important test will be to project |RVB> onto the results of exact diagonalization of finite systems for the Hubbard model on the anisotropic triangular lattice.

Making the Hartree-Fock-Gorkov approximation leads to two coupled gap equations, $\Delta_{\mathbf{k}} = -\sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}}$ and

$$\begin{split} \chi_{\mathbf{k}} &= \tilde{\varepsilon}_{\mathbf{k}} - \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} \frac{\chi_{\mathbf{k}'}}{2E_{\mathbf{k}'}}, \text{ where } V_{\mathbf{k}} = -\frac{3}{2} g_{S} [J(\cos k_{x} + \cos k_{y}) + J'\cos(k_{x} + k_{y})], \quad \tilde{\varepsilon}_{\mathbf{k}} = \tilde{\mu} - 2 g_{I} [t(\cos k_{x} + \cos k_{y}) + t'\cos(k_{x} + k_{y})], \text{ and } E_{\mathbf{k}} = \sqrt{[\tilde{\varepsilon}_{\mathbf{k}} + \chi_{\mathbf{k}}]^{2} + |\Delta_{\mathbf{k}}|^{2}}. \quad d \text{ is minimized variationally and the renormalized chemical potential, } \tilde{\mu}, \text{ is chosen to ensure half-filling [20].} \\ \text{The two mean fields are a Hartree-Fock term, } \chi_{\mathbf{k}} = \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} \langle \hat{c}_{\mathbf{k}'\uparrow}^{\dagger} \hat{c}_{\mathbf{k}'\downarrow} \rangle_{\mathrm{BCS}}, \text{ and an anomalous term, } \Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} \langle \hat{c}_{\mathbf{k}'\downarrow}^{\dagger} \hat{c}_{-\mathbf{k}'\downarrow} \rangle_{\mathrm{BCS}}, \text{ where } \hat{c}_{\mathbf{k}\sigma} \text{ is the Fourier transform of } \hat{c}_{i\sigma}. \end{split}$$

We solve the coupled gap equations self-consistently in reciprocal space on a 120×120 mesh. We do not enforce any symmetry constraints on the order parameters and find that it has $d_{x^2-y^2}$ symmetry; this is the pairing symmetry most compatible with experiments on $\frac{1}{2}$ LOS [6].

For the Hubbard model $g_t = Z$, the quasiparticle weight (the factor by which many-body effects reduce the bandwidth and Drude weight and enhance the effective mass, m^*). In Fig. 2 we plot g_t against U for several values of t'/t. For all values of t'/t we find that at some critical value, U_c , there is a first order transition from a superconducting state $(g_t \neq 0)$ to an insulating state $(g_t = 0)$. This is consistent with the first order superconductor-insulator transition observed experimentally in $\frac{1}{2}$ LOS [12,23]. Note that near the Mott transition g_t is reduced (and hence m^* is enhanced by a factor of 3 or 4), consistent with the large effective mass seen in the layered organic superconductors close to the insulating state [7]. Previous weak coupling approaches [4] do not capture this large mass renormalization. g_t is closely related to the reduction in the Drude weight due to strong correlations. Figure 2 is quantitatively similar to exact calculations of the Drude weight for the Hubbard model on an isotropic triangular model (c.f., Fig. 4 of Ref. [19]).



FIG. 2 (color online). $g_t \sim Z$ as a function of U for various values of t'/t, throughout J = t/3 and $J' = t'^2/3t$ [15]. Here we plot t' = 0.7t (dashed line), t' = 0.3t (dot-dashed line), and t' = 0 (solid line). For each value of t'/t we find a first order Mott transition at some critical value of U, U_c , from a superconducting state ($g_t \neq 0$) to an insulating state ($g_t = 0$). The inset shows the phase diagram for the model.

The fact that $g_t < 1$ leads to a reduced superfluid stiffness [20] as is observed in $\frac{1}{2}$ LOS. However, if we interpret our results in the simplest manner [21] they suggest that the most correlated materials have the most strongly suppressed superfluid stiffness, which is the opposite trend to that found experimentally [7,11].

 $\tilde{\Delta}_{\mathbf{k}} = \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} \langle \hat{c}_{\mathbf{k}'\uparrow} \hat{c}_{-\mathbf{k}'\downarrow} \rangle_{\text{RVB}} = g_t \Delta_{\mathbf{k}}$ is the superconducting order parameter. Figure 3 shows the mean of $|\Delta_{\mathbf{k}}|$ and $|\tilde{\Delta}_{\mathbf{k}}|$ as functions of *U* for several values of t'/t. $\tilde{\Delta}_{\mathbf{k}} \neq \Delta_{\mathbf{k}}$ indicates a pseudogap, which is predicted to be largest near the Mott transition and have $d_{x^2-y^2}$ symmetry. The angle dependence of the pseudogap could be measured by angle resolved photoemission or angle resolved magnetoresistance oscillations. We plot the mean of $|\Delta_{\mathbf{k}}|$ and $|\tilde{\Delta}_{\mathbf{k}}|$ as functions of t'/t for fixed *U* in the inset to Fig. 3. Varying t'/t can lead to a suppression of superconductivity and can even drive the Mott transition as can be seen from the phase diagram of the model (inset to Fig. 2).

Our results suggest that the effects of the anisotropy of the triangular lattice are important for the organic superconductors. We suggest that the large value of t'/t and hence of J'/J stabilizes the RVB state in $\frac{1}{2}$ LOS [18]. The RVB state naturally explains the first order transition between the Mott insulator and a $d_{x^2-y^2}$ superconductor. Further, our results suggest that the simple picture [1,3] in which the only role of hydrostatic and chemical pressure is to vary U/W is not sufficient to explain the phase diagram of $\frac{1}{2}$ LOS. It appears that the value of t'/t, and hence J'/J also plays a crucial role in determining the



FIG. 3 (color online). $\overline{|\Delta_{\mathbf{k}}|}$ and $|\tilde{\Delta}_{\mathbf{k}}|$ (both in units of *t*) as functions of *U* for various values of t'/t and J = t/3 and $J' = t'^2/3t$ [15]. $\tilde{\Delta}_{\mathbf{k}} = g_t \Delta_{\mathbf{k}}$ and the bar indicates averaging over the Brillouin zone (i.e., $\overline{f}_{\mathbf{k}} = \sum_{\mathbf{k}} f_{\mathbf{k}} / \sum_{\mathbf{k}}$). Here we plot t' = 0.7t(blue: $|\tilde{\Delta}_{\mathbf{k}}|$ solid line; $|\overline{\Delta}_{\mathbf{k}}|$ dashed line), t' = 0.3t (red: $|\tilde{\Delta}_{\mathbf{k}}|$ double dot-dashed line; $|\overline{\Delta}_{\mathbf{k}}|$ long-dashed line), and t' = 0(black: $|\tilde{\Delta}_{\mathbf{k}}|$ dot-double-dashed line; $|\overline{\Delta}_{\mathbf{k}}|$ dot-dashed line). The inset shows $|\overline{\Delta}_{\mathbf{k}}|$ (dashed line) and $|\tilde{\Delta}_{\mathbf{k}}|$ (solid line) against t'/t with U = 9t.

behavior of these materials. t'/t controls the degree of nesting of the Fermi surface and therefore directly controls the stability of the Mott insulator, whereas J'/J determines $V_{\mathbf{k}}$ which controls the stability of the superconducting phase. This is why variations in t'/t can even drive the Mott transition at a fixed U. Clearly, the physics of the anisotropic triangular lattice is qualitatively different from that of square lattice.

Combining our results with those from DMFT studies of the Hubbard model allows one to reproduce the main features of the phase diagram of $\frac{1}{2}$ LOS (Fig. 1). This is consistent with the claim [3] that the Hubbard model is the minimal model for $\frac{1}{2}$ LOS. (We stress that this theory is not applicable to the quarter-filled layered organic superconductors [10] or the Bechgaard salts [9].) However, caution is required here. Although calculations (e.g., [12]) based on the Hubbard model can give good quantitative agreement with experiments on $\frac{1}{2}$ LOS, one does not know *a priori* how to map the experimental parameter space (pressure, temperature, and chemical composition) onto the theoretical parameter space (t'/t, U/t, etc.). Therefore, an outstanding problem is to discover whether quantum chemistry predicts the large variations of the Hubbard parameters with pressure required for quantitative agreement with experiment.

We have presented an RVB theory of the Hubbard-Heisenberg model on the anisotropic triangular lattice. We argued that the RVB state may be a good trial wave function for $\frac{1}{2}$ LOS because the values of J'/J deduced from quantum chemistry and experiment are comparable to those for which the RVB state appears to be a good approximation. Our calculations show a first order Mott transition from an insulating state to a $d_{x^2-y^2}$ superconductor. A similar first order Mott transition is seen in experiments on $\frac{1}{2}$ LOS. The Mott transition can be driven by increasing *either* U/t or t'/t. Further, at a fixed U, superconductivity is strongly suppressed by increasing t'/t. This suggests that the value of t'/t may be more important in the layered organic superconductors than has previously been appreciated. The superconducting state has a reduced superfluid stiffness as is observed in the $\frac{1}{2}$ LOS. The RVB theory predicts that there is a pseudogap with $d_{x^2-y^2}$ symmetry.

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Note added.—After completing this work we became aware of some similar results reported elsewhere [29,30].

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