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Pairing and superconductivity driven by strong quasiparticle renormalization in two-dimensional organic charge transfer salts

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We introduce and analyze a variational wave function for quasi two-dimensional κ-(ET)$_2$ organic salts containing strong local and nonlocal correlation effects. We find an unconventional superconducting ground state for intermediate charge carrier interaction, sandwiched between a conventional metal at weak coupling and a spin liquid at larger coupling. Most remarkably, the excitation spectrum is dramatically renormalized and is found to be the driving force for the formation of the unusual superconducting state.

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The proximity to a Mott insulating phase affects the behavior of a correlated material in a fundamental way[1, 2]. Since most Mott insulators are also magnetically ordered, it is often not clear whether unconventional behavior observed in nearby phases is due to the proximity to a Mott transition, to a magnetic phase transition, or a combination of both. Ideal materials to sort this out are obviously spin liquids, systems where the Mott insulating phase is magnetically disordered. Recently, such behavior was found in the magnetically frustrated, insulating organic charge transfer salt κ-(ET)$_2$Cu$_2$(CN)$_3$ by Shimizu *et al.*[3]. No magnetic long-range order was found down to $T \approx 30\,$mK. While the low-T susceptibility is suppressed, consistent with the opening of a spin gap, the observed power-law dependence, $1/T_1 \propto T^2$, of the NMR-spin liquid relaxation rate[3] supports gapless (possibly nodal) excitations of the spin liquid. Under pressure, κ-(ET)$_2$Cu$_2$(CN)$_3$ becomes, like many similar κ-(ET)$_2$X systems[4, 5, 6], a superconductor[7].

In quasi two-dimensional κ-(ET)$_2$X salts[4, 5, 6] dimers of ET = bis[ethylenedithio]-tetrathiafulvalene molecules are arranged in an anisotropic triangular lattice, with a charge state of one hole per dimer. The insulating state is, in most cases, antiferromagnetically ordered and separated from a pressure induced superconducting phase by a first order transition[8]. In the superconducting state a number of experiments strongly support the existence of nodes of the pairing gap[9, 10, 11, 12, 13, 14, 15, 16]. A gap with nodes was determined in spin fluctuation theories[17, 18, 19, 20, 21]; the location of the nodes of most of these calculations[17, 18, 19, 20] was however in disagreement with experiments[14, 15]. More importantly, the absence of magnetic long range order in κ-(ET)$_2$Cu$_2$(CN)$_3$ and the rather strong first order transition to an antiferromagnet in other systems, seem to be at odds with key assumptions of the spin fluctuation approach.

In this paper we introduce and analyze a variational resonating valence bond (RVB) wave function for systems close to a Mott transition, tuned by the interaction strength, i.e. for fixed carrier concentration but variable pressure. Starting with a simple metal for low interaction strengths, we find a dramatic renormalization of the quasiparticle spectrum for intermediate strength of the interaction. The system becomes a spin liquid of singlets with strong but short ranged spin correlations and a rapidly growing gap which persists as the interaction strength is increased. We further find that superconductivity is strong only in the transition regime between the simple metal and the spin liquid, see Fig.1. The nature of the renormalized spectrum and the nodal structure in the superconducting state are a strong function of the electronic dispersion. We claim that our proposed wavefunction, with its ability to describe unconventional order parameters with nodes and effects of strong correlations, is a strong candidate for the description of κ-

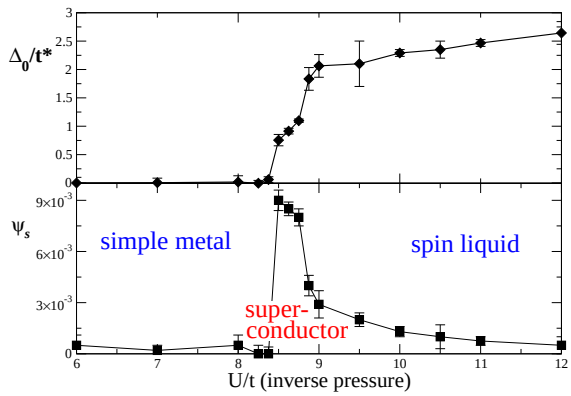

FIG. 1: Single particle gap, Δ_0 in units of the renormalized hopping t^* (see text), and superconducting order parameter, ψ_s, as a function of U/t. For $U/t \lesssim 8.5$ the system is a Fermi liquid metal. Pairing and superconductivity build up in the intermediate coupling regime for $U/t \sim 8-10$ in a non-BCS fashion. While the pairing amplitude grows with U/t, superconductivity is non-monotonic. For $U/t \gtrsim 10$, ψ_s is negligible and the system becomes a spin liquid.

$(ET)_2Cu_2(CN)_3$ and related materials.

We start from the single band Hubbard model

$$H = \sum_{ij;\sigma} t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \tag{1}$$

where $c^\dagger_{i\sigma}$ is the creation operator for a hole in the bonding state of a $(ET)_2$-dimer[5, 17, 22]. The hopping elements, t_{ij}, between dimers at sites i and j determine the bare band structure, $\varepsilon_{\mathbf{k}} = 2t\,(\cos k_x + \cos k_y) + 2t' \cos(k_x + k_y)$, as measured in magneto-oscillation experiments in the metallic regime[6], see inset of Fig.2. U is the Coulomb repulsion between holes on the same dimer. Typical parameters are $t \approx 0.05 - 0.1$eV, and $U \simeq 5 - 10t$, whereas the ratio t'/t varies from $\simeq 0.6$ for X=Cu[N(CN)$_2$]Br to $t'/t \simeq 1.0$ for the spin liquid compound with X=$Cu_2(CN)_3$.

In systems where the Mott transition occurs due to varying charge carrier concentration, important strong correlations are captured by the t-J model. A great deal of insight into this model has been gained by using a variational wave function[1, 23, 24] $|\Psi_{\rm RVB}\rangle = e^{iS} P_0 |\Phi_{\rm BCS}\rangle$, where P_0 projects out all doubly occupied states and S generates the unitary transformation to the $t-J$ model (see Refs.[23, 24, 25, 26, 27]). Here,

$$|\Phi_{\rm BCS}\rangle \propto \left(\sum_{\mathbf{k}} \varphi_{\mathbf{k}} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow} \right)^{N/2} |0\rangle \tag{2}$$

is a BCS wave function of N particles with $\varphi_{\mathbf{k}} = \Delta_{\mathbf{k}} / \left[\xi_{\mathbf{k}} + \sqrt{\xi^2_{\mathbf{k}} + \Delta^2_{\mathbf{k}}} \right]$ and $\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu_{\rm v}$. The gap $\Delta_{\mathbf{k}}$ as well as $\mu_{\rm v}$ are variational parameters[23, 24, 25, 26, 27].

In the organics the Mott transition occurs at half filling via changing pressure, i.e. changing the ratio t/U. Recently, a generalization of the $t-J$-model to pressure induced Mott transitions was suggested[28]. Here we use another approach and perform our calculation explicitly for finite U/t. This could be achieved using a Gutzwiller projected[29] pair wave function, $|\Psi_{\rm GW}\rangle = g^D |\Phi_{\rm BCS}\rangle$, with $D = \sum_i n_{i\uparrow} n_{i\downarrow}$. Even though this wave function treats the interaction term in Eq.1 properly, it is known to poorly treat the kinetic energy and thus the physics of the superexchange coupling, $J = \frac{4t^2}{U}$. A promising way to improve this shortcoming was proposed in Ref.[30]. g^D was replaced by $g^D h^\Theta$ with an additional variational parameter h. Θ is the total number of doubly occupied sites which have no empty neighbor connected by a hopping element. This causes an "attraction" of doubly occupied and empty sites, that arise as intermediate steps for the superexchange process and dramatically improves the ground state energy[30].

The propagation of quasi-particles in a magnetically frustrated system is likely affected by the strong, but local spin correlations and we expect that the renormalized spectrum, $\varepsilon^*_{\mathbf{k}}$, differs from the bare dispersion, $\varepsilon_{\mathbf{k}}$.

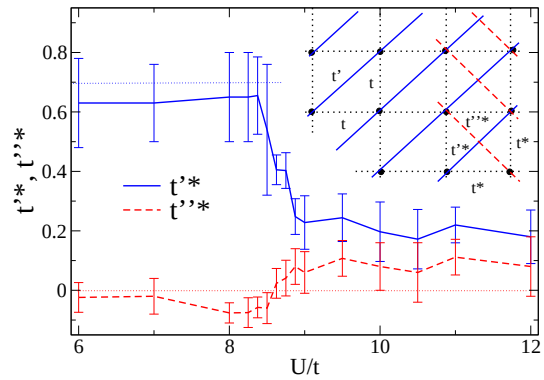

FIG. 2: The renormalized hopping elements along the two diagonals (see right part of the inset) as a function of U/t. For $t' = 0.7t$, the diagonal t'^* is strongly suppressed whereas t''^* is enhanced over their bare values (horizontal lines), suggesting a reorganization of the quasiparticle dispersion for $U \sim 8.5t$.

This is a common observation of mean field or variational approaches[31] to the $t-J$ model and was recently demonstrated in cluster dynamic mean field calculations of the present model[32]. Thus, we allow for a renormalization of the energy spectrum and use $\xi_{\mathbf{k}} = \varepsilon^*_{\mathbf{k}} - \mu_{\rm v}$ in the BCS-wave function. Since $|\Phi_{\rm BCS}\rangle$ depends only on the ratio $\xi_{\mathbf{k}}/\Delta_{\mathbf{k}}$, we cannot determine $\varepsilon^*_{\mathbf{k}}$ or the gap in absolute units, but, for example, in units of t^*, the renormalization of t. t^* itself cannot be determined.

Combining all these aspects, we propose the following wave function for organic charge transfer salts close to the Mott transition:

$$|\Psi\rangle = g^D h^\Theta |\Phi_{\rm BCS}\rangle . \tag{3}$$

The matrix element $E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ are evaluated using the Monte Carlo approach of Ref.[24, 33] for a 12×12 lattice. E is then minimized with respect to the variational parameters h, g, $\mu_{\rm v}$, $\Delta_{\mathbf{k}}$ and $\varepsilon^*_{\mathbf{k}}$ using a simulated annealing algorithm. The results shown below are mainly for $t'/t = 0.7$ and varying U/t, but we discuss other t'-values as well.

Correlated Superconductor: The ground state of the triangular lattice in the Heisenberg limit, $U/t \to \infty$ exhibits long range order[37]. From Ref.[34] we further know that for $t'/t = 0.7$ and $U/t \lesssim 10 - 12$ the model is in a spin liquid insulating state without long range magnetic order. We expect that such a spin liquid has a natural tendency towards Cooper pair formation and superconductivity[1]. We calculate the single particle gap $\Delta_{\mathbf{k}}$ and compare with the actual superconducting order parameter, ψ_s. Our central result is shown in Fig.1a depicting the U dependence of the pairing amplitude of $\Delta_{\mathbf{k}}$. Out of a large class of different symmtries analyzed for $t' = 0.7t$, the optimal form of the gap is $\Delta_0 (\cos k_x - \cos k_y)$. For small $U \lesssim 7t$, Δ_0 is negligible; it starts building up for $U/t \sim 8.5$, rising sharply and attaining a large value of $\Delta_0/t^* \sim 3$. Whether the

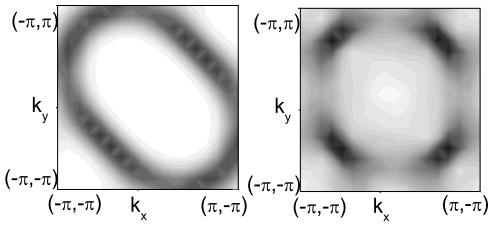

FIG. 3: Contour plot of $|\nabla n_{\mathbf{k}}|$ for $U = 0$ (left) and for $U/t = 9$ (right). The strongly renormalized dispersion in the interacting case generates a four-fold symmetric structure. $|\nabla n_{\mathbf{k}}|$ is largest along the diagonals.

pairing amplitude Δ_0 is related to superconductivity is determined by the pairing correlation function,

$$F_{\mathbf{a},\mathbf{b}}(\mathbf{r}-\mathbf{r}') = \left\langle \Psi \left| B^{\dagger}_{\mathbf{r},\mathbf{a}} B_{\mathbf{r}',\mathbf{b}} \right| \Psi \right\rangle, \tag{4}$$

with $B_{\mathbf{r},\mathbf{a}} = \frac{1}{2}\left(c_{\mathbf{r}+\mathbf{a},\downarrow} c_{\mathbf{r}\uparrow} - c_{\mathbf{r}+\mathbf{a},\uparrow} c_{\mathbf{r},\downarrow}\right)$. In a superconductor, $F_{\mathbf{a},\mathbf{b}} \to \pm |\psi_s|^2$ for large $|\mathbf{r}-\mathbf{r}'|$. The sign depends on the direction of the nearest neighbor vectors $\mathbf{a}$ and $\mathbf{b}$. Our results for $|\psi_s|^2$ as function of U/t are shown in Fig.1b. The order parameter becomes rapidly large around $U \simeq 8.5t$, just where Δ_0 grows. For larger values of U, superconductivity becomes weak, despite the fact that Δ_0 keeps growing. As shown in Ref.[35], a wave function of the form in Eq.3, is unable to yield a true insulating state and it is not clear whether the state for $U \simeq 10t$ is a fragile superconductor along the lines of Ref.[36] or an insulator. In this strict sense our wave function describes a fragile conductor rather than a spin liquid. We believe, however, that this limitation is of minor importance as far as the distinctive features of the superconductivity are concerned: the large value of the gap, the very fragile superfluid stiffness and their very different dependences on U/t. A robust superconducting ground state only exists in the intermediate transition regime.

Renormalization of the excitation spectrum: We find rather remarkably that the crucial factor for the emergence of the superconducting state is a qualitative change in the excitation spectrum.

As mentioned above, we determine the optimal excitation spectrum, $\varepsilon^*_{\mathbf{k}}$ by minimizing the energy. In addition to renormalizations of existing hopping elements, i.e. $t \to t^*$ and $t' \to t'^*$, we include hopping elements not present in $\varepsilon_{\mathbf{k}}$. Allowing for all second and third neighbor hopping elements, one relevant new hopping along the other diagonal t''^* emerges (see inset of Fig.2). Our results for t'^* and t''^* are shown in Fig.2. A strong renormalization $\varepsilon_{\mathbf{k}} \to \varepsilon^*_{\mathbf{k}}$ sets in coincident with the rapid increase of Δ_0. For $U \gtrsim 8t$, t'^* is strongly reduced but the additional hopping element, $t''^* \sim t'^*$, develops. As shown in Fig.3, $n_{\mathbf{k}} = \left\langle \Psi \left| c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} \right| \Psi \right\rangle$ becomes more symmetric than for the initial Hamiltonian and the effective dispersion corresponds to that of a weakly frustrated system. At the crossover, $U/t \approx 8.5$, the non-local variational parameter h rapidly decreases from $h \lesssim 1$ to small values, where the probability of doubly occupied sites being near an empty site is enhanced, thereby promoting superexchange physics. Setting $h = 1$ no gap or renormalized dispersion occurs for $U/t < 11$. Our variational, $T = 0$, calculations are completely consistent with the interesting effects recently found within a cluster dynamical mean field theory at finite T by Parcollet *et al.*[32], where for $U \approx 9t$ new real space components of the self energy emerge between precisely the lattice sites connected by t''^*.

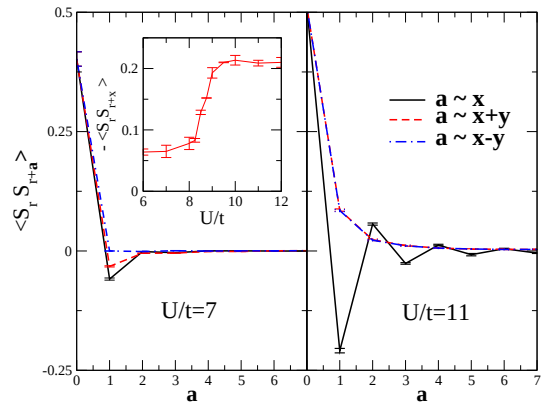

FIG. 4: Spatial dependence of the spin-spin correlation function different U. For larger U magnetic correlations along the two diagonals become indistinguishable even though the bare hopping elements are very different. The inset shows the U/t dependence of the nearest neighbor spin correlation.

Magnetic Correlations: The magnetic correlations of the spin liquid state at larger U are strong but remain short ranged. This can be seen in Fig.4 where we show our results for the spin correlation function $\left\langle \Psi \left| s^{\alpha}_{\mathbf{r}} s^{\alpha}_{\mathbf{r}+\mathbf{a}} \right| \Psi \right\rangle$ along different directions of $\mathbf{a}$, for $U = 7t$ and $U = 11t$, respectively. For large U, there is, in agreement with the renormalized dispersion of Figs.2 and 3, almost no difference in the magnetic correlations along the two diagonals (essentially indistinguishable in Fig.4), even though the bare hopping element in one direction is zero. The state at large U resembles the short range order of an *unfrustrated* square lattice. The key difference is of course that the square lattice for $U = 11t$ is deep in the Néel ordered state, while the present model is in a spin liquid state[34]. In the inset of Fig.4 we show the nearest neighbor spin correlation as function of U/t.

Finally we discuss the behavior for different t'-values, including the perfect triangular lattice at $t' = t$. For $t' > t$, no new hopping element occurs, but t'^*/t^* becomes much larger than its bare value. For $t' = 1.5t$ and $U = 12t$ we obtain $t'^* \approx 7.5t^*$. Again, an effective dispersion with weak frustration emerges; now with a tendency

to form weakly coupled chains. At the same time, the gap changes from d-wave to $\Delta_{\mathbf{k}} = \Delta_0 (\cos k_x + \cos k_y) - \Delta_0' \cos(k_x + k_y)$, with $\Delta_0 \sim \Delta_0'$. This corresponds roughly to a rotation of the nodes by $\pi/4$, as found experimentally in organic superconductors[14, 15], however for a system where t' is believed to be slightly smaller than t. For $t' = t$, relevant for κ-$(ET)_2Cu_2(CN)_3$, a gap only occurs if we allow for a renormalization of the spectrum. Then, one of the three bare hopping elements on the triangular lattice is spontaneously reduced compared to the other two. A gap with equal size and opposite sign forms along those two nearest neighbor bonds with the larger effective hopping. This demonstrate how crucial the renormalization of the spectrum for pairing and supercondictivity is. It also shows that the physics of the triangular lattice at half filling but intermediate U is much richer than the behavior at weak coupling or in the strong coupling, Heisenberg limit.

In summary, we have proposed a wave function for systems close to a pressure tuned Mott transition and analyzed spin liquid formation and pairing in the ground state of the Hubbard model on an anisotropic triangular lattice. This geometry is relevant for quasi two-dimensional κ-$(ET)_2X$ organic superconductors. In the κ-$(ET)_2Cu_2(CN)_3$ member of this family, genuine spin liquid behavior was recently observed[3]. As a function of increasing correlation strength, corresponding to decreasing pressure, we find a rapid transitions between a weak coupling, simple metal regime and a strongly coupled spin liquid region with a number of interesting new properties, most remarkably a complete reorganization of the quasiparticle spectrum. The latter occurs in and close to the spin liquid regime and might be hard to observe via magnetooscillation experiments, but should affect optical or Raman experiments. The large gap of the spin liquid state has nodes, consistent with the observation of gapless modes in the low-T spin lattice relaxation rate[3]. Superconductivity emerges in the spin liquid - metal crossover and is expected to become weak for larger pressure. The renormalized dispersion of the theory is either that of a square lattice or of weakly coupled chains, depending on the ratio t'/t of the hopping elements.

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