Symmetry of the Superconducting Order Parameter in Frustrated Systems Determined by the Spatial Anisotropy of Spin Correlations

B. J. Powell and Ross H. McKenzie

Department of Physics, University of Queensland, Brisbane, Queensland 4072, Australia
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We study the resonating valence bond theory of the Hubbard-Heisenberg model on the half-filled anisotropic triangular lattice. Varying the frustration changes the wave vector of maximum spin correlation in the Mott insulating phase. This, in turn, changes the symmetry of the superconducting state that occurs at the boundary of the Mott insulating phase. We propose that this physics is realized in several families of quasi-two-dimensional organic superconductors.

One of the major themes in condensed matter physics over the last few decades has been the deep connection between magnetism and unconventional superconductivity. This is one of the key ideas to have emerged from the study of the cuprates [1], ruthenates [2], cobaltates [3,4], heavy fermions [5], organic superconductors [6], ^{3}He [7], and ferromagnetic superconductors [8]. In the cuprates $d_{x^2-y^2}$ symmetry superconductivity emerges from the doping of a Mott insulator with Néel order. Many theories [1,9–11], including resonating valence bond (RVB), suggest that in the metallic state spin correlations which are maximal near the wave vector (π, π) mediate superconductivity. In RVB theory [1,9] superconductivity arises from the same strong correlations that give rise to antiferromagnetism in the Mott insulator. Alternative theories of the cuprates emphasize instead the role of different physics, such as stripes, phase fluctuations, or orbital currents [11].

When frustration is introduced into a system the insulating state may not be Néel ordered and the spin correlations may not be strongest at (π, π). Therefore, a natural question to ask is what kinds of superconducting states occur when the spin correlations are different from the commensurate (π, π) correlations? In this Letter we study an RVB theory of the Hubbard-Heisenberg model on the half-filled anisotropic triangular lattice (ATL) to investigate this question. This is partially motivated by the fact that this model may describe whole families of organic superconductors [6]. As we vary the frustration in our model, the peak in the spin fluctuations in the insulating state moves continuously from (π, π), characteristic of the square lattice, via $(2\pi/3, 2\pi/3)$, characteristic of the triangular lattice, to $(\pi/2, \pi/2)$ characteristic of quasi-one-dimensional (Q1D) behavior. This changes the symmetry of the superconducting state (see Fig. 1), from "$d_{x^2-y^2}$" for weak frustration to "$d + id$" at the maximum frustration to "$d_{xy} + s$" in the Q1D regime. We argue that these effects are realized in organic superconductors such as κ-(ET)$_2$Cu[N(CN)$_2$]Br, κ-(ET)$_2$Cu$_2$(CN)$_3$, β'-[Pd(dmit)$_2$]$_2X$, and β-(ET)$_2$I$_3$ [6,12].

The Hamiltonian of the Hubbard-Heisenberg model is
$$\mathcal{H} = -t\sum_{\{ij\}\sigma}\hat{c}^\dagger_{i\sigma}\hat{c}_{j\sigma} - t'\sum_{\langle ij\rangle\sigma}\hat{c}^\dagger_{i\sigma}\hat{c}_{j\sigma} + J\sum_{\{ij\}}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j +$$
$J'\sum_{\langle ij\rangle}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + U\sum_i\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} - \mu\sum_{i\sigma}\hat{c}^\dagger_{i\sigma}\hat{c}_{i\sigma}$, where $\hat{c}^{(\dagger)}_{i\sigma}$ annihilates (creates) an electron on site i with spin σ, $\hat{\mathbf{S}}_i$ is the Heisenberg spin operator, and $\{ij\}$ and $\langle ij\rangle$ indicate sums over nearest and next nearest neighbors across one diagonal, respectively [6,13] (Fig. 2). We study this model at exactly half filling, as this is appropriate for the β, β', κ, and λ phase organic superconductors [6]. Studies of related doped models [3] suggest that the superconducting state evolves continuously upon doping.

We study this Hamiltonian via the RVB variational ansatz [9,15,16], $|\text{RVB}\rangle = \hat{P}_G|\text{BCS}\rangle$, where $|\text{BCS}\rangle$ is
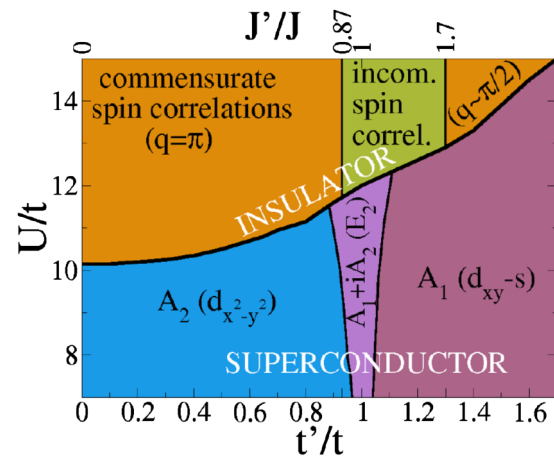

FIG. 1 (color online). Phase diagram of the Hubbard-Heisenberg model on the half-filled ATL. As the frustration, $J'/J = (t'/t)^2$, is varied the spin correlations change from commensurate (π, π) characteristic of the square lattice for $t'/t < 0.93$, to incommensurate (q, q) in the highly frustrated regime, to commensurate $(\pi/2, \pi/2)$ for $t'/t \gtrsim 1.3$ characteristic of weakly coupled chains (see Fig. 2). The spin correlations mediate superconductivity, and the changes in the spin correlations cause changes in the symmetry of the superconducting state, which changes from "$d_{x^2-y^2}$" (A_2) for small t'/t to "$d + id$" ($A_1 + iA_2$) for $t' \sim t$ to "$s + d_{xy}$" (A_1) for large t'/t.
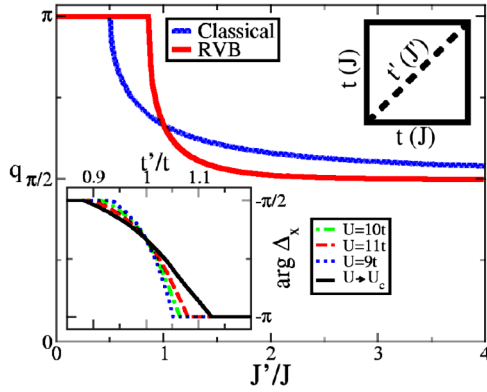
FIG. 2 (color online). The wave vector (q, q), where the spin correlations, which mediate superconductivity, are strongest. RVB theory shows that quantum effects increase the region where commensurate correlations are found relative to the classical theory. The lower inset shows the angle θ, which determines the symmetry of the superconducting order parameter. $\theta = -\pi/2$ implies A_2 ("$d_{x^2-y^2}$") superconductivity; $\theta = -\pi$ implies A_1 ("$s + d_{xy}$") superconductivity; and $-\pi/2 < \theta < -\pi$ implies an "$A_1 + iA_2$" ("$d + id$") state. Note, in particular, that $\theta = -2\pi/3$ for $t' = t$, independent of U. The upper inset is a sketch of the ATL indicating the relevant hopping integrals (exchange parameters) to nearest neighbors (solid lines) and across one diagonal (dashed line).

the BCS wave function and $\hat{P}_G$ is the partial Gutzwiller projector, which we treat in the Gutzwiller approximation. The problem reduces to solving the BCS and Gutzwiller variational problems simultaneously. This requires two mean fields: $\chi_\mathbf{k} = \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} \langle \hat{c}^\dagger_{\mathbf{k}'\uparrow} \hat{c}_{\mathbf{k}'\uparrow} \rangle$ and $\Delta_\mathbf{k} = \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} \langle \hat{c}_{\mathbf{k}'\uparrow} \hat{c}_{-\mathbf{k}'\downarrow} \rangle$, where $\hat{c}_{\mathbf{k}\sigma}$ is the Fourier transform of $\hat{c}_{i\sigma}$, and d is the fraction of doubly occupied sites. The pairing interaction, $V_\mathbf{k} = -6(1 - 2d)^2 [J(\cos k_x + \cos k_y) + J' \cos(k_x + k_y)]$, arises from exchange between near neighbors; see Fig. 2. This potential directly links the symmetry of the superconductivity with the magnetic degrees of freedom. We assume singlet superconductivity. It then follows from the functional form of $V_\mathbf{k}$ and basic trigonometry that the mean fields may be written as $\Delta_\mathbf{k} = \Delta_x \cos k_x + \Delta_y \cos k_y + \Delta_d \cos(k_x + k_y)$ and $\chi_\mathbf{k} = \chi_x \cos k_x + \chi_y \cos k_y + \chi_d \cos(k_x + k_y) - \tilde{\mu}$, the renormalized chemical potential $\tilde{\mu}$ ensures half filling. The symmetry of the ATL is represented by the group C_{2h} [6]. Thus symmetry requires that $|\Delta_x| = |\Delta_y|$, $\chi_x^2 = \chi_y^2$, and $\theta \equiv \arg\Delta_x = -\arg\Delta_y$ [17]. Thus $\Delta_\mathbf{k} = |\Delta_x| \cos\theta(\cos k_x + \cos k_y) + |\Delta_d| \cos(k_x + k_y) + i|\Delta_x| \sin\theta(\cos k_x - \cos k_y)$.

For simplicity we consider only Mott insulating states that are spin liquids, i.e., do not possess long-range magnetic order. We are aware that for some parameters, e.g., large U/t and small t'/t, that states with magnetic order may have slightly lower energy. However, the d-wave spin liquid states considered here are quite competitive in energy [1,18]. Further, other work shows that the instability of such ordered states to superconductivity, as U/t de-

creases, occurs for similar parameters as for spin liquid states. Hence, we suggest that this simplifying assumption will not change our main results relating the superconducting symmetry to the spatial anisotropy of the spin correlations in the parent Mott insulator.

Within the Gutzwiller approximation, $d = 0$ in the insulating phase, and the model is equivalent to the Heisenberg model. Therefore, results in the insulating phase do not explicitly depend on U. However, in the insulating state the Hubbard model overrepresents the Heisenberg model. This leads to an $SU(2)$ degeneracy of the insulating phase of the RVB theory [1,3]. Physically, this means that in the Mott insulator the mean fields are not physically distinct and the physical order parameters are $D = \sqrt{\Delta_x^2 + \chi_x^2} = \sqrt{\Delta_y^2 + \chi_y^2}$ and $D' = \sqrt{\Delta_d^2 + \chi_d^2}$. It is straightforward to show that the spin correlations are peaked at the wave vector (q, q), where $q = \arccos(D^2/2D'^2)$. We solve the variational problem numerically on a discrete k-space mesh. Figure 2 compares the wave vector found in this way from the RVB theory with the classical result, $q = \arccos(J/2J')$ [19]. For $J'/J < 0.87$ ($t'/t < 0.93$) we find that the spin correlations are commensurate and peaked at (π, π), consistent with a tendency towards Néel ordering. We also find commensurate spin correlations [peaked at $(\pi/2, \pi/2)$] for large J'/J. This is the classical ordering wave vector for uncoupled chains. It is difficult to determine exactly when the correlations becomes commensurate, as there is a smooth crossover (see Fig. 2). However, it is clear that $q \sim \pi/2$ for $J'/J \gtrsim 1.7$ ($t'/t \gtrsim 1.3$). This shows that quantum effects enhance the stability of the region with commensurate spin correlations compared to the classical result. This effect is also found by other theoretical methods [20]. In the region $0.87 < J'/J \lesssim 1.7$ ($0.93 < t'/t \lesssim 1.3$) the insulating state is characterized by incommensurate spin correlations (except at the high symmetry point $t' = t$, see below). In the metallic phase the two mean fields are physically distinct. $\chi_\mathbf{k}$ varies smoothly as the frustration t'/t is varied (Fig. 3), but three distinct superconducting phases are observed as is indicated by the behavior of $\Delta_\mathbf{k}$ (Figs. 2–4).

For small t'/t we find that $\Delta_d = 0$ and $\theta = -\pi/2$, thus $\Delta_\mathbf{k} = \Delta_x(\cos k_x - \cos k_y)$. This is the prototypical form for a "$d_{x^2-y^2}$" superconductor. Formally, $\Delta_\mathbf{k}$ transforms according to the A_2 representation of C_{2v}. This is consistent with the fact that for small t'/t the spin correlations in the insulating state are peaked at (π, π) (cf. Fig. 2).

For large t'/t we find that $\Delta_x, \Delta_y, \Delta_d \neq 0$ and $\theta = -\pi/2$. Thus the order parameter takes the form $\Delta_\mathbf{k} = |\Delta_x|(\cos k_x + \cos k_y) + |\Delta_d|(\cos k_x \cos k_y - \sin k_x \sin k_y)$. The first three terms are usually referred to as "extended s (xs)" as they transform according to the trivial representation but may have accidental nodes. The fourth term would be referred to as a "d_{xy}" state on the square lattice, where the "xs" and "d_{xy}" states belong to different irreducible representations of C_{4v}. We therefore refer to this state as the "$s + d_{xy}$" state. However, we stress that $\Delta_\mathbf{k}$ transforms
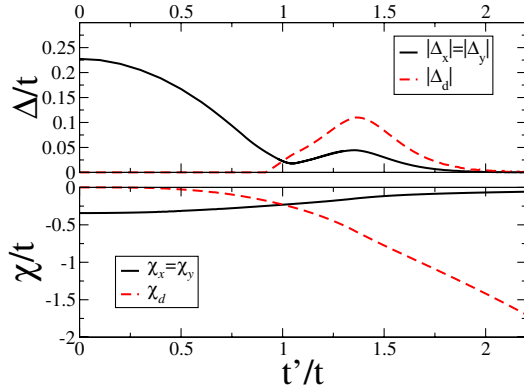
FIG. 3 (color online).   Variation of the RVB mean fields as the frustration is varied for $U = 10t$. χ_x, χ_y, and χ_d all vary smoothly, but two phase transitions occur between superconducting states. The first occurs when Δ_d becomes finite, but the second involves the angle θ (inset of Fig. 2). Δ_x, Δ_y, and Δ_d become small at large t'/t due because the bandwidth $W \propto t'$ in this regime and so we are moving away from the Mott transition as t'/t increases for $t' \gg t$ (cf. Fig. 1).

solely as the A_1 representation of C_{2v}, a direct consequence of the lower symmetry of the ATL [21]. In this regime the spin correlations are (nearly) commensurate at $(\pi/2, \pi/2)$, as expected for weakly coupled chains. Thus it is these Q1D correlations that cause the superconductor to take "$s + d_{xy}$" symmetry.

For $t' \sim t$, Δ_x, Δ_y, $\Delta_d \neq 0$ and $-\pi < \theta < -\pi/2$. Thus $\Delta_{\mathbf{k}}$ has a nontrivial complex phase and breaks time reversal symmetry (TRS): this might be detected by muon spin relaxation experiments [2,21,22]. The real part is the same as $\Delta_{\mathbf{k}}$ for large t'/t and transforms according to the A_1 representation. The imaginary part takes the same form as $\Delta_{\mathbf{k}}$ for small t'/t and transforms according to the A_2 representation. We therefore refer to this state either as the $A_1 + iA_2$ or "$d + id$" state. In this regime we have competition between spin correlations characteristic of the square lattice, which promote "$d_{x^2-y^2}$" superconductivity, and those along the diagonal which favor a "$s + d_{xy}$" state. The compromise between these frustrated interactions is the $A_1 + iA_2$ state with broken TRS. Figure 4 details how $\Delta_{\mathbf{k}}$ varies with the frustration for $t' \sim t$.

Exactly at $t' = t$ the lattice becomes hexagonal and has C_{6v} symmetry. In the insulating phase we find commensurate spin fluctuations peaked at $(2\pi/3, 2\pi/3)$. In the superconducting state "xs" terms transform like the A_1 representation of C_{6v}. However, the "$d_{x^2-y^2}$" and "d_{xy}" terms transform as the E_2 representation. E_2 is two-dimensional and spanned by the "$d_{x^2-y^2}$" and "d_{xy}" terms. Thus, "$d + id$" states that transform as the E_2 representation are expected on symmetry grounds on the hexagonal lattice for appropriate values of the Ginzburg-Landau coefficients [21,23]. This has already led to the prediction of broken TRS in κ-(ET)$_2$Cu$_2$(CN)$_3$ and β'-[Pd(dmit)$_2$]$_2$X on phe-
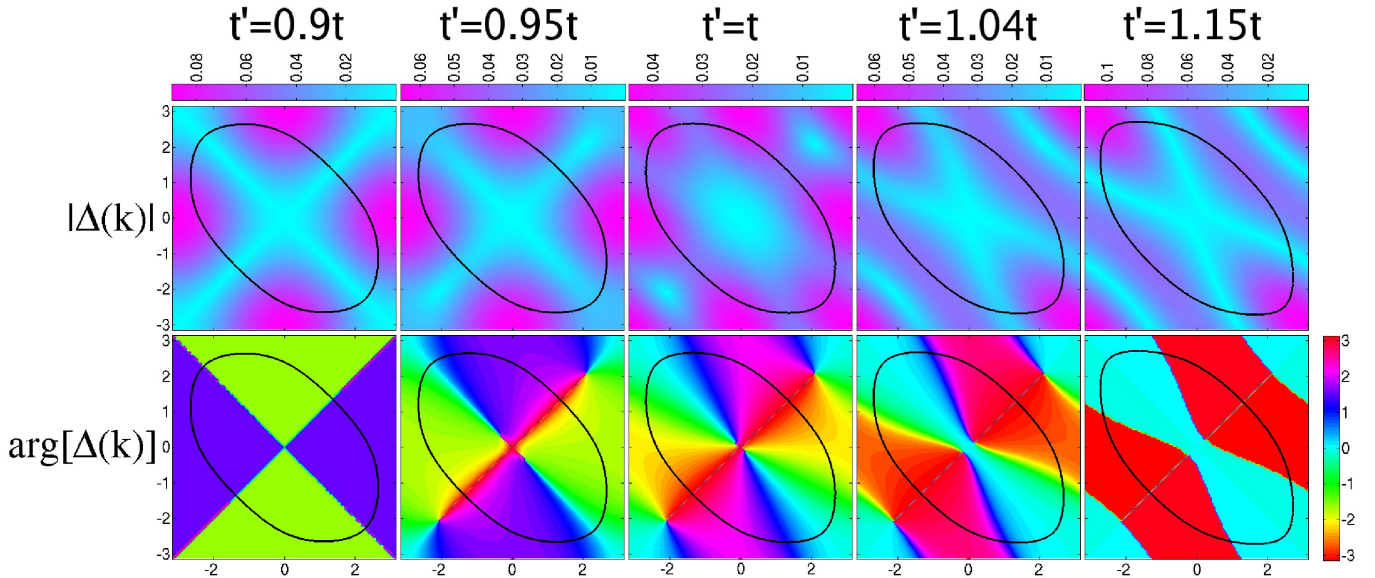

FIG. 4 (color online).   The k dependence of superconducting order parameter, $\Delta(\mathbf{k})$, as the frustration (t'/t) is varied. Each plot covers the first Brillouin zone, and the solid lines denote the noninteracting Fermi surfaces. For $t'/t < 0.92$ we have a "$d_{x^2-y^2}$" superconductor where $\Delta_{\mathbf{k}}$ transforms as the A_2 representation of C_{2v} and has symmetry required nodes along the lines $k_x = \pm k_y$. This superconducting state is driven by the strong spin correlations at wave vector (π, π). For $t'/t > 1.06$ we find an "$s + d_{xy}$" order parameter which transforms like the A_1 representation of C_{2v}. This superconducting state is favored by the strong spin correlations near $(\pi/2, \pi/2)$. We find that this state has nodes, although they are not required by symmetry and therefore their location is dependent on t'/t and U/t. For $t' = t$ the lattice maps onto the hexagonal lattice and the ground state is a "$d + id$" state which transforms as the E_2 representation of C_{6v}. Intermediate states such as those found at $t'/t = 0.95$ and 1.04 still show the effects of the strongly frustrated triangular spin correlations and form "$A_1 + iA_2$" states. The "$A_1 + iA_2$" states found for $0.92 < t'/t < 1.06$ all break time reversal symmetry and are fully gapped. The results shown are for $U = 10t$.

nomenological grounds [21]. For $t' \sim t \neq t'$ the lattice is slightly distorted away from C_{6v} symmetry, and this leads to either the "$d_{x^2-y^2}$" (for $t' \lesssim t$) or "$s + d_{xy}$" (for $t' \gtrsim t$) component giving a greater contribution to $\Delta_{\mathbf{k}}$ [21]. This is clearly seen in Figs. 2 and 4. Experiments on Cs_2CuCl_4 [24] and other calculations [20] suggest that RVB underestimates the size of the region where $q \simeq 2\pi/3$. As these frustrated spin fluctuations drive $A_1 + iA_2$ superconductivity, this suggests that RVB theory may underestimate the stability of this phase and the size of the region of the phase diagram (Fig. 1) where $A_1 + iA_2$ superconductivity occurs.

Our phase diagram (Fig. 1) differs in the region around $t' \sim t$ from that recently proposed by others [25]. These differences arise because those works did not consider the possibility of insulating states with incommensurate spin correlations or "$d + id$" superconducting states.

There is significant evidence that RVB physics is enhanced on frustrated lattices [6,18] and that it is relevant to layered organic superconductors [6,16,25]. Further, the RVB theory predicts a pseudogap in the metallic state above the superconducting critical temperature. Below about 50 K such a pseudogap is suggested by NMR relaxation rate and Knight shift data [6,26]. Additionally, the insulating state of κ-$(ET)_2Cu_2(CN)_3$ is a spin liquid [6,14]. Thus these materials provide an testing ground for the ideas presented here. The band structures suggest that these materials span the parameter range where the different superconducting order parameters occur [6]. For example, $t' < t$ in κ-$(ET)_2Cu[N(CN)_2]Cl$ and κ-$(ET)_2Cu[N(CN)_2]Br$, which suggests that they have "$d_{x^2-y^2}$" (A_2) order parameters, $t' \sim t$ in κ-$(ET)_2Cu_2(CN)_3$, and β'-$[Pd(dmit)_2]_2X$, and we propose that they have "$d + id$" ($A_1 + iA_2$) order parameters, and $t' > t$ in β-$(ET)_2I_3$, which suggests that it has an "$s + d_{xy}$" (A_1) order parameter [6]. These results are consistent with our current knowledge of the superconducting states of these materials, but much controversy remains over the experimental situation [6,21]. It has also been argued that the superconducting state of the doped triangular lattice compound $Na_xCoO_2 \cdot yH_2O$ is an RVB state with "$d + id$" pairing [3,4]. Ferromagnetic fluctuations are strong in doped triangular lattice systems [27] and so the possibility of triplet superconductivity needs to be considered carefully in both doped and half-filled systems [7].

We have studied the RVB theory of the Hubbard-Heisenberg model on the ATL. Varying the frustration t'/t changes the spatial anisotropy of the spin correlations. This drives changes in the symmetry of the superconducting state. We propose that as "$d_{x^2-y^2}$" superconductivity results from proximity to a Néel ordered state, so "$d + id$" superconductivity arises from proximity to a spiral state and "$s + id_{xy}$" superconductivity is driven by Q1D spin fluctuations. The generality of the connection between (π, π) spin correlations and "$d_{x^2-y^2}$" [1,9–11] suggests that our results are valid beyond the Hamiltonian studied and the approximations used in this Letter. This clearly

begs the question: Which superconducting states are driven by proximity to other magnetic orderings?

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