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## Indications of unconventional superconductivity in doped and undoped triangular antiferromagnets

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The possibility of superconductivity in doped and undoped triangular antiferromagnets is discussed. Using the Bethe-Salpeter (BS) equation, it is shown that the exchange of random-phase approximation paramagnons on a triangular lattice Hubbard model leads to strong pairing correlations at and near half filling. The dominant states for this system correspond to *d*-wave singlet (even-frequency) and *s*-wave triplet (odd-frequency) pairing. Analytical techniques applied to the hole-doped *t*-*J* model yield similar results. A  $t_1 - t_2$  Hubbard model interpolating between square ( $t_1=0$ ) and triangular ( $t_1=t_2$ ) lattices has a tendency to only *d*-wave singlet pairing for  $t_1/t_2 \le 0.8$ . Experimental consequences for organic compounds  $\kappa$ -(BEDT-TTF)<sub>2</sub>X are discussed. [S0163-1829(99)50202-6]

Since the discovery of high-temperature superconductivity, two-dimensional (2D) doped antiferromagnets (AF) have been studied intensively. Experimental results and a large body of theoretical work suggest that the pairing state is highly anisotropic and probably a  $d_{x^2-y^2}$  singlet. In addition, materials with 2D spin arrangements on nonsquare lattices have also been synthesized. For example, experiments suggest the realization of a triangular spin- $\frac{1}{2}$  AF in NaTiO<sub>2</sub>,<sup>1</sup> as well as in surface structures<sup>2</sup> such as K/Si(111):B. Delafossite cuprates  $RCuO_{2+\delta}$ , with R a rare-earth element, have Cu ions sitting on a triangular lattice.<sup>3</sup> Other compounds with this geometry have also been prepared.<sup>4</sup> Recently, theoretical arguments in the context of organic superconductors suggest that  $\kappa$ -(BEDT-TTF)<sub>2</sub>X, where X is an ion, is described by the half-filled Hubbard model on an anisotropic triangular lattice with one electron per site.<sup>5</sup> Metallicity is obtained by working below the critical coupling that leads to an insulating phase.

The presence of unconventional superconductivity on a square-lattice AF suggests that similar unusual phenomena may occur in other 2D AF arrangements, such as a triangular lattice. Although most of the materials described above do not contain a finite concentration of mobile carriers, it is important to analyze on theoretical grounds the properties of holes in this environment and especially the characteristics of a possible superconducting state. This information may induce further experimental work in nonsquare lattice doped spin systems. Precisely in this paper the issue of pairing in triangular and anisotropic triangular AF is addressed.

The model to be discussed in the first part of this paper contains a nearest-neighbor hopping term  $t_2$  on a 2D square lattice and an additional hopping term  $t_1$  along *one* diagonal of each plaquette, so that  $t_1=0$  corresponds to a square lattice (bandwidth 8  $t_2$ ) whereas  $t_1=t_2$  is an isotropic triangular lattice (bandwidth 9  $t_2$ ). For details see Ref. 5. The interaction will be modeled by an on-site Hubbard repulsion  $Un_{i\uparrow}n_{i\downarrow}$ .

To study the effective interaction between electrons arising from the exchange of paramagnons the RPA approximation is used, as done before for the analogous problem on the square lattice<sup>6</sup> where further work<sup>7</sup> using more sophisticated techniques showed that indeed indications of *d*-wave pairing are present in this context. Then, the BS approach is powerful enough to capture the essence of the pairing tendencies in Hubbard-like models. The effective pairing potentials for the singlet and the triplet channels are

$$V_{s}(p,p') = U + \frac{U^{3}\chi_{0}^{2}(p'-p)}{1 - U^{2}\chi_{0}^{2}(p'-p)} + \frac{U^{2}\chi_{0}(p'+p)}{1 - U\chi_{0}(p'+p)},$$
  
$$V_{t}(p,p') = -\frac{U^{2}\chi_{0}(p'-p)}{1 - U^{2}\chi_{0}^{2}(p'-p)},$$
(1)

with  $p = (\mathbf{p}, i\omega_n)$  and  $\omega_n$  being a fermionic Matsubara frequency.  $\chi_0(\mathbf{q}, \omega)$  denotes the spin susceptibility:

$$\chi_0(\mathbf{q},\omega) = \frac{1}{N} \sum_{\mathbf{p}} \frac{f(\boldsymbol{\epsilon}_{\mathbf{p}+\mathbf{q}}) - f(\boldsymbol{\epsilon}_{\mathbf{p}})}{\omega - (\boldsymbol{\epsilon}_{\mathbf{p}+\mathbf{q}} - \boldsymbol{\epsilon}_{\mathbf{p}}) + i0^+}, \quad (2)$$

where  $\epsilon_{\rm p}$  are the noninteracting electron energies.

These interactions Fourier transformed into real space at  $t_1 = t_2$  (triangular lattice) and in the static limit ( $\omega = 0$ ) are shown in Fig. 1. The density is chosen to be slightly below half filling, i.e.,  $\langle n \rangle \approx 0.9$ . The singlet pairing interaction is repulsive on site, but attractive for pairs of electrons at nearest-neighbor sites. The triplet interaction  $V_t$  behaves qualitatively similar to  $V_s$  except for the difference in sign, i.e., it is repulsive for nearest-neighbor pairs. Note that the triangular system does not obey perfect nesting at half filling. Thus, the tendency to form a spin-density wave state is not as strong as on the square lattice Hubbard model. However,

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FIG. 1. Effective singlet  $(V_s)$  and triplet  $(V_t)$  interaction in real space for  $U/t_2=4$ ,  $t_1=t_2$ ,  $\omega=0$ , and a density of  $\langle n \rangle \approx 0.9$  (results at half filling are similar). The numbers are normalized such that the on-site interaction has unit magnitude. (The reference site is marked by a rectangle.) The ratio of on-site interactions is  $V_s(0)/V_t(0) \approx -3$ . With decreasing band filling the range and magnitude of the interactions decrease.

for large U and half filling the model maps onto the  $S = \frac{1}{2}$  triangular AF (Ref. 8) which is believed to have an ordered 120° magnetic ground state.<sup>9</sup>

To investigate two-particle bound states it is convenient to classify them according to symmetry properties in momentum space. The point symmetry group of the isotropic triangular lattice is  $C_6$  which has six irreducible representations  $(s, p_x, p_y, d_{x^2-y^2}, d_{xy}, f_{x^3-3xy^2})$ . The results below show that the triangular system has possible instabilities in the *s*-,  $p_{x^-}$ ,  $d_{xy^-}$ , and  $f_{x^3-3xy^2}$  channels. These pairing symmetries in momentum space are illustrated in Fig. 2 using the Brillouin zone of the triangular system. There are three equivalent  $d_{xy}$  solutions (related by 60° rotation), one of them continuously evolves into the well-known square lattice  $d_{x^2-y^2}$  symmetry when reducing  $t_1$  and going to the square Brillouin zone.

To search for possible pairing instabilities in the problem let us here investigate the leading eigenvalues  $\lambda$  and eigenfunctions  $\phi(p)$  of the Bethe-Salpeter (BS) equation,

$$\lambda \phi(p) = -\frac{T}{N} \sum_{p'} V(p,p') G(p') G(-p') \phi(p') . \quad (3)$$

Self-energy contributions are neglected, and the singleparticle Green's function is  $G(p) = (i\omega_n - \epsilon_p)^{-1}$ . When the largest eigenvalue  $\lambda$  reaches 1, a superconducting instability to a state with a pair wave function  $\phi(p)$  occurs.

The BS equation can have singlet and triplet solutions which correspond to pair wave functions with even or odd parity when transforming from  $(\mathbf{p}, i\omega_n)$  to  $(-\mathbf{p}, -i\omega_n)$ . The usual *s*- and *d*-wave singlet solutions are even both in frequency and momentum whereas the usual triplet solutions (*p* and *f*) are even in frequency and odd in momentum. As discussed by Berenzinskii and by Balatsky and Abrahams,<sup>10</sup> also odd-frequency pair wave functions are permitted by symmetry. Then, one can obtain even-momentum triplets  $[\phi(-\mathbf{p}, i\omega_n) = \phi(\mathbf{p}, i\omega_n) = -\phi(\mathbf{p}, -i\omega_n)]$  and odd-



FIG. 2. Momentum dependence of the pair wave functions corresponding to s,  $p_x$ ,  $d_{xy}$ , and  $f_{x^3-3xy^2}$  symmetries. The graphs show the sign and the zeros of the pair wave function at selected points of the Brillouin zone.

momentum singlets  $[\phi(-\mathbf{p},i\omega_n) = -\phi(\mathbf{p},i\omega_n) = \phi(\mathbf{p}, i\omega_n)]$ . In a model with strong on-site repulsion there are two ways for the pairs to "avoid" the repulsion. One is by constructing a pair wave function with zero on-site amplitude, i.e., with nonzero angular momentum. The second way is by having an odd- $\omega$  dependence which implies a vanishing equal-time pair amplitude (and spontaneous breaking of time reversal symmetry).

The present investigation shows that the dominant pairing channels in the triangular lattice model treated with the BS equation are *d*-wave singlet (*even* in frequency) at intermediate  $U/t_2$  switching to s-wave triplet (odd in frequency) at large  $U/t_2$ , although a small deviation from this geometry using the  $t_1 - t_2$  model establishes a *d*-wave state as the only dominant one. (For small  $U/t_2 \le 2.5$  and  $t_1 = t_2$  the transition temperature is smaller than  $10^{-3} t_2$ .) This curious competition for the triangular lattice can be understood intuitively as follows, starting with the even- $\omega$  case first: The singlet potential favors pairing with zero on-site amplitude due to the Hubbard repulsion. This effect suppresses s-wave singlets, as is the case in the square lattice near half filling.<sup>6</sup> In the family of even- $\omega$  solutions the next possibility is a *d*-wave singlet. However, in contrast to the square lattice where  $d_{x^2-y^2}$  pairing is favored,<sup>6</sup> the tendency towards d-wave solutions is not as strong in the triangular system. This can be understood from the BS equation: The susceptibility  $\chi_0$  and the effective potential are strongly peaked at the ordering wave vector Q  $=(\frac{4}{3}\pi,0)$  for the triangular system. The kernel of the BS equation for  $T \rightarrow 0$  basically couples values of  $\phi(p)$  at Fermi surface momenta which differ by Q. The particular value of **Q** for the triangular system weakens  $d_{x^2-y^2}$  and  $d_{xy}$ -wave singlet solutions. How about p and f symmetries in the even- $\omega$  sector? Here the effective triplet potential is repulsive for nearest neighbors, and it tends to suppress all triplet pairing with zero amplitude on site. This reasoning lead us to believe that odd- $\omega$  pairing may be relevant for the triangular lattice. In the triplet channel, the s-wave solution can take advantage of the on-site interaction which remains attractive at nonequal times, thus avoiding the suppression by the Pauli principle. Note that in previous BS studies on the square lattice it was observed that odd- $\omega$  solutions actually compete in strength with the even- $\omega$  d-wave possibility.<sup>11</sup>

To verify this intuitive picture, the BS equation was solved on a finite lattice (up to  $32^2$  sites) with a cutoff on the Matsubara frequencies of  $8 t_2$ . The eigenvalues reach unity only at and close to half filling. The transition temperature is determined by the temperature where this largest eigenvalue reaches unity. In Fig. 3 the leading eigenvalues are shown for the triangular lattice  $(t_1 = t_2)$  at half filling, U/t = 3.5, vs temperature. In this regime the dominant eigenvalue corresponds to *d*-wave singlet pairing. Small deviations from the perfect triangular lattice using the  $t_1 - t_2$  model also give a stable *d*-wave singlet solution at a temperature  $T = 0.08 t_2$ [Fig. 4(a)]. This regime is likely of relevance for organic superconductors.<sup>5</sup> However, it is interesting to observe that for  $U/t \ge 4$  and half filling the *d*-wave even- $\omega$  and the three odd- $\omega$  solutions strongly compete in the considered temperature range  $0.01 < T/t_2 < 0.1$  [Fig. 4(b)]. Actually, the eigenvalue corresponding to the s-wave pairing instability is the largest in this regime, and thus odd- $\omega$  s-wave triplets are



FIG. 3. Bethe-Salpeter eigenvalues vs temperature for the isotropic triangular lattice,  $U=3.5 t_2$ , and half filling (*d*-wave singlets, solid; *s*-wave triplets, dash dot; *p*-wave singlets, dashed; *f*-wave singlets, dotted).

favored, as expected from the previous discussion. Since self-energy contributions are neglected the critical temperature for the pairing instability, which is around  $0.02 t_2$ , should only be considered as a rough estimate. Compared with the results obtained on a square lattice<sup>11</sup> (~0.1  $t_2$ ), the triangular lattice seems to have a critical temperature substantially smaller.

Thus far, the calculations have addressed the weakcoupling limit. In the second part of this paper an isotropic triangular AF doped with holes described by the *t*-*J* model will be discussed. At half filling the *t*-*J* model reduces to the triangular Heisenberg antiferromagnet (THAF) (Ref. 8) with spins  $\frac{1}{2}$ . It is by now widely believed that its ground state possesses magnetic long-range order<sup>9</sup> which can be described as 120° order, namely the ground state of the classical spin model with the addition of quantum fluctuations.

The one-hole problem in the triangular t-J model was studied analytically before using the self-consistent Born approximation (SCBA).<sup>12,13</sup> Since the SCBA neglects closed loops in the hole motion (which are more important here than for the square lattice since only three hopping steps are necessary for one loop) in this paper an alternative analytical approach based on the picture of magnetic polarons will be used. The spin excitations are described by a set of string operators locally distorting the background spin configuration<sup>14–16</sup> which is assumed to be long-range ordered. The one-hole spectral function can be evaluated using the Mori-Zwanzig projection technique. For details see Refs.



FIG. 4. Bethe-Salpeter eigenvalues vs band filling for  $U = 4 t_2$ . (a)  $t_1/t_2 = 0.8$  and  $T = 0.08 t_2$ . (b)  $t_1/t_2 = 1.0$  (triangular lattice) and  $T = 0.02 t_2$ . The inset in (a) shows the symmetry of the *d*-wave solution in the triangular lattice Brillouin zone which becomes  $d_{x^2-y^2}$  for the square lattice case.



FIG. 5. (a) One-hole dispersion calculated from the polaron picture at J/t=0.1 (dashed) and 0.4 (solid). The energy zero level has been set at the center of mass of the band. The inset shows the path in momentum space corresponding to the horizontal axis. (b) Onehole spectral function at J/t=0.4 and momentum ( $\frac{4}{3}\pi$ ,0) which is the minimum of the quasiparticle (QP) band. A sharp QP peak is observed.

16 and 17. Figure 5(a) contains the calculated one-hole dispersion  $\epsilon_{\mathbf{p}}^{\text{hole}}$  for different couplings J/t. In Fig. 5(b) the one-hole spectral function at J/t = 0.4 and the momentum corresponding to the band minimum  $\mathbf{p} = (\frac{4}{3}\pi, 0)$  are shown. A sharp peak at the bottom of the spectrum suggests that a description in terms of quasiparticles (QP) is appropriate. Note that the one-hole dispersion shown in Fig. 5(a) is in qualitative agreement with exact diagonalization (ED) data on a 12-site cluster<sup>12</sup> as well as with SCBA and 21-site ED results from Ref. 13. (A detailed discussion will be given elsewhere.<sup>17</sup>)

Now let us consider a fermionic model constructed from the dressed one-hole properties and including an interaction between the QP. The use of a dressed QP dispersion implicitly assumes that in the normal state short-range antiferromagnetism exists, namely the AF correlation length is not negligible. This is a standard assumption in AF scenarios for the cuprates and can be checked experimentally using, e.g., NMR techniques. For simplicity, the QP interaction is taken from the RPA calculation described in the first part of the paper. For singlet pairing it basically consists of an on-site repulsion, a nearest-neighbor attraction, and a next-nearestneighbor repulsion. Note here that the  $\omega$  dependence of the interaction is important for possible odd- $\omega$  pairing. Previous literature in the context of the square lattice<sup>7,18</sup> has shown that in *both* weak and strong coupling the most important part of the interaction for the study of pairing is the nearest neighbor attraction (singlet channel). Thus, for the qualitative purposes of the present strong-coupling study it is reasonable to assume that a similar result holds in triangular lattices.

To investigate the existence of pairs within this model once again the BS equation Eq. (3) will be solved. Now the single-particle Green's function is determined by the onehole QP dispersion from the strong-coupling calculation:  $G(p) = (i\omega_n - \epsilon_p^{hole})^{-1}$ . For the calculation the RPA interaction V(p,p') corresponding to an electronic density  $\langle n \rangle$ 



FIG. 6. Temperature dependence of the Bethe-Salpeter eigenvalues for *s*-wave triplets, and *p*-wave, *d*-wave, and *f*-wave singlets, now calculated from the strong-coupling dispersion and the RPA interaction.

=0.9 will be used. In Fig. 6 the leading eigenvalues are plotted as a function of temperature for the different pairing symmetries, working with a low-band *hole* filling (10%). The results qualitatively agree with those obtained in the Hubbard model.

Odd-frequency pairing such as the one described here has experimental interesting consequences, as discussed in Ref. 19. First, there is no gap in the excitation spectrum at any  $\mathbf{k}$ . Second, the magnitude of the Hebel-Slichter peak in the NMR relaxation rate is strongly reduced compared to the BCS case. Other nontrivial consequences of odd-frequency pairing include the tunneling between an odd-frequency and a BCS superconductor. However, regarding the organic superconductors  $\kappa$ -(BEDT-TTF)<sub>2</sub>X, our results suggest that their low-temperature properties will likely correspond to a *d*-wave singlet state being the analog of the widely discussed  $d_{x^2-y^2}$  state of square lattices which arises from antiferromagnetic fluctuations.

Summarizing, in this paper the possibility of superconductivity in doped and undoped triangular and anisotropic antiferromagnets has been investigated. The pairing interaction is assumed to arise from the exchange of paramagnons. Both weak-coupling and strong-coupling approaches suggest that the system presents a pairing instability in an unconventional channel. A d-wave singlet superconducting state similar to the square lattice dominates for anisotropic lattices, and even for the isotropic ones at intermediate U/t. However, at large U/t pairing in the s-wave triplet odd-frequency channel is also possible. Hopefully the present calculations will motivate experimentalists to study in more detail antiferromagnetic triangular lattice compounds. Recent results<sup>5</sup> suggest that the physics described here may already be realized in organic superconductors. If angle-resolved photoemission experiments were possible in this context,<sup>20</sup> nodes should be observed for a *d*-wave singlet state. Specific heat and penetration depth measurements<sup>5,21</sup> already suggest the existence of gapless excitations in these materials.

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