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THE RESONATING VALENCE BOND STATE AND HIGH-T_C SUPERCONDUCTIVITY - A MEAN FIELD THEORY

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A mean field type theory is developed for the insulating RVB state and high temperature superconductivity in doped La_2CuO_4 and other high-T_c oxides. The T_c as a function of the doping parameter δ drops sharply around $\frac{t}{U} \sim \delta$. The zero temperature gap versus T_c relation depends sensitively on the choice of the parameters. Gutzwiller projection, suppression of T_c by phase fluctuations for small δ and screening effects are briefly discussed.

The recent discovery[1] of high-T_c superconductivity in a number of doped lanthanum copper oxides has generated strong interest in the basic properties of these substances and possible new mechanisms[2,3] for superconductivity. High temperature susceptibility data[4] on insulating La_2CuO_4 suggests that Cu^{2+} is in an $S = 1/2$. orbitally non-degenerate state, with a copper $d_{x^2-y^2}$ orbital strongly hybridizing with the neighboring oxygen p-levels. Based on the magnetic data of Ganguly and Rao, a predominately electronic and magnetic mechanism for superconductivity in these compounds has been suggested by Anderson[2]. It is hypothesized that the insulating state of pure La_2CuO_4 is the resonating valence bond (RVB) state or quantum spin liquid proposed in 1973[5]. There are pre-existing spin singlet pairs in the RVB state and they become charged superconducting Cooper pairs by strong enough doping.

In this communication we present a mean field theory for the RVB state and the high-T_c superconductivity. Our theory explicitly takes into account the singlet correlations induced between electrons on neighbouring sites by the Hubbard U and shows how superconductivity results in a model with pure repulsive interaction. It is shown that the general picture seems to be consistent with what was proposed by Anderson[2]. We found that the RVB wave function for the insulator comes out as a self-consistent solution to the problem. In the insulating phase there exist neutral fermionic excitations with effective mass of the order of J^{-1}, where J is the antiferromagnetic exchange integral. Charge excitations are projected out by the Gutzwiller procedure, so that the state behaves like a fermi liquid with $F_0^s = \infty$. We calculate T_c as a function of doping parameter δ; it has a sharp fall around $t/U \sim \delta$, where t and U are the usual " Hubbard" parameters. The relation between the zero-temperature gap and T_c is found to be very sensitive to the parameters. At the end we discuss the Gutzwiller projection,and how much it may change the picture. We also discuss phase fluctuations and suppression of T_c for small δ. The screening of the Hubbard U is also briefly discussed. For the exact half filled band case our theory has some mathematical resemblence to a theory recently discussed by Noga[6]. We also would like to point out that antiferromagnetic spin-fluctuation-mediated even-parity pairing in heavy fermion superconductors has been discussed by Miyake et.al[7]

Since the high-T_c superconducting transition appears near a metal-insulator transition, it is believed that a nearly half-filled "Hubbard" model describes the system:

$$H = -t \sum_{<ij>} (C_{i\sigma}^{+} C_{j\sigma} + h.c.) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \qquad (1)$$

and we will explicitly introduce a chemical potential μ modeling the doping process later. We consider a 2-dimensional square lattice and perform a mean field theory. The usual argument of weaker coupling between Cu Layers can be used to stabilise the 2-d mean field phase that we find. After a canonical transformation[8,9], we obtain an approximate effective Hamiltonian which is defined only in the non-doubly occupied subspace:

$$\begin{aligned} H = & -t \sum_{<ij>} (1 - n_{i-\sigma}) C_{i\sigma}^{+} C_{j\sigma} (1 - n_{j-\sigma}) \\ & + \mu \sum_{i} C_{i\sigma}^{+} C_{i\sigma} + J \sum_{<ij>} (\vec{S}_i \cdot \vec{S}_j - 1/4\, n_i n_j) \end{aligned} \qquad (2)$$

with $J = 4t^2/U$, $S_i^{+} = C_{i\uparrow}^{+} C_{i\downarrow}$, etc. For a half-filled band in the singly occupied site subspace, eq.(2) becomes $H = J \sum_{<ij>} (\vec{S}_i \cdot \vec{S}_j - 1/4)$. We will concentrate on the Hamiltonian(2) which can be uesd for the non-half filled band case. We will relax the restriction to singly occupied subspace and work in the entire Hilbert space for pure mathematical convenience and to get a general idea of the physics of the situation. Part of this restriction is taken into account by approximating the hopping term $-t(1 - n_{i-\sigma}) C_{i\sigma}^{+} C_{j\sigma} (1 - n_{j-\sigma})$ by $-t\delta C_{i\sigma}^{+} C_{j\sigma}$,where δ is the fractional difference of n from the half-filled case. We will discuss at the end, using a Gutzwiller projection, the effect

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of removing the double occupancy restriction. Thus the Hamiltonian can be written in terms of fermion operators:

$$H = -t\delta \sum_{<ij>} (C^+_{i\sigma} C_{j\sigma} + h.c.) + J \sum_{<ij>} \left[\frac{1}{2} (C^+_{i\uparrow} C_{i\downarrow} C^+_{j\downarrow} C_{j\uparrow} + h.c.) + \frac{1}{2} (n_{i\uparrow} n_{j\downarrow} + n_{i\downarrow} n_{j\uparrow}) \right] \quad (3)$$

We note that the two-body term can be written in terms of valence bond "singlet" pair creation and annihilation operators defined by

$$b^+_{ij} = \frac{1}{\sqrt{2}} (C^+_{i\uparrow} C^+_{j\downarrow} - C^+_{i\downarrow} C^+_{j\uparrow}). \quad (4)$$

$$H = -t\delta \sum_{<ij>} (C^+_{i\sigma} C_{j\sigma} + h.c.) - J \sum_{<ij>} b^+_{ij} b_{ij} \quad (5)$$

where $n_i = n_{i\uparrow} + n_{i\downarrow}$. The negative sign of the second term above suggests that the singlet objects (approximate bosons) will try to undergo "Bose condensation" into zero momentum state. The numerical simulations of Hirsch[8] strongly suggests that the bond singlet pairing tendency dominates. Hirsch's results also suggests that when the Hubbard U is not very large, the RVB state may be stabilized by quantum fluctuations for the exactly half filled band.

When we go to momentum space and make a Hartree-Fock factorization in eq.(6), the resulting Hamiltonian is

$$H = \sum_{\vec{k}\sigma} (\epsilon_k - \mu) C^+_{k\sigma} C_{k\sigma} - J \sum_k \left(\Delta \gamma_k C^+_{k\uparrow} C^+_{-k\downarrow} + h.c. \right) - N(\Delta^2 + p^2) \quad (6)$$

where the self-consistent order parameters Δ and p are defined as $\sqrt{2} < b_{ij} > = \Delta$, $p = < C^+_{i\sigma} C_{j\sigma} >$, for $ij >$ nearest neighbors and zero otherwise; $\epsilon_k = (2t\delta + pJ)(\cos k_x a + \cos k_y a)$ for two dimensions; $\gamma_k = \epsilon_k/(2t\delta + pJ)$. The Hamiltonian is of BCS type. Diagonalizing eq.(6) by Bogoliubov transformation gives quasiparticle energy

$$E_k = \sqrt{(\epsilon_k - \mu)^2 + J^2 \gamma_k^2 \Delta^2}. \quad (7)$$

The corresponding quasiparticle operators, α_k, β_k, are related to C's by a unitary transformation, and therefore they are fermions. The Hartree-Fock order parameters δ and p are to be found self-consistently by minimizing the free energy. The gap and chemical potential equations are:

$$\frac{1}{N} \sum_k \frac{\tanh \beta E_k/2}{E_k} \gamma_k^2 = \frac{2}{J} \quad (8)$$

$$\frac{1}{N} \sum_k \frac{\tanh \beta E_k/2}{E_k} (\epsilon_k - \mu) = \delta \quad (9)$$

$$p = -\frac{1}{2N} \sum \frac{\tanh \beta E_k/2}{2E_k} \gamma_k (\epsilon_k - \mu)$$

Before we discuss the general solution to eq.(8,9), let's first look at some of the unusual consequence of this simple theory in the insulating phase in which $\delta = \mu = 0$. It's easy to see that eq.(9) is trivially satisfied with $p = 0$ and the quasiparticle operators are given by

$$\alpha_k = \begin{cases} \frac{1}{\sqrt{2}} (C_{k\uparrow} + C^+_{-k\downarrow}), & \text{if } |k| < k_F \\ \frac{1}{\sqrt{2}} (C_{k\uparrow} - C^-_{-k\downarrow}), & \text{if } |k| > k_F \end{cases} \quad (10)$$

Similar relations hold for β_k. The quasiparticle energy becomes

$$E_k = \Delta J |\gamma_k| = \Delta J |\cos k_x a + \cos k_y a| \quad (11)$$

Thus we get from first principles the RVB state constructed by Anderson

$$|G> = P_N \prod_{\vec{k}} \left(u_k + v_k C^+_{k\uparrow} C^+_{-k\downarrow} \right) |0>$$

with

$$\sum_k \frac{v_k}{u_k} = \sum_k a(k) = 0; \quad |a(k)| = 1 \quad (12)$$

Note that $a(k)$ does change sign across a "fermi surface' as is pointed out by Anderson.

As a consequence of the signs in eq.(10), $\alpha^+_k \alpha^+_{k'}$ creates a charged excitation if $\vec{k}$ and $\vec{k}'$ are both on the same side of the "pseudo-fermi surface", and a neutral spin excitation if they are on opposite sides. When we project out charged excitations in the insulating state, only the latter spectrum will persist; it will resemble closely the excitation spectrum of a simple fermi gas. There will be a gap for charged excitations, which will more or less gradually disappear with temperature. Spin excitations will have no gap, but their spectrum is restricted in $\vec{k}, \omega$ space by the condition that $\vec{k}'$ and $\vec{k}$ be on opposite sides of the pseudo-fermi surface.

The excitation spectrum(11) implies a linear temperature dependence of low temperature specific heat due to the fermionic nature of the quasiparticles, $C(T) \propto \gamma T$, where γ is proportional to the effective mass of the quasiparticle which is of order of J^{-1}. In the presence of a weak magnetic field the degeneracy of the two branches will be lifted giving rise to a Pauli-like susceptibility . Thus the experimental measurement of specific heat and suseptibility of the pure La_2CuO_4 at low temperature would be a decisive test of the pressent theory. When $T > 3J/16(1/N \sum_k \gamma_k^2)$, Δ vanishes, and the susceptibility obeys a Curie-Weiss law, since an energy J is needed to break up a valence bonded pair. This has been partially confirmed by experiment (see Ref.4).

It is important to recognize that there can be no true "ODLRO" for exactly half-filled band and that the phase of the mean field Δ is to be averaged over. Thus there can be no BCS type transition in the insulating case. In essence, the phase correlation length for charged excitations is zero, and as we remark later

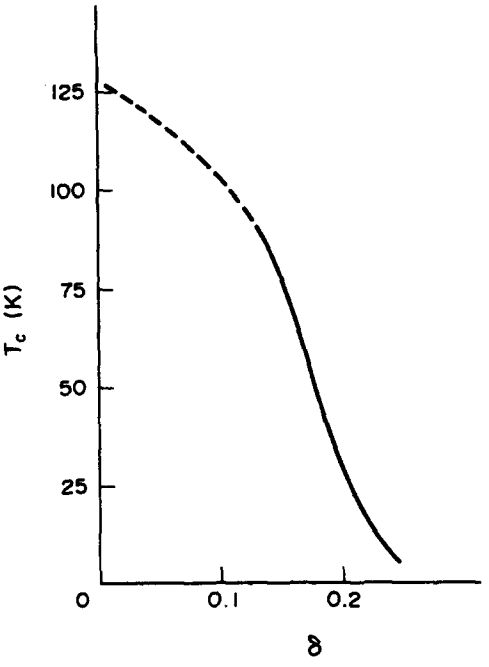
the corresponding reduction in T_c when charged excitations are present is striking (as well as the low critical currents that implies). We see no way of formally expressing the fact that spin excitations nonetheless exhibit a sharp fermi surface except to appeal to the theoretical possibility that $F_0^s \cdot \propto$.

Now let's look at the superconducting state in which the band is non-half filled due to doping. The quasiparticle energy is given by eq.(9). From the mean field point of view, as soon as the system is metallized, it should become superconducting and open up a gap. However, in the low doping concentration limit($\delta \ll 1$), the phase fluctuations play an important role and the mean field theory fails. At this limit, T_c and the gap are governed by strong phase fluctuations. A rough estimate of T_c will be given for $\delta \ll 1$ later. But for large enough $\delta(> 5\%)$ we expect that the mean field theory works. We have choosen a set of parameters(t, U, δ) and calculated the gap as a function of T. The ratio of the zero temperature gap to T_c depends sensitively on the choice of the parameters. In our model the true energy gap is related to the order parameter Δ by

$$Gap = \frac{3\delta J\Delta/2}{\sqrt{1+(3\Delta J/2W)^2}} \qquad (13)$$

where $2W$ is the band width($\sim t\delta$). For some choice of the parameters $2Gap/T_c$ is close to the BCS value. Some experimental results are needed to get a good idea about t and U. Another interesting feature of our model is the dependence of T_c on δ. The difficulty arises because of lack of information about the metallic screening. In the insulating phase $J = 4t^2/U$ is of order 200K. In the metallic phase, however, U becomes smaller and t remains essentially unchanged. Thus one expects that J increases. Nevertheless, if we assume a reasonable value for J, we found T_c as a function of δ drops sharply around $\delta \sim 0.15 - 0.20$. This is easily understood physically: when increasing δ, the band gets wider. $W \sim t\delta$; when W is compatible to the bonding energy J, electron pairs will break up by gaining kinetic energy and superconducivity disappears. One can easily see that T_c becomes very small when $W > J$. Our numerical calculation confirms this (see Fig.1). We have assumed that the self consistent parameter p is zero in our calculation of T_C. However Wilkins[10] points out that inclusion of p shifts the phase boundary of figure 1. The numerical analysis also indicates that T_c is very sensitive to the hopping integral t. larger t leads to higher T_c. Therefore within limits, pressure will enhance T_c. Although we have only done at this stage a preliminary study on the superconducting state, our theory seems to be able explain a wide variety of experimental observations. We leave the thermodynamics and many other details of the model for future investigation. Before concluding the letter, we discuss the small δ limit and Gutzwiller projections.

For small δ the phase fluctuations dominate and T_c is severely suppressed. The motion of singlet pairs



1) T_c vs δ for a choice of parameters $J = 0.05eV$ and band width $2W = 0.4eV$. The dashed region is the phase fluctuation dominated region, where we expect a drastic reduction in T_c.

in the ground state is not accompanied by any charge flow in the insulator. On the other hand, once we dope the system with holes, the singlet pairs next to the holes can carry charge as they move. In other words, the motion of holes can be thought of as motion of singlet pair carrying a charge. The effective mass associated with this motion has been shown by Hsu[11] to be of the order of the band electron mass (m^*). Thus we can model the small doping limit as a collection of charged valence bond pair bosons. To get a rough estimate of the T_c associated with the superconductivity of these charged bosons, we use the Bose-Einstein condensation formula: $T_c \sim (2\pi/m^*)(n/2.61)^{2/3}$. So $T_c \sim \delta^{2/3}$. A simple calculation shows that when $\delta < 1\%$, T_c is negligibly small. Then T_c builds up very quickly with δ. When $k_B(T_c)$ exceeds J the modelling in terms of bosons breaks down because valence bond pairs break for $k_BT > J$. Further study is underway to understand the small δ behavior, where screening and localization effects also become important.

Finally about the Gutzwiller projection: We have performed a Gutzwiller projection on the RVB state for the exactly half filled band in one dimension and find that the energy almost coincides with Bethe's ground state energy[12]. The RVB state energy before doing the Gutzwiller projection in one dimension is $-0.608J$ which is lower than the exact energy $\approx -.4431J$. (This is no contradition to variational principle, because we go outside the Hilbert Space, as for example in the spin wave theory). But after the

projection the RVB energy becomes $-.4422J$. So we have demonstrated that in one dimension the energy of our RVB state after the Gutzwiller projection is much closer to the exact result than that of the Neel' state. The one dimension chain has no frustration of course, and the reason that RVB state has lower energy than Neel's state is due to quantum fluctuations. We expect the similar result for the square lattice which has strong quantum fluctuations for not so large U. Additional quantum fluctuation in this two dimensional case could be due to the strong electron phonon interaction and the next nearest neighbor interaction.

The quasiparticle excitation spectrum in the insulator is not qualitatively affected by projecting out the doubly occupied states, since our excitation is chargeless characterizing the spin fluctuations. In the spirit of fermi liquid theory, the Gutzwiller projection amounts to a mass renormalization which will change the band width of the quasiparticle. The general features of the quasiparticle are preserved qualitatively. We have not been able to perform Gutzwiller projections on our superconducting state satisfactorily for finite δ. Our analysis for the non-half filled band can be taken in the spirit of fermi liquid theory for superconductivity. The band parameters such as effective mass are fermi liquid parameters. The onsite Hubbard U induces nearest neighbor singlet correlation between quasiparticles which results in superconductivity. The main aim of this paper has been to show and explain how the antiferromagnetic singlet correlations induce high temperature superconductivity and how quickly this superconductivity is suppressed with high doping.

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