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Neutral fermion, charge-e boson excitations in the resonating-valence-bond state and superconductivity in La_2CuO_4-based compounds

Z. Zou and P. W. Anderson
Joseph Henry Laboratories of Physics, Princeton University, Princeton, New Jersey 08544
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We derive the neutral fermion excitation spectrum in the resonating-valence-bond state based on a fermion-boson field theory. It is formally shown that charge-e bosons are created upon doping while the neutral fermion excitation remains gapless, predicting a linear low-temperature specific heat $C\propto\gamma T$ in the superconducting state. Bose condensation in doped samples leads to the observed superconductivity with true "off-diagonal long-range order."

Since the original work by Anderson[1] on the resonating-valence-bond (RVB) theory of high-T_c superconductivity, considerable progress has been made. Baskaran, Zou, and Anderson (BZA)[2] have developed a mean-field theory in which many of Anderson's conjectures are confirmed, especially the existence of a pseudo-Fermi surface in the insulator. Kivelson, Rokhsar, and Sethna[3] have pointed out that there exist three kinds of excitations in the RVB state: fermion solitons, which we call spinons; charge $\pm e$ bosons; and true electrons or holes.

In a recent Letter,[4] we identified the mysterious high-T "twitch" transition[5] in La_2CuO_4 with the mean-field RVB transition of the Heisenberg model of BZA; we argued that doping the pure La_2CuO_4 in the RVB state is compensated by creation of boson excitations, as long as the system remains in the RVB state; we also argued that after projection with the Mott-Hubbard condition $n_i=1$ the bare fermions $C_{i\sigma}^\dagger$ turn into "spinon" degrees of freedom $S_{i\sigma}^\dagger$ which have no true kinetic energy in the insulating state; the $S_{i\sigma}$ is treated as strictly neutral, even after doping ($n_i\neq 1$), and spinon excitations remain gapless. This is strongly supported by the linear temperature-dependent low-temperature specific heat in the superconducting phase as well as in the normal phase for both La-based and Y-based compounds.[6] In this paper we demonstrate how this is formally done in the Hubbard model with the help of the so-called "slave boson" technique developed in the study of heavy-fermion systems by Coleman,[7] Barnes,[8] etc. This technique was used by Kotliar and Ruckenstein[9] to study the metal-insulator transition for the finite-U Hubbard model, where they derived the same result as that of the Gutzwiller approximation. However, in the previous work the "slave boson" was introduced merely for mathematical convenience. To the best of our knowledge, its physical meaning is not well understood. In the present work, we show that in the RVB state "slave bosons" have real physical meaning if properly treated; they are related to the soliton holes that are introduced by doping the insulating RVB vacuum state; and they carry a conserved quantum number, charge. A similar but different approach has been used recently by Newns[10] to study the high-temperature superconductivity.

We shall start from the finite-U Hubbard model:

$$H=-t\sum_{\langle ij\rangle\sigma}C_{i\sigma}^\dagger C_{j\sigma}+U\sum_i n_{i\uparrow}n_{i\downarrow}-\mu\sum_{i\sigma}C_{i\sigma}^\dagger C_{i\sigma}\,. \quad (1)$$

Let us consider site i: there are four possible states, $|0\rangle$, $|\alpha\rangle$, $|\beta\rangle$, and $|\alpha\beta\rangle$, corresponding to an empty site, one up (down) spin state and a doubly occupied site. Using Hubbard[11] projection operators, we have the completeness relation for each site i:

$$|0\rangle\langle 0|+|\alpha\rangle\langle\alpha|+|\beta\rangle\langle\beta|+|\alpha\beta\rangle\langle\alpha\beta|=1\,. \quad (2)$$

Since $|ip\rangle$ ($p=0,\alpha,\beta,\alpha\beta$) form a complete set for site i, any operator affecting only the electron of site i can be written in terms of $|ip\rangle\langle ip|$.[11] In particular,

$$C_{i\sigma}=|0\rangle\langle\sigma|+\sigma|-\sigma\rangle\langle\alpha\beta|\,, \quad (3)$$

where $\sigma=\alpha,\beta$. Note that for $\sigma=\beta$ a minus sign is needed in Eq. (3) to preserve the anitcommutation relations.[12]

As was shown by Hubbard,[11] some of the projection operators are fermionlike, some bosonlike; their commutators or anticommutators form an algebra. These algebraic properties of projection operators are exactly reproduced by a combined fermion-boson field theory, namely, by mapping, for instance,

$$|0\rangle\langle 0|\to e_i^+e_i,\quad |0\rangle\langle\alpha|\to e_i^\dagger S_{i\alpha}\,,$$

$$|\alpha\beta\rangle\langle\alpha|\to d_i^\dagger S_{i\alpha},\quad |\alpha\beta\rangle\langle\alpha\beta|\to d_i^\dagger d_i\,,$$

etc. Here e_i, d_i are boson fields satisfying $[e_i,e_j^\dagger]=\delta_{ij}$, $[d_i,d_j^\dagger]=\delta_{ij}$, and $[e_i,d_i^\dagger]=0$, etc., and $S_{i\sigma}$ are fermions satisfying $[S_{i\sigma},S_{j\sigma'}^\dagger]_+=\delta_{ij}\delta_{\sigma\sigma'}$. One can easily convince himself that the mapping from projection operators to fermion-boson field theory is self-consistent. Thus the true (bare) electron operators are expressed as, using Eq. (3),

$$C_{i\sigma}^\dagger=e_iS_{i\sigma}^\dagger+\sigma d_i^\dagger S_{i-\sigma}\,, \quad (4)$$

where $\sigma=+(\alpha)$ or $-(\beta)$. We note that $C_{i\sigma}^\dagger$ in Eq. (4) still satisfies the anticommutation relations provided that

$$e_i^\dagger e_i+d_i^\dagger d_i+\sum_\sigma S_{i\sigma}^\dagger S_{i\sigma}=1\,, \quad (5)$$

corresponding to the completeness conditions (2).

Substituting Eq. (4) into Eq. (1), we obtain

$$\begin{aligned} &H = H_0 + tH' , \\ &H_0 = -t \sum_{\langle ij\rangle\sigma} (e_i e_j^\dagger - d_i d_j^\dagger) S_{i\sigma}^\dagger S_{j\sigma} + U\sum_i d_i^\dagger d_i \\ &\qquad + \mu \sum_i (e_i^\dagger e_i - d_i^\dagger d_i) - \mu N , \\ &H' = -\sum_{\langle ij\rangle} [(e_i d_j + e_j d_i) S_{i\alpha}^\dagger S_{j\beta}^\dagger + \text{H.c.}] , \end{aligned} \tag{6}$$

where N is the number of the lattice sites. Let us pause for a moment to discuss the nature of the transformation (4). Physically $e^\dagger$ corresponds to creating an empty site and $d^\dagger$ a doubly occupied site; therefore $e^\dagger$ and $d^\dagger$ have opposite charges (e and $-e$, respectively). So we see immediately from Eq. (4) that we can treat $S_{i\sigma}^\dagger$ as a neutral particle. One may check the consistency of this assignment by a direct calculation of the currents due to bosons: The current of particle l ($l = e$, d, or C) is given by

$$\mathbf{j}_l = \frac{\partial \mathbf{P}_l}{\partial t} = i[H, \mathbf{P}_l] , \tag{7}$$

where $\mathbf{P}_l$ is the polarization operator for particle l; in the tight-binding model $\mathbf{P}_l$ is given by, for instance, $\mathbf{P}_e = q_e \sum_i \mathbf{R}_i e_i^\dagger e_i$ (with $q_e = e$). A straightforward calculation using the Hamiltonian (6) shows that the total current $\mathbf{j}_c = \mathbf{j}_e + \mathbf{j}_d$, implying that the charges of $S_{i\sigma}$ are identically zero. Thus we can assign the charges of the bare electrons to bosons and the spins to spinons.

One is tempted to do a mean-field theory on the Hamiltonian (6) (namely, replace e_i and d_i by their classical values).[10] However, this is incorrect because the Hamiltonian (6) contains many virtual processes which ought to be eliminated before we let the bosons condense to a zero-momentum state. This is achieved by a canonical transformation[13] $\tilde{S}$, which eliminates the H' term in H to the order of t/U: $tH' + [H_0, \tilde{S}] = 0$. For sufficiently large U (larger than the critical U_c for the Mott transition), we neglect terms of order of $(t/U)^2$ and restrict ourself within the subspace determined by Eq. (5), yielding

$$\begin{aligned} &\tilde{S} = \frac{t}{U} \sum_{\langle ij\rangle} (e_i^\dagger d_j^\dagger + e_j^\dagger d_i^\dagger) S_{j\beta} S_{i\alpha} - \text{H.c.} , \\ &H_{\text{eff}} = H_0 - J \sum_{\langle ij\rangle} (S_{i\alpha}^\dagger S_{j\beta}^\dagger S_{j\beta} S_{i\alpha} + S_{i\alpha}^\dagger S_{j\alpha} S_{j\beta}^\dagger S_{i\beta}) , \end{aligned} \tag{8}$$

where $J = 4t^2/U$ and H_0 is defined in (6). One can set $d = 0$ in (8) since they involve large energy U (self-consistent solution always leads to $d = 0$ for large U). One could in principle integrate out fermion degrees of freedom obtaining a free-energy functional F; it is easy to see from Eq. (8) that

$$\frac{\partial F}{\partial \mu} = e^2 N - N = -N_0 , \tag{9}$$

where N_0 is the total number of electrons, yielding $e^2 = \delta$ (concentration of holes). Thus we have proved that the boson amplitudes correspond to the hole amplitudes. At low temperature bosons will undergo Bose condensation with true off-diagonal long-range order (ODLRO) leading to superconductivity. As we shall see in the following, the Hamiltonian (8) contains essentially almost all the physics we need.

We first discuss the insulating state. The second term in H can be written as $(J/4)\sum_{\langle ij\rangle} (\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j - 1)$ in the half-filled band, where $\boldsymbol{\sigma}/2$ is the spin operator for spinons. There are no bosons in the insulator, $e^2 = d^2 = 0$. Our main purpose in this paper is to calculate the excitation spectrum of spinons and we do not attempt to prove the existence of the RVB state. It is assumed, instead, that we have a RVB ground state[1,4] at $T = 0$, of which a typical configuration of valence bonds is schematically shown in Fig. 1 with all the electrons in the singlet pairs. We want to create excitations on this RVB vacuum state. The simplest excitation one can imagine is a dangling spin[3] (spin soliton). It is important to recognize that spin-up and spin-down solitons are always created in pairs; they behave like particle-antiparticle pairs, or in another words the number of spin solitons is not conserved. In the absence of holes, although there are no direct hopping matrix elements for spinons, they can gain coherence energy by exchanging particle pairs with the RVB background. As is illustrated in Fig. 1, spinon and antispinon are simultaneously created and then annihilated at the nearest sites, resulting in an equivalent hopping. Based on these physical considerations, we adopt the following strategy to calculate the spinon spectrum: (1) We work in a grand canonical ensemble allowing the spinon number to fluctuate between $|N\rangle$ and $|N \pm 2\rangle$, etc., since the kinetic energy of spinons comes entirely from this kind of coherent fluctuations. (2) We then perform a mean-field theory on Hamiltonian (8), looking for $\langle S_{i\sigma}^\dagger S_{j-\sigma}^\dagger - S_{i\sigma}^\dagger S_{j\sigma}^\dagger \rangle = \Delta$. This has been done in BZA's paper,[2] where the excitation spectrum is given by

$$E_k = \Delta J \,|\cos k_x + \cos k_y| . \tag{10}$$

In doped systems, the motion of boson holes is compensated by the motion of spinons. The same type of mean-field calculation gives the excitation spectrum

$$E_k = E_0 \,|\cos k_x + \cos k_y| , \tag{11}$$

where $E_0 (\Delta^2 J^2 + 4t^2\delta^2)^{1/2}$. The result obtained here is different from that of BZA's paper, where a gap is opened upon once we move away from the half-filling. The reason

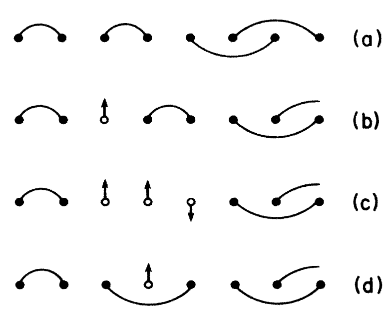

FIG. 1. (a) A typical configuration of valence bonds in the RVB; (b) to (d), hopping process of a dangling spin (spin soliton) via simultaneous creation and then destruction of a soliton-antisoliton pair in the RVB.

that the spinon excitation remains gapless lies in the fact that the number of spinons is not conserved and that the RVB vacuum serves as a reservoir of particles. The chemical potential μ does not appear in the expression for E_k in (11), since the charges are compensated by creation of charge e boson holes [see Eq. (9)]. The gaplessness is supported by a theorem due to Lieb and Mattis[14] which applies here without modification. This is an important result because it implies that in the superconducting phase the contribution to specific heat from spinons is linear in temperature $C \propto \gamma T$, with a more or less conventional metallic γ. This prediction is confirmed by experimental data.[6] To compare with the experimental data, we make a rough numerical estimate of γ: effective mass of the spinons is given by $\hbar/E_0 a^2$; a simple exercise of two-dimensional Fermi statistics yields $\gamma \approx \pi k_B^2/6E_0 a^2$. If we take $J=1000$ (a reasonable value obtained elsewhere;[15] see also Ref. 4) and $\delta=0$ (insulator), we obtain $\gamma \sim 1.8$ mJ/K^{2}mole, which is close to the observed values. Considering the uncertainty in the parameter (J and t), one should not take this number literally; the actual value may differ by 2 to 3 mJ/K^{2}mole. Many workers have reported this $C \sim \gamma T$ behavior both in the insulating and superconducting state with slightly different γ. The "variation" of γ can be due to magnetic impurities in the samples, since the spinons carry spins and may be bonded to the impurities, i.e., some of the spinons may be frozen out.

An objection might be raised with regard to the treatment of the constraint (5). The constraint should be strictly enforced in the insulator in order to arrive at the RVB liquid state without breaking the gauge symmetry. However, as we said, we are not deriving the RVB ground state in this paper, but intend mainly to study the excitations of the assumed ground state and try to look at their experimental consequences. The concept of the pseudo Fermi surface (PFS) is useful only for low-energy excitations at low T. At low T we have relatively few spin solitons and the particle-antiparticle condition implies $S^\dagger_{k\sigma}=S_{-k,-\sigma}$ for $\mathbf{k}$ near the PFS. We can satisfy the constraint by overcompleteness of $S_{i\sigma}$, since one-half as many degrees of freedom satisfy the constraint by anticommunation relations. Hence the quasiparticles are no longer subject to the local constraints because they can be annihilated into RVB background or created from the background. A spinon cannot hop directly from site to site unless there are holes next to it. The situation resembles the formation of the heavy-fermion band in Kondo lattices in which the localized electrons with opposite spins on neighboring sites have antiferromagnetic (AFM) interactions and they can simultaneously hybridize with the conduction electron background[16] forming a coherent heavy fermion band. So we believe that our calculation of spinon excitation is not bad after all, though more refined work is clearly needed.

Next, we discuss AFM versus RVB. Clearly there is a competition between the AFM and the RVB in the insulator. While we are unable to specify in the present work which state will energetically more favorable, the AFM state has been observed[17] in "pure" (slightly oxygen-deficient) La_2CuO_4, therefore the AFM may or may not be more stable than RVB in the insulator. However, as we shall see, a small percentage of doping will destroy this AFM ordering. In the AFM state we have two sublattices "red" and "black" and there are no direct matrix elements connecting the sites on the same sublattice. The hopping term in Eq. (8) vanishes in the AFM because the motion of a hole will induce a string of defects in the ordered state. Thus a large amount of kinetic energy is lost. By balancing the gain in kinetic energy against the energy difference between RVB and AFM, one can show that less than 2% doping will kill the AFM ordering.[4]

The Hamiltonian (8) also describes the normal state. One important conclusion drawn from (8) is that the boson mass is of order of the band-electron mass.[4] The hopping term in (8) may be well approximated as

$$-t\rho_0 \sum_k e_k^\dagger e_k - t \sum_{k \neq k', q\sigma\tau} e^{i(\mathbf{k}+\mathbf{k}'-\mathbf{q})\cdot\tau} e_k^\dagger e_{k'} S^\dagger_{-k+q,\sigma} S_{-k'+q,\sigma} , \tag{12}$$

where ρ_0 is the fermion background amplitude. The first term shows that the bandwidth of the bosons is of order t, from which the high T_c results; and the second term describes the scattering processes between holes and spinons, which are of the same order as the bandwidth. In the normal state ($T > T_c$) only those spinons that lie within a range of order T from the PFS are available to scatter the boson holes, therefore we expect a large linear temperature-dependent resistivity[4] $\rho \sim T$. This $\rho \sim T$ behavior is one of the most striking properties of all high-T_c material. A strong experimental fact which may confirm the presence of bosons is the absence of an extrapolated residual resistivity for reasonably good samples. Detailed calculations of $\rho \sim T$ behavior will be published later.

Finally, we address the question of the flux quantization within our formalism: As was discussed by Anderson, Baskaran, Zou, Hsu[4] the Josephson frequency will still be $2\ \mathrm{eV}/\hbar$ in spite of boson charge e. Since the bosons are spinless, it is necessary to require a two-electron tunneling in order to conserve the spin angular momentum. We also argued in the previous work that holes can have only ODLRO and not true macroscopic coherence.[4] We can see this clearly from the following argument based on the present theory: Our Hamiltonian (8) has full U(1) symmetry; it is invariant, in particular, under the transformation P, $PC_iP^{-1}=-C_i$, $Pe_iP^{-1}=-e_i$, and $PS_iP^{-1}=-S_i$. For a fermion system the symmetry P cannot be spontaneously broken (Yang's theorem[18]), thus $\langle\Psi|e|\Psi\rangle=0$. Another way to see this is if $\langle\Psi|e|\Psi\rangle\neq 0$, we would have a ground-state wave function Ψ

$$|\Psi\rangle = \sum_N a_N |N,e\rangle , \tag{13}$$

where $|N,e\rangle$ is a state with N bosons (N=positive integers). However, we also have the local constraint (5), $e_i^\dagger e_i + \sum_\sigma C^\dagger_{i\sigma} C_{i\sigma} = 1$ (since $d_i^\dagger d_i = 0$). Thus the local fluctuations of the boson number are compensated by electron number fluctuations, leading to

$$|\Psi\rangle = \sum_N \tilde{a}_N |N,C\rangle , \tag{14}$$

where $|N,C\rangle$ is a state with N electrons. But an electron system is not allowed to have particle number fluctuations such as $|N\rangle \rightarrow |N \pm 1\rangle$, so we conclude that if a boson is created in one region of the sample, then a boson must be annihilated in another region of the sample. In other words, we have a true ODLRO. We therefore believe that the unit of flux quantization in a whole sample is $\hbar c/2e$ not $\hbar c/e$. The situation here differs from that of H_e^3 and H_e^4 mixture in which the numbers of H_e^3 and H_e^4 atoms can fluctuate independently.

In conclusion, we have derived in this paper the excitation spectrum for the spinon based on a boson-fermion field theory. It is formally shown that the hole due to doping behaves like a boson with bandwidth of order $\sim t$. In the normal state boson-spinon scattering leads to the observed temperature dependence of resistivity $\rho \sim T$; Bose condensation of holes results in the transition to the superconducting state with true ODLRO, in which the spinon excitations remain gapless giving rise to a linear temperature-dependent specific heat. While our theory contains essentially all relevant physics, many questions remain: for example, in the large doping limit the RVB state is destroyed and the holes tend to bind together with the spinons; we expect a crossover from Bose-condensed superconducting state to a BCS-like state with order parameter $\langle C_{k\uparrow}^{\dagger} C_{-k\downarrow}^{\dagger} \rangle$; the crossover behavior is not well understood at present. Nonetheless, we believe that the formalism developed here serves as a starting point for further investigations.

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