ABSENCE OF PAIRING MECHANISM DUE TO COUPLING OF OXYGEN HOLES TO LOCALIZED SPINS IN HIGH-T_c SUPERCONDUCTORS

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A canonical transformation method is used to derive an effective Hamiltonian which describes $Cu(3d)$ spins and $O(2p)$ holes within the CuO_2 plane in the charge transfer regime. It is found that spin-carrier interactions present in second order overrule the pairing mechanisms as proposed by Emery and Hirsch. The results suggest that mixed valence regime is more realistic for high T_c superconductors.

1. INTRODUCTION

In the search for an electronic mechanism of high T_c superconductivity, a few possibilities have been suggested so far. The most prominent of them is the resonating valence bond (RVB) mechanism of Anderson et al. [1] which assumes that the effective Hubbard Hamiltonian is at work and the doping creates defects in the spin lattice. On the other hand, photoemission data suggest that the holes are created rather in $O(2p)$ orbitals within CuO_2 planes of a high T_c superconductor [2]. Two mechanisms of superconductivity based on this picture have been suggested by Emery [3] and Hirsch [4]. They both should originate from effective carrier-carrier attraction which results from the hybridization V between $Cu(3d)$ and $O(2p)$ states in fourth order of perturbation theory. Here we investigate whether these mechanisms may indeed be effective in high T_c superconductors.

A realistic model Hamiltonian which describes the $Cu(3d_{x^2-y^2})$ and $O(2p_{x(y)})$ orbitals in a high T_c superconductor is of the form

$$H = \varepsilon_d \sum_{i\sigma} n_{di\sigma} + U \sum_i n_{di\uparrow} n_{di\downarrow} + \varepsilon_p \sum_{j\sigma} n_{j\sigma}$$
$$+ \sum_{jj'\sigma} t_{jj'} a_{j\sigma}^+ a_{j'\sigma} + \sum_{<ij>\sigma} V_{ij}(d_{i\sigma}^+ a_{j\sigma} + h.c.). \quad (1)$$

The operators $d_{i\sigma}^+$ and $a_{i\sigma}^+$ create holes in a $d_{x^2-y^2}$ orbital at Cu site and in $p_{x(y)}$ orbital at O site, respectively. Kinetic energy is due to the $p - p$ hopping $t_{jj'}$ and the $d - p$ hybridization V_{ij}. The energy scale is defined by two parameters: (i) the charge transfer energy $\Delta = \varepsilon_p - \varepsilon_d$ and (ii) the Coulomb integral U for $Cu(3d_{x^2-y^2})$ orbital. Depending on their values, one is in different physical regimes. For large U and Δ, the Hamiltonian (1) either reduces to an effective Hubbard model (if $\Delta \gg U$), or a charge transfer correlation gap is obtained (if $U \gg \Delta$). If either U or Δ become of the order of the relevant bandwidth, we enter metallic

regimes, being of either Mott-Hubbard (if $\Delta \gg U$) or mixed valence (if $U \gg \Delta$) type. The analysis of photoemission data [2] gives evidence that high T_c superconducting oxides are characterized in any case by $U > \Delta$. Thus, these systems are either in the charge transfer regime and exhibit a correlation gap, or they are itinerant mixed valence systems. Below we analyze in more detail the physics in the charge transfer regime.

2. CANONICAL PERTURBATION EXPANSION AND SPIN-CARRIER INTERACTION

The basic idea of a canonical perturbation expansion is to construct an effective Hamiltonian which replaces interconfigurational hopping processes by effective interactions. In the case of the Hubbard Hamiltonian in the strongly correlated regime it gives an effective RVB Hamiltonian [5]. Here we generalize this method to the Anderson lattice Hamiltonian (1).

In the charge transfer regime, one has localized spins at Cu atoms and doping creates holes in $O(2p)$ orbitals. The zeroth order Hamiltonian H_0 is just given by the term proportional to the $p - p$ hopping $t = t_{jj'}$. There are two transitions which change the configuration of a single Cu atom: (i) from a Cu site to one of the surrounding O atoms and (ii) from an O atom to Cu atom, characterized by the energy difference Δ and $U - \Delta$, respectively. An effective Hamiltonian may be derived by introducing projection operators which correspond to these configurations [6]. In second order one obtains

$$H_{eff}^{(2)} = \left(\frac{1}{\Delta} + \frac{1}{U - \Delta}\right) \sum_{<ijj'>} V_{ji} V_{ij'}$$

$$[S_i^z(a_{j\uparrow}^+ a_{j'\uparrow} - a_{j\downarrow}^+ a_{j'\downarrow}) + S_i^+ a_{j\downarrow}^+ a_{j'\uparrow} + S_i^- a_{j\uparrow}^+ a_{j'\downarrow}]$$

$$+ \frac{1}{2}\left(\frac{1}{\Delta} - \frac{1}{U - \Delta}\right) \sum_{<ijj'>\sigma} V_{ji} V_{ij'} a_{j\sigma}^+ a_{j'\sigma}, \quad (2)$$

where O sites j and j' are coupled by second order processes. $H_{eff}^{(2)}$ contains spin-carrier (Kondo-like) interaction and a new $p - p$ hopping term.

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The simplest way to study the consequences of the derived interaction on the electronic states is to use the mean-field approximation. One finds that the quasiparticle energies depend on the underlying magnetic order of the spin lattice. As an example, we have studied a one dimensional chain which consists of interchanging Cu and O atoms. In the absence of direct $p - p$ hopping (i.e. at $t = 0$) and taking $V = V_{ij}$, one finds that the bottom of the band is located at $-2V^2/(U - \Delta)$ and $-4V^2/(U - \Delta)$ in an antiferromagnet and in a ferromagnet, respectively. Thus, one carrier polarizes its surrounding ferromagnetically and leads to the formation of magnetic polaron. The same was observed with finite hopping t, as shown in Fig. 1.

In order to go beyond the mean-field approximation, we have solved exactly a small cluster of two Cu and two O atoms on a square, filled with two spins and one O hole. Under neglect of t the quantum fluctuations are quite important. Basing on this observation, Zhang and Rice [7] suggested that the internal degrees of freedom of the CuO_4 clusters can be neglected and that the system can be mapped on a RVB Hamiltonian. We think that this is not obvious since t is quite large in the real systems and this quantity tends to suppress the fluctuations. Further, one may have doubts concerning the validity of the one step renormalization procedure of Zhang and Rice [7].

3. DISCUSSION OF FOURTH ORDER PROCESSES

As pointed out by Emery [3], effective attractive interactions follow from the Hamiltonian (1) in fourth order. Their origin is analogous to that of spin-spin
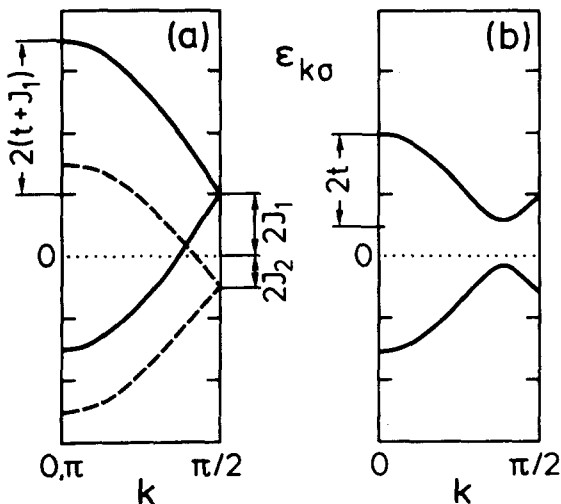
superexchange. For instance, in the one dimensional chain of Sec. 2 one finds the effective interaction of the form $-J(k, k')a_{k\uparrow}^+ a_{-k\downarrow}^+ a_{-k'\downarrow} a_{k'\uparrow}$ with $J(k, k') > 0$. Such processes could indeed lead to hole pairing if second order terms would give only band renormalization. In fact, the latter terms give rather complicated dynamics and by simple phase space arguments it can be seen that this results in repulsive interactions of order V^2/Δ and $V^2/(U - \Delta)$ and that Emery's interactions are small corrections to those.

In contrast to Emery, Hirsch [4] emphasizes spin-carrier interaction. His argument is that a moving carrier creates defects in an ordered spin lattice, while two carrier may hop together without disturbing the magnetic order. There are a couple of reasons that this pairing mechanism is also unlikely. First of all, he assumes that the carrier moves in an antiferromagnetic lattice only due to spin-flip processes, i.e. he considers only transitions of the $1/(U - \Delta)$ type. In fact, the $1/\Delta$ processes without spin-flip are of equal importance [8]. Furthermore, the mechanism of pairing based on fourth order processes is again much weaker than the spin-carrier processes which act in the opposite direction. This is also supported by our analysis of spin-spin and spin-carrier interactions in a finite cluster [6].

An important problem is to bridge the gap between the effective RVB Hamiltonian [1] and the two-band model. In view of the presented results, one may have strong doubts that this task is ever possible in the localized (charge transfer) regime. Further, we have shown that one finds also in the two-band model only *repulsive* interactions on small length scales as in the single band Hamiltonian [9]. The results presented above suggest that two-band model in the localized regime is rather unrealistic for high T_c superconductors. In fact, experimental data indicate that a well developed correlation gap is absent. Thus, we think that the charge degrees of freedom are important and one should search for a possibility of electronic mechanism of superconductivity in the mixed valence regime.

Fig. 1. Quasiparticle energies $\varepsilon_{k\sigma}$ (in arbitrary units) for a one dimensional $Cu - O$ chain in mean-field approximation for (a) ferromagnetically and (b) antiferromagnetically ordered Cu spins. Solid (dashed) lines in (a) represent majority (minority) spin in the folded Brillouin zone, $J_1 = V^2/\Delta$ and $J_2 = V^2/(U - \Delta)$.

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