PHYSICAL REVIEW B VOLUME 37, NUMBER 7 1 MARCH 1988

Effective Hamiltonian for the superconducting Cu oxides

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(Received 9 October 1987)

Although assuming that doping creates holes primarily on oxygen sites, we derive explicitly a single-band effective Hamiltonian for the high-T_c Cu-oxide superconductors. Cu-O hybridization strongly binds a hole on each square of O atoms to the central Cu^{2+} ion to form a local singlet. This moves through the lattice in a similar way as a hole in the single-band effective Hamiltonian of the strongly interacting Hubbard model.

Since the discovery of high-T_c superconducting oxides[1] there has been considerable controversy over the choice of the appropriate microscopic Hamiltonian. Although it is generally agreed now that Anderson's starting point,[2] namely, strong on-site Coulomb interactions among a partially filled band of Cu $3d$ levels, is correct, it is not so generally agreed that a single-band effective Hamiltonian, as Anderson proposed, is sufficient. Since various spectroscopic methods[3] have shown that the holes introduced in the superconductors reside primarily on O sites and do not form Cu^{3+} ions, there have been various works which have proposed that this introduces an essential difference.[4] However, Anderson[5] has recently restated that a single-band effective Hamiltonian is adequate. In this Rapid Communication we explicitly derive a single-band effective Hamiltonian starting from a two-band model using methods which follow from Anderson's original treatment of magnetic insulators.[6] The key point of our work is that the hybridization strongly binds a hole on each square of O atoms to the central Cu^{2+} ion to form a local singlet. This singlet then moves through the lattice of Cu^{2+} ions in a similar way as a hole (or doubly occupied site) in the single-band effective Hamiltonian. Further, two holes feel a strong repulsion against residing on the same square, so that we recover the single-band model.

We consider a Hamiltonian describing a single layer of square planar coordinated Cu and O atoms:

$$H=\sum_{i,\sigma}\epsilon_d d_{i\sigma}^{\dagger}d_{i\sigma}+\sum_{l,\sigma}\epsilon_p p_{l\sigma}^{\dagger}p_{l\sigma}+U\sum_i d_{i\uparrow}^{\dagger}d_{i\uparrow}d_{i\downarrow}^{\dagger}d_{i\downarrow}+H' \ . \tag{1}$$

In Eq. (1), the vacuum is defined as filled Cu d^{10} and O p^6 states. The operators $d_{i\sigma}^{\dagger}$ create Cu $(3d_{x^2-y^2})$ holes at site i, and $p_{l\sigma}^{\dagger}$ create O $(2p_x, 2p_y)$ holes at site l. U is the on-site Coulomb repulsion at a Cu site. We set the atomic energy of the Cu holes $\epsilon_d=0$ and consider the case $\epsilon_p>0$. The hybridization term is given by

$$H'=\sum_{i,\sigma}\sum_{l\in\{i\}}V_{il}d_{i\sigma}^{\dagger}p_{l\sigma}+\text{H.c.} \ , \tag{2}$$

where sum over l runs over the four O sites around a given Cu site i. The hybridization matrix V_{il} is assumed to be proportional to the wave-function overlap of Cu and O holes. Taking the phase of the wave functions into account we may write

$$V_{il}=(-1)^{M_{i,l}}t_0 \ , \tag{3}$$

where t_0 is the amplitude of the hybridization, and $M_{i,l}=2$ if $l=i-\frac{1}{2}\hat{x}$ or $i-\frac{1}{2}\hat{y}$, and $M_{il}=1$ if $l=i+\frac{1}{2}\hat{x}$ or $i+\frac{1}{2}\hat{y}$. We use the Cu-Cu distance as the length unit. In the following we shall consider the case $t_0\ll U$, ϵ_p, $U-\epsilon_p$.

Undoped La_2CuO_4 has 1 hole/Cu. At $t_0=0$, and with $(U,\epsilon_p)>0$ all the Cu sites are singly occupied, and all the O sites are empty in the hole representation. If t_0 is finite but small, the virtual hopping process involving the doubly occupied Cu-hole states produces a superexchange antiferromagnetic (AF) interaction[6] between neighboring Cu holes. The Hamiltonian (1) reduces[6] to a $S=\frac{1}{2}$ Heisenberg model on the square lattice of Cu sites:

$$H_S=J\sum_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j, \quad J=\frac{4t_0^4}{\epsilon_p^2 U}+\frac{4t_0^4}{2\epsilon_p^3} \ . \tag{4}$$

In Eq. (4), $\mathbf{S}_i$ are spin $-\frac{1}{2}$ operators of Cu holes, and $\langle ij\rangle$ denotes nearest-neighbor pairs. A flood of experimental data on undoped La_2CuO_4 has found strong[7] and, in particular, two-dimensional AF correlation[8] consistent with Eq. (4).

Upon doping, additional holes are introduced in the CuO_2 layers. In the atomic limit $t_0\to 0$, the additional holes sit either at Cu sites if $\epsilon_p>U$ or at O sites if $\epsilon_p<U$. In the first case, the hybridization may be included by eliminating O sites to give an effective Hamiltonian for motion on Cu sites alone. This is obviously a single-band Hubbard model. In the second case, it is not so apparent that one can eliminate the O sites, and the issue remains controversial at present.[4,5] Below we shall examine the second case and show that the physics of the CuO_2 layer is also described by the single-band effective Hamiltonian.

To explore this idea further, let us consider the energy of an extra hole in La_2CuO_4. To the zeroth order in t_0 this energy is ϵ_p for any O hole state. However, the system may gain energy from the Cu–O hybridization, which leads to a AF superexchange interaction between O and Cu holes. Therefore, our first task is to choose a proper set of the localized O-hole states.

Consider the combinations of the four oxygen hole states around a Cu ion. They can form either symmetric

or antisymmetric state with respect to the central Cu ion:

$$P_{i\sigma}^{(S,A)} = \frac{1}{2}\sum_{l\in\{i\}}(\pm 1)^{M_i,l}p_{l\sigma} , \tag{5}$$

where $-(+)$ corresponds to the $S(A)$ state, and the phase of the p- and d-state wave functions are defined in Fig. 1. Both S and A states may combine with the d-wave Cu hole to form either singlet- or triplet-spin states. To the second order in perturbation theory, the energies of the singlet and triplet states for S in Eq. (5) are $-8(t_1+t_2)$ and 0, respectively, where $t_1=t_0^2/\epsilon_p$ and $t_2=t_0^2/(U-\epsilon_p)$, while A has energy $-4t_1$. In the band-structure language, S forms bonding and antibonding states while A is nonbonding.[9] The large binding energy in the singlet S state is due to the phase coherence. This energy should be compared with the energy of an O hole sitting at a fixed site l. In the latter case, the binding energy of a singlet combination of a O hole and its neighboring Cu hole is only $-2(t_1+t_2)$, $\frac{1}{4}$ of the square S state. Because the effective hopping energy of the O hole is t_1 or t_2 (depending on the spin configuration), much smaller than the energy separation of these localized states, we may safely project out the antisymmetric O-hole states, and work in the subspace of the S states of Eq. (5). The energy of the two O holes residing on the same square, i.e., the configuration $P_{i\uparrow}^{(S)}P_{i\downarrow}^{(S)}d_{i\sigma}$ is $-(6t_1+4t_2)$ much higher than the energy of the two separated O holes. So the two holes feel a strong repulsion on the same square.

The localized states of (5) are, however, not orthogonal because the neighboring squares share a common O site. Thus,

$$\langle P_{i\sigma}^{(S)} \mid P_{j\sigma'}^{(S)\dagger}\rangle = \delta_{\sigma\sigma'}(\delta_{i,j} - \tfrac{1}{4}\delta_{\langle ij\rangle,0}) , \tag{6}$$

where $\delta_{\langle ij\rangle,0}=1$ if i,j are nearest neighbors. In analogy to the treatment of Anderson for the isolated spin quasiparticle,[6] we construct a set of Wannier functions (N_S = number of squares):

$$\phi_{i\sigma} = N_S^{-1/2}\sum_{\mathbf{k}}P_{\mathbf{k}\sigma}\exp(i\mathbf{k}\cdot\mathbf{R}_i) , \tag{7}$$

$$P_{\mathbf{k}\sigma} = N_S^{-1/2}\beta_{\mathbf{k}}\sum_i P_{i\sigma}^{(S)}\exp(-i\mathbf{k}\cdot\mathbf{R}_i) , \tag{8}$$

where $\beta_{\mathbf{k}}$ is a normalization factor

$$\beta_{\mathbf{k}} = [1-\tfrac{1}{2}(\cos k_x+\cos k_y)]^{-1/2} . \tag{9}$$

The functions $\phi_{i\sigma}$ are orthogonal, and are complete in the symmetric O-hole space. $\phi_{i\sigma}$ combines with the Cu hole at site i to form a spin singlet $(-)$ or triplet $(+)$:

$$\psi_i^{\pm} = (1/\sqrt{2})(\phi_{i\uparrow}d_{i\downarrow} \pm \phi_{i\downarrow}d_{i\uparrow}) , \tag{10}$$

with energies in second-order perturbation theory, of

$$E_{\pm} = \sum_{\{w\}}|\langle\psi_i^{\pm}\mid H'\mid w\rangle|^2/\Delta E_w , \tag{11}$$

where w runs over all possible intermediate states, and ΔE_w is the 0th-order energy difference between ψ and w, i.e., $\Delta E_w=\epsilon_p-U$ or $-\epsilon_p$ depending on whether or not the state w contains a doubly occupied Cu hole. From now on, for simplicity, we set $\epsilon_p=U-\epsilon_p$, i.e., $t_1=t_2=t$. The physics is expected to be essentially the same. We find that

$$E_{\pm} = -8(1\mp\lambda^2)t , \tag{12}$$

with

$$\lambda = N_s^{-1}\sum_{\mathbf{k}}\beta_{\mathbf{k}}^{-1}\simeq 0.96 .$$

The energies of Eq. (12) are very close to those of a single square. Since $E_+-E_-\simeq 15t\gg t$, we can ignore transitions between $\{\psi_i^-\}$ and $\{\psi_i^+\}$ and the system can be treated within the singlet $\{\psi_i^-\}$ subspace. We wish to point out that it is the phase coherence that produces the large energy separation of the different symmetry state from the spin-singlet state of the Cu hole and the symmetric O hole. The importance of the phase coherence does not seem to have been recognized in previous work except for Hirsch[4] who considered the S combination of O states in the case of a fixed spin direction on the Cu site, and a recent paper by Rice and Wang[10] on optical properties.

Having a set of proper Wannier wave functions with large binding energy, the next task is to study the motion of these singlet states due to the hopping process Eq. (2). Since the O holes are created in the background with singly occupied Cu holes, when ψ^- moves from site i to j, a Cu hole moves simultaneously from site j to i. This motion is represented by the process $\psi_i^- d_{j\sigma}\rightarrow\psi_j^- d_{i\sigma}$, with kinetic energy described by an effective hopping Hamiltonian

$$H_t = \sum_{i\neq j,\sigma}t_{ij}(\psi_j^- d_{i\sigma})^+\psi_i^- d_{j\sigma} . \tag{13}$$

In Eq. (13) the effective hopping matrix element t_{ij} is given within second-order perturbation theory by

$$t_{ij} = \sum_{\{w\}}\langle\psi_i^- d_{j\sigma}\mid H'\mid w\rangle\langle w\mid H'\mid(\psi_j^- d_{i\sigma})^+\rangle/\Delta E_w . \tag{14}$$

Using Eqs. (5), (7), (8), and (10), the right-hand side of Eq. (14) can be evaluated in the original O-site represen-

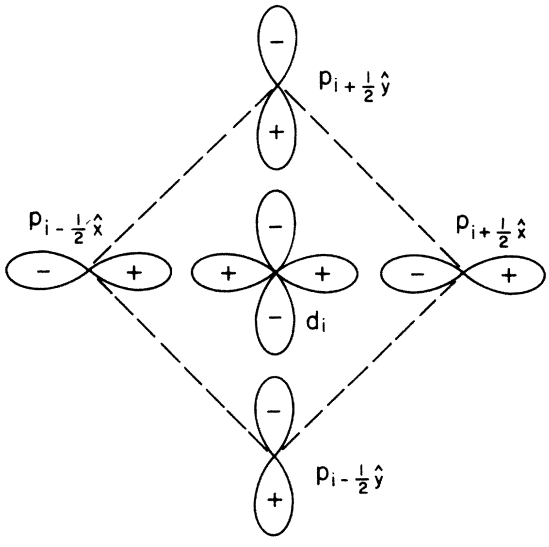

FIG. 1. Schematic diagram of the hybridization of the O hole ($2p^5$) and Cu hole ($3d^9$). The signs + and − represent the phase of the wave functions.

tation $p_{l\sigma}$. There are two different kinds of the two-step-hopping processes in t_{ij}. One involves spin exchange between the Cu and O holes, denoted by $t_{ij}^{(a)}$. The other is the effective O-hole hopping. After some algebra, we get $(i \neq j)$

$$t_{ij} = t_{ij}^{(a)} - \tfrac{1}{2} t \delta_{\langle ij \rangle, 0} \ , \tag{15}$$

$$t_{ij}^{(a)} = 8\lambda t \frac{1}{N_s} \sum_{\mathbf{k}} \beta_{\mathbf{k}}^{-1} \exp[i\mathbf{k} \cdot (\mathbf{i} - \mathbf{j})] \ . \tag{16}$$

From Eqs. (15) and (16), we obtain $t_{ij} \simeq -1.5t$ for the nearest neighbor i and j, and all other effective hopping matrix elements are very small. For instance, the next-nearest-neighbor term $t_{ij} \simeq -0.16t$, smaller by one order in magnitude.

From Eq. (13), when a Cu d hole is created at site i, the singlet state is destroyed at the same site. Therefore, the state ψ_i^- is equivalent to the empty state of the d hole at site i. The effective hopping Hamiltonian (13) is then reduced to the form, after dropping the empty-state operators,

$$H_t = \sum_{i \neq j, \sigma} t_{ij} (1 - n_{i,-\sigma}) d_{i\sigma}^{\dagger} d_{j\sigma} (1 - n_{j,-\sigma}) \ . \tag{17}$$

For the same reason, Eq. (4) holds for the doped system, which describes the AF interaction between the d holes. The singlet state has no magnetic interaction with all other d holes. Summarizing our results, we finally obtain an effective Hamiltonian H_{eff} given by

$$H_{\text{eff}} = H_t + H_s \ , \tag{18}$$

where H_t and H_s contain only Cu d holes, and are given by Eqs. (17) and (4), respectively. The effective hopping matrix elements are all negligibly small except the nearest-neighbor term. The Hamiltonian (18) is just the effective Hamiltonian of the single-band Hubbard model in the large-U limit.[5]

In conclusion, we have explicitly derived a single-band effective Hamiltonian for Cu-O based compounds starting from a two-band model in agreement with Anderson.[5]

We wish to thank Y. Takahashi, P. Prelovsek, and R. Joynt for useful discussions, and the Swiss National Fonds for financial support. We appreciate the help of P. A. Lee for a critical discussion of the expression for parameter J in Eq. (4). One of us (T.M.R.) would like to acknowledge the hospitality of the IBM Thomas J. Watson Research Center during the initial part of this work.

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