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HOW STRONGLY ARE ELECTRONS CORRELATED IN THE HIGH-T_c SUPERCONDUCTING MATERIALS?

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Electron correlations within CuO_2 layers, a common structural unit in La–Ba–Cu–O and Y–Ba–Cu–O systems, are studied by using a tight-binding model Hamiltonian. It is found that electron correlations are particularly strong within $Cu(3d_{x^2-y^2})$ orbitals. They do not only considerably suppress charge fluctuations, but also change the electron densities. As a consequence, the average number of holes at Cu sites increases and local moments are formed. Our results agree qualitatively with the experimentally observed magnetic moments in the antiferromagnetic phase and support the point of view that these systems are similar to valence fluctuating systems.

1. Introduction

Since the discovery of high-T_c superconducting oxides (HTSO) [1], there has been increasing evidence that electron correlations are sizeable in these materials [2–8]. Antiferromagnetic long-range order has been observed in La_2CuO_4 [2, 3]. The observed value of the magnetic moment of $0.5\mu_B$ per Cu atom cannot be reproduced by band structure calculation performed within local density approximation (LDA) [4]. This suggests that Coulomb interactions within $Cu(3d_{x^2-y^2})$ orbitals are large. This is also evident from the recent photoemission experiments [5–7] which show that the density of states at the Fermi level is small and that the d electron peak lies at lower energy than expected from band structure calculations. A nonmetallic behaviour of La_2CuO_4 [8] also suggests that Hubbard U is large.

It has been suggested by a number of model calculations that strong electron correlations may play an important role in the mechanism of superconductivity [9, 10]. So far, however, the correlations effects have not been quantified. Here we investigate how strong the correlation effects really are in these systems. We use a tight-binding Hamiltonian to model the band states formed by $Cu(3d_{x^2-y^2})$, $O(2p_x)$ and $O(2p_y)$ orbitals within a Cu–O plane which is a common structural unit in La–Ba–Cu–O and Y–Ba–Cu–O systems. Electron correlations are calculated by using a local ansatz (LA), as formulated for d electron systems by Oleś and Stollhoff [11].

2. Tight-binding model for electron correlations in Cu–O plane

As noticed by Mattheiss [12], the three bands formed by $Cu(3d_{x^2-y^2})$ and $O(2p_x, 2p_y)$ orbitals in the band structure of La_2CuO_4 may be well described by an effective tight-binding Hamiltonian. Similar quasi-two-dimensional bands were also reported in the band structure of $YBa_2Cu_3O_{7-x}$ [13]. Therefore, we use here

$$\begin{aligned} H = {} & \varepsilon_d^0 \sum_{m\sigma} n_{dm\sigma} + \varepsilon_p^0 \sum_{i\sigma} n_{pi\sigma} \\ & - V_0 \sum_{mi\sigma} (d_{m\sigma}^+ a_{i\sigma} + a_{i\sigma}^+ d_{m\sigma}) \\ & + U_d \sum_m n_{dm\uparrow} n_{dm\downarrow} \\ & + U_p \sum_i n_{pi\uparrow} n_{pi\downarrow} + U_{dp} \sum_{mi} n_{dm} n_{pi} , \end{aligned} \tag{1}$$

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where $d^+_{m\sigma}$ and $a^+_{i\sigma}$ create an electron in an atomic Cu($3d_{x^2-y^2}$) and O($2p_x$, $2p_y$) orbital, respectively. $n_{dm} = \Sigma_\sigma n_{dm\sigma} = \Sigma_\sigma d^+_{m\sigma} d_{m\sigma}$ stands for the density of $d_{x^2-y^2}$ electrons at site m. The site-diagonal one- and two-electron terms are (ε_d, U_d) and (ε_p, U_p) for Cu(3d) and O(2p) states, respectively. The only other nonvanishing terms are the hybridization V_0 and an interaction U_{dp} between electrons on neighboring (Cu and O) sites. The Coulomb elements U_d, U_p and U_{dp} are effective parameters. They are reduced by screening processes involving, e.g., s electrons from the respective atomic values which are 32, 22 and 8 eV, respectively.

The model Hamiltonian (1) can be made equivalent to Mattheiss's effective tight-binding model [12] when a Hartree–Fock (HF) approximation is made. It reduces then to

$$H_{HF} = \varepsilon_d \sum_{m\sigma} n_{dm\sigma} + \varepsilon_p \sum_{i\sigma} n_{pi\sigma} - V \sum_{mi\sigma} (d^+_{m\sigma} a_{i\sigma} + a^+_{i\sigma} d_{m\sigma}) . \quad (2)$$

The parameters of H_{HF} are related to those of (1) through

$$\varepsilon_d = \varepsilon_d^0 + \tfrac{1}{2} U_d n_d^{(0)} + 4 U_{dp} n_p^{(0)} ,$$

$$\varepsilon_p = \varepsilon_p^0 + \tfrac{1}{2} U_p n_p^{(0)} + 2 U_{dp} n_d^{(0)} ,$$

$$V = V_0 + U_{dp} \langle d^+_{m\sigma} a_{i\sigma} \rangle , \quad (3)$$

where $n_d^{(0)} = \Sigma_\sigma \langle n_{dm\sigma} \rangle$, $n_p^{(0)} = \Sigma_\sigma \langle n_{pi\sigma} \rangle$, and the averages $\langle \cdots \rangle$ are calculated with the HF ground state $|\phi_0\rangle$ which is easily found. Here we consider only nonmagnetic states and assume an electron density of one hole per unit cell. Thus, the HF bands are described in our model by two parameters: the distance between the HF levels $\Delta = \varepsilon_d - \varepsilon_p$ and the hybridization V.

Electron correlations are treated within the LA in which the correlated ground state $|\psi_0\rangle$ has the following form

$$|\psi_0\rangle = \exp[-\Sigma_n \eta_n O_n] |\phi_0\rangle . \quad (4)$$

The variational parameters η_n are found by the minimization of the ground state energy

$$E_0 = \langle \psi_0 | H | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle . \quad (5)$$

For the local operators O_n we use

$$O_m^{(1)} = n_{dm\uparrow} n_{dm\downarrow} ,$$

$$O_i^{(1)} = n_{pi\uparrow} n_{pi\downarrow} ,$$

$$O_{mi}^{(2)} = n_{dm} n_{pi} ,$$

$$O_m^{(0)} = n_{dm} . \quad (6)$$

The operators $O^{(1)}_{m(i)}$ and $O^{(2)}_{mi}$ reduce charge fluctuations within orbital m (or i) and between two orbitals m and i, respectively. They describe the most important two-particle excitations in the system. The operators $O^{(0)}_m$ describe one-particle excitations and reoptimize the d-electron density in the presence of correlations. This optimization takes place due to the coupling between the one- and two-particle excitations. In the calculation of the ground state energy E_0 we use a local cluster expansion of the correlation energy. The respective quantities $\langle O_n H \rangle$, $\langle O_n H O_{n'} \rangle$ and $\langle O_n O_{n'} \rangle$ are evaluated by making use of the so-called $\boldsymbol{R} = 0$ approximation in which only the leading local terms are preserved. The above approximations ensure that the correct atomic limit is obtained. For more details of the computation scheme the reader is referred to ref. [11].

After determining the variational parameters η_n, one is able to determine various one- and two-electron densities in the correlated ground state $|\psi_0\rangle$. The average $d_{x^2-y^2}$ electron number is

$$n_d = \langle \psi_0 | n_{dm} | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle . \quad (7)$$

Similarly, one finds for the mean-square deviation of the $d_{x^2-y^2}$ electron number

$$(\Delta n_d^2)_{corr} = \langle \psi_0 | (n_{dm} - n_d)^2 | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle . \quad (8)$$

This quantity is small if the electrons correlate strongly and tend to localize. Therefore, we quantify the strength of electron correlations by a parameter [14]

$$\Sigma_d = [(\Delta n_d^2)_{HF} - (\Delta n_d^2)_{corr}] / (\Delta n_d^2)_{HF} , \quad (9)$$

where $(\Delta n_d^2)_{HF}$ is calculated as in (8) but with $|\phi_0\rangle$ replacing $|\psi_0\rangle$. The value of Σ_d lies between zero and $\Sigma_{d,max} = (2 - n_d)/n_d$ and indicates strong correlation if the latter is approached. It describes also the formation of local moments in $Cu(3d_{x^2-y^2})$ orbitals, as being proportional to the enhancement of the moment

$$L_d^2 = [\langle \psi_0 | S_{dm}^2 | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle - \langle S_{dm}^2 \rangle] / \langle S_{dm}^2 \rangle = \Sigma_d , \quad (10)$$

where S_{dm} is the spin operator for electrons at site m. A similar parameter Σ_p may be also introduced for O(2p) electrons.

Knowing n_d and Σ_d, one is able to determine the probabilities p_i of the configurations $d^i_{x^2-y^2}(i = 0, 1, 2)$ in the ground state $|\psi_0\rangle$. They correspond to $3d^8$, $3d^9$ and $3d^{10}$ configurations of a Cu atom, respectively. One finds

$$p_1 = n_d(1 - \tfrac{1}{2}n_d)(1 + \Sigma_d) , \quad (11)$$

$$p_2 = \tfrac{1}{4}n_d[n_d - (2 - n_d)\Sigma_d] , \quad (12)$$

and $p_0 = 1 - p_1 - p_2$. Below we analyze the strength of electron correlations in HTSO by using these quantities.

3. Results and discussion

Electron correlations in HTSO depend on the electron–electron interaction, the hybridization V_0 and on the distance between the HF levels Δ. These parameters are fixed as follows for the Cu–O plane. Our previous studies [15] have demonstrated that atomic values of the Coulomb interaction have to be used in order to obtain the correct interatomic correlation energies for bonds formed by s and p electrons. The same applies in principle to d electrons. However, since our Hamiltonian (1) describes only Cu(3d) and O(2p) electrons (i.e. it does not describe all valence electrons), we have to reduce the values of the respective Coulomb integrals to the effective ones in order to simulate the effect of screening due to s electrons. Such values can be then used in our model to calculate electron correlations. Because of some uncertainties in the actual screening, we consider here two sets of parameters U_d, U_p and U_{dp} which should characterize the Cu(3d) and O(2p) states in HTSO: (A) $U_d = 25$, $U_p = 18$, $U_{dp} = 7$ eV and (B) $U_d = 15$, $U_p = 12$, $U_{dp} = 4$ eV. They correspond to a weak and strong screening, respectively. The intersite Coulomb interaction of 7 eV in (A) was thereby assumed to be almost unscreened, while a screened value of 4 eV is taken in (B). In our opinion, the sets (A) and (B) may be considered as an upper and lower limit for the parameters which are appropriate to evaluate electron correlations in the ground state. We stress that they have to be distinguished from the effective parameters which enter the interpretation of, e.g., the photoemission experiments [5–7] and contain relaxation effects.

The remaining parameters may be deduced as follows. By using the formulas of Harrison [16] one finds $V_0 = 1.3$ eV which we assume here. It gives $V = 2.35$ and 1.9 eV for the two parameter sets defined above. On the other hand, the band structure data obtained within LDA seem to suggest that $V_{LDA} \approx 1.8$ eV [12]. Thus, $V > V_{LDA}$ as expected, because the HF bands are broader than the ones from LDA. Finally, we determine the value of Δ in such a way that the charge distribution derived from core spectroscopy data [5] is correctly reproduced by our model. For that purpose, we reinterpret the experimental results of Fujimori et al. [5] by using a model of van der Laan et al. [17]. It allows to determine the average number of d electrons n_d by using an experimental information about the energetic distance ΔE_{ms} between the satellite and the main line, the relative intensities I_s/I_m, as well as one additional parameter related to the electronic structure. It has been shown that a mixing matrix element T which couples the $3d^9$ and $3d^{10}L$ configurations is very realistically approximated by LDA calculations [18]. Therefore, a value of $T = 2V_{LDA} = 3.6$ eV should be combined with the data of Fujimori et al. [5] for ΔE_{ms} and I_s/I_m. As a result, one obtains $n_d = 1.27$ which is then used to fix the value of Δ in our model. With the two used sets of parameters, we find $\Delta_A = 0.3$ and $\Delta_B = 1.2$ eV. It should be noticed that correlations lead to a considerable shift of electronic

charge from Cu(3d) to O(2p) orbitals. For the corresponding HF states one has $n_d^{(0)} = 1.49$ and 1.43, respectively.

The results of our calculations are summarized in table I. The correlations within Cu(3d) orbitals are found to be particularly strong. This is demonstrated by the ratio $\Sigma_d/\Sigma_{d,max}$ which exceeds 0.8 for both parameter sets. Since our calculation is based on a variational expansion, we estimate the values for $\Sigma_{d(p)}$ from below. It is found that the ground state $|\psi_0\rangle$ contains in principle only the configurations $3d^9$ and $3d^{10}$ of Cu. The respective probabilities are $p_1 = 0.70(0.68)$, $p_2 = 0.29(0.30)$ for the parameter sets (A) and (B), respectively. The configuration $3d^8$ is thus almost entirely suppressed and has the weight $p_0 = 0.01(0.02)$. In the HF state $|\psi_0\rangle$ corresponding to set (A) one has $p_1 = 0.38$, $p_2 = 0.56$ and $p_0 = 0.06$. The values of σ_d demonstrate that local moments built up at Cu(3d) orbitals, which is not the case for O(2p) orbitals. The local moments at $d_{x^2-y^2}$ orbitals would give a magnetic moment of $0.8\mu_B$ in the Néel state, assuming that $g = 2.3$ as in ref. [3]. When quantum fluctuations are taken into account, this agrees well with the experimental value of $0.5\mu_B$ [2, 3].

At the end we would like to note that a number of models for superconductivity in HTSO seem to require a complete suppression of charge fluctuations in La_2CuO_4 [9, 10]. We cannot support this point of view. Instead, we find that although the correlations are strong, charge fluctuations are still considerable because of $n_d = 1.27$. Charge transfer excitations seem to be therefore of importance, as suggested recently [19]. Therefore, the HTSO seem to resemble more fluctuating valence systems than, e.g., heavy-fermion systems. Realistic models for superconductivity should take that feature into account.

Table I
Electron correlation parameters for $Cu(3d_{x^2-y^2})$ and $O(2p_{x(y)})$ orbitals within the Cu–O plane for the parameter sets (A) and (B) described in the text.

Quantity	Set (A)	Set (B)
Σ_d	0.516	0.465
Σ_p	0.098	0.082
$\Sigma_d/\Sigma_{d,max}$	0.90	0.81
$\Sigma_p/\Sigma_{p,max}$	0.70	0.67

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