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The Effective Hamiltonian of the Singlet–Triplet Model for Copper Oxides

M. M. Korshunov* and S. G. Ovchinnikov**

* Krasnoyarsk State University, Krasnoyarsk, 660062 Russia
e-mail: kite ent co@xoommail.com

**Kirenskiĭ Institute of Physics, Siberian Division, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia
e-mail: sgo@post.krascience.rssi.ru

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Abstract—The effective Hamiltonian for a realistic multiband p–d model is developed. In the case of electron doping, the Hamiltonian coincides with that for the standard t–J model. For hole doping, the singlet–triplet t–J model takes place. © 2001 MAIK "Nauka/Interperiodica".

In recent years, more and more attention has been paid to investigations of the electronic structure and properties of systems with strong electron correlations (SEC), as an understanding of the processes occurring in these systems is the key in the explanation of the phenomenon of high-temperature superconductivity (HTSC). It is widely believed that the most interesting in this respect is the consideration of a CuO_2 layer, as such high values of the critical temperatures T_c of compounds containing this layer are most likely to be due to the presence of this layer and to the transformation of the electronic structure in it caused by doping. One of the problems appearing here is to construct an adequate model which will make it possible to describe the main HTSC properties completely enough.

The aim of this work is to find the effective Hamiltonian for the multiband p–d model [1] in the case of the presence of two-particle singlet and triplet states in the system in addition to the one-particle states. It is shown that this singlet–triplet model is asymmetric with respect to electron and hole doping.

The single-band Hubbard model [2] is one of the simplest models describing, at the same time, the main low-energy properties of the systems with SEC. However, the chemical composition of copper oxides can in no way be taken into account in this model. This drawback was partly eliminated in the three-band p–d model, which is a generalization of the Hubbard model for the CuO_2 layer [3]. A lot of spectral methods with high excitation energies, such as x-ray spectroscopy and x-ray electron spectroscopy, have been described in the framework of this model.

There are some essential points that still remain unclear. One point is the difference in behavior between the electron- and hole-doped systems. The issue is that a spin exciton, associated with singlet–triplet excitation of the two-hole term, is created in the hole-doped systems. This excitation is absent in the electron-doped systems [4]. Another fact which is ignored by the three-band model is the nonzero occupancy of d_{z^2} orbitals, which is evident from experiments on the polarization dependence of CuL_3 x-ray absorption spectra [5]. The correlation between the T_c and the occupancy of d_{z^2} orbitals was also detected there. Taking this into account, it can be stated that a more realistic model of the CuO_2 layer must involve $d_{x^2-y^2}$ and d_{z^2} orbitals of copper, as well as p_x and p_y orbitals of each oxygen ion. When considering the systems which involve the apical oxygen, it is necessary to account for the p_z orbital of oxygen. A similar model was proposed in [1], the Hamiltonian of which has the form

$$H_{p-d} = \sum_r H_d(r) + \sum_i H_p(i)$$
$$+ \sum_{\langle r, i \rangle} H_{pd}(r, i) + \sum_{\langle i, j \rangle} H_{pp}(i, j), \tag{1}$$

where

$$H_d(r) = \sum_{\lambda, \sigma} \left[\varepsilon_\lambda^d d_{\lambda r \sigma}^+ d_{\lambda r \sigma} + \frac{U_\lambda^d}{2} n_{\lambda r}^\sigma n_{\lambda r}^{\bar{\sigma}} \right.$$
$$\left. - \sum_{\lambda', \sigma'} \left(J_{\lambda\lambda'}^{dd} d_{\lambda r \sigma}^+ d_{\lambda r \sigma} d_{\lambda' r \sigma'}^+ d_{\lambda' r \sigma} - \sum_{r'} V_{\lambda\lambda'}^{dd} n_{\lambda r}^\sigma n_{\lambda' r'}^{\sigma'} \right) \right],$$

$$H_p(i) = \sum_{\alpha, \sigma} \left[\varepsilon_\alpha^p p_{\alpha i \sigma}^+ p_{\alpha i \sigma} + \frac{U_\alpha^p}{2} n_{\alpha i}^\sigma n_{\alpha i}^{\bar{\sigma}} \right.$$

$$\left. - \sum_{\alpha', \sigma'} \left(J_{\alpha\alpha'}^{pp} p_{\alpha i \sigma}^+ p_{\alpha i \sigma'} p_{\alpha' i \sigma'}^+ p_{\alpha' i \sigma} - \sum_{i'} V_{\alpha\alpha'}^{pp} n_{\alpha i}^\sigma n_{\alpha' i'}^{\sigma'} \right) \right],$$

$$H_{pd}(r, i) = \sum_{\alpha, \lambda, \sigma, \sigma'} ((t_{\lambda\alpha}^{pd} p_{\alpha i \sigma}^+ d_{\lambda r \sigma} + \text{H.c.}) + V_{\alpha\lambda}^{pd} n_{\alpha i}^\sigma n_{\lambda r}^{\sigma'}),$$

$$H_{pp}(i, j) = \sum_{\alpha, \beta, \sigma} (t_{\alpha\beta}^{pp} p_{\alpha i \sigma}^+ p_{\beta j \sigma} + \text{H.c.}).$$

Here, r and i are sites of copper and oxygen; $\lambda = \{ d_{x^2 - y^2}, d_{z^2} \}$ and $\alpha = \{p_x, p_y, p_z\}$ are orbital indices for a given site of copper and oxygen, respectively; ε^d and ε^p are the energies of $d_{x^2 - y^2}$ and d_z^2 holes on copper and of the p_x, p_y, p_z states of oxygen, measured from the level of the chemical potential μ; U^d and U^p are the on-site Coulomb interactions; t^{pd} is the transfer integral between the nearest neighbors of copper and oxygen; t^{pp} is the oxygen–oxygen transfer integral; V^{dd}, V^{pp}, and V^{pd} are the interatomic Coulomb interactions; and J^{dd} and J^{pp} are the exchange interaction integrals.

As can be seen, the Hamiltonian (1) accounts for all the main types of the relevant interactions in copper oxides. The simplest calculation in this model has been done for CuO_4 [4] and CuO_6 clusters [6] by the precise-diagonalization method. It has been shown that the energy difference between the two-particle singlet $^1A_{1g}$ and triplet $^3B_{1g}$ is intimately related to the involvement of the d_{z^2} orbitals. With this orbital neglected, it turns out that the triplet with energy ε_{2t} lies above the singlet with energy ε_{2S} by an amount of the order of 2 eV and, therefore, can be ignored in a low-energy description, which leads to the three-band model. However, as the energy of the d_{z^2} orbitals approaches the energy of the $d_{x^2 - y^2}$ orbitals, the singlet–triplet splitting decreases, and, at certain values of the parameters, the crossover of the singlet and triplet occurs. A similar result was obtained for the CuO_6 cluster by the self-consistent-field method [7] and also by the perturbation theory [8]. This gives reason for a thorough investigation of the processes associated with the presence of not only the two-particle singlet in the system but also the triplet.

For copper oxides and, particularly, a CuO_2 layer, the CuO_6 cluster is the unit cell they have in common. This cell was considered in [9], where by using the cluster

perturbation theory first stated in [10] the following Hamiltonian was obtained on the basis of Eq. (1):

$$H = \sum_f \left(\varepsilon_1 \sum_\sigma X_f^{\sigma\sigma} + \varepsilon_{2S} X_f^{SS} + \varepsilon_{2t} \sum_M X_f^{tMtM} \right)$$

$$+ \sum_{\langle f, g \rangle, \sigma} [t_{fg}^{00} X_f^{\sigma 0} X_g^{0\sigma} + 2\sigma t_{fg}^{0b} (X_f^{\sigma 0} X_g^{\bar{\sigma} S} + X_f^{S\bar{\sigma}} X_g^{0\sigma})$$

$$+ t_{fg}^{bb} X_f^{S\bar{\sigma}} X_g^{\bar{\sigma} S}] + \sum_{\langle f, g \rangle, \sigma} t_{fg}^{aa} (\sigma\sqrt{2} X_f^{t0\bar{\sigma}} - X_f^{t2\sigma\sigma}) \quad (2)$$

$$\times (\sigma\sqrt{2} X_g^{\bar{\sigma} t0} - X_g^{\sigma t2\sigma}) + \sum_{\langle f, g \rangle, \sigma} t_{fg}^{ab}$$

$$\times [(\sigma\sqrt{2} X_f^{t0\bar{\sigma}} - X_f^{t2\sigma\sigma})(-\nu X_g^{0\sigma} + 2\sigma\gamma_b X_g^{\bar{\sigma} S}) + \text{H.c.}].$$

Here, the energies ε_1, ε_{2S}, and ε_{2t} are related to the level of the chemical potential μ and superscripts 0, a, and b on the transfer integral t_{fg} indicate the appearance of the quasiparticle in the lower (0), the upper singlet (b), and in the upper triplet (a) Hubbard bands.

In this case, the local basis is constituted by the functions which correspond to the no-hole and one-hole terms, namely, $|0\rangle$ for $n_h = 0$ and $|\sigma\rangle \equiv \{|\uparrow\rangle, |\downarrow\rangle\}$ for $n_h = 1$, and also to the two-hole terms with the singlet state (S) $|2\rangle \equiv |\downarrow, \uparrow\rangle$ and the triplet state (t) $|tM\rangle \equiv \{|t0\rangle, |t2\sigma\rangle, |t2\bar{\sigma}\rangle\}$.

For this basis, the condition of its completeness is written as

$$X_i^{00} + \sum_\sigma X_i^{\sigma\sigma} + X_i^{SS} + \sum_M X_i^{tMtM} = 1. \quad (3)$$

Using the Hamiltonian (2) as the original one, we can obtain an effective Hamiltonian of the singlet–triplet model by excluding the interband (between the lower and upper Hubbard bands) transitions from it. For this purpose, we use the method proposed in [11].

First, we define projection operators P_1 and P_2

$$P_1 = \left(X_i^{00} + \sum_\sigma X_i^{\sigma\sigma} \right) \left(X_j^{00} + \sum_\sigma X_j^{\sigma\sigma} \right). \quad (4)$$

The operator P_2 can be determined from the condition for completeness of the basis of the projection operators

$$P_2 = 1 - P_1. \quad (5)$$

It is clear that P_1 and P_2 follow the rule for multiplication of projection operators

$$P_n P_m = \delta_{mn} P_n. \quad (6)$$

Left and right multiplications of the Hamiltonian (2) by

the operators P_n yield the following four relationships:

$$P_1 H P_1 = \varepsilon_1 \sum_{i,\sigma} X_i^{\sigma\sigma} + \sum_{\langle i,j\rangle,\sigma} t_{ij}^{00} X_i^{\sigma 0} X_j^{0\sigma}, \tag{7}$$

$$P_1 H P_2 = \sum_{\langle i,j\rangle,\sigma} [2\sigma t_{ij}^{0b} X_i^{\bar\sigma S} X_j^{\sigma 0} \\ - \nu t_{ij}^{ab}(\sigma\sqrt{2} X_i^{\bar\sigma t0} - X_i^{\sigma t2\sigma}) X_j^{\sigma 0}], \tag{8}$$

$$P_2 H P_1 = (P_1 H P_2)^+, \tag{9}$$

$$P_2 H P_2 = \sum_i \left(\varepsilon_{2S} X_i^{SS} + \varepsilon_{2t} \sum_M X_i^{tMtM} \right) + \sum_{\langle i,j\rangle,\sigma} t_{ij}^{bb} X_i^{S\bar\sigma} X_j^{\bar\sigma S} \\ + \sum_{\langle i,j\rangle,\sigma} t_{fg}^{aa}(\sigma\sqrt{2} X_i^{t0\bar\sigma} - X_i^{t2\sigma\sigma})(\sigma\sqrt{2} X_j^{\bar\sigma t0} - X_j^{\sigma t2\sigma}) \\ + \sum_{\langle i,j\rangle,\sigma} t_{ij}^{ab} 2\sigma\gamma_b[X_i^{S\bar\sigma}(\sigma\sqrt{2} X_j^{\bar\sigma t0} - X_j^{\sigma t2\sigma}) + \text{H.c.}]. \tag{10}$$

As can be seen from the above relationships, $P_1 H P_1$ and $P_2 H P_2$ describe the processes in the lower and upper Hubbard bands, respectively. The interband transitions are described by the terms $P_1 H P_2$ and $P_2 H P_1$.

The interband transitions may be further excluded by using an operator method of the perturbation theory. We present the Hamiltonian in the form

$$H_\eta = H' + \eta H'', \tag{11}$$

where $H' = P_1 H P_1 + P_2 H P_2$, $H'' = P_1 H P_2 + P_2 H P_1$, and η is a formal parameter (we ultimately put it equal to unity). The essence of this method is in the following: applying the canonical transformation

$$\tilde{H} = \exp(-i\eta F) H \exp(i\eta F), \tag{12}$$

we can choose the operator F such that the terms of the Hamiltonian $\tilde{H}$ that are linear in η, namely, the terms responsible for the interband transitions, will be equal to zero.

As can be readily shown, the requirement imposed brings about the following equation for the operator F:

$$H'' + i[H', F] = 0. \tag{13}$$

Then, $\tilde{H}$ is defined as

$$\tilde{H} = \tilde{H}(\eta = 1) = H' + \frac{1}{2} i[H'', F]. \tag{14}$$

Omitting the solutions of Eqs. (13) and (14) presented in [11], we obtain as a result

$$\tilde{H} = P_1 H P_1 + P_2 H P_2 = \frac{1}{E_{\text{ct}}}[P_1 H P_2, P_2 H P_1], \tag{15}$$

where $E_{\text{ct}} = \langle P_2 H P_2 \rangle - \langle P_1 H P_1 \rangle$ is the charge-transfer energy between the lower and upper Hubbard bands.

When studying the low-energy processes, one can consider the processes in the lower and upper Hubbard bands separately, because there is an appreciable energy gap (2–4 eV) between them.

For the systems with electron doping (*n*-type systems), the Fermi level ε_F is situated in the lower Hubbard band. In this case, the influence of the upper band can be ignored resulting in the common *t*–*J* model (see, e.g., [11, 12]). The corresponding Hamiltonian has the form

$$H_{t-J} = \sum_{i,\sigma} \varepsilon_1 X_i^{\sigma\sigma} + \sum_{\langle i,j\rangle,\sigma} t_{ij}^{00} X_i^{\sigma 0} X_j^{0\sigma} \\ + \sum_{\langle i,j\rangle,\sigma} J_{ij}\left(\mathbf{S_i S_j} - \frac{1}{4} n_i n_j\right), \tag{16}$$

with J_{ij} being the exchange integral

$$J_{ij} = 4\frac{(t_{ij}^{0b})^2}{E_{ct}}. \tag{17}$$

It has also been accounted for that

$$\mathbf{S_i S_j} - \frac{1}{4} n_i n_j = \frac{1}{2}\sum_\sigma (X_i^{\sigma\bar\sigma} X_j^{\bar\sigma\sigma} - X_i^{\sigma\sigma} X_j^{\bar\sigma\bar\sigma}).$$

For the systems with hole doping (*p*-type systems), the ε_F is situated in the upper band. In this case, we have a model which takes into account the transitions involving the two-particle singlet and triplet. We shall further refer to this model as the singlet–triplet model.

By applying the commutation relations for the Hubbard operators and omitting the three-center terms, we find the Hamiltonian of the singlet–triplet model in the form

$$\tilde{H} = H_0 + H_t + H_J, \tag{18}$$

where H_t is the kinetic part of the Hamiltonian and H_J is the term involving all processes associated with the exchange interaction.

In an explicit form, these terms are written as

$$H_0 = \sum_i \left(\varepsilon_1 \sum_\sigma X_i^{\sigma\sigma} + \varepsilon_{2S} X_i^{SS} + \varepsilon_{2t} \sum_M X_i^{tMtM} \right),$$

$$H_t = \sum_{\langle i,j\rangle,\sigma} t_{ij}^{bb} X_i^{S\bar\sigma} X_j^{\bar\sigma S} \\ + \sum_{\langle i,j\rangle,\sigma} t_{fg}^{aa}(\sigma\sqrt{2} X_i^{t0\bar\sigma} - X_i^{t2\sigma\sigma})(\sigma\sqrt{2} X_j^{\bar\sigma t0} - X_j^{\sigma t2\sigma}) \\ + \sum_{\langle i,j\rangle,\sigma} t_{ij}^{ab} 2\sigma\gamma_b[X_i^{S\bar\sigma}(\sigma\sqrt{2} X_j^{\bar\sigma t0} - X_j^{\sigma t2\sigma}) + \text{H.c.}],$$

$$H_J = \frac{1}{2} \sum_{\langle i, j \rangle, \sigma} (J_{ij} + \delta J_{ij}) \left(\mathbf{S_i S_j} - \frac{1}{4} n_i n_j \right)$$

$$- \frac{1}{2} \sum_{\langle i, j \rangle, \sigma} \delta J_{ij} X_i^{\sigma\sigma} X_j^{\sigma\sigma}.$$

Here, δJ_{ij} is a correction to the exchange integral J_{ij} in Eq. (17) due to the contribution from the triplet

$$\delta J_{ij} = 2v^2 \frac{(t_{ij}^{ab})^2}{E_{ct}}. \qquad (19)$$

In closing, it should be noted that the obtained effective Hamiltonian of the singlet–triplet model in Eq. (18) is the generalization of the t–J model to the case of the presence of the two-particle triplet in the system. However, the allowance for this triplet results in quite appreciable changes in the Hamiltonian, such as the renormalization of the exchange integral in Eq. (17) and also the appearance of the term of the "density–density" type, $X_i^{\sigma\sigma} X_j^{\sigma\sigma}$.

A more important feature of the singlet–triplet model is the asymmetry regarding the systems of the n and p type. This effect was experimentally observed. In particular, the fact that holes suppress antiferromagnetism more strongly than electrons do was observed in $La_{2-x}Sr_xCuO_4$ in contrast to $Nd_{2-x}Ge_xCuO_4$ [13]. The conditions for the existence of the superconducting phases are also different for the hole and electron superconductors. Restricting ourselves to only the electronic mechanisms of superconductivity, we also see that the spin-fluctuation mechanism, known for the t–J model (see review [14]), operates in n-type superconductors, while, in addition to the spin-fluctuation mechanism of the creation of the pairs, the pairing due to the singlet–triplet transitions can occur in p-type superconductors with the complicated band structure at the top of the valence band described by the Hamiltonian H_t. A similar pairing mechanism was proposed for multiband metals as early as 1969 [15].

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