Consistent low-energy reduction of the three-band model for copper oxides with O-O hopping to the effective $t$-$J$ model

V.I. Belinicher and A.L. Chernyshev
Institute of Semiconductor Physics, 630090, Novosibirsk, Russia

Abstract

A full three-band model for the CuO$_2$ plane with inclusion of all essential interactions - Cu-O and O-O hopping, repulsion at the copper and oxygen and between them - is considered. A general procedure of the low-energy reduction of the primary Hamiltonian to the Hamiltonian of the generalized $t$-$t'$-$J$ model is developed. An important role of the direct O-O hopping is discussed. Parameters of the effective low-energy model (the hopping integral, the band position and the superexchange constant $J$ are calculated. An analysis of the obtained data shows that the experimental value of $J$ fixes the charge transfer energy $\Delta = (\epsilon_p - \epsilon_d)$ in a narrow region of energies.

PACS Numbers: 74.70.Ya, 72.80.Ga
I. Introduction

Since the discovery of high-\(T_c\) superconductors, major theoretical efforts were devoted to finding the simplest model which would contain all details relevant to superconductivity. Anderson first suggested [1] that the two-dimensional single-band \(t\)-\(J\) model fits well for this role.

Now there is a general agreement that the CuO\(_2\) planes are common to all high-temperature superconductors. A realistic model for these planes was proposed from the first principles by Emery [2], Varma, Schmitt - Rink and Abrahams [3], and Gaididei and Loktev [4].

During last years there was a polemic about the equivalency of the \(t\)-\(J\) model and the Emery model [2] in the low-energy limit. The principal step was made in the work of Zhang and Rice [5], where they proposed the idea of the local singlet and idea of the Wannier representation for O-states. The problem of the low-energy reduction has been intensively investigated [6]–[9]. The singlet - triplet effective Hamiltonian was obtained in works of Yushankhai and Lovtsov [9] and Shen and Ting [7]. In our recent work [10] the quantitative comparison of the exact solution for the three-band model with the solution for the generalized \(t\)-\(J\) model was performed. However, the situation seems not completely clarified since (1) most of the above-named works were dealing with the unrealistic region of parameters \(t \ll U_d, \Delta\), where \(t\) is the Cu-O hopping integral, \(U_d\) is the Coulomb repulsion at the Cu site, \(\Delta = (\epsilon_p - \epsilon_d)\) is the charge-transfer energy, and (2) all above named works did not consistently take into account the direct O-O hopping.

In this work we develop a general approach to the consistent low-energy reduction of the three-band model. For this we following by Zhang and Rice [5] transform the primary Hamiltonian of the model from the terms of the usual oxygen states to the terms of symmetrical and antisymmetrical orthonormalized oxygen states on O - clusters. Further we introduce a new basis of the local states with the certain number of particles. Since only the systems with filling close to unity are of interest, we restrict ourselves to one- and two-hole local states. After that, the diagonalization of the local part of the Hamiltonian presents no special problems. It should be noted that we consider the direct O-O hopping. We have found that it does not change crucially the picture of the local states but play an important role for the effective hopping parameters. Next, we hold only the lowest two-hole local singlet state and consider its transitions over the background of the lowest one-hole (spin) states. Thus, we get the \(t\)-\(t'\)-\(J\) model. All other states we take into account perturbatively, by applying the canonical transformation. In this way we obtain the general form of the second-order corrections to the \(t\)-\(t'\)-\(J\) model and the expression for the superexchange constant \(J\).

At the beginning, we investigate three limiting cases of the complete three-band model. Because the Gilbert spaces in these limiting cases are restricted, mathematical treatment is simplified. Further, we investigate the general case of the three-band model in the region of parameters where the charge-transfer insulator [11] is the ground state of the undoped system. We conclude that the \(t\)-\(J\) model is valid for the doped charge-transfer insulator, i.e. corrections to it are small. Corrections to the hopping integrals at the
second and other neighbors are not relatively small, and thus the simple $t$-$t'$-$J$ model does not follow from the three-band model. Since the experimental value of the superexchange constant $J$ is known very well, we determine the value of the charge-transfer energy $\Delta$ through $J$. We have found that a narrow region of energies for $\Delta$ is suitable.

We also consider the repulsion at the O site $U_p$ and the repulsion between the Cu and O ions $V_{pd}$ terms in the framework of our approach. Their influence on the values of $\Delta$ and the first hopping integral $t_1$ is discussed. Thus, we perform a consistent and full consideration of the three-band model.

In Sec. II we represent the three-band Hamiltonian in terms of new oxygen states. In Sec. III we diagonalize the local Hamiltonian and rewrite it in terms of the Hubbard operators. In Sec. IV the low-energy reduction procedure is developed. In Sec. V three limiting cases of the three-band model are considered. In Sec. VI the quantitative analysis is performed. In Sec. VII the $U_p$ and $V_{pd}$ terms are considered. Section VIII presents our conclusions. In Appendices A and B the explicit form of the required matrix elements are presented. In Appendix C the three-hole states are considered. In Appendix D the shifts of the energies of local states connected with $U_p$ and $V_{pd}$ terms are presented.

II. Three-band Hamiltonian

The three-band model studied in this paper was originally proposed by Emery [2]. It is given by the following Hamiltonian

$$H = \epsilon_d \sum_{l,\alpha} n_{l\alpha}^d + \epsilon_p \sum_{m,\alpha} n_{m\alpha}^p + U_d \sum_l n_{l\uparrow}^d n_{l\downarrow}^d + \Delta H + H'$$

$$\Delta H = U_p \sum_m n_{m\uparrow}^p n_{m\downarrow}^p + V_{pd} \sum_{\langle lm \rangle, \alpha, \beta} n_{l\alpha}^d n_{m\beta}^p,$$

where $l$ and $m$ denote summation over the Cu- and O-sites respectively, $n_{l\alpha}^d = d_{l\alpha}^+ d_{l\alpha}$, $n_{m\alpha}^p = p_{m\alpha}^+ p_{m\alpha}$, $(d_{l\alpha}^+ (d_{l\alpha}))$ creates (annihilates) the Cu $(3d_{x^2-y^2})$ hole, $(p_{m\alpha}^+ (p_{m\alpha}))$ creates (annihilates) an O $(p_x, p_y)$ hole. $U_d$ and $U_p$ are intrasite Coulomb repulsion at the copper and oxygen respectively, $V_{pd}$ is the intersite repulsion between the nearest Cu and O holes.

The hybridization Hamiltonian $H'$ includes Cu-O and O-O hopping terms:

$$H' = t \sum_{\langle lm \rangle} (d_{l\alpha}^+ p_{m\alpha} + H.c.)$$

$$-t_p \sum_{\langle mm' \rangle} (p_{m\alpha}^+ p_{m'\alpha} + H.c.),$$

where $\langle l, m \rangle$ denotes the nearest-neighbor Cu and O sites and $\langle mm' \rangle$ denotes the nearest-neighbor O sites. The quantities $t$ and $t_p$ are positive. In Eq. (2.3) the sign convention corresponds to the change of the signs of the operators at the odd sites, which corresponds to the shift of quasimomentum space by $(\pi/a, \pi/a)$. As was proposed in [2], such transformation makes all O-O hopping constants of the same sign and negative.
The three-band model (2.1), (2.3) and its modifications have been studied recently by many authors \([6, 19, 20]\). One of the simplifications used in all analytical works was neglecting the repulsion at the oxygen and between the nearest neighbor copper and oxygen. To take into account the main effect, we will firstly consider the model (2.1) - (2.3) without \(U_p\) and \(V_{pd}\) terms and later include these terms as the perturbation.

The Fourier-transformed Hamiltonian (2.1) - (2.3) with the above named restriction is given by

\[
H_0 = \epsilon_d \sum_{k,\alpha} d_{k\alpha}^+ d_{k\alpha} + \epsilon_p \sum_{k,\alpha} (p_{k\alpha x}^+ p_{k\alpha x} + p_{k\alpha y}^+ p_{k\alpha y}) \\
+ U_d \sum_{k_1 + k_2 = k_3 + k_4} d_{k_1\uparrow}^+ d_{k_2\uparrow}^+ d_{k_3\downarrow} d_{k_4\downarrow},
\]

(2.4)

and

\[
H' = 2t \sum_{k\alpha} \{d_{k\alpha}^+ [p_{k\alpha x} \cos(k_x/2) + p_{k\alpha y} \cos(k_y/2)] + H.c.\} \\
- t_p \sum_{k\alpha} \{2[\cos((k_x + k_y)/2) + \cos((k_x - k_y)/2)] p_{k\alpha x}^+ p_{k\alpha y} + H.c.\} \\
\]

(2.5)

where

\[
d_k = \sum_l d_l \exp(-i \mathbf{r}_l), \quad p_{k\alpha(x/y)} = \sum_{m \in \{x\alpha(y)\}} p_m \exp(-i \mathbf{r}_m),
\]

(2.6)

\(m \in \{x(y)\}\) denotes the \(x(y)\) O-sublattices. Hereafter, the lattice constant is equal to unity. It is reasonable to introduce the symmetrical and antisymmetrical orthonormalized \(p\)-operators combination as

\[
q_k = (\cos(k_x/2)p_{k\alpha x} + \cos(k_y/2)p_{k\alpha y})(1 + \gamma_k)^{-1/2},
\]

\[
\tilde{q}_k = (-\cos(k_y/2)p_{k\alpha x} + \cos(k_x/2)p_{k\alpha y})(1 + \gamma_k)^{-1/2},
\]

where \(\gamma_k = (1/2)(\cos(k_x a) + \cos(k_y a))\).

Thus, the \(pd\)-hybridization term in \(H'\) includes only the symmetrical state \(\tilde{\{\}}\). In terms of these operators (2.7) we rewrite the Hamiltonian (2.4), (2.5) as:

\[
H_0 = \epsilon_d \sum_{k,\alpha} d_{k\alpha}^+ d_{k\alpha} + \epsilon_p \sum_{k,\alpha} (q_{k\alpha}^+ q_{k\alpha} + \tilde{q}_{k\alpha}^+ \tilde{q}_{k\alpha}) \\
+ U_d \sum_{k_1 + k_2 = k_3 + k_4} d_{k_1\uparrow}^+ d_{k_2\uparrow}^+ d_{k_3\downarrow} d_{k_4\downarrow},
\]

(2.7)

\[
H' = 2t \sum_{k\alpha} \lambda_k \{d_{k\alpha}^+ \tilde{q}_{k\alpha} + H.c.\} \\
- t_p \sum_{k\alpha} \{\mu_k [q_{k\alpha}^+ q_{k\alpha} - \tilde{q}_{k\alpha}^+ \tilde{q}_{k\alpha}] + \nu_k [q_{k\alpha}^+ \tilde{q}_{k\alpha} + \tilde{q}_{k\alpha}^+ q_{k\alpha}]\}
\]

were quantities \(\lambda_k, \mu_k, \nu_k\) are

\[
\lambda_k = (1 + \gamma_k)^{1/2},
\]

\[
\mu_k = 8 \cos^2(k_x/2) \cos^2(k_y/2)(1 + \gamma_k)^{-1/2},
\]

\[
\nu_k = 4 \cos(k_x/2) \cos(k_y/2) (\cos^2(k_x/2) - \cos^2(k_y/2))(1 + \gamma_k)^{-1/2}.
\]
It is not convenient to treat this Hamiltonian in the $k$-space due to the strong hole repulsion at the copper sites or large value of the parameter $U_d$ in this Hamiltonian. For taking into account this term precisely, we return to lattice representation for our Hamiltonian. After inverse Fourier transformation, Hamiltonian (2.7) has the form:

$$H_0 = \epsilon_d \sum_{l,\alpha} d_{l\alpha}^+ d_{l\alpha} + \epsilon_p \sum_{l,\alpha} (q_{l\alpha}^+ q_{l\alpha} + \tilde{q}_{l\alpha}^+ \tilde{q}_{l\alpha})$$

$$+ U_d \sum_l d_{l\uparrow}^+ d_{l\uparrow}^+ d_{l\downarrow} d_{l\downarrow}$$

$$H' = 2t \sum_{\langle l' \rangle \alpha} \lambda_{l'} (d_{l\alpha}^+ q_{l'\alpha} + H.c.)$$

$$- t_p \sum_{\langle l' \rangle \alpha} \left\{ \mu_{l'} (q_{l\alpha}^+ q_{l'\alpha} - \tilde{q}_{l\alpha}^+ \tilde{q}_{l'\alpha}) + \nu_{l'} (q_{l\alpha}^+ \tilde{q}_{l'\alpha} + H.c.) \right\} ,$$

where

$$(q_l, \tilde{q}_l) = \sum_k (q_{k}, \tilde{q}_k) \exp(-i \mathbf{k} \cdot \mathbf{r}_l) ,$$

$$\{\lambda, \mu, \nu\}_{l'} \equiv \{\lambda, \mu, \nu\} (1 - l')$$

$$= \sum_{\mathbf{k}} \{\lambda, \mu, \nu\}_k \exp(-i \mathbf{k} (1 - l')) ,$$

where summation over $\mathbf{k}$ is produced over the Brillouin zone, coefficients $\lambda, \mu, \nu$ decrease rapidly with increasing $|1 - l'|$. The values of $\lambda, \mu$ and $\nu$ for small $|1 - l'|$ are given in Table I. It is easy to get that $\nu_0 \equiv \nu_{00} = 0$ and $\nu_{n,n} \equiv \nu(n\mathbf{x} + n\mathbf{y}) = 0$.

One can divide Hamiltonian (2.8) into the local and hopping parts

$$H_{loc} = \epsilon_d \sum_{l,\alpha} d_{l\alpha}^+ d_{l\alpha} + (\epsilon_p - \mu_0 t_p) \sum_{l,\alpha} q_{l\alpha}^+ q_{l\alpha}$$

$$+ U_d \sum_l d_{l\uparrow}^+ d_{l\uparrow}^+ d_{l\downarrow} d_{l\downarrow}$$

$$+ 2t \lambda_0 \sum_{l',\alpha} (d_{l\alpha}^+ q_{l'\alpha} + H.c.) ,$$

$$H_{hop} = 2t \sum_{l',\alpha} \lambda_{l'} (d_{l\alpha}^+ q_{l'\alpha} + H.c.)$$

$$- t_p \sum_{l',\alpha} \left\{ \mu_{l'} (q_{l\alpha}^+ q_{l'\alpha} - \tilde{q}_{l\alpha}^+ \tilde{q}_{l'\alpha})$$

$$+ \nu_{l'} (q_{l\alpha}^+ \tilde{q}_{l'\alpha} + H.c.) \right\} ,$$

hereafter sum over $l, l'$ means that $l \neq l'$. Now, one can discuss the reasons for transformation from the Hamiltonian (2.7) - (2.3) to (2.10). The copper $d$-state hybridizes only with the symmetrical oxygen $q$-state [4]. Taking into account the direct O-O hopping
does not change this picture. After this separation out of the strongly interacting \(d\) and \(q\) local states, one can find the full energy spectrum of the one- or two-hole local states and solve the problem of the low-energy two-hole state at the background of the one-hole states (spins) consistently. The direct O-O hopping only slightly shifts the energies of the oxygen states with the opposite symmetry. But its contribution to the effective hopping parameters will be very important (see Sec. V). The transformed Hamiltonian (2.10) with the definitions (2.9) is equivalent to the Hamiltonian (2.1), (2.3) without the additional Coulomb terms \(U_p\) and \(V_{pd}\) and describes the three-band model exactly.

### III. Diagonalization of the local Hamiltonian

In this paper we study the model relating to high-temperature superconductors, which are the systems with a nearly half-filled band. Thus, we shall concentrate our attention on the case of one hole over unit filling in the framework of the three-band model. Namely, we determine the space of one- and two-hole local states of the CuO\(_2\) plane. A primary set of states in the one-hole sector is

\[
|d_\alpha\rangle \equiv d_\alpha^+|0\rangle, \quad |q_\alpha\rangle \equiv q_\alpha^+|0\rangle, \quad |\tilde{q}_\alpha\rangle \equiv \tilde{q}_\alpha^+|0\rangle.
\]

(3.1)

The two-hole singlet sector has a set of states

\[
|\psi\rangle \equiv d_1^+d_2^+|0\rangle, \quad |\varphi\rangle \equiv q_1^+q_2^+|0\rangle, \quad |\chi\rangle \equiv (1/\sqrt{2})(d_1^+q_2^+ - d_2^+q_1^+)|0\rangle, \\
|\tilde{\varphi}\rangle \equiv \tilde{q}_1^+\tilde{q}_2^+|0\rangle, \quad |\tilde{\chi}\rangle \equiv (1/\sqrt{2})(\tilde{q}_1^+\tilde{q}_2^+ - \tilde{q}_2^+\tilde{q}_1^+)|0\rangle, \\
|\tilde{\eta}\rangle \equiv (1/\sqrt{2})(q_1^+\tilde{q}_2^+ - q_2^+\tilde{q}_1^+)|0\rangle.
\]

(3.2)

The two-hole triplet sector is

\[
|\tau\rangle \equiv (d_1^+q_2^+, d_2^+q_1^+, (1/\sqrt{2})(d_1^+q_2^+ + d_2^+q_1^+))|0\rangle, \\
|\tilde{\tau}\rangle \equiv (d_1^+\tilde{q}_2^+, d_2^+\tilde{q}_1^+, (1/\sqrt{2})(d_1^+\tilde{q}_2^+ + d_2^+\tilde{q}_1^+))|0\rangle, \\
|\zeta\rangle \equiv (q_1^+\tilde{q}_2^+, q_2^+\tilde{q}_1^+, (1/\sqrt{2})(q_1^+\tilde{q}_2^+ + q_2^+\tilde{q}_1^+))|0\rangle,
\]

(3.3)

where \(|0\rangle\) is the vacuum state (state without holes on a cluster). Hence, we have three one-hole and nine two-hole states. As will be shown below, some of these states do not play any role in a low-energy model. In this part of the work we shall consider only the local part \(H_{loc}\) of the Hamiltonian (2.10). It is convenient to express this Hamiltonian in terms of the Hubbard operators rather than in terms of the usual Fermi operators. Such representation of the Hamiltonian (2.10) in the one- and two-hole sector in terms of states (3.1)-(3.3) has the form:

\[
H_{loc}^1 = \sum_{l,\alpha} (\epsilon_d X_{l}^{d\alpha d\alpha} + (\epsilon_p - \mu_0 t_p) X_{l}^{q\alpha q\alpha})
\]
\[ H_{\text{loc}}^2 = \sum_l \left\{ \left( (U_d + 2\epsilon_d) X_l^{\phi\psi} + 2(\epsilon_p - \mu_0 t_p) X_l^{\phi\varphi} \\
+ (\epsilon_d + \epsilon_p - \mu_0 t_p) X_l^{\chi\chi} + 2\sqrt{2}t\lambda_0 (X_l^{\chi\psi} + X_l^{\chi\varphi} + H.c.) \right) \right\} \] (3.4)

where the upper index 1,2 marks one- and two-hole sector of the local Hamiltonian, \( X_{i}^{ab} \) is the Hubbard operator at the site \( l \):

\[ X_{i}^{ab} \equiv |a \rangle \langle b |, \ a, b = \{ d\alpha, q\alpha, \bar{q}\alpha, \psi, \varphi, \chi, \bar{\chi}, \eta, \tau m, \zeta m, \bar{\tau} m \}, \] (3.5)

where index \( \alpha = \pm 1/2 \) in \( H^1 \) is a spin projection, \( m \equiv \pm 1, 0 \) in \( H^2 \) denotes triplet components.

The representation of \( H_{\text{loc}} \) (2.10) in terms of the Hubbard operators Eq. (3.4) allows us to solve simply the one-site problem. The diagonalization of \( H_{\text{loc}}^1, H_{\text{loc}}^2 \) is performed at each site independently. After the diagonalization, \( H_{\text{loc}}^1, H_{\text{loc}}^2 \) is given by

\[ H_{\text{loc}}^1 = \sum_{l,\alpha} \left\{ \epsilon_f X_l^{f\alpha} + \epsilon_g X_l^{g\alpha} \right\}, \] (3.6)

where

\[ \epsilon_{f,g} = -\Delta_1 \mp R_1, \ \Delta_1 = (\Delta + \mu_0 t_p)/2, \]
\[ R_1 = (\bar{\Delta}^2 + 4t^2\lambda_0^2)^{1/2} \]
\[ \bar{\Delta} = (\Delta - \mu_0 t_p)/2, \ \Delta = \epsilon_p - \epsilon_d, \] (3.7)

\(|f\alpha\rangle\) and \(|g\alpha\rangle\) are the lower and higher one-hole cluster states

\[ |f\alpha\rangle = U|d\alpha\rangle - V|q\alpha\rangle, \]
\[ |g\alpha\rangle = V|d\alpha\rangle + U|q\alpha\rangle, \] (3.8)

Our approach gives us the reasons to assume that in the low-energy limit at unit filling the background of the CuO\(_2\) plane consists of the lowest \(|f\alpha\rangle\)-states (3.8) at each cluster. Such state is a linear combination of the \(d\)-hole state and the orthonormalized symmetrical \(q\)-hole state at the nearest oxygens. Virtual transitions of holes in the \(|f\alpha\rangle\)-states (spins)
at the neighbor sites and back provide the antiferromagnetic type of interaction between these spins.

In $H^2_{loc}$ (3.4) there are different sectors, separated by the square brackets, which are diagonalized independently. The first sector includes the three singlets $dd$, $qq$, and $dq$. One can prove that diagonalization of this sector gives the lowest singlet with the eigenenergy well below than the eigenenergies of other states. Thus, the diagonalized two-hole part of the Hamiltonian (3.4) is

$$H^2_{loc} = \sum_l \left\{ E_- X^{cc}_l + \sum_y E_- X^{yy}_l \right\}, \quad (3.9)$$

where $E_-$ is the energy of the lowest singlet $|c\rangle$, $E_y$ are the energies of the upper states, $y$ is the set of the two-hole local states without $|c\rangle$. For the analytical expression of the eigenenergies and for the set of eigenstates see Sections V, VI. After diagonalization of the local part (3.4) of the full Hamiltonian (2.10), one can introduce the nondiagonal Hubbard operators and rewrite the hopping Hamiltonian (2.10) in terms of transitions between local eigenstates at different sites.

### IV. Low-energy reduction

#### A. Zero order

As was noted, we assume that at unit filling there are holes in the lowest $|f\alpha\rangle$-states (spins) at each cluster. We will demonstrate below that these spins interact antiferromagnetically. A general expression for the superexchange constant $J$ is derived in Section IV.D.

For the case of one hole over unit filling we take into account only the lowest singlet and its transitions from site to site. All upper two-hole states and transitions to them are projected out. Such procedure gives the $t$-$t'$-$J$ model with hopping at all neighbors in the explicit form:

$$H_{t-t'} = E_- \sum_l X^{cc}_l + \sum_{ll',\alpha} t_{ll'} X^{f\alpha,c}_l X^{c,f\alpha}_l, \quad (4.1)$$

where $|c\rangle$ is the lowest singlet, $|f\alpha\rangle$ is the lowest one-hole state, $t_{ll'}$ are the effective hopping parameters from $l$ to $l'$ site. In more usual terms this Hamiltonian (4.1) may be written as

$$H_{t-t'} = E_- \sum_l (1 - \hat{n}_l^c + \hat{d}_l^c) + \sum_{ll',\alpha} t_{ll'} \tilde{c}_{l\alpha}^+ \tilde{c}_{l'\alpha}$$

$$\tilde{c}_{l\alpha} = c_{l\alpha}(1 - \hat{n}_{l,-\alpha}) \quad \tilde{c}_{l\alpha}^+ = (\tilde{c}_{l\alpha})^+ \quad \hat{n}_l = (c_l^+ c_l) \quad \hat{d}_l^c \equiv c_l^+ c_{l\uparrow} c_{l\downarrow}.$$  \quad (4.2)

Here $c_{l\alpha}^+$, $c_{l\alpha}$ are the electron creation and annihilation operators.

In the next part of the work we will consider the second-order perturbation theory, which gives us a criterion of validity of the $t$-$t'$-$J$ model (4.1). Thus, if corrections to the energy and the hopping integrals for the lowest singlet from virtual transitions to the upper states are small, one can argue that this model (4.1) is valid.
B. Schrieffer-Wolff transformation

By diagonalization of the local part of the primary Hamiltonian (3.4) we obtain a set of local states. For the low-energy processes one can consider only the lowest states and include all others perturbatively. We use the Schrieffer-Wolff (S-W) transformation \[ H \Rightarrow \tilde{H} = \exp(-S)H \exp(S) \], \( S^+ = -S \).

for getting the second-order correction to the pure \( t-t'-J \) model. On this way we use the smallness of the \( \{\lambda, \mu, \nu\}_{ll'} \) constants for \( |l - l'| \neq 0 \). The first-order generator of transformation \( S \) and second-order correction are given by

\[ [H_0, S] = -H', \quad \delta H^2 = (1/2)[H', S], \]

For the case of one hole over unit filling \( H_0 \equiv H^2_{loc} + H^1_{loc} + H_{t-t'} \) (3.6, 3.9, 4.1) and \( H' \) includes all terms of \( H_{hop} \) (2.10) which are relevant to the transition between the lowest singlet and all of the upper two-holes states. In terms of the nondiagonal Hubbard operators the Hamiltonian \( H' \) is given by

\[ H_{hop} = \sum_{ll'} \sum_{\alpha\beta,y} \left[ F_{ll'}^{f,\beta,y} X_l^{\gamma,\alpha} X_{l'}^{\beta,c} + H.c. \right] + \sum_{ll'} \sum_{\alpha\beta,y} \left[ F_{ll'}^{g,\beta,y} X_l^{\gamma,\alpha} X_{l'}^{\beta,c} + H.c. \right], \]

where \( y \) is the set of the two-hole states, the prime in the sum (4.3) denotes absence of contribution of the lowest singlet state; \( f_\alpha \) and \( g_\beta \) are the one-holes states (3.8). The second term in Eq.(4.3) is essential only for correction to the energy \( E_{-} \) of the \( c \)-singlet. The first term in Eq.(4.3) provides corrections both to the energy and to the hopping integrals. \( F_{ll'}^{x,\beta,y} \) are the matrix elements of transitions between \( |0l\rangle \otimes |f_\alpha l\rangle \) and \( |x\beta l'\rangle \otimes |yl\rangle \) states \( (x = f, g) \). Their explicit form is presented in Appendix A.

In the case of unit filling, \( H_0 \) for Eq.(4.4) is

\[ H_0 \equiv H^2_{loc} + H^1_{loc} \]

and \( H' \) is

\[ H' = \sum_{ll'} \sum_{\alpha\beta,y} D_{ll'}^{y,\alpha\beta} \left[ X_l^{\gamma,\alpha} X_{l'}^{\beta,c} + H.c. \right], \]

where \( |0\rangle \) is the state without holes, \( D_{ll'}^{y,\alpha\beta} \) are the matrix elements of transition of two holes at different sites into the two-holes state \( y \) : \( |f_\alpha l\rangle \otimes |f_\beta l'\rangle \Rightarrow |0l\rangle \otimes |y\rangle \) (see Appendix B). Corresponding generators of the S-W transformation are given in Appendices A,B.

C. Second-order corrections

Here we derive a general form of corrections to the \( t-t'-J \) model. By applying the S-W transformation (4.3), (4.4) to the Hamiltonian \( H' \) (4.3) one can get correction to the
Hamiltonian of $c$-singlet \[10\]
\[
\delta H_E = -\sum_{ll'} M_{ll'} X_{ll'}^c \hat{N}_l 
\]
with
\[
M_{ll'} = \sum_y' \frac{|F_{ll'}^{f,y}|^2}{E_y - E_-} + \sum_y \frac{|F_{ll'}^{g,y}|^2}{E_y - E_- + \epsilon_g - \epsilon_f}, \tag{4.8}
\]
and $\hat{N}_l = X_{l\uparrow\uparrow} + X_{l\downarrow\downarrow}$.

Corrections to the hopping Hamiltonian have the form \[10\]
\[
\delta H_t = \sum_{lnl'} \sum_{y} T_{lnl'}^{y} \left\{ x_y X_{l}^{f_{\alpha,c}} X_{l'}^{c,f_{\alpha}} \hat{N}_n 
+ z_y X_{l}^{f_{\alpha,c}} X_{l'}^{c,f_{\beta}} (\sigma_{\alpha\beta} S_n) \right\}, \tag{4.9}
\]
where
\[
S_l = (1/2)\sigma_{\alpha\beta} X_{l}^{\alpha\beta},
\]
here $x_y = 1/2$ for singlets and $x_y = 3/4$ for triplets; $z_y = 1$ for singlets and $z_y = -1/2$ for triplets
\[
T_{lnl'}^{y} = \frac{F_{lnl'}^{y} F_{l'l}^{y}}{E_y - E_-}. \tag{4.10}
\]

In Eqs. (4.8), (4.10) we express parameters $M$ and $T$ through the matrix elements without spin structure. They are connected with the primary matrix element as
\[
F_{ll'}^{x_{\beta,y}} = \delta_{\alpha\beta} F_{ll'}^{x_{\alpha,y}}, \tag{4.11}
\]
for $y=$ singlet and
\[
F_{ll'}^{x_{\beta,y}} = (2\beta)[m_{\alpha\beta}] F_{ll'}^{x_{\alpha,y}}, \tag{4.12}
\]
for $y=$ triplet, where $[m_{\alpha\beta}] = \langle 1/2\alpha | 1/2\beta, 1m \rangle$ are the Clebsh-Gordon coefficients, $m = \pm 1, 0$ are spin-1 projections, $\alpha, \beta = \pm 1/2$ are the spin-$1/2$ projections, $\bar{\beta} = -\beta$. One can see that the corrections (4.7), (4.9) to the $t$-$t'$-$J$ Hamiltonian (4.4) depend on the filling ($\hat{N}$-term in $\delta H_E$ and $\delta H_t$) and magnetic order ($S$ term in $\delta H_t$ ). Such terms can not be expressed through the simple direct hopping.

In Section V we will analyze quantitatively the relative magnitudes of the second-order corrections. Validity of the $t$-$J$ model, as well as correctness of inclusion of hopping at the next neighbors are well checked by this analysis.
D. Superexchange interaction

In our approach the superexchange interaction arises in the second order of the perturbation theory over hopping of holes at neighboring cluster and back. The situation is similar to calculation of the superexchange interaction in the simple Hubbard model \(4t^2/U\). Of course, in the case of small \(t\) our result for the superexchange constant must be proportional to \(t^4\) as was calculated in earlier works \([6, 19]\) in the fourth order of perturbation theory. From Eq. (4.6) one can get

\[
\delta H^2 = H_J = \sum_{l,l'} (J_{ll'}S_lS_{l'} + Y_{ll'}\hat{N}_l\hat{N}_{l'}).
\]  

(4.13)

Such form (4.13) is more general than in the \(t-J\) model. Firstly, there are interactions between all pairs of spins. Due to the rapid decrease of the constant \(\{\lambda, \mu, \nu\}\), \((J_{ll'}^{(2,3)} \sim 10^{-2}J_{ll'})\), one can omit all next-nearest neighbor terms in Eq. (4.13) and get the Heisenberg term of the usual \(t-J\) Hamiltonian. Secondly, \(Y_{ll'} \neq -(1/4)J_{ll'}\) because the hole may virtually hop into triplet states and back, i.e.

\[
J_{ll'} = \sum_y x_y \frac{|D_{ll'}^y|^2}{\epsilon_y + \epsilon_0 - 2\epsilon_f},
\]

\[
Y_{ll'} = -\sum_y z_y \frac{|D_{ll'}^y|^2}{\epsilon_y + \epsilon_0 - 2\epsilon_f},
\]  

(4.14)

with \(x_y = 2\) and \(z_y = 1/2\) for \(y =\text{singlet}\), \(x_y = -1\) and \(z_y = +3/4\) for \(y =\text{triplet}\). \(D_{ll'}^y\) are connected with the matrix elements \(D_{ll',\alpha\beta}^y\) as follows

\[
D_{ll',\alpha\beta}^y = (2\alpha)\delta_{\alpha\beta}D_{ll'}^y
\]  

(4.15)

for \(y =\text{singlet}\),

\[
D_{ll',\alpha\beta}^y = [m\alpha\beta]D_{ll'}^y
\]  

(4.16)

for \(y =\text{triplet}\). One can check that in the limit \(t \rightarrow 0\) the reduced matrix element \(D_{ll'}^y\) is proportional to \(t\) and the superexchange constant \(J_{ll'}\) has contribution proportional to \(t^2\). But such contributions from the singlet and the triplet two-hole states are cancelled, and we get usual result which is proportional to \(t^4\).

V. Limiting cases

In the previous parts of the work we consistently reformulated the three-band model and passed from the terms of the primary Fermi operators of the hole at the copper and at the oxygens to the one- and two-holes states Hubbard operators on the cluster. For the problem of one hole over unit filling we established the general form of the low-energy the \(t-t'-J\) model (4.1), the general form of the corrections to it (4.7), (4.9), and the general form of the spin interaction at unit filling (4.13). Now we will consider three limiting cases, all with special constraints on the Gilbert space of the problem. Such constraints simplify the mathematical treatments and provide the possibility to get results in the analytical form.
A. The case of $\Delta \ll U_d$

This case was considered by Lovtsov and Yushankai [9]. We include into this problem direct O-O hopping and make consideration more complete.

Such limit ($U_d \Rightarrow \infty$) pushes up in energy the state with double occupation of the copper. Thus, one can ignore $|\psi\rangle$-singlet state (5.2). After such simplification diagonalization of the two-particle sector of the Hamiltonian (5.4) presents no problems. Corrections to the energy and to the first hopping parameter are 4.1% and 3.1%, respectively. Thus, the $t$-$J$ model is valid for this case. It seems that inclusion of hopping at the second and third neighbor to the $t$-$t'$-$J$ model is justified because corrections to them are small enough.

$$H_{loc}^2 = \sum_i \left\{ E_+ X_i^{cc} + E_- X_i^{bb} + 2\mu_0 t_p X_i^{\tilde{c}\tilde{b}} + \tilde{E}_- \left( X_i^{\tilde{c}\tilde{c}} + \sum_{m=\pm 1,0} X_i^{t1\omega t1m} \right) + \tilde{E}_+ \left( X_i^{\tilde{b}\tilde{b}} + \sum_{m=\pm 1,0} X_i^{t2\omega t2m} \right) - (\Delta + \mu_0 t_p) \sum_{m=\pm 1,0} X_i^{\tau\omega \tau m} \right\},$$

where $c, b$ are the lowest and highest singlets of $q-d$ sector, $\tilde{c}, \tilde{b}$ are the lowest and highest $\tilde{q}-d$ singlets, $t1, t2$ are the lowest and highest $\tilde{q}-d$ triplets, $\tau$ and $\tilde{\varphi}$ are determined in Eqs. (3.2), (3.3). All energies are counted from $\epsilon_p$ (hereafter $\epsilon_p = 0$). $E_\pm = -\Delta_2 \pm R$, $\Delta_2 = 1/2(\Delta + 3\mu_0 t_p)$, $R = (\Delta^2 + 8t^2 \lambda_0^2)^{1/2}$, $\tilde{E}_\pm = -\tilde{\Delta} \pm R_1$, $\tilde{\Delta} = (\Delta - \mu_0 t_p)/2$. New eigenstates are connected with the primary set of states (5.2), (5.3), as

$$|c\rangle = -a|\varphi\rangle + b|\chi\rangle, \quad |b\rangle = b|\varphi\rangle + a|\chi\rangle, \quad b = ((R + \tilde{\Delta})/2R)^{1/2}, \quad a = ((R - \tilde{\Delta})/2R)^{1/2},$$

$$|\tilde{c}\rangle = U|\tilde{\varphi}\rangle - V|\tilde{\eta}\rangle, \quad |\tilde{b}\rangle = V|\tilde{\varphi}\rangle + U|\tilde{\eta}\rangle,$$

$$|t1\rangle = U|\tilde{\tau}\rangle - V|\tilde{\zeta}\rangle, \quad |t2\rangle = V|\tilde{\tau}\rangle + U|\tilde{\zeta}\rangle,$$

$U$ and $V$ are determined in Eq. (5.8) The energies of the local states at $U_d \Rightarrow \infty$ (5.1) for values of the hopping parameters $t = 1.4$ eV, $t_p = 0.7$ eV and $\Delta = 3.66$ eV are given in Table II.

Next, we follow the scheme of Sec. III. Explicit forms of parameters of the $t$-$t'$-$J$ model are

$$E_c = E_- = -(\Delta + 3\mu_0 t_p)/2 - R,$$

$$t_{ll} = 2t_\lambda_{ll} V b(U + \sqrt{2}V a) + t_p \mu_{ll} (\sqrt{2}aV + U b)^2/2,$$

Hopping parameters for the first four neighbors at values of parameters mentioned above are given in Table II. One can see the important role of the direct O-O hopping. Its contribution to the full amplitude of hopping at the nearest neighbor $\approx 50\%$. Explicit form of the matrix elements $F^{\mu\nu}_{ll}$ and $D^\nu_{ll}$, one can get from Eqs. (5.2), (5.3), (4.4), and (2.10). They are given in Appendices A and B. Relative magnitudes of corrections to the hopping and energy are presented in Tab. II. Corrections to the energy and to the first hopping parameter are 4.1% and 3.1%, respectively. Thus, the $t$-$J$ model is valid for this case. It seems that inclusion of hopping at the second and third neighbor to the $t$-$t'$-$J$ model is justified because corrections to them are small enough.
B. The case \((U_d - \Delta) \ll U_d\)

This case was considered by the authors [10] without the O-O direct hopping. In Ref. [10] we assumed that at unit filling there is one hole (spin) per copper site. In terms of the present work we ignored the admixture of the \(|q\rangle\)-state to \(|d\rangle\)-state. We also assumed that there are no doubly occupied oxygen degrees of freedom. Both assumptions are valid over the parameter \(\sim t/U_d\). Such constraints lead to \(U = 1, V = 0\) (see Eq. (3.8)) and rather simple form of the diagonalized Hamiltonian \(H^2_{loc}\)

\[
H^2_{loc} = \sum_l \left\{ E_{-} X^c_{l} + E_{+} X^{bh}_{l} - (\delta + \mu_0 t_p) \sum_{m=\pm,0} X^\tau_{l \tau} \right\},
\]

where \(E_{\pm} = -\Delta_1 \pm R, \Delta_1 = 1/2(U_d - 3\Delta - \mu_0 t_p), R = (\tilde{\Delta}^2 + 8t^2\lambda_0^2)^{1/2}, \tilde{\Delta} = (U_d - \Delta + \mu_0 t_p)/2, \quad \text{and} \quad \)

\[
|c\rangle = -a|\psi\rangle + b|\chi\rangle, \quad |b\rangle = b|\psi\rangle + a|\chi\rangle,
\]

\[
b = ((R + \tilde{\Delta})/2R)^{1/2}, \quad a = ((R - \tilde{\Delta})/2R)^{1/2}.
\]

The explicit form of parameters of the \(t-t'-J\) model is following

\[
E_c = E_- = -(U_d - 3\Delta - \mu_0 t_p)/2 - R
\]

\[
t_{ll'} = 2t\lambda_{ll'}\sqrt{2ab} + t_p \mu_{ll'} b^2/2.
\]

The spectrum of the local energies and first four hopping integrals at \(U_d = 8\) eV and \(\Delta = 3.65\) eV are given in Table III. One can see that direct O-O hopping is less important than for the case A. It is evident, because part of the oxygen degrees of freedom is excluded from consideration. Expressions for the matrix elements of transitions to the excited states \(F^{xy}_{ll'}\), \(D^{y}_{ll'}\) one can easily get from (5.5), (5.5), and (2.10). They are given in Appendices A and B. A correction to the energy is not so small as for the case A. (see Table III). It is close to 13%, a correction to the first hopping is close to 40%. Thus, the \(t-J\) model may be valid. Inclusion of hopping at next neighbors requires consideration of corrections in the form (4.9) because they are not relatively small. They have a complicated structure. One can see a discrepancy in our approach. We assume that \((U_d - \Delta) \ll U_d\), i.e. \(\Delta \approx U_d\), while the realistic region for \(\Delta\) (for which \(J \approx 126\) meV) is close to 3.6 eV. Such situation is explained by the importance of the oxygen states for the three-band model.

C. The special case of the complete model

Here we consider the complete three-band model (3.4) without any constraints on the Gilbert space. Let us put \((U_d - 2\Delta) = -2\mu_0 t_p\). Such choice of the parameters leads to
accidental degeneracy of the energies of the $qq$ and $dd$ singlets. The $q-d$ singlets sector of the Hamiltonian (3.4) is written as

$$H_{loc}^2 = \sum_l \left\{ [E_{\psi}X_l^{\psi\psi} + E_{\varphi}X_l^{\varphi\varphi} - (\Delta + \mu_0 t_p)X_l^{XX} + 2\sqrt{2}t\lambda_0(X_l^{\chi\chi} + X_l^{\chi\varphi} + H.c.)] + \ldots \right\},$$  

(5.7)

where $E_{\psi} = E_{\varphi} = E_0 = U_d - 2\Delta = -2\mu_0 t_p$. Simplification in this case is as follows: linear combination of $|\psi\rangle$ and $|\varphi\rangle$ (3.2) singlets

$$|c2\rangle = (1/\sqrt{2})(|\psi\rangle - |\varphi\rangle)$$  

(5.8)

does not hybridize with the $qd$ singlet $|\chi\rangle$ (3.2). After diagonalization of $H_{loc}^2$ we have:

$$H_{loc}^2 = \sum_l \left\{ E_- X_l^{1c1} + E_0 X_l^{2c2} + E_+ X_l^{3c3} + 2\mu_0 t_p X_l^{2\tilde{\varphi}} + \tilde{E}_- \left( X_l^{\tilde{\varphi}\tilde{\varphi}} + \sum_{m=\pm 1,0} X_l^{1tm\;tm} \right) + \tilde{E}_+ \left( X_l^{\tilde{\varphi}\tilde{\varphi}} + \sum_{m=\pm 1,0} X_l^{2tm\;2tm} \right) - (\Delta + \mu_0 t_p) \sum_{m=\pm 1,0} X_l^{\tau m\;\tau m} \right\},$$  

(5.9)

where $E_{\pm} = -\Delta_2 \pm R$, $E_0 = -2\mu_0 t_p$, $\Delta_2 = U_d/4 + 2\mu_0 t_p$, $\tilde{E}_{\pm} = -\tilde{\Delta} \pm R_1$, $\tilde{\Delta} = U_d/4$, $R_1 = (\tilde{\Delta}^2 + 4t^2 \lambda_0^2)^{1/2}$, and $R = (\tilde{\Delta}^2 + 16t^2 \lambda_0^2)^{1/2}$. Thus, the real hybridization parameter is $16t\lambda_0/U_d$! It means that the perturbation approach over $t/U_d$ [3, 8] is unjustified for this system. The states $|\tilde{c}\rangle, |\tilde{b}\rangle, |t1\rangle$ and $|t2\rangle$ are defined in Eq. (5.2)

$$|c1\rangle = -a(|\varphi\rangle + |\psi\rangle)/\sqrt{2} + b|\chi\rangle, \quad |c3\rangle = b(|\varphi\rangle + |\psi\rangle)/\sqrt{2} + a|\chi\rangle,$$

$$b = ((R + \Delta)/2R)^{1/2}, \quad a = ((R - \Delta)/2R)^{1/2}.$$  

(5.10)

Since in this case $\Delta = U_d/2 + \mu_0 t_p$, one can determine an adequate value of $U_d$ at fixed $t$, $t_p$ and $J$. In the case being considered, the experimental value of $J$ is achieved at $U_d = 8.13$ eV and $\Delta = 5.1$ eV. Expressions for the parameters of the $t-t'$.J model are

$$E_{c1} \equiv E_- = -(U_d/4 + 2\mu_0 t_p) - R,$$
$$t_{2\mu} = 2t\lambda\mu (UV + ba) + t_p \mu t_{2\mu} (aV + bU)^2/2.$$  

(5.11)

The local energies and hopping parameters for this special case are given in Table IV.

The matrix $F_{\mu\nu}^{xy}$ and $D_{\mu\nu}^{xy}$ elements which are required for the derivation of corrections to the energy $E_-$, the hopping constants $t_{2\mu}$ and the superexchange constant $J$ are given in Appendices A, B. As in the first limiting case, O-O hopping plays an important role for the magnitude of effective hopping of the lowest $c1$-singlet. Correction to the energy is close to 4.6%, correction to the first hopping constant is close to 2.5%. Thus, the $t$-$J$ model is valid with the same precision. Absolute magnitude of the second hopping integral (hopping at the next-nearest neighbors) is small due to the partial compensation.
of the amplitudes of Cu-O and O-O hopping (see Eq. (5.11) and Table IV). As a result, correction to them is rather large ≈ 78%, and the \( t-t' -J \) model is not valid. Relative magnitude of terms with transition at the next neighbors (farther than nearest) is of the order of 10%. This is also the parameter of accuracy of the \( t-J \) model as the low-energy limit of the three-band model.

VI. The general case

In this part of the work we consider reduction of the three-band model to the effective \( t-t' -J \) model in the general region of parameters when the charge transfer insulator is the ground state of undoped system. The general case differs from the special case considered above only by the absence of degeneracy of the local \(|dd\rangle\) and \(|qq\rangle\) two-hole states. The local Hamiltonian is defined by Eq.(5.7) with \( E_{\psi} = U_d - 2\Delta \) and \( E_{\varphi} = -2\mu t_p \). We stress that \( E_{\psi} \neq E_{\varphi} \) in this case. The expression for the diagonalized Hamiltonian \( H_{loc}^2 \) coincides completely with Eq.(5.9) but the eigenstates \(|ci\rangle\) have the more general form

\[
|ci\rangle = U_i|\psi\rangle + V_i|\varphi\rangle + W_i|\chi\rangle, \tag{6.1}
\]

where coefficients \( U_i, V_i, W_i \) are determined from the solution of a system of three linear equations. The energies \( E_{-}, E_{0}, E_{+} \) are roots of the corresponding cubic equation. Effective hopping parameters are

\[
t_{ll'} = 2t\lambda_{ll'}(\sqrt{2}U_1V_1V - W_1U) + t\mu_{ll'}(\sqrt{2}V_1V - W_1U)^2/2, \tag{6.2}
\]

Other matrix elements which are required for the derivation of the constants \( F_{x,y}^{ll'} \) (4.5), (4.12) and \( D_{y}^{ll'} \) (4.6), (4.15), (4.16) are presented in Appendices A,B.

Parameters of the effective \( t-t' -J \) model are calculated at the following values of parameters of the three-band model: \( t = 1.4 \) eV, \( t_p = 0.7 \) eV, \( U_d = 8 \) eV and \( \Delta = 5.1 \) eV according to different band calculations \[13, 14, 21\] and the detailed analysis of experiment \[22\].

In Table V the magnitudes of the hopping parameters at the first four neighbors are given. The important role of O-O hopping is shown: for the first hopping parameter it is close to 30%, for others is close to 50%. Relative magnitudes of corrections to the energy and first hopping are 3% and 2.5% respectively. Thus, the \( t-J \) model is valid with the same precision. Due to compensation of contribution of the \( p-d \) and \( p-p \) hopping to the effective hopping integral at the second neighbors (they have the opposite sign), the correction to it is not small (82%). Thus, the model with transitions at the neighbors farther than nearest must include the terms of the form (4.9), which depend on filling and the spin state of neighbor sites.

Applicability of a perturbation scheme in the realistic region of parameters of the three-band model is provided by smallness of the ratio of the effective hopping parameters between different local states to the energy gap between them. This ratio is of the order of 10% which gives the accuracy of the \( t-J \) model for the CuO\(_2\) plane. Relative magnitude of the \( t' \)-terms (hopping at the next neighbors) in the \( t-t' -J \) model is also of the order of
10%. In Table V the fundamental ratio \( t_1/J = 4.2 \) for \( U_d = 8 \) eV is presented. It only weakly depends on \( U_d \) and \( \Delta \). This value is slightly larger than the generally accepted \( t/J \approx 3 \).

Different parameters of the three-band model are known with different accuracy. Notice that the value of the superexchange constant for La\(_2\)CuO\(_4\) is known with high accuracy which imposes restrictions on the values of the parameters of the three-band model. Therefore one can try to determine the value of the least known parameter \( \Delta \) as a function of other parameters of the model. At fixed values of \( t \) and \( t_p \) presented above and \( J = 126 \) meV we get \( \Delta \) as a function of \( U_d \) in the physically reasonable region: \( \Delta \leq U_d \leq 12 \) eV in Fig. 1. One can see that the reasonable region of \( \Delta \) lies between 4.75 eV and 5.75 eV which is in complete agreement with the band calculations of Sushkov and Flambaum [15] but larger than the generally accepted value \( \Delta = 2.75 - 3.75 \) eV [22].

VII. Inclusion of \( V_{pd} \) and \( U_p \) terms

Here we consider the role of the intrasite repulsion at the oxygens \( U_p \) and the intersite repulsion \( V_{pd} \). We suppose that the main effect is taken into account (strong hybridization \( d- \) and \( q- \) states), so that one can take the above named terms as the perturbation. Therefore, we do not consider the contribution of these terms to the second-order corrections to the energies and the hopping integrals of the form (1.7), (1.9). Our aim is to get the renormalization of the first hopping integral and the charge-transfer energy due to the Hamiltonian \( \Delta H \) (2.2). Using the representation (2.7) for \( q_l \) and \( \bar{q}_l \) operators one can easily get

\[
\Delta H_{pd} = V_{pd} \sum_{l,l_1,l_2,\alpha,\beta} n_{l\alpha}^d \left\{ f_{qq}(l_1 - 1, l_2 - 1) q_{l_1,\beta}^+ q_{l_2,\beta} \right. \\
+ f_{qq}(l_1 - 1, l_2 - 1) \left[ \bar{q}_{l_1,\beta}^+ q_{l_2,\beta} + H.c. \right] \\
\left. + f_{qq}(l_1 - 1, l_2 - 1) \bar{q}_{l_1,\beta}^+ \bar{q}_{l_2,\beta} \right\},
\]

(7.1)

Since we are interested in the renormalization of the lowest singlet parameters, we can omit all terms with antisymmetrical oxygen operators \( \bar{q} \). Similar procedure for \( U_p \)-term leads to

\[
\Delta H = V_{pd} \sum_{l,l_1,l_2,\alpha,\beta} f_{l,l_1,l_2} n_{l\alpha}^d q_{l_1,\beta}^+ q_{l_2,\beta} \\
+ U_p \sum_{l,l_1,l_2,l_3} h_{l,l_1,l_2,l_3} (q_{l_1,\beta}^+ q_{l_1,\beta}) (q_{l_2,\gamma}^+ q_{l_3,\gamma})
\]

(7.2)

where \( f_{l,l_1,l_2} = f_{qq}(l_1 - 1, l_2 - 1), h_{l,l_1,l_2,l_3} = h(l_1 - 1, l_2 - 1, l_3 - 1), \) and

\[
f_{qq}(l_1 - 1, l_2 - 1) = \sum_{k,k'} f_{k,k'} \exp(i\mathbf{k}(l_1 - 1) - ik'(l_2 - 1))
\]

\[
h(l_1 - 1, l_2 - 1, l_3 - 1) = \sum_{k,k',k''} h_{k,k',k''} \exp(i\mathbf{k}(l_1 - 1) - ik'(l_2 - 1) + ik''(l_3 - 1))
\]

(7.3)
Thus, we have the four-fermion terms with the complicated relation between many states at different sites. All later arguments are based on a very rapid decrease of the constant \( f_{l^l} \) and \( h_{l^1,l^2,l^3} \) with \(|l_l| \leq 1\). Our calculation gives \( f_0 \equiv f(0,0) = 0.9180 \), \( f_1 = f(1,0) = f(0,1) = 0.1343 \), and \( S_f \equiv \sum_{l^1 \neq l' \neq l} f_{l^1,l^2,l^3} = 0.0092; h_0 = h(0,0,0) = 0.29 \) and \( h_1 = h(1,0,0) = h(0,1,0) = h(0,0,1) = 0.0096 \). Therefore, one can turn from (7.2) to the effective Hamiltonian

\[
\Delta H_{\text{loc}}^{\text{eff}} = V_{pd} \sum_{l'\alpha,\beta} f_{l^l} n^d_{l\alpha} n^\beta_{l'\beta} + U_p \sum_{l^l} h_{l^l} n^q_{l^l} n^q_{l^l},
\]

\[
\Delta H_{\text{hop}}^{\text{eff}} = V_{pd} f_1 \sum_{(l^l),\alpha,\beta} n^d_{l\alpha} \{ q^+_{l^l,\alpha} q^q_{l^l,\beta} + H.c. \} + U_p h_1 \sum_{l^l} \{ n^q_{l^l} \{ q^+_{l^l} q^q_{l^l} + H.c. \} \}
\]

where in \( \Delta H_{\text{loc}}^{\text{eff}} \) \( f_{l^l} \equiv f(Y - 1, Y - 1) \).

Let us consider the system at unit filling and calculate the shift of the energies of the local states due to \( \Delta H_{\text{loc}}^{\text{eff}} \). At unit filling there is the state \( |f\alpha\rangle = U |\alpha\rangle - V |q\alpha\rangle \) at each site. Hence, the shift of the energy of \( d \) - hole at the site \( l \) will be

\[
\Delta \epsilon_d = V_{pd} V^2 \sum_{l \neq l'} f_{l^l} = V_{pd} V^2 (2 - f_0)
\]

for the \( q_l \) state

\[
\Delta \epsilon_q = V_{pd} U^2 (2 - f_0) + U_p V^2 (1/2 - h_0)
\]

numbers 2 and 1/2 are the sums over all \( l' \) for \( f_{l^l} \) and \( h_{l^l} \) respectively. The coefficients \( U \) and \( V \) are defined in Eq.(3.8) with

\[
R_1 = (\bar{\Delta}^2 + 4t^2 \lambda^2_{\alpha 0})^{1/2}, \quad \bar{\Delta} = (\epsilon_q - \epsilon_d)/2,
\]

Thus, Eqs.(7.3), (7.4), (7.5), and (7.8) are the system of equations, which can be solved numerically. After solving we have new values \( \bar{\bar{U}} \) and \( \bar{\bar{V}} \), and consider one hole over unit filling. It is easy to get the shift of the local energies of the additional hole. For some details see Appendix D.

The matrix elements of \( \Delta H_{\text{hop}}^{\text{eff}} \) (7.4) produce the addition to the first hopping integral.

\[
\Delta t_1 = -(f_1 V_{pd} \bar{\bar{U}}) W_1 + \sqrt{2} h_1 U_{j_1} \bar{\bar{V}} V_1) (W_1 \bar{\bar{U}} - \sqrt{2} V_1 \bar{\bar{V}})
\]

The expressions for the matrix elements \( \Delta D_{l^l}^{ll} \) which are essential for the constant \( J \) (4.14), are given in Appendix B.
Different band calculations \([13, 14, 21]\) give the consistent magnitudes for \(V_{pd}\) and \(U_p\):
\[
V_{pd} = 1.2 \text{ eV}, \quad U_p = 4 \text{ eV}
\]
The calculations present no special problems. Fig. 2 and Table VI present our results. The lower curve in Fig. 2 demonstrates that for reasonable region of \(U_d\) \((5 - 11 \text{ eV})\), at fixed \(V_{pd}, U_p, t\) and \(t_p\), \(\Delta\) varies in the region \(2.5 - 3.5 \text{ eV}\), which coincides very well with the band calculations \([21]\) and analysis of experiments \([22]\).

Different contributions to the first hopping parameter \(t_1\) are presented in Table VI for \(U_d = 8.0 \text{ eV}\) and \(\Delta = 3.0 \text{ eV}\). Inclusion of \(\Delta H\) tends to decrease \(t_1\). The ratio \(t_1/J = 3.38\), which is close to the results of the other works \([14, 18]\).

**VIII. Stability of the system**

There are few conditions which determine stability of the system under study. One can take an analogy from the classical Hubbard system: the energy of two electrons at different sites \(\{l, 1_l\}\) is lower than the energy of two electrons at the same site and an empty site \(\{2_l, 0_l\}\) by the energy of the Hubbard intrasite repulsion \(U_H\). Thus, the ground state of the system at unit filling is the state with one electron per site which is a dielectric if \(U_H\) is sufficiently larger than band width \(wzt\), where \(z\) is the number of neighbors and \(w\) is the constant of the order of unity.

Since we have reduced our problem to the system of the Hubbard type but with many states at each site, we can formulate the stability conditions in terms of energies of these states. The conditions will be
\[
E^2 + E^0 - 2E^1 > 0 \tag{8.1}
\]
and
\[
E^3 + E^1 - 2E^2 > 0 \tag{8.2}
\]
where the indexes \(n = 1, 2, 3\) denote the states with \(n\) holes at site. From this one can easily get the charge-transfer gap (an analogue of \(U_H\)) as the difference between \((E^2 + E^0)\) and \(2E^1\), where \(E^2\) is the energy of the lowest singlet and \(E^1\) is the energy of the lowest one-hole state
\[
\Delta E(2, 0 - 1, 1) = E_- + E^0 - 2E_f = 3.2 \text{ eV} > 0 \tag{8.3}
\]
for the above mentioned parameters.

An interesting quantity is also the difference between \(\{2_l, 2_l\}\) and \(\{3_l, 1_l\}\) states
\[
\Delta E(3, 1 - 2, 2) = E^3 + E_f - 2E_- = 2.7 \text{ eV} \tag{8.4}
\]
where \(E^3\) is the lowest three-hole state (see Appendix C). This energy difference \(\Delta E(3, 1 - 2, 2)\) is also analogue of the energy of the Hubbard repulsion \(U_H\).
IX. Conclusion

We conclude by summarizing our results. We have studied the low-energy properties of the CuO$_2$ plane near unit filling in the framework of the three-band model. We have considered the full three-band model in the form that was put forward by Emery [2], in the realistic region of the parameters, without any additional assumptions about the smallness of some of them.

Thus, we have taken into account the direct O-O hopping, intrasite repulsion at the oxygens $U_p$, and intersite repulsion $V_{pd}$, which have not been considered earlier. We have presented the consistent approach to the mapping of the three-band model to its low-energy limit. Following the idea of Zhang and Rice [5], we expressed the primary Hamiltonian in terms of symmetrical and antisymmetrical oxygen states. Next, we turned to the terms of the local states with certain number of the particles and transitions between them. The diagonalization of the local part of the Hamiltonian provided the set of eigenstates. The lowest of them is the singlet state with the energy well below than others. We have derived the low-energy Hamiltonian for the lowest singlet and its transitions ($t$-$t'$-$J$ model), and have taken into account all upper states by the special type of the unitary transformation.

Thus, we obtained the effective single-band Hamiltonian which is essentially the $t$-$J$ model one. Transitions to the next neighbors are not simple hopping due to the important role of the correction, which has a complicated structure.

Our approach allows to establish the quantitative boundary of the validity of the $t$-$J$ model as the low-energy limit of the three-band model, to get the corrections to it in an explicit form, and to take into account the transitions at the next neighbors. It is evident, that one can determine the value of the charge-transfer energy $\Delta$ from the well-defined value of $J$ at fixed other parameters of the three-band model. We have established that $\Delta$ varies in a narrow region of energies.

The lowest one-hole state for the undoped CuO$_2$ plane is (3.8)

$$|f\alpha\rangle = U|d\alpha\rangle - V|q\alpha\rangle \quad \alpha = \uparrow, \downarrow.$$  \hfill (9.1)

The lowest two-hole singlet state for the doped CuO$_2$ plane is (6.1)

$$|c1\rangle = U_1|d \uparrow d \downarrow\rangle + V_1|q \uparrow q \downarrow\rangle + W_1(|d \uparrow q \downarrow\rangle - |d \downarrow q \uparrow\rangle)/\sqrt{2}$$  \hfill (9.2)

where $|d\alpha\rangle$ is the state of a hole at the copper with projection $\alpha$; $|q\alpha\rangle$ is the state of a hole at the symmetrical oxygen which represents the Wannier state formed from the four oxygen states around the copper ion; $|d \uparrow d \downarrow\rangle$, $|q \uparrow q \downarrow\rangle$ and $(|d \uparrow q \downarrow\rangle - |d \downarrow q \uparrow\rangle)/\sqrt{2}$ are the two-hole singlet states.

The following set of parameters of the three band model (2.1) - (2.3) seems the most acceptable at present: $\Delta = \epsilon_p - \epsilon_d = 3$ eV, $U_d = 8$ eV, $U_p = 4$ eV, $V_{pd} = 1.2$ eV, $t = 1.4$ eV, $t_p = 0.7$ eV.

For this set of parameters of the three band model we have the following values of the coefficients $U$, $V$, $U_1$, $V_1$, $W_1$ (7.1), (7.2) which determine the probability of location of holes at the copper and the oxygen: $U = 0.85$, $V = 0.52$, $U_1 = -0.38$, $V_1 = -0.64$, $W_1 = 0.67$. 

19
The fundamental parameters of the t-J model $t_1$ and $J$ are: $t_1 = 0.427$ eV, $J = 0.126$ eV and $t_1/J = 0.34$.

The charge transfer gap $\Delta E = 3.2$ eV and the effective Hubbard repulsion of holes $U_H = 2.7$ eV.
Acknowledgments

This work was supported, in part, by a Soros Foundation Grant awarded one of us (V.I.B.) by the American Physical Society. This work was supported partly by the Soros-Akademgorodok Foundation, by the Council on Superconductivity of Russian Academy of Sciences, Grant No. 90214, and by the Program 'Universities of Russia as the centers of fundamental researches'.

Appendix A: Matrix elements for the singlet transitions

Here we present the explicit form for the matrix elements of the transition of the additional hole from the lowest to excited states. Thus,

$$F_{l'l',\alpha}^{x,y} = \langle l'y\mid l'x\beta\mid H_{hop}\mid cl'\rangle\langle f\alpha l\rangle,$$  \hspace{1cm} (A.1)

where $H_{hop}$ determined in eq.(2.10). A generator of the $S - W$ transformation is

$$S = -\sum_{l'l'\alpha}\sum'_{y} \frac{F_{l'l',\alpha}^{f,y}}{E_{y} - E_{-}} \left\{ X_{l}^{y,\alpha} X_{l'}^{f,y} - H.c. \right\}$$

$$- \sum_{l'l'\alpha,y} F_{l'l',\alpha}^{g,y} \frac{F_{l'l',\alpha}^{g,y}}{E_{y} - E_{-} + \epsilon_{g} - \epsilon_{f}} \left\{ X_{l}^{y,\alpha} X_{l'}^{g,y} - H.c. \right\}. \quad (A.2)$$

As was noted, the spin structure of the matrix elements can be separated out (see Eqs. (4.11), (4.12)). So, for the first limiting case (Sec. V.A) the matrix elements are

$$F_{l'l'}^{f,b} = 2t\lambda l l' V(Uab - (b^{2} - a^{2})V/\sqrt{2}) - t_{p}l l' (Vb\sqrt{2} - Ua)(Ub + Va\sqrt{2})/2,$$

$$F_{l'l'}^{f,\tau} = 2t\lambda l l' V^{2}a - t_{p}l l' U(Ub + Va\sqrt{2})/\sqrt{2},$$

$$F_{l'l'}^{f,c} = t_{p}l l' (Ub + Va\sqrt{2})/2,$$

$$F_{l'l'}^{f,t1} = -t_{p}l l' (Ub + Va\sqrt{2})/\sqrt{2},$$

$$F_{l'l'}^{f,\tilde{c}} = F_{l'l'}^{f,\tilde{\phi}} = F_{l'l'}^{f,\tilde{\tau}} \equiv 0,$$

$$F_{l'l'}^{g,c} = 2t\lambda l l' (bU^{2} - (a^{2})V/2 + aUV\sqrt{2}) - t_{p}l l' (Vb - \sqrt{2}Ua)(Ub + Va\sqrt{2})/2,$$

$$F_{l'l'}^{g,b} = t\lambda l l' (abU^{2} - UV(b^{2} - a^{2})\sqrt{2}) - t_{p}l l' (Ua - Vb\sqrt{2})(Vb - Ua\sqrt{2})/2,$$

$$F_{l'l'}^{g,\tau} = -\sqrt{2}t\lambda l l' (b - UVa\sqrt{2}) + t_{p}l l' U(Vb - \sqrt{2}Ua)/\sqrt{2},$$

$$F_{l'l'}^{g,\tilde{\epsilon}} = -t_{p}l l' (Ub - Ua\sqrt{2})/2,$$

$$F_{l'l'}^{g,t1} = -t_{p}l l' (Vb - Ua\sqrt{2})/\sqrt{2},$$

$$F_{l'l'}^{g,\tilde{b}} = F_{l'l'}^{g,\tilde{\phi}} = F_{l'l'}^{g,\tilde{\tau}} \equiv 0.$$
For the second limiting case (Sec. V.B.) there are matrix elements only with \( x = f \)

\[
F^{f,b}_{ll'} = -\sqrt{2}t\lambda V(b^2 - a^2) + t_p\mu U b a / 2 ,
\]
\[
F^{f,\tau}_{ll'} = 2t\lambda V a + t_p\mu U b / \sqrt{2} ,
\]
\[
F^{f,\tilde{c}}_{ll'} = t_p\mu U b / 2 ,
\]
\[
F^{f,\tilde{\tau}}_{ll'} = t_p\mu U b / \sqrt{2} .
\]

The matrix elements for the third case (Sec. V.C.)

\[
F^{f,c_2}_{ll'} = t\lambda U V(U^2 - V^2) - t_p\mu U V(Ub + Va) / 2 ,
\]
\[
F^{f,c_3}_{ll'} = t\lambda V(b^2 - a^2) + t_p\mu V((b^2 - a^2)UV - (U^2 - V^2)ba) / 2 ,
\]
\[
F^{f,\tau}_{ll'} = \sqrt{2}t\lambda V(U^2 - V^2)a + t_p\mu U(Ub + Va) / \sqrt{2} ,
\]
\[
F^{f,\tilde{c}}_{ll'} = -t_p\mu U(Ub + Va) / 2 ,
\]
\[
F^{f,\tilde{\tau}}_{ll'} = -t_p\mu U(Ub + Va) / \sqrt{2} ,
\]
\[
F^{f,b}_{ll'} = F^{f,\tilde{c}}_{ll'} = F^{f,\tilde{\tau}}_{ll'} = 0 ,
\]

The matrix elements for the general case (Sec. VI.) are

\[
F^{f,\tilde{c}_i}_{ll'} = -t\lambda U[(\sqrt{2}U_i U - W_i V)(\sqrt{2}V_i V - W_i V) + (\sqrt{2}V_i V - W_i U)(\sqrt{2}V_i V - W_i U)]
- t_p\mu U(\sqrt{2}V_i V - W_i U)(\sqrt{2}V_i V - W_i U) / 2 ,
\]
\[
F^{g,\tilde{c}_i}_{ll'} = -t\lambda U[(\sqrt{2}V_i V + W_i U)(\sqrt{2}V_i V - W_i V) - (\sqrt{2}V_i V + W_i U)(\sqrt{2}V_i U - W_i V)]
+ t_p\mu U(\sqrt{2}V_i U + W_i V)(\sqrt{2}V_i V - W_i U) / 2 ,
\]
where \( i = 1, 2, 3 \) is the number of the singlet from \( q - d \) sector. Other matrix elements are

\[
F^{f,\tau}_{ll'} = 2t\lambda V(U_1 V^2 - U_1 U^2) - t_p\mu U(U(\sqrt{2}V_1 V - W_1 U)) / \sqrt{2} ,
\]
\[
F^{f,\tilde{c}}_{ll'} = t_p\mu U(\sqrt{2}V_1 V - W_1 U) / 2 ,
\]
\[
F^{f,\tilde{\tau}}_{ll'} = -t_p\mu U(\sqrt{2}V_1 V - W_1 U) / \sqrt{2} ,
\]
\[
F^{f,b}_{ll'} = F^{f,\tilde{c}}_{ll'} = F^{f,\tilde{\tau}}_{ll'} = 0 ,
\]
\[
F^{f,\tau}_{ll'} = -\sqrt{2}t\lambda U(W_1 + (U_1 + U_1)UV \sqrt{2}) + t_p\mu U(\sqrt{2}V_1 U + W_1 V) / \sqrt{2} ,
\]
\[
F^{g,\tilde{c}}_{ll'} = t_p\mu U(\sqrt{2}V_1 U + W_1 V) / \sqrt{2} .
\]
\[
\begin{align*}
F_{i'i'}^{g,c} &= -t_{p\nu'i'}(\sqrt{2}V_1 U + W_1 V)/2 , \\
F_{i'i'}^{g,c} &= -t_{p\nu'i'}(\sqrt{2}V_1 U + W_1 V)/\sqrt{2} , \\
F_{i'i'}^{g,b} &= F_{i'i'}^{g,\phi} = F_{i'i'}^{g,t_2} \equiv 0 .
\end{align*}
\]

**Appendix B: Matrix elements for the virtual transitions**

For the case of unit filling we need to determine the matrix elements of the virtual transition of a hole at neighboring clusters. Thus, we are interested in the following quantities

\[
D_{il',\alpha\beta}^y = \langle ly|\langle l'0||H_{\text{hop}}||f\alpha l'|| f\beta l\rangle .
\]  \hspace{1cm} (B.1)

The spin structure can be separated out (see Eqs. (4.13), (4.16)). A generator of the \(S - W\) transformation has the form

\[
S = - \sum_{il',\alpha\beta,y} \frac{D_{il',\alpha\beta}^y}{E_y + E_0 - 2\epsilon_f} \left\{ X_{l'y}^\alpha X_{l'}^\beta - H.c. \right\} .
\]  \hspace{1cm} (B.2)

For the first limiting case (Sec.V.A.)

\[
\begin{align*}
D_{il'}^c &= \sqrt{2}t\lambda_{ii'}(b + aUV\sqrt{2}) + t_{p\mu l'i'}V(Ub + Va\sqrt{2})/\sqrt{2} , \\
D_{il'}^b &= \sqrt{2}t\lambda_{ii'}(a - bUV\sqrt{2}) + t_{p\mu l'i'}V(Ua - Vb\sqrt{2})/\sqrt{2} , \\
D_{il'}^* &= 2t\lambda_{ii'}(U^2 - V^2) + t_{p\mu l'i'}UV , \\
D_{il'}^\xi &= t_{p\nu l'i'}V/\sqrt{2} , \\
D_{il'}^1 &= t_{p\nu l'i'}V , \\
D_{il'}^2 &= D_{il'}^{\phi} = D_{il'}^{t_2} \equiv 0 .
\end{align*}
\]  \hspace{1cm} (B.3)

For the second limiting case (Sec.V.B.)

\[
\begin{align*}
D_{il'}^c &= -\sqrt{2}t\lambda_{ii'}b , \\
D_{il'}^b &= -\sqrt{2}t\lambda_{ii'}a , \\
D_{il'}^\xi &= -2t\lambda_{ii'} , \\
D_{il'}^1 &= D_{il'}^{\phi} \equiv 0 .
\end{align*}
\]  \hspace{1cm} (B.4)

For the third limiting case (Sec.V.C.)

\[
\begin{align*}
D_{il'}^{11} &= \sqrt{2}t\lambda_{ii'}(b + 2aUV) + t_{p\mu l'i'}V(Ub + Va)/\sqrt{2} , \\
D_{il'}^{22} &= t_{p\mu l'i'}V^2/\sqrt{2} , \\
D_{il'}^{33} &= \sqrt{2}t\lambda_{ii'}(2bUV - a) - t_{p\mu l'i'}V(Ua - Vb)/\sqrt{2} ,
\end{align*}
\]
\[
D_{ll'}^\tau = 2t\lambda (U^2 - V^2) + t_p\mu VU , \\
D_{ll'}^\tilde{c} = t_p\nu V/\sqrt{2} , \\
D_{ll'}^1 = t_p\nu V , \\
D_{ll'}^\tilde{b} = D_{ll'}^\tilde{c} = D_{ll'}^{t2} \equiv 0 . 
\]

For the general case (Sec. VI.) matrix elements are
\[
D_{ci}^1 = -\sqrt{2}t\lambda (\sqrt{2}V_1(U_i + V_i) - W_i) - t_p\mu VU/\sqrt{2} , \\
D_{ci}^\tau = 2t\lambda (U^2 - V^2) + t_p\mu UV , \\
D_{ci}^\tilde{c} = t_p\nu V/\sqrt{2} , \\
D_{ci}^1 = t_p
\]

The additions to the matrix elements from \( U_p \) and \( V_{pd} \) terms, which are essential for calculation of \( J \) (Sec. VII)
\[
\Delta D_{(ll')}^c = V_{pd}f_1UVW_1 - U_ph_1V_1V^2 , \\
\Delta D_{(ll')}^\tau = V_{pd}f_1UV . 
\]

**Appendix C: Three-hole states**

There are twenty of the three-hole cluster states
\[
|\Psi_q^\alpha\rangle \equiv q^{+}_\alpha d^{+}_q d^{\uparrow}_q |0\rangle , \quad |\tilde{\Phi}_q^\alpha\rangle \equiv q^{+}_\alpha \tilde{d}^{+}_q d^{\uparrow}_q |0\rangle , \\
|\Phi^d_q^\alpha\rangle \equiv d^{+}_\alpha q^{+}_q q^{\uparrow}_q |0\rangle , \quad |\tilde{\Phi}^d_q^\alpha\rangle \equiv \tilde{q}^{+}_\alpha q^{+}_q q^{\uparrow}_q |0\rangle , \\
|\Phi^d_q^\tilde{\alpha}\rangle \equiv d^{+}_\alpha \tilde{q}^{+}_q q^{\uparrow}_q |0\rangle , \quad |\tilde{\Phi}^d_q^\tilde{\alpha}\rangle \equiv q^{+}_\alpha \tilde{q}^{+}_q q^{\uparrow}_q |0\rangle , \quad \text{and} \\
|\Lambda_{\alpha\beta\gamma}\rangle \equiv d^{+}_\alpha q^{+}_\beta \tilde{q}^{\uparrow}_\gamma |0\rangle .
\]

The hybridization term (2.11) provides the transitions only between
\[
|\Phi^d_q^\alpha\rangle \leftrightarrow |\tilde{\Phi}^d_q^\alpha\rangle , \\
|\Psi_q^\alpha\rangle \leftrightarrow |\Phi^d_q^\alpha\rangle , \\
|\Psi_q^{\tilde{\alpha}}\rangle \leftrightarrow |\Phi^d_q^{\tilde{\alpha}}\rangle \leftrightarrow (2\sigma)|\Lambda_{\alpha\beta\gamma}\rangle .
\]

Four other states \( |\Lambda_{\sigma\sigma\alpha}\rangle \) are noninteracting and degenerating in energy
\[
E^3_{\Lambda_{\sigma\sigma\alpha}} = -\Delta
\]

counted from \( \epsilon_p = 0 \).
By diagonalization of the Hamiltonian (2.10) one can easily get that the eigenfunctions $|\tilde{\Psi}_{q,\alpha}\rangle$ and $|\tilde{\Phi}_{q,\alpha}\rangle$ in the three-holes sector are connected with the $q-d$ sector of the two-hole states (5.9). Three-hole eigenfunctions are

$$|G_{\alpha,i}\rangle \equiv \tilde{q}_{\alpha}^i |c_i\rangle ,$$

and their energies

$$E^3(G_{\alpha,i}) \equiv E^{2+\tilde{q}}_1 = \mu_0 t_p + E^2_i ,$$

where $E^2_i \equiv E_{\pm,0}$ are the energies of the local singlets (6.1). Diagonalization of the other sectors (C.2) provides the eigenenergies

$$\tilde{E}^3_{\pm} = -\left(\Delta + 3\mu_0 t_p\right)/2 \pm \left(\left(\Delta - \mu_0 t_p\right)/2\right)^2 + 4t^2\lambda^2_0\right)^{1/2} ,$$

for the $(\tilde{\Phi}_{\alpha}, \tilde{\Phi}^q_{\alpha})$ sector

$$E^3_{\pm} = -\left(U_d - 3\Delta - 3\mu_0 t_p\right)/2 \pm \left(\left(U_d - \Delta + \mu_0 t_p\right)/2\right)^2 + 4t^2\lambda^2_0\right)^{1/2} ,$$

and for the $(\Psi^q_{\alpha}, \Phi^d_{\alpha})$ sector.

Since we are interested in the lowest three-hole state, we analyze the spectrum of the energies (C.3), (C.6). For a wide region of $U_d$ and $\Delta$ 

$$E^{2+\tilde{q}}_1 < E^3_{-} ,$$

and all other states lie much higher. Renormalization of these energies due to the $U_p$ and $V_{pd}$ terms remains all our consideration to be correct.

For the above mentioned parameters $U_d = 8$ eV, $\Delta = 3$ eV, $U_p = 4$ eV, and $V_{pd} = 1.2$ eV one can get

$$E^{2+\tilde{q}}_1 = -0.5 \text{ eV} ,$$

$$E^3_{-} = -3.73 \text{ eV} .$$

Thus, the Hubbard repulsion $U_H$ is

$$U_H = E^3 + E^1 - 2E^2 = -3.73 - 4.27 + 2 \cdot 5.36 \simeq 2.7 \text{ eV} .$$

Appendix D: Shifts of energies of the two-hole states

Shifts of energies of the primary set of the two-hole states, due to $U_p$ and $V_{pd}$ terms are

$$\Delta E_\varphi = 2V_{pd}U^2(2 - f_0) + U_p(h_0 + V^2(1/2 - h_0)) ,$$

$$\Delta E_\psi = 2V_{pd}V^2(2 - f_0) ,$$

$$\Delta E_\chi = 2V_{pd} + U_pV^2(1/2 - h_0) ,$$

$$\Delta E_\tau = 2V_{pd} + U_pV^2(1/2 - h_0) .$$

(D.1)
References

[1] P.W. Anderson, Science 235, 1196 (1987)
[2] V.J. Emery, Phys. Rev. Lett. 58, 2794 (1987).
[3] C.M. Varma, S. Schmitt-Rink and E. Abrahams, Solid State Commun. 62, 681 (1987).
[4] Yu.B. Gaididei and V.M. Loktev, Phys. Stat. Sol. (b) 147, 307 (1988).
[5] F.C. Zhang and T.M. Rice, Phys. Rev. B 37, 3759 (1988).
[6] F.C. Zhang and T.M. Rice, Phys. Rev. B 41, 7243 (1990).
[7] J.L. Shen and C.N. Ting, Phys. Rev. B 41, 1969 (1990).
[8] H.B. Pang, T. Xiang, Z.B. Su and L. Yu, Phys. Rev. B 41, 7209 (1990).
[9] S.V. Lovtsov and V.Yu. Yshankhai, Physica C 179, 159 (1991).
[10] V.I. Belinicher and A.L. Chernyshev, Phys. Rev. B 47, 390 (1993).
[11] J.G. Zaanen, G.A. Sawtzky and J.W. Allen, Phys. Rev. Lett. 55, 418 (1985).
[12] D.M. Frenkel, R.J. Gooding, B.I. Shraiman, and E.D. Siggia, Phys. Rev. B 41, 350 (1990).
[13] W.E. Pickett, Rev. Mod. Phys. 61, 433 (1989).
[14] J. Fink at al., Physica C 185-189, 45 (1991).
[15] V.V. Flambaum and O.P. Sushkov, Physica C 175, 347 (1991).
[16] S. Maekawa, Y. Ohita, and T. Tohyama, Physica C 185-189, 168 (1991).
[17] G.L. Bir and G.E. Pikus, Symmetry and deformational effects in Semiconductors, Wiley, New York, 1974.
[18] M.S. Hybertsen, E.B. Stechel, M. Schluter and D.R. Jennison, Phys. Rev. B 41, 11068 (1990).
[19] V.J. Emery and G. Reiter, Phys. Rev. B 38, 4547 (1988).
[20] Weiyi Zhang and K. Bennemann, Phys. Rev. B 45, 12487 (1992).
[21] M.S. Hybertsen, W.M.C. Foulkes and M. Schluter, Phys. Rev. B 45, 10032 (1992).
[22] H. Eskes, L.H. Tjeng, and G.A. Sawatzky, Phys. Rev. B 41, 288 (1990).
TABLE I.
Coefficients $\lambda(l-l')$, $\mu(l-l')$, and $\nu(l-l')$ as functions of $(l-l') = nx + my$.

| n,m | $\lambda_{n,m} = \lambda_{m,n}$ | $\mu_{n,m} = \mu_{m,n}$ | $\nu_{n,m} = -\nu_{m,n}$ |
|-----|-------------------------------|------------------------|------------------|
| 0, 0 | 0.9581                        | 1.4567                 | 0.0              |
| 1, 0 | 0.1401                        | 0.5497                 | 0.2678           |
| 1, 1 | -0.0235                       | 0.2483                 | 0.0              |
| 2, 0 | -0.0137                       | -0.1245                | 0.0812           |
| 2, 1 | 0.0069                        | -0.0322                | 0.0609           |
| 2, 2 | 0.0035                        | 0.0231                 | 0.0              |

TABLE II.
Energies of the local states, the first four hopping parameters, the second-order corrections to them on a ferromagnetic background, correction to the energy $E_-$, the superexchange constant $J$, the ratio of $(t_1/J)$ for the case $\Delta \ll U_d$ at $\Delta = 3.66$ eV.
| neighbor number, $n$ | direct hopping parameters, $t_n$, (eV) | contribution of direct O-O hopping, $t_{pp}^n$, (eV) | contribution of Cu-O hopping, $t_{pd}^n$, (eV) | second-order corrections, $\delta t_n$, (%) |
|---|---|---|---|---|
| 1 | 0.43 | 0.24 | 0.19 | 3.1 |
| 2 | 0.078 | 0.11 | -0.032 | 9.6 |
| 3 | -0.074 | -0.055 | -0.019 | 14.4 |
| 4 | 0.005 | -0.014 | 0.009 | 110. |

| correction to the energy $E_{-}$, (%) | superexchange constant $J$, (meV) | ratio $|t_1/J|$ |
|---|---|---|
| 4.1 | 126.1 | 3.4 |
TABLE III.
Energies of the local states, the hopping parameters at the first four neighbors, the second-order corrections to them on a ferromagnetic background, correction to the energy $E_-$, the superexchange constant $J$, and the ratio $t_1/J$ for the case $U_d - \Delta \ll U_d$ at $U_d = 8$ eV, $\Delta = 3.65$ eV.

| neighbor number, $n$ | direct hopping parameters, $t_n$, (eV) | contribution of direct O-O hopping, $t_{pp}^n$, (eV) | contribution of Cu-O hopping, $t_{pd}^n$, (eV) | second-order corrections, $\delta t_n$, (%) |
|---------------------|---------------------------------|---------------------------------|---------------------------------|--------------------------------|
| 1                   | 0.38                            | 0.15                            | 0.23                            | 4.6                            |
| 2                   | 0.030                           | 0.068                           | -0.038                          | 313.                           |
| 3                   | -0.057                          | -0.034                          | -0.022                          | 91.                            |
| 4                   | 0.0022                          | -0.0089                         | 0.011                           | 165.                           |
| correction to the energy $E_-$, (%) | superexchange constant $J$, (meV) | ratio $|t_1/J|$ | 13.0 | 126.6 | 3.0 |
TABLE IV.
Energies of the local states, the hopping parameters at the first four neighbors, the second-order corrections to them on a ferromagnetic background, correction to the energy $E_-$, the superexchange constant $J$, and the ratio $t_1/J$ for the special case at $U_d = 8.13$ eV.

| one-hole local energies, (eV) | $E_f = -6.42$ | $E_g = 0.31$ | $E_d = 1.02$ |
| two-hole local energies, (eV) | $E_- = -9.81$ | $E_0 = -2.04$ | $E_+ = 1.66$ | $E_\phi = -6.10$ |

| neighbor number, $n$ | direct hopping parameters, $t_n$, (eV) | contribution of direct O-O hopping, $t_{pp}^n$, (eV) | contribution of Cu-O hopping, $t_{pd}^n$, (eV) | second-order corrections, $\delta t_n$, (%) |
|---------------------|-------------------------------|-----------------|-----------------|----------------|
| 1                   | 0.53                          | 0.19            | 0.34            | 2.5            |
| 2                   | 0.028                         | 0.085           | -0.057          | 79.5           |
| 3                   | -0.076                        | -0.043          | -0.033          | 22.9           |
| 4                   | 0.0056                        | -0.011          | 0.0166          | 25.2           |

| correction to the energy $E_-$, (%) | superexchange constant $J$, (meV) | ratio $|t_1/J|$ |
|-------------------------------------|----------------------------------|-------------|
| 4.66                                | 126.2                            | 4.18        |
TABLE V.
Energies of the local states, the hopping parameters at the first four neighbors, the second-
order corrections to them on a ferromagnetic background, correction to the energy $E_-$, the
superexchange constant $J$, and the ratio $t_1/J$ for the general case at $U_d = 8$ eV, $\Delta = 5.1$ eV.

| one-hole local energies, (eV) | two-hole local energies, (eV) |
|-----------------------------|-------------------------------|
| $E_f = -6.43$ | $E_\phi = 1.02$ |
| $E_g = 0.31$ | $E_0 = -2.12$ |
| $E_\psi = 1.61$ | $E_\tau = -6.12$ |

| neighbor number, n | direct hopping parameters, $t_n$, (eV) | contribution of direct O-O hopping, $t'n^p$, (eV) | contribution of Cu-O hopping, $t'n^p$, (eV) | second-order corrections, $\delta t_n$, (%) |
|--------------------|------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 1                  | 0.528                                    | 0.187                           | 0.341                           | 2.5                             |
| 2                  | 0.0274                                   | 0.0846                          | -0.0572                         | 82.2                            |
| 3                  | -0.0758                                  | -0.0424                         | -0.0334                         | 23.0                            |
| 4                  | 0.0057                                   | -0.011                          | 0.0167                          | 24.8                            |

| correction to the energy $E_-$, (%) | superexchange constant $J$, (meV) | ratio $|t_1/J|$ |
|------------------------------------|---------------------------------|----------------|
| 3.02                               | 126.4                           | 4.18           |

31
TABLE VI. Contributions of $p - d$ hopping, $p - p$ hopping, $V_{pd}$ and $U_p$ terms to the effective hopping parameter of the lowest singlet at the nearest neighbors, the superexchange constant $J$ and the ratio $t/J$ at $U_d = 8$ eV, $U_p = 4$ eV, $V_{pd} = 1.2$ eV, $\Delta = 3.0$ eV.

| effective hopping parameter, $t_1$, (eV) | $p - d$ contribution, (eV) | $p - p$ contribution, (eV) | $V_{pd}$ contribution, (eV) | $U_p$ contribution, (eV) |
|-----------------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 0.427                                   | 0.351                     | 0.202                     | -0.113                    | -0.013                    |

| superexchange constant $J$, (meV) | ratio $|t_1/J|$ |
|-----------------------------------|-----------------|
| 126.26                            | 3.38            |