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

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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.

I. INTRODUCTION

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

Now there is general agreement that the CuO_2 planes are common to all high-temperature superconductors. A realistic model for these planes was proposed from first principles by Emery,[2] Varma, Schmitt-Rink, and Abrahams,[3] and Gaididei and Loktev.[4]

Also some other realistic models have been put forward and investigated on small clusters by Mila[5] and Eskes, Tjeng, and Sawatzky.[6–8]

During the 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,[9] where they proposed the idea of the local singlet and the idea of the Wannier representation for O states. The problem of the low-energy reduction has been intensively investigated.[10–13] The singlet-triplet effective Hamiltonian was obtained in works of Yushankhai and Lovtsov[13] and Shen and Ting.[11] In our recent work[14] a quantitative comparison of the exact solution for the three-band model with the solution for the generalized t-J model was performed. The role of both essential hybridization terms Cu-O and O-O for the renormalization of energies of local states was considered in Refs. 5–8.

However, the situation seems not completely clarified since (1) most of the above-named works dealt 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, and $\Delta=(\epsilon_p-\epsilon_d)$ is the charge-transfer energy, and (2) all of the above-named works did not consistently take into account direct O-O hopping. The approaches of Refs. 5–8 did not allow one to calculate effective hopping integrals for the lowest singlet.

In this work we develop a general approach to the consistent low-energy reduction of the three-band model. For this, following Zhang and Rice,[9] we 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 basis of the local states with a 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 direct O-O hopping. We have found that it does not change crucially the picture of the local states but plays an important role for the effective hopping parameters. Next, we keep 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 Hilbert 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[15] 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 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 Δ through J. We have found that a narrow region of energies for Δ 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 Δ and the first hopping integral t_1 is discussed.

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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.

A more detailed version of this paper is available.[16]

II. THREE-BAND HAMILTONIAN

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

$$H=\epsilon_d \sum_{l,\alpha} n^d_{l\alpha}+\epsilon_p \sum_{m,\alpha} n^p_{m\alpha}+U_d \sum_l n^d_{l\uparrow} n^d_{l\downarrow}+\Delta H+H' , \tag{2.1}$$

$$\Delta H=U_p \sum_m n^p_{m\uparrow} n^p_{m\downarrow}+V_{pd} \sum_{\langle lm\rangle,\alpha,\beta} n^d_{l\alpha} n^p_{m\beta} , \tag{2.2}$$

where l and m denote summation over the Cu and O sites, respectively, $n^d_{l\alpha}=d^\dagger_{l\alpha}d_{l\alpha}$, $n^p_{m\alpha}=p^\dagger_{l\alpha}p_{l\alpha}$, $d^\dagger_{l\alpha}(d_{l\alpha})$ creates (annihilates) the Cu $(3d_{x^2-y^2})$ hole, and $p^\dagger_{l\alpha}(p_{l\alpha})$ creates (annihilates) an O (p_x,p_y) hole. U_d and U_p are the intrasite Coulomb repulsion at the copper and oxygen sites, respectively, and 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:

$$H'=t \sum_{\langle lm\rangle\alpha} (d^\dagger_{l\alpha}p_{m\alpha}+\text{H.c.})-t_p \sum_{\langle mm'\rangle\alpha} (p^\dagger_{m\alpha}p_{m'\alpha}+\text{H.c.}) , \tag{2.3}$$

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 Ref. 17, such a 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.[10,18,19] One of the simplifications used in all analytical works was neglecting the repulsion at the oxygen and between the nearest-neighbor copper and oxygen sites. To take into account the main effect, we will first consider the model (2.1)–(2.3) without U_p and V_{pd} terms and later include these terms as the perturbation.

It is reasonable to introduce the symmetrical and antisymmetrical orthonormalized p operator combination as

$$q_{\mathbf{k}}=[\cos(k_x/2)p_{\mathbf{k}x}+\cos(k_y/2)p_{\mathbf{k}y}](1+\gamma_{\mathbf{k}})^{-1/2} ,$$

$$\tilde{q}_{\mathbf{k}}=[-\cos(k_y/2)p_{\mathbf{k}x}+\cos(k_x/2)p_{\mathbf{k}y}](1+\gamma_{\mathbf{k}})^{-1/2} ,$$

where $\gamma_{\mathbf{k}}=(1/2)[\cos(k_x a)+\cos(k_y a)]$. Hereafter, the lattice constant is equal to unity.

It is evident that the pd-hybridization term in H' includes only the symmetrical state.[9] In terms of these operators after substitution of (2.4) in (2.1),(2.3) and inverse Fourier transformation, the Hamiltonian has the form

$$\begin{aligned} H_0=&\epsilon_d \sum_{l,\alpha} d^\dagger_{l\alpha}d_{l\alpha}+\epsilon_p \sum_{l,\alpha} (q^\dagger_{l\alpha}q_{l\alpha}+\tilde{q}^\dagger_{l\alpha}\tilde{q}_{l\alpha}) \\ &+U_d \sum_l d^\dagger_{l\uparrow}d_{l\uparrow}d^\dagger_{l\downarrow}d_{l\downarrow} , \\ H'=&2t \sum_{\langle ll'\rangle\alpha} \lambda_{ll'}(d^\dagger_{l\alpha}q_{l'\alpha}+\text{H.c.}) \\ &-t_p \sum_{\langle ll'\rangle\alpha} \{\mu_{ll'}(q^\dagger_{l\alpha}q_{l'\alpha}-\tilde{q}^\dagger_{l\alpha}\tilde{q}_{l'\alpha}) \\ &+\nu_{ll'}(q^\dagger_{l\alpha}\tilde{q}_{l'\alpha}+\text{H.c.})\} , \end{aligned} \tag{2.4}$$

where

$$\begin{aligned} \{\lambda,\mu,\nu\}_{ll'}\equiv&\{\lambda,\mu,\nu\}(l-l') \\ =&\sum_{\mathbf{k}} \{\lambda,\mu,\nu\}_{\mathbf{k}}\exp[-i\mathbf{k}(l-l')] , \end{aligned} \tag{2.5}$$

with quantities

$$\lambda_{\mathbf{k}}=(1+\gamma_{\mathbf{k}})^{1/2} ,$$

$$\mu_{\mathbf{k}}=8\cos^2(k_x/2)\cos^2(k_y/2)(1+\gamma_{\mathbf{k}})^{-1/2} ,$$

$$\nu_{\mathbf{k}}=4\cos(k_x/2)\cos(k_y/2) \times[\cos^2(k_x/2)-\cos^2(k_y/2)](1+\gamma_{\mathbf{k}})^{-1/2} ,$$

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

One can divide the Hamiltonian (2.4) into local and hopping parts,

$$\begin{aligned} H_{\text{loc}}=&\epsilon_d \sum_{l,\alpha} d^\dagger_{l\alpha}d_{l\alpha}+(\epsilon_p-\mu_0 t_p)\sum_{l,\alpha} q^\dagger_{l\alpha}q_{l\alpha} \\ &+(\epsilon_p+\mu_0 t_p)\sum_{l,\alpha} \tilde{q}^\dagger_{l\alpha}\tilde{q}_{l\alpha}+U_d \sum_l d^\dagger_{l\uparrow}d_{l\uparrow}d^\dagger_{l\downarrow}d_{l\downarrow} \\ &+2t\lambda_0 \sum_{l,\alpha} (d^\dagger_{l\alpha}q_{l\alpha}+\text{H.c.}) , \\ H_{\text{hop}}=&2t \sum_{ll'\alpha} \lambda_{ll'}(d^\dagger_{l\alpha}q_{l'\alpha}+\text{H.c.}) \\ &-t_p \sum_{ll'\alpha} \{\mu_{ll'}(q^\dagger_{l\alpha}q_{l'\alpha}-\tilde{q}^\dagger_{l\alpha}\tilde{q}_{l'\alpha}) \\ &+\nu_{ll'}(q^\dagger_{l\alpha}\tilde{q}_{l'\alpha}+\text{H.c.})\} ; \end{aligned} \tag{2.6}$$

hereafter, the sum over l,l' means that $l\neq l'$.

Now, one can discuss the reasons for the transformation from the Hamiltonian (2.1)–(2.3) to (2.6). The copper d state hybridizes only with the symmetrical oxygen q state.[9] Taking into account 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

TABLE I. Coefficients $\lambda(l-l')$, $\mu(l-l')$, and $\nu(l-l')$ as functions of $(l-l')=n\mathbf{x}+m\mathbf{y}$.

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

states and solve the problem of the low-energy two-hole state at the background of the one-hole states (spins) consistently. This spectrum is well determined, in the sense that the local states on different sites (clusters) mixed weakly. Roughly, we know that for our representation (2.4) the ratio of the effective hopping parameters between the different states to the energy gap between them for the CuO_2 plane is of the order 1/10. It is a strong justification for our perturbation scheme.

The direct O-O hopping only slightly shifts the energies of the oxygen states with opposite symmetry. But its contribution to the effective hopping parameters will be very important (see Sec. V). The transformed Hamiltonian (2.6) with the definitions (2.6) 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

$$|d_\alpha\rangle\equiv d_\alpha^\dagger|0\rangle,\quad |q_\alpha\rangle\equiv q_\alpha^\dagger|0\rangle,\quad |\bar q_\alpha\rangle\equiv \bar q_\alpha^\dagger|0\rangle\ . \tag{3.1}$$

The two-hole singlet sector has a set of states

$$\begin{aligned}&|\psi\rangle\equiv d_\uparrow^\dagger d_\downarrow^\dagger|0\rangle,\quad |\varphi\rangle\equiv q_\uparrow^\dagger q_\downarrow^\dagger\rangle\ ,\\ &|\chi\rangle\equiv S(d^\dagger,q^\dagger\rangle|0\rangle\ ,\end{aligned} \tag{3.2}$$

$$\begin{aligned}&|\bar\varphi\rangle\equiv \bar q_\uparrow^\dagger \bar q_\downarrow^\dagger|0\rangle,\quad |\tilde\chi\rangle\equiv S(d^\dagger,\bar q^\dagger)|0\rangle\ ,\\ &|\bar\eta\rangle\equiv S(q^\dagger,\bar q^\dagger)|0\rangle\ ,\end{aligned} \tag{3.3}$$

where $S(a^\dagger,b^\dagger)=(1/\sqrt{2})(a_\uparrow^\dagger b_\downarrow^\dagger-a_\downarrow^\dagger b_\uparrow^\dagger)$.

The two-hole triplet sector is

$$\begin{aligned}&|rm\rangle\equiv t_m(d^\dagger,q^\dagger)|0\rangle,\quad |\bar\tau m\rangle\equiv t_m(d^\dagger,\bar q^\dagger)|0\rangle\ ,\\ &|\zeta m\rangle\equiv t_m(q^\dagger,\bar q^\dagger)|0\rangle\ ,\end{aligned} \tag{3.4}$$

where $t_m(a^\dagger,b^\dagger)=(a_\uparrow^\dagger b_\uparrow^\dagger, a_\downarrow^\dagger b_\downarrow^\dagger,(1/\sqrt{2})(a_\uparrow^\dagger b_\downarrow^\dagger+a_\downarrow^\dagger b_\uparrow^\dagger)$ for $m=\pm1,0$, and $|0\rangle$ is the vacuum state (state without holes on a cluster). Hence, we have three one-hole and nine two-hole states. Classification of the cluster states on the same footing was proposed in Refs. 5 and 6, but on the basis of nonorthonormalized 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 $H_{\rm loc}$ of the Hamiltonian (2.6). It is convenient to express this Hamiltonian in terms of the Hubbard operators rather than in terms of the usual Fermi operators. Such a representation of the Hamiltonian (2.6) in the one- and two-hole sectors in terms of states (3.1)–(3.4) has the form

$$\begin{aligned}H_{\rm loc}^1=&\sum_{l,\alpha}\{\epsilon_d X_l^{d\alpha,d\alpha}+(\epsilon_p-\mu_0 t_p)X_l^{q\alpha,q\alpha}+(\epsilon_p+\mu_0 t_p)X_l^{\bar q\alpha,\bar q\alpha}+2t\lambda_0(X_l^{d\alpha,q\alpha}+\text{H.c.})\}\ ,\\ H_{\rm loc}^2=&\sum_l\{[(U_d+2\epsilon_d)X_l^{\psi,\psi}+2(\epsilon_p-\mu_0 t_p)X_l^{\varphi,\varphi}+(\epsilon_d+\epsilon_p-\mu_0 t_p)X_l^{\chi,\chi}+2\sqrt{2}t\lambda_0(X_l^{\chi,\psi}+X_l^{\chi,\varphi}+\text{H.c.})]\\ &+2(\epsilon_p+\mu_0 t_p)X_l^{\bar\varphi,\bar\varphi}+[(\epsilon_d+\epsilon_p+\mu_0 t_p)X_l^{\tilde\chi,\tilde\chi}+\epsilon_p X_l^{\bar\eta,\bar\eta}+2t\lambda_0(X_l^{\tilde\chi,\eta}+\text{H.c.})]+(\epsilon_d+\epsilon_d-\mu_0 t_p)\sum_{m=\pm1,0}X_l^{\tau m,\tau m}\\ &+\sum_{m=\pm1,0}[(\epsilon_d+\mu_0 t_p)X_l^{\bar\tau m,\bar\tau m}+\epsilon_p X_l^{\zeta m,\zeta m}+2t\lambda_0(X_l^{\zeta m,\bar\tau m}+\text{H.c.})]\}\ ,\end{aligned} \tag{3.5}$$

where the upper index 1,2 marks the one- and two-hole sectors of the local Hamiltonian and $X_l^{a,b}$ is the Hubbard operator at the site l:

$$\begin{aligned}&X_l^{a,b}\equiv|al\rangle\langle bl|\ ,\\ &a,b=\{d\alpha,q\alpha,\bar q\alpha,\psi,\varphi,\chi,\tilde\chi,\eta,\tau m,\zeta m,\bar\tau m\}\ ,\end{aligned} \tag{3.6}$$

where the index $\alpha=\pm\frac{1}{2}$ in H^1 is a spin projection; $m\equiv\pm1,0$ in H^2 denotes triplet components.

The representation of $H_{\rm loc}$ (2.6) in terms of the Hubbard operators Eq. (3.5) allows us to solve simply the one-site problem. The diagonalization of $H_{\rm loc}^1, H_{\rm loc}^2$ is performed at each site independently. After the diagonalization, $H_{\rm loc}^1$ is given by

$$H_{\rm loc}^1=\sum_{l,\alpha}\{\epsilon_f X_l^{f\alpha f\alpha}+\epsilon_g X_l^{g\alpha g\alpha}+(\epsilon_p+\mu_0 t_p)X_l^{\bar q\alpha\bar q\alpha}\}\ , \tag{3.7}$$

where $\epsilon_{f,g}=-(\Delta+\mu_0 t_p)/2\mp R_1$, $R_1=(\tilde\Delta^2+4t^2\lambda_0^2)^{1/2}$, $\tilde\Delta=(\Delta-\mu_0 t_p)/2$, $\Delta=\epsilon_p-\epsilon_d$, and $|f\alpha\rangle$ and $|g\alpha\rangle$ are the lower and higher one-hole cluster states,

$$|f\alpha\rangle=U|d\alpha\rangle-V|q\alpha\rangle,\quad |g\alpha\rangle=V|d\alpha\rangle+U|q\alpha\rangle\ , \tag{3.8}$$

with $U=[(R_1+\tilde{\Delta})/2R_1]^{1/2}$ and $V=[(R_1-\tilde{\Delta})/2R_1]^{1/2}$.

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 $|f\alpha l\rangle$ 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 an antiferromagnetic type of interaction between these spins.

In $H^2_{\rm loc}$ (3.5) 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 (3.5) is

$$H^2_{\rm loc}=\sum_l \left\{ E_- X_l^{cc}+\sum_y E_- X_l^{yy} \right\} , \tag{3.9}$$

where E_- is the energy of the lowest singlet $|c\rangle$, E_y are the energies of the upper states, and 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 Sec. V and VI. After diagonalization of the local part (3.5) of the full Hamiltonian (2.6), one can introduce the nondiagonal Hubbard operators and rewrite the hopping Hamiltonian (2.6) 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 Sec. 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 a procedure gives the t-t'-J model with hopping at all neighbors in the explicit form

$$H_{t-t'}=E_- \sum_l X_l^{cc}+\sum_{ll'\alpha} t_{ll'} X_l^{f\alpha,c} X_l^{c,f\alpha} , \tag{4.1}$$

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

$$\begin{aligned} &H_{t-t'}=E_- \sum_l (1-\hat{n}_l^c+\hat{d}_l^c)+\sum_{ll',\alpha} t_{ll'} \tilde{c}_{l\alpha}^\dagger \tilde{c}_{l'\alpha} , \\ &\tilde{c}_{l\alpha}=c_{l\alpha}(1-\hat{n}_{l,-\alpha}), \tilde{c}_{l\alpha}^\dagger=(\tilde{c}_{l\alpha})^\dagger , \\ &\hat{n}_l=(c_l^\dagger c_l), \hat{d}_l^c \equiv c_\uparrow^\dagger c_\uparrow c_\downarrow^\dagger c_\downarrow . \end{aligned} \tag{4.2}$$

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

In the next part of the work we will consider 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 hoping 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 (3.5) we obtain a set of the local states. For the low-energy processes one can consider only the lowest states and include all others perturbatively. We use the Schrieffer-Wolff (SW) transformation[20]

$$H \Longrightarrow \tilde{H}=\exp(-S)H\exp(S), S^\dagger=-S , \tag{4.3}$$

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

$$[H_0,S]=-H', \quad \delta H^2=(1/2)[H',S] . \tag{4.4}$$

For the case of one hole over unit filling $H_0 \equiv H^2_{\rm loc}+H^1_{\rm loc}+H_{t-t'}$ [Eqs. (3.7), (3.9), and (4.1)] and H' includes all terms of $H_{\rm hop}$ (2.6) 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

$$\begin{aligned} H'_1=&\sum_{ll'\alpha\beta} {\sum_y}' F^{f\beta,y}_{ll'\alpha} \{X_l^{y,f\alpha} X_{l'}^{f\beta,c}+\text{H.c.}\} \\ &+\sum_{ll'\alpha\beta,y} F^{g\beta,y}_{ll',\alpha} \{X_l^{y,f\alpha} X_{l'}^{g\beta,c}+\text{H.c.}\} , \end{aligned} \tag{4.5}$$

where y is the set of the two-hole states and the prime in the sum (4.5) denotes the absence of a contribution of the lowest singlet state; $f\alpha$ and $g\beta$ are the one-holes states (3.8). The second term in Eq. (4.5) is essential only for correction to the energy E_- of the c singlet. The first term in Eq. (4.5) provides corrections both to the energy and to the hopping integrals. $F^{x\beta,y}_{ll'\alpha}$ are the matrix elements of transitions between $|cl'\rangle\otimes|f\alpha l\rangle$ and $|x\beta l'\rangle\otimes|yl\rangle$ states ($x=f,g$),

$$F^{x\beta,y}_{ll'\alpha}=\langle ly|\otimes\langle l'x\beta\|H'_1\|cl'\rangle\otimes|f\alpha l\rangle . \tag{4.6}$$

Also, there is another term which makes the contribution to correction to the energy,

$$H'_2=\sum_{ll',z}\sum_{\alpha\beta\gamma\delta} G^{z,\alpha\beta\gamma}_{ll',\delta}\{X_l^{0,f\delta} X_{l'}^{\Lambda\alpha\beta\gamma,c}+\text{H.c.}\} , \tag{4.7}$$

where $\Lambda\alpha\beta\gamma$ are the three-hole states, z is their index, and

$$G^{z,\alpha\beta\gamma}_{ll',\delta}=\langle l0|\otimes\langle l'\Lambda\alpha\beta\gamma\|H'_2\|cl'\rangle\otimes|f\delta l\rangle . \tag{4.8}$$

In the case of unit filling, H_0 and H' for Eq. (4.4) are

$$\begin{aligned} &H_0 \equiv H^2_{\rm loc}+H^1_{\rm loc} , \\ &H'=\sum_{ll'\alpha\beta,y} D^y_{ll',\alpha\beta}\{X_l^{y,f\alpha} X_{l'}^{0,f\beta}+\text{H.c.}\} , \end{aligned} \tag{4.9}$$

where $|0\rangle$ is the state without holes and $D^y_{ll',\alpha\beta}$ are the

matrix elements of the transition of two holes at different sites into the two-holes state y, $|f\alpha l\rangle\otimes|f\beta l'\rangle\Longrightarrow|0l\rangle\otimes|yl'\rangle$,

$$D^{y}_{ll',\alpha\beta}=\langle ly|\otimes\langle l'0\|H'\|f\alpha l'\rangle\otimes|f\beta l\rangle\ . \tag{4.10}$$

One can get the explicit form of the matrix elements $F^{yx}_{ll'}, G^{z}_{ll'}$, and $D^{y}_{ll'}$ from Eqs. (4.5), (4.7), (4.9), and (2.6) (see Ref. 16).

C. Second-order corrections

Here we derive a general form of corrections to the t-t'-J model. By applying the SW transformation (4.3), (4.4) to the Hamiltonian H' (4.5), (4.7), (4.9) one can get a generator and corrections to the Hamiltonian of the c singlet,[14]

$$\begin{aligned}\delta H_E&=-\sum_{ll'}M_{ll'}X^{cc}_{l}\hat{N}_{l'}\ ,\\ M_{ll'}&=\sum_{y}{}'\frac{|F^{f,y}_{ll'}|^2}{E_y-E_-}+\sum_{y}\frac{|F^{g,y}_{ll'}|^2}{E_y-E_-+\epsilon_g-\epsilon_f}\\ &\quad+\sum_{z}\frac{|G^{z}_{ll'}|^2}{E_z+E_0-E_--\epsilon_f}\ ,\end{aligned} \tag{4.11}$$

where $\hat{N}_l=X^{\uparrow\uparrow}_l+X^{\downarrow\downarrow}_l$.

Corrections to the hopping Hamiltonian of the c singlet (4.1) have the form[14]

$$\begin{aligned}\delta H_t=\sum_{lnl'\alpha\beta}\{\,&T^{N}_{lnl'}X^{f\alpha,c}_{l}X^{c,f\alpha}_{l'}\hat{N}_n\delta_{\alpha\beta}\\ &+T^{S}_{lnl'}X^{f\alpha,c}_{l}X^{c,f\beta}_{l'}(\sigma_{\alpha\beta}\mathbf{S}_n)\}\ ,\end{aligned} \tag{4.12}$$

where

$$\begin{aligned}&\mathbf{S}_l=(1/2)\sigma_{\alpha\beta}X^{\alpha\beta}_{l}\ ,\\ &T^{N}_{lnl'}=-\tfrac{1}{2}T^{c}_{lnl'}+\sum_{y}{}'x_yT^{y}_{lnl'}\ ,\\ &T^{S}_{lnl'}=T^{c}_{lnl'}+\sum_{y}{}'z_yT^{y}_{lnl'}\ ;\end{aligned}$$

here $x_y=\frac{1}{2}$ for singlets and $x_y=\frac{3}{4}$ for triplets, $z_y=1$ for singlets and $z_y=-\frac{1}{2}$ for triplets, and

$$\begin{aligned}T^{c}_{lnl'}&=D^{c}_{ln}D^{c}_{nl'}/(E_-+E_0-2\epsilon_f)\ ,\\ T^{y}_{lnl'}&=F^{y}_{ln}F^{y}_{nl'}/(E_y-E_-)\ .\end{aligned} \tag{4.13}$$

E_0 is the energy of the $|0\rangle$ state.

Corrections to the hopping Hamiltonian which have a form similar to (4.12) were considered by Psaltakis[21] on the basis of the Hubbard model. In Eqs. (4.11) and (4.13) we express the parameters M and T through the matrix elements without spin structure. They are connected with the primary matrix element as

$$\begin{aligned}&F^{x\beta,y}_{l\bar{l}',\alpha}=\delta_{\alpha\beta}F^{x,y}_{l\bar{l}'},\quad F^{x\beta,y}_{l\bar{l}',\alpha}=(2\beta)[m\alpha\bar{\beta}]F^{x,y}_{l\bar{l}'}\ ,\\ &\text{for } y=\text{singlet and triplet, respectively}\ ,\\ &G^{z,\alpha\beta\gamma}_{ll',\delta}=\delta_{\alpha\delta}\delta_{\beta\bar{\gamma}}G^{z}_{ll'}\ ,\end{aligned} \tag{4.14}$$

where $[m\alpha\bar{\beta}]=\langle 1/2\alpha|1/2\bar{\beta},1m\rangle$ are the Clebsch-Gordon coefficients, $m=\pm1,0$ are spin-1 projections, $\alpha,\beta=\pm\frac{1}{2}$ are the spin-$\frac{1}{2}$ projections, and $\bar{\beta}=-\beta$. Similar relations for D-matrix elements are given in the next section. One can see that the corrections (4.11), (4.12) to the t-t'-J Hamiltonian (4.1) depend on the filling ($\hat{N}$ term in δH_E and δH_t) and magnetic order ($\mathbf{S}$ term in δH_t). Such terms cannot be expressed through a simple direct hopping.

In Sec. V we will analyze quantitatively the relative magnitudes of the second-order corrections. The validity of the t-J model, as well as the correctness of the inclusion of hopping at the next neighbors is checked well by this analysis.

D. Superexchange interaction

In our approach the superexchange interaction arises in the second order of perturbation theory over the hopping of holes at a neighboring cluster and back. The situation is similar to the 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[10,18] in the fourth order of perturbation theory. From Eq. (4.9) one can get the generator of the SW transformation and superexchange term,

$$\begin{aligned}S&=-\sum_{ll'\alpha\beta,y}\frac{D^{y}_{ll',\alpha\beta}}{E_y+E_0-2\epsilon_f}\{X^{y,f\alpha}_{l}X^{0,f\beta}_{l'}-\text{H.c.}\}\ ,\\ \delta H^2=H_J&=\sum_{\langle ll'\rangle}(J_{ll'}\mathbf{S}_l\mathbf{S}_{l'}+Y_{ll'}\hat{N}_l\hat{N}_{l'})\ .\end{aligned} \tag{4.15}$$

Such a form (4.15) is more general than in the t-J model. First, there are interactions between all pairs of spins. Due to the rapid decrease of the constant $\{\lambda,\mu,\nu\}$, ($J_{\langle ll'\rangle_{2,3}}\sim10^{-2}J_{\langle ll'\rangle}$), one can omit all next-nearest-neighbor terms in Eq. (4.15) and get the Heisenberg term of the usual t-J Hamiltonian. Second, $Y_{ll'}\neq-(1/4)J_{ll'}$ because the hole may virtually hop into triplet states and back, i.e.,

$$\begin{aligned}J_{ll'}&=\sum_{y}x_y\frac{|D^{y}_{ll'}|^2}{E_y+E_0-2\epsilon_f}\ ,\\ Y_{ll'}&=-\sum_{y}z_y\frac{|D^{y}_{ll'}|^2}{E_y+E_0-2\epsilon_f}\ ,\end{aligned} \tag{4.16}$$

with $x_y=4$ and $z_y=1$ for $y=$singlet, $x_y=-2$ and $z_y=\frac{3}{2}$ for $y=$triplet. $D^{y}_{ll'}$ are connected with the matrix elements $D^{y}_{ll'\alpha\beta}$ as follows:

$$D^{y}_{ll',\alpha\beta}=(2\alpha)\delta_{\alpha\bar{\beta}}D^{y}_{ll'},\quad D^{y}_{ll',\alpha\beta}=[m\alpha\beta]D^{y}_{ll'}\ , \tag{4.17}$$

for $y=$singlet and triplet, respectively.

One can check that in the limit $t\Longrightarrow0$ the reduced matrix element $D^{y}_{ll'}$ is proportional to t and the superexchange constant $J_{ll'}$ has a contribution proportional to t^2. But such contributions from the singlet and the triplet two-hole states are canceled, and we get the 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 oxygen sites to the one- and two-holes state Hubbard operators on the cluster. For the problem of one hole over unit filling we established the general form of the low-energy t-t'-J model (4.1), the general form of the corrections to it (4.11), (4.12), and the general form of the spin interaction at unit filling (4.15). Now we will consider three limiting cases, all with special constraints on the Hilbert space of the problem. Such constraints simplify the mathematical treatments and provide the possibility to get results in an analytical form.

A. The case of $\Delta \ll U_d$

This case was considered by Lovtsov and Yushankai.[13] We include into this problem direct O-O hopping and make consideration more complete.

Such a limit ($U_d \Longrightarrow \infty$) pushes up in energy the state with double occupation of the copper site. Thus, one can ignore $|\psi\rangle$-singlet state (3.2). After such simplification diagonalization of the two-particle sector of the Hamiltonian (3.5) presents no problems,

$$H^2_{\rm loc}=\sum_l \left\{ E_- X_l^{c,c}+E_+ X_l^{b,b}+2\mu_0 t_p X_l^{\bar\varphi,\bar\varphi}+\tilde E_- \left[X_l^{\bar c,\bar c}+\sum_{m=\pm1,0} X_l^{t1m,t1m} \right] \right.$$
$$\left. +\tilde E_+ \left[X_l^{\tilde b,\tilde b}+\sum_{m=\pm1,0} X_l^{t2m,t2m} \right] -(\Delta+\mu_0 t_p) \sum_{m=\pm1,0} X_l^{\tau m,\tau m} \right\}, \tag{5.1}$$

where c,b are the lowest and highest singlets of the q-d sector, $\bar c,\tilde b$ are the lowest and highest $\bar q$-d singlets, $t1,t2$ are the lowest and highest $\bar q$-d triplets, and τ and $\bar\varphi$ are determined in Eqs. (3.2), (3.4). All energies are counted from ϵ_p (hereafter $\epsilon_p=0$). $E_\pm=-\Delta_2\pm R$, $\Delta_2=1/2(\tilde\Delta+3\mu_0 t_p)$, $R=(\tilde\Delta^2+8t^2\lambda_0^2)^{1/2}$, $\tilde E_\pm=-\tilde\Delta\pm R_1$, and $\tilde\Delta=(\Delta-\mu_0 t_p)/2$. New eigenstates are connected with the primary set of states (3.2), (3.4) as

$$|c\rangle=-a|\varphi\rangle+b|\chi\rangle,\quad |b\rangle=b|\varphi\rangle+a|\chi\rangle\ ,$$
$$|\bar c\rangle=U|\bar\chi\rangle-V|\bar\eta\rangle,\quad |\tilde b\rangle=V|\bar\chi\rangle+U|\bar\eta\rangle\ , \tag{5.2}$$
$$|t1\rangle=U|\bar\tau\rangle-V|\zeta\rangle,\quad |t2\rangle=V|\bar\tau\rangle+U|\zeta\rangle\ ,$$

where $b=[(R+\tilde\Delta)/2R]^{1/2}$, $a=[(R-\tilde\Delta)/2R]^{1/2}$, and U and V are determined after Eq. (3.8). The energies of the local states at $U_d\Longrightarrow\infty$ (5.1) for values of the hopping parameters $t=1.4$ eV, $t_p=0.7$ eV, and $\Delta=3.66$ eV are $E_-=-7.38$ eV (lowest singlet), $E_\tau=-4.68$ eV (next two-hole state triplet), and others considerably above.

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

$$E_c=E_-=-(\Delta+3\mu_0 t_p)/2-R\ ,$$
$$t_{ll'}=2t\lambda_{ll'}Vb(bU+\sqrt{2}Va)+t_p\mu_{ll'}(\sqrt{2}aV+Ub)^2/2\ . \tag{5.3}$$

Hopping parameters for the first neighbors at values of the parameters mentioned above are $t_1=0.43$ eV, $t_2=0.078$ eV, and $t_3=-0.074$ eV. One can see the important role of the direct O-O hopping. Its contribution to the full amplitude of hopping at the nearest neighbor is $\approx 50\%$ and it plays a major role for hopping at the next-nearest neighbor. Corrections to the energy and to the first hopping parameters 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 neighbors to the t-t'-J model is justified because corrections to them are small enough (9.6% and 14.4%, respectively).

B. The case $(U_d-\Delta)\ll U_d$

This case was considered by the authors[14] without O-O direct hopping. In Ref. 14 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 a rather simple form of the diagonalized Hamiltonian $H^2_{\rm loc}$,

$$H^2_{\rm loc}=\sum_l \left\{ E_- X_l^{c,c}+E_+ X_l^{b,b}-(\Delta+\mu_0 t_p) \sum_{m=\pm1,0} X_l^{\tau m,\tau m} \right.$$
$$\left. -(\Delta-\mu_0 t_p) \left[X_l^{\tilde\chi,\tilde\chi}+\sum_{m=\pm1,0} X_l^{\bar\tau m,\bar\tau m} \right] \right\},$$

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

$$|c\rangle=-a|\psi\rangle+b|\chi\rangle,\quad |b\rangle=b|\psi\rangle+a|\chi\rangle\ , \tag{5.4}$$

with $b=[(R+\tilde\Delta)/2R]^{1/2}$ and $a=[(R-\tilde\Delta)/2R]^{1/2}$. The explicit form of the parameters of the t-t'-J model is

$$E_c=E_-=-(U_d-3\Delta-\mu_0 t_p)/2-R\ ,$$
$$t_{ll'}=2t\lambda_{ll'}\sqrt{2}ba+t_p\mu_{ll'}b^2/2\ , \tag{5.5}$$

where $E_-=-7.38$ eV, $t_1=0.38$ eV, $t_2=0.03$ eV, $t_3=-0.057$ eV at $U_d=8$ eV, and $\Delta=3.65$ eV. One can see that direct O-O hopping is less important than for the case given in Sec. V A. It is evident, because part of the oxygen degrees of freedom is excluded from consideration. Correction to the energy is not so small as for the case given in Sec. V A. It is close to 13%; a correction to the first hopping is close to 4.0%. Thus, the t-J model may be valid. Inclusion of hopping at next neighbors re-

quires consideration of corrections in the form (4.12) because they are not relatively small ($\delta t_2/t_2 \simeq 300\%$, $\delta t_3/t_3 \simeq 90\%$). 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 Δ [for which $J \simeq 126$ meV (Ref. 22)] is close to 3.6 eV. Such a 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 (3.5) without any constraints on the Hilbert space. Let us put $(U_d-2\Delta)=-2\mu_0 t_p$. Such a choice of parameters leads to accidental degeneracy of the energies of the qq and dd singlets. The q-d singlet sector of the Hamiltonian (3.5) is written as

$$H^2_{\rm loc}=\sum_l \{[\, E_\psi X_l^{\psi,\psi}+E_\varphi X_l^{\varphi,\varphi}-(\Delta+\mu_0 t_p)X_l^{\chi,\chi} +2\sqrt{2}t\lambda_0(X_l^{\chi,\psi}+X_l^{\chi,\varphi}+\text{H.c.})]\}+\cdots , \quad (5.6)$$

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 $|c2\rangle=(1/\sqrt{2})(|\psi\rangle-|\varphi\rangle)$ does not hybridize with the qd singlet $|\chi\rangle$ (3.2). After diagonalization of $H^2_{\rm loc}$ we have

$$H^2_{\rm loc}=\sum_l \left\{ E_- X_l^{c1,c1}+E_0 X_l^{c2,c2}+E_+ X_l^{c3,c3}+2\mu_0 t_p X_l^{\bar\varphi,\bar\varphi}+\tilde E_- \left[X_l^{\bar c,\bar c}+\sum_{m=\pm1,0} C_l^{t1m,t1m} \right] +\tilde E_+ \left[X_l^{\bar b,\bar b}+\sum_{m=\pm1,0} X_l^{t2m,t2m} \right] -(\Delta+\mu_0 t_p)\sum_{m=\pm1,0} X_l^{\tau m,\tau m} \right\} , \quad (5.7)$$

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 (Refs. 9 and 12) is unjustified for this system. The states $|\bar c\rangle$, $|\bar b\rangle$, $|t1\rangle$, and $|t2\rangle$ are defined in Eq. (5.2),

$$|c1\rangle=-a(|\varphi\rangle+|\psi\rangle)/\sqrt{2}+b|\chi\rangle , \qquad |c3\rangle=b(|\varphi\rangle+|\psi\rangle)/\sqrt{2}+a|\chi\rangle , \quad (5.8)$$

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

$$E_{c1}\equiv E_-=-(U_d/4+2\mu_0 t_p)-R , \qquad t_{ll'}=2t\lambda_{ll'}(UV+ba)+t_p\mu_{ll'}(aV+bU)^2/2 . \quad (5.9)$$

The local level with energy E_- lies well below the others ($E_-=-9.81$ eV). The first excited two-hole state has the energy $E_\tau=-6.1$ eV. Hopping parameters are $t_1=0.53$ eV, $t_2=0.028$ eV, and $t_3=-0.076$ eV.

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. The 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. (5.9)]. As a result, correction to them is rather large $\approx 78\%$, and the t-t'-J model is not valid. The relative magnitude of terms with a 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 a 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 the 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. (5.6) 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 $H^2_{\rm loc}$ coincides completely with Eq. (5.7) but the eigenstates $|ci\rangle$ have the more general form

$$|ci\rangle=U_i|\psi\rangle+V_i|\varphi\rangle+W_i|\chi\rangle , \quad (6.1)$$

where the coefficients U_i, V_i, W_i are determined from a solution of a system of three linear equations. The energies E_-, E_0, E_+ are roots of the corresponding cubic equation. The effective hopping parameters are

$$t_{ll'}=2t\lambda_{ll'}(\sqrt{2}U_1U-W_1V)(\sqrt{2}V_1V-W_1U) +t_p\mu_{ll'}(\sqrt{2}V_1V-W_1U)^2/2 . \quad (6.2)$$

The 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[23–25] and a detailed analysis of the experiment.[6]

In Table II 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 it is close to 50%. Rela-

TABLE II. 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)	$E_f=-6.43$	$E_g=0.31$	$E_{\tilde{q}}=1.02$	
Two-hole local energies (eV)	$E_-=-9.85$	$E_0=-2.12$	$E_+=1.61$	$E_\tau=-6.12$
	$\tilde{E}_-=-5.41$	$\tilde{E}_+=1.33$	$E_{\tilde{\varphi}}=2.04$	

Neighbor number n	Direct hopping parameters t_n (eV)	Contribution of direct O-O hopping t_n^{pp} (eV)	Contribution of Cu-O hopping t_n^{pd} (eV)	Second-order corrections δt_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 $\lvert t_1/J\rvert$
3.02		126.4		4.18

tive 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 the 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 (4.12), 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 the 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. The 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 II the fundamental ratio $t_1/J=4.2$ for $U_d=8$ eV is presented. It only weakly depends on U_d and Δ. 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_2CuO_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 Δ 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 Δ as a function of U_d in the physically reasonable region: $\Delta\le U_d\le 12$ eV. We obtain that the reasonable region of Δ lies between 4.75 eV and 5.75 eV which is in complete agreement with the band calculations of Sushkov and Flambaum[26] but larger than the generally accepted value $\Delta=2.75$–3.75 eV.[6]

VII. INCLUSION OF V_{pd} AND U_p TERMS

Here we consider the role of the intrasite repulsion at the oxygen sites 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 (4.11), (4.12). Our aim is to get the renormalization of the first hopping integral and the charge-transfer energy due to the Hamiltonian ΔH [Eq. (2.2)]. Since we are interested in the renormalization of the lowest singlet parameters, we can omit all terms with antisymmetrical oxygen operators $\tilde{q}$. Using the representation (2.4) for q_l and $\tilde{q}_l$ operators we obtain

$$\Delta H = V_{pd}\sum_{l,l_1,l_2,\alpha,\beta} f_{l,l_1,l_2} n^d_{l\alpha} q^\dagger_{l_1,\beta} q_{l_2,\beta} + U_p \sum_{l,l_1,l_2,l_3} h_{l,l_1,l_2,l_3}(q^\dagger_{l,\uparrow}q_{l_1,\uparrow})(q^\dagger_{l_2,\downarrow}q_{l_3,\downarrow}) , \tag{7.1}$$

where $f_{l,l_1,l_2}=f(l_1-l,l_2-l)$, $h_{l,l_1,l_2,l_3}=h(l_1-l,l_2-l,l_3-l)$, and

$$\begin{aligned} f_{l,l_1,l_2} &= \sum_{\mathbf{k},\mathbf{k}'} f_{\mathbf{k},\mathbf{k}'} \exp[i\mathbf{k}(l_1-l)-i\mathbf{k}'(l_2-l)] , \\ h_{l,l_1,l_2,l_3} &= \sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''} h_{\mathbf{k},\mathbf{k}',\mathbf{k}''} \exp[\, i\mathbf{k}(l_1-l)-i\mathbf{k}'(l_2-l) \\ &\qquad +i\mathbf{k}''(l_3-l)] , \end{aligned} \tag{7.2}$$

with

$$\begin{aligned} f_{k,k'} &= 2\{\cos(k_x/2)\cos(k'_x/2)\cos[(k_x-k'_x)/2] \\ &\quad +(x\to y)\}(1+\gamma_{\mathbf{k}})^{-1/2}(1+\gamma_{\mathbf{k}'})^{-1/2} , \\ h_{k,k',k''} &= 2\{\cos(k_x/2)\cos(k'_x/2)\cos(k''_x/2) \\ &\quad \times\cos[(k_x+k'_x-k''_x)/2]+(x\to y)\} \\ &\quad \times(1+\gamma_{\mathbf{k}})^{-1/2}(1+\gamma_{\mathbf{k}'})^{-1/2}(1+\gamma_{\mathbf{k}''})^{-1/2} \\ &\quad \times(1+\gamma_{\mathbf{k}+\mathbf{k}'-\mathbf{k}''})^{-1/2} . \end{aligned} \tag{7.3}$$

Thus, we have the four-fermion terms with the compli-

cated relation between many states at different sites. All later arguments are based on a very rapid decrease of the constant f_{l,l_1,l_2} and h_{l,l_1,l_2,l_0} with $|l_n-l|$. Our calculation gives $f_0\equiv f(0,0)=0.9180$, $f_1=f(1,0)=f(0,1)=0.1343$, and $S_f\equiv\sum_{l_1\neq l_2\neq l}f_{l_1,l_2,l_3}=0.0092$; $h_0\equiv h(0,0,0)=0.29$ and $h_1\equiv h(1,0,0)=h(0,1,0)=h(0,0,1)=0.0096$. Therefore, one can turn from (7.1) to the effective Hamiltonian

$$\Delta H^{\rm eff}_{\rm loc}=V_{pd}\sum_{ll',\alpha,\beta}f_{ll'}n^d_{l\alpha}n^g_{l'\beta}+U_p\sum_{ll'}h_{ll'}n^g_{l\uparrow}n^g_{l'\downarrow}\ ,$$
$$\Delta H^{\rm eff}_{\rm hop}=V_{pd}f_1\sum_{\langle ll'\rangle,\alpha,\beta}n^d_{l\alpha}\{q^\dagger_{l,\beta}q_{l',\beta}+{\rm H.c.}\}$$
$$+U_ph_1\sum_{\langle ll'\rangle}(n^g_{l\uparrow}\{q^\dagger_{l,\downarrow}q_{l',\downarrow}+{\rm H.c.}\}$$
$$+n^g_{l\downarrow}\{q^\dagger_{l,\uparrow}q_{l',\uparrow}+{\rm H.c.}\})\ , \tag{7.4}$$

where in $\Delta H^{\rm eff}_{\rm loc}$, $f_{ll'}\equiv f_{l,l',l'}$, and $h_{ll'}\equiv h_{l,l',l',l'}$.

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

$$\Delta\epsilon_d=V_{pd}V^2\sum_{l\neq l'}f_{ll'}=V_{pd}V^2(2-f_0)\ , \tag{7.5}$$

for the q_l state, and

$$\Delta\epsilon_q=V_{pd}U^2(2-f_0)+U_pV^2(\tfrac{1}{2}-h_0)\ . \tag{7.6}$$

The numbers 2 and $\frac{1}{2}$ are the sums over all l' for $f_{l'l}$ and $h_{l'l}$, respectively. The coefficients U and V are defined after Eq. (3.8) by

$$R_1=(\bar\Delta^2+4t^2\lambda_0^2)^{1/2},\quad \bar\Delta=(\epsilon_q-\epsilon_d)/2\ . \tag{7.7}$$

Thus, Eqs. (7.4), (7.5), (7.6), and (7.7) are the system of equations, which can be solved numerically. After solving we have new values $\tilde U$ and $\tilde V$, consider one hole over unit filling and get the shift of the local energies of the additional hole.

The matrix elements of $\Delta H^{\rm eff}_{\rm hop}$ [Eq. (7.3)] produce the addition to the first hopping integral,

$$\Delta t_1=(-f_1V_{pd}\tilde UW_1+\sqrt{2}h_1U_p\tilde VV_1)(W_1\tilde U-\sqrt{2}V_1\tilde V)\ . \tag{7.8}$$

The matrix elements $\Delta D^\gamma_{ll'}$ which are essential for the constant J (4.16) are also derived and included into the calculations.

Different band calculations[23–25] give consistent magnitudes for V_{pd} and U_{pd}: $V_{pd}=1.2$ eV and $U_p=4$ eV. The calculations present no special problems.

Different contributions to the first hopping parameter t_1 are presented in Table III for $U_d=8.0$ eV and $\Delta=3.0$ eV. Inclusion of ΔH tends to decrease t_1. The ratio $t_1/J=3.38$, which is close to the results of the other works.[24,27]

Taking into account the additional Coulomb repulsions (V_{pd}, U_p) change the possible region of Δ at fixed J. For a reasonable region of U_d(5–11 eV) the charge-transfer energy varies in the narrow region 2.6–3.5 eV which coincides very well with the band calculations[25] and analysis of experiments.[6]

VIII. STABILITY OF THE SYSTEM

There are a few conditions which determine the stability of the system under study. One can take an analogy from the classical Hubbard system: The energy of two electrons at different sites ($\{1_l,1_{l'}\}$) 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 bandwidth wzt, where z is the number of neighbors and w is a 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

$$E^2+E^0-2E^1>0\ \text{ and }\ E^3+E^1-2E^2>0\ , \tag{8.1}$$

where the indexes $n=0,1,2,3$ denote the states with n holes at site. From this one can easily get the charge-transfer gap (an analog 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,

$$\Delta E(2,0-1,1)=E_-+E^0-2E_f=3.2\ \text{eV}>0\ , \tag{8.2}$$

for the above-mentioned parameters.

TABLE III. 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, and $\Delta=3.0$ 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 $\lvert t_1/J\rvert$	
	126.26		3.38	

An interesting quantity is also the difference between $(\{2_l,2_{l'}\})$ and $(\{3_l,1_{l'}\})$ states. On the basis of our approach one can solve the three-hole problem and analyze the energy spectrum of three-hole states. We considered the full set of these states (20), get the energy of the lowest ones, and obtain

$$\Delta E(3,1-2,2)=E^3+E_f-2E_-=2.7 \text{ eV} , \quad (8.3)$$

where E^3 is the energy of the lowest three-hole state. This energy difference $\Delta E(3,1-2,2)$ is also an analog 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 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 a consistent approach to the mapping of the three-band model to its low-energy limit. Following the idea of Zhang and Rice,[9] we expressed the primary Hamiltonian in terms of symmetrical and antisymmetrical oxygen states. Next, we turned to the terms of the local states with a certain number of particles and transition 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 next neighbors are not simple hopping due to the important role of the correction, which has a complicated structure.

Our approach allows one 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 Δ from the well-defined value of J at other fixed parameters of the three-band model. We have established that Δ varies in a narrow region of energies.

The lowest one-hole state for the undoped CuO_2 plane is [Eq. (3.8)]

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

The lowest two-hole singlet state for the doped CuO_2 plane is [Eq. (6.1)]

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

where $|d\alpha\rangle$ is the state of a hole at the copper with projection α; $|q\alpha\rangle$ 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, and $t_p=0.7$ 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 [Eqs. (9.1), (9.2)] which determine the probability of location of holes at the copper and the oxygen sites: $U=0.85$, $V=0.52$, $U_1=-0.38$, $V_1=-0.64$, and $W_1=0.67$.

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.

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