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Derivation and numerical study of the singlet-triplet model for cuprate superconductors

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We perform a low-energy reduction of the three-band Hubbard Hamiltonian (H_{3b}), keeping in the relevant Hilbert subspace not only local singlets (Zhang-Rice singlets), but also triplet states between Cu holes and O holes at the Wannier function of the same site, with x^2-y^2 symmetry. We solve exactly the resulting Hamiltonian H_T in a system of 2×2 unit cells. From the analytical dependence of the parameters of H_T and the numerical results, one can see that the local triplet states can be practically neglected for finite O-Cu on-site energy difference Δ, very large Cu on-site Coulomb repulsion U_d, and O-O hopping $t_{pp}=0$. This fact is in contrast with the mapping of H_{3b} to a one-band model using nonorthogonal singlets, which is very accurate when the Cu^+ configuration can be neglected. Although the amount of local triplet states in the low-energy eigenstates is in general small, it increases with t_{pp} and for large t_{pp} it is necessary to introduce higher-order corrections in the one-band model to accurately represent the low-energy physics. In all cases even when local triplets are not important, the t-J model should be supplemented with other terms, to describe the lowest-energy levels. We also discuss briefly the effect of nonbonding O orbitals.

I. INTRODUCTION

One of the most important problems concerning the low-energy properties of high-T_c superconductors and the mechanism of superconductivity is the reduction of the complex electronic structure of these materials, to a hopefully relatively simple effective Hamiltonian that describes accurately enough the ground state and the low-lying excitations. Experimental evidence[1] indicates that most of the holes reside in the orbitals included in the three-band Hubbard model H_{3b}.[2,3] However, while, for example, for the transport properties and the superconductivity, one is interested in energy scales < 0.1 eV, H_{3b} contains energies such as the on-site Cu Coulomb repulsion $U_d \sim 10$ eV.[4] One would like to integrate out the high-energy degrees of freedom by a suitable procedure.

Zhang and Rice[5] have first reduced H_{3b} to an effective t-J model. They assumed a ratio of O-Cu hopping to on-site energy difference $t_{pd}/\Delta \ll 1$ and showed that the singlet state constructed with a Cu hole and an O hole, at the Wannier function centered at the Cu site and with the same symmetry as the Cu orbital, has less energy than the corresponding triplet state. Retaining only the singlets, the mapping to the one-band model became possible. This procedure has been criticized because the effect of local triplet states is of the same order in t_{pd}/Δ (Ref. 6) and in fact $t_{pd}/\Delta \sim 0.4$ (Ref. 4) is not so small. However, several analytical calculations using the *cell perturbation method*, which explicitly takes into account covalency effects, have shown that in fact the Zhang-Rice singlet is stabilized by a sizable t_{pd}.[7–12] The advantage of this method is that the *cell* composed of the Cu orbital and the above-mentioned O Wannier function with all local interactions is solved exactly, and that perturbations in the intercell hopping and interactions converge rapidly due to large stabilization energy of the ground state of the cell, which for two holes is essentially the Zhang-Rice singlet. Belinicher and Chernyshev have carried out a detailed analysis of the reduction to a one-band t-J model including all relevant interactions.[12]

Another approach to obtain a simpler effective Hamiltonian is to perform a canonical transformation which eliminates t_{pd} in H_{3b}.[6,13–15] The resulting spin-fermion model H_{sf} contains Cu spins and O fermions, Cu-O exchange J_K, Cu-Cu exchange J, and O-O hopping combined with Cu-O spin-flip t_1 (t_2) if fluctuations via Cu^+ (Cu^{3+}) dominate. Although for realistic values of t_{pd} the perturbation series converges slowly, an accurate representation of H_{3b} and its photoemission spectra has been obtained with H_{sf} *provided* that its parameters are adjusted to fit the energy levels of a CuO_4 cluster.[13] In this way, as in the cell perturbation method, the local problem is solved (almost) exactly. In turn, H_{sf} can be mapped into a generalized t-J model[16] either using the above orthogonal Wannier functions, or the mapping through nonorthogonal singlets used before by Zhang.[17] It has been shown that when $J=t_{pp}=0$, the mapping using orthogonal (non-orthogonal) Zhang-Rice states is almost exact (exact) when $t_2=0$ ($t_1=0$).[16,17] The second fact has been confirmed by exact diagonalization in a Cu_4O_8 cluster with periodic boundary conditions.[18,19] However, since in this cluster there are only three (instead of four) independent Wannier functions, the accuracy of the mapping using orthogonal singlets could not be reproduced. In the present work we *first* change the basis to orthogonal O Wannier functions centered around Cu ions and *then* take four unit cells for the numerical study.

Except for certain ideal, unrealistic parameters, there is always a certain admixture of local singlets with lo-

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cal triplets, which affects the quality of the mapping to a one-band model. If the admixture is small, it can be included in the one-band model perturbatively. In the present work we include the triplets explicitly and study their effect on the mappings to effective one-band models, such as the one-band generalized Hubbard[10] and the generalized t-J model,[8,12] where the triplet states were neglected. We derive a singlet-triplet Hamiltonian H_T from H_{3b}, we study the dependence of the parameters of H_T on those of H_{3b}, and we calculate the effects of the triplets on the electronic structure solving exactly a 2×2 cluster with 25% doping (five holes) after eliminating the states with zero hole occupancy at any site by means of a canonical transformation. The singlet-triplet model has been studied previously for infinite U_d and $t_{pp}=0$ using analytical approximations.[9] We focus our study on the behavior of the energy levels and degree of local singlet-triplet admixture. We also discuss briefly the effect of the nonbonding O orbitals. To discuss the mapping of other properties, like photoemission spectra, it is necessary to address the transformation of the corresponding operators to obtain the correct spectral weight.[10,11,13,19,20] This is beyond the scope of the present work.

Another point of interest addressed here concerns the nature, magnitude, and sign of the corrections to the effective t-J model. It has been recently found that a small term t'' which combines next-nearest-neighbor hopping with nearest-neighbor spin-flip stabilized a superconducting resonance-valence-bond state for realistic t and J, if t'' has the opposite sign as the corresponding term obtained from a canonical transformation of the Hubbard model.[21] This appropriate sign has been obtained for $t_{pp}/t_{pd}\sim 0.6$ from the mapping using nonorthogonal singlets[16] and numerical fitting of the levels.[18]

In Sec. II we briefly explain the singlet-triplet model H_T and its derivation from H_{3b}. In Sec. III we show the resulting energy levels of the cluster, compare them with the corresponding levels obtained neglecting the triplet states, and explain the results on the basis of the dependence of the parameters of H_T with those of H_{3b}. Section IV contains the conclusions.

II. THE SINGLET-TRIPLET MODEL

We start from the three-band model in the form

$$H_{3b}=\Delta\sum_j p^\dagger_{j\sigma}p_{j\sigma}+U_d\sum_i d^\dagger_{i\uparrow}d_{i\uparrow}d^\dagger_{i\downarrow}d_{i\downarrow}+t_{pd}\sum_{i\delta\sigma}(p^\dagger_{i+\delta\sigma}d_{i\sigma}+\text{H.c.})-t_{pp}\sum_{j\gamma\sigma}p^\dagger_{j+\gamma\sigma}p_{j\sigma}. \quad (1)$$

The sum over i (j) runs over all Cu (O) ions. The vector δ (γ) connects a Cu (O) site with one of its four nearest O atoms. The operator $d^\dagger_{i\sigma}$ ($p^\dagger_{j\sigma}$) creates a hole with symmetry $d_{x^2-y^2}$ (p_σ) at site i (j) with spin σ. The phases of half of the orbitals have been changed in such a way that for all δ and γ, t_{pd}, $t_{pp}>0$. The intratomic O Coulomb repulsion U_p and the interatomic Cu-O repulsion U_{pd} have been neglected for simplicity. For one added hole, the main effect of the latter is to renormalize Δ.[12]

The first step in the cell perturbation method[8,10,12] is to change the basis of the O orbitals to linear combinations which hybridize ($\alpha_{k\sigma}$) and do not hybridize ($\gamma_{k\sigma}$) with $d_{k\sigma}$ orbitals, due to the term in t_{pd} in each point $\mathbf{k}$ of the reciprocal space. The Wannier functions of the $\alpha_{k\sigma}$ are centered at the Cu sites and may be written in the form:[10]

$$\alpha_{i\sigma}=\frac{1}{N}\sum_k e^{-i\mathbf{k}\cdot\mathbf{R}_i}[1+\tfrac{1}{2}\cos(k_xa)+\tfrac{1}{2}\cos(k_ya)]^{-\frac{1}{2}}\times\sum_m e^{i\mathbf{k}\cdot\mathbf{R}_m}\frac{1}{2}\sum_\delta p_{i+\delta\sigma}. \quad (2)$$

After the change of basis one obtains

$$H_{3b}=\sum_i H_i+H_{\text{hop}}, \quad (3)$$

with

$$H_i=[\Delta-\mu(0)t_{pp}]\sum_\sigma \alpha^\dagger_{i\sigma}\alpha_{i\sigma}+[\Delta+\mu(0)t_{pp}]\sum_\sigma\gamma^\dagger_{i\sigma}\gamma_{i\sigma}+U_d d^\dagger_{i\uparrow}d_{i\uparrow}d^\dagger_{i\downarrow}d_{i\downarrow}+2t_{pd}\lambda(0)\sum_\sigma(d^\dagger_{i\sigma}\alpha_{i\sigma}+\text{H.c.}), \quad (4)$$

$$H_{\text{hop}}=2t_{pd}\sum_{i,l\neq 0}\lambda(l)d^\dagger_{i+l\sigma}\alpha_{i\sigma}-t_{pp}\left[\sum_{i,l\neq 0}\mu(l)(\alpha^\dagger_{i+l\sigma}\alpha_{i\sigma}-\gamma^\dagger_{i+l\sigma}\gamma_{i\sigma})+\nu(l)(\alpha^\dagger_{i+l\sigma}\gamma_{i\sigma}+\text{H.c.})\right], \quad (5)$$

and the functions of the lattice vectors λ, μ, and ν are given in Ref. 12. They decay rapidly with increasing argument and as a consequence, most of the original hoppings and interactions are contained in $\sum_i H_i$, which is solved exactly. In our 2×2 cluster with periodic boundary conditions, all $\nu\equiv 0$ and the nonbonding $\gamma_{i\sigma}$ orbitals decouple completely.

In the standard reduction of H_{3b} to a one-band model,[8,10,12] one usually retains only the ground state of the cell Hamiltonian H_i for zero, one, or two holes in the cell [see Eqs. (18) and (19) below]. These states are mapped, respectively, into the following states of the one-band Hubbard model at site i, namely, $|0\rangle$, $c^\dagger_{i\sigma}|0\rangle$, and $c^\dagger_{i\uparrow}c^\dagger_{i\downarrow}|0\rangle$.[10] Eliminating the states of no hole occupancy by means of standard methods, one would obtain an effective t-J model.[8,12] Here, however, we will retain at this stage still all three states, and in addition, for two holes, we also retain the triplet states between Cu and bonding O orbitals. We represent these states using boson operators b_{iM}, depending on the spin projection $M=1,0,-1$. For example:

$$\alpha_{i\uparrow}^{\dagger}d_{i\uparrow}^{\dagger}|0\rangle = b_{i1}^{\dagger}|0\rangle. \qquad (6)$$

Also, the singlet ground state is represented here as $a_i^{\dagger}c_{i\uparrow}^{\dagger}c_{i\downarrow}^{\dagger}|0\rangle$ where a_i is another boson operator and the $c_{i\sigma}$ are fermion operators. Similarly, the ground states of H_i for zero and one particles are represented by $a_i^{\dagger}|0\rangle$ and $a_i^{\dagger}c_{i\uparrow}^{\dagger}|0\rangle$. Thus, the constraint

$$a_i^{\dagger}a_i + \sum_M b_{iM}^{\dagger}b_{iM} = 1 \qquad (7)$$

should be satisfied and $a_i^{\dagger}a_i = 1$ for all i indicates a perfect mapping to a one-band model. This bosonic representation has no great advantages if one is solving exactly a small system. However, if the bosons are allowed to condense and the terms in U and U_T below are treated within the slave-boson formalism,[22] one has a simple mean-field solution of the problem which is also superconducting if the bosons b are condensed in some direction.

After evaluating $H_{\rm hop}$ in the restricted basis, we obtain the following singlet-triplet Hamiltonian:

$$H_T = H_1 + H_2 + H_3, \qquad (8)$$

with

$$H_1 = U\sum_i a_i^{\dagger}a_i n_{i\uparrow}n_{i\downarrow} + \sum_{il\sigma} c_{i+l\sigma}^{\dagger}c_{i\sigma}\Big\{ t_{AA}^l(1-n_{i,-\sigma})(1-n_{i+l,-\sigma}) + t_{AB}^l[n_{i,-\sigma}(1-n_{i+l,-\sigma}) + n_{i+l,-\sigma}(1-n_{i,-\sigma})] + t_{BB}^l n_{i,-\sigma}n_{i+l,-\sigma}\Big\} a_{i+l}^{\dagger}a_{i+l}a_i^{\dagger}a_i, \qquad (9)$$

$$H_2 = U_T\sum_{iM} b_{iM}^{\dagger}b_{iM} + \sum_{il\sigma} t_d^l c_{i+l,\sigma}^{\dagger}c_{i\sigma}(2b_{i,2\sigma}^{\dagger}b_{i+l,2\sigma} + b_{i,0}^{\dagger}b_{i+l,0})a_{i+l}^{\dagger}a_i + \sum_{il\sigma}\sqrt{2}t_d^l c_{i+l,-\sigma}^{\dagger}c_{i\sigma}(b_{i,2\sigma}^{\dagger}b_{i+l,0} + b_{i,0}^{\dagger}b_{i+l,-2\sigma})a_{i+l}^{\dagger}a_i + \sum_{il\sigma} t_c^l\left[c_{i+l,\sigma}^{\dagger}c_{i\sigma}^{\dagger}(1-n_{i+l,-\sigma})a_{i+l}^{\dagger}a_{i+l}a_i^{\dagger}b_{i,2\sigma} + \frac{1}{\sqrt{2}}c_{i+l,\sigma}^{\dagger}c_{i,-\sigma}^{\dagger}(1-n_{i+l,-\sigma})a_{i+l}^{\dagger}a_{i+l}a_i^{\dagger}b_{i,0} + \text{H.c.}\right], \qquad (10)$$

$$H_3 = \sum_{il\sigma} t_e^l\left[c_{i+l\sigma}^{\dagger}c_{i\sigma}^{\dagger}n_{i+l,-\sigma}a_{i+l}^{\dagger}a_{i+l}a_i^{\dagger}b_{i,2\sigma} + \frac{1}{\sqrt{2}}c_{i+l\sigma}^{\dagger}c_{i,-\sigma}^{\dagger}n_{i+l,-\sigma}a_{i+l}^{\dagger}a_{i+l}a_i^{\dagger}b_{i,0} + \text{H.c.}\right], \qquad (11)$$

where H_1 contains only the singlet ground state for each doubly occupied cell. For $a_i^{\dagger}a_i = 1$ for all i, it reduces to the generalized one-band Hubbard model derived previously.[10,11] Similarly H_2 contains only local triplets, while H_3 hybridizes local singlets with local triplets.

The matrix elements can be calculated straightforwardy from the eigenstates of H_i.[11,12] Those involving the triplet states are

$$t_c^l = 2t_{pd}\lambda(l)(\cos^2\phi - \sin^2\phi) + t_{pp}\mu(l)\sin\phi\cos\phi, \qquad (12)$$

$$t_d^l = -2t_{pd}\lambda(l)\sin\phi\cos\phi - \tfrac{1}{2}t_{pp}\mu(l)\cos^2\phi, \qquad (13)$$

$$t_e^l = 2t_{pd}\lambda(l)(A_3\cos^2\phi - A_2\sin^2\phi) + t_{pp}\mu(l)\left[\frac{A_1}{\sqrt{2}}\cos^2\phi + A_2\sin\phi\cos\phi\right]. \qquad (14)$$

Here the coefficients A_i are all positive and describe the singlet ground state of H_i for two holes,

$$|i2\rangle = \left[\frac{A_1}{\sqrt{2}}(d_{i\uparrow}^{\dagger}\alpha_{i\downarrow}^{\dagger} - d_{i\downarrow}^{\dagger}\alpha_{i\uparrow}^{\dagger}) - A_2\alpha_{i\uparrow}^{\dagger}\alpha_{i\downarrow}^{\dagger} - A_3 d_{i\uparrow}^{\dagger}d_{i\downarrow}^{\dagger}\right]|0\rangle. \qquad (15)$$

Similarly for one hole,

$$|i\sigma\rangle = (\cos\phi\ d_{i\sigma}^{\dagger} - \sin\phi\ \alpha_{i\sigma}^{\dagger})|0\rangle. \qquad (16)$$

The meaning of the different matrix elements is the following: The superscript l denotes the distance between the two sites involved in the hopping. t_{AA}^l describes the hopping of a hole of a singly occupied site to a site without holes. The hopping of a hole of a singlet (triplet) to a site without holes, and the reverse process is t_{AB}^l (t_c^l). The hopping from a singlet to a singly occupied site, leaving in the latter site a singlet (triplet with maximum spin projection) is t_{BB}^l (t_e^l). Finally, the hopping from a triplet with maximum spin projection to a singly occupied site leaving in the latter site a singlet (triplet with maximum spin projection) is t_e^l (t_d^l). Matrix elements involving triplets with projection zero are related to those already mentioned by symmetry.

H_T generalizes to $U_d \neq \infty$ and $t_{pp} \neq 0$ the Hamiltonian studied previously.[9] It describes the states of the lowest energy of H_{3b}, integrating out high-energy states in the scale of U_d and roughly $(\Delta^2 + 8t_{pd}^2)(1/2)$.

We want to address here the question of to what extent the triplet can be eliminated performing a further low-energy reduction.

III. RESULTS

A measure of the singlet-triplet mixing is given by the quotient between the nearest-neighbor hopping t_e [see

Eq. (11)] and the average energy difference between triplets and singlets $U_T - U$. This quotient is represented in Fig. 1 as a function of Δ. For $U_d = \infty$, this was already shown in Ref. 8. The effect of the O-O hopping t_{pp} is mainly to increase t_e (although it also increases $U_T - U$) and then to increase the amount of local triplet states in the low-energy manifold and to deteriorate the mapping to a one-band model. For $t_{pp} = 0$ and very large U_d and Δ, the singlet-triplet mixing is very low. From Eqs. (14) and (15), it is clear that the largest component of the singlet A_1 does not contribute to t_e^l when $t_{pp} = 0$. This agrees with the result of Ref. 16. For infinite U_d, $U_T - U$ decreases with Δ as $1/\Delta$, while if $t_{pp} = 0$ [$t_{pp} \neq 0$), $t_e^l \sim 1/\Delta^3$ ($t_e^l \sim t_{pp}\mu(l)/\sqrt{2}$] for large Δ [see Eq. (14) and Fig. 2]. As a consequence of the different behavior of t_e^l for large U_d and Δ, in this limit the mapping to a one-band model is very good for $t_{pp} = 0$, while it is the worst limit when $t_{pp} \neq 0$ (see Fig. 1 for $\Delta \sim 10$). However, for finite U_d, the amount of Cu^{3+} states increases with Δ and then $U_T - U$ also increases and the quotient $|t_e^l|/(U_T - U)$ passes through a maximum as a function of Δ. From Figs. 1 and 2 and this discussion it is clear that the effect of a finite U_d, neglected in previous work,[8,9] can modify dramatically the singlet-triplet mixing and thus the quality of the mapping to a one-band model.

In order to estimate the effects of the nonbonding O orbitals $\gamma_{i\sigma}$, not included in H_T, we have calculated the hopping matrix element between a state containing a local two-particle singlet of the Zhang-Rice type [Eq. (15)] and a state containing the following two-particle singlet:

$$|i2'\rangle = \frac{1}{\sqrt{2}}(\gamma_{i\uparrow}^\dagger|i\downarrow\rangle - \gamma_{i\downarrow}^\dagger|i\uparrow\rangle), \tag{17}$$

where $|i\sigma\rangle$ is given by Eq. (19).

The result for nearest-neighbor hopping is

$$t_\gamma = t_{pp}\nu(1,0)\left(\frac{A_1}{2}\cos\phi + \frac{A_2}{\sqrt{2}}\sin\phi\right). \tag{18}$$

The quotient between t_γ and the energy difference between both states is represented in Fig. 3. Comparing with Fig. 1, we see that in spite of the fact that the states involving nonbonding orbitals lie lower in energy than the local triplet states, the corrections introduced by the nonbonding orbitals to the effective one-band model are smaller in magnitude than the correction due to triplet states.

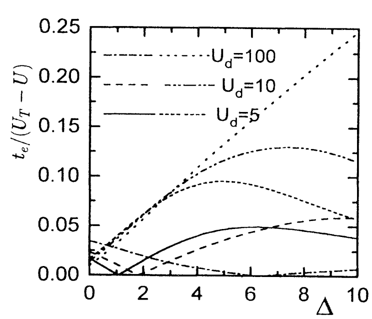

FIG. 1. Ratio of the nearest-neighbor singlet-triplet hopping [t_e^l for $l = (1,0)$] and the on-site triplet-singlet energy difference, as a function of Δ for different values of U_d and two values of t_{pp}: $t_{pp} = 0$ (three lower curves for $\Delta = 5$) and $t_{pp} = 0.5$.

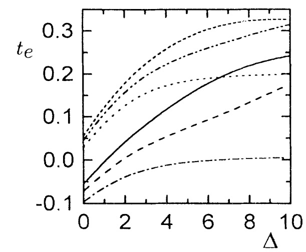

FIG. 2. Singlet-triplet hopping for the same parameters as Fig. 1.

If one wishes to retain only the Hilbert space of a one-band model, local triplet states and nonbonding O orbitals should in general be included as virtual states in a perturbative expansion leading to the one-band Hamiltonian (using the equations of Sec. II, this procedure is straightforward). When the Hilbert space retained is that of the t-J model (i.e., if also the states $|0\rangle$ of nc hole occupancy are eliminated), other terms in addition to the nearest-neighbor hopping and exchange appear. One of them is a three-site term of the form,

$$H_{t''} = t'' \sum_{i\delta\neq\delta'\sigma} c_{i+\delta'\sigma}^\dagger c_{i+\delta\sigma}(\tfrac{1}{2} - 2\mathbf{S}_i \cdot \mathbf{S}_{i+\delta}), \tag{19}$$

where δ, δ' are nearest-neighbor lattice vectors. It is a next-nearest-neighbor hopping via a singly occupied nearest-neighbor site which carries a singlet in the intermediate state. This three-site term has been found to be important to fit numerically the energy levels of a Cu_4O_8 cluster[18] and to stabilize a superconducting resonance-valence-bond (RVB) state in a 4×4 cluster.[21] The sign of t'' necessary to obtain the superconducting RVB state

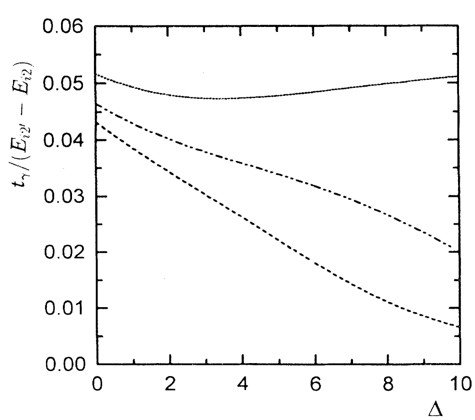

FIG. 3. Ratio of the nearest-neighbor hopping between Zhang-Rice states and states involving nonbonding singlets (see text) and the corresponding energy difference as a function of Δ for three different values of U_d.

is opposite to that arising from a canonical transformation of the Hubbard model.[21] The latter sign is positive in our representation (but negative in that of Ref. 21).[25]

The next-nearest-neighbor hopping t' is already present in H_T. It changes sign with t_{pp} as seen in Fig. 4, and is important for the shape of the Fermi surface and magnetic properties.[16,24] Our results agree qualitatively with previous studies of these terms.[8,16,24,25] When the local triplet states are eliminated from the Hilbert space, the correction to t' in second order in t_e is $-t_e^2/[2(U_T-U)]$ and

$$t'' = \frac{t_{AB}^2}{U} - \frac{t_e^2}{2(U_T-U)}, \qquad (20)$$

where the first term arises from the elimination of the no hole states just as in the transformation from the Hubbard model. Numerically[18] and from a mapping using nonorthogonal singlets[16] it has been found that t'' changes sign as a function of t_{pp}. In general Eq. (20) gives a positive sign. However, for some parameters ($U_d \sim 10$, $\Delta \sim 6$), we also obtain a change of sign as a function of t_{pp} (for $t_{pp} \sim 0.6$). In lowest order, the O nonbonding states do not correct t' and t''. To obtain a more quantitative estimate of the small term t'', particularly for large values of t_{pp}, it is necessary to add higher-order corrections, the effects of O-O repulsion, Cu-O repulsion, and eventually other excited states of the cell Hamiltonian H_i neglected here.

We have considered the Hamiltonian H_T defined by Eqs. (8) to (16) in a system of 2×2 unit cells, with periodic boundary conditions and five holes (25% doping). In order to reduce the size of the Hilbert space, we have eliminated the states with no hole occupancy at any cell by means of a standard canonical transformation. This introduces several terms in the Hamiltonian. The most important are Cu-Cu superexchange of magnitude $J = 4t_{AB}^2/U - 2t_c^2/U_T$ and three-site hopping terms. Although the cluster is small, we expect that (except for the form of the Wannier functions already discussed and taken into account and the absence of nonbonding orbital) the finite-size effects for the low-energy part of the different models are equivalent, so that they do not affect the validity of the conclusions regarding the mapping of the low-energy levels.[16,18] Note that when the mapping of the spin-fermion model to the t-J is exact (see Sec. I) in the thermodynamic limit, it is also exact in the 2×2 cluster as shown by previous numerical work.[19]

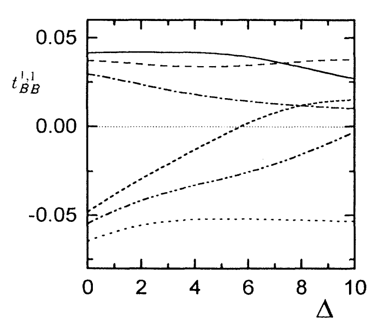

FIG. 4. Next-nearest-neighbor hopping as a function of Δ for $t_{pd} = 1$, and different values of U_d and t_{pp} (from bottom to top for $\Delta \sim 0$) $t_{pp} = 0.5$ and $U_d = 100$, 10, 5, $t_{pp} = 0$ and $U_d = 100$, 10, 5.

We fix the unit of energy as $t_{pd} = 1$. In Fig. 5 we show the resulting energy levels of the system for $t_{pp} = 0.2$, $U_d = 10$, and $\Delta = 4$, and compare them with the corresponding result for the one-band model H_1 with all $a_i^\dagger a_i = 1$. These energy levels have been shifted rigidly in order that the average energy of the low-lying energy levels is the same. All the eigenstates of H_T which have correspondence with an eigenstate of H_1 (the lowest nine in Figs. 5 and 6), have mainly local singlet character (see Fig. 7), while the remaining eigenstates of H_T have mainly local triplet character. Note that in spite of the fact that the difference between the highest level of mainly local singlet character (the quartet of M_2^4 symmetry[23]) and the lowest level of mainly local triplet character, is lower than the energy band spanned by the states of mainly local singlet character, the energy of the latter is well reproduced by H_1 with $a_i^\dagger a_i = 1$ (neglecting completely the triplet contribution). This is due to the fact that H_3 is small, as we have explained at the beginning of this section.

Increasing t_{pp}, the amount of triplet states in the low-energy manifold increases, and as shown in Fig. 6, it is not possible to obtain a quantitative agreement with the levels of H_T using the one-band model H_1 alone. The difference with Fig. 5 can be understood in terms of the larger value of the singlet-triplet matrix element t_e with increasing t_{pp} as shown in Fig. 1. The rightmost parts of Figs. 5 and 6 do not contain corrections due to triplet states as virtual states. Including the correction $-t_e^2/2(U_T-U)$ for t' and t'', and $-2t_c^2/U_T$ for J, there is a noticeable improvement in the comparison for the lowest five energy levels. Also the ordering of all energy levels is corrected. The highest energy levels of the local singlet manifold are more affected by the mixing with the triplets and corrections of higher order in t_{pp} seem

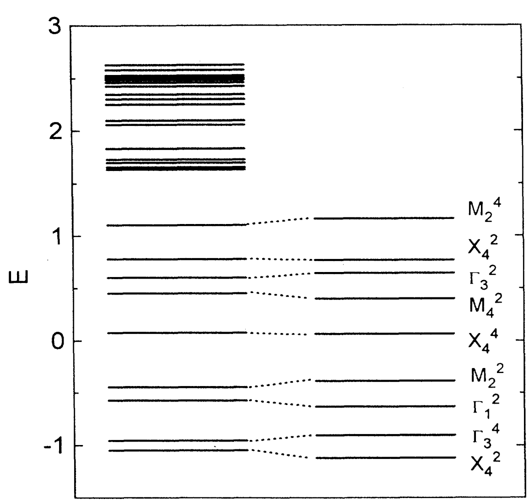

FIG. 5. Energy spectrum of H_T (left) and H_1 with all $a_i^\dagger a_i = 1$ (right) for $U_d = 10$, $\Delta = 4$, $t_{pd} = 1$, $t_{pp} = 0.2$ Ref. 23.

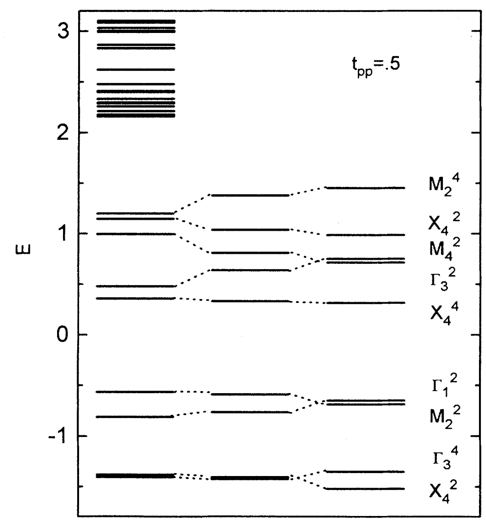

FIG. 6. Left and right columns, same as Fig. 5 with $t_{pp} = 0.5$. Middle column: result for H_1 including corrections due to singlet-triplet admixture.

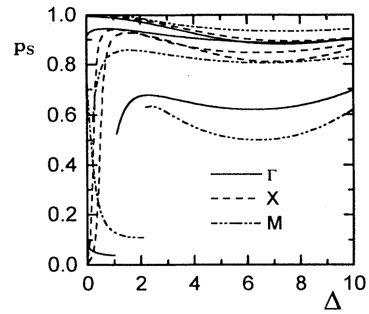

FIG. 7. Amount of local singlet character of the eigenstates of the low-energy manifold, as a function of Δ for $U_d = 10$, $t_{pd} = 1$, $t_{pp} = 0.5$.

necessary to obtain a more quantitative agreement with the energy levels of H_T.

In Fig. 7 we show the amount of singlet character p_S of the states of the low-energy manifold. This amount increases for energies near the ground-state energy. For the four levels of lowest energy $p_S \gtrsim 90\%$. At low Δ, for the levels of highest energy within the low-energy manifold, there is a crossing of energy levels because the Cu^{2+} configuration becomes unstable against Cu^{+}.

IV. CONCLUSIONS

We have studied the effect of local triplet states on the electronic structure of the CuO_2 planes and on the mapping to one-band models using orthogonal O Wannier functions. The mapping is very accurate when the configuration Cu^{3+} can be neglected (large U_d) and the O-O hopping $t_{pp} = 0$. For realistic values of U_d and t_{pp}, local triplet states are present in the low-energy manifold and should be included perturbatively if a description in terms of a one-band model is wished. The perturbative corrections can be performed in a systematic way from the Hamiltonian H_T derived in Sec. II. The effect of t_{pp} is different if nonorthogonal Wannier functions are used in the mapping.[16]

The effect of states containing nonbonding orbitals is smaller than that of the local triplet states.

Even neglecting the triplet states, the reduction to a generalized t-J model contains nearest-neighbor hopping and three-site terms which modify the physics of the *bare* t-J model. These conclusions agree with previous analytical results obtained using the spin-fermion model as an intermediate step of the mapping from the three-band Hubbard model to a generalized t-J model using orthogonal singlets.[16,18] The dependence of the next-nearest-neighbor hopping t' on the parameters of the three-band model agrees with different previous studies.[8,16,24,4] Concerning the three-site term t'' [Eq. (23)], there are some differences between the results of the mapping using nonorthogonal singlets, which predicts a change of sign as a function of t_{pp} for realistic values of the other parameters,[16,21] and the present results, for which the change of sign occurs in a more restricted region of parameters.

In the present study we have not included Cu-O repulsion U_{pd} and intratomic O repulsion U_p. The effect of both terms is to introduce interactions between neighboring local singlets, and new corrections to the hopping and three-site terms.[7] A very large U_{pd} might lead to a breakdown of the one-band model.[7]

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