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Effective Hamiltonian for cuprate superconductors

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We compare numerical results of O and Cu occupations and optical and magnetic excitations for the three-band Hubbard model in a Cu_4O_8 cluster, with those obtained with an effective Hamiltonian $H_{\rm eff}$ in which the Cu-O hopping t_{pd} is eliminated by means of a canonical transformation. This transformation up to order t_{pd}^4 is not quantitatively valid when the relevant energy differences are of the order of $\sqrt{8}\, t_{pd}$ or less. However an $H_{\rm eff}$ with the form of the second-order one, but which retains all higher-order terms contained in a CuO_4 (Cu_2O_7) cluster for zero or one added hole (one added electron) to the undoped system, leads to a very good agreement with the results using the full Hilbert space. This $H_{\rm eff}$ makes possible the numerical study of the three-band Hubbard model for realistic parameters, using larger clusters.

I. INTRODUCTION

Experimental evidence about the symmetry of holes in high-T_c superconductors,[1,2] as well as constrained-density-functional calculations[3,4] support the following model to describe the electronic structure of superconducting CuO_2 planes:[5,6]

$$H = H_0 + H_1 + H_2, \tag{1}$$

$$\begin{aligned} H_0 = {} & \epsilon_d \sum_{i\sigma} d^\dagger_{i\sigma} d_{i\sigma} + (\epsilon_d + \Delta) \sum_{j\sigma} p^\dagger_{j\sigma} p_{j\sigma} \\ & + U_d \sum_i d^\dagger_{i\uparrow} d_{i\uparrow} d^\dagger_{i\downarrow} d_{i\downarrow} + U_p \sum_j p^\dagger_{j\uparrow} p_{j\uparrow} p^\dagger_{j\downarrow} p_{j\downarrow} \\ & + U_{pd} \sum_{i\delta\sigma\sigma'} d^\dagger_{i\sigma} d_{i\sigma} p^\dagger_{i+\delta\sigma'} p_{i+\delta\sigma'}, \end{aligned} \tag{2}$$

$$H_1 = t_{pd} \sum_{i\delta\sigma} [p^\dagger_{i+\delta\sigma} d_{i\sigma} + \text{H.c.}], \tag{3}$$

$$H_2 = -t_{pp} \sum_{j\gamma\sigma} p^\dagger_{j+\gamma\sigma} p_{j\sigma}. \tag{4}$$

$d^\dagger_{i\sigma}$ creates a hole with spin σ on the Cu $3d_{x^2-y^2}$ orbital at site i. $p^\dagger_{j\sigma}$ creates a hole with spin σ on the O orbital at site j which points towards its nearest-neighbor Cu atoms. $i+\delta (j+\gamma)$ labels the four O atoms nearest to the Cu (O) atom at site i (j). The phases of half of the d and p orbitals have been changed in such a way that t_{pd} and t_{pp} are positive and independent of δ and γ, respectively.[7]

This model has been used to explain the pairing mechanism,[8–11], electronic structure,[12] and angle resolved photoemission experiments[13] in high-T_c superconductors. The pairing mechanism has been extended to BiO_3 based superconductors[7,14] and n-type superconductors.[11,15,16]. The shortcoming of the three-band Hubbard model described above is its large Hilbert space, since at present strong-correlation effects can be properly taken into account by numerical methods and the largest cluster for which the ground state of H can be obtained exactly contains only four unit cells.[17–20] The small degree of covalency suggested by the experimentally measured Cu valence[21] and the relatively high value of the localized magnetic moment[22] seems to justify the perturbative treatments in H_1 that can be found in the literature,[23,24] in which high-energy excited states are projected out of the relevant Hilbert space. A further simplification of the resulting effective Hamiltonian $H_{\rm eff}$ (including terms up to order t_{pd}^2 and with $t_{pp} = 0$) leads to the widely studied t-J model.[25]

In the present work we investigate to what extent such an $H_{\rm eff}$ can reproduce results obtained from H, for parameters near those calculated using constrained-density-functional theory[5,6] in a Cu_4O_8 cluster (2×2 unit cells) with periodic boundary conditions. We find that to obtain a quantitative agreement, it is necessary and sufficient to include some terms beyond fourth order in t_{pd}. In Sec. II we discuss the form of $H_{\rm eff}$ for the undoped system, one added hole and one added electron taking $t_{pp} = 0$. In Sec. III we use $H_{\rm eff}$ to calculate the photoemission and inverse photoemission spectra, Cu and O occupations and spin correlation functions, and we compare the results with known ones using H and the full Hilbert space. In Sec. IV we include $H_2 (t_{pp} \neq 0)$ and recalculate the main properties for a set of parameters which are supported by theoretical and experimental work. Section V contains a discussion.

II. EFFECTIVE HAMILTONIAN

We keep for the moment $H_2 = 0$ and eliminate terms linear and cubic in H_1 by means of two successive canonical transformations.[26] As shown by Proetto and López for intermediate valence systems,[26] the effective Hamiltonian including terms up to order t_{pd}^4 is

$$H^4_{\rm eff} = H_0 + \tfrac{1}{2}\,[S, H_1] + \tfrac{1}{8}\,[S,[S,[S,H_1]]]\,, \tag{5}$$

where the matrix element of S between any two eigenstates $\mid n\rangle, \mid m\rangle$ of H_0 with energies E_n and E_m is

$$\langle n \mid S \mid m\rangle = \frac{\langle n \mid H_1 \mid m\rangle}{E_n - E_m}. \tag{6}$$

Finally, we eliminate the terms of order t^2_{pd} in $H^4_{\rm eff}$ which mix the degenerate ground state of H_0 with excited states. The resulting $H_{\rm eff}$ has a different form for the electron-doped and the hole-doped system because of the different nature of the low-energy eigenstates of H_0. The undoped system can be described in both ways. The electron-doped system is characterized by a degenerate ground state of H_0 in which all eigenstates have all holes in Cu atoms and none of them is doubly occupied: the ionic species present are Cu^+, Cu^{+2}, and O^{-2} [we note, however, that the corrected eigenstates have an important content of O^- that will be apparent in the photoemission spectra (Fig. 1)]. Within this subspace $H_{\rm eff}$ takes a form which is also particular to the topology of the $\mathrm{Cu_4O_8}$ cluster due to its small size [some of the four Cu atoms nearest-neighbour (NN) to a given Cu atom coincide for periodic boundary conditions]. For one added electron we find using Eqs. (5) and (6) (neglecting for simplicity a few terms of oder t^4_{pd} which vanish for $U_{pd} = 0$):

$$H^e_{\rm eff} = -C_e - t_e \sum_{i\delta\sigma} d^\dagger_{i+2\delta\sigma} d_{i\sigma} + \frac{J}{2} \sum_{i\delta} (\mathbf{S}_i \cdot \mathbf{S}_{i+2\delta} - \tfrac{1}{4}). \tag{7}$$

The constant C_e, which is important in determining the charge-transfer gap can be written in the form:

$$C_e = A_1 + 2A'_1 - 4B_1 - 4B'_1, \tag{8}$$

where A_1 contains all diagonal second- and fourth-order processes contained in a $\mathrm{CuO_4}$ cluster (an occupied Cu atom with its NN O atoms) with its four NN Cu atoms occupied. A'_1 has a similar meaning for the case in which two of these Cu atoms are occupied and two unoccupied. $B_1 (B'_1)$ is a fourth-order term involving two NN occupied (one occupied and the other empty) Cu sites. t_e, J, A_1, A'_1, B_1, and B'_1 are all positive and given by

$$\begin{aligned}
t_e &= \frac{t^2_{pd}}{\Delta}\left\{1 - \frac{t^2_{pd}}{\Delta}\left[\frac{3}{\Delta} + \frac{4\Delta + 2U_{pd}}{(\Delta + U_{pd})^2}\right]\right\},\\
J &= \frac{4t^4_{pd}}{(\Delta + U_{pd})^2}\left(\frac{1}{U_d} + \frac{2}{2\Delta + U_p}\right),\\
A_1 &= \frac{4t^2_{pd}}{\Delta + U_{pd}}\left[1 - 4\frac{t^2_{pd}}{(\Delta + U_{pd})^2}\right],\\
A'_1 &= 2t^2_{pd}\left\{\frac{1}{\Delta} + \frac{1}{\Delta + U_{pd}} - 2t^2_{pd}\left[\frac{1}{\Delta^3} + \frac{1}{(\Delta + U_{pd})^3}\right.\right.\\
&\qquad\left.\left. + \frac{2\Delta + U_{pd}}{\Delta^2(\Delta + U_{pd})^2}\right]\right\}\\
B_1 &= \frac{2t^4_{pd}}{(\Delta + U_{pd})^3};\, B'_1 = \frac{t^4_{pd}}{\Delta^3}
\end{aligned} \tag{9}$$

When only holes are added to the system, the ground state of H_0 contains only Cu^{+2}, O^{-2}, and a number of O^- ions equal to the number of added holes, for realistic values of Δ, U_d, U_p, and U_{pd}.[3,4] The resulting effective Hamiltonian $H_{\rm eff}$ is more complicated than the one for the one-electron-doped case $H^e_{\rm eff}$. Up to order t^2_{pd}, but including the Cu-Cu superexchange, $H_{\rm eff}$ has the form:[23,24]

$$\begin{aligned}
H^h_{\rm eff} = &-C + (\Delta + 2U_{pd}) \sum_{j\sigma} n_{j\sigma} - t_2 \sum_{i\sigma,\delta'\neq\delta} p^\dagger_{i+\delta'\sigma} p_{i+\delta\sigma}\\
&+(t_1 + t_2) \sum_{i\sigma\sigma',\delta'\neq\delta} d^\dagger_{i\sigma} d_{i\sigma'} p^\dagger_{i+\delta'\sigma'} p_{i+\delta\sigma}\\
&+J_K \sum_{i\delta} (\mathbf{S}_i \cdot \mathbf{S}_{i+\delta} - n_{i+\delta}/4)\\
&+\frac{J}{2} \sum_{i\delta} (\mathbf{S}_i \cdot \mathbf{S}_{i+2\delta} - \tfrac{1}{4})
\end{aligned} \tag{10}$$

As before, the signs in Eq. (10) were chosen so that all parameters are positive. $t_1 (t_2)$ is an effective O-O hopping which involves an intermediate state containing one Cu^+ (Cu^{+3}) ion. For more than one added hole and $U_{pd} \neq 0$, the t_i are operators which depend on the charge in the first coordination shell around the Cu ion.[24] C is a diagonal operator, J_K is a Cu-O exchange, and J represent

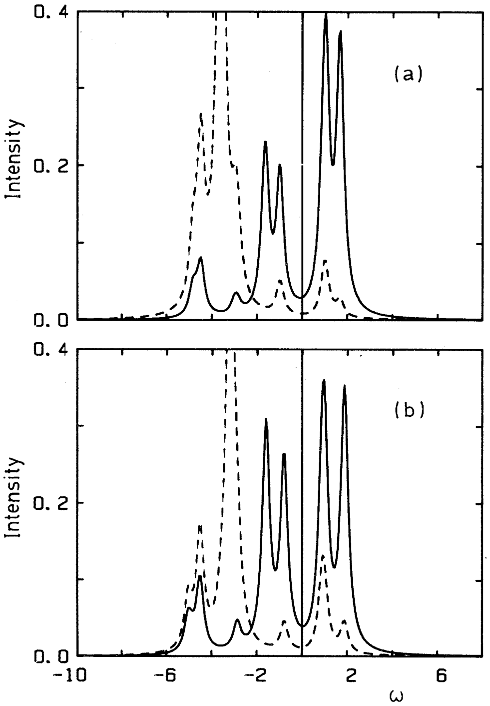

FIG. 1. Photoemission spectra of the undoped system as a function of the difference of energy from the Fermi energy. Solid (dashed) line is the Cu (O) electronic spectral density. Parameters are $t_{pd} = 1, U_d = 6, U_p = 3$, and (a) $\Delta = 4, U_{pd} = 0$, (b) $\Delta = 2, U_{pd} = 1$. The units are arbitrary.

the usual Cu-Cu superexchange as before [Eqs. (7) and (9)].

Since as explained below, H_{eff} containing terms up to t_{pd}^4 only is of very limited use, we shall only explain the main features of the fourth-order terms, instead of writing the lengthy expressions.

(1) Most of the contributions retain the form of Eq. (10). The remaining ones give rise to O-O hopping at larger distances and O-O exchange. We neglect them.

(2) Also, most of the contributions are contained in a CuO_4 cluster composed of a Cu atom and its four NN O atoms. For example a correction to t_2 can be represented by a process in which an O hole of one of these cluster hops to the Cu^{+2} ion (which contains a hole with opposite spin), then one hole of the resulting Cu^{+3} ion hops to the same or another NN O atom, comes back and finally one Cu hole jumps to an O different from the original one. For a given initial and final state there are eight ways of choosing the second intermediate state.

(3) The corrections to t_1 and t_2 are (roughly) proportional to two times the coordination of the Cu atom. Thus, when the parameters are such that the system is approaching a charge-transfer instability of the Cu valence to Cu^+ or Cu^{+3}, H_{eff} becomes rapidly meaningless. For example, the corrections to t_2 mentioned in (2) amount to -8 $[t_{pd}/(U_d - \Delta - 2U_{pd})]^2$ times the second-order value of t_2. If we take $U_d = 6, \Delta = 4$ in units to t_{pd}, as in Refs. 10, 13, and 19, t_2 becomes negative and the energy levels have nothing to do with those of the original Hamiltonian [Eqs. (1) to (3)].

(2) and (3) are also valid for the electron-doped case, as can be seen by inspection of Eqs. (7) to (9). By comparison with the photoemission spectra calculated in Ref. 19, we find that near a charge-transfer instability against Cu^+ (small Δ) or against Cu^{+3} (small U_d - Δ - $2U_{pd}$), H_{eff}^h and H_{eff}^e up to t_{pd}^2 only, are better than the fourth-order ones, in the sense that the energy levels of H can be rather well reproduced by the former if the origin and energy scale and adjusted. However, without such an adjustment, the energy gap calculated using the second order H_{eff}^e and H_{eff}^h turns out to be negative (instead of near $2t_{pd}$) for both sets of parameters studied in Ref. 19.

In spite of the above-mentioned failure of the fourth-order corrections, the form of these corrections suggested to us the procedure that we finally adopted to construct H_{eff}^h and H_{eff}^e. We begin explaining first H_{eff}^h: we adopt for it the form of Eq. (10). However, t_1, t_2, J_K, and part of the diagonal corrections are calculated fitting exactly all the levels of H_{eff}^h with the corresponding ones of H within a CuO_4 cluster (with one or two holes). In this way the most important corrections of order t_{pd}^n are summed up to $n \to \infty$. J and a "bond" diagonal correction are calculated from the energy difference between two singly occupied CuO_4 clusters and a Cu_2O_7 cluster, solving the latter in second-order perturbation theory, starting from a state built from eigenfunction of CuO_4 clusters as explained below. The procedure is similar to a recently used cell-perturbation method.[27]

Specifically if $n = 0, 1$ is the total number of added holes we obtain

$$C = (N - 2n)A_1 + 2nA_2 - \tfrac{1}{2}\sum_{i\delta}(1 - n_{1+\delta})B_1, \tag{11}$$

where A_i is the part of the diagonal correction due to a single CuO_4 cluster with i holes and B_1 is due to the overlap between two neighboring, singly occupied CuO_4 clusters. Equating the ground state energies of H and H_{eff}^h for a singly occupied CuO_4 cluster one gets:

$$A_1 = \left[(\Delta + U_{pd})^2/4 + 4t_{pd}^2\right]^{1/2} - (\Delta + U_{pd})/2. \tag{12}$$

Both H and H_{eff}^h in a CuO_4 cluster are invariant under *any* permutation of the O atoms. For two holes and total spin 1, the ground state of H_{eff}^h belongs to the three-fold degenerate irreducible representation (3,1) of S_4. This degeneracy is lifted by H_2 (Sec. IV). The excited states are totally symmetric. Fitting all these levels to the corresponding ones of H we get

$$t_1 = \left\{\left[\Delta^2/4 + 4t_{pd}^2\right]^{1/2} - \Delta/2\right\}/4, A_2 = 3t_1. \tag{13}$$

For the singlet states the ordering in energy of the irreducible representations is the opposite. The ground state of H is a mixture of four totally symmetric states: the first with one hole in the Cu atom, the second with two holes in the Cu ion, the third with two holes in different O atoms and the last with both holes in the same O atoms. In this basis the matrix of H has the form:

$$\begin{pmatrix} 0 & \sqrt{8}t_{pd} & \sqrt{6}t_{pd} & \sqrt{2}t_{pd} \\ \sqrt{8}t_{pd} & U_d - \Delta - 2U_{pd} & 0 & 0 \\ \sqrt{6}t_{pd} & 0 & \Delta & 0 \\ \sqrt{2}t_{pd} & 0 & 0 & \Delta + U_p \end{pmatrix}. \tag{14}$$

The first excited energies (three-fold degenerate) for S=0 are given by the lowest eigenvalue of the matrix

$$\begin{pmatrix} 0 & \sqrt{2}t_{pd} & \sqrt{2}t_{pd} \\ \sqrt{2}t_{pd} & \Delta & 0 \\ \sqrt{2}t_{pd} & 0 & \Delta + U_p \end{pmatrix}. \tag{15}$$

Calling E_g and E_e the lowest eigenvalues of these two matrices, the fitting procedure gives

$$t_2 = \frac{E_e - E_g}{8} - t_1/2, \quad J_K = 2(t_2 - t_1) - E_e. \tag{16}$$

An analytical approximation for t_2 and J_K can be obtained solving the matrices given by Eqs. (13) and (14) in an adequately chosen 2×2 sector and treating the rest in perturbation theory. This approximation is very good for realistic values of U_p and if the fluctuations of the Cu valence towards +1 and +3 are not both simultaneously important. It also allows an analytical expression for all the parameters of H_{eff}^h.

B_1 was calculated as the difference between the ground state energy of a doubly occupied Cu_2O_7 cluster for total spin S=1 and the corresponding one for two separated CuO_4 singly occupied clusters. J is the difference between the ground state energies of the Cu_2O_7 cluster for $S = 1$ and $S = 0$. To obtain analytical expressions for B_1 and J retaining the most important corrections of order beyond t_{pd}^4, we have calculated the energy of the

Cu_2O_7 cluster for given S starting from the state $| \phi\rangle$ constructed from the ground state of two neighboring CuO_4 clusters, but projecting out the double occupation of the common O atom[28] and normalizing. The action of the Hamiltonian on this state can be written in the form:

$$H \mid \phi\rangle = 2E_1 \mid \phi\rangle + \sum_i c_i \mid \psi_i\rangle, \tag{17}$$

where the $| \psi_i\rangle$ are eigenstates of H_0, E_1 is the ground state energy of a singly occupied CuO_4 cluster and the c_i are coefficients of order t_{pd}^2 for $t_{pd} \to 0$. $\langle\phi \mid \psi_i\rangle$ is also of order t_{pd}^2. In leading order in perturbation theory, the ground state energy becomes

$$\begin{aligned} E = 2E_1 &+ \sum c_i \langle\phi \mid \psi_i\rangle \\ &- \sum_i \frac{| c_i |^2}{\langle\psi_i \mid H_0 \mid \psi_i\rangle - 2E_1} \end{aligned} \tag{18}$$

Using this for both values of S we obtain

$$\begin{aligned} B_1 = & \frac{t_{pd}^4}{R^2(2R+\Delta+U_{pd})} \\ & \times \left\{ 1 - \frac{6U_{pd}[1+U_{pd}/(\Delta+2R)]}{2R+\Delta+U_{pd}} \right\} \end{aligned} \tag{19}$$

$$\begin{aligned} J = \frac{t_{pd}^4}{R^2} & \left[\frac{1}{U_d + 2R - \Delta - U_{pd}} \right. \\ & \left. + \frac{2}{U_p + 2R + \Delta - U_{pd}} \left(\frac{2\Delta + 2U_{pd}}{2R+\Delta+U_{pd}} \right)^2 \right], \end{aligned} \tag{20}$$

where

$$R = \left[(\Delta + U_{pd})^2 /4 + 4t_{pd}^2 \right]^{1/2}. \tag{21}$$

This completes the specification of H_{eff}^h. The first term of B_1 and J coincide with the fourth-order pertubative results given by Eqs. (9) for $t_{pd} \to 0$ as it should be. The other parameters of H_{eff} also can be checked to coincide with the result of the canonical transformation up to second order t_{pd} (Ref. 24) when t_{pd} is small enough. However, the present treatment is free from the divergences of the canonical treatment near a charge-transfer instability.

Similarly, for one electron added to the Cu_4O_8 cluster with periodic boundary conditions, we take the form of Eqs. (7) and (8), but instead of using Eq. (9), $-A_1$ is determined by the ground state energy of a singly occupied CuO_4 with its four NN Cu atoms occupied [Eq. (12)]. $-A_1'$ is the ground state energy of the cluster with only two opposite Cu NN atoms occupied. We take B_1 and J given by Eqs. (19) and (20) (although there is a small difference with the correct result for $U_{pd} \neq 0$). Finally t_e and B_1' are determined from the two lowest eigenvalues of a Cu_2O_6 singly occupied cluster with periodic boundary conditions. t_e equals the difference of these eigenvalues and $2B_1'$ is given by the average energy plus A_1'. Since the procedure used is analogous as before and contrary to H_{eff}^h, the form of H_{eff}^e is specific of the cluster chosen, we do not write here the expressions of the parameters of H_{eff}^e.

B_1 is positive for small U_{pd}. All other parameters of H_{eff}^h and H_{eff}^e are positive for all reasonable parameters of H.

III. RESULTS FOR $H_2 = 0$

One of the most severe tests for H_{eff} is to reproduce simultaneously both the photoemission and inverse phtoemission spectra of the undoped system, calculated with H and the full Hilbert space. The Cu and O spectral weights for single-particle excitations, defined for example in Sec. III of Ref. 19, depend on the energies and structure of the ground state and all excited states of total spin $\frac{1}{2}$ with one added hole and one added electron. To compare with the results of Ref. 19 we take $t_{pd} = 1, U_p = 3, U_d = 6$ and (a) $\Delta = 4, U_{pd} = 0$ or (b) $\Delta = 2, U_{pd} = 1$. Using the procedure of Sec. II the parameters of H_{eff}^h and H_{eff}^e become (a) $t_1 = 0.20, t_2 = 0.15, J_K = 0.58, A_1 = 0.83, B_1 = 0.012, t_e = 0.35, C_e = 2.38$ and J=0.030; (b) $t_1 = 0.31, t_2 = 0.10, J_K = 0.58, A_1 = 0.83, B_1 = 0.0031, t_e = 0.50, C_e = 3.1$, and J=0.040.

The obtained analytical expressions for t_2 and J_K, treating exactly the fluctuations via Cu^{+3} and perturbatively the rest of the matrices (13) and (14), give values ~ 10% higher. The gap is 1.96 and 1.69 in cases (a) and (b), respectively. The value of the gap is extremely sensitive to the values of the parameters. For example, an increase in $t_1(t_2)$ by a small amount δ reduces the gap in 5δ (8δ). As a consequence the value of the gap using H_{eff} in fourth-order perturbation theory is unreasonable for the above-mentioned parameters of H. To calculate the on-site Cu and O spectral weights with H_{eff} we have to transform the on-site creation (or annihilation) operators. To obtain analytical expressions, we assume that fluctuations via Cu^{+3} are more important for H_{eff}^h and the effect of Cu^+ and O^0 states is calculated perturbatively. Following a similar procedure as in Sec. II we obtain for operators acting on the undoped system:

$$\begin{aligned} T d_{i\sigma}^\dagger T^\dagger = & \frac{\beta}{2} \sum_\delta p_{i+\delta\sigma}^\dagger n_{i\sigma} \\ & - \left[\frac{\alpha\delta}{\sqrt{8}} + \frac{\beta}{4}(\gamma - 1) \right] \sum_\delta p_{i+\delta\sigma}^\dagger n_{i\bar{\sigma}} \\ & + \left[\frac{\alpha\delta}{\sqrt{8}} + \frac{\beta}{4}(\gamma + 1) \right] \sum_\delta p_{i+\delta\bar{\sigma}}^\dagger d_{i\sigma}^\dagger d_{i\bar{\sigma}} \end{aligned}$$

$$T d_{i\sigma} T^\dagger = \alpha d_{i\sigma}, \quad T p_{j\sigma} T^\dagger = -\frac{\beta}{2} \sum_{i=n.n.j} d_{i\sigma} \tag{22}$$

where $\alpha, \beta, \gamma, \delta$ are all positive,

$$\begin{aligned} \alpha^2 &= 1 - \beta^2 = \frac{1}{2} + \frac{\Delta + U_{pd}}{4R}, \\ \gamma^2 &= 1 - \delta^2 = \frac{1}{2} + \frac{\Delta}{4[\Delta^2/4 + 8t_{pd}^2]^{1/2}}, \end{aligned} \tag{23}$$

and R is given by Eq. (21). These transformed operators were obtained requiring that the matrix elements of the operator between eigenstates of H in the CuO_4 cluster be the same as matrix element of the transformed operator between the corresponding eigenstates of H_{eff}. To linear order in t_{pd}, these expressions coincide with the canonical transformation using $T = \exp(S)$ with S given by Eq. (6). For simplicity, for the transformed operator of $p^{\dagger}_{j\sigma}$ acting on the undoped system we used

$$TOT^{\dagger} = O + [\tilde{S}, O] + \frac{1}{2}[\tilde{S}, [\tilde{S}, O]] \tag{24}$$

with $O = p^{\dagger}_{j\sigma}$, and we retained in the second member only terms proportional to $p^{\dagger}_{j\sigma}$ and $\tilde{S}$ is given by Eq. (6), but with the energies E_i renormalized in such a way that the second member of Eq. (24) for $O = H$ reproduces H^{h}_{eff} for $B_1 = J = 0$. $\tilde{S}$ differs from S in terms of order t^{3}_{pd}. For the parameters mentioned above we obtain (a) $Tp^{\dagger}_{j\sigma}T^{\dagger} \cong 0.80p^{\dagger}_{j\sigma}$, (b) $Tp^{\dagger}_{j\sigma}T^{\dagger} \cong 0.60p^{\dagger}_{j\sigma}$.

The resulting photoemission spectra are shown in Fig. 1. The agreement with Fig. 8 of Ref. 19 is noticeable. The broadening of the peaks is the same as that used in Ref. 19. In general, the positions and intensities of all peaks are quantitatively reproduced, particularly in the hole doped region ($\omega \leq 0$), except for the greatest and lowest ω. H_{eff} left out the lower Hubbard band (states with a large amount of Cu^{+3}) and states with a large amount of O holes for electron-doped systems. The position of the peak of highest energy ω is shifted to higher energy with respect to the result of the original Hamiltonian.[19] This is due to a near degeneracy of the corresponding eigenstates with others containing important amounts of O holes (rightmost peak of Fig. 8, Ref. 19), which we have considered only as virtual states and not in high enough order in perturbation theory. Although the overall shape of the spectra is well reproduced, the agreement with the exact results improves if higher values of J are used.

The value of J and the low-energy excitations of the undoped system are probed by the Fourier-transform of the spin-spin correlation function. Using the same procedure that leads to Eqs. (22) to (24), we obtain for the transformed Cu site occupation number $n_{i\sigma} = d^{\dagger}_{i\sigma}d_{i\sigma}$ for the undoped or electron-doped systems:

$$Tn_{i\sigma}T^{\dagger} = \alpha^2 n_{i\sigma} \tag{25}$$

In Fig. 2, we represent the *z-z* component of the above-mentioned correlation function, for comparison with the exact results of Ref. 18. With H_{eff} the position of the peak at wave vector $q = (\pi/a, \pi/a)$ is $2J$ (the factor 2 is due to the periodic boundary conditions) and for $(\pi/a, 0)$ the energy is $4J$. Comparison of our result with those of Refs. 18 and 19 suggests that our value of J is nearly two times smaller. We have found that Eq. (20) gives a value of J which is reduced in 25% with respect to the exact triplet-singlet energy difference in a Cu_2O_7 cluster with two holes. However the main reason for the difference is a finite-size effect that we have avoided in our treatment: in a Cu_4O_8 cluster with periodic boundary conditions there is a process of fourth order in t_{pd} by which two Cu holes can be interchanged without involving double occupancy in any intermediate state. In addition, in Refs. 18 and 19, the ratio between the energies of both peaks is not 2, but is larger for low values of Δ.[18] This is likely to be due to four-spin cyclic exchange processes (eighth order in t_{pd}),[18,29] which we have neglected. The intensities of the peaks in Fig. 2 are in good agreement with those obtained in Ref. 18. The differences of order of 20% might be due to different criteria for the broadening of the peaks.

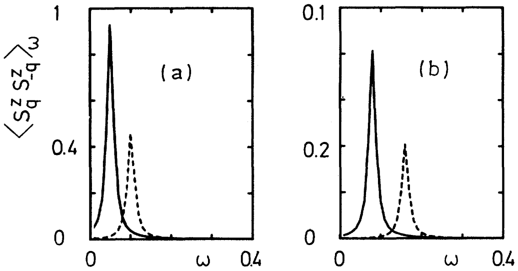

FIG. 2. Time and space Fourier transform of the spin-spin correlation function as a function of frequency for wave vectors $\mathbf{q} = (\pi/a, \pi/a)$ (solid line) and $\mathbf{q} = (\pi/a, 0)$ (dashed line). Parameters are $t_{pd} = 1, U_d = 8, U_p = 4, U_{pd} = 1$, and (a) $\Delta = 4$, (b) $\Delta = 2$. The units are arbitrary.

Exact results for the Cu site occupation number $n_i = \sum_{\sigma} n_{i\sigma}$ for the undoped system, $t_{pd} = 1, U_d = 10, U_p = 0$ and several values of Δ and U_{pd} were represented in Ref. 20. For $\Delta + U_{pd} = 3$ the result is $n_{\text{Cu}} = 0.72$, while Eqs. (25), (23), and (21) give $n_{\text{Cu}} = 0.80$. For larger values of $\Delta + U_{pd}$ both results approach that of second-order perturbation theory. For the 25% hole-doped system, the expression of the operator $Tn_iT^{\dagger}$ is very lengthy and we do not reproduce it here. For this system and $t_{pd} = 1, U_d = 6, U_p = 0, \Delta = 2$ and $U_{pd} = 1$, the exact result is $n_i = 0.75$.[20] We obtain $n_i = 0.73$. The total O occupation is 5-4 n_i. Increasing the value of Δ to 4, one of the denominators of ordinary perturbation theory diverges. In this case we obtain n_i=0.93 whereas the exact result is 0.96. For the parameters used in Ref. 10, we obtain less than 7% of the hole added to the undoped system that goes to Cu atoms in agreement with Ref. 10.

For the Cu antiferromagnetic structure factor:

$$S(\mathbf{Q}) = 4\sum_i e^{i\mathbf{Q}\cdot\mathbf{R}_i}\langle S^z_o S^z_i \rangle, \tag{26}$$

where $S^z_i = (n_{i\uparrow} - n_{i\downarrow})/2$ and $\mathbf{Q} = (\pi/a, \pi/a)$ we obtain the simple result $S(\mathbf{Q}) = 8\alpha^2/3$ for the undoped system, and the agreement with the exact results of Ref. 20 is similar to that of the Cu occupation n_i.

IV. INCLUSION OF DIRECT O-O HOPPING

Constrained-density-functional calculations predict a ratio t_{pp}/t_{pd} between 0.4 and 0.5.[3,4] However, a comparison with values found for other oxides and assuming a d^{-2} distance dependence of t_{pp} suggests $0.15 < t_{pp}/t_{pd} < 0.2$.[30] These values are also suggested by a fit of the shape of the Fermi surface.[30,31]

The effect of t_{pp} is included adding $TH_2T^\dagger$ to H_{eff}, using Eqs. (4) and (24). The leading term of the second member of Eq. (24) with $O = H_2$ is H_2. The main correction term is of order $t_{pd}^2 t_{pp}$ and includes effective hopping and spin-flip-hopping processes, some of which connect O sites at a distance of $(5/2)^{1/2}$ lattice parameters. Since near a charge-transfer instability and particularly for $t_{pp}/t_{pd} < 0.2$, the terms of order t_{pd}^4 are more important than those of order $t_{pd}^2 t_{pp}$, we adopt for simplicity the form $H'_{\text{eff}} = H_{\text{eff}} + H_2$ for the effective Hamiltonian for $H_2 \neq 0$. The parameters are determined as in Sec. II fitting the energy of the levels of H'_{eff} and H in adequately chosen small clusters. However in this case for a CuO_4 cluster with two holes the fitting is no more perfect due to the lowering of symmetry: the three-fold degenerate irreducible representation (3,1) of S_4 splits into two in the group C_{4v}. For the sake of brevity we do not reproduce the expressions of the parameters of H'_{eff} in terms of those of H here.

Based on theoretical calculations[3,4] and experimental data[32,21] which suggest that fluctuations via Cu^+ are more favorable than those via Cu^{+3}, we study here the following sets of parameters: U_d=10 eV, U_p=5 eV, Δ=3 eV, U_{pd}=1 eV and (a) t_{pd}=1.6 eV, $t_{pp} = 0.2t_{pd}$; (b) t_{pd}=1.3 eV, t_{pp}=0.4 t_{pd}.

The value of t_{pd} was chosen to result in a gap of nearly 2 eV (Refs. 33 and 34) (a) 2.05 eV, (b) 2.03 eV. The resulting parameters of H'_{eff} in eV are (a) $t_1 = 0.51, t_2 = 0.12, J_K = 1.02, A_1 = 1.93, B_1 = 0.025, t_e = 0.92, C_e = 5.56$; (b) $t_1 = 0.37, t_2 = 0.12, J_K = 0.89, A_1 = 1.51, B_1 = 0.019, t_e = 0.82, C_e = 4.27$; and in both cases we replaced J by the experimental value 0.12 eV.[33,35,36] The resulting photoemission spectra of the undoped system are shown in Fig. 3. Comparison with Fig. 1 shows that as t_{pp} increases, the main change is that the second peak nearer to the Fermi energy for hole injection ($\omega \leq 0$) moves closer to the Fermi energy. The separation of the main peaks for $\omega \geq 0$ increases for these sets of parameters. The peak nearest to the Fermi energy for $\omega \leq 0$, correponds to a Zhang-Rice singlet.[25] The next one corresponds to a state of some local triplet character of M_4 symmetry. The rapid decrease of the difference between the energy of these peaks with increasing t_{pp} might reflect a limit in the validity of the t-J model.[25] This point deserves further study.

The average Cu on-site occupancies for the undoped and 25% hole-doped systems for the parameters used are, respectively, (a) 0.73 and 0.84, (b) 0.75 and 0.88. The added hole has (a) 58% or (b) 47% O character. Since a larger amount of O character of the added hole is expected,[1,2] the value of t_{pd} is probably too large.

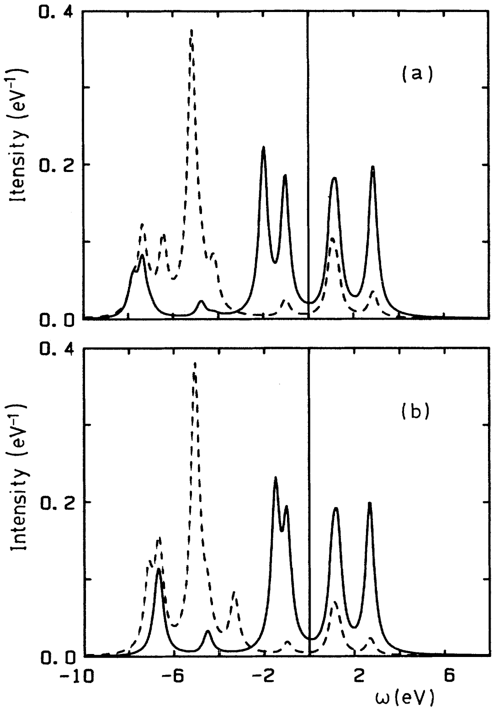

FIG. 3. Same as Fig. 1 for $t_{pp} \neq 0$. Parameters are U_d=10 eV, U_p=5 eV, Δ=3 eV, U_{pd}=1 eV and (a) t_{pd}=1.6 eV, $t_{pp} = 0.2t_{pd}$, (b) t_{pd}=1.3 eV, $t_{pp} = 0.4t_{pd}$. The value of J in H_{eff} has been increased to 0.12 eV.

V. DISCUSSION

Based on results of a standard canonical transformation, but renormalizing adequately the relevant energies, we have derived an effective Hamiltonian H_{eff} which reproduces results obtained from the three-band Hubbard model H for realistic values of the parameters. For the electron-doped system and $t_{pp} = 0$, H^e_{eff} has the form of the t-J model,[25] while for hole-doped systems H^h_{eff} contains two O bands interacting with Cu spins. The controversial question of whether this model can be further reduced to a one-band model[25,27,31,37] will be studied elsewhere. Results for small t_{pd} (Ref. 24) suggest that the dispersion for one-added hole is different in H^h_{eff} and the t-J model. Also the wave function of the Zhang-Rice singlet state derived by Schüttler and Fedro[37] contains a larger amount of neutral O atoms than our corresponding results for the CuO_4 cluster with two holes.

Although similar H_{eff} have been derived previously,[23,24] this is the first time that an H_{eff} reproduces several results obtained with H for realistic parameters on a quantitative level. Except for the value of J analytical expressions for the parameters of H^h_{eff} are accurate enough. The photoemission spectra were also calculated using inhomogeneous Hartree-Fock and the random-phase approximation,[38] obtaining results in good agreement with the exact ones.[19] However, our results are better and for the size of the cluster studied (Cu_4O_8) require less computational effort.

Recently, a finite-size scaling approach has been employed to study the energy[39] and the spectral density[40] of the t-J model with one added hole. Since for the single-hole doped situation the Hilbert space of H^h_{eff} is only eight times larger than that of the t-J model, a similar study of H^h_{eff} should be possible.

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