Many-body derivation of quasiparticle bands and effective interactions of fermions in CuO_2 layers

P. Entel and J. Zielinski*
Theoretische Tieftemperaturphysik, Universität-GH-Duisburg, 4100 Duisburg 1, West Germany
(Received 11 September 1989; revised manuscript received 2 February 1990)

We discuss normal-state properties and the phase diagram of high-T_c copper oxide superconductors on the basis of a five-states model (one d state and two bonding and two nonbonding p states per unit cell) for interacting electrons in a single CuO_2 layer. In particular, quasiparticle bands and densities of states have been derived by applying a generalized Hubbard-I scheme to the five-states model and to the reduced three-states model. We find that in both cases and for realistic values of model parameters the insulating gap opens between an antibonding band of almost pure p character and the antibonding band of mainly d character. The insulating state is thus of the charge-transfer type and introducing holes into the p-like antibonding band metallizes the system. This would mean that in the presence of an attractive interaction at least a part of the Cooper pairs are formed out of only weakly correlated p-type quasiparticles. Insight of the normal-state behavior can be gained from a discussion of the spectral distribution of strongly correlated and more localized d electrons among mobile p electrons or holes. The work is supplemented by a brief discussion of the residual interactions among quasiparticles and by a comparison of our model with more strong-coupling models like the t-J model. Finally, we present formal solutions for the Green's functions by using a more refined decoupling scheme. The influence of the resulting lifetime effects and Kondo-type features on the quasiparticle spectra is briefly discussed.

I. INTRODUCTION

Despite intensive research activities there is no real agreement about how the basic physical properties of the copper oxide systems are to be explained. Several theoretical models of quite distinct natures have been formulated. In spite of the variety of models there are some generally accepted ideas. It seems clear that correlated electrons in CuO_2 layers contribute to most of the unusual features of the normal, the magnetic, and the superconducting state. For specific discussions of some of the electronic properties of high-T_c materials we refer to Refs. 1–4. Furthermore, it is obvious that the coupling between layers is important for the formation of a coherent magnetic or superconducting state.[5–7] A particular interesting feature might be connected with the observation that the Coulomb interaction between charge carriers in layered materials can be attractive over an extensive fraction of reciprocal space.[8] On the other hand the involvement of lattice degrees of freedom in normal-state and superconducting properties is far from being clear.[9]

In this paper we would like to add to the known features another important feature of high-T_c systems by showing that in the vicinity of the Fermi energy mobile carriers consist of nearly free quasiparticles and that the main spectral weight of strongly correlated particles lies well below the Fermi level. Our investigations are based on a generalized five-states model composed of interacting electrons in $3d_{x^2-y^2}$ and $2p_{x,y}$ orbitals (two bonding and two nonbonding p orbitals per unit cell) of a planar CuO_2 square lattice. This model originates from the accomplishment of the three-states model[10] by the two nonbonding p orbitals and by allowing for direct O-O hopping. There are many versions of similar electronic Hamiltonians and we refer to Refs. 1–4 for details of the present knowledge of one-electron band structures and correlated electron models.

The three-states model (without direct O-O hopping) is of particular interest since it has been shown that it reduces to an effective one-band Hubbard model in the strong-coupling limit. However, the question whether the effective one band t-J model and the three-states Emery model contain the same and most important features of high-T_c systems is still in debate.[11] Our investigations show that the quasiparticle spectrum of the metallic state obtained for the five- and three-states model (O-O hopping included) is different from the corresponding spectrum of the t-J model and that the inclusion of O-O hopping and nonbonding p orbitals might be of crucial importance. However, we have to admit that our approximations are rather crude and could forbid a direct comparison of results obtained so far for the five-states model and the t-J model. The drawbacks of our treatment will be critically discussed at each level.

The t-J and related models are of interest since analytical investigations and numerical simulations of small systems show that superexchange-driven formation of Cooper pairs is possible. For discussions of different aspects of real-space pairing of fermion spins to total spin zero we refer to Ref. 12–25. Since Cooper pairs consist of holes introduced by doping, the nature of the Cooper pairs depends on whether holes go onto oxygen or copper sites. Our results for quasiparticle band structure clearly show

that holes predominantly go onto oxygen sites. In our treatment the dispersion of the quasiparticle bands near the Fermi energy is mainly due to O-O hopping and to a much less extent to covalent Cu-O mixing. If this were true, then the superexchange mechanism for pair formation would be not so effective since holes on oxygen sites are less correlated than holes on copper sites.

To what extent does this contradict the Zhang-Rice argument? If one sticks to the three-states model and neglects direct O-O hopping then as shown by Zhang and Rice,[11] one hole on the central Cu and a hole distributed over neighboring O sites form a spin singlet that is strongly bound to the central Cu site. Since the excited triplet state has a much larger energy than the singlet state and since two such composite particles feel a repulsive interaction, the reduced three-states model reduces at low enough hole concentration to an effective one-band Hubbard model. If O-O hopping is included, for example, within the five-states model, then it is more likely the oxygen ion that plays the central role and one would have to generalize the procedure used by Zhang and Rice. To this one could consider two holes on the central oxygen ion (one in the bonding and one in the nonbonding orbital) which form a spin singlet. This singlet is allowed to travel to the nearest-neighbor oxygen sites, or a single hole could travel to the nearest-neighbor Cu sites. Moreover, one could consider two holes in one and the same oxygen orbital, etc. In addition one would have to consider all possible transitions of a single hole. In this way one would create a much larger object than in the original work of Zhang and Rice, which is perhaps still of singlet nature, but its excited states are not simple triplet states and may lie close in energy. Whether this would still strongly couple the oxygen hole spin to a central Cu spin is not obvious. We briefly come back to this question when discussing effective interactions in Sec. V.

Besides the superexchange mechanism and more refined concepts based on this mechanism such as the resonant valence bond[12,13] and the spin-bag mechanism,[14] different types of charge-transfer mechanism have been proposed.[26–28] Recently, the exchange of charge fluctuations as an underlying mechanism for hole-hole attraction was discussed within the spinless version of the three-states model.[29] Our results for the five-states model show that for a completely filled antibonding quasiparticle band of nearly pure p character the ground state is a charge-transfer insulator with an insulating gap larger than 5 eV. In our opinion this gap is too large to be of any importance for a d-p excitonic mechanism. Charge fluctuations of the type $Cu^{2+}O_2^{2-} \leftrightarrow Cu^{+}O^{2-}$, in which only carriers in band states beneath the insulating gap are involved, are not so effective because only a few percent of d states are admixed to the band that contains the Fermi level.

Normal-state properties are of particular interest since they determine to a large extent also the low-temperature properties. There are only a few attempts to calculate normal-state properties of high-T_c systems with the help of the three-states model. To our knowledge, in most cases direct O-O transfer terms were neglected. All one-electron band structure calculations based on the local-density approximation yield a metallic ground state for undoped high-T_c systems and one really has to use many-body techniques to obtain an insulating ground state. Quite recently, Balseiro *et al.*[30] calculated the metal-insulator phase diagram of the three-states model (without O-O hopping) by using the slave-boson technique. Their results show that for one hole per elementary unit, La_2CuO_4 is a charge-transfer insulator and that a slight increase in the number of holes causes rapid metallization.

In Sec. II we discuss the five-states model and relevant energy parameters. In Sec. III we present results for the quasiparticle spectra obtained with the help of a generalized Hubbard-I scheme[31] for the five-states model. These results essentially confirm the observations of Balseiro *et al.* Furthermore, our results clearly indicate that in the presence of an attractive interaction, Cooper pairs are formed out of only weakly correlated p-like quasiparticles. In Sec. IV results for the three-states model are discussed. Section V deals with effective interactions within the reduced three-states model (without O-O hopping). Finally in Sec. VI a more refined decoupling procedure is presented and the influence of lifetime effects and Kondo-type features is briefly discussed.

II. FIVE-STATES MODEL HAMILTONIAN

In this section we derive an effective Hamiltonian for high-T_c systems. In the absence of correlations, electrons in CuO_2 planes are well described by Bloch functions of the form,

$$\langle \mathbf{r}|\varphi_{\mathbf{k}}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i\mathbf{k}\cdot\mathbf{n}} [a_{\mathbf{k}} \langle \mathbf{r}-\mathbf{n}|d_{x^2-y^2}\rangle + e^{i\mathbf{k}\cdot\mathbf{a}_1/2}(b_{\mathbf{k}x}\langle x-\mathbf{n}-\mathbf{a}_1/2|p_x\rangle + b_{\mathbf{k}y}\langle y-\mathbf{n}-\mathbf{a}_1/2|p'_y\rangle) ,$$
$$+ e^{i\mathbf{k}\cdot\mathbf{a}_2/2}(c_{\mathbf{k}x}\langle x-\mathbf{n}-\mathbf{a}_2/2|p'_x\rangle + c_{\mathbf{k}y}\langle y-\mathbf{n}-\mathbf{a}_2/2|p_y\rangle)] . \quad (1)$$

Eigenvalues and coefficients are easily calculated from

$$\begin{bmatrix} (\varepsilon_d-\varepsilon_{\mathbf{k}}) & -2i\gamma S_{1\mathbf{k}} & 2i\gamma S_{2\mathbf{k}} & 0 & 0 \\ 2i\gamma S_{1\mathbf{k}} & (\varepsilon_p-\varepsilon_{\mathbf{k}}) & 4\beta S_{1\mathbf{k}}S_{2\mathbf{k}} & 0 & 4\beta' C_{1\mathbf{k}}C_{2\mathbf{k}} \\ -2i\gamma S_{2\mathbf{k}} & 4\beta S_{1\mathbf{k}}S_{2\mathbf{k}} & (\varepsilon_p-\varepsilon_{\mathbf{k}}) & 4\beta' C_{1\mathbf{k}}C_{2\mathbf{k}} & 0 \\ 0 & 0 & 4\beta' C_{1\mathbf{k}}C_{2\mathbf{k}} & (\varepsilon_{p'}-\varepsilon_{\mathbf{k}}) & 4\beta S_{1\mathbf{k}}S_{2\mathbf{k}} \\ 0 & 4\beta' C_{1\mathbf{k}}C_{2\mathbf{k}} & 0 & 4\beta S_{1\mathbf{k}}S_{2\mathbf{k}} & (\varepsilon_{p'}-\varepsilon_{\mathbf{k}}) \end{bmatrix} \begin{bmatrix} a_{\mathbf{k}} \\ b_{\mathbf{k}x} \\ c_{\mathbf{k}y} \\ b_{\mathbf{k}y} \\ c_{\mathbf{k}x} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} , \quad (2)$$

with $\varepsilon_{d,p,p'}$ as energy of the atomic d, bonding p, and nonbonding p' levels, and

$$S_{\alpha\mathbf{k}}=\sin\frac{k_\alpha a}{2},\quad C_{\alpha\mathbf{k}}=\cos\frac{k_\alpha a}{2},\quad \alpha=1,2\ , \tag{3}$$

where 1 (2) refers to the x (y) direction.

The arrangement of orbitals and definitions of the different hybridization constants γ, β, and β' are displayed in Fig. 1. In the usual formulation of the three-states model only dashed bonding p orbitals are taken into account and direct O-O hopping due to $\beta\neq 0$ is neglected. If the case $\beta\neq 0$ is considered then one should also take direct transfer between bonding and nonbonding p orbitals (as represented by blank circles in Fig. 1) into account. For $\beta'=0$ the nonbonding states are decoupled from the bonding states.

For the reduced three-states model ($\beta=0$) the nonbonding band is dispersionless and bonding and antibonding bands are given by

$$\varepsilon_{\mathbf{k}}^{\pm}=\tfrac{1}{2}\{\varepsilon_d+\varepsilon_p\pm[(\varepsilon_d-\varepsilon_p)^2+16\gamma^2(S_{1\mathbf{k}}^2+S_{2\mathbf{k}}^2)]^{1/2}\}\ , \tag{4}$$

while d and p character are determined by the Bloch coefficients,

$$\begin{pmatrix} a_{\mathbf{k}}^{\pm}\\ b_{\mathbf{k}}^{\pm}\\ c_{\mathbf{k}}^{\pm}\end{pmatrix}=\frac{a_{\mathbf{k}}^{\pm}}{\varepsilon_p-\varepsilon_{\mathbf{k}}^{\pm}}\begin{pmatrix}\varepsilon_p-\varepsilon_{\mathbf{k}}^{\pm}\\ -2i\gamma S_{1\mathbf{k}}\\ 2i\gamma S_{2\mathbf{k}}\end{pmatrix}\ , \tag{5}$$

$$a_{\mathbf{k}}^{\pm}=\frac{|\varepsilon_p-\varepsilon_{\mathbf{k}}^{\pm}|}{[(\varepsilon_p-\varepsilon_{\mathbf{k}}^{\pm})^2+4\gamma^2(S_{1\mathbf{k}}^2+S_{2\mathbf{k}}^2)]^{1/2}}\ . \tag{6}$$

For example, this gives the following expression for the ratio of spectral weights of carriers with d- and p-like symmetry at the logarithmic singularity,

$$\frac{1}{16\gamma^2}\{\varepsilon_d-\varepsilon_p\pm[(\varepsilon_d-\varepsilon_p)^2+16\gamma^2]^{1/2}\}^2\ . \tag{7}$$

Introducing field operators in terms of creation operators of Bloch electrons,

$$\Psi_\sigma^\dagger(\mathbf{r})=\sum_{n,\mathbf{k}}\langle\mathbf{r}|\varphi_{\mathbf{k}}\rangle a_{n\mathbf{k}\sigma}^\dagger\ , \tag{8}$$

leads to creation operators of Wannier electrons of the form

$$d_{\mathbf{n}\sigma}^\dagger=\frac{1}{\sqrt{N}}\sum_{n,\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{n}}a_{n\mathbf{k}}^* a_{n\mathbf{k}\sigma}^\dagger\ , \tag{9}$$

$$p_{\alpha\mathbf{m}_1\sigma}^\dagger=\frac{1}{\sqrt{N}}\sum_{n,\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{m}_1}b_{\alpha n\mathbf{k}}^* a_{1n\mathbf{k}\sigma}^\dagger\ , \tag{10}$$

$$p_{\alpha\mathbf{m}_2\sigma}^\dagger=\frac{1}{\sqrt{N}}\sum_{n,\mathbf{k}}e^{-i\mathbf{k}\cdot m_2}c_{\alpha n\mathbf{k}}^* a_{2n\mathbf{k}\sigma}^\dagger\ , \tag{11}$$

where n is the band index and $\mathbf{m}_{1,2}=\mathbf{n}+\mathbf{a}_{1,2}/2$.

In what follows, we will use a much simpler representation defined by

$$d_{\mathbf{n}\sigma}^\dagger=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{n}}d_{\mathbf{k}\sigma}^\dagger\ , \tag{12}$$

$$p_{\alpha\mathbf{m}_\alpha\sigma}^\dagger=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{m}_\alpha}p_{\alpha\mathbf{k}\sigma}^\dagger\ , \tag{13}$$

$$p_{\beta\mathbf{m}_\alpha\sigma}^{\prime\dagger}=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{m}_\alpha}p_{\beta\mathbf{k}\sigma}^{\prime\dagger},\quad \beta\neq\alpha\ . \tag{14}$$

Then the resulting Hamiltonian in $\mathbf{k}$ representation is given by

$$\begin{aligned}\mathcal{H}_0=&\sum_{\mathbf{k},\sigma}\varepsilon_d d_{\mathbf{k}\sigma}^\dagger d_{\mathbf{k}\sigma}+\sum_{\alpha\mathbf{k}\sigma}(\varepsilon_p p_{\alpha\mathbf{k}\sigma}^\dagger p_{\alpha\mathbf{k}\sigma}+\varepsilon_{p'}p_{\alpha\mathbf{k}\sigma}^{\prime\dagger}p_{\alpha\mathbf{k}\sigma}^{\prime})\\&+2i\gamma\sum_{\alpha,\mathbf{k},\sigma}(-1)^\alpha S_{\alpha\mathbf{k}}(d_{\mathbf{k}\sigma}^\dagger p_{\alpha\mathbf{k}\sigma}-p_{\alpha\mathbf{k}\sigma}^\dagger d_{\mathbf{k}\sigma})\\&+4\beta\sum_{\alpha\neq\beta,\mathbf{k},\sigma}S_{\alpha\mathbf{k}}S_{\beta\mathbf{k}}(p_{\alpha\mathbf{k}\sigma}^\dagger p_{\beta\mathbf{k}\sigma}+p_{\alpha\mathbf{k}\sigma}^{\prime\dagger}p_{\beta\mathbf{k}\sigma}^{\prime})\\&+4\beta'\sum_{\alpha,\mathbf{k},\sigma}C_{1\mathbf{k}}C_{2\mathbf{k}}(p_{\alpha\mathbf{k}\sigma}^{\prime\dagger}p_{\alpha\mathbf{k}\sigma}+\text{H.c.})\ .\end{aligned} \tag{15}$$

$\mathcal{H}_0$ reproduces the eigenvalues of (2) and the resulting band structure is shown in Fig. 2(a) and respective density of states in Fig. 2(b).

We now add to (15) the most important Coulomb interactions defined by

$$\begin{aligned}\mathcal{H}_1=&U_{dd}\sum_{\mathbf{n}}n_{d\mathbf{n}\uparrow}n_{d\mathbf{n}\downarrow}+U_{pp}\sum_{\alpha,\mathbf{m}_\alpha}n_{\alpha\mathbf{m}_\alpha\uparrow}n_{\alpha\mathbf{m}_\alpha\downarrow}\\&+V_{dp}\sum_{\alpha\langle\mathbf{n}\mathbf{m}_\alpha\rangle}n_{d\mathbf{n}}n_{\alpha\mathbf{m}_\alpha}\ .\end{aligned} \tag{16}$$

The first two terms describe on-site correlations while the last term describes Coulomb interactions among d and p carriers. Intrasite O-O interactions between carriers in orbitals of different symmetry as well as intersite O-O interactions will not be considered in this paper. Without the direct O-O hopping terms and without nonbonding p' orbitals, the extended Hubbard Hamiltonian $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1$ is sometimes referred to as Emery model[10] if used in the hole representation. The hole representation used by Emery is based on the vacuum that consists of Cu^+ (all d states singly occupied) and of O^{2-} (all p

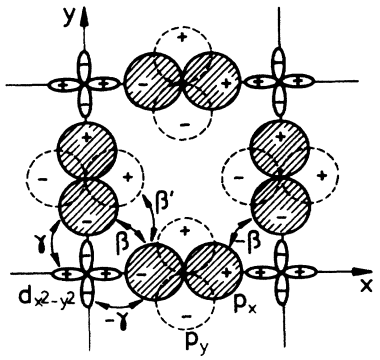

FIG. 1. A schematic representation of the orbitals and transfer terms included in the five-states model Hamiltonian Eqs. (15) and (16). The five-states model consists of one d state and the two bonding and two nonbonding p states per unit cell.

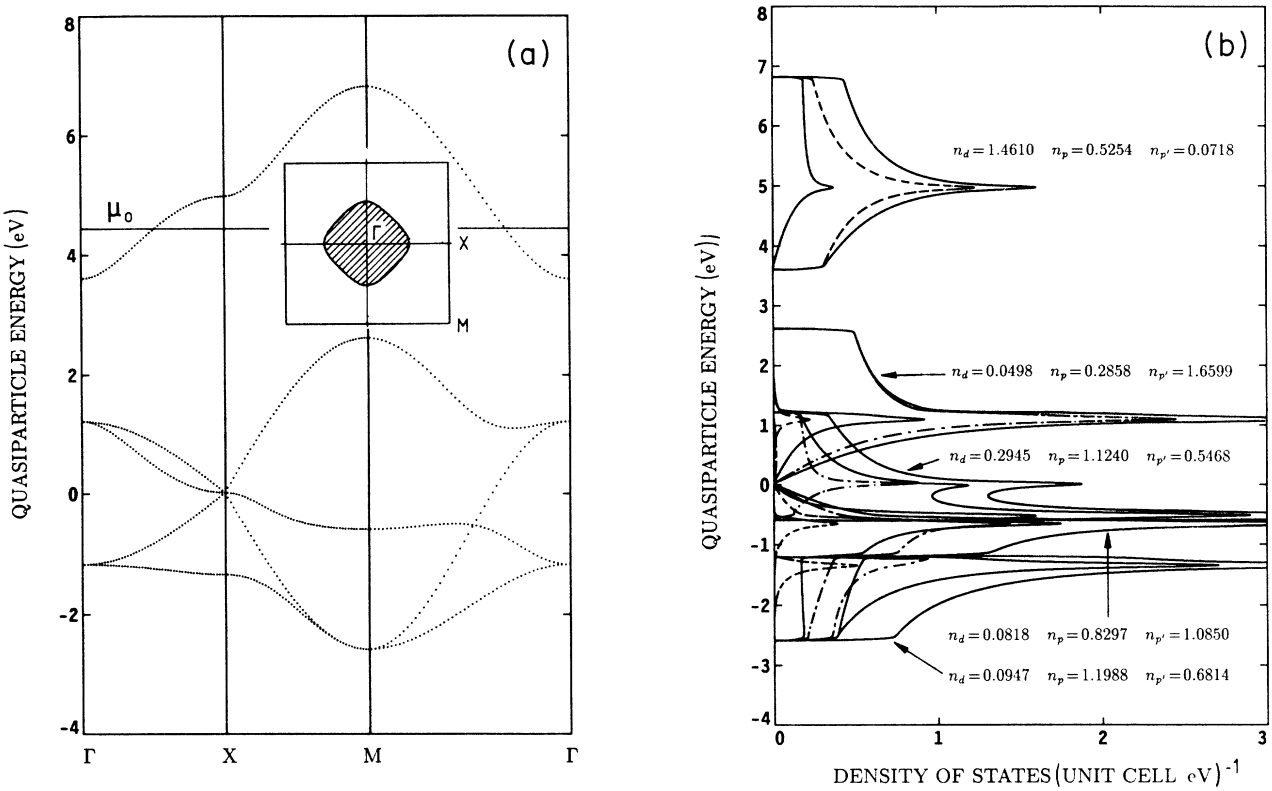

FIG. 2. (a) One-electron band structure of the five-states model Eq. (15) (uncorrelated case). $\beta'=-0.3$; the other energy parameters are listed in (19). $\beta'\neq 0$ lifts the fourfold degeneracy of the first four bands at Γ. The inset shows the Fermi surface for 8.36 electrons per CuO_2 unit cell ($n_d=0.852$, $n_p=3.512$, $n_{p'}=3.996$, where p and p' stand for bonding and nonbonding p orbitals, respectively). (b) Respective one-electron densities of states, ρ_d (dashed lines), ρ_p (solid lines), $\rho_{p'}$ (dashed-dotted lines), and total densities of states ρ_t (solid lines). $n_{d,p,p'}$ are the occupation numbers of each band.

states occupied). If we transform to hole creation and destruction operators by

$$\begin{aligned} D^{\dagger}_{\mathbf{k}\sigma}&=d_{\mathbf{k}\sigma},\quad P^{\dagger}_{\alpha\mathbf{k}\sigma}=p_{\alpha\mathbf{k}\sigma},\quad P'^{\dagger}_{\alpha\mathbf{k}\sigma}=p'_{\alpha\mathbf{k}\sigma}\ ,\\ D_{\mathbf{k}\sigma}&=d^{\dagger}_{\mathbf{k}\sigma},\quad P_{\alpha\mathbf{k}\sigma}=p^{\dagger}_{\alpha\mathbf{k}\sigma},\quad P'_{\alpha\mathbf{k}\sigma}=p'^{\dagger}_{\alpha\mathbf{k}\sigma}\ , \end{aligned} \tag{17}$$

then the Hamiltonian formally remains invariant if we make the replacements $\varepsilon_d\rightarrow\varepsilon_d^h=-\varepsilon_d-U_{dd}-8U_{dp}$, $\varepsilon_p^{(1)}-\varepsilon_p^{1h}=-\varepsilon_p-U_{pp}-4V_{dp}$, and $\gamma\rightarrow-\gamma$, $\beta^{(1)}\rightarrow-\beta^{(1)}$, together with an appropriate rescaling of the chemical potential. In the following we stay in the electron notation.

A comment should be added with respect to the two different representations in (9)–(11) and (12)–(14). If one is interested in the momentum dependence of the different interaction terms in (16) for a discussion of the formation of spin- or charge-density-wave states it might be worthwhile to consider the more complicated Bloch representation (9)–(11). In the present paper we will stick to the more simple plane-wave representation (12)–(14).

It seems as if the nonbonding bands that owe their dispersion to the $pp\sigma$ and $pp\pi$ transfer integrals, $\beta^{(\prime)}$, are less affected by correlations than the other bands. They are approximately given by

$$z=\varepsilon_p+4\beta' C_{1\mathbf{k}}C_{2\mathbf{k}}\pm 4\beta S_{1\mathbf{k}}S_{2\mathbf{k}}\ , \tag{18}$$

where $\varepsilon_{p'}=\varepsilon_p$ has been used. The actual energetic position of the nonbonding orbital with respect to the bonding orbital is a subtle question and is not known.[1]

If for a moment the assumption is made that the insulating gap forms between the upper antibonding band of d character and such a band of less correlated oxygen $p^{(\prime)}$ quasiparticles, then in the doped case one would have conductivity as well as superconductivity of nearly free O $p^{(\prime)}$ electrons (holes).

Since there are experimental hints that mainly oxygen charge carriers are involved in normal conduction and presumably also in superconductivity,[32] the inclusion of O-O hopping is really of crucial importance. Without this term, hole or electron motion can only occur through the Cu sites and may be impeded by localization effects due to large U_{dd} and V_{dp} values.

The actual values of parameters in (15) and (16) are not known. Using a constrained local-density approach, Hybertsen *et al.*[33] recently have derived the following values (electron representation):

$$\begin{aligned} -\gamma=E_{x,x^2-y^2}&=\frac{\sqrt{3}}{2}V_{pd\sigma}=-1.30,\quad U_{dd}=10.5\ ,\\ -\beta=E_{x,y}&=\frac{\sqrt{2}}{2}(V_{pp\sigma}-V_{pp\pi})=0.65\ ,\\ U_{pp}&=4.00\ ,\\ \varepsilon_d-\varepsilon_p&=\varepsilon_p^h-\varepsilon_d^h-U_{dd}+U_{pp}-4V_{dp}\ ,\\ V_{dp}&=1.20\ . \end{aligned} \tag{19}$$

All energies are in eV. Further values can be found in Refs. 34–36. In addition to (19), we have included O-O hopping of the form,

$$\beta' = E_{\alpha\alpha} = \frac{\sqrt{2}}{2}(V_{pp\sigma} - V_{pp\pi}) + V_{pp\pi}, \quad \alpha = x,y \ . \tag{20}$$

With respect to the energy separation $-\varepsilon_d - \varepsilon_p$ in electron notation we will use 3.6 eV, which places the bare atomic d level on top of the p level. Strong enough correlations at the oxygen sites still lead to a charge-transfer insulator. By going from $\varepsilon_d - \varepsilon_p > 0$ to $\varepsilon_d - \varepsilon_p < 0$ we gradually reduce the charge-transfer gap whereas spectral weights are not drastically influenced.

As mentioned previously, many authors have considered different simplified versions of $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$. A widely used simplification consists of retaining correlations only between carriers of d type and neglecting $\beta^{(\prime)}$, U_{pp}, and V_{dp} altogether. The remaining Hamiltonian has interested features. In the strong correlation limit it leads to frustration effects among copper d spins on a planar square lattice and simultaneously favors Cooper pair formation in the case of doping.[15] Still further simplification leads to the so-called t-J model.[2] It remains to be proven that these simplified model Hamiltonians contain the essential physics of high-T_c systems.

In this work we show that with respect to normal-state properties it might be important to retain all interactions and transfer terms and that the insulating state of the charge transfer type can only be obtained for the full five- or three-states model. In the actual calculation we shall employ a generalized version of the Hubbard-I approximation which needs to be justified, since it violates Luttinger's theorem. So far, the metal-insulator transition was studied by applying the slave-boson technique to the reduced three-states model (i.e., without O-O hopping).[30] However, the disadvantage of this method lies in the fact that all bandwidths shrink to zero at the metal-insulator transition for the case that the model Hamiltonian contains only one type of transfer term (as in the one-band Hubbard or in the reduced three-states model[30]). Since O-O hopping is crucial this kind of work should be repeated by making use of the full five-states model. This is under present investigation. The Gutzwiller method is difficult to apply to a multiband system; also it has the same advantages and disadvantages as the slave-boson method. Therefore, in order to get a first insight into the spectral weight of quasiparticles over an extended energy range we will use the Hubbard-I scheme. The energies in (19) and (20) are the input. Hence the result will very much depend on (19) and (20) and the Hubbard-I scheme which will put $p^{(\prime)}$ spectral weight on top of d spectral weight ($U_{pp} \approx \varepsilon_d - \varepsilon_{p'}$). Since d spectral weight of the Hubbard split band at $\varepsilon_d + U_{dd}$ lies on top of this, one obtains in a very simple manner a charge-transfer insulator. However, we will show that by using a constraint that fixes the total d-electron number, one can somewhat improve the Hubbard-I scheme. One can also add a constraint that would lead to the fulfillment of the Luttinger theorem. However, this does not work together with the Hubbard approximation.

III. GENERALIZED HUBBARD-I SCHEME AND NORMAL-STATE QUASIPARTICLES FOR THE FIVE-STATES MODEL

In the actual calculation we have retained in (15) and (16) all but the V_{dp} term. One of the implications of this term is further localization of charges on neighboring copper-oxygen sites. We assume that this localization can be mimicked by an enhanced energy separation between bare atomic energies of $p^{(\prime)}$ and d levels. The final result for the one-particle propagators can be written down in a more compact and transparent form without this term as

$$M_{\mathbf{k}\sigma}(\omega)\mathbf{G}^{(i)}_{\mathbf{k}\sigma}(\omega) = \mathbf{a}^{(i)} \ , \tag{21}$$

where

$$\mathbf{M}_{\mathbf{k}\sigma}(\omega) = \begin{pmatrix} \mathcal{G}^{-1}_{d\sigma}(\omega) & 2i\gamma S_{1\mathbf{k}} & -2i\gamma S_{2\mathbf{k}} & 0 & 0 \\ -2i\gamma S_{2\mathbf{k}} & \mathcal{G}^{-1}_{p\sigma}(\omega) & -4\beta S_{1\mathbf{k}} S_{2\mathbf{k}} & 0 & -4\beta' C_{1\mathbf{k}} C_{2\mathbf{k}} \\ 2i\gamma S_{2\mathbf{k}} & -4\beta S_{1\mathbf{k}} S_{2\mathbf{k}} & \mathcal{G}^{-1}_{p\sigma}(\omega) & -4\beta' C_{1\mathbf{k}} C_{2\mathbf{k}} & 0 \\ 0 & 0 & -4\beta' C_{1\mathbf{k}} C_{2\mathbf{k}} & \mathcal{G}^{-1}_{p'\sigma}(\omega) & -4\beta S_{1\mathbf{k}} S_{2\mathbf{k}} \\ 0 & -4\beta' C_{1\mathbf{k}} C_{2\mathbf{k}} & 0 & -4\beta_{1\mathbf{k}} S_{2\mathbf{k}} & \mathcal{G}^{-1}_{p'\sigma}(\omega) \end{pmatrix} , \tag{22}$$

$$\mathbf{G}^{(i)T}_{\mathbf{k}\sigma}(\omega) = (\langle\langle d_{\mathbf{k}\sigma} | A_i \rangle\rangle, \ \langle\langle p_{1\mathbf{k}\sigma} | A_i \rangle\rangle, \ \langle\langle p_{2\mathbf{k}\sigma} | A_i \rangle\rangle, \ \langle\langle p'_{2\mathbf{k}\sigma} | A_i \rangle\rangle, \ \langle\langle p'_{1\mathbf{k}\sigma} | A_i \rangle\rangle) \ , \tag{23}$$

$$A_1 = d^\dagger_{\mathbf{k}\sigma}, \quad A_2 = p^\dagger_{1\mathbf{k}\sigma}, \quad A_3 = p^\dagger_{2\mathbf{k}\sigma}, \quad A_4 = p'^\dagger_{2\mathbf{k}\sigma}, \quad A_5 = p'^\dagger_{1\mathbf{k}\sigma} \ , \tag{24}$$

the ith component of $\mathbf{a}^i$ equals 1, all other components are zero. The atomic-limit-like propagators are given by

$$\mathcal{G}_{\xi\sigma} = \frac{1 - \langle n_{\xi-\sigma} \rangle}{z - \varepsilon_\xi} + \frac{\langle n_{\xi-\sigma} \rangle}{z - \varepsilon_\xi - U_{\xi\xi}}, \quad \xi = d,p,p' \ . \tag{25}$$

The propagators (24) originate from a decoupling on the second stage of the equations of motion, which is equivalent to the replacement of $(z - \varepsilon_\xi)$ by atomic-limit-like propagators in the exact Green's functions derived with $\mathcal{H}_0$ alone.[37] Superconductivity as well as Hall-effect measurements were recently discussed on the basis of the t-J model by using a similar decoupling procedure.[38,39] To the set of Eqs. (22)–(25) we have to add the corresponding equation for the chemical potential

$$\sum_\sigma (\langle n_{d\sigma} \rangle + 2\langle n_{p\sigma} \rangle + 2\langle n_{p'\sigma} \rangle) = n \ , \tag{26}$$

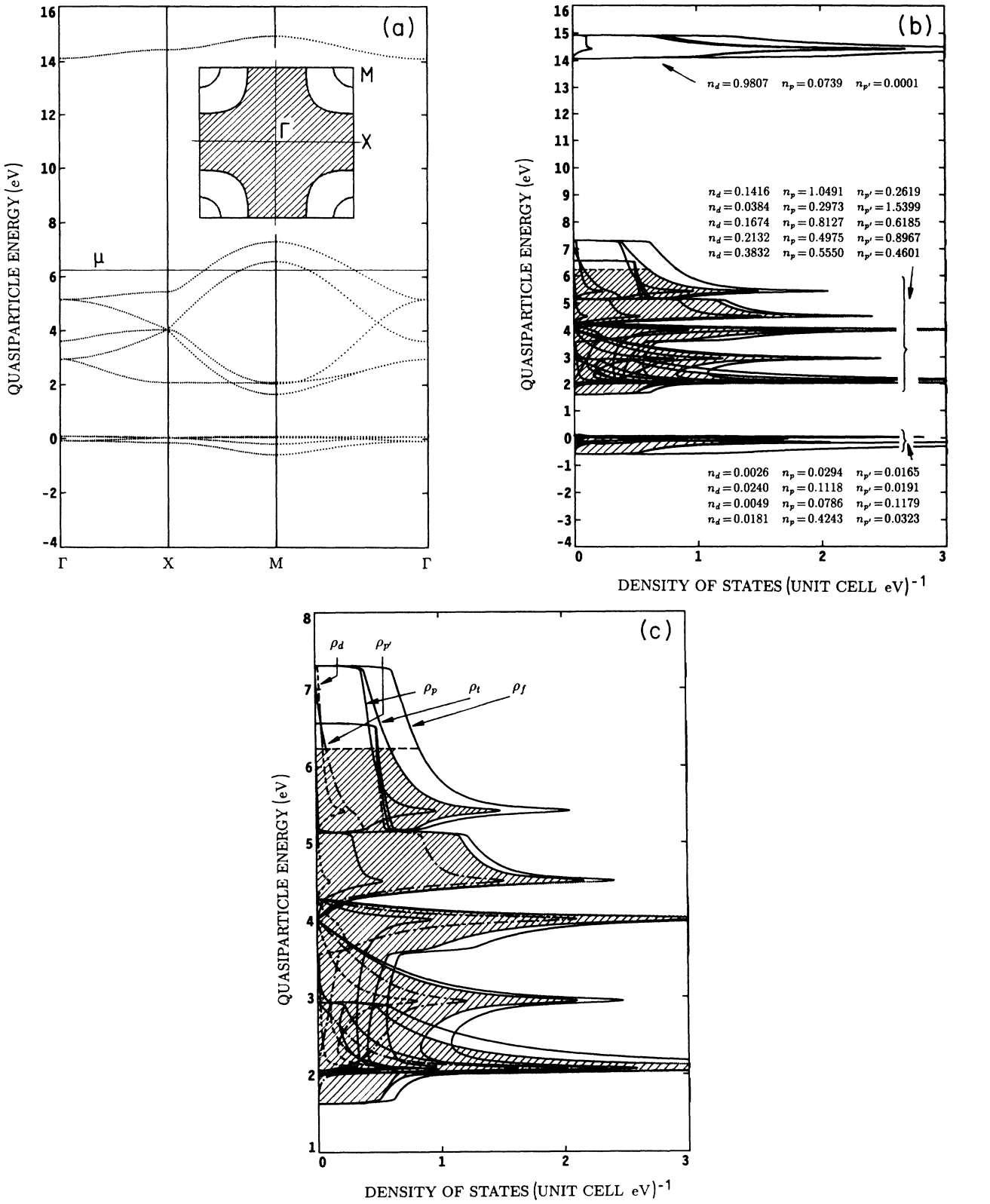

FIG. 3. (a) Quasiparticle band structure for the five-states model as obtained within the generalized Hubbard-I scheme for 8.36 electrons per unit cell. $\beta' = -0.3$; all other parameter values are defined in (19). The Fermi surface consists of two hole pockets centered at M, whereby the smaller pocket consists of nonbonding p states. (b) Respective total quasiparticle density of states and partial d, p, and p' contributions. The free-electron density of states (which is always the largest one) is shown for comparison. $n_{d,p,p'}$ are within numerical accuracy the occupation numbers of each band. The shaded area marks the occupied region. (c) Respective quasiparticle densities of states of the band package beneath the insulating gap on an extended scale showing more clearly that states near the Fermi surface mainly are of p and p' character.

where n is the number of electrons per CuO_2 unit formula. Resulting quasiparticle bands and density of states for the five-states model are shown in Figs. 3(a)–3(c) for $n=8.36$ electrons (i.e., 0.64 holes with respect to the insulating state of CuO_2 which corresponds to $n=9$ electrons per unit cell). All numerical calculations are done for $T=100$ K. With respect to the parameter values we stick to those derived recently by Hybertsen *et al.*[33] and which are given above.

One general feature of our results is that we obtain ten quasiparticle bands for the five-states model (six for the case of three-states). This holds also for arbitrarily small values of U_{dd} and U_{pp} and is in this limit a typical artifact of the original Hubbard-I approximation. However, for strong enough correlations as in our case ($U_{dd}=10.5$ eV, $U_{pp}\geq 4$ eV) the appearance of Hubbard subbands and the associated spectral weights might be not too unrealistic. For infinitely strong correlations, $U_{dd}, U_{pp}\rightarrow\infty$, we are left with five (three) bands at finite energies.

Figure 3(a) shows the quasiparticle band structure and the position of the chemical potential that cuts two bands, of which the upper one is of predominant p character with a small admixture of d and p' states, whereas the lower one is of predominant p' type with p states admixed. This can be seen from Fig. 3(b) in which the occupation numbers of each band are listed, and from Fig. 3(c), which shows the band package beneath the insulating gap on an extended scale. The occupation numbers are always given for the whole band (regardless of the filling) and were taken from the density of states.

For approximately nine electrons per unit formula the system is an insulator where the metal insulator transition is more of the charge transfer than of the Mott-Hubbard type. This result is remarkable in view of the simplicity of the underlying theory. But as discussed before, it seems to be sufficient to fulfill the condition that the charge-transfer energy $\Delta=(\varepsilon_d-\varepsilon_p+2V_{dp})/2$, is small enough as compared to U_{dd}, in order to be in the regime where charge transfer is important. Upon doping the system rapidly metallizes. The inset in Fig. 3(a) shows that for a doping of 0.64 holes per unit cell (with respect to the insulating ground state) the Fermi surface consists of two-hole pockets of p and p' character at each corner of the Brillouin zone. Of interest could be the fact that for $\varepsilon_{p'}>\varepsilon_p$ a quasidegenerate situation can be realized, in which the two-hole pockets nearly coincide. Coupling of the small energy separation between the p and p' bands to local deformation could then result in large hole-phonon interactions (which reminds one of the possible superconducting coupling mechanism in heavy-fermion systems[40]).

The quasiparticle density-of-states curves were evaluated with the help of

$$\rho_\xi(\omega)=\frac{a^2}{(2\pi)^2}\sum_{\mathbf{k},\sigma}\frac{-1}{\pi}\,\mathrm{Im}G_{\xi\mathbf{k}\sigma}(\omega),\quad \xi=d,p,p'\ , \tag{27}$$

where the resulting δ functions have been replaced by

$$\delta(\omega-z_i)=\frac{1}{\sqrt{\pi}}\lim_{\tau\rightarrow 0}\left[\frac{1}{\sqrt{\tau}}e^{-(\omega-z_i)^2/\tau}\right]. \tag{28}$$

Here, z_i ($i=1,\ldots,10$) are the poles of the propagators and τ is appropriately chosen to yield smooth density-of-states curves (we used $\tau=10^{-3}$, 5000 points in the irreducible part of the Brillouin zone and 2500 intervals on the energy scale of each band; this led to 10 h of CPU time for the evaluation of the density-of-states curves). Note that we cannot make use of one-particle schemes like the tetrahedron method for the density-of-states calculation, since spectral weight in each band changes with filling and change of parameter values.

The present speculation that quasiparticles in the vicinity of the Fermi energy are only weakly correlated p and p' holes is of particular interest and would rule out pairing mechanisms based on superexchange or charge excitations of the type $Cu^{2+}O^{2-}\leftrightarrow Cu^{+}O^{-}$. If the present speculation were true then charge excitations of holes in the two-anion oxygen networks of bonding and nonbonding type would be more important. However, we would like to add that the present findings could be partially connected with the Hubbard-I scheme employed in this work, which does not allow us to calculate residual interactions among the quasiparticles.

The original Hubbard-I approximation for the single-band Hubbard model is the result of a kind of strong-coupling expansion. In spite of its simplicity it allows a first insight into the Mott-Hubbard transition. The extended Hubbard-I scheme that has been used in this work is more refined and the results show that for appropriate parameter values a charge-transfer insulator instead of a Mott insulator can be obtained. However, two negative aspects are connected with the Hubbard-I scheme. First, lifetime effects (which will be discussed later) are not taken into account. Second, the Luttinger theorem is not fulfilled. Results for the quasiparticle density of states for electrons on a square lattice described by the single-band Hubbard model have shown that with increase in U the singularity in the generalized density of states rapidly vanishes.[27] This fact is connected with the fulfillment of Luttinger's theorem.

In principle there is a systematic way to improve the Hubbard-I scheme by using the method of projecting operators.[41–43] This method conserves the fourth moments of the propagators (only third moments are conserved within the Hubbard-I approximation) and can be extended to conserve higher moments. So, for example, magnetic and nonmagnetic solutions and critical values for correlation energies have been discussed with the help of the four-momentum method.[44] However, at no stage is the Luttinger theorem fulfilled. Therefore, we used the lowest nontrivial order, which has the advantage to be numerically tractable.

In order to see the impact of Luttinger's theorem on the present work we have added a constraint which keeps the volume enclosed by the Fermi surface for a given filling fixed while U_{dd} and U_{pp} can be varied. This can be done by adding to the Hamiltonian a term of the form

$$\eta\left[\frac{1}{N}\sum_{n,\mathbf{k},\sigma}f(\varepsilon^0_{n\mathbf{k}\sigma})-\frac{1}{N}\sum_{\xi,\mathbf{k},\sigma}\hat{n}_{\xi\mathbf{k}\sigma}\right], \tag{29}$$

where $\varepsilon^0_{n\mathbf{k}\sigma}$ are the electronic energies in the absence of

correlations (n is the band index) and $n_{\xi\mathbf{k}\sigma}=\langle \hat{n}_{\xi\mathbf{k}\sigma}\rangle$ has to be calculated with the help of (22)–(25),

$$n_{\xi\mathbf{k}\sigma}=-\frac{1}{\pi}\int d\omega\, f(\omega)\mathrm{Im}G_{\xi\mathbf{k}\sigma},\quad \xi=d,p,p' . \tag{30}$$

Unfortunately, this constraint of including equal volume inside the Fermi surface for noncorrelated and correlated cases cannot be fulfilled within the Hubbard-I scheme (this one immediately realizes by considering the behavior of the two weight functions for a single-band Hubbard model). But such a constraint can be useful if more refined approximations are used. Thus we investigate at present the application of the slave-boson method to our five-states model together with such a constraint.

A definite improvement of the Hubbard-I scheme can be obtained by partially fulfilling constraints such as (29). Remembering that in the 1:2:3 compound the valence of the Cu ion depends on the amount of oxygen ($Y^{3+}Ba_2^{2+}Cu_3^{1.666+}O_6^{2-}$, $Y^{3+}Ba_2^{2+}Cu_3^{2+}O_{6.5}^{2-}$, $Y^{3+}Ba_2^{2+}Cu_3^{2.333+}O_7^{2-}$ etc.), one might think of fixing the total number of electrons per unit cell as well as the d-electron number. This can be done by adding to the Hamiltonian the global constraint

$$\lambda\left[n_d-\frac{1}{N}\sum_{\mathbf{k},\sigma} d^{\dagger}_{\mathbf{k}\sigma}d_{\mathbf{k}\sigma}\right] . \tag{31}$$

This procedure resembles the slave-boson technique. λ plays the role of a chemical potential for d electrons. The influence of this constraint on the behavior of quasiparticles has been investigated in detail for the three-states and will be discussed in the next section. It will be shown that due to the amount of d-electron charge at the Cu site one can either have a charge-transfer insulator or a Mott insulator.

A final comment concerns high-temperature superconductivity. If as discussed above, there are mainly less strongly correlated p and p' holes at the Fermi surface, then superconductivity should be discussed in the frame of an extended Hamiltonian by adding to (15) and (16) attractive interactions of the type

$$\begin{aligned}\mathcal{H}_2=&-U^{11}_{pp'}\sum_{\mathbf{m}_1} p^{\dagger}_{1\mathbf{m}_1\uparrow}p'^{\dagger}_{2\mathbf{m}_1\downarrow}p'_{2\mathbf{m}_1\downarrow}p_{1\mathbf{m}_1\uparrow}-U^{22}_{p'p}\sum_{\mathbf{m}_2} p'^{\dagger}_{1\mathbf{m}_2\uparrow}p^{\dagger}_{2\mathbf{m}_2\downarrow}p_{2\mathbf{m}_2\downarrow}p'_{1\mathbf{m}_2\uparrow}\\
&-U^{12}_{p'p'}\sum_{\langle \mathbf{m}_1\mathbf{m}_2\rangle} p'^{\dagger}_{2\mathbf{m}_1\uparrow}p'^{\dagger}_{1\mathbf{m}_2\downarrow}p'_{1\mathbf{m}_2\downarrow}p'_{2\mathbf{m}_1\uparrow}-U^{12}_{pp}\sum_{\langle \mathbf{m}_1\mathbf{m}_2\rangle} p^{\dagger}_{1\mathbf{m}_1\uparrow}p^{\dagger}_{2\mathbf{m}_2\downarrow}p_{2\mathbf{m}_2\downarrow}p_{1\mathbf{m}_1\uparrow}\\
&-U^{12}_{pp'}\sum_{\langle \mathbf{m}_1\mathbf{m}_2\rangle} p^{\dagger}_{1\mathbf{m}_1\uparrow}p'^{\dagger}_{1\mathbf{m}_2\downarrow}p'_{1\mathbf{m}_2\downarrow}p_{1\mathbf{m}_1\uparrow}-U^{12}_{p'p}\sum_{\langle \mathbf{m}_1\mathbf{m}_2\rangle} p'^{\dagger}_{2\mathbf{m}_1\uparrow}p^{\dagger}_{2m_2\downarrow}p_{2\mathbf{m}_2\downarrow}p'_{2\mathbf{m}_1\uparrow} .\end{aligned} \tag{32}$$

The first two terms describe negative $U_{pp'}$ terms for two holes at each of the two oxygen basis atoms at $\mathbf{m}_{1=x}$ and $\mathbf{m}_{2=y}$ (i.e., one hole in the bonding p and one hole in the antibonding p' orbital). Such terms could exist, since introducing two holes at an oxygen site into two different orbitals saves correlation energy. In how far the response of the surrounding lattice would compensate this energy gain is unclear and remains to be calculated. It is well known that such terms lead to an effective Hamiltonian that describes hopping of local Cooper pairs if states with a single hole per oxygen site are projected out. Originally negative-U centers were obtained by taking into account the interaction of an electron with local displacements of a given atom within the one-band Hubbard model.[45]

The remaining terms describe attractive hole-hole interactions with holes on neighboring oxygen atoms. These terms can arise from usual electron-phonon interactions and from excitations of the p and p' plasma. Probably the last two terms will be rather small due to the smaller nearest-neighbor overlap of bonding and nonbonding orbitals. There is some resemblance of the above interactions with corresponding interactions in the bipolaron model. For a recent review of the bipolaron theory see Ref. 46.

IV. GENERALIZED HUBBARD-I SCHEME AND NORMAL-STATE QUASIPARTICLES FOR THE THREE-STATES MODEL

The three-states model is obtained from the five-states model by neglecting the β' transfer terms in (22). This formally decouples bonding p and nonbonding p' orbitals and the resulting propagators can be written in compact form as

$$\langle\langle d_{\mathbf{k}\sigma}|d^{\dagger}_{\mathbf{k}\sigma}\rangle\rangle=\frac{1-16\beta^2(S_{1\mathbf{k}}S_{2\mathbf{k}})^2\mathcal{G}^2_{p\sigma}(z)}{\mathcal{G}^{-1}_{d\sigma}(z)-\mathcal{D}_{\sigma}} , \tag{33}$$

$$\langle\langle p_{\alpha\mathbf{k}\sigma}|p^{\dagger}_{\alpha\mathbf{k}\sigma}\rangle\rangle=\frac{1-4\gamma^2S^2_{\beta\neq\alpha}\mathcal{G}_{p\sigma}(z)\mathcal{G}_{d\sigma}(z)}{\mathcal{G}^{-1}_{p\sigma}(z)-\mathcal{P}_{\sigma}(z)} , \tag{34}$$

$$\langle\langle p'_{\alpha\mathbf{k}\sigma}|p'^{\dagger}_{\alpha\mathbf{k}\sigma}\rangle\rangle=\frac{\mathcal{G}^{-1}_{p'\sigma}}{\mathcal{G}^{-2}_{p'\sigma}-(4\beta S_{1\mathbf{k}}S_{2\mathbf{k}})^2} , \tag{35}$$

where

$$\begin{aligned}\mathcal{D}_{\sigma}(z)=&4\{\gamma^2(S^2_{1\mathbf{k}}+S^2_{2\mathbf{k}})\mathcal{G}_{p\sigma}(z)\\
&+4\beta(S_{1\mathbf{k}}S_{2\mathbf{k}})^2[\beta\mathcal{G}^{-1}_{d\sigma}(z)-2\gamma^2]\mathcal{G}^2_{p\sigma}(z)\} ,\end{aligned} \tag{36}$$

$$\begin{aligned}\mathcal{P}_{\sigma}(z)=&4\{\gamma^2(S^2_{1\mathbf{k}}+S^2_{2\mathbf{k}})\mathcal{G}_{d\sigma}(z)\\
&+4\beta(S_{1\mathbf{k}}S_{2\mathbf{k}})^2[\beta-2\gamma^2\mathcal{G}_{d\sigma}(z)]\mathcal{G}_{p\sigma}(z)\} .\end{aligned} \tag{37}$$

Numerical results obtained for the three-states model are displayed in Figs. 4–9. In all figures the corresponding contributions of the decoupled nonbonding orbitals are omitted.

Fig. 4(a) shows the quasiparticle bands and Figs. 4(b) and 4(c) the respective densities of states. The insulating gap opens between the lower-lying bonding-nonbonding bands of mainly p character and the higher-lying antibonding band of essentially d character as before for the

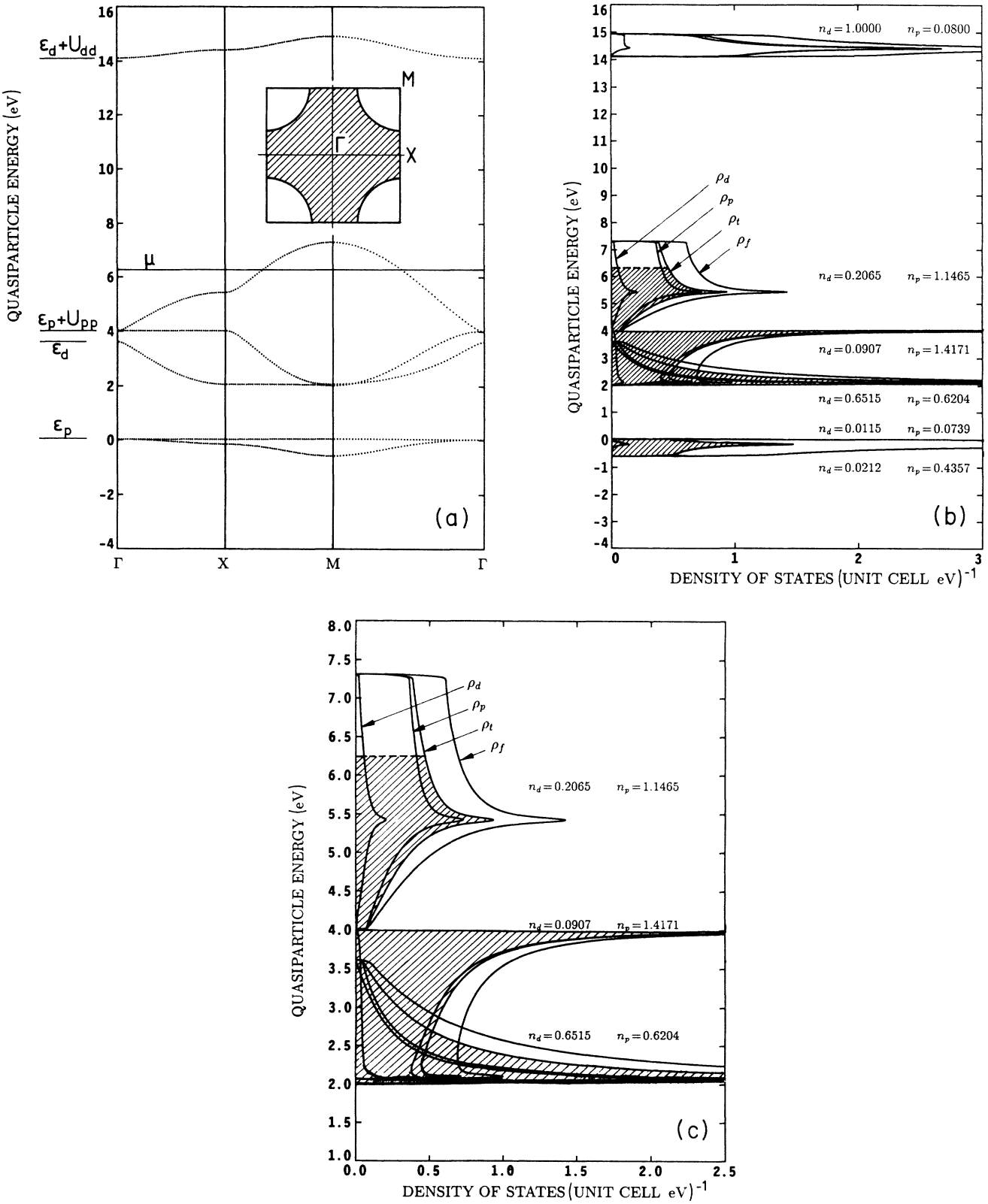

FIG. 4. (a) Quasiparticle band structure of the three-states model (which consists of one d state and the two bonding p states per unit cell) as obtained within the generalized Hubbard-I scheme for 4.5 electrons per unit cell. Parameter values are defined in (19). The Fermi surface now consists of only one hole pocket at each M point (in contrast to the five-states model). (b) Respective total quasiparticle density of states and partial d and p contributions. Again for comparison the free-electron density of states is shown. $n_{d,p}$ are within numerical accuracy the occupation numbers of each band. (c) Respective quasiparticle densities of states on an extended scale showing more clearly the charge distribution in the three bands beneath the insulating gap.

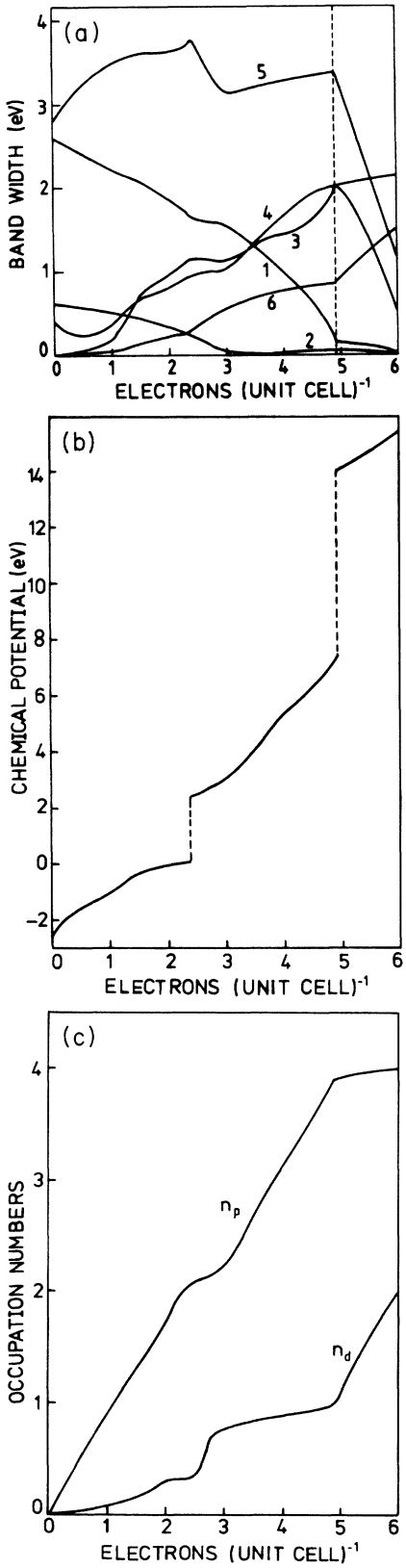

FIG. 5. (a) Three-states model: variation of quasiparticle bandwidths with filling. The discontinuity at $n \approx 5$ electrons per unit cell corresponds to the filling for which the metal-insulator transition occurs. (b) Three-states model: variation of the chemical potential ($T = 100$ K) with filling. (c) Three-states model: variation of the occupation numbers $n_{d,p}$ with filling.

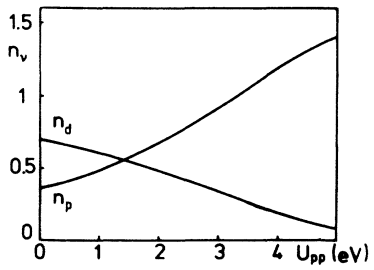

FIG. 6. Three-states model: variation of the occupation numbers in the band below the insulating gap as function of U_{pp} for $n = 4.9$ electrons per unit cell.

five-states model. From the specific distribution of d spectral weights below the gap in Figs. 4(b) and 4(c) it is clear that the insulating state is of the charge-transfer type. The Fermi surface consists of one p-like hole pocket centered at each corner of the Brillouin zone.

It is quite interesting to see how the total band structure changes if we fill in electrons. Since correlations only play an active role in the presence of carriers, the actual form and width of each band strongly depends on the electron filling. Thus, for zero filling we obtain the corresponding uncorrelated bands of $\mathcal{H}_0$. The remarkable variation of the bandwidths as function of filling is shown in Fig. 5(a). It is also obvious from this figure how the crossover occurs from nearly free fermions to strongly correlated fermions with increasing electron density. For example, for the chosen energy separation of atomic levels, $\varepsilon_d - \varepsilon_p = 3.6$ eV (electron notation), the lowest-lying band 1 corresponds at low filling to the antibonding band of mixed symmetry where the degree of admixture of p- and d-like symmetry is determined by the energy separation and by the hybridization energy γ. With increasing filling the different strong correlations among p and d electrons determine the final spectral weight. At

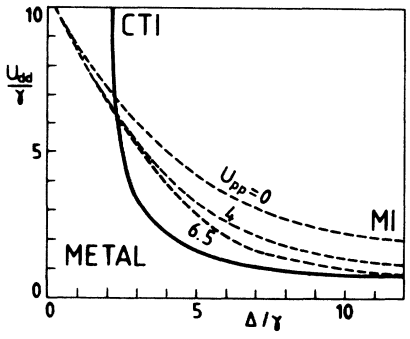

FIG. 7. Metal-insulator phase diagram of the three-states model in the (U_{dd},Δ) plane, where Δ is the charge-transfer energy, $\Delta = (\varepsilon_d - \varepsilon_p + 2V_{dp})/2$ with $V_{dp} = 0$ in this work. (CTI) and (MI) indicate the parameter space of charge-transfer and Mott insulators, respectively. The solid line is the transition line as obtained by Balseiro *et al.* (Ref. 30) in their slave-boson mean-field calculation. U_{pp} has little influence on the phase diagram in the sense that already for moderate values of U_{pp} the insulating state is of the charge-transfer type (i.e., $n_p > n_d$ in the band beneath the gap, see also Fig. 6.

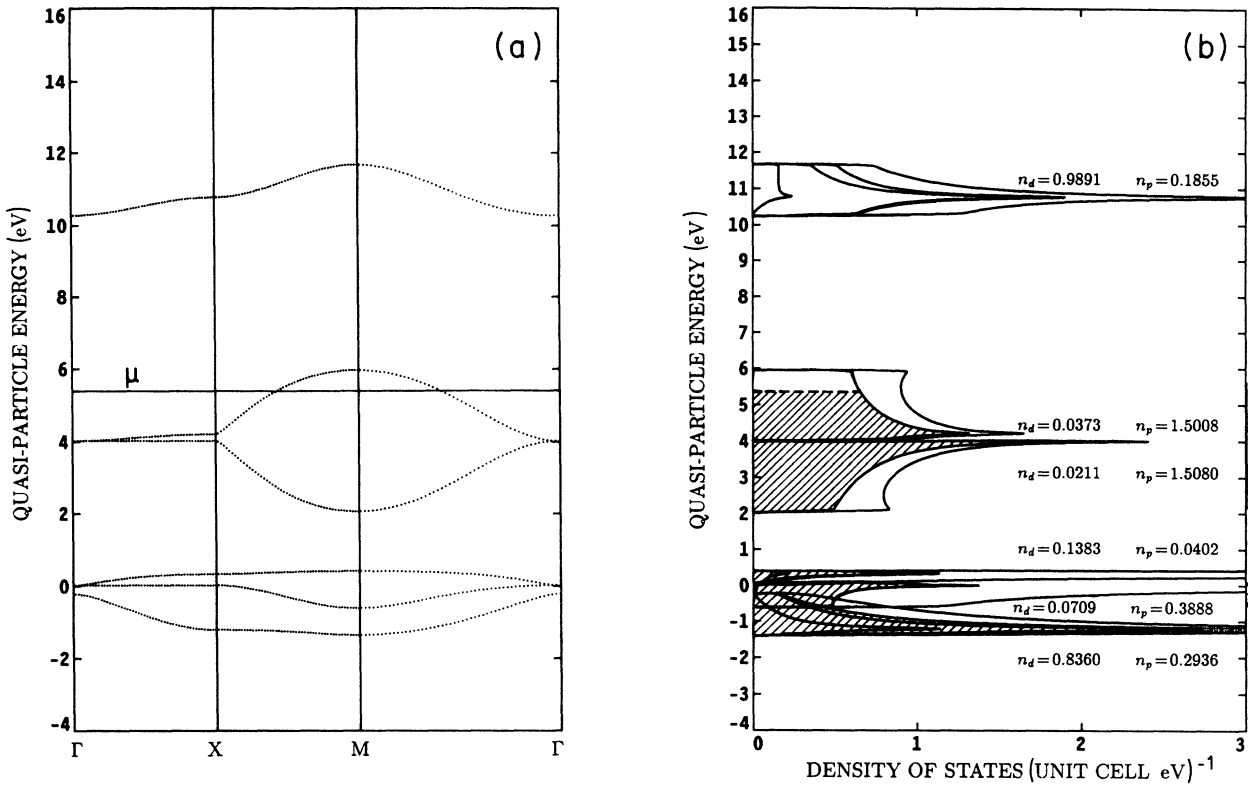

FIG. 8. (a) Quasiparticle bands for the three-states model for a total number of 4.5 electrons per unit cell, whereby the number of d electrons per unit cell ($=1$) is kept fixed by using the constraint Eq. (30). Same energy parameters values as without constraint. (b) Respective quasiparticle densities of state. Note, that due to the constraint ($\lambda=5.447$) bands with d-like character have come down in energy, which causes the insulating gap to shrink from 6.5 to 4 eV. Note also the different spectral weights in (b) as compared to the results in Fig. 4 that were obtained without constraint.

complete filling (six electrons) this band is nearly dispersionless, it is depleted of d electrons and can accommodate only ≈ 0.5 p electrons. It is furthermore visible that the role of band 3 and 6 (dispersionless at low filling) is taken over by band 1 and 2 at high filling.

Besides band narrowing effects charge-transfer effects play an important role. Figure 5(a) shows that the widths of band 3 and 4 increase with filling. With increasing electron densities these bands can accommodate more and more p electrons and less d electrons. Furthermore, this figure clearly reveals a discontinuity at approximately $n=5$ electrons. Apart from band 4 (which corresponds to the antibonding band with dominant p-type spectral weight) all other bands show a discontinuity at this critical electron density. Actually the metal-insulator transition occurs for this critical value of $n_c \simeq 5$. Within numerical accuracy the actual transition occurs for an electron number which lies slightly below five (or slightly below nine for the five-states model). Thus the experimental fact that for $1+\delta$ ($\delta \ll 1$) holes per CuO_2 complex the system rapidly metallizes is approximately reproduced by our calculations.

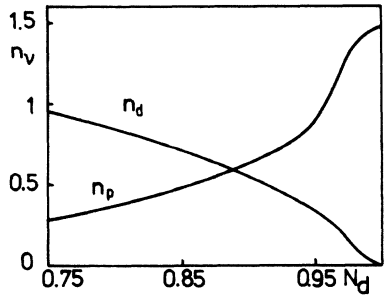

FIG. 9. Three-states model: variation of the occupation numbers in the band below the insulating gap for a total number of 4.5 electrons per unit cell as function of the d-electron number N_d per unit cell (and otherwise the same energy parameters as before). Note the rapid change of the spectral weights if N_d decreases from 1.

Figures 5(b) and 5(c) show the variation of the chemical potential and the total number of d and p electrons as function of filling. Altogether, Figs. 5(a)–5(c) show several discontinuities that point towards the possibility of metal-insulator transitions at different fillings. However, it is obvious from the figures that the discontinuity is most pronounced for $n \approx 5$ electrons.

Of further interest is the sign of the O-O transfer integrals. Note first that for $\beta<0$ the sequence of bands below the insulating gap is bonding above nonbonding band. For $\beta>0$ this order is reversed, which causes the Fermi level to lie in the nonbonding band. Unfortunately we cannot evaluate the correct sign of β within our approach. It seems that one-electron band structure calcu-

lations favor $\beta<0$.

A further remark concerns the gap width. We have obtained a rather large insulating gap of the order of $U_{dd}-U_{pp}\approx 6.5$ eV. This is probably too large and is connected with our choice $\varepsilon_d-\varepsilon_p=3.6$ eV. Electron energy-loss studies on high-T_c systems probe in plane unoccupied O $2p$ states above the Fermi surface[47] and thus confirm our results that mainly p and p' states are at the Fermi surface, but these studies also show that the insulating gap is of the order of 1.7 eV. In our calculation the large gap can only be reduced by either making $U_{dd}-U_{pp}$ much smaller or by reversing the order of atomic levels, ε_p and ε_d, respectively. Note, however, that the slave-boson calculation[30] also yields a rather large mass gap (>4 eV for the same set of parameter values). We think that the final width of the insulating gap could be of crucial importance for normal-state as well as for superconducting properties. If this gap could be made arbitrarily small then volume fluctuations would lead to fluctuating bandwidths and a superconducting pairing mechanism similar to the mechanism based on the Kondo volume collapse in heavy-fermion systems[39] is conceivable.

As discussed in the Introduction, the role of U_{pp} is to put p spectral weight on top of d spectral weight within the Hubbard-I scheme. Figure 6 shows how the occupation numbers in the band beneath the insulating gap change with U_{pp}.

Figure 7 shows the metal-insulator phase diagram in the (U_{dd},Δ) plane obtained in this work. It resembles the phase diagram that was calculated by Balseiro *et al.*[30] with the help of the slave-boson technique. The variation of the border line between metallic and insulating states is in our work less pronounced than in Balseiro's work. Small variations of U_{pp} have not much impact on the phase diagram as long as $U_{pp}<U_{dd}$ holds. The quasiparticle band structure that was obtained in Ref. 30, consists of bonding and antibonding and dispersionless nonbonding bands (because O-O hopping was neglected). In the slave-boson mean-field theory the renormalized hole mass is a simple function of doping and becomes infinite for vanishing doping. The semiconducting state is then characterized by dispersionless antibonding and bonding bands (whereas bandwidths remain finite in our work). Balseiro *et al.* emphasize that the inclusion of the interatomic V_{dp} term might be crucial for the occurrence of superconductivity, since two holes added to the charge-transfer insulator are bounded for $V_{dp}>|\varepsilon_d-\varepsilon_p|$.

We conclude this section by briefly discussing constraints like (31). Constraints, by which we can fix individual particle numbers, have a big impact on the generalized Hubbard-I scheme. Figures 8(a) and 8(b) show band structure and density-of-states results for the case that we fix the number of d electrons per unit cell to $N_d=1$ and the total number of electrons to $N_d+N_p=4.5$. This constraint has the effects that (i) the lowest-lying band is now of pure d character [compare the spectral weights of Figs. 8(b) and 4(b)]; and (ii) the insulating gap has become smaller (≈ 4 eV) and resembles in magnitude the value obtained in Ref. 30. In Fig. 9 we show the occupation numbers in the band below the gap for different values of N_d and $N_d+N_p=4.5$. Note the rapid change of the spectral weights if N_d decreases from 1. Note also that with decreasing d-electron number the metal-insulator transition changes from the charge-transfer to the Mott-Hubbard type.

V. EFFECTIVE INTERACTIONS NEAR THE $U_{dd}=\infty$ FIXED POINT

In this section residual interactions among particles will be discussed for the reduced three-states model, which corresponds to the Emery model and which is the basis of the t-J model. The reduced three-states model is obtained by neglecting direct O-O hopping (i.e., we take $\beta=0$). Moreover, since we are interested in the strong-coupling limit, we will set $U_{dd}\to\infty$ and $U_{pp}=0$. In what follows Hubbard operators will be used for d electrons,

$$U_{dd}\to\infty:\ d^{\dagger}_{\mathbf{n}\sigma}\to X^{\sigma 0}_{\mathbf{n}},\quad d_{\mathbf{n}\sigma}\to X^{0\sigma}_{\mathbf{n}}\ ; \tag{38}$$

this automatically excludes double occupancy of d states.[48] The decoupling of d- and p-electron degrees of freedom is carried through by eliminating the d-p transfer term to order $O(\gamma^4)$. Before presenting results, we would like to make a comment.

(i) The projective perturbation theory in $1/U_{dd}$ for eliminating double occupied states leads to an effective one-band strong-coupling model with an exchange constant $J\simeq\gamma^2/U_{dd}\approx 0.16$. For $U_{dd}\to\infty$ and U_{pp} finite the exchange is of the order $J\simeq\gamma^2/U_{pp}\approx 0.42$. If we take the limit $U_{dd}\to\infty$, $U_{pp}=0$, and make a canonical perturbation theory with respect to γ to fourth order, then the resulting exchange is $J\simeq\gamma^4/(\varepsilon_d-\varepsilon_p)^3\approx 0.06$ and is considerably smaller. Thus, one should not neglect U_{pp} terms when discussing exchange terms in the strong-coupling limit. However, the aim of this section is to show that at large doping it might be worthwhile to consider more terms than those contained in the effective one-band model. To this it is sufficient to consider $U_{pp}=0$.

(ii) With respect to superconductivity and the possible importance of $p^{(\prime)}$-$p^{(\prime)}$ interaction terms like (32) one should go back to the original five-states model and eliminate γ together with β and β' to a given order. Such a canonical perturbation theory could then be accomplished by projecting out double occupancy of d states. The resulting terms will be discussed at the end of this section.

The reduced three-states model in the limit $U_{dd}\to\infty$ is given by

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1\ , \tag{39}$$

$$\mathcal{H}_0=\sum_{\mathbf{n},\sigma}\varepsilon_d X^{\sigma\sigma}_{\mathbf{n}}+\sum_{\mathbf{n},\sigma}\varepsilon_{d0}X^{00}_{\mathbf{n}}+\sum_{\alpha,\mathbf{k},\sigma}\varepsilon_p p^{\dagger}_{\alpha\mathbf{k}\sigma}p_{\alpha\mathbf{k}\sigma}\ , \tag{40}$$

$$\mathcal{H}_1=\frac{1}{\sqrt{N}}\sum_{\alpha,\mathbf{n},\mathbf{k},\sigma}(-1)^{\alpha}S^{\alpha}_{\mathbf{k}}(e^{i\mathbf{k}\cdot\mathbf{n}}X^{\sigma 0}_{\mathbf{n}}p_{\alpha\mathbf{k}\sigma}-e^{-i\mathbf{k}\cdot\mathbf{n}}p^{\dagger}_{\alpha\mathbf{k}\sigma}X^{0\sigma}_{\mathbf{n}})\ . \tag{41}$$

In order to eliminate uneven powers of γ to any desired order one can use an onionlike procedure:

$$\mathcal{H}_{\text{eff}}=\cdots e^{S_c}e^{S_l}\mathcal{H}e^{-S_l}e^{-S_c}\cdots\ , \tag{42}$$

where S_l (S_c) eliminates the term linear (cubic) in γ. This leads to

$$[S_l,\mathcal{H}_0]=-\mathcal{H}_1,\quad [S_c,\mathcal{H}_0]=-\tfrac{1}{3}[S_l,[S_l,\mathcal{H}_1]]\ , \tag{43}$$

$$\mathcal{H}_{\rm eff}=\mathcal{H}_0+\tfrac{1}{2}[S_l,\mathcal{H}_1]+\tfrac{1}{8}[S_l,[S_l,[S_l,\mathcal{H}_1]]]+O(\gamma^6)\ , \tag{44}$$

where S_l is given by

$$S_l=-\frac{2i\gamma}{\varepsilon_p-\tilde{\varepsilon}_d}\frac{1}{\sqrt{N}}\sum_{\alpha,\mathbf{n},\mathbf{k},\sigma}(-1)^{\alpha}S^{\alpha}_{\mathbf{k}}(e^{i\mathbf{k}\cdot\mathbf{n}}X^{\sigma 0}_{\mathbf{n}}p_{\alpha\mathbf{k}\sigma}+e^{-i\mathbf{k}\cdot\mathbf{n}}p^{\dagger}_{\alpha\mathbf{k}\sigma}X^{0\sigma}_{\mathbf{n}})\ . \tag{45}$$

with $\tilde{\varepsilon}_d=\varepsilon_d-\varepsilon_{d0}$.

The last term on the right-hand side of (44) contains among two-particle interactions, terms with six operators. These have been systematically truncated. The final result can be written in rather compact form if spin operators are defined by

$$\begin{aligned}\sigma^x_{\mathbf{n}}&=X^{\uparrow\downarrow}_{\mathbf{n}}+X^{\downarrow\uparrow}_{\mathbf{n}}\ ,\\ \sigma^y_{\mathbf{n}}&=-i(X^{\uparrow\downarrow}_{\mathbf{n}}-X^{\downarrow\uparrow}_{\mathbf{n}})\ ,\\ \sigma^z_{\mathbf{n}}&=X^{\uparrow\uparrow}_{\mathbf{n}}-X^{\downarrow\downarrow}_{\mathbf{n}}\ ,\end{aligned} \tag{46}$$

with $\sigma^z_{\mathbf{n}}=2S^z_{\mathbf{n}}/\hbar$, etc. and are generalized to spin operators involving more than one lattice site,

$$\sigma^x_{\mathbf{nm}}=\frac{1}{\sqrt{2}}(X^{\uparrow 0}_{\mathbf{n}}+X^{\uparrow 0}_{\mathbf{m}})\frac{1}{\sqrt{2}}(X^{0\downarrow}_{\mathbf{n}}+X^{0\downarrow}_{\mathbf{m}})+\frac{1}{\sqrt{2}}(X^{\downarrow 0}_{\mathbf{n}}+X^{\downarrow 0}_{\mathbf{m}})\frac{1}{\sqrt{2}}(X^{0\uparrow}_{\mathbf{n}}+X^{0\uparrow}_{\mathbf{m}})\ , \tag{47}$$

$$\sigma^y_{\mathbf{nm}}=-i\left[\frac{1}{\sqrt{2}}(X^{\uparrow 0}_{\mathbf{n}}+X^{\uparrow 0}_{\mathbf{m}})\frac{1}{\sqrt{2}}(X^{0\downarrow}_{\mathbf{n}}+X^{0\downarrow}_{\mathbf{m}})-\frac{1}{\sqrt{2}}(X^{\downarrow 0}_{\mathbf{n}}+X^{\downarrow 0}_{\mathbf{m}})\frac{1}{\sqrt{2}}(X^{0\uparrow}_{\mathbf{n}}+X^{0\uparrow}_{\mathbf{m}})\right]\ , \tag{48}$$

$$\sigma^z_{\mathbf{nm}}=\frac{1}{\sqrt{2}}(X^{\uparrow 0}_{\mathbf{n}}+X^{\uparrow 0}_{\mathbf{m}})\frac{1}{\sqrt{2}}(X^{0\uparrow}_{\mathbf{n}}+X^{0\uparrow}_{\mathbf{m}})-\frac{1}{\sqrt{2}}(X^{\downarrow 0}_{\mathbf{n}}+X^{\downarrow 0}_{\mathbf{m}})\frac{1}{\sqrt{2}}(X^{0\downarrow}_{\mathbf{n}}+X^{0\downarrow}_{\mathbf{m}})\ . \tag{49}$$

It was originally pointed out by Parmenter that within the strong-coupling limit of the Hubbard-model terms involving spin operators as in (47)–(49) should be taken into account.[49] All the spin operators obey the usual commutation relations, but $(S^x_{\mathbf{n}})^2=(S^y_{\mathbf{n}})^2=(S^z_{\mathbf{n}})^2=\hbar^2/4$ is only fulfilled for $X^{\downarrow\downarrow}_{\mathbf{n}}+X^{\uparrow\uparrow}_{\mathbf{n}}=\hat{1}$. In addition we use the following abbreviations:

$$\Delta_2=\frac{\gamma^2}{\varepsilon_p-\tilde{\varepsilon}_d},\quad \Delta_4=\frac{\gamma^4}{(\varepsilon_p-\tilde{\varepsilon}_d)^3}\ , \tag{50}$$

$$S_{\alpha\mathbf{k}}=\sin\frac{k_\alpha a}{2},\quad C_{\alpha\mathbf{k}}=\cos k_\alpha a\ , \tag{51}$$

$$\eta^{\alpha\beta}_{\mathbf{kq}}=(-1)^{\alpha+\beta}S_{\alpha\mathbf{k}}S_{\beta\mathbf{q}},\quad \lambda_{\mathbf{k}}=\sum_{\alpha}(S_{\alpha\mathbf{k}})^2\ , \tag{52}$$

$$\begin{aligned}\xi&=\frac{1}{N}\sum_{\alpha,\beta,\mathbf{k}}\eta^{\alpha\beta}_{\mathbf{kk}}\langle p^{\dagger}_{\alpha\mathbf{k}-\sigma}p_{\beta\mathbf{k}-\sigma}\rangle\ ,\\ \varphi_{\mathbf{kq}}&=\sum_{\alpha}[C_{\alpha\mathbf{k}}+C_{\alpha\mathbf{q}}]\langle X^{-\sigma-\sigma}_{\mathbf{n}}\rangle\ .\end{aligned} \tag{53}$$

The following notations are used for summing over lattice sites: $\langle\mathbf{mn}\rangle$, NN sites; $\langle\mathbf{mn}l\rangle$, $\mathbf{n}$ is NN of $\mathbf{m}$ and l is NN of $\mathbf{n}$; $\langle\langle\mathbf{mn}\rangle\rangle$, NNN sites (in x or y direction); $((\mathbf{mn}))$, NNN sites (over cross).

The fourth-order effective Hamiltonian is then given by

$$\mathcal{H}_{\rm eff}=\tilde{\mathcal{H}}_0+\mathcal{H}_1\ , \tag{54}$$

$$\tilde{\mathcal{H}}_0=\sum_{\mathbf{n}}\varepsilon_{d0}X^{00}_{\mathbf{n}}+\sum_{\mathbf{n}\sigma}[\varepsilon_d-4\Delta_2+20\Delta_4]X^{\sigma\sigma}_{\mathbf{n}}+\sum_{\langle\mathbf{mn}\rangle\sigma}[\Delta_2-8\Delta_4]X^{\sigma 0}_{\mathbf{m}}X^{0\sigma}_{\mathbf{n}}+\sum_{\langle\langle\mathbf{mn}\rangle\rangle\sigma}2\Delta_4X^{\sigma 0}_{\mathbf{m}}X^{0\sigma}_{\mathbf{n}}+\sum_{((\mathbf{mn}))\sigma}\Delta_4X^{\sigma 0}_{\mathbf{m}}X^{0\sigma}_{\mathbf{n}}+\sum_{\alpha,\beta,\mathbf{k},\sigma}[\varepsilon_p\delta_{\alpha\beta}+4\eta^{\alpha\beta}_{\mathbf{kk}}(\Delta_2-4\lambda_{\mathbf{k}}\Delta_4)]p^{\dagger}_{\alpha\mathbf{k}\sigma}p_{\beta\mathbf{k}\sigma}\ . \tag{55}$$

The fourth-order effective interactions are contained in $\tilde{\mathcal{H}}_1$ and consist of the following.

(i) A term describing magnetic interactions and charge correlations among d electrons including frustration effects:

$$\tfrac{1}{4}\Delta_4\left[\sum_{\langle\mathbf{mn}\rangle\sigma}(1+4\xi)\underline{\sigma}_{\mathbf{m}}\cdot\underline{\sigma}_{\mathbf{n}}+\sum_{\langle\mathbf{mn}l\rangle\sigma}\underline{\sigma}_{\mathbf{n}}\cdot(\underline{\sigma}_{\mathbf{m}l}-\tfrac{1}{2}\underline{\sigma}_{\mathbf{m}}-\tfrac{1}{2}\underline{\sigma}_{l})-\sum_{\langle\mathbf{mn}\rangle\sigma\sigma'}(1-4\xi)X^{\sigma\sigma}_{\mathbf{m}}X^{\sigma'\sigma'}_{\mathbf{n}}-\sum_{\langle\mathbf{mn}l\rangle\sigma\sigma'}X^{\sigma 0}_{\mathbf{m}}X^{\sigma'\sigma'}_{\mathbf{n}}X^{0\sigma}_{l}\right]\ . \tag{56}$$

(ii) A term describing charge correlations among p electrons:

$$-8(1-\langle X^{-\sigma-\sigma}_{\mathbf{n}}\rangle)\Delta_4\frac{1}{N}\sum_{\alpha,\beta,\gamma,\delta}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q},\sigma}\eta^{\alpha\beta}_{\mathbf{k}+\mathbf{q},\mathbf{k}'-\mathbf{q}}\eta^{\gamma\delta}_{\mathbf{k}'\mathbf{k}}p^{\dagger}_{\alpha\mathbf{k}+\mathbf{q}\sigma}p^{\dagger}_{\beta\mathbf{k}'-\mathbf{q}-\sigma}p_{\gamma\mathbf{k}'-\sigma}p_{\delta\mathbf{k}\sigma}\ . \tag{57}$$

(iii) A term describing charge correlations among d and p electrons:

$$\frac{1}{N}\sum_{\alpha,\beta}\sum_{\mathbf{n},\mathbf{k},\mathbf{q},\sigma}\eta_{\mathbf{kq}}^{\alpha\beta}e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{n}}\{-2\Delta_2+4\Delta_4[2(\lambda_{\mathbf{k}}+\lambda_{\mathbf{q}})-\varphi_{\mathbf{kq}}+2\xi]\}p_{\alpha\mathbf{k}\sigma}^{\dagger}X_{\mathbf{n}}^{-\sigma-\sigma}p_{\beta\mathbf{q}\sigma}\ . \tag{58}$$

(iv) A term describing spin-flip scattering of d and p electrons:

$$\frac{1}{N}\sum_{\alpha,\beta}\sum_{\mathbf{n},\mathbf{k},\mathbf{q},\sigma}\eta_{\mathbf{kq}}^{\alpha\beta}e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{n}}\{-2\Delta_2+4\Delta_4[2(\lambda_{\mathbf{k}}+\lambda_{\mathbf{q}})-\varphi_{\mathbf{kq}}]\}p_{\alpha\mathbf{k}\sigma}^{\dagger}X_{\mathbf{n}}^{-\sigma 0}p_{\beta\mathbf{q}-\sigma}X_{\mathbf{n}}^{0\sigma}\ . \tag{59}$$

(v) Another term describing charge and spin correlations:

$$-2\Delta_4\frac{1}{N}\sum_{\alpha,\beta}\sum_{\langle\mathbf{mn}\rangle}\sum_{\mathbf{k},\mathbf{q},\sigma}\eta_{\mathbf{kq}}^{\alpha\beta}(e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{m}}+e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{n}})(p_{\alpha\mathbf{k}\sigma}^{\dagger}X_{\mathbf{m}}^{-\sigma 0}X_{\mathbf{n}}^{0-\sigma}p_{\beta\mathbf{q}\sigma}+p_{\alpha\mathbf{k}\sigma}^{\dagger}X_{\mathbf{m}}^{-\sigma 0}p_{\beta\mathbf{q}-\sigma}X_{\mathbf{n}}^{0\sigma})\ . \tag{60}$$

(vi) A term describing excitonic correlations:

$$3\Delta_4\frac{1}{N}\sum_{\alpha,\beta}\sum_{\langle\mathbf{mn}\rangle}\sum_{\mathbf{k},\mathbf{q},\sigma}\eta_{\mathbf{kq}}^{\alpha\beta}(e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{m}}X_{\mathbf{n}}^{\sigma 0}X_{\mathbf{m}}^{-\sigma 0}p_{\alpha\mathbf{k}-\sigma}p_{\beta\mathbf{q}\sigma}+e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{m}}p_{\beta\mathbf{q}\sigma}^{\dagger}p_{\alpha\mathbf{k}-\sigma}^{\dagger}X_{\mathbf{m}}^{0-\sigma}X_{\mathbf{n}}^{0\sigma})\ . \tag{61}$$

(vii) A Falicov-type of interaction term:

$$8\Delta_4\xi\sum_{\alpha,\beta,\gamma,\delta}\sum_{\mathbf{n},\mathbf{k},\mathbf{q},\sigma}\eta_{\mathbf{kq}}^{\alpha\beta}e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{n}}p_{\alpha\mathbf{k}\sigma}^{\dagger}p_{\beta\mathbf{q}\sigma}X_{\mathbf{n}}^{\sigma\sigma}\ . \tag{62}$$

The Hermitian conjugate should be added to each of these interaction terms.

Some physical implications of these interactions have been discussed earlier [15]. However, a few comments should be added here.

The perturbation theory presented here leads to an effective Hamiltonian, which besides translation degrees of freedom included in $\tilde{\mathcal{H}}_0$, contains effective interactions of second ($\propto\Delta_2$) and fourth order ($\propto\Delta_4$) in γ. This method which can be regarded as the lattice generalization of the Schrieffer-Wolff transformation,[50] was recently applied to the Anderson lattice model.[51] As was noticed in,[51] the resulting Hamiltonian can be used to calculate fourth-order contributions to the ground-state energy due to magnetic interactions between localized electrons. Such contributions would follow from matrix elements of $\tilde{\mathcal{H}}_1$ connecting two possible degenerate ground states of $\tilde{\mathcal{H}}_0$, which differ only in the z projection of the spin of two localized electrons. Since $\tilde{\mathcal{H}}_1$ is not diagonal on the same basis as $\tilde{\mathcal{H}}_0$, there exist excited states of $\tilde{\mathcal{H}}_0$ that are connected to the two degenerate states through $\tilde{\mathcal{H}}_1$. Proetto *et al.* showed that for the periodic Anderson model the second-order contribution gives rise to a longer-ranged Ruderman-Kittel interaction, while the fourth-order contribution leads to a pronounced peak of the modified Lindhard function. The total effective interaction between localized moments can be written as

$$\mathcal{T}_{\text{eff}}=\langle i|H^{(4)}|f\rangle+\sum_{\nu}\frac{\langle i|H^{(2)}|\nu\rangle\langle\nu|H^{(2)}|f\rangle}{E_0-E_\nu}\ , \tag{63}$$

where $|i\rangle$ and $|j\rangle$ are the two degenerate states, E_0 is the ground-state energy of $\tilde{\mathcal{H}}_0$, E_ν is the energy of intermediate states, and $H^{(2)}$ and $H^{(4)}$ stand for the second- and fourth-order contributions. It would be worthwhile to perform the same calculations with the effective interactions obtained in this work and to discuss the importance of the different terms as a function of the hole concentration. However, this is a tedious problem, since the transfer terms in $\tilde{\mathcal{H}}_{\text{eff}}$ give rise to correlation effects due to the nature of the Hubbard operators.

Another comment concerns the magnetic interactions in (56). The spin-spin interaction involving two sites will be antiferromagnetic for holes while the spin-spin interaction involving three sites gives rise to antiferromagnetic and ferromagnetic interactions and thus leads to frustration in the case of doping. Such a term also appears for finite U_{dd} and U_{pp}; this is discussed is more detail in Ref. 49. At finite doping these terms certainly help to destroy the magnetically ordered state.

Finally we would like to say that this perturbation expansion is reasonable if

$$\frac{\gamma}{\Delta}\ll 1,\quad\frac{\gamma}{U_{dd}}\ll 1,\quad\frac{\gamma}{U_{dd}-\Delta}\ll 1 \tag{64}$$

holds, where Δ is the charge-transfer energy defined previously (i.e., the energy cost of transferring an electron from the O site to the Cu site or a hole from the Cu to the O site). The first two inequalities just state that we have a correlation gap while the last relation defines the region, in which perturbation theory can be applied. We would like to mention that recently Zaanen *et al.*[52] have performed a similar calculation up to fourth order with the help of the projection operator method. They have kept U_{dd} finite. For finite U_{dd} the relevant denominators in the expansion are Δ and $(U_{dd}-\Delta)$, which shows that perturbation theory in the case $U_{dd}\to\infty$ leads for $\tilde{\mathcal{H}}_{\text{eff}}/\gamma$ to an expansion in uneven powers of $\gamma/\Delta\approx 0.36$. A close inspection of (55)–(62) shows that second- and fourth-order contributions always appear with different signs and that second-order contributions dominate. This is important for (58)–(59) which can be transformed into a Kondo-lattice-like Hamiltonian (and remaining charge correlation terms). This means that with increase of doping the superexchange terms become less and less important than spin-spin interactions and charge correlations between localized and delocalized carriers. Perhaps this is a hint that attractive interactions among carriers obtained in fourth order will probably not lead to a superconducting ground state as assumed in Ref. 10. Apart from details these observations remain valid for finite

values of U_{dd}.[52] Thus the relevant terms at low doping are Kondo-like interactions, charge correlations, and superexchange interactions. With increase in doping the second-order contributions will probably dominate and due to the different sign might lead to repulsive interactions among holes on neighboring sites. For more details of a similar discussion we refer to Ref. 52.

VI. KONDO-TYPE FEATURES AND LIFETIME EFFECTS

The discussion of relevant interactions in the last section has shown that the reduced three-states model can be considered as an extended version of the Anderson model. Therefore it might be interesting to look for Kondo-type features either in the three- or in the five-states model. To this we have calculated the propagators of the reduced three-states model by using a more refined decoupling procedure. The decoupling procedure actually used in this paper is of the same type as the one utilized by Theumann[53] and others[54] for the discussion of the Kondo effect in the single-impurity model. It gives rise to a Kondo resonance in the impurity case, but the Kondo temperature turns out to be wrong. As recently shown, the same decoupling procedure (together with a $1/N$ expansion, where N is the orbital degeneracy) if applied to the Anderson lattice model, not only reproduces the impurity results,[55] but becomes exact in the limit $N\rightarrow\infty$. If the decoupling procedure is applied to the Anderson model without the $1/N$ expansion, then no pronounced Kondo effect was observed.[56] However, Kondo-type features were seen (in the sense that with decreasing temperature the density of states develops a small peak at the Fermi level[57]). The suppression of the Kondo resonance in the lattice case is due to large lifetime effects which survive at $T=0$. Hence it follows that the condition

$$\mathrm{Im}\Sigma(\omega)\propto(\omega-\mu_0)^2 \tag{65}$$

is not satisfied. This means, that not only Luttinger's theorem is not fulfilled, but also that there is no discontinuity of the momentum distribution function at the Fermi momentum. This also means that the Kondo contributions to the self-energy will not diverge at the Fermi level, since divergencies of the real part of terms like

$$\frac{1}{N}\sum_{\mathbf{k}}\frac{\langle c^{\dagger}_{\mathbf{k}-\sigma}c_{\mathbf{k}-\sigma}\rangle}{z-\varepsilon_{\mathbf{k}}} \tag{66}$$

occur only at discontinuities of the distribution function. In spite of these failures, numerical results obtained for the specific heat and magnetic susceptibility turned out to be quite reasonable.[56]

In this section we would like to show that on the basis of the decoupling procedure cited above, Kondo-type features for the reduced three-states model are even less pronounced than for the Anderson lattice model [for which at least Kondo-type terms like (66) appear]. Since the resulting expressions are rather lengthy we will only discuss the limit $U_{dd}\rightarrow\infty$ while U_{pp} and V_{dp} and β' are set equal to zero. As before, Hubbard operators will be used for the creation and destruction operators of infinitely strongly correlated d electrons. In compact notation the propagators are given by

$$\langle\langle X^{0\sigma}_{\mathbf{k}}|X^{\sigma 0}_{\mathbf{k}}\rangle\rangle=\frac{N_d d_{\mathbf{k}}}{D_{\mathbf{k}}}\ , \tag{67}$$

$$\langle\langle p_{\alpha\mathbf{k}\sigma}|X^{\sigma 0}_{\mathbf{k}}\rangle\rangle=\frac{(-1)^{\beta}}{D_{\mathbf{k}}}2i\gamma S_{\alpha\mathbf{k}}N_d(z-\varepsilon-4\beta S^2_{\beta\mathbf{k}})\ ,\quad \beta\neq\alpha\ , \tag{68}$$

$$\langle\langle p_{\alpha\mathbf{k}\sigma}|p^{\dagger}_{\alpha\mathbf{k}\sigma}\rangle\rangle=\frac{1}{D_{\mathbf{k}}}[(z-\varepsilon_d+M_d)(z-\varepsilon_p)-4\gamma^2S^2_{\beta\mathbf{k}}N_d],\quad \beta\neq\alpha\ , \tag{69}$$

$$\langle\langle p_{1\mathbf{k}\sigma}|p^{\dagger}_{2\mathbf{k}\sigma}\rangle\rangle=\langle\langle p_{2\mathbf{k}\sigma}|p^{\dagger}_{1\mathbf{k}\sigma}\rangle\rangle=\frac{4S_{1\mathbf{k}}S_{2\mathbf{k}}}{D_{\mathbf{k}}}[\beta(z-\varepsilon_d+M_d)-\gamma^2N_d]\ . \tag{70}$$

In this limit the three-pole structure of propagators has changed due to the presence of frequency-dependent functions giving rise to lifetime effects. The denominator $D_{\mathbf{k}}$ is given by

$$D_{\mathbf{k}}(z)=(z-\varepsilon_d+M_{d\mathbf{k}})d_{\mathbf{k}}-\sum_{\alpha\neq\beta}4\gamma^2S^2_{\alpha\mathbf{k}}(z-\varepsilon_p-4\beta S^2_{\beta\mathbf{k}})[1-F(z)]\ , \tag{71}$$

while the remaining functions are defined as follows:

$$d_{\mathbf{k}}(z)=(z-\varepsilon_p)^2-(4\beta S_{1\mathbf{k}}S_{2\mathbf{k}})^2\ , \tag{72}$$

$$N_d(z)=1-\langle X^{-\sigma-\sigma}\rangle-F(z)\ , \tag{73}$$

$$F(z)=\frac{1}{N}\sum_{\mathbf{k},\nu}\frac{2i\gamma}{d_{\mathbf{k}}}(-1)^{\nu}S_{\nu\mathbf{k}}[\langle X^{-\sigma 0}_{\mathbf{k}}p_{\nu\mathbf{k}-\sigma}\rangle(z-\varepsilon_p)+4\beta S_{1\mathbf{k}}S_{2\mathbf{k}}\langle X^{-\sigma 0}_{\mathbf{k}}p_{\beta\mathbf{k}-\sigma}\rangle]\ ,\quad \beta\neq\nu\ , \tag{74}$$

$$M_{d\mathbf{k}}(z)=\frac{4\gamma^2}{d_{\mathbf{k}}}\langle X^{-\sigma-\sigma}\rangle\sum_{\alpha}[S^2_{\alpha\mathbf{k}}(z-\varepsilon_p)+4\beta(-1)^{\alpha+\beta}(S_{\alpha\mathbf{k}}S_{\beta\mathbf{k}})^2]+M_d(z)\ , \tag{75}$$

and

$$M_d(z)=\frac{1}{N}\sum_{\alpha,\mathbf{k}}\frac{4\gamma^2}{d_{\mathbf{k}}}\Big\{[S^2_{\alpha\mathbf{k}}(z-\varepsilon_p)+4\beta(-1)^{\alpha+\beta}(S_{\alpha\mathbf{k}}S_{\beta\mathbf{k}})^2](\langle X^{-\sigma 0}_{\mathbf{k}}X^{0-\sigma}_{\mathbf{k}}\rangle-2\langle X^{-\sigma-\sigma}\rangle)-\sum_{\nu}(-1)^{\alpha+\nu}S_{\alpha\mathbf{k}}S_{\nu\mathbf{k}}[\langle p^{\dagger}_{\nu\mathbf{k}-\sigma}p_{\alpha\mathbf{k}-\sigma}\rangle(z-\varepsilon_p)+4\beta S_{1\mathbf{k}}S_{2\mathbf{k}}\langle p^{\dagger}_{\nu\mathbf{k}\sigma}p_{\beta\mathbf{k}\sigma}\rangle]\Big\}\quad \beta\neq\alpha\ . \tag{76}$$

The functions $M_{d\mathbf{k}}$ and M_d can be considered as self-energies, while the remaining terms in $D_{\mathbf{k}}$ are kind of vertex corrections which renormalize γ.

The general structure of the propagators reminds of many-body Kondo-type features known from corresponding expressions for the Anderson lattice model.[55,56,58] One might expect that Kondo-type resonances can appear due to internal momentum summations in $F(z)$ and $M_d(z)$. However, there is a remarkable difference between the usual form of propagators leading to a Kondo resonance and the propagators in the present work.

First, the bare energies of d and p electrons are dispersionless. Dispersion is created by allowing for hybridization. Second, Kondo-type terms are of the form

$$\frac{1}{N}\sum_{\nu,\mathbf{k}}\frac{(-1)^{\alpha+\nu}S_{\alpha\mathbf{k}}S_{\nu\mathbf{k}}\langle p^{\dagger}_{\nu\mathbf{k}-\sigma}p_{\nu\mathbf{k}-\sigma}\rangle(z-\varepsilon_p)}{(z-\varepsilon_p)^2-(4\beta S_{1\mathbf{k}}S_{2\mathbf{k}})^2} \quad (77)$$

and are considerably different from (66). Lifetime effects will again suppress the Kondo resonance since the expectation values have no discontinuity at the Fermi momentum. In addition the Kondo-type features will be further suppressed due to the specific analytical structure of the last relation. All other contributions of similar structure (including terms which contain $\langle X^{\sigma 0}_{\mathbf{k}}X^{0\sigma}_{\mathbf{k}}\rangle$) are higher-order contributions. Since the expectation value in (77) has not a discontinuity at the Fermi momentum and since (77) has a different analytical structure as compared with (66), we expect only a very weak resonance.

A detailed numerical analysis of the impact of lifetime effects on the charge-transfer insulator at small hole concentration is under current investigation. At present the convergence achieved while solving the self-consistency equations is not high enough to see any resonance. If it would turn out that there is a pronounced Kondo effect in the reduced three-states model then one should switch over to the five-states model because this would allow us to describe two interpenetrating lattices of strongly bound singlets (as in the t-J model) and weakly correlated nonbonding p' carriers.

VII. FINAL REMARKS

We have calculated a few normal-state properties of highly correlated fermions of the two-dimensional CuO_2 lattice. We think that the results such as the phase diagram and quasiparticle spectrum are relevant for high-T_c copper oxide superconductors.

The spectrum and phase diagram show that undoped CuO_2 (which corresponds to approximately nine electrons in the bands) is a charge-transfer insulator. For realistic parameter values spectral weight of d and p electrons is distributed in such a way that in the doped case (i.e., taking electrons away in the vicinity M) the Fermi level comes to lie in a band of mainly $p^{(\prime)}$-type symmetry. To what extent this result has to be changed if d and p carriers are strongly bound into spin singlets remains an open question. Probably this would lead to the appearance of d spectral weight at the Fermi level (which would not be much different from the appearance of a Kondo resonance). It is unclear, whether considerable d-type spectral weight at the Fermi level would contradict the observation that most high-T_c systems should behave as charge-transfer insulators. However, the charge-transfer insulator state has not always to be very pronounced. Our calculations show that the nature of the insulating state (charge or Mott-Hubbard insulator) depends on the amount of d-type charge localized at the Cu sites.

In any case, whether strongly bound d-p singlets exist or not, we expect that weakly correlated nonbonding p' carriers are present at the Fermi level. This means that in the presence of attractive interactions at least a partial fraction of fermions that originate from these orbitals are bound into Cooper pairs. The actual number of Cooper pairs consisting of weakly correlated fermions is difficult to estimate. It depends to a large extent on the energetic position of the nonbonding orbitals with respect to the bonding ones. If at the same time strongly bound d-p singlets were present at the Fermi level one might face the interesting situation that one system might behave Fermi-liquid-like, the other not.

To what extent the present reflections would rule out purely electronic mechanisms for superconductivity is an open question. The weakly correlated fermions at the Fermi surface will certainly strongly couple to local lattice distortions. Moreover, excitations of this weakly correlated Fermi gas may be important. However, we do not claim that an electronic driven superconducting instability has become impossible. There is clear evidence that strongly correlated fermions possess an inherent tendency to form local singlet pairs. This has been confirmed by mean-field-like calculations for the single-band Hubbard model in the large-U limit[59,60] or by numerical studies of the two-dimensional Hubbard model. For recent numerical work in this context and further references we refer to Ref. 61.

One should also note that besides the influence of spin or charge fluctuations electron-phonon interactions could be of crucial importance for high-T_c superconductivity. There is experimental evidence that La_2CuO_4 has a tilt soft mode of the octahedra around a [110] axis.[62] At present we investigate the problem of to what extent the coupling of weakly correlated $p^{(\prime)}$ holes to phonons and above all, the coupling of excitations of this weakly correlated Fermi gas to phonons, might help us to understand high-T_c superconductivity. To this we have coupled via volume-dependent O-O transfer integrals the holes to the most important modes of the oxygen octahedra, and excitations of the weakly correlated Fermi gas are taken to induce attractive interactions among the more correlated d-p particles and vice versa. Results will be published elsewhere.[63]

The magnitude of the charge-transfer gap obtained in this work is of the order $U_{dd}-U_{pp}\approx 6.5$ eV. If this were true then probably any excitoniclike mechanism for high-T_c superconductivity as originally proposed would be ruled out. With respect to the validity of the present calculation, we would like to say that if the generalized Hubbard-I scheme is combined with the constraint Eq. (31), which ensures a certain degree of localization of d electrons, then the resulting electronic spectrum of a

CuO_2 layer should bare a few realistic features. If we make use of the constraint (31) then the insulating gap obtained in this work (≈ 4 eV) corresponds to the value that was obtained in Ref. 30. Unfortunately, the Luttinger theorem cannot be fulfilled within Hubbard-I and the constraint (30).

The interesting problem of the rapid decrease of the Néel temperature upon doping cannot be discussed within the generalized Hubbard-I scheme. To treat this problem we have to use the four-momentum method discussed briefly in Sec. III by extending the calculation to the two-sublattices case. As has been stated before, the increase of frustration with increasing hole concentration might be primarily responsible for the rapid decrease of the Néel temperature.

ACKNOWLEDGMENTS

We wish to thank S. G. Mishra for collaboration at an early stage of this work and J. L. Shen, C. S. Ting, and M. S. Hybertsen, E. B. Stechel, M. Schluter, and D. R. Jennison for unpublished work which we received after completion of the present paper. Shen *et al.* provided further comments on the validity of the *t-J* model while Hybertsen *et al.* showed that under certain restrictions the *t-J* model might still be valid, even if direct O-O hopping terms are taken into account. One of the authors (J. Z.) would like to acknowledge partial support from the Alexander von Humboldt Foundation and from the Polska Akademia Nauk, Grant No. CPBF 01.12.

*Permanent address: Institute of Physics, Silesian University, 40-007 Katowice, Poland.

[1]K. C. Hass, Solid State Phys. **42**, 213 (1989).
[2]T. M. Rice, Phys. Scr. T **29**, 72 (1989).
[3]P. Entel, J. Zielinski, M. Matschke, and S. G. Mishra, in *Electronic Correlation and Disorder Effects in Metals,* edited by S. N. Behera (World Scientific, Singapore, 1990).
[4]W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).
[5]Z. Tesanovic, Phys. Rev. B **36**, 2364 (1987).
[6]P. Haldar, K. Chen, B. Maheswaran, A. Roig-Janicki, N. K. Jaggi, R. S. Markiewicz, and B. C. Giessen, Science **241**, 1198 (1988).
[7]J. Zielinski and M. Matlak, Phys. Status Solidi B **151**, 203 (1989).
[8]Daniel C. Mattis, J. Opt. Soc. Am. B **6**, 496 (1989).
[9]L. N. Bulaevskii, O. V. Dolgov, A. A. Golubov, M. O. Ptitsyn, and S. I. Vedeneev, Mod. Phys. Lett. B **3**, 101 (1989).
[10]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987); V. J. Emery and G. Reiter, Phys. Rev. B **38**, 4547 (1988).
[11]C. Gros, R. Joynt, and T. M. Rice, Phys. Rev. B **36**, 8190 (1987); F. C. Zhang and T. M. Rice, *ibid.* B **37**, 3759 (1988).
[12]P. W. Anderson, Science **235**, 1196 (1987); P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987); P. W. Anderson, in *Frontiers and Borderlines in Many-Particle Physics Proceedings of the International School of Physics "Enrico Fermi,"* Course CIV, Varenna, 1987, edited by R. A. Broglia and J. R. Schrieffer (North-Holland, Amsterdam, 1988), p. 1.
[13]G. Baskaran, Z. Zou, and P. W. Anderson, Solid State Commun. **63**, 973 (1987).
[14]J. R. Schrieffer, X. G. Wen, and S. C. Zhang, Phys. Rev. Lett. **60**, 944 (1988); Phys. Rev. B **39**, 11 663 (1989).
[15]P. Entel, S. G. Mishra, and M. Matschke, Physica C **153-155**, 1171 (1988).
[16]M. W. Long, Z. Phys. B **69**, 409 (1988).
[17]J. Zaanen and A. M. Oles, Phys. Rev. B **37**, 9423 (1988).
[18]A. Muramatsu, R. Zeyher, and D. Schmeltzer, Europhys. Lett. **7**, 473 (1988).
[19]H. Fukuyama, H. Matsukawa, and Y. Hasegawa, J. Phys. Soc. Jpn. **58**, 364 (1989).
[20]J. H. Jefferson, J. Phys. Condens. Mat. **1**, 1621 (1989).
[21]E. R. Gagliano, A. G. Rojo, C. A. Balseiro, and B. Alascio, Solid State Commun. **64**, 901 (1987); C. A. Balseiro, A. G. Rojo, E. R. Gagliano, and B. Alascio, Phys. Rev. B **38**, 9315 (1988).
[22]M. Ogata and H. Shiba, J. Phys. Soc. Jpn. **57**, 3074 (1988).
[23]M. Imada, J. Phys. Soc. Jpn. **57**, 3128 (1988).
[24]Y. Suzumura, Y. Hasegawa, and H. Fukuyama, J. Phys. Soc. Jpn. **57**, 2768 (1988).
[25]J. E. Hirsch and S. Tang, Phys. Rev. **40**, 2179 (1989).
[26]C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Commun. **62**, 681 (1987).
[27]W. Weber, Z. Phys. B **70**, 323 (1988); W. Weber, A. L. Shelankov, and X. Zotos, in *Proceedings of the NEC Symposium on Mechanisms of High Temperature Superconductivity* (Springer, Berlin, 1989).
[28]D. L. Cox, M. Jarell, C. Jayaprakash, H. R. Krishnamurthy, and J. Deisz, Phys. Rev. Lett. **62**, 2188 (1989).
[29]H. Castillo, C. Balseiro, B. Alascio, and H. Ceva, Phys. Rev. B **40**, 224 (1989).
[30]C. A. Balseiro, M. Avignion, A. G. Rojo, and B. Alascio, Phys. Rev. Lett. **62**, 2624 (1989).
[31]J. Hubbard, Proc. R. Soc. London, Ser. A **276**, 238 (1963).
[32]N. Nücker, J. Fink, J. C. Fuggle, P. J. Durham, and W. Temmermann, Phys. Rev. B **37**, 5158 (1989).
[33]M. S. Hybertsen, M. Schlüter, and N. E. Christensen, Phys. Rev. B **39**, 9028 (1989).
[34]A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988).
[35]F. Mila, Phys. Rev. B **38**, 11 358 (1988).
[36]M. J. DeWeert, D. A. Papaconstantopoulos, and W. E. Pickett, Phys. Rev. B **39**, 4235 (1989).
[37]S. Doniach and E. H. Sondheimer, *Green's Functions for Solid State Physicists* (Benjamin, New York, 1974).
[38]S. Misawa, J. Phys. Soc. Jpn. **58**, 3298 (1989).
[39]H. Fukuyama and Y. Hasegawa, Physica B **148**, 204 (1987).
[40]P. Fulde, J. Keller, and G. Zwicknagl, Solid State Phys. **41**, 2 (1988).
[41]A. J. Fedro and R. S. Wilson, Phys. Rev. B **11**, 2148 (1975).
[42]J. Zielinski and J. Czakon, Acta Phys. Pol. A **55**, 63 (1979).
[43]A. E. Ruckenstein and S. Schmitt-Rink, in *Progress in High Temperature Superconductivity,* edited by G. Baskaran, A. E.

Ruckenstein, E. Tosatti, and Yu Lu (World Scientific, Singapore, 1990), Vol. 23.
[44]W. Nolting and W. Borgiel, Phys. Rev. B **39**, 6962 (1989).
[45]P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).
[46]R. Micnas, J. Ranninger, and S. Robaszkiewicz, Rev. Mod. Phys. **62**, 113 (1990).
[47]J. Fink, N. Nücker, H. Romberg, M. Alexander, S. Nakai, B. Sheerer, P. Adelmann, and D. Ewert, Physica C **162-164**, 1415 (1989); N. Nücker, M. Alexander, H. Romberg, P. Adelmann, and J Fink (unpublished).
[48]J. Hubbard, Proc. R. Soc. London, Ser. A **285**, 542 (1965).
[49]R. H. Parmenter, Phys. Rev. Lett. **59**, 923 (1987).
[50]J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).
[51]C. Proetto and A. López, Phys. Rev. B **24**, 3031 (1981).
[52]J. Zaanen and A. M. Oleś, Phys. Rev. B **37**, 9423 (1988).
[53]A. Theumann, Phys. Rev. **178**, 978 (1968).
[54]H. Mameda and F. Takano, Prog Theor. Phys. **43**, 1459 (1970).
[55]G. Czycholl, Phys. Rev. B **31**, 2867 (1985); Phys. Rep. **143**, 277 (1986).
[56]T. A. Costi, J. Phys. C **19**, 5665 (1986).
[57]T. A. Costi (private communication).
[58]H. G. Baumgärtel and E. Müller-Hartmann, in *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 57.
[59]J. Zielinski, M. Matlak, and P. Entel, Phys. Lett. A **136**, 441 (1989).
[60]C. Bastide, C. Lacroix, and A. da Rosa Simoes, Physica C **159**, 347 (1989).
[61]S. R. White, D. J. Scalapino, R. L. Sugar, E. Y. Loh, J. E. Gubernatis, and R. T. Scalettar, Phys. Rev. B **40**, 506 (1989).
[62]L. Pintschovius, J. M. Bassat, P. Odier, F. Gervais, G. Chevrier, W. Reichardt, and F. Gompf, Phys. Rev. B **40**, 2229 (1989).
[63]P. Entel and J. Zielinski (unpublished).