Effect of orbital relaxation on the band structure of cuprate superconductors and implications for the superconductivity mechanism

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Where the doped holes reside in cuprate superconductors has crucial implications for the understanding of the mechanism responsible for their high-temperature superconductivity. It has been generally assumed that doped holes reside in hybridized Cu $d_{x^2-y^2}$-O $p\sigma$ orbitals in the CuO_2 planes, based on results of density functional band-structure calculations. Instead, we propose that doped holes in the cuprates reside in O $p\pi$ orbitals in the plane, perpendicular to the Cu-O bond, that are raised to the Fermi energy through local orbital relaxation, that is not taken into account in band-structure calculations that place the bands associated with these orbitals well below the Fermi energy. We use a dynamic Hubbard model to incorporate the orbital relaxation degree of freedom and find in exact diagonalization of a small Cu_4O_4 cluster that holes will go to the O $p\pi$ orbitals for relaxation energies comparable to what is expected from atomic properties of oxygen anions. The bandwidth of this band becomes significantly smaller than predicted by band-structure calculations due to the orbital relaxation effect. Within the theory of hole superconductivity the heavy hole carriers in this almost full band will pair and drive the system superconducting through lowering of their quantum kinetic energy.

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I. INTRODUCTION

The question of which atomic orbitals in the Cu-oxide superconductors host the carriers that drive the system superconducting was recognized as essential already in the early days of the high-T_c cuprate era since it is likely to play a key role in the understanding of the mechanism of superconductivity. Band-structure calculations based on density functional theory (DFT) yield a metallic ground state with a broad band of states with a dominant Cu $d_{x^2-y^2}$-O $p\sigma$ orbital character crossing the Fermi energy [1–9]. O $p\sigma$ orbitals are directed along the Cu-O bond (see Fig. 1). Despite the fact that these calculations yield a metallic rather than an insulating state in the undoped case, it has been generally accepted that holes doped into the insulating state go into this band and are the carriers responsible for superconductivity.

The possibility that instead doped holes occupy planar oxygen orbitals pointing in a direction perpendicular to the Cu-O bond ($p\pi$ orbitals) was proposed early on by Guo and co-workers [10] based on quantum chemical calculations. Also simple electrostatic considerations suggest that doped holes (positive carriers) should prefer to occupy O $p\pi$ orbitals since they give rise to larger carrier concentration near the center of Cu-O plaquettes (furthest away from the Cu^{++} ions) where the electrostatic potential is most negative. This was also found in detailed calculations of Madelung potentials [11]. However, it is generally believed that the strong hybridization between O $p\sigma$ and Cu $d_{x^2-y^2}$ orbitals along the Cu-O bonds renders those orbitals more favorable for hole doping as predicted by the DFT calculations.

Experimentally it is possible to ascertain that doped holes occupy planar O orbitals ($p_{x,y}$ rather than p_z) from x-ray absorption [12] and electron-energy-loss spectroscopy [13] studies, but it is not possible to differentiate between $p\sigma$ and $p\pi$ holes.

The bands arising from direct overlap of oxygen orbitals are predicted by DFT theory to have a width of approximately 6 to 7 eV [14] and be located with the top at a distance of 1 [6] to 2.5 eV [14] below the Fermi energy, thus remaining completely filled by electrons and hence inert when the system is doped with holes. In this paper we question this point of view and argue that it is in error, resulting from ignoring the important effect of *local orbital relaxation* of the filled oxygen orbitals when an electron is removed. We argue that when this effect is taken into account the O $p\pi$ bands rise to the Fermi energy and as a consequence host the hole carriers responsible for superconductivity in the cuprates [15,16].

II. BAND STRUCTURE

As pointed out by Mattheiss and others [1–9], the main features of the band structure of the cuprates obtained from density functional calculations can be reproduced with simple tight-binding models that include the Cu $d_{x^2-y^2}$ and O p_x, p_y orbitals. Since superconductivity is clearly driven by transport in the planes, we consider only the Cu $d_{x^2-y^2}$ and O p_x, p_y orbitals in the planes. There is one Cu and two O atoms in the unit cell which we denote by O_1 and O_2. Figure 1 shows the orbitals schematically. The oxygen orbitals in the direction of the Cu-O bond are denoted $p\sigma$, and the ones perpendicular to the Cu-O bond are denoted $p\pi$.

We denote the d-$p\sigma$ hopping amplitude by t_d and the direct hopping amplitudes between oxygen orbitals by t_1 for π-π or σ-σ hopping and t_2 for π-σ hopping. Following estimates by McMahan *et al.* [14] and Stechel and Jennison [17] we take $t_1 = 0.65$, $t_2 = 0.35$, and $t_d = 1.75$, all in eV. For site energies we take $\epsilon_d = -5.2$, $\epsilon_{p\sigma} = -5.5$, and $\epsilon_{p\pi} = -4.7$ eV. Because of electrostatics, $\epsilon_{p\pi}$ is higher than $\epsilon_{p\sigma}$.

The resulting band structure obtained by diagonalization of the 5×5 matrix of Bloch states is shown in Fig. 2 in the direction $(0,0) - (\pi,\pi)$, i.e., $\Gamma \to X$. Figure 3 shows the weights of the different orbitals in the band states for bands 1–5 ordered from lowest to highest energy. Band 2, that is not shown in Fig. 3, is mostly $p\sigma$, with some $p\pi$ contribution and no contribution from the d orbitals. The band of interest to

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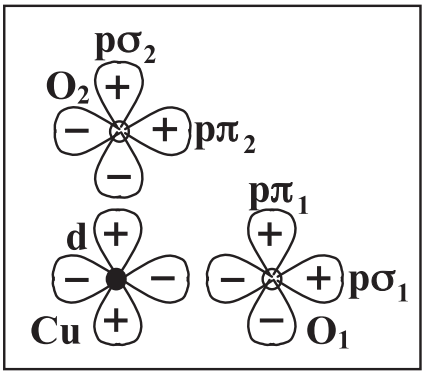

FIG. 1. Unit cell in the Cu-O plane with five electronic orbitals: Cu $d_{x^2-y^2}$ and O p_σ, p_π orbitals. There are two oxygen atoms in the unit cell denoted by O_1, O_2.

us is band 4, which is almost entirely of $p\pi$ character at its highest energies near the X point as shown in the lower left panel of Fig. 3.

The Fermi level corresponds to energy 0. This tight-binding band structure, extending from −9.2 to 1 eV, resembles the main features of the band structures obtained from density functional calculations [1–9]. The Fermi level cuts the Cu $d_{x^2-y^2}$-O $p\sigma$ antibonding band that extends from energy −3.6 to 1 eV, hence according to this band structure when the system is doped with holes they should occupy this band. This is the general consensus. The antibonding oxygen $p\pi$ band (band 4) is full, and its top is approximately 2 eV below the Fermi level, hence it should remain full and inert when the system is doped with holes according to this band structure.

There are two problems with this argument, the first one is well recognized, but the second one is not.

The first problem is that the band structure in Fig. 2 does not reflect the fact that the undoped system is insulating. This is attributed to the strong Coulomb repulsion of electrons in the Cu $d_{x^2-y^2}$ orbital, which is argued to open up a gap (Mott-Hubbard gap) when the band is half-filled, corresponding to the undoped case. Hence, band 5 in Fig. 2 is argued to split into two upper and lower Hubbard bands when the system is undoped with the Fermi level in the gap between the two bands rendering it insulating.

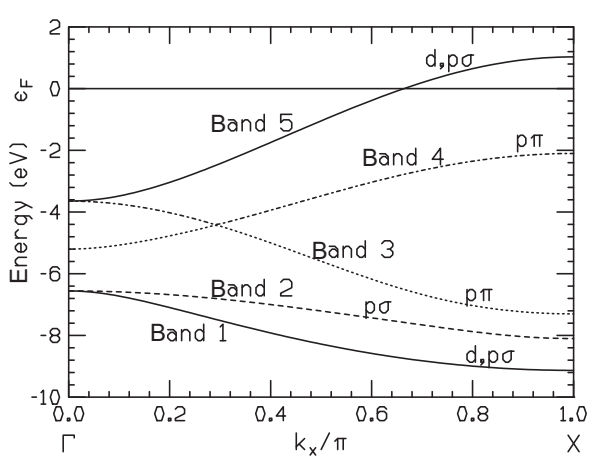

FIG. 2. Band structure in the Cu-O planes in the Γ-X direction [(0,0) to (π,π)] from a tight-binding calculation with five orbitals per unit cell (see Fig. 1). Parameters used are $t_{\pi\pi} = t_{\sigma\sigma} \equiv t_1 = 0.65$, $t_{\pi\sigma} \equiv t_2 = 0.35$, $t_{d\sigma} \equiv t_d = 1.75$, $\epsilon_d = -5.2$, $\epsilon_{p\sigma} = -5.5$, and $\epsilon_{p\pi} = -4.7$ (see text).

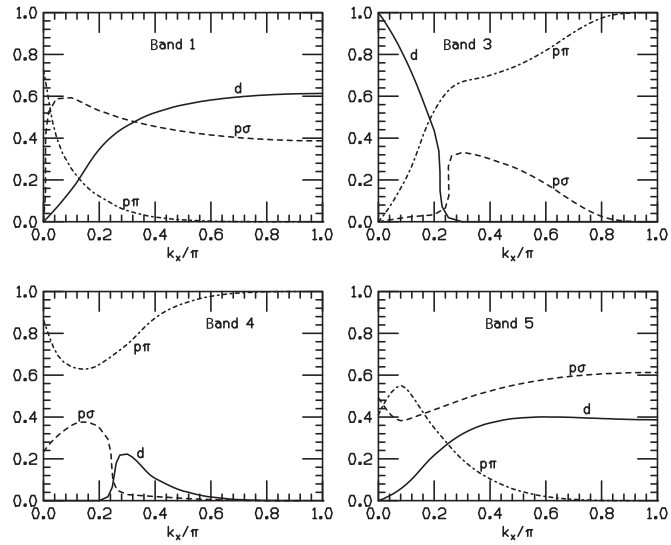

FIG. 3. Weights of the different orbitals in the band states. Bands 1–5 are numbered from lowest to highest energy. Band 2 (not shown) has only contributions from $p\sigma$ (mostly) and $p\pi$ and none from d for all values of k.

There have been various calculations performed using these ideas that take the Mott-Hubbard gap into account [4,8,14,17–24]. The general consensus is that doped holes still go into the Cu $d_{x^2-y^2}$-O $p\sigma$ band and are responsible for the transport in the underdoped through overdoped regimes. However, these calculations rely on approximations that are not necessarily well controlled.

The second problem is that the antibonding $p\pi$ band (band 4 in Fig. 2), which comes to about 2 eV below the Fermi level at the X point, is assumed to be rigid. Here we argue that this assumption is incorrect and that in reality the energy of holes doped into this band is raised by several eV by *orbital relaxation* and that as a result doped holes will go into this band rather than into the Cu-O $p\sigma$ band. In other words, the energetics of orbital relaxation, not reflected in the band structure shown in Fig. 2, makes it easier to remove electrons from band 4 rather than from the band above it (band 5 in Fig. 2).

III. ORBITAL RELAXATION

When an atomic orbital is doubly occupied, its size expands. This is certainly well known from atomic physics [25], but surprisingly its consequences are not properly taken into account in band-structure calculations nor in the many-body Hamiltonians commonly used for solids. In a series of papers we have argued that this effect is essential to understand the physics of electrons in electronic energy bands that are more than half-full [26–30] and have proposed a new class of model Hamiltonians, "dynamic Hubbard models" to take it into account. The magnitude of this effect increases as the net

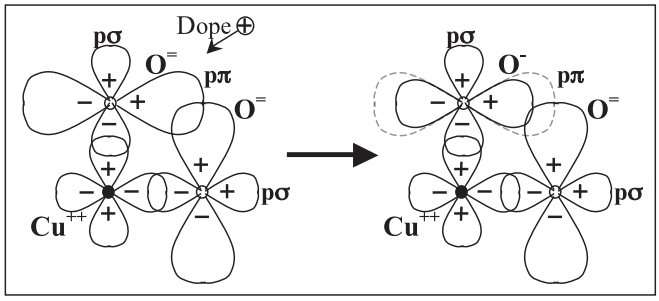

FIG. 4. Atomic orbitals in the CuO_2 unit cell for the undoped case (left) and when an electron is removed (hole is added) (right). If the hole goes into the $p\pi$ orbital, it will shrink as shown schematically with the dashed and full lines in the right panel of the figure.

charge of the ion decreases as discussed, e.g., in Ref. [26]. Hence this effect will be large for $O^{=}$ anions [31], e.g., compared to the isoelectronic F^{-} and Ne^{0} ions. As emphasized by Bussmann-Holder *et al.* [32] and Bilz *et al.* [33], the oxygen $O^{=}$ is unstable in free space, and it is stabilized in the solid by long-range Coulomb forces only, resulting in a high polarizability [34].

In the undoped situation the oxygen ion is nominally $O^{=}$, which suggests that it has a large amount of excess negative charge. The $p\sigma$ orbitals share electrons with neighboring Cu^{++} ions, hence the total excess negative charge in the $O^{=}$ ions is not 2 but somewhat less, approximately 1.5, still large. Regarding the individual p orbitals, the oxygen $p\pi$ orbitals in the plane as well as the p_z orbitals are doubly occupied and hence will be enlarged by Coulomb repulsion. Instead, the oxygen $p\sigma$ orbitals are less enlarged because they share their electrons with the neighboring Cu ions.

As mentioned earlier, experiments show that when the system is doped with holes, i.e., when electrons are removed from the system, these electrons come from planar orbitals. Let us assume that an electron from a $p\pi$ orbital is removed as shown in Fig. 4. As a consequence, the size of the orbital is reduced because it goes from being doubly occupied and hence enlarged by Coulomb repulsion to being singly occupied. This has two important consequences: (i) The overlap with neighboring orbitals will change, changing the effective mass and bandwidth of carriers in this band because of Franck-Condon overlap matrix elements [31], and (ii) because of the energy lowering caused by orbital relaxation, the energy cost in removing this electron will be smaller than what would be predicted from the band structure shown in Fig. 2.

As a simple illustration, consider the states of one and two electrons in an atomic p orbital shown in Fig. 5. The wave function for one electron is

$$\varphi_\alpha(r,\theta) = \left(\frac{\alpha^5}{\pi}\right)^{1/2} r\cos\theta e^{-\alpha r}. \tag{1}$$

The single-electron energy is

$$E(1) = \alpha^2 - \alpha Z, \tag{2}$$

with Z as the ionic charge and the Coulomb repulsion for two electrons in this orbital is

$$U = \tfrac{501}{640}\alpha, \tag{3}$$

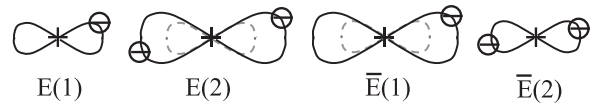

FIG. 5. States with one and two electrons in an atomic p orbital. $E(1)$ and $E(2)$ are the energies of the lowest-energy states with one and two electrons, respectively. The orbital expands when the second electron is added. $\bar{E}(1)$ is the energy of one electron in the expanded orbital, and $\bar{E}(2)$ is the energy of two electrons in the unexpanded orbital.

all in atomic units [length in units of a_0 and energy in units of $e^2/(2a_0)$]. For a single electron in the orbital the orbital exponent is

$$\alpha = \frac{Z}{2}, \tag{4}$$

and the atomic energy is

$$E(1) = -\frac{Z^2}{4}. \tag{5}$$

For two electrons in the orbital, the energy is minimized by the orbital exponent,

$$\bar{\alpha} = \frac{Z}{2} - \delta, \tag{6a}$$

$$\delta = \frac{501}{2560,} \tag{6b}$$

reflecting the expansion of the orbital, and the energy in the two-electron atom is

$$E(2) = -2\left[\frac{Z}{2} - \delta\right]^2. \tag{7}$$

The overlap matrix element between the wave functions for the expanded and nonexpanded orbital is

$$S = \int d^3r\, \varphi_\alpha^*(\vec{r})\varphi_{\bar{\alpha}}(\vec{r}) = \frac{(\alpha\bar{\alpha})^{5/2}}{\left(\frac{\alpha+\bar{\alpha}}{2}\right)^5}, \tag{8}$$

and becomes arbitrarily small for Z approaching $2\delta = 0.39$. The single-electron energy is higher in the expanded orbital,

$$\bar{E}(1) = -\left[\left(\frac{Z}{2}\right)^2 - \delta^2\right], \tag{9}$$

but the electrons pay this price in order to minimize the total energy. If the orbital is not allowed to expand, the total energy of the two-electron orbital is

$$\bar{E}(2) = -Z\left[\frac{Z}{2} - 2\delta\right], \tag{10}$$

larger than Eq. (7) by

$$\bar{E}(2) - E(2) = 2\delta^2, \tag{11}$$

which is twice the cost in single-electron energy in expanding the orbital,

$$\bar{E}(1) - E(1) = \delta^2. \tag{12}$$

Thus, we can define the *relaxation energy per electron* as

$$\epsilon_R = \tfrac{1}{2}[\bar{E}(2) - E(2)] = \bar{E}(1) - E(1). \tag{13}$$

This is both the *reduction* in energy per electron achieved by expanding the orbital versus keeping it unexpanded when a second electron is put in as well as the *excess* energy of the electron remaining in the orbital after the second electron is removed if it does not relax to the unexpanded orbital.

We can relate this relaxation energy to the bare and effective Coulomb repulsions. The bare Coulomb repulsion is the Coulomb energy if the orbital is not allowed to expand

$$U_{\text{bare}} = \bar{E}(2) - 2E(1) = 2\,\delta Z, \tag{14}$$

which is the same as Eq. (3) with unexpanded orbital exponent $\alpha = Z/2$. The "effective U" is given by

$$U_{\text{eff}} = E(2) - 2E(1) = 2\,\delta Z - 2\delta^2, \tag{15}$$

so that

$$\epsilon_R = \tfrac{1}{2}(U_{\text{bare}} - U_{\text{eff}}). \tag{16}$$

For a single p orbital this yields for the relaxation energy,

$$\epsilon_R = \delta^2 = 0.52 \text{ eV}. \tag{17}$$

However, this estimate does not take into account the presence of other electrons in the atom. In particular, when the $p\pi$ orbital expands the Coulomb interaction energy of an electron in that orbital with electrons in other p orbitals is also reduced so that the relaxation energy should be substantially larger than Eq. (17). We can obtain a quantitative estimate for oxygen ions using Eq. (16). The effective U for two electrons in the oxygen ion O^n is given by

$$U_{\text{eff}}(O^n) = E(O^n) + E(O^{n+2}) - 2E(O^{n+1}), \tag{18}$$

with $E(O^n)$ as the electronic energy for the ion O^n. This can be obtained from the difference in ionization energies,

$$U_{\text{eff}}(O^n) = I(n+2) - I(n+1), \tag{19}$$

with

$$I(n) = E(O^n) - E(O^{n-1}), \tag{20}$$

the nth ionization energy for $n \leqslant 1$ and $I(0)$, $I(-1)$ are the first and second electron affinities of O^0.

The experimental values for ionization energies and electron affinities and resulting effective U's are given in Table I. Note that the effective U's for two electrons in the O^0, O^+, and O^{++} ions are all on the order of 20 eV or slightly larger. This is also approximately the value for Slater's $F^0(2p,2p)$ parameter, the spherically averaged Coulomb repulsion for two electrons in p orbitals in O^0,

$$F^0(2p,2p) = \frac{93\mu c}{128} = 21.94 \text{ eV}, \tag{21}$$

with $2\mu c = 4.44$ from Tables 15-6 and 15-7 in Ref. [25]. When the ion becomes negatively charged the orbitals expand, and the effective U decreases substantially to 12.17 and 10.20 eV for two electrons in O^- and in $O^=$, respectively. Thus, we conclude that the "bare U" for two electrons in the neutral oxygen atom O^0 is on the order of 20 eV and the effective U for two electrons in the negative anion $O^=$ is on the order of 10 eV. According to Eq. (16) this then yields

$$\epsilon_R \sim 5 \text{ eV} \tag{22}$$

for the lowering of energy *per electron* due to the orbital expansion when an electron is added to O^- to form $O^=$. Conversely, when adding a hole to $O^=$, i.e., removing an electron from $O^=$, the energy of the final state is $\sim$5 eV *lower* than would be estimated if the orbital relaxation effect is not taken into account.

In concluding from Fig. 2 that when the cuprate plane is doped with holes and the oxygen $p\pi$ band remains full, the effect of orbital relaxation is *not* taken into account. Even a new band-structure calculation with a low level of doping will not capture this effect since it will only take into account the *average* charge distribution which will not change much for low doping compared to the undoped state. Instead we argue that even doping with a single hole changes the outcome qualitatively when the orbital relaxation effect is taken into account.

Thus, the conclusion from the band structure shown in Fig. 2 that band 4 remains full when the system is doped with holes needs to be reconsidered. Let E_{initial} and E_{final} be the initial and final energies of the system upon bringing an electron from the top of band 4 to the Fermi energy, and

$$\Delta = E_{\text{final}} - E_{\text{initial}}, \tag{23}$$

the energy cost of this. According to the band structure shown in Fig. 2,

$$\Delta \sim 2.1 \text{ eV}, \tag{24}$$

and other calculations yield estimates in the range of 1 to 2.5 eV [6,14]. These calculations (using density functional or tight-binding methods) assume the charge distribution and kinetic, potential, and interaction energies of electrons in the system *when the system is undoped* and do not change upon infinitesimal doping since on average the charge distribution does not change. Thus, they do not take into account the relaxation of the orbital when an electron is removed. A correct calculation taking this effect into account would yield instead for the final energy,

$$E'_{\text{final}} = E_{\text{final}} - \epsilon_R, \tag{25}$$

since the atomic energy is lowered by ϵ_R through the process of orbital relaxation. As a consequence,

$$\Delta' = E'_{\text{final}} - E_{\text{initial}} = \Delta - \epsilon_R, \tag{26}$$

and it will change sign from positive to negative if $\epsilon_R > \Delta$, which is the case for the cuprate superconductors according to the estimates discussed above. This then implies that when the

TABLE I. nth ionization energy $I(n)$ and effective electron-electron repulsion $U_{\text{eff}}(O^{n-1}) = I(n+1) - I(n)$ for two electrons in the O^{n-1} ion.

n	$I(n)$ (eV)	$U_{\text{eff}}(O^{n-1})$ (eV)
−1	−8.75	10.20
0	1.45	12.17
1	13.62	21.5
2	35.12	19.82
3	54.94	22.47
4	77.41	

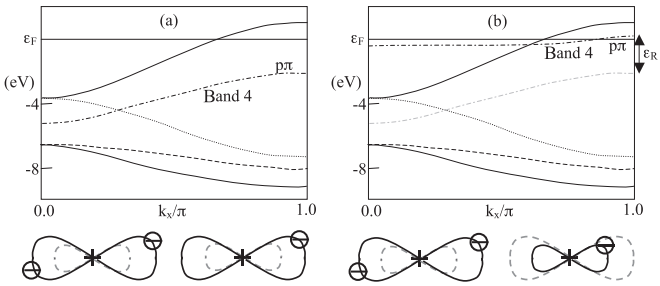

FIG. 6. Effect of orbital relaxation on the band structure (b) (schematic) compared to the case when orbital relaxation is not taken into account (a). The energies of the states of band 4, arising from overlap of oxygen $p\pi$ orbitals, are lifted by an amount given by the orbital relaxation energy ϵ_R with respect to the energies when orbital relaxation is not taken into account. In addition, the bandwidth of band 4 becomes significantly smaller due to the modulation of the hopping amplitude by the overlap matrix elements.

insulating system is doped with holes, the holes will occupy the oxygen $p\pi$ band, or in other words that the states near the top of the band of band 4 rise to the Fermi level. An additional important effect is that the bandwidth will become significantly smaller because the hopping amplitude is reduced by the square of the overlap matrix element S between expanded and unexpanded atomic states Eq. (8) [26]. The resulting band is shown schematically in Fig. 6.

IV. DYNAMIC HUBBARD MODEL CALCULATION

To take into account the effect of orbital relaxation quantitatively we use a dynamic Hubbard model [26,29] and diagonalize it exactly for the small cluster shown in Fig. 7 with four Cu sites with one d orbital each and four O sites with a $p\sigma$ and a $p\pi$ orbital each. There is in addition a spin-1/2 degree of freedom associated with each oxygen $p\pi$ orbital to represent the orbital expansion/contraction. We denote by $d^\dagger_{i\sigma}$, $c^\dagger_{i\sigma}$, and $p^\dagger_{i\sigma}$ the creation operators for electrons in orbitals d, $p\sigma$, and $p\pi$, respectively, and n_{di}, n_{ci}, and n_{pi} the corresponding electronic site occupations. The Hamiltonian is given by

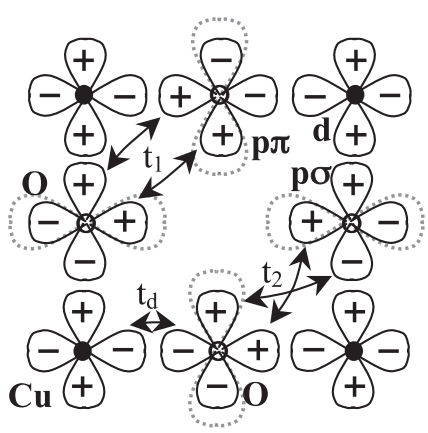

FIG. 7. Eight-site cluster for the exact diagonalization calculation. There is one electronic d orbital at each of the four Cu sites, a $p\sigma$ and a $p\pi$ orbital at each of the four O sites, and an auxiliary spin degree of freedom at each O site to describe the expansion/contraction of the $p\pi$ orbitals indicated by the dotted lines.

$$H = \sum_i \epsilon_d n_{di} + \sum_i \epsilon_c n_{ci} + \sum_i h_i + H_{\rm kin}, \tag{27a}$$

$$H_{\rm kin} = t_d \sum_{ij\sigma}(d^\dagger_{i\sigma} c_{j\sigma} + \text{H.c.}) + t_1 \sum_{ij\sigma}(c^\dagger_{i\sigma} c_{j\sigma} + \text{H.c.}) + t_1 \sum_{ij\sigma}(p^\dagger_{i\sigma} p_{j\sigma} + \text{H.c.}) + t_2 \sum_{ij\sigma}(c^\dagger_{i\sigma} p_{j\sigma} + \text{H.c.}), \tag{27b}$$

$$h_i = \epsilon_c + \epsilon_0(n_{pi\uparrow} + n_{pi\downarrow}) + \omega_0\sigma^i_x + g\omega_0\sigma^i_z + (U_p - 2g\omega_0\sigma^i_z)n_{pi\uparrow}n_{pi\downarrow}, \tag{27c}$$

$$\epsilon_c = \omega_0\sqrt{1+g^2}. \tag{27d}$$

The justification for the site Hamiltonian h_i is given in the references, particularly, Refs. [26,27,30]. The auxiliary spin degree of freedom describes the expansion/contraction of the O $p\pi$ orbital depending how many holes are at the site as discussed in Sec. III. We have discussed several possible versions of this model in Ref. [30], all giving rise to the same physics, the simplest one given by Eq. (27c). The parameters of the model are determined by comparison with properties of the atom as discussed in the following.

The ground-state energy of the Hamiltonian h_i when the orbital is doubly occupied is

$$E(2) = 2\epsilon_0 + U_p. \tag{28}$$

If we take an electron out of this orbital and do not let the orbital relax the energy is [30]

$$\bar{E}(1) = \epsilon_c + \epsilon_0 + \frac{g^2-1}{\sqrt{1+g^2}}\omega_0. \tag{29}$$

Therefore, we choose the parameters in the Hamiltonian h_i so as to give

$$E(2) = 2\epsilon_{p\pi}, \tag{30a}$$

$$\bar{E}(1) = \epsilon_{p\pi}. \tag{30b}$$

If the orbital is allowed to relax, the lowest energy of h_i with one electron is

$$E(1) = \epsilon_0, \tag{31}$$

so that the relaxation energy is

$$\epsilon_R = \bar{E}(1) - E(1) = \omega_0\sqrt{1+g^2} + \frac{g^2-1}{\sqrt{1+g^2}}\omega_0. \tag{32}$$

The overlap matrix element between relaxed and unrelaxed orbitals is

$$S = \frac{1}{\sqrt{1+g^2}}, \tag{33}$$

which corresponds to the overlap matrix element between expanded and unexpanded orbitals Eq. (8), and determines the bandwidth of the renormalized band when the orbital relaxation effect is taken into account. We take it here as a free parameter. For given S and relaxation energy ϵ_R the parameters

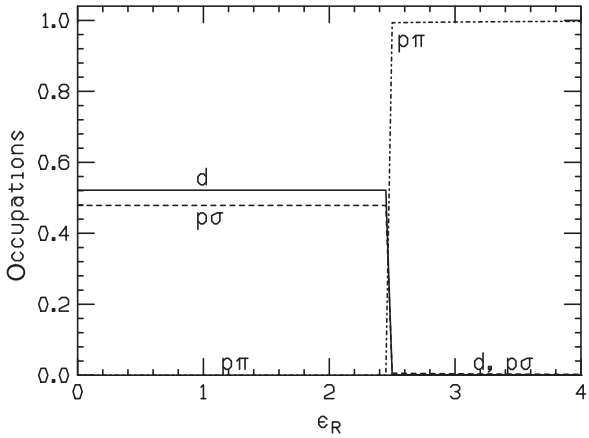

FIG. 8. Occupation of the orbitals in the cluster of Fig. 7 in the ground state when there is one hole in the cluster as a function of the orbital relaxation energy ϵ_R (in eV) for $S = 0.333$.

in the Hamiltonian h_i are then,

$$g = \sqrt{\frac{1}{S^2} - 1}, \tag{34a}$$

$$\omega_0 = \frac{\epsilon_R}{\sqrt{1 + g^2 + \frac{g^2-1}{\sqrt{1+g^2}}}}, \tag{34b}$$

$$\epsilon_0 = \epsilon_{p\pi} - \epsilon_R, \tag{34c}$$

$$U_p = 2\epsilon_R. \tag{34d}$$

Finally, to match the band-structure results of Fig. 2 we take $\epsilon_d = -5.2$, $\epsilon_{p\sigma} = -5.5$, $\epsilon_{p\pi} = -4.7$, $t_1 = 0.65$, $t_2 = 0.35$, and $t_d = 1.75$.

We consider only the dynamics of the one added hole to the cluster, assuming the other four holes are "frozen" on the Cu sites. This is a reasonable approximation in view of the fact that the undoped system is insulating due to the strong Coulomb interactions. The Hilbert space for one hole in this cluster has 192 states (12 states for the hole and 16 states for the auxiliary spins), and thus the Hamiltonian Eq. (27) is easily diagonalized in this subspace. Considering instead the motion of five holes would require dealing with 232 320 states in the Hilbert space making the calculation unmanageable. We calculate the occupation of the orbitals d, $p\sigma$, and $p\pi$ as functions of the relaxation energy ϵ_R and plot the occupations for the lowest-energy state for the case of $S = 0.333$ in Fig. 8.

The results are qualitatively as expected. For zero or small relaxation energy the hole resides in the d and $p\sigma$ orbitals, i.e., band 5 in Fig. 2. Note in Fig. 8 that the occupation of the d orbitals is slightly larger than that of the $p\sigma$ orbitals, contrary to the results shown in Fig. 3, lower right panel. This is simply due to the finite size of the cluster used. When the relaxation energy exceeds a critical value $\epsilon_{Rc} \sim 2.5$ eV the hole occupies the oxygen $p\pi$ orbital, i.e., the top of band 4 in Fig. 2. In other words, the states at the top of that band are now at the Fermi energy as shown schematically in Fig. 6, right panel.

The critical value $\epsilon_{Rc} \sim 2.5$ eV is similar to the distance between the top of band 4 and the Fermi energy in Fig. 2 or between the top of band 4 and the top of band 5 in Fig. 2. This critical value depends somewhat on the value assumed for the overlap matrix element S and decreases monotonically from $\epsilon_{Rc} = 2.7$ to $\epsilon_{Rc} = 1.6$ eV for S going from 0 to 1.

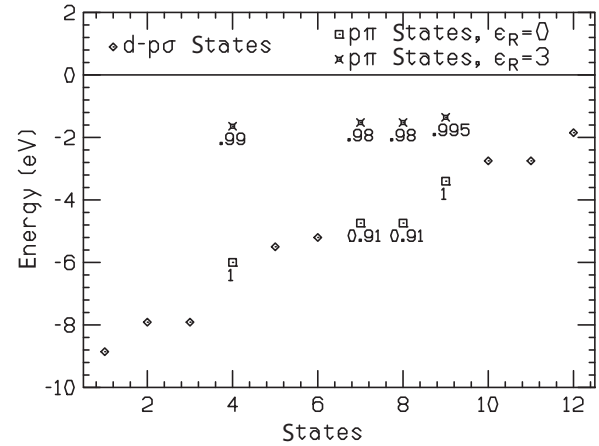

FIG. 9. Energy eigenvalues for the cluster of Fig. 7 with one hole in the absence of orbital relaxation and when orbital relaxation is included with the dynamic Hubbard model with $S = 0.333$ and $\epsilon_R = 3$. The four $p\pi$ states in the cluster are moved up in energy by several eV when orbital relaxation is included. The numbers next to the symbols indicate the $p\pi$ occupation for the state. Note also that the spread in energy of the $p\pi$ states becomes much smaller in the presence of orbital relaxation.

In Fig. 9 we show the energy eigenvalues for all the electronic states with one hole in the cluster in the absence of orbital relaxation and the change in the energy of the $p\pi$ states when the effect of orbital relaxation is included. The diamonds and squares denote the states in the absence of orbital relaxation of d-$p\sigma$ and $p\pi$ characters, respectively, as determined by the occupations of the sites. For the states denoted by the diamonds the $p\pi$ occupation is zero or very small. Note that the highest-energy states in the absence of orbital relaxation are diamonds, corresponding to the d-$p\sigma$ states of band 5 in Fig. 2, which are the states where holes would be created in the absence of orbital relaxation. When orbital relaxation is included, the $p\pi$ states (squares) go up in energy and become the states denoted by the crosses, which are higher in energy than the highest d-$p\sigma$ states, indicating that doped holes will be created in those states. The numbers next to the squares and crosses give the hole occupation of the $p\pi$ orbitals for those states. Note also that the spread in energy of the states denoted by the crosses is much smaller than the states denoted by the squares, reflecting the band narrowing caused by orbital relaxation. Examination of the states denoted by the crosses shows that they are small "electronic polarons" with the auxiliary spin distortion representing the expansion/contraction of the orbital following the occupation of the $p\pi$ orbitals as expected.

V. CONSEQUENCES FOR NORMAL-STATE PROPERTIES AND FOR SUPERCONDUCTIVITY

If the doped holes in the cuprate superconductors occupy the O $p\pi$ rather than the O $p\sigma$ orbitals this has fundamental consequences for the understanding of both the normal state of the cuprates and the mechanism of superconductivity. In

particular, Chen and Goddard III [35], Stechel and Jennison [17], and Birgenau *et al.* [36] have proposed superconductivity mechanisms based on magnetic interactions between oxygen $p\pi$ hole carriers and Cu spins, and Ikeda [37] has proposed an exciton mechanism for pairing of O $p\pi$ holes induced by interactions with d-$p\sigma$ excitations.

Here we focus on the physics predicted by the theory of hole superconductivity [38]. The hole carriers doped into the O $p\pi$ states shown in Fig. 9 that were raised to the Fermi energy by orbital relaxation will be highly dressed by the orbital relaxation processes with quasiparticle weight given by [39,40]

$$z = S^2 \tag{35}$$

for infinitesimal hole doping. If we assume that half of the missing electron in the Cu-O $p\sigma$ bond resides on the Cu and half on the O it corresponds to $Z = 0.5$ in Eq. (2), yielding $\bar{\alpha} = 0.054$ in Eq. (6) and $S = 0.263$ from Eq. (8). If we assume the $d^{9.45}$ occupation for the Cu ion predicted by band-structure calculations [14] it corresponds to $Z = 0.45$, $\bar{\alpha} = 0.029$, and $S = 0.106$. These estimates illustrate that the value of S (and hence z) is very sensitive to the charge distribution but in any event is likely to be much smaller than unity.

As the doping level increases, the quasiparticle weight increases as [40]

$$z(n) = S^2\left[1 + \frac{n_h}{2}\Upsilon\right]^2, \tag{36}$$

with n_h as the hole concentration and Υ as the "undressing parameter"[40],

$$\Upsilon = \frac{1}{S} - 1, \tag{37}$$

which should be particularly large for negative ions, such as $O^=$. This will give rise to a vanishingly small quasiparticle weight for infinitesimal hole doping ($z = 0.106^2 = 0.01$ if we use the $d^{9.45}$ value) that grows upon doping leading to increasing coherence in the normal state. This behavior is seen experimentally [41,42] but attributed to physics of the t-J model and the Mott-Hubbard gap in the O d-$p\sigma$ band instead of the physics and band discussed here. In addition, within our theory the same parameter Υ determines the correlated hopping interaction Δt that gives rise to pairing and superconductivity [16] driven by lowering of kinetic energy [43],

$$\Delta t = \Upsilon t_h, \tag{38}$$

with $t_h = tS^2$ and $t = t_{\pi\pi} = t_1$ as the bare $p\pi$-$p\pi$ hopping. Through the same physics, the model predicts increased coherence [39,40] and increased low-energy optical spectral weight [44,45] as the system goes superconducting, which is seen experimentally in photoemission [41] and optical [46,47] experiments.

The mechanism of hole superconductivity [38] only operates when a band is almost full, hence it can only be relevant to the cuprates if the doped holes go into a $p\pi$ band rather than a $p\sigma$ band that is half-full in the undoped case. The predicted doping dependence of T_c [48] closely resembles the doping dependence seen in the cuprates [49]. Many other predictions of the model are in agreement with observations [45,48,50]. In addition the model predicts a strong tendency to charge inhomogeneity [28] as seen experimentally.

VI. DISCUSSION

The question of the nature of the charge carriers in the high-T_c cuprates is undoubtedly a complicated one, both because of the existence of strong correlations induced by the Hubbard U on the Cu sites [51] and because of the effects of strong orbital relaxation in the negative $O^=$ anions focused on in this paper. Band-structure calculations capture neither of these effects. For the past 25 years the physics community has focused its attention on the former of these effects and has ignored the latter. With this paper we attempt to restore some balance to this situation.

It is possible that in fact doped carriers occupy *both* Cu-O $p\sigma$ bands as the Mott-Hubbard gap closes *and* an O $p\pi$ band lifted to the Fermi energy by orbital relaxation. We have considered such a two-band model [52] and found that high-temperature superconductivity would also result, driven by the kinetic pairing interaction of the O $p\pi$ carriers that would induce a weaker pairing of the Cu-O $p\sigma$ carriers. Angle-resolved photoemission experiments have detected a superconducting gap opening in the k-space region consistent with belonging to the approximately half-full d-$p\sigma$ band [41,53] and to date have not shown the presence of the $p\pi$ holes nor the associated superconducting gap that our model predicts close to the (π,π) point in the Brillouin zone. Presumably this is explained by the fact that the quasiparticle weight associated with this band Eq. (36) is very small. A more detailed explanation for why the opening of the superconducting gap seen in photoemission is associated with the d-$p\sigma$ rather than the $p\pi$ band is given in Ref. [40], Sec. VII.

More generally, the purpose of this paper is to point out that the effect of orbital relaxation on the band structure *cannot be ignored* when negative ions are involved and that it is not taken into account in standard band-structure calculations. Similar physics is emphasized in the approach developed by Fulde [54], Stoyanova *et al.* [55], and Hozoi *et al.* [56] as a substitute for standard band-structure approaches. Within dynamical mean-field theory [57] it is also possible to take the effects focused on in this paper into account [58], although this has not yet been performed in the context of a realistic band-structure calculation.

To summarize, we argue that the arguments and calculations in this paper indicate that orbital relaxation of the oxygen $p\pi$ orbitals in the cuprate superconductors raises an O $p\pi$ band to the Fermi level when holes are doped into the system, hence that the carriers responsible for superconductivity in the cuprates are holes in a full $p\pi$ band rather than in a half-filled d-$p\sigma$ band as generally assumed. In a band close to full and in the presence of strong orbital relaxation the theory of hole superconductivity predicts that high-temperature superconductivity results with many characteristic features seen in the high-T_c cuprates.

To conclude we point out that a strong argument in favor of our point of view is that if it is correct for the cuprates it is likely to also explain the high-temperature superconductivity of several other materials, such as MgB_2 [59], iron pnictides, and

dichalcogenides [60] and explain the reason for why all high-temperature superconducting materials appear to have *negative ions* [61,62], an observation also made by Overhauser [63]. It also suggests an explanation for why elements under high pressure are superconducting [64] for the fact that electron-doped cuprates have hole carriers in the regime where they become superconducting [65] and for the pervasive presence of hole carriers in superconducting materials ranging from the elements [66] to A15 compounds [67] to MgB_2 [68] to high-T_c cuprates.

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