Carrier location in high-T_c superconductors and the degree of Cu-O covalency

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We exactly solve a realistic three-band extended Hubbard model for the ground and low-lying excited states of a variety of finite clusters representing CuO_2 sheets. Because the virtual state involving the copper d^{10} valence fluctuation has its energy sharply lowered by the presence of a carrier hole, a strong stabilization results if the carrier holes are in oxygen orbitals that are strongly coupled to the copper sites: For example, in spite of strong correlation, at carrier densities of interest and with a reasonable choice of energy parameters, the carrier hole wave function is dominated by the $p\sigma$ orbital, rather than by the $p\pi$ orbital which is favored by the Madelung potential. Our previous conclusions concerning the carrier quasiparticles are supported by these calculations.

I. INTRODUCTION

All Cu-O based high-temperature superconductors have CuO_2 sheets which contain the supercurrent. Carriers are produced within these sheets by substituting metal atoms of reduced valency (doping)[1] or by a surplus of oxygen.[2,3] (Carriers could also be produced if a band from the oxide layer between the CuO_2 sheets dips below the Fermi level. There is some evidence that this may happen in the Bi and Tl materials.[4]) These factors remove electrons from the sheets, whose charges in the absence of carriers are nominally $Cu^{2+}(O^{2-})_2$. Spectroscopic studies suggest that the removed electrons result in holes which reside principally on the oxygen sites.[5] However, crystal symmetry splits the oxygen orbitals. Since the $p\sigma$ orbital points towards the two neighboring positive Cu ions, a hole in this orbital has its energy raised by the Madelung potential. Coulomb arguments thus favor hole occupancy of the $p\pi$ orbital which is perpendicular to the Cu-O-Cu axes in the x-y plane. The $p\pi$ orbital which is perpendicular to the plane is of intermediate energy.

In contrast, band structure calculations[6,7] show that the carrier holes reside in the antibonding band formed from the Cu $d(x^2-y^2)$ and the O $p\sigma$ orbitals. This band is highest in energy due to the large covalent interaction between the Cu and O neighbors. However, such covalency is limited by correlation effects which occur when the screened hole-hole Coulomb interactions are not negligible. The latter energies are included in model Hamiltonians as the Hubbard U parameters. Thus, in the limit of strong correlations, Coulomb factors determine the carrier hole location (the $p\pi$ orbitals in these materials); with weak correlations the covalent interactions dominate (causing $p\sigma$ carrier occupancy).

Obviously a most important question concerns the location of the carrier holes because the strength of the coupling of the carriers to the spin-$\frac{1}{2}$ Heisenberg system, composed of the Cu^{2+} sublattice, could be very different for $p\sigma$ vs $p\pi$ orbitals (indeed, we find the $p\pi$ coupling to be much less than that of the $p\sigma$). While most workers have assumed $p\sigma$ occupancy, recently Guo, Langlois, and Goddard[8] have proposed $p\pi$ carrier occupancy based on *ab initio* quantum chemical calculations which include limited correlation. In addition, Birgeneau, Kastner, and Aharony[9] proposed a magnetic frustration model which was analyzed assuming (but which is not necessarily dependent upon) $p\pi$ carrier occupancy. This assumption was based on the observation that correlation is strong, as evidenced by the existence of antiferromagnetic sister compounds to the superconducting materials, and that therefore Coulomb factors would win out.

Recently, we derived a realistic two-band extended Hubbard Hamiltonian for the CuO_2 sheet and obtained an understanding of the origin of the spin system and the nature of the charge carriers. In the following paragraphs, we summarize the major conclusions of Ref. 10.

We found that it is very important to include both the *inter*atomic Coulomb interactions and the oxygen-oxygen transfer integrals in the Hamiltonian and showed why it is not possible to leave out these energies and still have the essential physics in a two-band Hubbard model. In addition, we argued that it is very doubtful that a simple single-band model can recapture this physics from renormalization. (The importance of interatomic Coulomb interactions has also been recognized in the work of Varma, Schmitt-Rink and Abrahams,[11] although in conjunction with a different physical picture.)

Taking $Cu(d^{10})O(p^6)$ as the vacuum state, we found that with one hole per unit cell, a spin-$\frac{1}{2}$ system is formed because of Coulomb interactions (expressed by the intra- and interatomic Hubbard U parameters) which localize the holes on the Cu sites and cause the $Cu(d^9)$ configuration to be dominant. These significant Coulomb interactions result from the nearly closed shell nature of both the Cu and O ions which results in poor screening. The spin system was found to be well represented by the Heisenberg Hamiltonian.

We found that the spin system persists in the presence of carriers, at least at carrier densities of interest, because the localization is driven by local Coulomb interactions. This finding agrees with the conclusions derived from both neutron[12] and light scattering[13] experiments, although further work concerning sample homogeneity and the width of the magnon loss features in the Raman work

(presumably due to lifetime effects) would help to make this definitive. Carriers are produced when there is more than one hole per unit cell (we omit consideration of nonperiodic potentials which may bind a small number of carriers). We estimated the relative energy of different carrier hole placements and concluded that the carriers were on the oxygen sublattice due to the large value of the screened single-site copper hole-hole repulsion, $U_d \sim 9$ eV.

We considered the contributions of the various virtual states to the carrier energy and concluded that the most important virtual was the "d^{10}," which stabilized $p\sigma$ holes by ~ 1-2 eV in spite of the strong correlation between carrier holes (on the oxygen sublattice) and spin-system holes (on the copper sublattice). This virtual state can move a carrier with and without producing deviations in the local antiferromagnetic order of the spin subsystem. (Called "$1/\Delta$" processes in the work of Zaanen and Oles,[14] we refer to these as "dynamic exchange" and "exchange transport" processes depending, respectively, upon whether a spin excitation is produced or not.) The d^{10} virtual state is low lying in energy because it avoids double hole occupancies: a carrier hole momentarily on an oxygen $p\sigma$ can move to the $p\sigma$ orbital on another oxygen site via $p^5d^9p^6 \rightarrow p^5d^{10}p^5 \rightarrow p^6d^9p^5$. Since this process obviously exchanges the holes of the carrier and the Cu ion, their spins are also exchanged if they differ in alignment. Note that this process is very strong because locally it is Coulomb neutral. Thus the energy of the intermediate state (the d^{10}) relative to the other configurations is only the difference in the Cu $d(x^2-y^2)$ and O $p\sigma$ orbital energies, $\Delta\varepsilon \sim 1.5$ eV, while the matrix element that couples them is the Cu $d(x^2-y^2)$ to O $p\sigma$ transfer integral, $t_{pd} \sim 1.1$ eV (see below). Obviously, the mixing is very substantial.

The above d^{10} process causes strong interactions between the carrier and spin systems which cannot be treated perturbatively. This is the largest (though not the only) factor in the carrier-spin coupling and one that would be absent if the carriers were $p\pi$ type. These strong interactions lead to a new type of carrier quasiparticle which is neither a free hole nor a spin polaron: We named it a "spin-hybrid"[10] because while it moves with a relatively wide bandwidth, it has a high probability ($\sim$30–40%) of being associated with a deviation in the local antiferromagnetic order at any instant in time; i.e., it is a hybrid of different local spin-orbital configurations. We saw that the spin-hybrid quasiparticle leads to electronically driven pairing in the Cooper sense. We suggested that high-T_c superconductivity results from the attraction between these unique carrier quasiparticles.

In this communication, we extend our model Hamiltonian to include the $p\pi$ orbitals [the $d(xy)$ orbitals are discussed below] and report the results of numerical calculations for the ground and low-lying excited states of a variety of finite clusters representing the CuO_2 sheet with a carrier hole. These calculations represent the first exact solutions of the realistic Hamiltonian on finite systems of a size sufficient to shed insight into the carrier character.

In comparing the results for the smallest and the larger clusters, we find that with our choice of energy parameters,[10] $p\pi$ carrier occupancy is preferred only in the smallest cluster: As cluster size increases and the effects of the d^{10} virtual state increase, we observe the progressive lowering of the $p\sigma$ level until it is preferred by ~ 0.6 eV in the largest cluster that we consider (we estimate the value for the infinite solid to be still higher, perhaps ~ 1 eV). The conclusions of Ref. 10 concerning the nature of the carrier quasiparticles are thus supported by these calculations.

II. THE MODEL HAMILTONIAN AND ITS SOLUTION

Since the results reported below are the exact solution of the model for the finite systems which we consider, any question concerning the applicability of the results must address the energy parameters and/or the model Hamiltonian. The origin of the parameters is explained in detail in Ref. 10 and only summarized here.

The three-band [for $d(x^2-y^2)$, $p\sigma$, and $p\pi$] extended-Hubbard Hamiltonian is given by

$$H_0 = \sum_{i\sigma} \varepsilon_i n_{i\sigma} + \sum_{ij\sigma}{}' t_{ij} \psi^\dagger_{i\sigma} \psi_{j\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow} + \tfrac{1}{2} \sum_{i\sigma_1 j\sigma_2}{}' (U_{ij} n_{i\sigma_1} n_{j\sigma_2} + K_{ij} \psi^\dagger_{j\sigma_2} \psi_{i\sigma_2} \psi^\dagger_{i\sigma_1} \psi_{j\sigma_1}) , \quad (1)$$

where the prime on the summations implies $i \neq j$. The nonzero energy parameters are summarized in Table I. As explained in Ref. 10, the single-site values of $U_d \sim 9$ eV and $U_p \sim 6$ eV were obtained from the analysis of core-valence-valence Auger data on related materials. These numbers have received further support from *ab initio* calculations by three different groups.[15–17] [In this paper we will use $U_p(\sigma\sigma) = U_p(\pi\pi) = 6$ eV for single-site repulsion when both holes are in the same oxygen $2p$ orbital, and $U_p(\sigma\pi) = 5.4$ eV when they are in different $2p$ orbitals on the same oxygen site.] The values for the interatomic Coulomb interactions, $U_{pd} \sim 1.5$ eV and $U_{pp} \sim 1.0$ eV (the same for $p\sigma$ and $p\pi$), were estimated using the bounds of the dielectric limit on the lower side (with $\varepsilon_\infty \sim 10$) and by the consequences of the assumption that screening is more effective when holes are apart than together on the upper side. This meant that U_{pd} should be reduced from the bare (e^2/r) value with a proportion at least as great as the single site value of U_d (~ 9 eV) is reduced from the gas phase value of 16.5 eV. Band-structure calculations by Mattheiss[6] were used to estimate the difference in the $d(x^2-y^2)$ and $p\sigma$ orbital energies by assuming that the band structure could be considered a mean-field solution of the extended Hubbard model Hamiltonian, as pointed out by Emery.[18] Thus, since the one-electron copper $3d$ and oxygen $2p$ energies are close, $\Delta\varepsilon \equiv \varepsilon_d - \varepsilon_{p\sigma} \sim U_d/4 - U_p/8 \sim 1.5$ eV (Refs. 10 and 18) so that the Cu site is preferred in the Hubbard Hamiltonian, based on the values of U given above. (Other workers[15,16] have recently suggested a slightly larger value of 2 eV;

TABLE I. Nonzero energy parameters used in the three-band extended-Hubbard Hamiltonian. The energies apply a basis set which has local antibonding orientations between all d and p orbitals. The origin of the parameters and the considerable uncertainty of several of them is discussed in the text and more fully in Ref. 10.

Coulomb terms				
Single site	Interatomic	Transfer integrals	Orbital energies	Direct exchange energies
$U_d=9.0$ eV	$U_{pd}=1.5$ eV	t_{pd} (σ only) $=1.07$ eV	$\varepsilon_d\equiv 0.0$ eV	$K_{dp\sigma}=-0.18$ eV
$U_p(\sigma\sigma)=6.0$ eV	$U_{pp}=1.0$ eV	t_{pp} ($\sigma\sigma$ or $\pi\pi$) $=0.53$ eV	$\varepsilon_{p\pi}=-0.7$ eV	$K_{dp\pi}=-0.015$ eV
$U_p(\pi\pi)=6.0$ eV		t_{pp} ($\sigma\pi$ or $\pi\sigma$) $=0.36$ eV	$\varepsilon_{p\sigma}=-1.5$ eV	$K_p(\sigma\pi)=-0.85$ eV
$U_p(\sigma\pi)=5.4$ eV				

this does not qualitatively affect the results.) The model transfer integrals are taken to reproduce the band-structure valence bandwidth in the limit that the $U\equiv 0$. This argument is based on the observation that density functional bandwidths compare well with experiment in systems where correlation effects do not dominate. To a good approximation,[10] this means that the sum $t_{pd}+t_{pp}$ is set by the calculated bandwidth. The exact values of the t's were chosen by three methods, all of which agree rather well. (1) Noting that the oxygen bandwidth of MgO is ~ 6 eV and there are no d orbitals on the metal atom, we can estimate a t_{pp} of ~ 0.25 eV in MgO which scales up for the CuO_2 sheet upon considering the ratio of the overlaps between O^{2-} ion orbitals at the oxygen-oxygen distance in MgO and the 10% smaller distance that occurs in CuO_2. (2) The ratio of the ion orbital overlaps between Cu and O suggests by Huckel reasoning that $t_{pp}/t_{pd}\sim\frac{4}{7}$, and (3) a fit to the band structure by McMahan, Martin, and Satpathy[16] also results in a value for t_{pp}. These arguments suggest $t_{pd}\sim 1.1$ eV and t_{pp} (both σ or both π) ~ 0.5–0.6 eV (Ref. 10) (note that in this work we always take the orientation of the atomic orbitals to be in the crystal reference frame as opposed to a local diatomic reference frame). As a self-consistency check, we require that our model reproduce the measured value of the superexchange, J, which it does with good accuracy.[10] (While J could be used to suggest a value for t_{pd} if the other parameters are fixed, since J is a complex function of all of the parameters, there is no justification in setting t_{pd} by fitting J.) The value of $\varepsilon_{p\pi}-\varepsilon_{p\sigma}$ was found from the energy splitting of O^{2-} orbitals which were calculated self-consistently in a Madelung potential well produced by point ions appropriate to the La_2CuO_4 material. This value is 0.8 eV, favoring hole occupancy of the $p\pi$ orbital. The direct exchange energies between the $d(x^2-y^2)$ and the $p\sigma$ and $p\pi$ orbitals (-0.18 eV and -0.015 eV, respectively; negative means ferromagnetic) were obtained from the two-electron integrals calculated using orthogonalized ionic orbitals with the appropriate distance between sites. Similarly, the single site $p\sigma$-$p\pi$ exchange energy $K_p(\pi\sigma)\sim -0.85$ eV. The $t_{pp}(\sigma\pi)$ transfer-integral value of 0.36 eV was scaled from the value of t_{pp} using the relative values of the $p\sigma p\sigma=p\pi p\pi$ vs $p\sigma p\pi$ overlap integrals. Interatomic Coulomb interactions further than second nearest neighbor were found to play no role in the qualitative results.

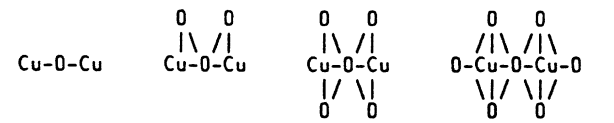
These values of the energy parameters should be considered to have some uncertainty. For example, our value for U_{pd} is a rough estimate,[10] with reasonable error bars being 2 ± 1 eV. As discussed in Ref. 10, we consider both U_p and U_d as determined from the Auger experiments to be lower bounds due to the complete screening of the Auger final state, particularly true in the Cu case. Our value for t_{pd} may be low;[16] raising it would raise the superexchange unless compensations occurred by changing other parameters. However, we have experimented with the parameters over reasonable ranges of uncertainty and find that the qualitative results reported are stable. We also report our quantitative results using the numbers from Table I so that other workers can reproduce our figures.

Our Hamiltonian can be used to write a configuration interaction matrix for calculations of n holes on N sites. For example, in the simplest case of a Cu-O-Cu cluster with two holes, we use a set of antisymmetrized spin-orbital bases of the form

$$[d_{1\alpha}(r_1)p\sigma_\beta(r_2)-p\sigma_\beta(r_1)d_{1\alpha}(r_2)]/\sqrt{2}\,,$$

etc., representing all possible placements of two holes on three sites with spins α or β. The Hamiltonian matrix for this basis can be constructed straightforwardly using Eq. (1), as is the extension to more sites and/or holes. Diagonalization of the Hamiltonian matrix then yields the ground state for our model and the low-lying excited states. Naturally, the matrix can be block factored (the 1920 three-hole configurations of our largest cluster described below block into 1360 of spin $\frac{1}{2}$ and 560 of spin $\frac{3}{2}$). The clusters are "embedded" in that interatomic Coulomb interactions are included (U_{pd}) between holes on the outermost oxygen atoms of the cluster and holes (considered fixed) on the next (missing) shell of Cu(d^9) ions.

In Ref. 10 we considered calculations on small clusters such as Cu_5O_4 (with five holes) in order to compute the superexchange and test the validity of the Heisenberg Hamiltonian in describing the spin system. Here we extend our basis set to include the $p\pi$ orbitals and consider the following clusters with two (spin system) or three (nominally one carrier and two spin system) holes each:



where the lines indicate the transfer-integral connections between sites.

III. RESULTS

For the three-hole clusters, the energies and spin states of the ground and low-lying excited states are shown in Table II as are the dominant basis functions in the carrier wave function. The $p\sigma$-dominated state is seen to progressively lower its energy relative to the $p\pi$-dominated states as we increase cluster size. The reason for the trend is explained by the d^{10} virtual process, which does not exist in cluster I and whose strength increases as we complete the oxygen coordination of the Cu sites by proceeding from cluster I to cluster IV (recall that we define the "d^{10}" process to involve a virtual state with holes on two different oxygen atoms). In cluster IV, the carrier density is not evenly distributed on the oxygens because the center oxygen has higher coordination than the others. The result of this is to prevent the full effect of the d^{10} process even though the coppers are fully coordinated, thus making the energy difference between the $p\sigma$ and the lowest $p\pi$ state (0.6 eV) a lower bound for the difference in the infinite solid.

The d^{10} process is not the only interaction between the oxygen and copper sites. Mixing with virtual states involving the d^8 and p^4 configurations is seen to reduce the energy splitting of the $p\sigma$ and $p\pi$ levels in cluster I from 0.8 eV ($\Delta\varepsilon$ between $p\sigma$ and $p\pi$) to $\sim$0.3 eV. Thus the d^{10} process only has to contribute the latter energy to cause the carriers to have $p\sigma$ character.

Another way to see the effect of the interactions between the $p\sigma$ carrier and the Cu site is to consider the following argument: If we compute any of the clusters without the Cu sites, the (one-electron) energy of the lowest $p\sigma$ orbital is almost exactly 0.8 eV above the lowest $p\pi$ orbital because each wave function is a cluster representation of the two purely antibonding levels that occur at the X point in the Brillouin zone and are only split by $\varepsilon_{p\sigma}-\varepsilon_{p\pi}$ (in other words, near X the two, $p\sigma$, and $p\pi$, purely antibonding levels do not mix due to orthogonality;[16] we called this phase "$\mathbf{k}=0$" in Ref. 10 because we chose for convenience the antibonding orientation of the local orbital bases; if we chose a conventional orientation, we would refer to these one-electron levels as having $\mathbf{k}$ at the X point, $[\pi/a_x,\pi/a_y,0]$ where a_x and a_y are lattice constants[6,7]). Thus in cluster IV, we see that the effect of the $p\sigma$ interactions with the Cu sites is to pull the $p\sigma$ carrier level 1.4 eV lower in energy relative to the $p\pi$ level. If we take $\sim$0.5 eV of this energy to represent the effect of virtual states other than the d^{10}, then we may ascribe $\sim$0.9 eV to the d^{10} process, which is at the lower bound of the estimate in Ref. 10 of 1–2 eV for the effect of the d^{10} process on the $p\sigma$ energy in the infinite solid. As our cluster IV value for the d^{10} energy is a lower bound, a reasonable estimate for the extended solid is that the $p\sigma$ would fall $\sim$1 eV below the $p\pi$. Thus, without strong mixing between the $p\sigma$ and $p\pi$ levels (see below), in order to have $p\pi$ carrier occupancy, the crystal field (i.e., Madelung potential) splitting of the $p\sigma$ vs $p\pi$ must exceed $\sim$1.8 eV, more than twice our estimate of 0.8 eV.

An obvious concern is the effect of cluster size. However, we believe that the clusters correctly predict the carrier character in the extended solid due to the following reasoning: Assume in the limit of a large cluster that the

TABLE II. The exact solution of the model Hamiltonian on the indicated finite clusters. The lowest several energy levels are referenced to the ground state. The $S_z=\frac{1}{2}$ orbital which dominates the carrier wave function is indicated together with the cluster spin. The $p\sigma$-$p\pi$ mixing is $<10\%$ except for the states indicated by the asterisk in cluster II where, for example, the lowest state has $\sim\frac{1}{3}$ of a hole in the $p\pi$ orbitals. The form of the spin wave function for those configurations which have the carrier hole between two Cu holes is also shown.

Cluster		Energy (eV)	Carrier	Spin	Cu-O-Cu wave function
I.	Cu-O-Cu	0.285	$p\sigma$	$\frac{1}{2}$	$\alpha\alpha\beta-2\alpha\beta\alpha+\beta\alpha\alpha$
		0.100	$p\pi$	$\frac{1}{2}$	$\alpha\alpha\beta-2\alpha\beta\alpha+\beta\alpha\alpha$
		0.025	$p\pi$	$\frac{1}{2}$	$\alpha\alpha\beta-\beta\alpha\alpha$
		0.000	$p\pi$	$\frac{3}{2}$	$\alpha\alpha\beta+\alpha\beta\alpha-\beta\alpha\alpha$
II.	O O | \ / | Cu-O-Cu	0.255	$p\pi^*$	$\frac{1}{2}$	$\alpha\alpha\beta-2\alpha\beta\alpha+\beta\alpha\alpha$
		0.248	$p\pi^*$	$\frac{1}{2}$	$\alpha\alpha\beta-\beta\alpha\alpha$
		0.215	$p\pi$	$\frac{3}{2}$	$\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha$
		0.000	$p\sigma^*$	$\frac{1}{2}$	$\alpha\alpha\beta-2\alpha\beta\alpha+\beta\alpha\alpha$
III.	O O | \ / | Cu-O-Cu | / \ | O O	0.463	$p\pi$	$\frac{1}{2}$	$\alpha\alpha\beta-2\alpha\beta\alpha+\beta\alpha\alpha$
		0.357	$p\pi$	$\frac{3}{2}$	$\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha$
		0.289	$p\pi$	$\frac{1}{2}$	$\alpha\alpha\beta-\beta\alpha\alpha$
		0.000	$p\sigma$	$\frac{1}{2}$	$\alpha\alpha\beta-2\alpha\beta\alpha+\beta\alpha\alpha$
IV.	O O /| \ /| O-Cu-O-Cu-O \\| / \\| O O	0.638	$p\sigma$	$\frac{1}{2}$	$\alpha\alpha\beta-\beta\alpha\alpha$
		0.630	$p\pi$	$\frac{3}{2}$	$\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha$
		0.567	$p\pi$	$\frac{1}{2}$	$\alpha\alpha\beta-\beta\alpha\alpha$
		0.000	$p\sigma$	$\frac{1}{2}$	$\alpha\alpha\beta-2\alpha\beta\alpha+\beta\alpha\alpha$

$p\sigma$ level would indeed lie ~ 1 eV below the $p\pi$ level, a value consistent with the trends seen in Table II. (Our largest cluster has only weak, $\sim 2\%$, mixing of $p\pi$ in the $p\sigma$ level and vice versa; we will ignore this.) We can then construct an oxygen (carrier) band structure for the extended system by including the effect of the Cu-$p\sigma$ interaction in a renormalized orbital energy for the $p\sigma$, making it ~ 1 eV below the $p\pi$. This simple model allows us to compute the amount of $p\pi$-$p\sigma$ mixing in the empty (hole) portion of the Brillouin zone as a function of carrier density. Since the square-lattice oxygen band structure is simple to work out, we only note here that using the transfer integrals of Table I, less than 2% of the carrier density is in the $p\pi$ orbitals even at 26% carrier concentration: For example, the Fermi momentum at relevant carrier densities is so close to Γ (or X with the conventional basis set) that the $p\sigma$-$p\pi$ orthogonality that occurs there continues to prevent strong $p\sigma$-$p\pi$ mixing in spite of the relatively large transfer integrals between these orbitals. Similar conclusions can be found if one considers coupling clusters together to make an infinite solid and the maximum matrix elements that can occur between clusters. These matrix elements mix the lowest two ($p\sigma$ and $p\pi$) cluster states, but with 1 eV separation and at carrier densities in the 10–20% range, mixing is at most $\sim 5\%$.

The Fermi momentum arguments given above mean that significant $p\sigma$-$p\pi$ mixing in the carrier wave functions will not occur at the carrier densities of these materials, so that the carriers will be essentially *either* $p\sigma$ or $p\pi$, not some combination of both, with the correct description depending on the competition between the energy lowering of the $p\sigma$ due to the d^{10} (and other virtuals) and the crystal-field energy difference between the $p\sigma$ and $p\pi$

A large energy which we left out of our three-band Hamiltonian is the transfer integral between the Cu $d(xy)$ and the O $p\pi$ orbitals. By scaling with the overlaps between ionic orbitals, we estimate that this transfer integral is ~ 0.6 of the $d(x^2-y^2)$ to $p\sigma$ matrix element. However, while one can construct a one-electron orbital in the $d(x^2-y^2)-p\sigma$ band that is fully antibonding (i.e., antibonding not only Cu to O but O to O also), it is not possible to do so in the $d(xy)$-$p\pi$ band: The lowest energy $p\pi$ hole state would be, within the one-electron approximation, antibonding between the oxygen $p\pi$ orbitals but *non*bonding between oxygen and Cu {having $g[xy(x^2-y^2)]$ symmetry about the Cu sites[16]}, and thus occur at the X-point in the Brillouin zone, as seen in the band-structure calculations.[6,7] Thus by leaving the $d(xy)$ out of our calculations, we have not altered the qualitative results.

We have also considered whether a different physical picture could result owing to uncertainty in the energy parameters. We mentioned above that if the Table I values are taken for the other parameters, the $p\pi$ would take the carriers only if the crystal-field splitting were greater than ~ 1.8 eV. This we consider unlikely as we[10] and McMahan *et al.*[16] obtained values for this quantity of 0.8 and 0.7 eV, respectively, using two very different approaches. However, one might expect that the d^{10} process would be weakened if one would change the parameters to lessen the time spent by copper holes on neighboring oxygen sites, for example by increasing $\Delta\varepsilon$ to 2 eV [between $d(x^2-y^2)$ and $p\sigma$].[15,16] We computed the largest cluster with this value and found that the opposite occurred: The $p\sigma$ state becomes 0.649 eV below the lowest $p\pi$ carrier state (in fact the second $p\sigma$ state is also lowered such that it becomes the first excited state of the cluster at 11 meV below the lowest $p\pi$). This can be understood by recalling that three-hole state energies are reported in Table II, not one-electron energies. Thus, the stabilization energy of the d^{10} process is a complex matter and apparently compensations occur when changing the d-$p\sigma$ hybridization so that the qualitative result is independent of reasonable variations of the energy parameters. In fact, when we increase both $\Delta\varepsilon$ and U_{pd} to 2 eV, we find that $p\sigma$ is even more strongly favored at 0.739 eV below the lowest $p\pi$ state. (Significant *lowerings* of U_{pd} without compensating increases in $\Delta\varepsilon$ cause the destruction of the spin system.[10] We have not yet taken our parameters into regimes where the system becomes unphysical.)

The $d(xy)$ orbital which is left out of our clusters will not appreciably contribute to the effective exchange between $p\pi$ carriers and the Cu spin system due to its nonbonding relationship to the preferred $p\pi$ hole level (at $\mathbf{k}=X$ in the band structure). Thus using our results we can estimate the magnitude of the effective exchange between hypothetical $p\pi$ carriers and the Cu spins. Note that the lowest $p\pi$ spin state in cluster I is $S=\frac{3}{2}$. This preferred local spin state was noted in both Refs. 8 and 9 and is due to the fact that the effective ferromagnetic $p\pi$-$d(x^2-y^2)$ exchange is larger than twice the Cu-Cu superexchange in the three hole cluster as the full value of the latter is blocked by the presence of the carrier hole. This would have a frustration effect on the spin order in a static picture in that the carriers want to align both neighboring Cu spins while the antiferromagnetic order wants to antialign them.[9] (A similar frustration effect can occur with $p\sigma$ carriers. The strength of this interaction is discussed in Ref. 10.) From our numbers and using reasoning found in Sec. IV of Ref. 10, it is possible to extract information about the effective $p\pi$-Cu exchange interaction and the degree of Cu-Cu superexchange blocking produced by the presence of the $p\pi$ hole. For example, taking the cluster I eigenvalues from Table II, we fit the energy of the $S=\frac{3}{2}$ state to $K_{\rm eff}(dp\pi)+J_b/2$ and the next higher two $S=\frac{1}{2}$ states to $-\frac{3}{2}J_b$ and $-2K_{\rm eff}(dp\pi)+J_b/2$, respectively. This results in $K_{\rm eff}(dp\pi)\sim -33$ meV (negative indicating ferromagnetic) and $J_b\sim 4$ meV, J_b representing the "blocked" superexchange. Since $J\sim 40$–60 meV,[10,12,13] superexchange is almost completely blocked by the presence of a $p\pi$ carrier hole, as was seen to also be the case for a $p\sigma$ carrier.[10]

Our cluster results suggest that a delocalized $p\pi$ hole may not frustrate the Cu spin order in spite of the above numbers: as soon as we delocalize the $p\pi$ carrier hole by considering a larger cluster, the lowest energy cluster spin state for a $p\pi$ carrier is $S=\frac{1}{2}$, not $S=\frac{3}{2}$. For example in cluster III, although we still block the superexchange with 45% of the $p\pi$ carrier hole on the center oxygen, the lowest spin state is $S=\frac{1}{2}$.

Finally, we report in Table III the orbital occupancies from calculations using the largest cluster. The one-

TABLE III. Hole populations in cluster IV by atom for various numbers of holes and states with different choices of energy parameters. The energy parameters are those of Table I except when modified as indicated. O(1) is the central oxygen, there are four O(2) and two O(3) oxygens. g.s. means ground state, the others are the lowest state with the carrier as indicated. $p\pi$ occupations are $< 20\%$ unless specifically indicated. Note the similarity of the Cu occupancy in the $2h$ and $3h(p\pi)$ calculations; this indicates that the Cu-$p\sigma$ hybridization is not substantially altered by the $p\pi$ presence.

Holes (state)	Parameters	Cu	O(1)	O(2)	O(3)
$2h$(g.s.)	· · ·	0.67	0.20	0.08	0.07
$3h(p\sigma)$	· · ·	0.74	0.41	0.18	0.19
$3h(p\pi)$	· · ·	0.66	0.15	0.09	0.10
		$p\pi$ occupations:	0.39	0.12	0.07
$2h$(g.s.)	$\Delta\varepsilon=2$ eV	0.72	0.17	0.06	0.06
$3h(p\sigma)$	$\Delta\varepsilon=2$ eV	0.79	0.39	0.17	0.17
$2h$(g.s.)	$\Delta\varepsilon=U_{pd}=2$ eV	0.76	0.15	0.06	0.06
$3h(p\sigma)$	$\Delta\varepsilon=U_{pd}=2$ eV	0.82	0.39	0.16	0.16
$2h$(g.s.)	all $U=0$	0.52	0.36	0.11	0.08
$3h(p\sigma)$	all $U=0$	0.82	0.36	0.17	0.16

electron occupancies are found by removing the U from the Hamiltonian and should mimic the band structure results, albeit with some cluster artifacts such as the nonuniformity of hole amplitude between the oxygens and the result of a finite $\Delta\varepsilon$ (which should actually be decreased to represent the mean-field $\Delta\varepsilon$;[18] the use of the Hubbard $\Delta\varepsilon$ will artifically increase the Cu hole amplitude and thus *reduce* the difference between the correlated and one-electron cluster results). Note that the Cu valency in the ground state of the two hole cluster is quite different from the one-electron result because of correlation (67% of a hole vs 52%, with the Table I parameters). This is in agreement with our observation[10] that the spin system forms due to correlation. A larger value for Cu hole occupancy (72%) results if $\Delta\varepsilon$ is increased to 2 eV.

This deviation from the one-electron description of the Cu valency can be interpreted as a destruction of Cu-O covalency. Indeed, this does occur due to the reduction of d^8 and p^4 configurations in the wave function. However, as we have seen, this loss of covalency does not prevent strong $p\sigma$ stabilization as a result of the d^{10} mechanism.

In conclusion, with reasonable parameters in a three-band extended-Hubbard model, we find it very likely that the charge carriers are of $p\sigma$ character in the high-T_c materials. Thus, the major conclusions of Ref. 10, concerning the importance of the d^{10} processes and its role in producing the strong carrier-spin system interactions which are the hallmark of the spin-hybrid carrier quasiparticles, are consistent with the results of exact solutions of our model Hamiltonian for finite clusters.

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