Proposal of an extended t-J Hamiltonian for high-Tc cuprates from ab initio calculations on embedded clusters.

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Abstract

A series of accurate ab initio calculations on Cu\textsubscript{p}O\textsubscript{q} finite clusters, properly embedded on the Madelung potential of the infinite lattice, have been performed in order to determine the local effective interactions in the CuO\textsubscript{2} planes of La\(_{2-x}\)Sr\(_{x}\)CuO\(_{4}\) compounds. The values of the first-neighbor interactions, magnetic coupling (\(J_{NN}=125\) meV) and hopping integral (\(t_{NN}=-555\) meV), have been confirmed. Important additional effects are evidenced, concerning essentially the second-neighbor hopping integral \(t_{NNN}=+110\) meV, the displacement of a singlet toward an adjacent colinear hole, \(h_{SD}^{abc}=-80\) meV, a non-negligible hole-hole repulsion \(V_{NN}-V_{NNN}=0.8\) eV and a strong anisotropic effect of the presence of an adjacent hole on the values of the first-neighbor interactions. The dependence of \(J_{NN}\) and \(t_{NN}\) on the position of neighbor hole(s) has been rationalized from the two-band model and checked from a series of additional ab initio calculations. An extended t-J model Hamiltonian has been proposed on the basis of these results. It is argued that the here-proposed three-body effects may play a role in the charge/spin separation observed in these compounds, that is, in the formation and dynamic of stripes.

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1 Introduction

The insulating cuprates, such as $\text{La}_2\text{CuO}_4$, which are the undoped parent compounds of the high-$T_c$ superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, are known to present antiferromagnetic couplings between nearest neighbor (NN) copper centered sites in the $\text{CuO}_2$ planes. Raman and neutron diffraction experiments evaluate this coupling to be around $J_{NN}=130 \text{ meV} (128\pm 6 \text{ meV} [1, 2], 134\pm 5 \text{ meV} [3, 4, 5]$, respectively). Nevertheless, the corresponding simple Heisenberg Hamiltonian does not reproduce entirely the features of the Raman spectrum [6, 7, 8, 9, 10, 11] and additional effects such as second-neighbor magnetic coupling $J_{NNN}$ and four-spin cyclic exchange have been invoked [12, 13, 14, 15]. While an upper bond for $J_{NNN} (|J_{NNN}| \leq 9 \text{ meV})$ has been given from Raman experiments [5], the amplitude of the four-spin operator in this kind of compounds is a matter of discussion. Previous works have shown that this cyclic operator corresponds to a fourth-order term in the Hubbard model, scaling as $\lambda t_{NN}^4 / U^3$, with $\lambda=40 [16, 17]$ or $\lambda=80 [18, 19]$, depending on the formal writing of the Hamiltonian.

Regarding the hole-doped material, where the conduction takes place in the $\text{CuO}_2$ planes, the holes can be seen as centered on copper atoms with large tails on the four neighboring oxygen atoms. They move from on site to an adjacent one through the effect of a hopping operator of amplitude $t_{NN}$, for which there is no direct experimental evaluation, but values around -0.5 eV are considered as reasonable [20]. One of the most widely employed model Hamiltonians used for the interpretation of the properties of these materials, through a hole-pairing mechanism, is the so-called $t-J$ model [21, 22] which combines spin coupling and hole hopping:

$$H = \sum_{ab} J_{NN} \cdot (S_a \cdot S_b - 1/4) + t_{NN} \cdot (a_a^\dagger a_b + a_b^\dagger a_a + s.c.) \delta(n_a + n_b, 1)$$

(1)

The adequacy of such a simple Hamiltonian to incorporate the physics of the problem is questionable. Hopping between second-neighbor sites may be non negligible. When one derives the $t-J$ Hamiltonian from the Hubbard Hamiltonian, three-site operators moving a singlet-coupled electron pair toward the hole appear at second order of perturbation theory, scaling as the $J_{NN}$ operator, i.e, as $t_{NN}^2 / U$, where $U$ is the on-site Coulombic repulsion. The transferability of $J_{NN}$ from the undoped to the doped material is not guaranteed, the presence of a neighboring hole may affect the coupling of two adjacent spins. The hole-hole repulsion $V_{ij}$ is likely to play a role, influencing the mean distance between the holes. Different extensions of the $t-J$ model have been employed in numerical simulations, for instance, $t-t'-J$ [23, 24, 25, 26] or $t-J-V$ [27, 28, 29], but the values given to the parameters are rather arbitrary, varying widely from one author to the other, the main objective being to exhibit qualitative collective effects. Among them the experimental evidence of the occurrence of stripes have focused attention in the recent past [30].

The goal of the present paper is to bring useful informations regarding the local effective interactions in undoped and hole-doped cuprates. To obtain them, the most accurate tools of ab initio quantum chemistry will be used. The method consists in considering few-site clusters, properly embedded in the field of the periodic environment, and to calculate the low part of the spectrum using the exact Hamiltonian, large basis sets and extensive Configuration Interactions. From this spectrum it is possible to fix the amplitudes of the effective interactions. The procedure has been successfully used to calculate the NN magnetic coupling in a series of perovskites [31], among them $\text{La}_2\text{CuO}_4$ for which a value of $J_{NN}=130 \text{ meV}$ is obtained. Similar calculations of the hopping integral in the hole-doped system ($t=-0.57 \text{ eV}$) have been also reported [32, 33]. These calculations concerned symmetrical two-site clusters, for which the determination of $J_{NN}$
and $t_{NN}$ is straightforward from the two lowest eigenvalues. This is no longer the case when one considers larger clusters to extract additional parameters, concerning next-nearest neighbor (NNN) interactions, neighboring-hole dependence of $J_{NN}$ and $t_{NN}$, hole-hole repulsions and four-spin cyclic operators. Their achievement requires some additional mathematical tools such as the Bloch definition of effective Hamiltonians and localization procedures (for instance, Boys method \[34\]). The methodology will be explained in Section II. Section III will present the results concerning the four-site square plaquette and three-site linear cluster with different number of electrons (holes). Calculations performed on undoped clusters provide the values of the NN, NNN and next NNN magnetic couplings (Scheme I). Also the amplitude of the four-spin cyclic exchange for this compound has been established. Hole-doped clusters give informations about the hopping integrals (NN, NNN and next NNN), the singlet-displacement operator and the dependence of the first-neighbor interactions (hopping integral and magnetic exchange) on the number and relative position of the adjacent holes. Section V presents a rationalization of the anisotropy of the effect of hole(s) in the vicinity on the values of $J_{NN}$ and $t_{NN}$ and reports additional exploratory calculations to evaluate the dependence of the bicentric parameters on the hole positions. Finally, Section VI summarizes the results, proposing a refined $t−J$ model, and discusses the possible effect of the additional operators on the charge/spin distribution on the lattice, with possible consequences for the stripping phenomena.

**Scheme I**

\[2\] Method

### 2.1 Mapping of a model Hamiltonian on an ab initio effective Hamiltonian

For such materials the unpaired electrons are essentially located on Cu $dx^2−y^2$ in-plane atomic orbitals, with non-negligible delocalization tails on the adjacent oxygen atoms. Such Cu-centered orbitals will be labelled \{a, b, c, ..\}. In the doped material the hole has much larger delocalization tails on O 2$p$ orbitals, but as shown by Zhang and Rice\[21, 22\] it remains possible to work within a one-band model Hamiltonian, the precise nature of its valence orbitals being implicit. For a finite cluster involving $p$ centers and $n ≤ p$ unpaired electrons, the model Hamiltonian works in a basis of $n$-electron localized determinants $\phi_i$, for which in the Heisenberg and $t−J$ Hamiltonians, the double occupancy of the orbitals is prohibited.

The ab initio calculations handle a large number of atomic orbitals, symmetry-adapted molecular orbitals (MOs) and expansions of the wave-functions on millions of determinants. Nevertheless, it is possible to construct from these calculations ab initio effective Hamiltonians which are in one-to-one correspondence with the model Hamiltonians. For an undoped cluster involving $p$ Cu atoms ($p$ sites), it is possible first to obtain from variational calculations a set of molecular orbitals containing doubly occupied MOs (core), unoccupied MOs (virtual MOs) and $p$ MOs with essentially single occupation, which define the ab initio one-electron valence space, $\{\phi_i\}$ in Figure 1. A unitary localizing transformation of the $p$ symmetry-adapted orbitals
will provide equivalent localized orbitals \( \{a', b', c', \ldots \} \) which can be seen as in strict one-to-one correspondence with the implicit valence orbitals of the model Hamiltonian. Fixing a double occupancy of the core orbitals, and putting \( n \) electrons in these orbitals, avoiding their double occupation, localized neutral determinants, \( \{ \phi_{i,\text{loc}}' \} \), are obtained which are in correspondence with the \( n \)-electron basis of the model Hamiltonian. Let be \( N_S \) the dimension of that space. The information obtained by the most refined ab initio calculations will be extracted according to the theory of the effective Hamiltonian proposed by Bloch[34]. When one knows the \( N_S \) eigenstates \( \Psi_m \) having the largest projections on the model space (which constitute the target space, stable subspace of \( H_{\text{exact}} \)) and their eigenvalues \( E_m \), the effective Hamiltonian is such that its eigenvalues are the exact ones, and its eigenvectors are the projections of the exact eigenvectors onto the model space:

\[
H_{\text{eff}}|P_S \Psi_m \rangle = E_m |P_S \Psi_m \rangle, \quad m = 1, N_S
\]

The spectral definition of \( H_{\text{eff}} \) is:

\[
H_{\text{eff}} = \sum_m |P_S \Psi_m \rangle E_m \langle P_S \Psi_m^\perp |
\]

where \( |P_S \Psi_m^\perp \rangle \) is the biorthogonal transformation of \( |P_S \Psi_m \rangle \). Actually the projections \( |P_S \Psi_m \rangle \) of the (orthogonal) states \( \Psi_m \) have no reason (expect for symmetry reasons) to be orthogonal, they define an overlap matrix \( s \):

\[
s_{mn} = \langle P_S \Psi_m |P_S \Psi_n \rangle
\]

and the biorthogonal vectors are defined by

\[
|P_S \Psi_m^\perp \rangle = s^{-1} |P_S \Psi_m \rangle
\]

The values of the norms of the projections, i.e. the diagonal elements of \( s \) matrix, give an indication on the quality of the description of these states by the truncated space \( S \). The model space and the exact eigenstates must be in strong correspondence, i.e. one must choose both spaces so that the vectors \( \Psi_m \) have the largest projections on the model space.

Then one may express this Hamiltonian in the basis of the localized determinants \( \{ \phi_{i,\text{loc}}' \} \) written in terms of the orbitals \( \{a', b', c', \ldots \} \) and the matrix elements

\[
\langle \phi_i' | H_{\text{eff}} | \phi_j' \rangle = \sum_m \langle \phi_i'|P_S \Psi_m \rangle E_m \langle P_S \Psi_m^\perp | \phi_j' \rangle
\]

can be identified to the matrix elements \( \langle \phi_i | H | \phi_j \rangle \) of the model Hamiltonian. In principle the effective Hamiltonians may be non-hermitian but the hermitization is straightforward [36].

The comparison between the ab initio effective Hamiltonian and the model Hamiltonian fixes the amplitudes of the integrals appearing in the latter and allows one to verify whether non-negligible additional interactions are not present. Figure 1 summarizes the whole process. Changing the size of the cluster, for instance going from a two-center/one-electron problem to a three-center/two-electron one, one may check the consistency of the procedure and the transferability of the effective interactions.

### 2.2 Computational details

The widely used embedded cluster technique has been employed to model the system. Finite clusters of the type \( \text{Cu}_p\text{O}_q \) (\( \text{Cu}_3\text{O}_{10} \) and \( \text{Cu}_4\text{O}_{12} \), Figure 2) have been selected, where the \( q \)
oxygen atoms are the first in-plane neighbors of the \( p \) Cu atoms. (Previous calculations have shown that the explicit involvement of the out of plane oxygen atoms does not change the values of the in-plane interactions \([32, 33]\)). The first-shell of atoms surrounding the cluster have been replaced by formal charges with pseudopotentials, in order to mimic the coulombic and exclusion effects. The rest of the lattice has been modeled by means of point charges, which values have been fixed according to Evjen’s method\([37]\), and which correctly represent the Madelung potential of the crystal\([38]\). This is a simplified approach in comparison with more elaborate methods proposed in the literature\([39]\).

The ten most internal electrons of Cu atoms have been represented by effective core pseudopotentials, the valence electrons being treated explicitly with triple-\( \zeta \) basis sets. A double-\( \zeta \) basis set has been used for oxygen atoms (preliminary calculations on bicentric clusters have shown that the inclusion of polarization functions on the bridging oxygen atoms has not an important effect neither on the magnetic coupling nor on the hopping integral)\([40]\).

For undoped clusters, the restricted-spin open-shell Hartree-Fock calculations variationaly define the singly occupied magnetic orbitals. These orbitals define a minimal valence complete active space (CAS). From this space it is possible to calculate the spectrum through a difference dedicated Configuration Interaction (DDCI) procedure \([41]\) which implies all the simple and double excitations on the top of this CAS, except the double excitations from the core to the virtual orbitals, which do not contribute to the energy difference at second-order of perturbation theory \([41]\).

An alternative solution consists in defining an enlarged CAS including the on-bond 2\( p \) orbital of the bridging oxygen atoms. These ligand-centered orbitals are the most participating on the intersite spin-exchange and electron transfer processes \([42]\). Performing all the single excitations on the top of this extended CAS, which corresponds to the two-band Hubbard model, one introduces dynamical polarization effects, i.e., screening by the non-active electrons, at lower computational cost than the preceding computational scheme.

3 Ab initio calculations on the plaquette and the linear clusters

As was mentioned above, two different clusters have been used to extract the effective interactions. A four-site square cluster (plaquette) of formula Cu\(_4\)O\(_{12}\) has been employed in order to determine the first- (NN) and second-neighbor (NNN) interactions, and also the four-spin cyclic exchange. Third-neighbor interactions (nNNN) has been estimated by means of the calculations carried out in a linear three-site cluster (Cu\(_3\)O\(_{10}\)). Comparing with the results obtained from the plaquette and previously studied binuclear clusters, it is possible to check the dependence of the NN interactions on the size of the fragment involved in the ab initio calculations.

Three fillings of the valence shell have been considered in order to evaluate the dependence of these interactions on the hole concentration. Undoped (4centre/4electron and 3centre/3electron problems), one hole-doped (4c/3e and 3c/2e) and two hole-doped (4c/2e and 3c/1e) situations have been analyzed. From the systems with two holes in the valence shells, it is possible to extract the amplitude of the hole-hole repulsions, an important magnitude for the study of the hole pairing mechanism. It is worth to notice that the here-referred hole-dopings are not in correspondence with the total doping of the lattice, induced by the replacement of La\(^{+3}\) by Sr\(^{+2}\).
A change in the occupation of the valence shell of these small clusters just induces a \textit{local} hole doping, which provides informations about the \textit{local} modifications of the effective parameters.

### 3.1 The localization process

In the plaquette, the four symmetry-adapted valence orbitals belong to the $A_{1g}$, $E_u$ and $B_{1g}$ representations in the $D_{4h}$ group. The localizing unitary transformation is straightforward since:

$$a_{1g} = \frac{(a + b + c + d)}{2} \quad (7)$$
$$e_{u(1)} = \frac{(a + b - c - d)}{2} \quad (8)$$
$$e_{u(2)} = \frac{(a - b - c + d)}{2} \quad (9)$$
$$b_{1g} = \frac{(a - b + c - d)}{2} \quad (10)$$

Figure 3 pictures one of these four localized valence orbitals for undoped and for the doped plaquettes, showing the strong localization of the magnetic orbitals and the $d - p$ hybridization occurring in the hole-doped systems[32, 33, 43].

In the linear cluster the localizing transformation of the three magnetic orbitals is no longer imposed by the symmetry. Two of these orbitals ($\varphi_g, \varphi'_g$) belong to the $A_g$ irreducible representation and the other one ($\varphi_u$) to the $B_{1u}$ symmetry. The rotation $U$, which transforms the \{\varphi_g, \varphi'_g, \varphi_u\} into the localized set \{\textit{a'}, \textit{b'}, \textit{c'}\} has been performed according to the Boys criterion [35], which maximizes the distance between the centroids of the orbitals. An alternative localization criterion, the minimization of the direct exchange integral $K_{ac}$, leads to the same rotation.

### 3.2 The magnetic interactions

Table 1 reports the results obtained from the plaquette and the linear clusters for the magnetic coupling, involving different fillings of the valence shell. For undoped cluster, the first-neighbor magnetic coupling $J_{NN}$ is $\sim 125$ meV. The calculated value is independent on the size of the considered cluster and it is in agreement with both the previously determined $J_{NN}$ in binuclear cluster and the estimations from Raman and neutron diffraction experiments ($128\pm6$ meV[1, 2], $134\pm5$ meV[3, 4, 5], respectively). The coupling between second-neighbors $J_{NNN}$ is also antiferromagnetic, with a value of $J_{NNN}=6.5$ meV in accordance with the experimental upper limit $|J_{NNN}| \leq 9$ meV[3]. A negligible antiferromagnetic coupling has been found between Cu atoms placed at a 2R distance (third-neighbors, next NNN): $J_{nNNN}=1$ meV.

Finally, the calculations on the plaquette provide a non-negligible value for the four-spin cyclic exchange of $K=14$ meV. The four-body operator can be written as:

$$H_K = K \sum_{ijkl} [(S_i \cdot S_j)(S_k \cdot S_l) + (S_i \cdot S_l)(S_j \cdot S_k) - (S_i \cdot S_k)(S_j \cdot S_l)] \quad (11)$$

This operator produces the cyclic permutation of the four spins on the plaquette (Scheme II) plus ordinary two-spin exchanges of all the pairs of spins of the plaquette including those of the diagonals. (A detailed discussion has been reported elsewhere [14].) Its value is somewhat smaller than some estimations used in numerical simulations [14, 13, 15], but larger than the critical value, $(K/J_{NN})_c=0.05 \pm 0.04$, estimated by Sakai and Hasegawa [15] for the appearance
of a magnetization plateau at half the saturation value in the $S = \frac{1}{2}$ antiferromagnetic spin ladders.

**SCHEME II**

When a hole is introduced in the cluster, the NN magnetic coupling is influenced by its presence, but in different directions depending on the relative position of this hole. Thus a hole in a colinear position to the two NN spins increases the coupling between these two spins (Scheme IIIa). However the NN magnetic coupling diminishes if the hole is placed in a position perpendicular to the bond (Scheme IIIb). The same trend is observed in the plaquette when a second-hole is introduced, $J_{NN}$ being 94 meV, to be compared with $J_{NN} = 104$ meV in presence of 1 hole and $J_{NN} = 125$ meV for undoped systems.

**SCHEME III**

### 3.3 Hopping integrals

As in the case of magnetic interactions, the first-neighbor hopping integral ($t_{NN}$) is also independent on the size of the cluster (Table 2), a value of -558 meV has been found in 1hole-doped linear cluster, -552 meV in 1hole-doped plaquette and -555 meV in previously reported binuclear cluster\[32, 33\]. This value is in accordance with a generally accepted value of -500 meV for these compounds\[20\].

An evaluation of second- and third-neighbor hopping integrals has also been possible. The NNN hopping integral $t_{NNN}=+112$ meV is unexpectedly large. The sign is in agreement with the negative overlap of the active orbitals placed at a $\sqrt{2}R$ distance, but its magnitude is large due to through bond processes, which involve the oxygen atoms. On the basis of the perturbation theory, there are two contributions to the $t_{NNN}$ hopping integral. One corresponds to a a third-order contribution, scaling as $-\frac{t_{pd}(t_{pd})^2}{\Delta E_{CT}}$, where $t_{pd}$ is the hopping integral between the O 2p and the Cu 3d orbitals, $t_{pp}$ is the hopping integral between the O 2p orbitals and $\Delta E_{CT}$ is the O 2p $\rightarrow$ Cu 3d charge-transfer excitation energy (Scheme IV). Since $t_{pp}$, $t_{pd}$ and $\Delta E_{CT}$ are negative quantities, the third-order contribution results in a positive magnitude. There exists an alternative pathway corresponding to a fourth-order contribution, scaling as $\frac{t_{pd}^4}{\Delta E_{CT}^3}$, with opposite sign. Since the third-order contribution is expected to be larger than the fourth-order one, the resulting sign of $t_{NNN}$ is positive.

A moderate amplitude of the hopping integral between third-neighbors (distance 2R) has been extracted from the calculations on the linear cluster. The extension of this coupling is controlled by through-bond interactions, but in contrast with the plaquette, only fourth-order
process can be written here, smaller in magnitude and with an opposite sign with respect to \( t_{NNN} \).

**SCHEME IV**

\[
\begin{array}{c}
3^{rd\ \text{order}} \\
\begin{array}{c}
\uparrow & \uparrow & \uparrow \\
\rightarrow & \downarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow \\
\end{array}
\end{array}
\]

\[
\begin{array}{c}
4^{th\ \text{order}} \\
\begin{array}{c}
\uparrow & \uparrow & \uparrow & \uparrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow \\
\end{array}
\end{array}
\]

When an additional hole is introduced in the system, the NN hopping integral is unchanged when the hole is placed in a perpendicular position to the bond (\( t_{NN} = -558 \text{ meV} \) in the 2hole-doped plaquette, Scheme Va), but its absolute value is augmented when the hole is placed in a colinear position to the bond (\( t_{NN} = -600 \text{ meV} \) in the 2hole-doped linear cluster, Scheme Vb).

**SCHEME V**

\[
\begin{array}{c}
\begin{array}{c}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow \\
\end{array}
\end{array}
\]

The presence of the extra hole does not influence significantly neither the second-neighbor (\( t_{NNN} = +130 \text{ meV} \) to be compared with +112 meV in absence of this additional hole) nor the third-neighbor (\( t_{NNNN} = -36 \text{ meV} \) versus -47 meV) hopping integrals.

### 3.4 Singlet displacement operator

An additional information coming from these calculations concerns the singlet-displacement operator(Table 3). It is a three-site/two-electron operator, which moves the pair of electron, coupled in a singlet, toward a hole placed in a neighbor position. Thus, a singlet on sites \( a \) and \( b, c \) containing a hole, is displaced to the positions \( b \) and \( c \), the hole being in \( a \) (Scheme VI):

**SCHEME VI**

\[
\begin{array}{c}
\begin{array}{c}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow \\
\rightarrow & \downarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow & \rightarrow \\
\end{array}
\end{array}
\]

8
It can be written as:

\[
    h_{SD}^{abc} [ |\bar{ab} - \bar{ab} \rangle \langle \bar{bc} - \bar{bc} | + |\bar{bc} - \bar{bc} \rangle \langle \bar{ab} - \bar{ab} | \delta(n_a + n_b + n_c, 2)
\]

where \(\delta(n_a + n_b + n_c, 2)\) controls the fact that the three centers bear only two electrons, i.e. that the singlet can only move toward a hole. As in the precedent parameters, the amplitude \(h_{SD}^{abc}\) depends on the relative position of the hole. If the singlet moves to a neighbor bond in the plaquette (i.e., the hole is placed in a perpendicular position to the singlet bond), the value is \(h_{SD}^{abc} = -41\) meV while it goes to \(h_{SD}^{abc} = -80\) meV if the hole is on the same axis than the singlet.

The presence of a second hole in the plaquette does not affect the amplitude of the singlet-displacement \((h_{SD}^{abc} = -37\) meV).

There exists also a small similar operator involving the diagonal of the square \((h_{SD}^{cbd} = 9\) meV):

\[
    h_{SD}^{cbd} [ |\bar{bc} - \bar{bc} \rangle \langle \bar{bd} - \bar{bd} | + |\bar{bd} - \bar{bd} \rangle \langle \bar{bc} - \bar{bc} | \delta(n_b + n_c + n_d, 2)
\]

moving the electrons as shown in Scheme VII. The value of this operator in presence of a second hole is very close to the preceding value: \(h_{SD}^{cbd} = 14\) meV.

SCHEME VII

3.5 Hole-hole repulsions

The absolute value of the hole-hole repulsion is not accessible, but the effective Hamiltonian gives the difference between two situations (Table 4). From the plaquette, we can extract the relative stability of two holes placed in NNN positions with respect to two holes in NN:

\[
    V_{NN} - V_{N_{NNN}} = V_{ab} - V_{ac} = 0.98 eV
\]

This is significantly larger than the values usually accepted for simulations [27, 28, 29]. One should stress on the fact that this value takes into account the dynamical repolarization effects of all the atoms explicitly treated in the calculation, i.e., the screening by the twelve in-plane oxygen atoms linked to the four Cu atoms of the plaquette. It misses the polarization of the rest of the environment. Taking into account the polarization of a large surrounding shell, with a value of the polarizability of the O\(^-\) ion, \(\alpha_O = 1.30\) \(\text{Å}^3\) (obtained from a series of finite-field ab initio calculations on an embedded CuO\(_4\) cluster), in agreement with experimental estimates [40], one diminishes the hole-hole repulsion difference to \(V_{NN} - V_{N_{NNN}} = 0.80\) eV which remains a rather large value. From the linear cluster, it is possible to estimate the energy gain obtained when placing two holes in nNNN positions (distance 2R) instead of adjacent positions (distance R): \(V_{NN} - V_{n_{NNN}} = V_{ab} - V_{ac} = 1.77\) eV, with a final value of \(V_{NN} - V_{n_{NNN}} = 1.47\) eV once the environment polarization effects have been taken into account.

These values of differences between hole-hole repulsions may seem very large and most of the calculations introducing this repulsion in a t-J-V model use to take smaller values \((J <
$V < 4J[27, 28, 29]$ when trying to exhibit hole-pairing phenomenon. The above calculated values are smaller than the corresponding electrostatic quantities calculated in a point charge approximation: $V_{NN} - V_{NNN} = 1.12$ eV and $V_{NN} - V_{NNN} = 1.90$ eV. The delocalization of the holes on the oxygen atoms should result in larger repulsions, especially for $V_{NN}$ since the two holes share an oxygen atom, and our values, which exhibit a significant screening, do not seem unrealistic.

4 Interpretation of the hole dependence of the one bond $J_{NN}$ and $t_{NN}$ parameters

The two preceding sections indicate that the presence of holes in the immediate vicinity of a bond may affect the values of the spin coupling and of the hopping integral on this bond, and that this effect is anisotropic, i.e., does not only depend on the minimal distance of the hole to the atoms of the bond. Hence it seems important to rationalize these effects if possible.

4.1 Rationalization from the two-band model

The hopping integral. The rationalization of this anisotropy is possible in terms of the two-band model. The $t$ hopping integral results from a second order effect (Scheme VIII, where the open circle represents a bridge oxygen atom and closed circles correspond to copper atoms):

\[
\begin{array}{ccc}
\phi_1 & \phi_{CT} & \phi_2 \\
\begin{array}{c}
\text{a} \\
\text{b}
\end{array} & \\
\begin{array}{c}
\text{a} \\
\text{b}
\end{array}
\end{array}
\]

$t$ scaling as

\[
t \sim \frac{t_{pd}^2}{\Delta E_{CT}}
\]

where $\Delta E_{CT}$ is the $2p$ O to $3d$ Cu charge transfer excitation energy. In presence of an additional hole, the energies of the model space determinants, $\phi_1$ and $\phi_2$, and of the intermediate charge transfer state, $\phi_{CT}$, will be modified. The model space determinant energies are no longer degenerate and one shall take their mean energy as the zero-order energy. Let consider now the effect on the bond directed along $x$ of an adjacent hole placed either on the $y$ direction, as occurs in the plaquette, or on the $x$ axis, as in the linear cluster (schemes Va and Vb). In situation (Va) the zero-order mean electrostatic energy with the hole is $\delta E_0 = \frac{\sqrt{2+1}}{\sqrt{2}} = 0.85 \frac{R}{R}$. In the corresponding charge transfer state the mean electrostatic energy with the hole is $\delta E_{CT} = \frac{2}{\sqrt{5}} = 0.89 \frac{R}{R}$, i.e., the excitation energy is increased by a small quantity:

\[
\Delta E_{CT} = \Delta E_{CT} + \delta E_{CT} - \delta E_0 = \Delta E_{CT} + 0.04 \frac{R}{R}
\]

which should diminish slightly the absolute value of the hopping integral. In contrast, for situation (Vb), $\delta E_0 = \frac{3}{4R}$ and $\delta E_{CT} = \frac{2}{3R}$ hence $\Delta E_{CT} = \Delta E_{CT} - 0.08 \frac{R}{R}$ which should increase the absolute value of $t$, in agreement with our calculation.
This analysis is quite rudimentary, it neglects the possible effects of the polarization of the orbitals on the $t_{pd}$ integrals and rests on a crude evaluation of the electrostatic effects on the denominators (holes considered as centered on Cu sites, neglecting their oxygen character), but it seems to agree with the computed trends.

*The magnetic coupling.*

The same kind of analysis may be tempted for the $J_{NN}$ coupling constant, which is now a fourth-order quantity (Scheme IX):

$$J_{NN} \sim \frac{-2t^4_{pd}}{U(\Delta E_{CT})^2}$$

which involves intermediate situations of opposite polarities, but with the same energy: $\Delta E_{CT1} = \Delta E_{CT2} = \Delta E_{CT}$. In the undoped system, $U_1=U_2=U$, which corresponds to the Coulombic repulsion of two electrons placed in the same 3d orbital.

**SCHEME IX**

![Diagram](image)

Adding an external hole will not modify the electrostatic zero-order energy, but will affect the energies of all intermediate states, so that the coupling becomes:

$$\frac{-t^4_{pd}}{\Delta E_{CT1}} \cdot \frac{1}{U_1} \text{ (for the top pathway)} + \frac{-t^4_{pd}}{\Delta E_{CT2}} \cdot \frac{1}{U_2} \text{ (for the bottom one)}.$$  

Notice that while $\Delta E_{CT1} = \Delta E_{CT} + \delta E_{CT1}$ and $\Delta E_{CT2} = \Delta E_{CT} + \delta E_{CT2}$ have no reason to be related, $U_1 = U + \delta U$ and $U_2 = U - \delta U$ whatever the outer charge distribution. The effective coupling is therefore:

$$-t^4_{pd} \left( \frac{1}{(\Delta E_{CT} + \delta E_{CT1})^2} \cdot \frac{1}{U + \delta U} + \frac{1}{(\Delta E_{CT} + \delta E_{CT2})^2} \cdot \frac{1}{U - \delta U} \right)$$

To the first order in $\frac{\delta U}{U}$ and $\frac{\delta E_{CT}}{\Delta E_{CT}}$ developments, one gets:

$$J_{NN} = \frac{-2t^4_{pd}}{U(\Delta E_{CT})^2} \left( 1 - \frac{\delta E_{CT1}}{\Delta E_{CT}} - \frac{\delta E_{CT2}}{\Delta E_{CT}} + \frac{\delta U}{U} - \frac{\delta U}{U} \right) + O(2)$$

The effect of the additional hole(s) will go through their electrostatic interaction in the charge transfer states. For the perpendicular situation (Scheme X) $\delta E_{CT1} = \frac{0.187}{R}$ and $\delta E_{CT2} = \frac{-0.105}{R}$. Hence, $\delta E_{CT1} + \delta E_{CT2} = \frac{0.082}{R}$ and $J_{NN}$ is diminished by the presence of the adjacent hole in
the $y$ direction, as observed in the corresponding ab initio calculations ($\Delta J_{NN}/J_{NN}=-17\%$).

**SCHEME X**

\[ \Delta E_{CT1} + \delta E_{CT1} \quad \Delta E_{CT1} + \delta E_{CT1} \]

\[ \Delta E_{CT2} + \delta E_{CT2} \quad \Delta E_{CT2} + \delta E_{CT2} \]

Oppositely, in the linear situation (Scheme XI) the quantities are: $\delta E_{CT1} = \frac{1}{16}R$ and $\delta E_{CT2} = \frac{1}{16}R$, so $\delta E_{CT1} + \delta E_{CT2} = \frac{1}{32}R$ is a negative quantity, hence the coupling constant should be increased. This is actually observed since $\Delta J_{NN}/J_{NN}=+25\%$. The variation of $J_{NN}$ in the model is of the right sign and its amplitude is larger than for the perpendicular orientation.

**SCHEME XI**

\[ \Delta E_{CT1} + \delta E_{CT1} \quad \Delta E_{CT1} + \delta E_{CT1} \]

\[ \Delta E_{CT2} + \delta E_{CT2} \quad \Delta E_{CT2} + \delta E_{CT2} \]

*The singlet-displacement operator.*

The same kind of rationalization applies to the two-electron/three-centre operator $h_{SD}^{abc}$. In the one-band model this effect scales as $t^2/U'$ (Scheme XII):
where $U' = U - 2V_{ab} + V_{ac}$, $V_{ij}$ being the electrostatic interaction between the charges (with respect to the basic undoped distribution). The denominator will be smaller for the linear configuration than for the perpendicular one since $V_{ac}$ is larger ($1/\sqrt{2}R$ instead of $1/2R$). This may explain the difference between the amplitudes of $h_{S_D}^{abc}$ found in the plaquette and in the linear cluster (Table III). The more realistic two-band model introduces an alternative mechanism, since there exist two paths to go from $ab\bar{c}$ to $\bar{b}c$, cf Scheme XIII:

The second path corresponds to the process appearing in the one-band model, which is not the case for the first one. Explicitly, the excitation energies are:

$$
\Delta E_1 = E_d - E_p - U_p = \Delta E_{CT} - U_d + \frac{2}{R} \tag{20}
$$

$$
\Delta E_2 = 2E_d - 2E_p + U_p - 2U_p - \frac{4}{R} + V_{1,II} = 2\Delta E_{CT} - U_d + V_{1,II} \tag{21}
$$

$$
\Delta E_3 = E_d - E_p - U_p + U_d - \frac{3}{R} + V_{a,II} = \Delta E_{CT} - \frac{1}{R} + V_{a,II} \tag{22}
$$

$$
\Delta E'_1 = \Delta E_3 \tag{23}
$$

$$
\Delta E'_2 = U_d - \frac{2}{R} + V_{ac} \tag{24}
$$

It is likely that $\Delta E'_2 > \Delta E_2$, i.e. that the additional path has a larger contribution. The overall effect is:

$$
\frac{t_{pd}^4}{\Delta E'_1} \left( \frac{1}{\Delta E_1} \cdot \frac{1}{\Delta E_2} + \frac{1}{\Delta E'_1} \cdot \frac{1}{\Delta E'_2} \right) \tag{25}
$$

ie, of the same order of magnitude as $J_{NN}$. Regarding the orientation effect it is clear that the denominators are larger for the perpendicular orientation than for the linear one, due to the hole-hole repulsions $V_{1,II}, V_{1,II}$ and $V_{13}$, and it is expected that $h_{S_D}^{abc}$ will be larger for the linear orientation, as found in the numerical ab initio calculations (-80 meV and -40 meV, respectively).
4.2 Further exploration of the influence of the hole on $J_{NN}$ and $t_{NN}$

In order to evaluate this influence, larger clusters would have to be considered, which is beyond our computational possibilities (the preceding CI expansions frequently reach $10^7$ determinants), and a simpler procedure has to be used. In the present set of calculations, a dinuclear $Cu_2O_7$ clusters have been chosen as before, adding one or two additional point charges on Cu sites of the environment, which become $Cu^{+3}$ centers, in order to grossly mimic the effect of the holes. For first-neighbor holes, this is a rather crude approximation, and its relevance has to be tested by comparison with the previously reported four- and three-center calculations. Actually, for a perpendicular position of the hole $J_{NN}=115$ meV (compared to 104 meV in the plaquette). For a colinear hole $J_{NN}=175$ meV, compared to 156 meV in the linear cluster. Hence the anisotropy of the first-neighbor hole is qualitatively reproduced. As an additional confirmation we have calculated the effect of two holes in the plaquette and we get the same value $J_{NN}=93$ meV as for the 2hole-containing plaquette. Table 5 gives the results for $J_{NN}$ concerning a series of possibilities with one remote hole, two holes in different positions, together with the variation of the electrostatic energy in the intermediate charge transfer states with respect to the non-doped case, expressed in eV. Figure 4a shows the correlation between the calculated $J_{NN}$ value with the variation of the electrostatic energy $\delta E_{CT1} + \delta E_{CT2}$ in the intermediate charge transfer states. The correlation is quite satisfactory and suggests the following law in eV:

$$J_{NN} = 0.131 - 0.053(\delta E_{CT1} + \delta E_{CT2})$$

An analogous fit of the hopping integral dependence on the variation of the electrostatic energy in the intermediate charge transfer state $\delta E_{CT} - \delta E_0$ has been tempted from the values of $t_{NN}$ (Table 5) calculated on binuclear complexes in presence of external hole(s). The correlation is less satisfactory (Figure 4b). The distortions of the active orbitals in presence of these close holes should be non-negligible and should affect the amplitudes of the hopping integral in a rather complex manner. However, it seems simpler to research a linear law rather than to produce and handle a dictionary of operator amplitudes considering exhaustively all possible occurrences. We therefore propose the following fit in eV for the first-neighbor hopping integral:

$$t_{NN} = -0.521 + 0.187(\delta E_{CT} - \delta E_0)$$

5 Discussion and Conclusions

The numerical results obtained here above suggest that the usual t-J or t-J-V model Hamiltonians neglect important physical effects, which should be incorporated into an extended model Hamiltonian. The main deviations from the t-J Hamiltonian are the following:

(i) the inclusion of the second-neighbor hopping, $t_{NNN} \simeq +110$ meV. The third-neighbor interaction $t_{nNNN} \simeq -40$ meV could tentatively be omitted. Recent analysis of angle-resolved photoemission spectroscopy data has shown that both $t_{NNN}$ and $t_{nNN}$ are necessary for understanding the dispersion and line shape of the spectral function in the t-J model [20]. Tohyama et al. [25] have estimated the ratio $t_{NNN}/t_{NN}$ and $t_{nNNN}/t_{NN}$ to be 0.12 and 0.08, respectively, by fitting the tight-binding Fermi surface to the experimental one in the overdoped sample [17] on the assumption that in the overdoped region the Fermi surface of the tight-binding band is the same as that of the t-t'-t"-J model. The values here-proposed are in good agreement with these ratio: $t_{NNN}/t_{NN} = -0.19$ and $t_{nNNN}/t_{NN}=0.08$ but not with the ratio $J/t_{NN}$ proposed by these authors ($J/t_{NNTohyama}=0.4$ vs $J/t_{NN}=0.22$).
(ii) the singlet displacement operator $h_{SD}$ has to be taken into account, at least for the colinear displacement, since $h_{SD} \simeq -80$ meV.

(iii) the hole-hole repulsion appears to be far from negligible. Due to possible screening effects and electrostatic mean cancellations by the Sr ions, it is certainly reasonable to neglect the hole-hole repulsions beyond the third-neighbors. Even if the calculated values $V_{NN} - V_{NNN}=0.8$ eV and $V_{NN} - V_{nNNN}=1.5$ eV were somewhat exaggerated, these interactions certainly play an important role.

(iv) the magnetic coupling and hopping integral between adjacent atoms depend in a stereospecific manner on the existence and position of hole(s) in the immediate vicinity. A simple correlation with the electrostatic energies of the intermediate ligand to metal charge transfer states has been proposed resulting in simple formulas, which should be used in a realistic model Hamiltonian. From the exploratory calculations appearing in Table 5, and for sake of simplicity, it seems sufficient to consider the first neighbors of the bond in the calculation of the electrostatic energy changes $\delta E_{CT1} + \delta E_{CT2}$ and $\delta E_{CT} - \delta E_0$ appearing in formulas (27) and (28), respectively.

One may therefore propose the following extended t-J model Hamiltonian:

$$H = \sum_{<pq>} t(\delta E) \cdot (\alpha^+_p \alpha_q + \alpha^+_q \alpha_p + \text{s.c.}) \delta(n_p + n_q, 1) - J(\delta E) \cdot (S_p \cdot S_q) +
$$

$$+ \sum_{<pr>} t_{NNN} \cdot (\alpha^+_p \alpha_r + \alpha^+_r \alpha_p + \text{s.c.}) \delta(n_p + n_r, 1) - J_{NNN} \cdot (S_p \cdot S_r) +
$$

$$+ \sum_{<pqrs> \text{plaque}} K \cdot [(S_p \cdot S_q)(S_r \cdot S_s) + (S_p \cdot S_s)(S_q \cdot S_r) - (S_p \cdot S_r)(S_q \cdot S_s)] +
$$

$$+ \sum_{<pqr> \text{connected}} h_{SD}^{pq} \cdot (\alpha^+_p \alpha^+_q \alpha_r \alpha_q + \alpha^+_q \alpha^+_q \alpha_r \alpha_q - \alpha^+_p \alpha^+_q \alpha_r \alpha_q - \alpha^+_q \alpha^+_p \alpha_r \alpha_q + \text{s.c.}) \delta(n_p + n_q + n_r, 2) +
$$

$$+ \sum_{pq \leq nNNN} V_{pq} \cdot \delta(n_p, 0) \cdot \delta(n_q, 0)$$

In this Hamiltonian, $t(\delta E)$ and $J(\delta E)$ reflect the dependence of the first-neighbor interactions on the number and position of the adjacent holes, which is controlled by the energy changes in the charge transfer intermediates. The second-neighbor interactions are not influenced by the presence of adjacent holes and the displacement of a singlet takes place toward an adjacent hole, so the positions occupied by the singlet and the hole have to be connected.

The here-proposed modifications with respect to the usual t-J or t-J-V Hamiltonians are important. We would like to point out that some local physical effects evidenced in the present work may have an impact on the spatial ordering of charges and spins and on their dynamics. In a crude static look at this problem one may notice that stripping separation of charges and spins (i) favors the mobility of holes in the charged column, since $t$ and $J$ values become especially larger, (ii) leads to a stronger magnetic coupling in the bonds perpendicular to the stripes (with a trend to form singlets on these bonds). The two last effects would result from the three body corrections on $t$ and $J$ created by the adjacent holes. Finally, (iii) the mobility of the stripes can be enhanced by the second-neighbor hopping integral and by the singlet displacement operator.

We think that our calculations are reliable enough and that their qualitative conclusions and quantitative estimates deserve to be considered in simulations of the collective properties of the lattice, whatever the method used for such a study.
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References
[1] P. E. Sulewski, P.A. Fleury, K.B. Lyons, S-W. Cheong, Z. Fisk Phys. Rev. B 41, 225 (1990).
[2] R.P. Singh, P.A. Fleury, K.B. Lyons, P.C. Sulewski, Phys. Rev. Lett. 62, 2736 (1989).
[3] G. Aeppli, S.M. Hayden, H.A. Mook, Z. Fisk, S-W. Cheong, D. Rytz, J.P. Remeika, G.P. Espinosa, A.S. Cooper Phys. Rev. Lett. 62, 2052 (1989).
[4] Y. Endoh, K. Yamada, R.J. Birgeneau, D.R. Gabbe, H.P. Jenssen, M.A. Kastner, C.J. Peters, P.J. Picone, T.R. Thurston, J.M. Tranquada, G. Shirane, Y. Hidaka, M. Oda, Y. Enomoto, M. Suzuki, T. Murakami Phys. Rev. B 37, 7443 (1988).
[5] S.M. Hayden, G. Aeppli, R. Osborn, A.D. Taylor, T.G. Perring, S.W. Cheong, Z. Fisk, Phys. Rev. Lett. 67, 3622 (1991).
[6] J.B. Parkinson, J. Phys. C 2, 2012 (1969).
[7] C.M. Canali, S.M. Girvin, Phys. Rev. B 45, 7127 (1992).
[8] M. Roger, J.M. Delrieu, Phys. Rev. B 39, 2299 (1989).
[9] E. Gagliano, S. Bacci, Phys. Rev. B 42, 8772 (1990).
[10] E. Dagotto, D. Poilblanc, Phys. Rev. B 42, 7940 (1990).
[11] F. Nori, E. Gagliano, S. Bacci, Phys. Rev. Lett. 68, 240 (1992).
[12] J. Eroles, C.D. Batista, S.B. Bacci, E.R. Gagliano, Phys. Rev. B 59, 1468 (1999).
[13] J. Lorenzana, J. Eroles, S. Sorella, Phys. Rev. Lett. 83, 5122 (1999).
[14] Y. Honda, Y. Kuramoto, T. Watanabe, Phys. Rev. B 47, 11329 (1993).
[15] T. Sakai, Y. Hasegawa, Phys. Rev. B 60, 48 (1999).
[16] J.P. Malrieu, D. Maynau, J. Am. Chem. Soc. 104, 3021 (1982).
[17] D. Maynau, J.P. Malrieu, J. Am. Chem. Soc. 104, 3029 (1982).
[18] A.H. MacDonald, S.M. Girvin, D. Yoshioka, Phys. Rev. B 37, 9753 (1988).
[19] A.H. MacDonald, S.M. Girvin, D. Yoshioka, Phys. Rev. B 41, 2565 (1990).
[20] V.J. Emery, G. Reiter, Phys. Rev. B 38, 4547 (1988).
[21] F.C. Zhang, T.M. Rice, Phys. Rev. B 37, 3759 (1988).
[22] F.C. Zhang, T.M. Rice, Phys. Rev. B 41, 7243 (1990).
[23] S. White, D.J. Scalapino, cond-mat/0006071.
[24] G.B. Martins, J.C.Xavier, C. Gazza, M. Vojta, E. Dagotto, cond-mat/0007196.
[25] T. Tohyama, S. Nagai, Y. Shibata, S. Maekawa, Phys. Rev. Lett. 82, 4910 (1999).
[26] C. Kim, P.J. White, Z.-X. Shen, T. Tohyama, Y. Shibata, S. Maekawa, B.O. Wells, Y. J. Kim, R.J. Birgeneau, M. A. Kastner, Phys. Rev. Lett. 80, 4245 (1998).
[27] C. Gazza, G. B. Martins, J. Riera, E. Dagotto, Phys. Rev. B 59, R709 (1999).
[28] J. Riera, E. Dagotto, Phys. Rev. B 57, 8609 (1998).
[29] J.H. Han, Q.H. Wang, D.H. Lee, cond-mat/0006041.
[30] For a recent review: J. Orenstein, A.J. Millis, Science 288, 468 (2000).
[31] I.P.R. Moreira, F. Illas, C.J. Calzado, J.F. Sanz, J.P. Malrieu, N. Ben Amor, D. Maynau, Phys. Rev. B 59, R6593 (1999).
[32] C.J. Calzado, J.F. Sanz, J.P. Malrieu, F. Illas, Chem. Phys. Lett. 307, 102 (1999).
[33] C.J. Calzado, J.F. Sanz, J.P. Malrieu, J. Chem. Phys. 112, 5158 (2000).
[34] Bloch C. Bloch, Nucl. Phys. 6, 329 (1958).
[35] S.F. Boys, Rev. Mod. Phys. 32, 306 (1960). S.F. Boys in Quantum Theory of Atoms, Molecules and Solid State, edited by P.-O. Lodwin (Academic Press, New York, 1966).
[36] J. des Cloizeaux, Nucl. Phys. 20, 321 (1960).
[37] H.M. Evjen, Phys. Rev. 39, 675 (1932).
[38] R.L. Martin, in Clusters Models for Surface and Bulk Phenomena, edited by G. Pacchioni and P. Bagus (Plenum, New York, 1992); R.L. Martin, P.J. Hay J. Chem. Phys. 98, 8680 (1993); R.L. Martin, Phys. Rev. B 53, 15501 (1996); Phys. Rev. B 54, 9647 (1996).
[39] For instance: M.A. Nygren, L.G.M. Pettersson, Z. Barandiarán, and L. Seijo, J. Chem. Phys. 100, 2010 (1994). M. Pohlchen, V. Staemler, J. Chem. Phys. 97, 2583 (1992).
[40] For metallic atoms, the ab initio relativistic core model potential proposed by Barandiarán (Z. Barandiarán, Jr., J. Chem. Phys. 70, 409 (1992)) has been used, where the Cu valence electrons are described by a (9s6p6d)/[3s3p4d] basis set. For the oxygen atoms, an all electron basis set (10s5p) contracted to [3s2p] is employed (T.H. Dunning, Jr., Phys. Rev. B 53, 2823 (1970); T.H. Dunning, Jr., P.J. Hay in Methods of electronic structure theory, edited by H. F. Schaefer III, Vol. 2 (Plenum Press 1977)).
[41] J. Miralles, O. Castell, R. Caballol, and J.P. Malrieu, Chem. Phys. 172, 33 (1993).
Two different strategies have been used to define the active orbitals, magnetic and ligand-centered orbitals. For undoped systems, where the magnetic orbitals are well represented by the Hartree-Fock eigenvectors, the ligand-centered orbitals can be rationally determined as eigenvectors of the difference of the density matrices, corresponding to the low-lying eigenstates (C.J. Calzado, J.P. Malrieu, J. Cabrero, R. Caballol, J. Phys. Chem. A accepted). For doped clusters, where the role of the oxygen atoms is more important, the active orbitals are redefined by means of an iterative procedure (iterative DDCI, IDDCI). (V.M. García, O. Castell, R. Caballol, and J.P. Malrieu, Chem. Phys. Lett. 238, 222 (1995)). Starting with the previously defined orbitals, one performs the single-excitation CI on the top of the minimal CAS. The diagonalization of the average density matrix for the relevant eigenstates provides revised doubly and partially occupied MOs, i.e. hole-adapted core orbitals and valence orbitals, with an appropriate hybridization of the Cu 3d and O 2p orbitals.

S. Uchida, T. Ido, H. Takagi, T. Arima, Y. Tokura, S. Tajima. Phys. Rev. B. 43, 7942 (1991).

C.J. Calzado, J.P. Malrieu, submitted.

H. Schmidt, Y. Kuramoto, Physica (Amsterdam) 167C, 263 (1990).

R. Kirsch, A. Gérard, and M. Wautelet, J. Phys. C 7, 3633 (1974).

A. Ino, C. Kim, T. Mizokawa, Z. X. Shen, A. Fujimori, M. Takaba, K. Tamasaku, H. Elisaki, S. Uchida, J. Phys. Soc. Jpn. 68, 1496 (1999).

MOLCAS version 4. K. Andersson, M. R. A. Blomberg, M. P. Fülscher, G. Karlström, R. Lindh, P. A. Malmqvist, P. Neogrády, J. Olsen, B. O. Roos, A. J. Sadlej, M. Schütz, L. Seijo, L. Serrano-Andrés, P. E. M. Siegbahn, P. O. Widmark, Lund University, Sweden, 1997.

CASDI program: N. Ben Amor, D. Maynau Chem. Phys. Lett. 286, 211 (1998).
6 Figure captions

Figure 1. Summary of the strategy used to extract effective interactions in La$_{2-x}$Sr$_x$CuO$_4$ systems.

Figure 2. Representation of the clusters employed in the ab initio calculations. (a) the plaquette Cu$_4$O$_{12}$, (b) the linear cluster Cu$_3$O$_{10}$. The first-neighbors of the cluster atoms have been also included. They have been modeled by means of the combination of a pseudopotential and a point charge, to mimic the both the exclusion and the Coulombic effects.

Figure 3. Localized active orbitals for the plaquette: (a) for undoped systems, centered in 3$d_{x^2−y^2}$, with important tails on the four in-plane neighbor oxygen atoms. (b) for hole-doped systems a strong 3$d−2p$ rehybridization takes places, the 2$p$ character increases substantially with respect to the undoped situation.

Figure 4. Linear correlation between the calculated first-neighbor interactions in binuclear clusters and the change of the electrostatic energy in the intermediate charge transfer states (in eV): (a) $J_{NN}$ versus $\Delta E_{CT1} + \Delta E_{CT2}$; (b) $t_{NN}$ versus $\Delta E_{CT} − \Delta E_0$. 
Table 1. Magnetic interactions in undoped and hole-doped clusters (in meV).

|                | $J_{NN}$ | $J_{NNN}$ | $J_{nNNN}$ | $K$ |
|----------------|----------|-----------|------------|-----|
| **Undoped clusters** |          |           |            |     |
| 125$^a$        |          |           |            |     |
| 122            |          |           |            |     |
| 124            | 6.5      |           |            |     |
| **Exp.**       | 128±6$^b$, 134±5$^c$ | ≤ 9$^d$ |           |     |
| **Doped clusters** |          |           |            |     |
| 156            |          |           | -11        |     |
| 104            | 3        |           |            |     |
| 94             | 10       |           |            |     |

a. A value of $J_{NN}$=130 meV has been previously reported [32,33], where polarization functions have been included in the basis set of the bridge oxygen atom. b. Ref. [1,2]. c. Ref. [3,4,5]. d. Ref. [5].
Table 2. Hopping integrals. Dependence on the presence of an additional hole (in meV).

|                  | $t_{NN}$ | $t_{NNN}$ | $t_{nNNN}$ |
|------------------|---------|-----------|------------|
| **1Hole-doped clusters** | ![Diagram](image1) | ![Diagram](image2) | ![Diagram](image3) |
|                  | -555 \(^a\) |           |            |
|                  | ![Diagram](image4) | ![Diagram](image5) | ![Diagram](image6) |
|                  | -558     |           | -47        |
|                  | ![Diagram](image7) | ![Diagram](image8) | ![Diagram](image9) |
|                  | -552     | +112      |            |
| **2Hole-doped clusters** | ![Diagram](image10) | ![Diagram](image11) | ![Diagram](image12) |
|                  | -600     |           | -36        |
|                  | ![Diagram](image13) | ![Diagram](image14) | ![Diagram](image15) |
|                  | -558     | +130      |            |

\(^a\) Ref. [32,33];
Table 3. Singlet-displacement operator (in meV). Effect of the presence of a second hole in the neighborhood of the singlet.

|                  | $h_{SD}^{\perp}$ | $h_{SD}^{\parallel}$ |
|------------------|------------------|-----------------------|
| **1 Hole-doped clusters** | ![Diagram](image1) | ![Diagram](image2) |
|                   | -41              | -80                   |
| **2 Hole-doped clusters** | ![Diagram](image3) | ![Diagram](image4) |
|                   | -37              |                       |
Table 4. Hole-hole repulsions (in eV).

| $V_{NN} - V_{N NN}$ | $V_{NN} - V_{nNN}$ |
|---------------------|---------------------|
|                     | \[ - \]             |
|                     | \[ - \]             |
|                     | \[ - \]             |
| \[ 1.77(1.47) \]    |                     |
| \[ 0.98(0.8) \]     | \[ \]               |

[Diagram showing the distribution of charges or spins with arrows indicating directions.]
Table 5. Magnetic coupling and hopping integral in binuclear clusters with hole(s) in adjacent position(s) and intermediate state energies (all in eV).

|       | Undoped | 1 Hole-doped |
|-------|---------|--------------|
|       | $J$     | $\delta E_{CT1} + \delta E_{CT2}$ | $t$ | $\delta E_{CT} - \delta E_0$ |
| 1     | 0.116   | 0.305        | -0.450 | 0.152 |
| 2     | 0.135   | -0.17        | -0.558 | -0.084 |
| 3     | 0.175   | -0.61        | -0.590 | -0.305 |
| 4     | 0.093   | 0.61         | -0.458 | 0.312 |
| 5     | 0.098   | 0.61         | -0.482 | 0.305 |
| 6     | 0.116   | 0.57         | -0.456 | 0.305 |
| 7     | 0.130   | -0.14        | -0.502 | 0.076 |
| 8     | 0.144   | -0.685       | -0.593 | -0.335 |
| 9     | 0.193   | -1.22        | -0.691 | -0.633 |
| 10    | 0.200   | -0.84        | -0.563 | -0.404 |
Figure 1. Calzado and Malrieu
Figure 2. Calzado and Malrieu
Figure 3. Calzado and Malrieu
Figure 4. Calzado and Malrieu