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Accurate *ab initio* determination of magnetic interactions and hopping integrals in La$_{2-x}$Sr$_x$CuO$_4$ systems

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The nature of magnetic interactions and electron transfer processes in La$_{2-x}$Sr$_x$CuO$_4$ systems are studied, by means of an *ab initio* embedded cluster model approach, using a difference dedicated configuration interaction (DDCI) procedure. For the undoped system, the crucial role played by the ligand to metal charge transfer (LMCT) configurations in the magnetic process makes necessary the use of an enlarged DDCI space, which explicitly takes account of the relaxation of these LMCT configurations. This procedure allows us to approach the experimental magnetic coupling constant value. In hole-doped systems, the value obtained for the electron transfer integral, *t*, is of 0.54–0.57 eV. The extra hole, characterized from the nature and occupation of differential natural orbitals, has a strong *p* character (approximately 50%) and is essentially localized in CuO$_2$ planes. These results are in agreement with the experimental evidence about these kinds of compounds. Neither the value of *t* nor the nature of the extra hole are seriously affected by the optimization of the orbitals used in the CI expansion. This suggests that a *t*–*J* effective Hamiltonian is an adequate model to study the electronic properties of these systems. © *2000 American Institute of Physics.* [S0021-9606(00)30210-0]

I. INTRODUCTION

Although superconductivity phenomena was detected in 1911 by Kamerlingh Onnes,[1] the discovery of the new high-temperature superconducting materials by Bednorz and Müller[2] in 1986 gave a new impetus to the field of superconductivity, stimulating numerous experimental and theoretical works.

The presence of copper oxide planes with a unit cell CuO$_2$ is a common feature of the high critical temperature (Tc) superconductors and it is believed that superconductivity is closely related with processes which take place within these planes. These materials are also characterized by the presence of mixed valency, i.e., the superconductivity is induced by doping with holes or electrons, in such a way that the *formal* copper oxidation state is not two.[3]

Understanding the behavior of these strongly correlated materials requires the use of model Hamiltonians, which explicitly treat the large Coulomb interactions. Mean-field approximations, as local density approximation (LDA) calculations, extremely successful at describing many crystalline solids, are not relevant for such materials. For instance, several LDA calculations have failed to reveal the antiferromagnetic nature of La$_2$CuO$_4$.[4]

Anderson[5] was the first to propose a single *d*-band effective Hamiltonian as an adequate model to analyze the electronic structure of cuprates. However, the controversy was opened when different experiments showed the strong oxygen character of the extra hole in doped cuprates and the absence of evidences for mixed-valent copper atoms.[6] These results have suggested the necessity to introduce the 2*p* oxygen band in the model Hamiltonian. These are the grounds of the three-band model of Emery,[7] which permits one to successfully interpret experimental data, such as x-ray photoemission spectra (XPS) and electron energy loss spectra (EELS) spectra, especially in the high-energy limit.[8] A disadvantage is that three-band Hamiltonians require more parameters than are accessible from experiments.

The *t*–*J* model of Zhang and Rice[9] tries to keep the advantages of both one- and three-band Hubbard models. It consists of a single-band effective Hamiltonian, which implicitly accounts for Cu 3*d* and O 2*p* hybridization, with similar results as a three-band model in the low-energy portion of the spectrum.[10,11] Indeed, Hybertsen *et al.*[12] have shown that the *t*–*J* wave functions have an overlap larger than 90% with the eigenfunctions of a three-band Hamiltonian. The *t*–*J* Hamiltonian only contains two parameters:

$$H = -t \sum_{\langle ij \rangle \sigma} [c_{i\sigma}^{+}(1-n_{i-\sigma})(1-n_{j-\sigma})c_{j\sigma} + \text{h.c.}]$$
$$+ J \sum_{\langle ij \rangle} (S_i S_j - \tfrac{1}{4} n_i n_j), \qquad (1)$$

where *t* refers to the hopping integral between adjacent *i* and *j* centers and *J* is the effective magnetic coupling between

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them. The present article, which develops the content of a recently reported letter,[13] shows that these parameters can be accurately obtained from high level *ab initio* quantum chemical calculations. The approach goes through the consideration of a finite cluster, involving at least two Cu atoms and the neighbor oxygen atoms, properly embedded in the field of the other lattice ions. *Ab initio* CI techniques may be applied to such a finite cluster. First the undoped systems are considered, in which each copper atom bears an unpaired electron, and we determine the corresponding magnetic orbitals by the SCF calculation of the upper multiplet. In order to determine the effective magnetic coupling constant between the two unpaired electrons, the energy difference between the lowest singlet and triplet states must be accurately calculated. The determination of the excitation energies may follow the logic of the so-called difference-dedicated configuration interaction (DDCI),[14] which generates the list of determinants contributing to the second-order of perturbation to the excitation energy. For a system with two-electron in two orbitals (*a* and *b*) in the magnetic limit (weak delocalization), the model space would consist of the two neutral valence-bond determinants, $|a\bar{b}|$ and $|b\bar{a}|$, and the corresponding list (DDCI-2 list) involves determinants presenting up to two inactive orbitals only (i.e., one hole and one particle, or two holes and two particles). Previous applications of that strategy to La$_2$CuO$_4$ system had only recovered a value of the magnetic coupling of -95 meV,[15] while the experimental value is close to -135 meV.[16,17] The present work reexamines the physics of this problem and shows the necessity to enlarge the list of determinants in order to allow the dynamical polarization of the ligand→metal charge transfer configurations, LMCT, to take place. The enlarged CI spaces produce accurate values of the coupling constant (-140 meV). The suggestion has led to a recent calculation of the magnetic coupling in perovskites of Ni and Cu,[18] which happens to be extremely successful.

Then the hole-doped analog (i.e., the La$_{2-x}$Sr$_x$CuO system) is considered. In order to determine the hopping integral *t*, which delocalizes the hole(s) on the lattice, we have considered the same clusters as before (Cu$_2$O$_7$ and Cu$_2$O$_{11}$) but with one electron less, and determined the energy difference between the lowest doublet states of *g* and *u* symmetry, the corresponding energy difference being considered as twice the hopping integral in the *t*−*J* model. The calculation of the energy difference follows the same logic as above, i.e., is based on a difference dedicated CI. The model space is the minimal one (one electron in two active molecular orbitals), and the CI list again includes all determinants contributing to the energy difference at the second order of perturbation.[19] The calculation has been performed first using the molecular orbitals of the triplet state of the undoped cluster, involving holes which are, at the zero-order level, essentially localized on the Cu atoms. The CI expansion shows an important delocalization of the holes on the oxygen atoms (about half Cu and half O), but already provides a reasonable value of the hopping integral (0.54–0.57 eV). Then the active space, i.e., the *g* and *u* orbitals are optimized by determination of approximated natural orbitals. This relaxation actually results in a strong mixing of the 3*d* Cu orbitals with the 2*p* orbitals
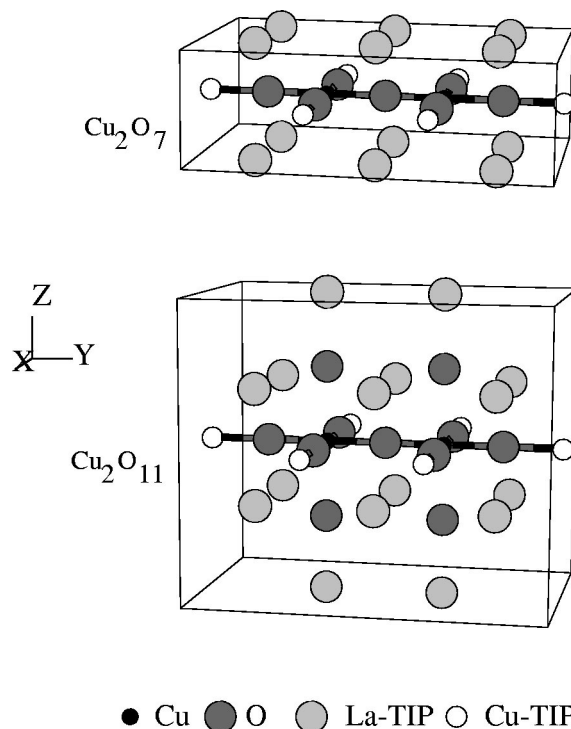

FIG. 1. Two- and three-dimensional clusters used to model the La$_{2-x}$Sr$_x$CuO$_4$ system.

of the surrounding orbitals, which become slightly dominant in the hole. But the resulting value of *t*, calculated from these optimized orbitals, remains the same. This confirms the validity of the Zhang–Rice analysis and the possibility of mapping the local interactions in an effective Hamiltonian of *t*−*J* character, spanned by the $3dx^2-y^2$ Cu orbitals with appropriate delocalization tails, as discussed in the final section.

II. CLUSTER MODELS AND ENVIRONMENT REPRESENTATION: COMPUTATIONAL DETAILS

La$_{2-x}$Sr$_x$CuO$_4$ has a perovskite-like structure and crystallizes in a body-centered tetragonal structure. It consists of CuO$_2$ layers separated by two LaO planes, which form the charge reservoir. Cu atoms are surrounded by corner-sharing oxygen octahedra.[20] In the undoped material, neighboring octahedra along a (110) direction are slightly tilted in opposite directions with respect to the *c*-axis. However, this distortion will not be taken into account to model the crystal, and the undistorted La$_{1.85}$Sr$_{0.15}$CuO$_4$ structure will be considered,[21] expecting that orthorhombic distortions do not have significant effects on the *t* and *J* values. For the determination of these values and the properties of doped and undoped systems, bimetallic clusters were used to model the system, including the nearest-neighbor oxygens, in such a way that they constitute two- and three-dimensional clusters (Cu$_2$O$_7$ and Cu$_2$O$_{11}$, respectively, Fig. 1). The minimum cluster representation, Cu$_2$O, is an inadequate model in both cases, and the corresponding results obtained for *J* and *t* were not included in this work. The clusters are surrounded by an array of point charges, in order to provide an adequate representation of the crystal Madelung potential. The charge values are fixed according to the method of Evjen.[22] In the

cluster–point charge interface, some total ion potentials (TIPs) are included to represent the Cu^{+2} and La^{+3} cations nearest to the cluster atoms. They prevent an artificial polarization of the cluster boundary oxygen electrons towards the positive point charges. Previous theoretical studies of Martin[23] and Wang et al.[24] have shown the importance of including both point charges and effective potentials to correctly describe the occupation of the $3d$ orbitals, the energy of the Cu $4s$ and $4p$ orbitals, and even the Cu–O bond lengths in geometry optimization calculations.

TIPs are represented by large core Hay–Wadt effective core potentials[25] (ECPs) with formal charges (+2 and +3 for Cu and La, respectively). For metallic atoms, the ECPs proposed by Stevens, Basch, and Kraus[26] are used to represent the ten innermost electrons. Cu valence electrons are described using a $(8s8p6d)/[4s4p3d]$ basis set. For the central oxygen atom of the cluster, an all-electron basis set is employed. Preliminary calculations testing the influence of basis function quality have shown the necessity to include polarization functions, at least in the central oxygen atom, in order to obtain the correct relative stabilization of singlet and triplet states in the undoped systems. The basis set finally used for this atom is $(10s5d1d)$ contracted to $[3s2p1d]$.[27] For the rest of the oxygen atoms, which do not contribute directly to the spin and electron transfer mechanisms, a $(6s6p)$ contracted to $[2s2p]$ basis set is used for the valence electrons, while the core $1s$ ones are described by an ECP.[28] We have checked that the polarizability of the oxygen dianions O^{-2} in the lattice, calculated with this $2s2p$ basis is 1.3 Å^3, in good agreement with the experimental data (0.5–3.2 Å^3) (Ref. 29) for oxygen ions in metallic oxides.

As a starting molecular orbital set, the restricted open shell Hartree–Fock (ROHF) wave function of the triplet state for the undoped system is used. In the D_{2h} symmetry point group, this state is of B_{2u} symmetry and can be written as $^3\phi_u = |\mathrm{core} gu|$. The two active orbitals g and u are essentially the symmetric (a_{1g}) and antisymmetric (b_{2u}) combination of the dx^2-y^2 orbitals of each of the two Cu cluster atoms (respectively, 93% and 90% d in character). As is well known, and as previously noticed by Martin[23] in the case of La$_2$CuO$_4$, Hartree–Fock approximation produces an overestimation of the on-site Coulomb repulsion (U_d) and an excessively ionic representation. We will show below that configuration interaction can correct this deficiency and recover the proper metal–ligand covalency.

III. UNDOPED SYSTEMS: MAGNETIC COUPLING CONSTANT DETERMINATION

The La$_2$CuO$_4$ is an antiferromagnetic insulator with an exchange constant experimentally determined by means of neutron scattering [$J = -134 \pm 5$ meV] (Ref. 16) and Raman measurements [$J = -128 \pm 6$ meV].[17] In the undoped system, each Cu^{+2} cation contains an unpaired electron essentially localized in a dx^2-y^2 orbital, according to the tetragonal ligand field. Each Cu^{+2} ion can be considered as a magnetic particle with spin $S = 1/2$. The Heisenberg–Dirac–Van Vleck Hamiltonian[30] is the most used model to deal with the interaction between magnetic particles. For two particles having total spin S, this Hamiltonian has the following expression:

$$\hat{H} = -J\hat{S}_1\hat{S}_2 = -J[\tfrac{1}{2}(\hat{S}_1^+\hat{S}_2^- + \hat{S}_1^-\hat{S}_2^+) + \hat{S}_{z_1}\hat{S}_{z_2}], \quad (2)$$

where J is the magnetic coupling constant, S_i is the total spin operator for center i, S_i^+ and S_i^- are the spin-up and spin-down operators for particle i, and S_{zi} is the operator for the z component of spin for particle i. The eigenvalues of the Heisenberg Hamiltonian are expressed as a function of J, in such a way that the difference between the lowest singlet and triplet eigenvalues gives the value of J:

$$E_S - E_T = J. \quad (3)$$

For antiferromagnetic systems, the singlet is the ground state and J is negative. The problem lies in the accurate determination of the energy values of these two states. For a two-center problem, represented by the localized dx^2-y^2 magnetic orbital, a and b, these two states can be expressed at a zero-order level as

$$\Psi_T^0 = \frac{1}{\sqrt{2}}(|a\bar{b}| - |b\bar{a}|), \quad \Psi_S^0 = \frac{1}{\sqrt{2}}(|a\bar{b}| + |b\bar{a}|). \quad (4)$$

Using delocalized magnetic orbitals $g = (a+b)/\sqrt{2}$ and $u = (a-b)/\sqrt{2}$ these states are

$$\Psi_T^0 = \frac{1}{\sqrt{2}}(|g\bar{u}| - |u\bar{g}|), \quad \Psi_S^0 = \frac{1}{\sqrt{2}}(|g\bar{g}| - |u\bar{u}|). \quad (5)$$

As has been previously established,[14,31] the $\phi_1 = |a\bar{b}|$ and $\phi_2 = |b\bar{a}|$ determinants constitute a model space, over which it is possible to build an effective 2×2 Hamiltonian. At the second order of the quasidegenerate perturbation theory (QDPT), the off-diagonal element H^{eff} of the matrix representation of this Hamiltonian is equal to[14,31]

$$\langle\phi_1|\hat{H}^{\mathrm{eff}(2)}|\phi_2\rangle = \langle\phi_1|\hat{H}|\phi_2\rangle + \sum_{\phi_\alpha \notin S} \frac{\langle\phi_1|\hat{H}|\phi_\alpha\rangle\langle\phi_\alpha|\hat{H}|\phi_2\rangle}{E_1^0 - E_\alpha^0}$$

$$= J/2, \quad (6)$$

where the determinants $|\phi_\alpha\rangle$ interact simultaneously with both of the two model space determinants, and they are the only ones which contribute to the energy differences $E_S - E_T$ at this level. The configuration interaction matrix built over this space is called DDCI-2.[14] DDCI stands for difference dedicated configuration interaction and the "2" indicates that this space includes excitations up to two degrees of freedom, i.e., consists of all the determinants built from the model space as excitations involving two inactive holes or two inactive particles, or one inactive hole and one inactive particle. As previously described,[14,32] the DDCI space is invariant under the unitary transformation of the active orbitals, and it is possible to generate the differential space in the original symmetry of the cluster, that is, using as active orbitals the delocalized ones and Eq. (5) as zero-order description for singlet and triplet states. Both Cu$_2$O$_7$ and Cu$_2$O$_{11}$ belong to the D_{2h} symmetry point group, and singlet and triplet are of A_{1g} and B_{2u} symmetries, respectively. The diagonalization of the DDCI-2 matrices gives the correct

TABLE I. Exchange coupling constant values J, meV, obtained with different DDCI spaces.

| Cluster	Space	n°det(T,S)	Orbital set	J (meV)
	DDCI-2	7680,7687	HF	−96
			IDDCI	−103
Cu$_2$O$_7$	DDCI-2+Single {LMCT}	12 454,12 461	HF	−135
	DDCI-3	411 084,411 091	HF	−138
			IDDCI	−142
	DDCI-2	11 772,11 779	HF	−99
			IDDCI	−111
Cu$_2$O$_{11}$	DDCI-2+Single {LMCT}	22 586,22 593	HF	−131
	DDCI-3	804 828,804 835	HF	−139
			IDDCI	−145

Experimental values: −128±6 meV[a], −134±5 meV[b]

[a]Reference 17.
[b]Reference 16.

sign of the J constant and roughly 80% of its value, as has been previously reported by Casanovas et al.[15] for La$_2$CuO$_4$ system and also computed in this work (Table I). As is shown in this table, the values obtained for the 2D and 3D clusters are practically identical, in agreement with the experimentally established two-dimensional nature of magnetism in this system.[16,17] Since the difference between experimental and theoretical values cannot be associated to collective effects, as Illas et al.[33] have recently demonstrated, this underestimation has to be related to an inadequate treatment of electronic correlation effects.

Actually, the value of the antiferromagnetic interaction is quite large, much larger than in many binuclear systems for which DDCI-2 appeared to be of sufficient accuracy.[31] We thought that the discrepancy in the present case might come from the large coefficient (≈ 0.1, see below) of the ionic valence–bond structure in the singlet state, which should be considered as belonging to the model space, now enlarged to involve beside ϕ_1 and ϕ_2, $\phi_3 = |a\bar{a}|$ and $\phi_4 = |b\bar{b}|$. ϕ_1 and ϕ_2 only differ by one orbital from ϕ_3 and ϕ_4 and in such a case and according to Slater's rules, the difference dedicated CI space has to be enlarged up to a DDCI-3 list, involving two inactive holes and one inactive particle ($2h-1p$) and one inactive hole and two inactive particles ($1h-2p$) configurations. This list increases the size of the CI matrix by a factor of 50–60, but as shown in Table I, gives a theoretical estimate which practically matches the experimental value. In Table II the analyses of the singlet and triplet wave functions are presented, both for DDCI-2 and DDCI-3 spaces. Together with the complete active space (CAS) determinants, other contributions are reported, corresponding to ligand to metal charge transfer configurations, LMCT, where single excitations from sp ligand-like orbitals to the g and u active orbitals take place (schematically represented by $L_g \rightarrow d$ and $L_u \rightarrow d$, where L_g and L_u represent, respectively, symmetric and antisymmetric combinations of s and p ligand basis functions, with minor contributions of the d-metal functions, scheme I).

SCHEME I.
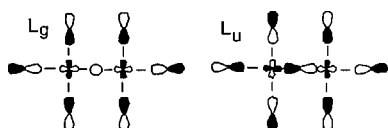
Two main effects can be distinguished when DDCI-3 space is used:

(i) the increase of the coef$|g\bar{g}|$/coef$|u\bar{u}|$ ratio in the singlet state,

(ii) the appearance of contributions external to the CAS, both for singlet and triplet states.

The former corresponds to an increase of the weight of ionic valence–bond determinants, ϕ_3 and ϕ_4 in the singlet description. The CAS projector P_{CAS} is defined as

$$P_{CAS} = \sum_{i \in CAS} |\phi_i\rangle\langle\phi_i|. \tag{7}$$

Operating over $|\Psi_S\rangle$ and $|\Psi_T\rangle$, we obtain

$$P_{CAS}|\Psi_s\rangle = \alpha|g\bar{g}| - \beta|u\bar{u}|,$$
$$P_{CAS}|\Psi_T\rangle = \gamma[|g\bar{u}| - |u\bar{g}|]. \tag{8}$$

Assuming that g and u are composed only by the symmetric and antisymmetric linear combination of the localized dx^2-y^2 orbitals, Eq. (8) result as

$$P_{CAS}|\Psi_s\rangle = \frac{\alpha+\beta}{\sqrt{2}}\left(\frac{|a\bar{b}|+|b\bar{a}|}{\sqrt{2}}\right) + \frac{\alpha-\beta}{\sqrt{2}}\left(\frac{|a\bar{a}|+|b\bar{b}|}{\sqrt{2}}\right), \tag{9}$$

TABLE II. Singlet and triplet wave functions for DDCI-2 and DDCI-3 spaces in the canonical MO basis set. ROHF MO as zero-order description. Only the contributions equal or larger than 0.05 are reported.

Cluster	Conf.	DDCI-2		DDCI-3	
		T	S	T	S
Cu$_2$O$_7$	$g\bar{g}$	⋯	0.7703	⋯	0.7380
	$u\bar{u}$	⋯	−0.6275	⋯	−0.5717
	$g\bar{u}$	−0.7037	⋯	−0.6629	⋯
	$u\bar{g}$	0.7037	⋯	0.6629	⋯
	$L_u \rightarrow d$	⋯	⋯	0.1152	0.1393
	$L_g \rightarrow d$	⋯	⋯	0.0933	0.0721
Cu$_2$O$_{11}$	$g\bar{g}$	⋯	0.7723	⋯	0.7379
	$u\bar{u}$	⋯	−0.6246	⋯	−0.5688
	$g\bar{u}$	−0.7037	⋯	−0.6616	⋯
	$u\bar{g}$	0.7037	⋯	0.6616	⋯
	$L_u \rightarrow d$	⋯	⋯	0.1002	0.1217
	$L_g \rightarrow d$	⋯	⋯	0.0862	0.0660

TABLE III. Valence–bond projections of singlet and triplet wave functions. ROHF MO as zero-order description.

Cluster	Coef.	DDCI-2	DDCI-3	DDCI-2+single {LMCT}
Cu_2O_7	$\sqrt{2}\gamma$	0.995	0.938	0.986
	$(\alpha+\beta)/\sqrt{2}$	0.988	0.926	0.975
	$(\alpha-\beta)/\sqrt{2}$	0.101	0.117	0.119
Cu_2O_{11}	$\sqrt{2}\gamma$	0.995	0.935	0.986
	$(\alpha+\beta)/\sqrt{2}$	0.987	0.924	0.975
	$(\alpha-\beta)/\sqrt{2}$	0.104	0.119	0.120

$$P_{CAS}|\Psi_T\rangle = \sqrt{2}\,\gamma\left(\frac{|a\bar{b}|-|b\bar{a}|}{\sqrt{2}}\right).$$

The values of the coefficients $(\alpha+\beta)/\sqrt{2}$ and $(\alpha-\beta)/\sqrt{2}$, which concern, respectively, the neutral and ionic valence–bond components, and $\sqrt{2}\gamma$ are presented in Table III. As is easy to check, the neutral/ionic ratio in the singlet state diminishes when the DDCI-3 space is used. The question now is why the effect of the ionic valence–bond singlet is enhanced when the DDCI-3 space is used.

The second effect is the appearance of contributions associated to charge transfer processes from orbitals centered in sp combinations of oxygen basis functions to orbitals $3d$ Cu in character. Actually, Van Oosten et al.[34] had obtained quite accurate results for exchange coupling in La_2CuO_4 system (-120 meV) from a low-dimensional nonorthogonal configuration interaction (NOCI) calculation. The method includes, in addition to the determinants ϕ_1, ϕ_2, ϕ_3, and ϕ_4, each of these with a specifically polarized core, the ligand→metal charge transfer determinants, involving the orbitals of the bridging ligand:

$$\phi_5 = \ldots Cu^+(\uparrow\downarrow) - L^+(\uparrow) - Cu^{+2}(\downarrow)..,$$

$$\phi_6 = \ldots Cu^+(\uparrow\downarrow) - L^+(\downarrow) - Cu^{+2}(\uparrow)..,$$

where L^+ is an O^- ion (L=$O^=$). These determinants appear in the DDCI-2 list as one-hole states. Their role is crucial to facilitate the Anderson mechanism. This mechanism is a second-order effect in through-space interactions (scheme II, M=Cu^{+2}),

SCHEME II.
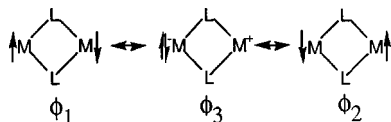
with the exchange coupling J proportional to $-(t^2/U)$, where U is the excitation energy from ϕ_1 to ϕ_3 and t is the hopping integral between the two magnetic orbitals, but it becomes a fourth-order effect when the ligand is on the M–M axis, according to the following process (scheme III, M=Cu^{+2}),

SCHEME III.
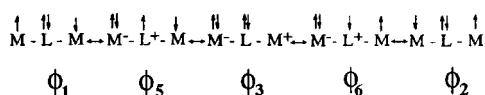
which involves ligand to metal hopping integrals (t_{LM}) and gives a contribution to the exchange proportional to $-(t_{LM})^4/(U')^2U$, where U' and U are the excitation energies from ϕ_1 to ϕ_5 and ϕ_1 to ϕ_3, respectively. In this scheme, the coefficients of the charge-transfer states and of the ionic forms, ϕ_3, are proportional to t_{LM}/U' and $(t_{LM})^2/UU'$, respectively.

The process will be underestimated if one does not introduce the specific dynamic repolarization occurring on the LMCT configurations. These repolarization effects are brought by the single excitations on the top of the determinants ϕ_5, ϕ_6..., i.e., by $2h-1p$ determinants which do not belong to the DDCI-2 list but to the DDCI-3 one. This explains why the LMCT determinants carry significant weights in the wave function descriptions only when the DDCI list is enlarged. The interaction of these determinants with their single excitations, single {LMCT}, produces an important lowering of the effective U' energies of the LMCT states and larger contributions to the singlet and triplet wave functions. It is worth while to notice that LMCT determinants are also single excitations with respect to the ionic ϕ_3 and ϕ_4 configurations, in such a way that the relaxation of the LMCT states produces a stabilization of the ionic valence bond configuration and an increase on its weight on the singlet description. Reducing the effective energy U', the coefficients of the LMCT forms and of the ionic determinants, ϕ_3, increase (respectively, $L_g \rightarrow d$ and $L_u \rightarrow d$ in Table II, and $(\alpha-\beta)/\sqrt{2}$ in Table III). The change of $(\alpha-\beta)/\sqrt{2} = (t_{LM})^2/UU'$ by 20% can be related to the change by 40% of the antiferromagnetic coupling, $J \sim (t_{LM})^4/U(U')^2 = (\alpha-\beta)^2/2U$.

From a practical point of view, it is important to notice that these singly excited {LMCT} determinants are not numerous, since one of the inactive holes is the L_g or L_u orbital of the ligands. The DDCI-2+single{LMCT} spaces are 40–50-fold smaller than DDCI-3 spaces but, as is shown in Table I, the experimental value of J is also recovered.

With regard to the nature of the molecular orbitals L_g and L_u, Fig. 2 represents the ROHF electronic density maps of g and u active orbitals and L_g and L_u orbitals for the Cu_2O_7 cluster. As can be seen in this figure, L_g and L_u correspond to the bonding combinations of the Cu dx^2-y^2 and sp oxygen orbitals (scheme I), whereas g and u are the antibonding combinations, with a strong d character. The electronic distribution of the two orbital pairs (g and L_g, u and L_u) are quite similar, making possible an optimal ligand–metal charge transfer in both these cases.

A. Dependence of the J value on the molecular orbital choice

In order to overcome the possible dependence of our results on the starting molecular orbital set, we have obtained the $S-T$ average natural orbitals by means of an iterative procedure, proposed by Garcia et al.[35] and implemented in the DDCI scheme. An average density matrix for the singlet and triplet states is built: $\bar{R}=(R_S+R_T)/2$. After the diagonalization of this matrix, a natural orbital set is obtained. With this new set, the DDCI procedure is repeated (iterative dDDCI, IDDCI) until both the orbitals and the $S-T$ energy
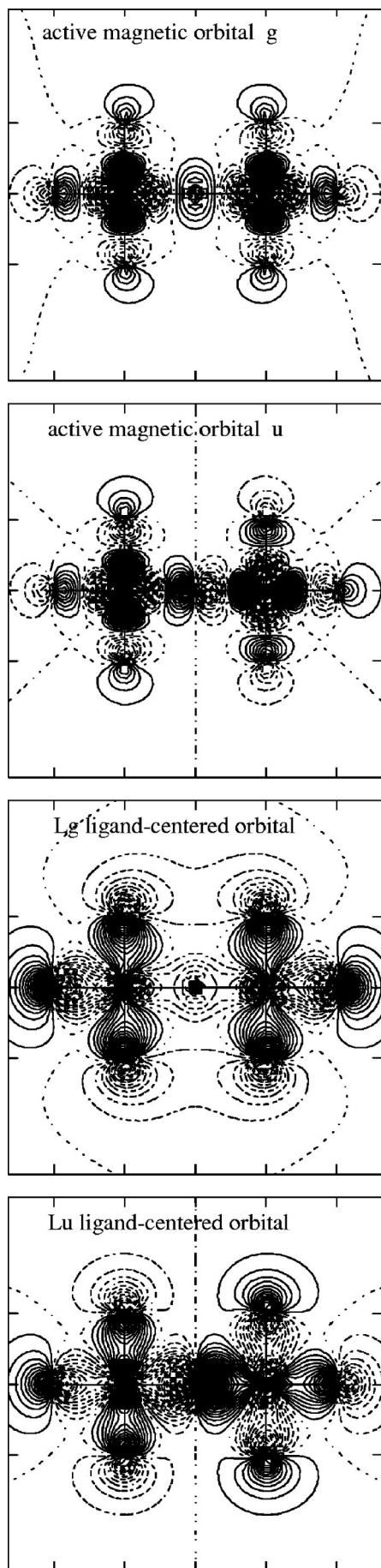
FIG. 2. Isodensity curves of magnetic g and u orbitals, and the most participating ligand orbital L$_g$ and L$_u$ for Cu$_2$O$_7$ cluster, plotted on the xy-plane.

ifference are self-consistent. Beside their interest for the determination of optimal molecular orbitals in the energy difference calculation, the density matrices and the natural orbitals are crucial instruments in the analysis of the wave function and they will be used for that purpose all through this work. Actually, the natural orbitals and occupation numbers make possible some concentration of information regarding wave functions developed on thousands of N-electron configurations.

The values of the exchange coupling obtained with the converged average natural orbital set is presented in Table I, for DDCI-2 and DDCI-3 spaces. The J values obtained with the canonical and natural orbital sets are similar and only a slight increase of the absolute value is observed when the natural orbital set is used. This effect is larger in the DDCI-2 space than in the DDCI-3. The IDDCI procedure only produces minor modifications on the magnetic orbitals (g and u have 92% and 89% of d character). Figures 3(a) and 3(b) correspond, respectively, to the triplet ROHF and natural IDDCI localized active orbital for Cu$_2$O$_7$, obtained from a $\pi/4$ rotation of the symmetry-adapted g and u orbitals. The minor change in the slope of these orbitals can be seen as a major participation of the p oxygen orbitals in the natural orbitals.

IV. DOPED SYSTEMS: NATURE OF THE HOLES

In La$_2$CuO$_4$, the substitution of La^{+3} ion by Sr^{+2} produces a defect of electrons in the CuO$_2$ planes, i.e., introduces holes in the system. When the Sr concentration (x) increases, different phase transitions take place. For $x < 0.05$ the system is an antiferromagnetic insulator, while for $0.05 < x < 0.3$ it becomes a superconductor. The maximum value of the critical temperature ($Tc = 40$ K) is observed at the optimal doping $x = 0.15$. Metallic behavior is observed for Sr doping larger than 0.3.[36]

The nature and distribution of carriers determine the superconductivity. This has motived numerous studies, experimental as well as theoretical. Different experimental evidence has shown that carriers in La$_{2-x}$Sr$_x$CuO$_4$ have a strong $2p$ oxygen character. Both XANES (x-ray absorption near edge structure)[6] and x-ray photoemission spectra[6] have indicated that the predominant Cu atoms configuration in doped copper oxides is $3d$,[9] whatever x. There is no evidence of mixed valency in these systems. Also the $1s$ oxygen EELS spectra suggest that holes are essentially placed in the $2p$ oxygen band.[6] Several theoretical works, as the intermediate neglect of differential overlap (INDO) results of Wang et al.[24] or the ab initio SCF/CI calculations reported by Martin[23] show that the additional hole has around 50% p character. In vacuum the ionization potential of Cu^{+2} ions is much larger than that of the O^{-2} anions. In infinite ionic lattices, however, this picture is no longer valid since the electrostatic potential pushes the Cu d band above the O p band, in a way that the highest partially occupied orbitals (the magnetic active orbitals in undoped systems) are essentially Cu $dx^2 - y^2$ in character. This delocalized monoelectronic picture would play in favor of a participation of the d shell in the ionization. Our work will examine the relative O/Cu composition of the holes.
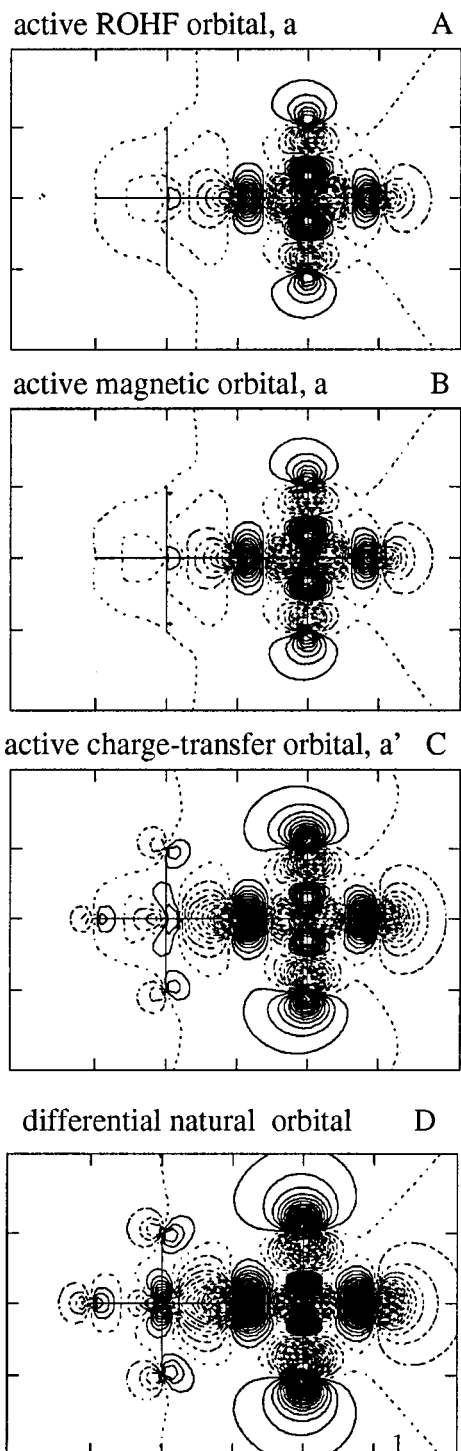
active ROHF orbital, a   A

active magnetic orbital, a   B

active charge-transfer orbital, a'   C

differential natural orbital   D

FIG. 3. Isodensity curves of active localized orbitals in Cu_2O_7 cluster, plotted on the xy-plane: (a) ROHF orbital, (b) natural IDDCI magnetic orbital, (c) natural IDDCI doped-system orbital, and (d) localized differential natural orbital.

As mentioned above, it is necessary to include properly the electronic correlation in order to adequately describe the ground state of the doped system. This will be the object of the present section.

A. The two state model

Let us consider one copper ion surrounded by four oxygen atoms. According to the original ideas of Zhang and

Rice,[9] a hole at the oxygen can be in a symmetric or antisymmetric state with respect to the central hole at the Cu ion. Holes in oxygen and Cu atoms will be coupled, resulting in a spin singlet or triplet state. These authors demonstrated that the spin singlet state has the lower energy, and assumed that it is possible to work in this singlet subspace without changing the physics of the problem. In this context, the movement of the hole is equivalent to the displacement of a Cu 1/2 spin and for a two-center cluster, the process can be summarized in Scheme IV,

SCHEME IV.

$$Cu^{+2}—O—Cu^{+3} \longleftrightarrow Cu^{+3}—O—Cu^{+2}$$
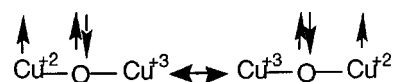
which represents two degenerated situations, where an unpaired electron (or a hole) oscillates between two equivalent positions. They can be expressed by two localized states:

$$\phi_a^{0+} = |\text{core}..a'|, \quad \phi_b^{0+} = |\text{core}..b'|. \tag{10}$$

Their symmetry-adapted linear combinations are

$$\Psi_g^{0+} = \frac{1}{\sqrt{2}} (\phi_a^{0+} + \phi_b^{0+}) = |\text{core}..g'|;$$

$$\Psi_u^{0+} = \frac{1}{\sqrt{2}} (\phi_a^{0+} - \phi_b^{0+}) = |\text{core}..u'|, \tag{11}$$

where the orbitals a' and b' (respectively, g' and u') should resemble, to some extent, those of the magnetic problem. This pair of determinants defines a new model space. As in the magnetic problem, at the second order of the quasidegenerate perturbation theory, the off-diagonal element of the matrix representation of the effective Hamiltonian built over this space is related to the electronic coupling constant, t:[19]

$$t = H_{ab}^{\text{eff}} = H_{ab}^{(0)} + \sum_\alpha \frac{\langle \phi_a^{0+} | \hat{H} | \phi_\alpha \rangle \langle \phi_\alpha | \hat{H} | \phi_b^{0+} \rangle}{E_a^0 - E_\alpha^0}. \tag{12}$$

Since ϕ_a^{0+} and ϕ_b^{0+} differ by only one spin-orbital, it is easy to show that the set of $|\phi_\alpha\rangle$ determinants include all the excitations up to three degrees of freedom (DDCI-3 list: single and double excitations except those which involve two inactive holes and two inactive particles).

As in the magnetic problem, the variational treatment of the DDCI list introduces higher order corrections and avoids the inaccuracies due to the smallness of the denominators in the second-order expressions. Using symmetry-adapted configurations, t is given by

$$t = \frac{E_g - E_u}{2}, \tag{13}$$

where E_g and E_u are the eigenvalues of the Ψ_g^+ and Ψ_u^+ states, which in the D_{2h} point group are of A_{1g} and B_{2u} symmetry, respectively. Once the DDCI list is built, the diagonalization of the difference dedicated CI matrix gives us the variational estimate of the hopping integral.

In Table IV the t values obtained for 2D and 3D clusters are collected. The size of the cluster does not affect the value of the transfer integral. This result suggests the two-

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TABLE IV. Absolute values of the hopping integral, obtained with DDCI-3 spaces and different MO sets.

Cluster	Triplet ROHF (eV)	IDDCI (eV)	$n°\det(g,u)$
Cu$_2$O$_7$	0.553	0.575	255520, 255432
Cu$_2$O$_{11}$	0.532	0.544	526767, 526639

dimensional character of the carriers in the doped copper oxides. The value of t oscillates between 0.53–0.55 eV in good agreement with the usually accepted value of 0.5 eV (Ref. 37) (for instance, 0.57–0.59 eV by Wang et al.,[24] 0.65 eV by Martin,[23] and 0.4 eV by Hybertsen et al.).[12]

In the basis of the canonical ROHF molecular orbitals, the projections in the CAS model space of the Ψ_g^+ and Ψ_u^+ DDCI-3 wave functions are 0.77 and 0.76, respectively. This means that only the 50% of the wave functions can be represented by the extra hole localized in one of the Cu dx^2-y^2 orbitals. The rest of the contributions comes from different O $2p \rightarrow$ Cu$3d$ charge-transfer excitations. An appealing point is that the most participating O $2p$ centered orbitals correspond to the same L_g and L_u orbitals which play an important role in the magnetic problem. There are three kinds of determinants participating in the ground state wave function description:

(i)   the model space determinants, M–L–M$^+$, M$^+$–L–M, where there is an extra hole in an active localized orbital:

$$\phi_a^{0+} = \text{Cu}^{+2}(\uparrow) - \text{L}(\uparrow\downarrow) - \text{Cu}^{+3}(.),$$
$$\phi_b^{0+} = \text{Cu}^{+3}(.) - \text{L}(\uparrow\downarrow) - \text{Cu}^{+2}(\uparrow);$$

(ii)   neutral charge-transfer excitations, M–L$^+$–M, with an extra hole in a ligand-centered orbital:

$$\phi_1^+ = \text{Cu}^{+2}(\uparrow) - \text{L}^+(\downarrow) - \text{Cu}^{+2}(\uparrow),$$
$$\phi_2^+ = \text{Cu}^{+2}(\uparrow) - \text{L}^+(\uparrow) - \text{Cu}^{+2}(\downarrow);$$

(iii)   ionic charge-transfer excitations, M$^+$–L$^+$–M$^-$, M$^-$–L$^+$–M$^+$, where the extra hole is in an oxygen orbital, and a metal–metal $d_A \rightarrow d_B$ transfer takes place simultaneously:

$$\phi_3^+ = \text{Cu}^{+3}(.) - \text{L}^+(\uparrow) - \text{Cu}^{+1}(\uparrow\downarrow),$$
$$\phi_4^+ = \text{Cu}^{+1}(\uparrow\downarrow) - \text{L}^+(\uparrow) - \text{Cu}^{+3}(.).$$

The first class (the model space) introduces the extra hole in a $3d$ orbital. But this represents only 50% of the doped ground state description. Charge transfer excitations put a hole in orbitals with strong character in $2p$ oxygen, increasing the electronic density in $3dx^2-y^2$, and therefore diminishing the $3d$ nature of the hole (screening the two holes in $3d$ orbitals). This effect has received the name of *electronic polaron*,[23] in the sense that an extra hole in a copper site produces not a nuclear distortion but an electronic distortion of the neighbor oxygen, and a strong $p-d$ rehybridization occurs (scheme V). In fact, the p character of active orbitals has increased after the hole doping. For instance, in the doped Cu$_2$O$_7$ cluster the active g and u orbitals have a 83% and 76% of d character, respectively, to be compared with

the state-averaged IDDCI natural orbitals obtained for the undoped system (86% and 87%). For the Cu$_2$O$_{11}$ cluster, a similar effect is observed in Scheme V.

SCHEME V.

Cu^{+3} L   Cu^{+2}
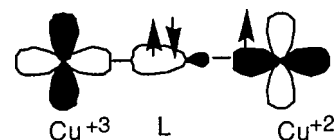
B. Dependence of the *t* value on the molecular orbital choice

It should be noted here that all the t calculations so far have been carried out using as active orbitals the magnetic orbitals determined for J. This is in agreement with the ideas behind the $t-J$ model, where a unique set of active orbitals is used. However, there has been a lot of controversy about the nature of the hole. Actually, there exists unanimity about its predominant oxygen character. This means that hole-adapted orbitals, a' and b', should be different than the original a and b orbitals. Moreover, the possible dependence of the DDCI results on the initial orbitals has been previously mentioned. To overcome these difficulties, some DDCI-3 calculations have been performed iterating the natural orbitals for the doped problem, using the iterative difference dedicated CI (IDDCI) method. This procedure does not change the value of t, as can be seen in Table IV. The most important effect of these hole adapted orbitals is the increase of the weight of the CAS determinants in the Ψ_g^+ and Ψ_u^+ description (the coefficients of the projections become 0.91–0.90), i.e., the concentration of the wave functions in an improved model space. The iterated g and u orbitals incorporate by themselves the $p-d$ hybridization, having a 71% and 66% d character, respectively, for the doped ground state of Cu$_2$O$_7$, as can be seen comparing the active magnetic and charge-transfer orbitals, a and a' [Figs. 3(b) and 3(c)]. This explains the larger contributions of the CAS determinants in the wave function description, increasing the validity of the two state model.

C. Nature of the hole

The determination of the hole nature in doped systems is not an easy task. Two different electronic arrangements, neutral (undoped) and ionic (doped) ones, based on different molecular orbital basis sets, need to be compared. The ''hole language,'' usual in this field, is not straightforward since it implicitly refers to an ideal closed shell description with d^{10} occupancy of Cu atoms. Moreover, the charge transfer processes, partially responsible for these covalent effects, are unlike in the neutral and ionic systems.

A new strategy to overcome these difficulties has been developed. It consists of building a differential density matrix, in the common atomic basis set, which explicitly describes the hole doping process. It is a general procedure, that could be useful to study other phenomena, where states related by hole doping are involved. The atomic-based density matrix for the neutral and ionic systems are built sepa-

rately. In our case, for the undoped system, an averaged singlet–triplet atomic density matrix (R_J) is stored after the IDDCI approach. In the doped system, the averaged doublet$_g$–doublet$_u$ atomic density matrix (R_t) is determined. Then, the differential density matrix, $R_J - R_t$, is obtained and diagonalized. The eigenvalues are between 1 and -1, and the addition of all of them has to be equal to 1. The eigenvectors with larger eigenvalues are the most participating in the excitation process. In Cu_2O_7 cluster, the ionization phenomenon can be seen as concerning essentially two orbitals of g and u character, with occupation numbers close to 0.5 (respectively, $n_g = 0.65$ and $n_u = 0.57$). These two orbitals have similar contributions of d orbitals and the outer oxygen p functions, differing essentially on the bridging oxygen. Their overall shape is quite similar to that of the natural magnetic orbitals of the undoped systems, but with a larger amplitude on oxygen atoms. It is possible to combine the g and u differential natural orbitals to obtain a localized differential natural orbital, which is pictured in Fig. 3(d), where the increased delocalization of the hole on the oxygen atoms appears clearly by comparison with Fig. 3(b). The p:d character ratio of this localized orbital is approximately 1:1, which permits us to conclude that the hole has around 50% p character, in agreement with experimental results,[3,6,7] and without the intrinsic arbitrariness of usual population analysis.

D. Effects of the inclusion of p orbitals in the active space

Since the extra hole in doped system has an important oxygen character, and although the $p-d$ hybridization resulting from the configuration interactions concentrates the description of the ground doped state on the model space, it seems adequate to check whether this description depends on the introduction in the model space of orbitals centered in oxygen atoms.

With this purpose, an active space CAS(3/3) is used. This space is composed of three electrons placed in the active g and u and in an oxygen-centered orbital with symmetry u, L_u. This one has a significant weight of the bridging oxygen and, as mentioned above, undergoes the largest deviation of the double occupation when the system is doped with an extra hole. After IDDCI the t value for the Cu_2O_7 cluster is 0.595 eV. The coefficients of the projection of the ground state on the model space is 0.898 [with respect to 0.913 obtained with the CAS(2/1)]. Neither the t value nor the description of the wave function nor the hole nature are seriously affected by the inclusion of the p orbital in the model space.

V. CONCLUSIONS

This work illustrates the ability of *ab initio* quantum chemistry to provide accurate evaluations of the elementary local interactions which govern the collective properties of spin or highly-correlated electron populations on periodic lattices. The amplitude of the local intersite magnetic coupling, electron transfer hopping integral, on-site bielectronic repulsions, and so on, which are the building stones of the

model Hamiltonians used to understand the heavy-fermion behavior, are not always accessible from experiment, and it is a major goal for quantum chemistry to provide such crucial information. Quantum chemistry may also predict the dependence of such interactions on the nuclear frame distortions, which may play a crucial role, for instance, in spin-Peierls phenomena.

The present work, as well as a recent systematic study of magnetic coupling in perovskites,[18] performed using the same methodology, show that the weak magnetic interactions are correctly predicted when:

(i)   the effect of embedding is appropriately treated,
(ii)   the magnetic orbitals are properly determined,
(iii)   a rationally defined difference dedicated configuration interaction is used.

This CI remains practicable for fragments as large as Cu_2O_{11} (involving 124 electrons in 163 molecular orbitals). In previous studies concerning binuclear complexes, where the ligands L between the magnetic centers, X and X', are quite far from the XX'-axis, accurate results had been obtained from a limited CI (of DDCI-2 type) which is no longer sufficient for the $X-L-X'$ architectures with collinear bridging ligands. Going to larger CI (of DDCI-3 type) gives an accurate value of the coupling constant. The study of the wave functions shows that the additional crucial physical effect is the dynamic polarization of the ligand to metal charge transfer states. This dynamic polarization cooperates to the indirect Anderson mechanism which stabilizes the singlet state (i.e., the antiferromagnetism). Adding the single excitations in addition to the ligand to metal charge transfer states to the DDCI-2 list is sufficient to obtain the correct value of the magnetic coupling. These results are compatible with those obtained from a nonorthogonal CI,[34] which consisted of a very limited CI between a few valence–bond configurations, including the ligand→metal charge transfer states, each of them using specifically relaxed orbitals. The use of larger CI spaces with a unique set of orthogonal orbitals is a rational procedure since it avoids the nonorthogonality ‘‘nightmare.’’ The (eventually iterative) determination of the natural orbitals resulting from the long CI expansions of the eigenstates make possible an unbiased analysis of the magnetic orbitals and of the respective participation of $3d$ Cu and $2p$ O orbitals.

The hole doped system has been studied in order to determine a value of the t-hopping integral, responsible for the hole delocalization, and to study the nature of the hole (on copper or on oxygen atoms). The differential natural orbitals, specially adapted to describe the hole-doping process, show that the hole is half and half $3d$ Cu and $2p$ O in nature (with some $2s$ oxygen component, too). Localized orbitals a' and b' for the doped system are less localized on the Cu atoms than the localized a and b orbitals for undoped magnetic systems, but their general shapes are similar and the overlap between a' and a is quite large. Hence the mapping of the doped electronic system into a $t-J$ model Hamiltonian spanned by atomic orbitals of essentially $3dx^2-y^2$ character seems reasonable. Actually, we have shown that the calculation of t from a CI based on a model space defined by the

two magnetic orbitals of the undoped problem gives the same value of t as obtained when starting from the iterative natural orbitals of the doped system. However additional work would be welcome in order to assess:

(i)   the transferability of the so-obtained hopping integral t (the transferability of magnetic coupling J having been verified by previous work),[33]

(ii)   the importance of the effective transfer between second-neighbors, which is a second-order effect, scaling as t^2/U, as shown by the first developments of $t-J$ effective Hamiltonians,[38]

(iii)   the importance of the hole–hole repulsion. Even the order of magnitude is not known, and this repulsion may play a crucial role in the hole pairing supposed to be responsible for the superconductivity.

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