

Effective t - J model Hamiltonian parameters of monolayered cuprate superconductors from *ab initio* electronic structure calculations

David Muñoz, Ibérico de P. R. Moreira, and Francesc Illas

Department de Química Física i Centre especial de Recerca en Química Teòrica, Universitat de Barcelona i Parc Científic de Barcelona, C/Martí i Franquès 1, E-08028 Barcelona, Spain

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The magnetic coupling constant of selected cuprate superconductor parent compounds has been determined by means of embedded cluster model and periodic calculations carried out at the same level of theory. The agreement between both approaches validates the cluster model. This model is subsequently employed in state-of-the-art configuration interaction calculations aimed to obtain accurate values of the magnetic coupling constant and hopping integral for a series of superconducting cuprates. Likewise, a systematic study of the performance of different *ab initio* explicitly correlated wave function methods and of several density functional approaches is presented. The accurate determination of the parameters of the t - J Hamiltonian has several consequences. First, it suggests that the appearance of high- T_c superconductivity in existing monolayered cuprates occurs with J/t in the 0.20–0.35 regime. Second, $J/t=0.20$ is predicted to be the threshold for the existence of superconductivity and, third, a simple and accurate relationship between the critical temperatures at optimum doping and these parameters is found. However, this quantitative electronic structure versus T_c relationship is only found when both J and t are obtained at the most accurate level of theory.

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I. INTRODUCTION

The discovery of superconductivity at 42 K in the doped La_2CuO_4 ceramic compound¹ has dramatically changed the picture of this important and fascinating phenomenon first encountered in 1911 in some pure metals² and, later, in many alloys. In fact, the elegant theory of superconductivity developed by Bardeen, Cooper, and Schrieffer³ (BCS) does not apply to doped La_2CuO_4 .⁴ In addition, La_2CuO_4 was just the first of a new family of superconductors generally termed as high-critical-temperature superconducting cuprates (HTSC's), because the phase transition to superconductivity appears at critical temperatures, T_c , much higher than those of metals and alloys.⁴ For a few years the maximum value of T_c has been increasing to reach 133 K for the Hg-based cuprates such as doped $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$.⁵ It must be noticed that this value of T_c corresponds to measurements carried out at ambient pressure; T_c reaches a value of 164 K under 31 GPa.^{6,7} Unfortunately, no new cuprates with higher T_c values have been yet synthesized and unraveling the mechanisms that govern high- T_c superconductivity appears to be necessary to design new families of HTSC's with even higher T_c values.^{4,8,9} Other superconducting materials without the typical copper-oxide planes have also been described in the past ten years. We mention $T_c=33$ K in electron-doped $\text{Cs}_x\text{Rb}_y\text{C}_{60}$,¹⁰ $T_c=30$ K in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$,¹¹ and $T_c=39$ K in the recently discovered MgB_2 .¹² However, these materials exhibit maximum T_c values substantially lower than those encountered in a large variety of HTSC's and, more importantly, some of them seem to behave according to the BCS theory.^{13,14}

All known HTSC's exhibit a layered crystal structure with well-defined Cu-O planes, strong magnetic interactions, and a rich phase diagram that depends on doping and on the temperature; a certain degree of doping is necessary to trig-

ger the appearance of the superconducting phase. Nevertheless, doping leads to a rather small change in the structure and other related properties of the parent, undoped, compound, and hence superconductor parent compounds have been used to understand the nature of the superconducting phase. The failure of the phonon-mediated BCS pairing mechanism to account for the superconductivity of these materials prompted a parallel research effort from the theoretical side. Many theoretical studies have been reported that aimed to disclose the fundamental microscopic interactions governing the pairing mechanism in high- T_c superconductors. Attempts to rationalize the electronic structure of HTSC's by means of the well-known local density approximation (LDA) of density functional theory (DFT) were unsuccessful because the LDA incorrectly describes these compounds as metals.¹⁵ To remedy this deficiency of the LDA, *ad hoc* corrections were developed; LDA+SIC (Refs. 16–18) attempts to correct the self-interaction repulsion (SIC) intrinsic to the LDA, whereas LDA+ U (Refs. 19–21) introduces explicitly the on-site Coulomb repulsion term U as an empirical fitting parameter. An alternative approach to the electronic structure of the HTSC's is based on the use of model Hamiltonians that aim to reduce complexity of the exact nonrelativistic Hamiltonian and to incorporate the essential physics into a few parameters. All HTSC's are very ionic compounds in which the Cu cations have essentially d^9 character with one unpaired spin per Cu site mainly located in the Cu $3d_{x^2-y^2}$ orbital that lies mostly within the Cu-O (XY) plane. However, this orbital is also strongly mixed with the O $2p_x$ and $2p_y$, and hence it was soon realized that a one-band model based solely in the Cu $3d_{x^2-y^2}$ orbitals was inadequate. Therefore, the initial attempts to relate electronic structure and superconductivity by means of model Hamiltonian approaches were based on the three-band Hubbard model proposed by Emery.^{22,23} Unfortunately, the number of

parameters entering the three-band model seems to be too large and a large amount of work was devoted to the reduction to a one-band model. Zhang and Rice²⁴ proposed a model Hamiltonian that simultaneously takes into account the magnetic interactions and the presence of holes in the antiferromagnetic Cu-O planes. This model Hamiltonian is a simplification of the three-band Hubbard model Hamiltonian of Emery²² that implicitly includes the $O(p)$ -Cu(d) hybridization and recovers the initial effective one-band description proposed earlier by Anderson.²⁵ This model Hamiltonian is usually written as

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

where the parameters t and J correspond to the effective hopping integral and the magnetic coupling constant between unpaired electrons in the i and j nearest-neighbor copper centers, respectively. In this expression, $J > 0$ stands for antiferromagnetic interactions.

The simple one-band t - J model Hamiltonian is thought to capture the essential physics of the phenomenon. Model Hamiltonian calculations for a set of parameters describing a realistic regime support this point of view,⁸ although a recent study of La_2CuO_4 suggests that some additional terms not included in the t - J Hamiltonian are also relevant.²⁶ Extended t - J Hamiltonians have also been invoked to explain metallic stripe formation.²⁷⁻²⁹ In any case, there are many indications that the t - J Hamiltonian largely contains the dominant interactions governing the low-lying states of the doped and undoped compounds. For instance, it is rather well accepted that the magnetic interactions play a fundamental role in the pairing mechanism and, hence, in the microscopic description of superconductivity in these cuprates.³⁰⁻³⁴ Recently, the importance of magnetic interactions in determining the critical temperature has been stressed by the model Hamiltonian calculations of Boninsegni and Manousakis,³⁵ Scalapino and White,³⁶ and by the accurate first-principles calculations of Muñoz, Illas, and Moreira.³⁷ All these works suggest a direct relationship between the magnitude of the antiferromagnetic coupling and the value of the critical temperature at optimal doping. On the other hand, Scalapino and White³⁶ have shown that for $J/t \sim 0.35$ hole pairing lowers the total energy, thus providing theoretical support for a pairing mechanism of high- T_c superconductivity based on the t - J model Hamiltonian.³³ Also, the numerical calculations of Boninsegni and Manousakis for finite two-dimensional lattices show that $J/t \sim 0.27$ is a lower limit for hole-pair formation. It is worth mentioning that several authors already anticipated the possibility of predicting superconductivity in the t - J model for a realistic regime of the relevant parameters.³⁸

The weak point of the model Hamiltonian-based calculations is that they are constrained to use values suggested either by experiment, intuition, or trial-and-error procedures. In fact, accurate experimental values of J are available for a small number of superconductor parent compounds only. In

addition, there is no simple direct way to measure the hopping integral, whose value is inferred by fitting a model to experimental data. For the prototypical La_2CuO_4 parent compound, J varies between 128 and 134 meV depending on the experimental technique and a value of $t \sim 0.55$ eV, is generally accepted for doped La_2CuO_4 ,³⁹ thus leading to $J/t \sim 0.24$. This ratio is not too far from the 0.35 value assumed by Scalapino and White,³⁶ but it is somehow lower than the lower limit for the existence of hole-pairing suggested by Boninsegni and Manousakis.³⁵ The lack of reliable values for the t and J parameters limits the applicability of the t - J model Hamiltonian and of its predictions which necessarily show a strong dependence on the set of parameters adopted.

Recently, it has been shown that J is a local property that can be predicted from *ab initio* calculations on embedded clusters that model the materials of interest.⁴⁰ Moreover, the *ab initio* computation of J for a rather large series of superconductor parent compounds has permitted one to establish that, as a general rule, the critical temperature increases with J .³⁷ The existence of such a trend suggests a possible correlation between the critical temperature and the microscopic parameters. Nevertheless, one must realize that a proper relationship must include the effect of doping the material, a necessary condition for the existence of superconductivity. Introducing holes in the embedded clusters used to represent the materials of interest permits to simulate the doping and provides a way to estimate the hopping integral using the same methodology that proved to be highly reliable for magnetic coupling. This strategy was initially used to derive *ab initio* t - J parameters for La_2CuO_4 (Ref. 39) and has been recently extended to obtain a complete set of t - J parameters for a broad class of superconducting cuprates that have the common feature of exhibiting a crystal structure with well-separated Cu-O planes. From this study a clear-cut relationship between T_c and J/t has been obtained.⁴¹ In the present work we further investigate the correctness of the above commented relationship between T_c and the calculated values of J/t by exploring the adequacy of the different models and computational methods to predict electronic-structure-derived parameters of the HTSC's.

II. PERIODIC AND EMBEDDED CLUSTER MODELS FOR MONOLAYERED CUPRATES

The main goals of this paper are to investigate the dependence of the effective t and J parameters of a representative set of HTSC's on the model and the computational method used to extract these parameters and to explore the reliability of the relationship between these parameters and the experimental T_c values recently reported.⁴¹ To this end the list of compounds studied in this work is the same previously studied in Ref. 41 and includes $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, Nd_2CuO_4 , $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, La_2CuO_4 , $\text{TlBa}_2\text{CuO}_5$, $\text{Sr}_2\text{CuO}_2\text{F}_2$, $\text{HgBa}_2\text{CuO}_4$, and $\text{Tl}_2\text{Ba}_2\text{CuO}_6$. This list of HTSC's expands a wide range of critical temperatures (at optimum doping) with values of $T_c = 10$ K for $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (Ref. 42); $T_c = 24$ K for Nd_2CuO_4 (Ref. 43); $T_c = 28$ K for $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (Ref. 44); $T_c = 42$ K for La_2CuO_4 (Ref. 45); $T_c = 45$ K for $\text{TlBa}_2\text{CuO}_5$ (Ref. 46); $T_c = 46$ K for $\text{Sr}_2\text{CuO}_2\text{F}_2$ (Ref. 47);

$T_c = 94$ K for $\text{HgBa}_2\text{CuO}_4$ (Ref. 48); and, finally, $T_c = 97$ K for $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ (Ref. 49).

For each one of the HTSC compounds described above periodic and embedded cluster models have been constructed. In all cases the experimental structure [$\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (Ref. 50), Nd_2CuO_4 (Ref. 51), $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (Ref. 44), La_2CuO_4 (Ref. 52), $\text{TlBa}_2\text{CuO}_5$ (Ref. 53), $\text{Sr}_2\text{CuO}_2\text{F}_2$ (Ref. 47), $\text{HgBa}_2\text{CuO}_4$ (Ref. 48), and $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ (Ref. 50)] has been used to build the different models, this is the only parameter external to theory used in the present study. For the periodic calculations two different unit cells have been used. These are the structural unit cell determined experimentally and the double of the conventional unit cell commonly used to represent the antiferromagnetic spin state.^{54–58} An embedded cluster model similar to those used in previous studies^{37–41,59–68} has been used to represent each one of these HTSC compounds. The cluster model has three well-separated regions; the first two regions are treated quantum mechanically, whereas the third region is treated in a classical way. The first quantum region contains two Cu sites and the surrounding O atoms in the basal plane: the electrons (valence or all depending on the level of theory) in this quantum region are explicitly taken into account in the cluster wave function or in the cluster electronic density. The choice of a planar quantum region is justified from previous work on La_2CuO_4 , which shows that apical oxygens have a negligible effect on the magnetic coupling constants.⁶³ The Cu_2O_7 region of the cluster model is surrounded by total ion potentials (TIP),⁶⁹ representing the oxygen nearest-neighbor cations and by an array of point charges. The TIP's are simple pseudopotentials with a net charge and no electrons; they constitute a bridge between the quantum-mechanical and the classical regions and include exclusion effects which prevent an artificial polarization of the anion electronic density towards the next-neighbor positive point charges.⁷⁰ Finally, the array of point charges accounts for the Madelung potential of these ionic systems. Figure 1 provides a representative scheme for $\text{HgBa}_2\text{CuO}_4$. The value of the point charges is chosen according to a fully ionic picture of these compounds. However, fractional charges chosen according to the Evjen's method⁷¹ are used for the ions in the cluster edge to guarantee the convergence of the truncated Madelung summation.⁷² In principle, one may claim that the choice of the point charges constitutes an external input to the theory. However, model calculations with scaled point charges have shown that the influence of the Madelung potential on the magnetic coupling constant is relatively small.⁶⁴ For the hopping parameter there is no previous experience, but there is no reason to expect any different behavior. This is because the main effect of the Madelung field is to shift the one-electron levels in a given direction. The fundamental difference between the distinct clusters lies in the geometrical structure and the composition of the material provided by the embedding potential, but all clusters have the same number of electrons, which for the undoped systems corresponds to a formal of $-10e$, although the overall model—cluster + embedding—is always neutral.

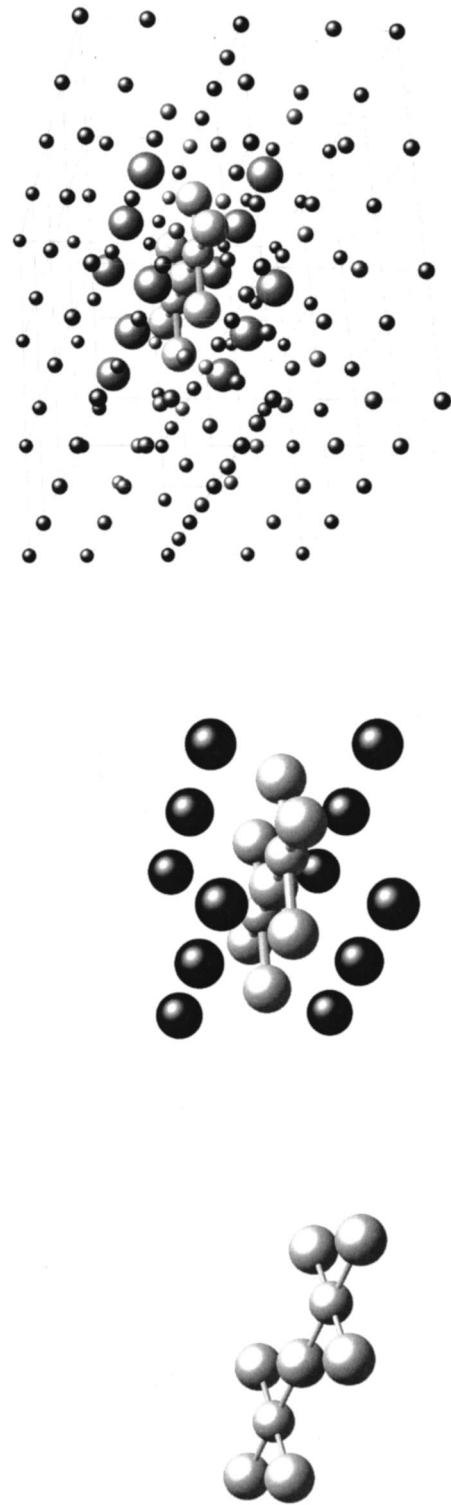


FIG. 1. Schematic representation of the embedded Cu_2O_7 cluster model used to represent $\text{HgBa}_2\text{CuO}_4$. The leftmost figure includes the atoms whose electrons are treated explicitly in the quantum-mechanical calculations, the figure in the center includes the atoms represented as total ion potentials, and the rightmost figure includes a subset of point charges used to include the Madelung potential effects.

III. EFFECTIVE PARAMETERS AND TOTAL ENERGY RELATIONSHIPS

The computation of the nearest-neighbor magnetic coupling constant J is based on the existing mapping between the eigenvalues and eigenstates of the Heisenberg Hamiltonian

$$H = \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \mathbf{S}_j = J \sum_{\langle ij \rangle} \mathbf{S}_i \mathbf{S}_j \quad (2)$$

and those of the exact nonrelativistic Hamiltonian. In the summation of Eq. (2) it has been explicitly assumed that there is only one relevant magnetic coupling and that is identical for all nearest-neighbor centers and that $J > 0$ corresponds to an antiferromagnetic interaction. [Notice that most often Eq. (2) bears a negative sign and antiferromagnetic interactions correspond to $J < 0$; the convention here is just the opposite to permit handling the t - J and Heisenberg Hamiltonians simultaneously.] For a system with two magnetic centers with spins with total spin quantum number $S_i = 1/2$, it is easy to show that the magnetic coupling constant is simply the energy difference between the singlet and triplet spin states that can be constructed by coupling the doublet spin states of each site.^{60,65}

$$E(S) - E(T) = -J. \quad (3)$$

However, in the periodic approach the constraint to use a single Slater determinant does not permit to obtain pure spin functions. In this case one needs to rely on the ferromagnetic (F) and antiferromagnetic (AF) states, which can be represented by a single Slater determinant, and use the fact that the F and AF states are eigenfunctions of the Ising Hamiltonian

$$H = \sum_{\langle ij \rangle} J_{ij} S_{zi} S_{zj} = J \sum_{\langle ij \rangle} S_{zi} S_{zj}. \quad (4)$$

None of the F and AF states are pure spin states, but it is easy to show that J can be obtained from the energy of these states. This strategy can also be used in the cluster model approach and requires the use of a broken symmetry approach. This has been suggested earlier by Noodleman *et al.*⁷³⁻⁷⁵ in the framework of the self-consistent field (SCF) $X\alpha$ method and by Yamaguchi and co-workers^{76,77} for the Hartree-Fock methods; for more details, see Refs. 65 and 78-81. For a cluster model with two magnetic centers with total spin $S = 1/2$, J is simply twice the energy difference corresponding to the F and AF states:

$$E(\text{AF}) - E(\text{F}) = -J/2. \quad (5)$$

For a periodic system one can make use of the fact that the Ising Hamiltonian contains scalar operators only and, hence, the magnetic interactions are additive. In this case J is easily obtained from

$$E(\text{AF}) - E(\text{F}) = -N_z J |S_z|^2, \quad (6)$$

where N is the number of magnetic centers on the cell, z is the number of nearest-neighbor magnetic centers of a given magnetic center, and S_z is the z component of total spin per center.^{54,55,82,83}

In the t - j Hamiltonian, the hopping integral t is meaningful only for the doped system. Then, t is defined as the energy to move an electron (or a hole) from a Cu site to its nearest-neighbor hole (or electron). The fact that to obtain the hopping integral one needs to consider a doped system makes it difficult to use any periodic approach because exceedingly large supercells will be required to simulate a moderate doping. The hopping integral t can be estimated using a cluster model with two Cu centers and one hole³⁹ plus the usual two-state framework.⁸⁴ For a system with two magnetic centers defined as left and right, the hopping integral represents the electronic coupling between the diabatic states corresponding to those having the hole localized on one magnetic site (i.e., right or left). This is nothing else than the off-diagonal element of the matrix representation of the Hamiltonian in the basis of these two configurations; this matrix element is twice the hopping integral. Alternatively, one can use a delocalized orbital basis. The “left” and “right” correspond to a localized description where the open-shell orbital is either on one site or on the other site of the cluster model. These two orbitals can be mixed in a positive (*bonding*) and a negative (*antibonding*) combination: this is a unitary transformation. Assuming that the diabatic states are orthogonal, t is given simply by half the energy difference between the two low-lying adiabatic electronic states in the delocalized basis.⁸⁵ In the particular case that the system has at least a symmetry inversion center the two different combinations will have different irreducible representations g and u and the corresponding electronic states will also have different symmetry. This fact can be exploited to compute t using DF techniques.⁸⁶ In these cases one simply has

$$E(g) - E(u) = -2t. \quad (7)$$

Since the need to consider a moderate doping precludes the use of a periodic approach, the comparison of results for the magnetic coupling obtained with the cluster and with the periodic approach is strictly necessary to validate the cluster model that is used to compute the hopping integral. Results in Sec. V will convince the reader that the cluster model provides an adequate representation of these systems.

IV. COMPUTATIONAL FRAMEWORK

Cluster and periodic calculations have been carried out in the framework of the linear combination of atomic orbitals (LCAO) expansion of the one-electron basis functions. The basis sets described below have been used to obtain the energies necessary to compute J and t using Eqs. (3), (5), (6), and (7). For the cluster model we have used a number of methods which range from Hartree-Fock to accurate configuration interaction and including several DFT approaches. The different methods can be divided in two main families depending on whether spin eigenfunctions or broken symmetry solutions are considered.

A. Basis sets

The one-electron basis functions—molecular orbitals or Bloch functions—are obtained by a suitable variational procedure and subsequently used to construct the Slater determinant(s) used in the different computational methods described below. The atomic orbitals, i.e., the localized basis functions, are linear combinations of contracted Gaussian-type orbitals (GTO) centered on the cluster or unit cell atoms. For the HTSC cluster models two series of cluster calculations have been carried out using appropriate configuration interaction (CI) wave functions, whereas a third series has been carried out using the broken symmetry approach and either unrestricted Hartree-Fock or DF calculations within several exchange-correlation functionals. In the first series of CI cluster model calculations, all electrons of the Cu_2O_7 cluster are explicitly considered. These have been described by means of the general atomic natural orbital (ANO) contraction scheme of Widmark *et al.*⁸⁷ especially designed to provide a compact representation of the atomic orbitals and aimed to give an optimal description of electronic correlation effects. For the Cu cluster atoms we use the $[5s,4p,3d]$ contraction of the $(17s,12p,9d)$ primitive set, for O bridging the two Cu cations the ANO basis set is the $[4s,3p,1d]$ contraction of the $(10s,6p,3d)$, and the six remaining surrounding oxygen atoms are described by a $[3s,2p]$ contraction of the same primitive set. Primitive sets and corresponding general contraction coefficients have been taken from Pierloot *et al.*⁸⁸ In this series of calculations the total number of basis functions is 130; there are 124 electrons distributed among 61 doubly occupied orbitals and two open-shell (active) orbitals. The 14 electrons from the $1s$ oxygen orbitals and the 10 [Ne]-core electrons of each Cu have not been included in the correlated calculations. Therefore, this series of CI calculations explicitly includes 90 electrons and 119 orbitals. The second series of CI calculations has been carried out using appropriate pseudopotentials to represent the core electrons of some of the cluster atoms. Hereafter, this will be referred to as the RECP basis; thus the relativistic effective core potentials (RECP's) of Hay and Wadt⁸⁹ were used to represent the $1s^2 2s^2 2p^6$ core electrons of the Cu atoms and the Durand-Barthelat pseudopotentials⁹⁰ to represent the $1s^2$ cores of the outermost cluster oxygen atoms. The corresponding GTO basis sets for Cu is an unsegmented $[4s,3p,3d]$ contraction of the $(5s,5p,5d)$ primitive set⁸⁹, a $[2s,2p]$ contraction of the $(6s,6p)$ primitive set used in previous works^{63,91} was used for the cluster edge oxygen atoms, and an all-electron $[4s,3p,1d]$ contraction of the $(9s,5p)$ primitive set used by Broughton and Bagus⁹² extended by a single d function.⁶³ Therefore, this second series of CI calculations involves a total number of 122 basis functions; there are 92 electrons which are distributed among 45 doubly occupied orbitals and two open-shell (active) orbitals. In this series the 92 electrons and 122 orbitals have been included in the correlated calculations. Notice that with these basis sets and explicitly correlated electrons the two corresponding CI expansions are perfectly comparable. The cluster model broken symmetry calculations have been carried out using the same standard all electron GTO basis used

in previous works,⁷⁹ which are $6-3111+g$ for Cu and $6-31g^*$ for the O atoms. The use of different basis sets permits to check the consistency of the results obtained for the t - J effective parameters and to define error bars for the computed quantities. Depending on the case and on the availability Hay and Wadt⁸⁹ or Durand and Barthelat⁹⁰ pseudopotentials have been used to describe the different cations that are represented as TIP's.

Finally, the periodic broken symmetry calculations have been carried out for a limited number of compounds due to technical limitations. Those are La_2CuO_4 , Nd_2CuO_4 , $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, and $\text{Sr}_2\text{CuO}_2\text{F}_2$. The nonsuperconducting but structurally related $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ cuprate has been also considered for completeness. The absence of superconducting transition in this compound is mostly related to the difficulties found in doping the parent compound^{93,94} rather than to an intrinsic limitation of its electronic structure to develop a high- T_c superconducting phase. The comparison to cluster calculations will indeed show that completing periodic calculations for the full list of compounds will not bring any additional conclusion. In the periodic calculations the Bloch functions are also combination of atom-centered Gaussian-type orbital basis sets.^{95,96} The Cu atomic basis contains $1s$, $4sp$, and $2d$ contracted GTO's obtained by means of a $8/6411/41$ contraction of the $(20s,12p,5d)$ primitive Gaussian set.⁹⁷ The oxygen basis set includes $1s$ and $3sp$ contracted GTO's obtained from a $(14s,6p)$ primitive set and a $8/411$ contraction scheme.⁹⁸ The cutoff threshold parameters ITOL 1–5 of the CRYSTAL code⁹⁹ for Coulomb and exchange integral evaluations have been set to 7, 7, 7, 7, and 14 strict values, respectively. The integration in reciprocal space has been carried out using a \mathbf{k} -space grid parameter of 8, yielding 65 points in the irreducible first Brillouin zone for the considered double cells. Here we remark that the antiferromagnetic phase, hereafter referred to as AF2, needs a double cell of the simple ferromagnetic cell which in all cases is the $14/mmm$ space group.

B. Methods involving spin eigenfunctions

This first family of *ab initio* electronic structure methods can only be applied to a finite model representation of the material. The complete active space configuration interaction (CASCI) method provides the simplest description. It starts from a spin-restricted Hartree-Fock calculation on the triplet state to obtain a set of molecular orbitals that are used to construct the different Slater determinants used in the CI expansion. Next, the open-shell molecular orbitals (which are g and u combinations of the atomic $d_{x^2-y^2}$ on each Cu site) define the complete active space (CAS) and two electrons are distributed in the two active orbitals in all possible ways. In this overwhelming simple case there are just two configurations with zero total z component of the total spin, $S_z=0$. These are precisely the singlet and triplet states defining J . Since the CASCI energy is invariant with respect to unitary transformations of the active orbitals, it is easy to show that the transformation

$$d_{\text{left}} = 1/\sqrt{2}(g+u), \quad d_{\text{right}} = 1/\sqrt{2}(g-u) \quad (8)$$

is unitary and defines orthogonal localized orbitals on each site. Therefore the active space contains the Slater determinants that can be constructed by having one electron in each Cu site (neutral forms) plus those that can be obtained by allowing simultaneously two electrons in each Cu site (ionic forms). This is precisely the equivalent of the Anderson mechanism for superexchange; the singlet may have an additional stabilization with respect to the triplet because the ionic forms cannot contribute to the triplet. The CASCI wave function can be improved in several ways. The first one is to enable the molecular orbitals to be self-consistent for either the singlet or triplet states; this gives rise to the complete active space self-consistent field (CASSCF) wave function.¹⁰⁰ The CASSCF method provides the best attainable solution for the given active space, but lacks electronic correlation effects external to the CAS that have been shown to be important in determining both J and t .^{101,85} This conclusion is supported by a many studies in different compounds including ionic perovskites, spin ladders, spin chains, and HTSC's.^{26,37-41,56-68} Electronic correlations for excitations out of the CAS have been accounted for by the CASPT2 (Refs. 102-104) and DDCI (Refs. 105 and 106) approaches. The CASPT2 method takes the CASSCF as zeroth-order wave function and estimates the remaining part of the (mainly) dynamical electron correlation effects by second-order perturbation theory. On the other hand, the DDCI scheme is based on the understanding that on a CI expansion many determinants equally contribute to the correlation energy of the two electronic states involved in the energy difference. Therefore, it is possible to select only the determinants that contribute to the energy difference between the states and include only those in the CI expansion. From the list of determinants constructed by single and double replacements from the determinants in the reference space, usually a CAS that represents the Anderson model, a selection is made based on arguments from quasidegenerate second-order perturbation theory. For a system with two unpaired electrons, it has been proved^{105,106} that in case of a degenerate reference space only the determinants $|K\rangle$ that fulfill the condition

$$\frac{\langle I|\hat{H}|K\rangle\langle K|\hat{H}|J\rangle}{E_K - E_0} \neq 0, \quad (9)$$

with $|I\rangle$ and $|J\rangle$ two different determinants belonging to the CAS and $|K\rangle \notin \text{CAS}$, contribute to the energy difference of the states involved. It can be easily shown that this condition selects determinants involving at most two orbitals outside the CAS. The complete diagonalization of the resulting CI matrix is usually referred to as DDCI2. For most real systems the selection condition does not apply strictly and even if the DDCI2 method gives very reasonable results it systematically underestimates the magnitude of the magnetic coupling constant.^{40,56-68} However, it has been shown recently that adding some well-defined set of determinants to the wave function gives an important contribution to the energy difference between the states of interest.^{40,107} These extra determinants involve at most three orbitals external to the CAS; the resulting method is labeled DDCI3. Calzado

*et al.*¹⁰⁷ and Cabrero *et al.*¹⁰⁸ have shown that the leading effect of adding the extra determinants to the DDCI2 list arises from the relaxation of the determinants connected to the ligand to magnetic-center charge-transfer (CT) excitations. These CT excitations are already present in the DDCI2 list, but their contribution remains rather small because the wave function lacks flexibility to account for the large orbital relaxation effects accompanying CT excitations.¹⁰⁹⁻¹¹¹ The inclusion of single excitations with respect to this CT excitations at the DDCI3 level lowers the CT excitations in energy and, hence, largely enhances the contribution of these determinants to the wave function. As a result, the DDCI3 calculated values of the magnetic coupling constant are in excellent agreement with available experimental data.^{37,40} An exhaustive comparison of the performance of DDCI and CASPT2 in predicting the magnetic coupling constant of a wide family of systems has been reported recently.¹¹² The number of determinants included in the DDCI3 list is 308 573 and 204 273 for the singlet and triplet using the ANO basis. For the RECP basis the number of determinants is 335 974 and 222 427, respectively. Therefore, any difference between these two basis is more likely to be due to a different description of the orbital shape rather than due to different treatments of electron correlation.

C. Broken-symmetry-based methods

The second families of methods are all based on the broken symmetry approach. In the case of using a cluster model to represent the material, a single Slater determinant is used to obtain solutions for $S_z=1$ and for $S_z=0$; none of them is a true spin eigenfunction. In part, this is because different spatial orbitals are obtained for the spin-up and spin-down spinorbitals. Quantum chemistry refers to these methods as spin unrestricted, whereas solid-state physics defines them as spin polarized. The $S_z=1$ solution is usually a good approximation to the triplet state, but the solution with $S_z=0$ is a broken symmetry one with energy midway between the singlet and triplet states.^{78,80} The simplest of these methods is the unrestricted Hartree-Fock (UHF) which can be regarded as an approximation to the CASCI or CASSCF method.^{65,80} UHF calculations can also be carried out for a periodic system and here the ferro- and antiferromagnetic solutions are those needed to obtain the magnetic coupling constant. In the present work we have carried out periodic UHF calculations for La_2CuO_4 , Nd_2CuO_4 , $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, and $\text{Sr}_2\text{CuO}_2\text{F}_2$ HTSC's and the related compound $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. The periodic calculations have been performed by using the supercell approach (double cells of the primitive crystallographic cell).

To improve the UHF description requires to include electronic correlation effects and this can be accomplished in different ways. In solid-state physics, density functional theory is the commonly used approach although it has also been used in the study of molecular systems (Ref. 80 and references therein). However, one must keep in mind that the commonly used local density approximation to DFT dramatically fails to predict the antiferromagnetic ground state of strongly correlated systems such as the HTSC's.¹⁵ Likewise, the improved version of DFT, termed the generalized gradi-

ent approximation (GGA), does not completely solve the LDA failure to describe magnetic systems. It has been suggested that a straightforward remedy of this deficiency is the use of hybrid functionals. These methods have been suggested by Becke¹¹³ and include a part of Fock exchange to improve the prediction of thermochemical properties. Martin and Illas have also shown that hybrid functionals largely improve the description of magnetic coupling in ionic solids with localized spins,⁷⁹ thus providing an alternative to GGA techniques. Following Martin and Illas, we have used several hybrid functionals starting with the semiempirical B3LYP functional,¹¹⁴ which contains $\sim 20\%$ of Fock exchange. The other hybrid approaches used in the present work follow the strategy of Martin and Illas.⁷⁹ These approaches mix Fock and Dirac-Slater exchange functionals with the LDA correlation functional. By tuning the parameter δ between 0 and 1, we can follow the progression from the pure LDA to pure HF exchange always maintaining the LDA correlation part:

$$E_{xc} = (1 - \delta)E_x^{\text{Slater}} + \delta E_x^{\text{HF}} + E_{\text{corr}}^{\text{LDA}}. \quad (10)$$

The choice of LDA for the remaining exchange and for the correlation contribution is that this permits to clearly differentiate the effect of Fock exchange without having to refer to external parameters and to particular forms of the gradient-corrected functionals. Moreover, the effect of the selected correlation functional on the calculated magnetic coupling constant is rather small and the same occurs for the DFT part of the exchange contribution.⁷⁹ Among the several possible mixtures we report here results for 35% and 50% of Fock exchange, respectively, and denote these approaches as Fock-35 and Fock-50. Notice that the latter is close, but not identical to the half-and-half functional proposed by Becke.¹¹³

The CASSCF and CASPT2 calculations have been carried out using the MOLCAS 4.0 package,¹¹⁵ and CASCI and DDCI were carried out by means of the CASDI code^{116,117} coupled either to MOLCAS (Ref. 118) or to the PSHF-CIPSI package¹¹⁹ depending on whether the ANO basis or the Hay-Wadt ECP and basis was used. The broken symmetry UHF and DFT calculations were performed by means of the GAUSSIAN98 suite of programs.¹²⁰ Finally, the periodic UHF calculations have been carried out using the CRYSTAL-98 computer code.⁹⁹

V. RESULTS AND DISCUSSION

In this section we comment the results obtained by the different methods and models for the magnetic coupling constant and for the electron charge transfer integral. In order to facilitate the reading and the comprehension of the large number of results included in the present paper the whole set of results is discussed in well defined and separated parts. First, the comparison of cluster and periodic calculations permits to validate the cluster model. Next, the state-of-the-art DDCI method is used to predict t and J values for a larger set of HTSC's. In a third subsection we report the results for t and J which are obtained by means of the DFT methods. Finally, the fourth subsection is devoted to study the relation-

TABLE I. Magnetic coupling for selected HTSC's, as obtained from periodic and cluster model calculations. Also included is the related compound $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ for completeness. Positive values of J correspond to antiferromagnetic coupling.

Compound	J (meV)	
	Periodic model	Cluster Model
Nd_2CuO_4	33.4	31.8
La_2CuO_4	36.1	38.3
$\text{Sr}_2\text{CuO}_2\text{F}_2$	33.7	34.9
$\text{Ca}_2\text{CuO}_2\text{Cl}_2$	31.7	32.5
$\text{Sr}_2\text{CuO}_2\text{Cl}_2$	28.5	29.1

ship between the critical temperature at optimum doping and the J/t ratio.

A. Comparison between cluster and periodic results

The representation of an extended system by means of a cluster model does always pose the problem to know to which extent does the model resemble the infinite system for the considered properties. Obviously, this depends very much on the physical property one is interested in. In the case of magnetic coupling it may be argued that the effective magnetic coupling parameter is a local two-body operator or that collective effects largely influence it. A fairly large amount of work has been devoted to answer this question by comparing periodic to cluster calculations^{37,67} or by using cluster models of increasing size.⁶⁶ From these works it seems quite clear that J is indeed a local property.⁴⁰ Nevertheless, it is appropriate to further verify the validity of this hypothesis at least for some of the compounds considered in the present work. Following the strategy of previous work^{56–58} we compare the value of the magnetic coupling constant obtained from cluster and periodic UHF calculations carried out using the basis sets reported in Sec. IV A.

The results for the magnetic coupling constant of La_2CuO_4 , Nd_2CuO_4 , and $\text{Sr}_2\text{CuO}_2\text{F}_2$, $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ are reported in Table I. It is worth mentioning that for La_2CuO_4 the present value is in full agreement with the previous work of Su *et al.*¹²¹ as expected from the close similarity between both calculations. The analysis of results in Table I shows that the influence of the model—periodic or cluster—on the UHF value of the magnetic coupling constant is fairly small. The difference between the J value obtained by the cluster and the periodic model does not exceed 2.5 meV or 8×10^{-5} hartree. This is an energy value which is almost within the numerical accuracy of the method and likely to be due to the use of a different GTO basis set rather than to a different description of the physical phenomenon due to the use of different material models. Therefore, it can be safely concluded that, as far as J is concerned, the embedded cluster models used in this work provide an adequate representation of the HTSC's under study. However, comparison to available experiments reveals that the UHF calculated values provide only a rough estimate of the measured value. Unfortunately, the experimental J is only known for three compounds of the list; those are Nd_2CuO_4 , La_2CuO_4 ,

TABLE II. Magnetic coupling values for the series of HTSC's, as obtained from the CASCI method and two basis sets. Positive values of J correspond to antiferromagnetic coupling.

Compound	J (meV)	
	ANO	RECP
Nd ₂ CuO ₄	24.5	23.9
La ₂ CuO ₄	30.7	31.5
Sr ₂ CuO ₂ F ₂	28.0	27.9
Ca ₂ CuO ₂ Cl ₂	25.6	26.4
TlBa ₂ CuO ₅	29.5	30.7
Tl ₂ Ba ₂ CuO ₆	28.5	30.1
HgBa ₂ CuO ₄	27.6	25.4
Bi ₂ Sr ₂ CuO ₆	21.6	19.4

and Sr₂CuO₂Cl₂ for which different techniques predict 125 ± 6 meV,¹²² 135 ± 6 meV,¹²³ and 125 ± 6 meV,⁹⁴ respectively. Clearly, UHF underestimates the magnitude of J by a factor of ~ 4 . Since both models provide equally good representations of the HTSC's, the difference with respect to experiment must be attributed to electron correlation effects not included in the Hartree-Fock wave function. This is in full agreement with previous studies, e.g., Refs. 37, 40, 59, 63, and 78.

B. Electronic correlation effects on the magnetic coupling constant

The UHF calculations do not include dynamical correlation effects and, in addition, correspond to wave functions without a definite multiplicity. The CASCI approach provides an equivalent physical description but using spin eigenfunctions. Clearly, the CASCI values of J are also too small (Table II) because the external correlation effects are still neglected. Nevertheless, results in Table II permit us to obtain an estimate of the influence of the basis set used to describe the electronic structure of these clusters. This is important because the CASCI wave function is very compact and differences can only be attributed to the atomic basis set and not to a different level of electronic correlation. The two different basis sets lead to the same physical description even at the quantitative level; the largest difference between both basis sets is 2 meV only. On the average choosing one or another basis set has a $\sim 4\%$ effect on the CASCI value of J . The resulting J values are comparable to, albeit slightly smaller than, their counterparts in Table I; these differences have a twofold origin. On the one hand, they correspond to a different basis set and on the other hand results in Table I have been obtained by means of a spin-unrestricted method which unavoidably includes an uncontrolled part of electronic correlation due to the introduction of spin contamination.

Extensive inclusion of external electronic effects by the different methods described in Secs. IVC and IVD largely improves the CASCI and UHF values, respectively. However, we must emphasize that the approach followed in each case is different. In the CASCI wave function, a part of the electronic correlation (usually defined as nondynamical cor-

TABLE III. Magnetic coupling values for the series of HTSC's, as obtained from the DDCI3 method and two basis sets. Positive values of J correspond to antiferromagnetic coupling. Available experimental data are included for comparison.

Compound	J (meV)		
	ANO	RECP	Expt.
Nd ₂ CuO ₄	149.9(131.7 ^a)	126.3	125 ± 6 ^b
La ₂ CuO ₄	149.3(150.2 ^a)	144.8	135 ± 6 ^c
Sr ₂ CuO ₂ F ₂	159.0(151.6 ^a)	139.9	
Ca ₂ CuO ₂ Cl ₂	148.4	138.6	
TlBa ₂ CuO ₅	166.9	155.7	
Tl ₂ Ba ₂ CuO ₆	186.3	182.3	
HgBa ₂ CuO ₄	164.0(144.7 ^a)	136.2	
Bi ₂ Sr ₂ CuO ₆	114.0	108.3	

^aValues obtained using a more extended basis for Cu and for the bridging oxygen.

^bReference 122.

^cReference 123.

relation) is explicitly taken into account. The remaining differential electronic correlation effect can be accounted for by adding to the CASCI wave function the determinants that contribute directly to the energy difference followed by a diagonalization of the corresponding enlarged CI matrix, whereas in the second case electronic correlation is estimated by means of some exchange-correlation functional. However, in all cases the effect of introducing electronic correlation is a large improvement over the values reported in Tables I and II. Overall, DDCI2 and CASPT2 do not bring in enough differential electronic correlation and the corresponding values are still too small, but 50%–60% and 75%–80% of the more accurate DDCI3 results reported in Table III. We must point out that for a large series of compounds including several HTSC's the DDCI3 values obtained using RECP and the corresponding basis appear to be remarkably close to available experimental data.^{37,40} Results in Table III show that except for three compounds—Nd₂CuO₄, Sr₂CuO₂F₂, and HgBa₂CuO₄—the values obtained with either basis set do not differ in more than 5%. However, for the above-mentioned compounds the deviation is much larger and reaches 15% for HgBa₂CuO₄. The reason for this difference has been assigned to the fact that in these three compounds either there is no apical ligand to the Cu atoms (as in Nd₂CuO₄) or it is very far away (as in Sr₂CuO₂F₂ and HgBa₂CuO₄). Since the ANO basis attempts to provide nearly atomic orbitals and these are an average from neutral, singly positive and negative Cu species, it is well possible that the resulting atomic virtual lack flexibility. In the three deviating cases this basis set limitation leads to significant inaccuracies on the final result of J . This interpretation is supported by the fact that the experimental value of J is known precisely for Nd₂CuO₄ [$J = 125$ meV (Ref. 122)] and it is close to the DDCI3 value obtained with the RECP and the corresponding basis ($J = 126$ meV). The comparison to experiment is also possible for La₂CuO₄, although in this case the two calculated values (149.3 and 144.8 for the ANO and RECP bases, respectively) are close to the experimental

TABLE IV. Magnetic coupling values for the series of HTSC's, as obtained from different broken symmetry approaches (cf. Sec. IV C). Positive values of J correspond to antiferromagnetic coupling.

Compound	UHF	Fock-50	J (meV)		
			Fock-35	B3LYP	LDA
Nd ₂ CuO ₄	31.8	71.2	141.4	139.1	654.3
La ₂ CuO ₄	38.3	74.3	134.7	209.8	820.0
Sr ₂ CuO ₂ F ₂	34.9	77.0	123.3	184.5	
Ca ₂ CuO ₂ Cl ₂	32.5	76.7	127.7	190.6	702.3
TlBa ₂ CuO ₅	42.0	88.9	138.2	195.1	895.6
Tl ₂ Ba ₂ CuO ₆	35.9	85.9	137.1	219.3	760.7
HgBa ₂ CuO ₄	35.4	70.3	103.8	188.4	
Bi ₂ Sr ₂ CuO ₆	38.3	69.7	112.1	309.3	

value of 135 ± 6 meV.¹²³ An alternative verification of the interpretation given above is provided by additional calculations with the ANO basis set using more extended sets such as $[6s,5p,4d]$ for Cu and $[5s,4p,2d]$ for the bridging oxygen or even larger sets. The calculated DDCI3 results for these three discordant compounds become 131.7, 151.6, and 144.7 meV, respectively. These refined values now nicely follow the trend observed for the remaining compounds. It is worth pointing out that enlarging the basis set does not practically affect the calculated CASCI values, thus indicating that the different description between the two basis relies mostly in the virtual space. To further confirm this unexpected basis set effect calculations have been also carried out for La₂CuO₄ with this ANO extended basis set. The resulting magnetic coupling constant is almost the same obtained with the more contracted set. These calculations show that the use of ANO basis sets in this context needs to be handled with special care. Nevertheless, it is worth pointing out the difficulty to compute this elusive property. Hence deviations of a few meV are not surprising, although being able to reach a more quantitative description is also rewarding.

Next we turn our attention to the results that are obtained by means of the broken symmetry approach carried out at different levels of theory. In Table IV we report a complete list of values obtained by means of the UHF, Fock-50, Fock-35, and B3LYP methods. The first obvious point concerns the close similarity between the UHF and CASCI values. This is not surprising and follows from the fact that UHF natural orbitals are a good approximation to those obtained from a CASCI (or CASSCF) wave function.¹²⁴ From a more physical point of view the orbitals involved in the nondynamical correlation contribution to the magnetic coupling constant are precisely the g and u combinations of the Cu($d_{x^2-y^2}$) orbitals and consequently exhibit fractional occupation numbers in either the CASCI or the unrestricted natural orbitals. The discussion concerning the DDCI3 has already made it clear that the difference between UHF (or CASCI) calculated J values and experiment lies in the electronic correlation effects. Introducing electronic correlation by means of a density functional approach largely improves the results but the calculated values are strongly dependent on the choice of the exchange-correlation functional E_{xc} . The dependence is so big that the LDA values are wrong by almost one order of

magnitude. Martin and Illas⁷⁹ have shown that the use of gradient corrected functional does not improve the results. Chevreau *et al.*¹²⁵ analyzed the charge density obtained from different methods and related the failure of the LDA and GGA to their excessive delocalization of charge density near the nuclei. This incorrect behavior is remedied, in part, by the use of hybrid functionals. However, Table IV shows that the widely used B3LYP methods largely overestimates the magnitude of the coupling constant. Following previous work⁷⁹ we have studied the dependence of the DF values of J with respect to the amount of Fock exchange included in the E_{xc} functional. The results in Table IV suggest that Fock-35 is a reasonable choice. However, the calculated values deviate considerably from the DDCI3 values with differences ranging from -25 to $+12\%$. Clearly, the choice of Fock-35 appears to be rather empirical, the amount of Fock exchange to be included depending either on the existence of experimental or of accurate calculated values. This fact discredits the use of DF techniques, especially of the LDA, to predict the magnetic coupling constants of HTSC's.

C. Hopping integral

The first problem encountered when computing the hopping integral t is the difficulty to evaluate the accuracy of a given result. This is because this quantity cannot be directly obtained from experiment. Therefore, the error bars must be acquired by comparing methods of increasing accuracy and exploring the effect of the parameters entering into a given method. The discussion about the magnetic coupling constants have made it clear that DDCI3 is the best available method and that the influence of the basis set does not exceed 5%. It is reasonable to assume that DDCI3 will perform equally good on the prediction of t . Table V reports the DDCI3 values of t obtained by using the RECP and ANO basis sets. In general, the values predicted by the two basis sets are of the same order of magnitude. However, those obtained by the ANO basis set are consistently larger than those obtained by the RECP basis by 10%–15%. The impossibility to compare to experiment does not permit us to find out about the accuracy of these results, and the difference between calculated values has to be taken as error bars arising from the use of a finite basis set.

TABLE V. Hopping integral t values for the series of HTSC's, as obtained from the DDCI3 method and two basis sets.

Compound	t (meV)	
	ANO	RECP
Nd ₂ CuO ₄	598	524
La ₂ CuO ₄	623	549
Sr ₂ CuO ₂ F ₂	617	562
Ca ₂ CuO ₂ Cl ₂	623	573
TlBa ₂ CuO ₅	631	568
Tl ₂ Ba ₂ CuO ₆	624	532
HgBa ₂ CuO ₄	560	513
Bi ₂ Sr ₂ CuO ₆	524	497

The calculated results of the hopping integral do also present a significant dependence on the computational method. However, this is much less than the one observed for the magnetic coupling constant. The results in the previous subsection clearly show that accounting for dynamical correlation effects leads to values of J which are larger than the UHF or CASCI one almost by a factor of 5. In the case of the hopping integral the situation is less dramatic. In fact, UHF already provides a reasonable estimate of the hopping integral: the UHF values are too large compared to those predicted by the more accurate DDCI3 method, but by a 50% only. On the other extreme, the LDA predicts values which appear to be too small when compared by DDCI3 and also by almost 50%. The different hybrid functionals provide results that are midway between UHF and LDA. In particular, Fock-35 seems to perform remarkably well (see Table VI).

The fact that the hopping integral is less sensitive than the magnetic coupling constant with the level of electronic correlation treatment has several important consequences. It is clear that the t - J Hamiltonian parameters derived from the LDA or GGA are unbalanced because the corresponding t has the right order of magnitude, whereas J is wrong by a much larger factor. In a limiting situation one may argue that t is not dramatically changing from compound to compound and that it is almost constant. This is justified from the fact that t is an effective one-electron property and consequently

 TABLE VI. Hopping integral t values for the series of HTSC's, as obtained from different broken symmetry approaches (cf. Sec. IV C). For the Bi₂Sr₂CuO₆ compound the absence of an inversion center of symmetry does not allow the DFT calculation of t ; cf. Eq. (7).

Compound	t (meV)				
	UHF	Fock-50	Fock-35	B3LYP	LDA
Nd ₂ CuO ₄	763	486	565	448	481
La ₂ CuO ₄	790	567	609	526	416
Sr ₂ CuO ₂ F ₂	781	406	622	618	452
Ca ₂ CuO ₂ Cl ₂	956	584	610	529	477
TlBa ₂ CuO ₅	801	336	479	445	416
Tl ₂ Ba ₂ CuO ₆	764	676	659	571	481
HgBa ₂ CuO ₄	756	499	565	496	452

less sensitive to electronic correlation effects. From second-order perturbation theory arguments on the effective one-band Hubbard Hamiltonian it follows that $J \sim 4t^2/U$, where U in the on-site two-electron repulsion Hubbard parameter. Therefore, accepting that t does not strongly vary from compound to compound one understands the enormous effect of electron correlation on the magnetic coupling constant. It is directly related to the fact that U is a two-electron effective parameter and hence enormously sensitive to the level of electron correlation treatment.

VI. RELATIONSHIP BETWEEN THE ELECTRONIC STRUCTURE AND CRITICAL TEMPERATURE

Following recent work⁴¹ we consider possible relationships between the critical temperature T_c and the electronic structure parameters of the t - J Hamiltonian. To this end we have explored the correlation between T_c and the t and J parameters. In particular, T_c has been represented against the J/t ratio obtained at the different levels of theory discussed in the present work. However, a clear relationship does only appear when using the t and J DDCI3 values and either with the RECP or ANO basis set (Fig. 2). However, for the DDCI3 values the critical temperature of these oxides follows a quasilinear dependence on J/t . In addition, this relationship holds within the computational uncertainty for t and J discussed above and the experimental error for T_c . Although the linear trend in Fig. 2 should be taken merely as an observation, it permits us to rationalize the variation of T_c along a representative series of superconducting oxides in terms of a simple t - J Hamiltonian. We have to point out that in spite of the existence of this linear relationship different authors have demonstrated that terms not included in the t - J Hamiltonian can be relevant.^{26,126} The effect of the additional terms in extended t - J models has been studied at length by Martins *et al.*,²⁷⁻²⁹ especially in the context of stripe formation. The linear plots in Fig. 2 strongly suggests that these terms do not seem to exhibit a strong control on the critical temperature of the material. In addition, White and Scalapino have also reported stripe formation within the standard t - J model.¹²⁷ From a linear fit it turns out that

$$T_c^{\max} \text{ (K)} = 969.1J/t - 197.7, \quad (11a)$$

$$T_c^{\max} \text{ (K)} = 674.0J/t - 134.9, \quad (11b)$$

with $R^2 = 0.922$ and $R^2 = 0.956$ for the ANO and RECP basis sets, respectively. In these regressions we excluded the Hg compound since it shows the largest deviation with respect to the whole set of results. As shown in Refs. 128 and 129, the uncertainty in T_c^{\max} for HgBa₂CuO₄, but also for Sr₂CuO₂F₂,¹³⁰ is larger than for the other compounds considered in this study.

The existence of this correlation permits to make a reliable and straightforward prediction about the critical temperature of any hypothetical new monolayered superconducting cuprate from *ab initio* microscopic parameters. In this sense, the absence of a superconducting transition in Sr₂CuO₂Cl₂ is related to the limitations in doping the pure compound since the present embedded cluster calculations

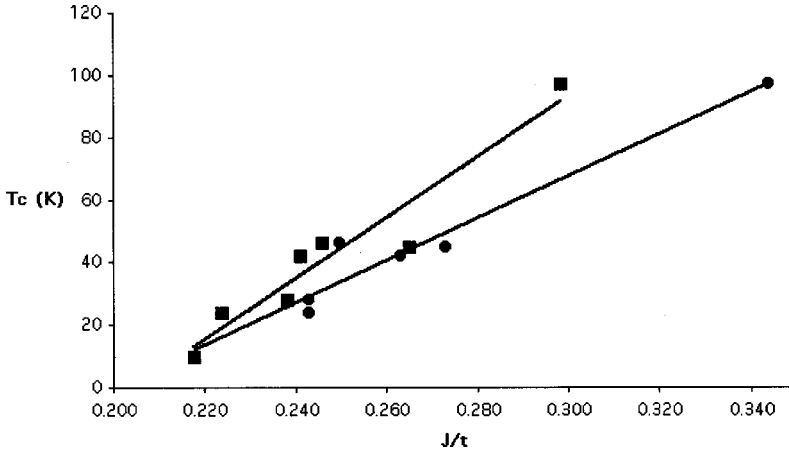


FIG. 2. Relation between the critical temperature at optimum doping, T_c^{\max} , and J/t derived from *ab initio* embedded cluster model calculations for a series of high- T_c superconductors with almost noninteracting Cu-O planes in their crystal structure. ● stands for results obtained with the RECP basis set, whereas ■ denotes results obtained by means of the ANO basis).

predict that this cuprate could be a HTSC. The predicted values for this compound correspond to $J = 120$ meV and $t = 510$ meV, giving rise to $J/t = 0.234$, which corresponds to an approximate T_c of 27 K. Moreover, this correlation predicts that, independently of the basis set, $J/t \sim 0.20$ is a lower limit for the existence of high- T_c superconductivity. A limiting value of J/t was also predicted from the finite lattice Green's Function Monte Carlo calculations of Boninsegni and Manousakis.³⁵ This conclusion is fully supported by the present *ab initio* calculations which indeed provide accurate values and error bars for the t and J parameters of the different monolayered HTSC's. The accuracy of the present set of parameters permits to suggest that $J/t \sim 0.20$ is a more realistic lower limit value. In addition, we show that the highest T_c^{\max} is attained for $J/t = 0.34$ and indicates that the $J/t = 0.35$ ratio often used in model calculations is probably too high.¹²⁷ Notice that the J and t parameters defining the t - J Hamiltonian are assumed to be independent of p , the amount of doping in holes per CuO_2 unit. Therefore, the above-reported correlation applies for different levels of doping since $T_c = T_c^{\max} f(p - p_{\text{optimum}})$; it only affects the parameters defining the straight line in Fig. 1, but maintains $T_c = 0$ at $J/t \sim 0.20$.

VII. CONCLUSIONS

The magnetic coupling constant of selected cuprate superconductor parent compounds has been determined by means of embedded cluster model and periodic calculations carried out at the unrestricted Hartree-Fock level of theory. The good agreement between both approaches permits us to firmly establish the validity of the embedded cluster model approach which in turn permits us to use sophisticated configuration-interaction-based methods to obtain accurate values of this quantity that require extensive incorporation of electronic correlation effects. In addition, the cluster model approach provides a simple way to incorporate doping and hence to obtain accurate values of the hopping integral. A systematic study is also presented about the influence of atomic basis sets on the calculated t and J values and of the performance of various configuration interaction and density functional techniques.

The present study shows a different behavior of t and J

with respect to the level of electron correlation introduced in the calculation. It has been shown that t is almost equally described by all methods introducing explicitly or implicitly dynamical correlation effects including perhaps the LDA. This behavior is related to the one-electron character of this effective parameter. However, the final value of the magnetic coupling constant appears to be extremely sensitive to the level of theory. The close similarity between the DDCI3 values and available experimental data for a limited number of compounds provides additional support to the present interpretation.

The accurate determination of the t and J parameters of the t - J Hamiltonian by means of state-of-the-art *ab initio* techniques has two important outcomes. First, it suggests that the appearance of high- T_c superconductivity in existing monolayered cuprates occurs within J/t in the 0.20–0.35 interval. This regime is in consonance with the assumptions of many authors that have intensively used the t - J Hamiltonian to study the properties and phase diagram of the HTSC's.^{8,27–29,33,35,36} The lower value is predicted to be a critical lower limit for the existence of superconductivity, and it is not far from previous estimates using completely different approaches.³⁵ Second, a simple and accurate relationship between the critical temperatures and these parameters is found. However, it is very important to realize that this quantitative electronic structure versus T_c relationship is only apparent when both J and t are obtained at the most accurate DDCI3 level of theory.

It is hoped that the relationship between T_c and J/t will be useful to assist the synthesis of new cuprates with even higher values of the critical temperature. The present *ab initio* values for t and J strongly suggest that the physical mechanisms responsible for high- T_c superconductivity in cuprates are implicitly accounted for in the t - J model Hamiltonian with an interplay of exchange- and screening-mediated interactions in the pairing mechanisms.

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