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Accurate Prediction of Large Antiferromagnetic Interactions in High-T_c $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n = 2, 3$) Superconductor Parent Compounds

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The in-plane nearest-neighbor Heisenberg magnetic coupling constant, J, of La_2CuO_4, Nd_2CuO_4, $Sr_2CuO_2Cl_2$, $YBa_2Cu_3O_6$, and undoped $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n = 1, 2, 3$) is calculated from accurate *ab initio* configuration interaction calculations. For the first four compounds, the theoretical J values are in quantitative agreement with experiment. For the Hg-based compounds the predicted values are -135 meV ($n = 1$) and ~ -160 meV ($n = 2, 3$), the latter being much larger than in previous cases and, for $n = 3$, increasing with pressure. Nevertheless, the physics governing J in all these layered cuprates appears to be the same. Moreover, calculations suggest a possible relationship between J and T_c.

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More than ten years have passed since the discovery of the high-T_c superconductivity in several cuprate compounds and, up to now, there has been no agreement on a complete theory capable of explaining their anomalous physical properties [1]. The layered crystal structure, the strong antiferromagnetic coupling between neighbor Cu^{2+} ions in these layers, and the strongly correlated nature of their electronic structure have been pointed out to play a very important role in the fundamental mechanisms of superconductivity [1,2]. The high-T_c superconductors are produced by moderate doping of "parent compounds" such as La_2CuO_4, Nd_2CuO_4, or $YBa_2Cu_3O_6$. It is widely accepted that proximity to the insulating phase and the interaction of dopant carriers with magnetic degrees of freedom are fundamental aspects for the existence of high-T_c superconductivity. Recent theories strongly suggest that magnetic coupling is at the very origin of the superconducting state [2]. Thus, the magnetic coupling constants defining the magnetic structure of these compounds are key magnitudes in establishing trends and theories based on model Hamiltonians.

Recently, several families of layered cuprates, containing Bi, Tl, or Hg, have been synthesized. The $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n = 1, 2, 3$) family [3–5] includes $HgBa_2Ca_2Cu_3O_{8+\delta}$, the compound with the highest transition temperature observed to date (133 K at ambient pressure and 164 K under 31 GPa) [4,6,7]. The difficult synthesis and the layered structure of those materials limits the capability of obtaining pure crystals large enough to perform accurate measurements of their magnetic properties. This restricts the theoretical understanding due to the difficulty to obtain reliable estimates of the model Hamiltonian parameters. Modern theoretical approaches to electronic structure could provide accurate values of these parameters, such as the nearest-neighbor Heisenberg magnetic coupling constant J, thus providing a more detailed description of these materials.

Unfortunately, because of the strong correlated nature of the electronic structure and the antiferromagnetic insulating character of these cuprates, band structure calculations based on the local density approximation (LDA) or on the generalized gradient approximation (GGA) of density functional theory (DFT) usually lead to metallic ground state solutions or to extremely small insulating gaps [8]. *Ad hoc* corrections to the LDA [9,10] give more realistic results but its use is rather scarce. Recently, Martin and Illas [11,12] have shown that the failure of LDA, or GGA, to properly describe magnetic interactions in wide gap ionic insulators is due to the inadequacy of the current exchange functionals, the correlation functional having a minor effect.

Comparison of *ab initio* periodic and cluster model calculations at the same level of theory, together with the analysis of results obtained using cluster models with several magnetic centers, have permitted us to firmly establish that the magnitude of J in wide gap ionic insulators is a local property which is determined by the two interacting magnetic centers only [13–15]. Therefore, it is possible to use a cluster model to obtain accurate values of J by means of a configuration interaction (CI) expansion of the electronic wave functions for the electronic states of interest. In particular, the recently developed difference dedicated configuration interaction (DDCI) technique [16] has proven to be capable of accurately predicting the value of J in a large family of wide gap ionic insulators [17]—$KNiF_3$, K_2NiF_4, La_2CuO_4, $KCuF_3$, K_2CuF_4—with well-established experimental data.

In this Letter, the *ab initio* cluster model approach is further validated by showing that it quantitatively predicts the in-plane J of La_2CuO_4, Nd_2CuO_4, and $YBa_2Cu_3O_6$ superconductor parent compounds and, also, of the $Sr_2CuO_2Cl_2$ related cuprate. This theoretical prediction is claimed to be accurate because the J values of these materials, which are experimentally well established, are reproduced by the calculations. Next, we use this theoretical approach to predict the J values of the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ series (with $n = 1, 2, 3$) which are not available from experiment. Given the accuracy of the present approach, the

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results obtained in this work are expected to be quantitative predictions of intrinsic interest in the understanding of the properties of Hg-based cuprates.

Accurate values of J can be obtained by means of quantum chemical calculations on an appropriate cluster model representation of the material. These models contain a Cu_2O_7 unit ($Cu_2O_7Cl_4$ for $Sr_2CuO_2Cl_2$) embedded in an adequate environment of total ion potentials (TIPs) and an array of point charges that account for Pauli repulsion and Madelung potential, respectively. For additional details about the model setup, see [14,18]. To construct the models, experimental geometries [3,5,6,19–22] are used. This constitutes the only input data external to theory. It may be argued that these cluster models are a too crude representation of the real system and, hence, that cluster model results cannot be trusted. In consequence, a periodical description would be unavoidable. However, this claim is in contradiction with recent results that show that *ab initio* unrestricted Hartree-Fock (UHF) cluster and periodic calculations of the magnetic coupling constant are almost the same [11,14,15]. Moreover, it has also been shown that, for a broad family of wide gap insulators, the cluster model calculations reproduce the experimental values of J [17], provided a suitable wave function is used. There is no other *ab initio* theoretical approach that may reach such a level of accuracy. Notice that periodic calculations are not free of problems. They are constrained to use the UHF method or some spin polarized variant of DFT, they cannot deal with pure spin eigenstates, and, finally, they fail to provide a quantitative estimate of J in cuprates and in other strongly correlated systems [8,11].

Once the material cluster models are constructed, *ab initio* CI wave functions and energies, for the electronic states defining J, are obtained. Since each Cu^{2+} cluster ion carries a localized $S = 1/2$ spin moment, coupling two magnetic centers results in a singlet, S, and a triplet, T, spin state and one simply has $J = E(S)\text{-}E(T)$. The CI wave functions for the S and T states are specific linear combinations of Slater determinants (*vide infra*) constructed using spin orbitals that, in turn, are expressed as linear combinations of atomic Gaussian-type basis functions. The basis sets, pseudopotentials, and cluster setup have been carefully tested [13,14]; further details are available upon request to the authors.

Detailed information about the physical mechanisms governing the magnitude of J can be obtained from different types of *ab initio* configuration interaction wave functions of increasing complexity. In the first one, the configuration list accounts for the Anderson superexchange mechanism. In practice, this corresponds to all Slater determinants that can be constructed from the different ways of distributing the unpaired electrons in the *active* open-shell orbitals (situations with one unpaired electron per center plus all metal-metal charge transfer situations) while leaving one set of *inactive* and one set of *virtual* objects doubly occupied and unoccupied in all configurations, respectively. In the language of quantum chemistry, this is a complete active space configuration interaction (CASCI) wave function. The second CI wave functions, DDCI-2, add to the previous one all the ligand to metal charge transfer, CT, situations plus all other second-order diagrams contributing to J, i.e., double spin polarization, kinetic exchange, etc. Finally, the DDCI-3 wave function adds to DDCI-2, the instantaneous relaxation of the metal to oxygen CT situations, already included in the DDCI-2 list, but with an effective energy which is too high because of the CI truncation. The basic idea behind DDCI-2 and DDCI-3 is to include only the many body diagrams that contribute to the energy difference between different electronic states on a given model space, here the CAS. From quasidegenerate perturbation theory it follows that the second-order effective Hamiltonian defined on a CAS model space is

$$\hat{H}^{\mathrm{eff}(2)}_{I,J} = \sum_{K \notin \mathrm{CAS}} \frac{\langle I|\hat{H}|K\rangle\langle K|\hat{H}|J\rangle}{E^0_J - E^0_K}, \tag{1}$$

where $\hat{H}$ is the exact nonrelativistic Hamiltonian. Therefore, only the $|K\rangle$ determinants interacting directly with $|I\rangle$ and $|J\rangle$ contribute to $\hat{H}^{\mathrm{eff}(2)}_{I,J}$ and, hence, to the energy differences in the eigenstates defined by $\hat{H}^{\mathrm{eff}(2)}$. In the DDCI method this set of $|K\rangle$ determinants defines the CI expansion. Hence, their contribution is summed up to infinite order instead of used to construct $\hat{H}^{\mathrm{eff}(2)}$. The DDCI-2 wave function contains the $\{|K\rangle\}$ list with up to 2 degrees of freedom, holes, or particles, with respect to the CAS, while DDCI-3 extents this list so as to include the determinants with 3 degrees of freedom; cf. [16,17].

In the language of the Hubbard Hamiltonian, one would say that the diagrams added to DDCI-2 to give DDCI-3 permit one to lower the on-site two-electron repulsion effective integral U, without largely affecting the effective hopping integral t. A second-order perturbation expansion in the Hubbard model gives $J \sim t^2/U$, so a smaller U implies a larger J. In the *ab initio* CI wave functions these different physical effects are explicitly introduced in the matrix representation of the exact nonrelativistic Hamiltonian which is contracted for each CI list and diagonalized to provide the energies of interest.

Table I reports the results for La_2CuO_4, Nd_2CuO_4, $YBa_2Cu_3O_6$, and $Sr_2CuO_2Cl_2$. The J values obtained from the CASCI wave function, i.e., only terms corresponding to the Anderson mechanism, are in a rough, qualitative agreement with experiment only. This is because many important physical mechanism (i.e., kinetic exchange, double spin polarization, ligand to metal, and metal to ligand charge transfer instantaneous situations) are missing in the CASCI wave function. All these second-order mechanisms are explicitly taken into account in the DDCI-2 wave function and, as a result, the calculated J values are largely improved with respect to experiment. However, a quantitative description is

TABLE I. Theoretical and experimental (neutron scattering) in-plane nearest-neighbor magnetic coupling constants (in meV) for La_2CuO_4, Nd_2CuO_4, and $YBa_2Cu_3O_6$ superconductor parent compounds and the related material $Sr_2CuO_2Cl_2$. Also indicated are the physical mechanisms included in each CI space discussed in the text.

Wave function	CASCI		DDCI-2		DDCI-3	Experiment
Physical mechanisms	Anderson model	+	Second-order diagrams [c.f. Eq. (1)]	+	Instantaneous orbital relaxation of charge transfer forms	
La_2CuO_4	−31.5		−93.9		−144.8	−135[a]
Nd_2CuO_4	−23.9		−76.3		−126.4	−126 ± 5[b]
$YBa_2Cu_3O_6$	−27.3		−86.2		−141.6	−120 ± 20[c]
$Sr_2CuO_2Cl_2$	−21.2		−68.6		−119.5	−125[d]

[a] B. Kreimer *et al.*, Phys. Rev. B **46**, 14 034 (1992).

[b] T. R. Thurston *et al.*, Phys. Rev. Lett. **65**, 263 (1990); M. Matsuda *et al.*, Phys. Rev. B **42**, 10 098 (1990).

[c] S. Shamoto *et al.*, Phys. Rev. B **48,** 13 817 (1993).

[d] D. Vaknin *et al.*, Phys. Rev. B **41**, 1926 (1990); M. Greven *et al.*, Z. Phys. B **96,** 465 (1995).

achieved only when enabling instantaneous orbital relaxation of the ligand to metal CT forms through DDCI-3. These DDCI-3 results are also in agreement with the calculations reported by Van Oosten *et al.* [23] except for $YBa_2Cu_3O_6$, for which their value is somewhat smaller than the present one.

Results described above (together with Ref. [17]) suggest that DDCI-3 can be used to obtain reliable predictions of the magnetic coupling constant of the Hg based cuprates for which experimental data is not available. The values obtained at different levels of theory, see Table II, show that general trends are very similar to those described above for the other cuprates. The mechanisms included in the Anderson model are enough to qualitatively predict the magnetic behavior, but are rather far from the DDCI-3 values. Interestingly enough, the contribution of the instantaneous orbital relaxation effects is almost the same in all compounds, the J_{DDCI-3}/J_{DDCI-2} ratio being always in the 1.6 ± 0.1 range. The final value of the magnetic coupling constant results solely from the particular crystal structure, i.e., the potential energy surface minimum which is determined by the crystal electronic structure. Therefore, magnetic coupling in all these cuprates is dominated by the same physical mechanisms. However, the leading terms are precisely those not included in the Anderson model. The DDCI-3 calculations for the Hg-based compounds permit one to predict reliable values for the magnetic coupling constants. Some of the resulting values are the largest reported so far for superconductor parent compounds. For Hg-1201 and Hg-1212 the predicted values are $J = -136.2$ and $J = -153.8$ meV, respectively. For the two magnetic planes in the Hg-1223 unit cell the DDCI-3 values are $J = -155.0$ meV for the two equivalent planes and $J = -165.2$ meV for the more symmetric central one. For the superconductor parent compounds, a representation of the experimental maximum value of T_c (under optimum dopage) versus the calculated J values suggests a possible relationship between these magnitudes. Of course, a strong antiferromagnetic cuprate does not lead to a high-T_c superconductor, but Fig. 1 seems to indicate that when a given compound exhibits a superconducting transition, the value of T_c increases with J. Another indication of this trend comes from the DDCI-3 J values for the symmetric plane of the Hg-1223 structures under pressure [6] leading to a $J \sim r^{-n}$ relationship with $n = 5.4$, Table III.

TABLE II. Theoretical prediction of in-plane nearest-neighbor magnetic coupling constants (in meV) for $HgBa_2CuO_4$ (Hg-1201), $HgBa_2CaCu_2O_6$ (Hg-1212), and $HgBa_2Ca_2Cu_3O_8$ (Hg-1223). For the last compound, two different magnetic planes appear in the unit cell: the central and most symmetric one (symm.) and two less symmetric CuO_2 planes (ext.).

Wave function	CASCI	DDCI-2	DDCI-3
Hg-1201	−25.5	−79.7	−136.2
Hg-1212	−29.4	−93.8	−153.8
Hg-1223 (symm.)	−30.5	−97.3	−165.2
Hg-1223 (ext.)	−30.0	−94.6	−155.0

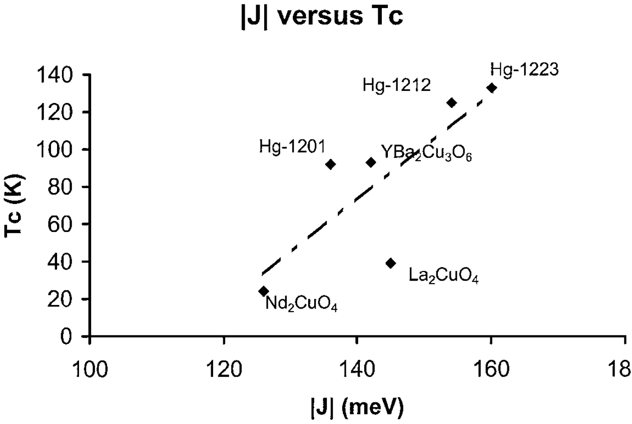

FIG. 1. Representation of experimental values of T_c versus DDCI-3 values of J for a series of high-T_c parent compounds. The straight line indicates a trend and is not intended to propose a linear relationship.

TABLE III. Values for the nearest-neighbor magnetic coupling constant (in meV) of the symmetric plane of the Hg-1223 superconductor parent compound calculated at the DDCI-3 level for $HgBa_2Ca_2Cu_3O_{8+\delta}$ structures under pressure. Structures have been taken from Ref. [6].

Pressure (GPa)	d(Cu-Cu) (Å)	J (meV)
0.5	3.8481	−164.0
3.5	3.8089	−176.1
6.0	3.7822	−182.8
8.6	3.7608	−185.7

The even larger values of J predicted for the structures under pressure together with the increase of T_c of these materials, also under pressure, supports the existence of a relationship between superconductivity and antiferromagnetic interactions in the high-T_c superconductors based in layered cuprates.

In conclusion, the values for the magnetic coupling constant of the Hg-based layered cuprates are predicted to be much larger than those corresponding to other superconductor parent compounds such as La_2CuO_4 or $YBa_2Cu_3O_6$. However, the physical mechanisms determining these large values are essentially the same in all compounds and the most important ones are not included in the Anderson's superexchange theory. Finally, we stress the fact that the largest values for T_c measured for the Hg-based superconductors are also accompanied by the largest values of the magnetic coupling constant, thus giving support to the arguments that relate magnetic coupling to high-T_c superconductivity.

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