Magnitude of interplane effective parameters in multilayered high-T_c cuprate superconductors

David Muñoz, Ibério de P.R. Moreira, and Francesc Illas
Departament de Química Física & Centre Especial de Recerca en Química Teòrica, Universitat de Barcelona & Parc Científic de Barcelona, C/ Martí i Franquès 1, E-08028 Barcelona, Spain
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Embedded clusters and periodic supercell approaches are used to obtain accurate *ab initio* values for the parameters of an extended *t-J* Hamiltonian for multilayered cuprates. In-plane and interplane magnetic coupling constants (J and $J_\perp$) and hopping integrals (t and $t_\perp$) are explicitly considered for various superconducting multilayered cuprates. For $YBa_2Cu_3O_6$, results are in good agreement with available experimental data thus supporting the reliability of the present extended *t-J* Hamiltonian parameters. The comparison of the magnitude of the different parameters in the extended *t-J* model strongly suggests that $t_\perp$ and $J_\perp$ play a key role in defining the differences in the critical temperature of bilayered cuprates.

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The discovery of the phenomenon of high-T_c superconductivity in copper perovskites[1] has prompted the development of theories trying not only to unravel the so far unknown physical mechanism governing this property but also the complex nature of the so called normal state of this kind of materials.[2,3] The physical description of these materials is complicated because this interesting phenomenon does only show up for specific nonstoichiometric compositions, doping playing a dominant role. However, even for the undoped parent compounds the description of the electronic structure remains challenging because the strongly correlated nature of these compounds cannot be correctly described by the current methods of solid state physics based on density functional theory. Local density approximation (LDA) fails even to describe the charge-transfer insulating character of these materials and predict them to behave as metals.[4] The improved generalized gradient approach (GGA) does not solve this problems and one has to rely in alternative methods such as LDA+U,[5] which, on the other hand, incorporate parameters which are external to the theory. Other approaches trying to overcome the LDA deficiencies by correcting for the self-interaction—LDA+SIC (Ref. 6) or GW approximations[7]—have only found a limited use.

The failure of the standard methods of solid state physics to describe even the electronic structure of the undoped materials has prompted alternative approaches to explicitly include electron-electron correlation effects in a more controlled way. An alternative and broadly used approach attempts to reduce the physics to a few dominant parameters defining a model Hamiltonian. These are simplifications of the exact nonrelativistic Hamiltonian including the physically relevant terms only. In the field of high-T_c superconductivity, one of the most widely used models is the *t-J* Hamiltonian proposed by Zhang and Rice[8]

$$H = -J\sum_{\langle ij\rangle}\left(\mathbf{S}_i\mathbf{S}_j - \frac{1}{4}n_i n_j\right) - t\sum_{\langle ij\rangle\sigma}[c^+_{i\sigma} \times (1-n_{i-\sigma})(1-n_{j-\sigma})c_{j\sigma} + \mathrm{H.c.}], \quad (1)$$

where J and t are effective parameters corresponding to the magnetic coupling constant, which governs the coupling of the spin moments on the Cu magnetic sites within the CuO_2 plane, and the hopping integral, which takes into account the transfer of one electron between these magnetic centers, also within the CuO_2 plane. This simple model, or extensions including longer range interactions within the plane,[9,10] is thought to incorporate the basic physics governing the properties of these compounds in the normal and superconductor states since doping is effectively introduced through the hopping integral.[11–13] Unfortunately, t cannot be directly measured and accurate values of J can only be obtained through sophisticated neutron scattering experiments. Hence, suitable estimates of t and J have been obtained empirically from fitting to a given theoretical model.[14] Recently, it has been shown that *ab initio* calculations on suitably embedded cluster models provide results of accuracy comparable to experiment.[15,16] It is worth pointing out that similar models and methods were used earlier on to estimate effective parameters in the simple monolayered materials, mostly in La_2CuO_4.[17–22] All these works employed a two center cluster model embedded in point charges. However, while Chen and Goodard[17] and Martin[18,19] used limited configuration interaction wave-function based methods, Hybertsen *et al.*[20–22] relied on the LDA method. However, it is nowadays well established that both LDA and GGA fail to describe these strongly correlated systems.[23–25] More recently, it has been shown that improving the embedding of these cluster models and using sophisticated configuration-interaction techniques for the calculation of energy differences provide an accurate description of the local electronic structure parameters of these systems[26–28] and, in particular, for cuprates.[29,30] In addition, *ab initio t* and J values for a large series of monolayered cuprate superconductors have been recently reported and a linear relationship between the J/t rate and T_c has been observed.[16]

Monolayered superconducting cuprates permit one to focus on models based on a single CuO_2 plane. However, one must realize that multilayered cuprates (those having more than one CuO_2 plane per unit cell) exhibit much higher values of T_c. For instance, $YBa_2Cu_3O_{6+x}$ contains two CuO_2 planes and the $T_c = 92$ K;[31] higher than that exhibited by most monolayered compounds. The influence of the extra planes appears in a natural way in the Hg family of cuprates.

The two-layered $HgBa_2CaCu_2O_{6+x}$ has $T_c=128$ K, considerably higher than the monolayered $HgBa_2CuO_{4+x}$ counterpart for which $T_c=97$ K.[32] A slightly higher value of T_c appears for the trilayered $HgBa_2Ca_2Cu_3O_{8+x}$ compound [$T_c=133$ K at ambient pressure and $T_c=164$ K under pressures of around 30 Gpa (Ref. 33)]. Unfortunately, the increase of T_c with the number of CuO_2 planes is not monotonous.[34]

The summary of experimental data above strongly suggests that *t-J* model for superconducting cuprates should be extended also to include the corresponding interaction terms between planes ($J_\perp$ and $t_\perp$). While important steps on that direction have been carried out in the past few years,[35–37] the problem of finding out reliable parameters for the corresponding model Hamiltonian still remains. The purpose of this paper to extend our previous work to multilayered cuprates providing accurate $J_\perp$ and $t_\perp$ values for several multilayered cuprates and to investigate the possible influence of these parameters on the higher T_c exhibited by these materials relative to most of the monolayered cuprates. Hence, $YBa_2Cu_3O_6$, $HgBa_2CaCu_2O_6$, $LaBa_2CaCu_2O_6$ have been chosen as representative of two-layered cuprates and $HgBa_2Ca_2Cu_3O_8$ as a paragon of the three-layered cuprates.

Accurate *ab initio* configuration interaction based calculations have been carried out for a number of embedded cluster models representing in-plane and inter-plane interaction paths. The embedded cluster models have been constructed using the procedure outlined in various previous papers.[15,16] This approach has been shown to be able to reproduce all available experimental data for magnetic coupling constants on high-T_c parent compounds. Moreover, the suitability of the present cluster model approach is doubly checked by comparing to periodic calculations carried out at the same level of theory. This is using the same approximate Hamiltonian (unrestricted Hartree Fock or UHF) and using a similar basis set to develop the atomic orbitals necessary to construct the *N*-electron wave function. In the latter case, *J* is obtained from broken symmetry solutions using the appropriate mapping approach.[38–40] The experimental crystal structure of the materials has been considered in all calculations (cluster and periodic) and this constitutes the only input data external to theory. Two types of electrically neutral cluster models have been used in this work, one for the interactions inside the CuO_2 planes and one for the interactions between planes. The cluster model for the first case consists of two copper centers linked by a bridging oxygen atom, and the remaining three next neighbor oxygen atoms of each copper center. The cations and other Cu ions surrounding this basic unit are represented by total ionic potentials (TIP) and the resulting model is further embedded in an array of point charges (PC) which reproduce the Madelung potential in the central region of the model (for additional details, see Ref. 16); this gives rise to a Cu_2O_7+TIPs+PCs model. The second cluster model is similar to the previous one but the two copper centers belong to two adjacent CuO_2 planes. The metal centers are surrounded by the four oxygen in-plane atoms coordinated to each Cu and the two planes are linked by four bridging cations. Notice that in these clusters the cations placed between the two CuO_2 planes are explicitly included. Hence, the resulting cluster models are $Cu_2O_8M_4$ +TIPs+PCs where $M=$Y for $YBa_2Cu_3O_6$, and $M=$Ca for $HgBa_2CaCu_2O_6$, $HgBa_2Ca_2Cu_3O_8$, and $LaBa_2CaCu_2O_6$.

The effective parameters of the extended *t-J* Hamiltonian ($t, J, t_\perp, J_\perp$) are obtained from the suitable energy differences of low lying electronic states and following the procedure outlined at length in previous work.[16] For the calculation of *t* and *J*, the atomic orbitals are linear combinations of contracted Gaussian type orbitals, GTO and the atomic cores have been represented by relativistic effective core potentials (ECP). The GTO basis sets for Cu is an unsegmented $[4s,3p,3d]$ contraction of a $(5s,5p,5d)$ primitive set, a $[2s,2p]$ contraction of the $(6s,6p)$ primitive set was used for the cluster edge oxygens and an all electron $[4s,3p,1d]$ contraction was used for the bridging oxygen. For the calculation of $t_\perp$ and $J_\perp$, the basis set for the Cu centers and the outermost O atoms is the same as for *t* and *J*, whereas an all electron basis has been used for Ca and a small core ECP for Y. The electronic states of interest are pure spin states represented by appropriate configuration interaction expansions with the Slater determinants built up from the molecular orbitals described as a linear combination of the above described basis sets which in turn are obtained from an initial self-consistent field calculation on the triplet state. In some cases it is not possible to obtain the effective parameters from energy differences only and one needs to rely on effective Hamiltonian theory.[41] However, for the set of parameters of interest in this work this is not the case. In fact, it is straightforward to proof that for a system with two magnetic centers with spins with total spin quantum number $S_i=1/2$, as in the case of the superconducting cuprates, the magnetic coupling constant is simply the energy difference between the singlet (S) and triplet (T) spin states of the corresponding embedded Cu_2O_7 or $Cu_2O_8M_4$ cluster models. These spin stated arise from the coupling of the local doublet spin state of each site:

$$J = E(S) - E(T). \tag{2}$$

Recent systematic work using a variety of basis sets and core effective potentials has shown that the *J* values computed using this approach are within the experimental range.[42] In a similar way, the hopping integral, which represents the electronic coupling between the diabatic states corresponding to those having one hole localized on one magnetic site (i.e., right or left), is just the off-diagonal element of the matrix representation of the Hamiltonian in the basis of these two configurations. For cluster models with inversion center, one can use a delocalized orbital and it is easy to show that[43]

$$t = -\frac{1}{2}\{E(g)\text{-}E(u)\}. \tag{3}$$

However, for the $t_\perp$ of $HgBa_2Ca_2Cu_3O_8$ it is not possible to design a cluster with this symmetry and Eq. (3) cannot be used. This parameter has been obtained using effective Hamiltonian formalism as specified in Ref. 41.

TABLE I. In-plane (J) and interplane ($J_\perp$) magnetic coupling constants (in meV) of $YBa_2Cu_3O_6$ and $LaBa_2CaCu_2O_6$ predicted by cluster and periodic approaches and within the UHF method. The minus sign indicates antiferromagnetic order.

	Periodic		Embedded cluster	
	J	$J_\perp$	J	$J_\perp$
$YBa_2Cu_3O_6$	−28.2	−0.5	−35.0	−0.7
$LaBa_2CaCu_2O_6$	−33.6	−0.2	−37.5	−0.1

To further validate the embedded cluster model approach used in this work to extract the effective parameters of an extended *t-J* model UHF broken symmetry calculations have been carried out for the cluster model and compared to those obtained for a periodic model using also a suitable GTO basis set (Table I). The values predicted by both models are almost the same as consistently found for other ionic compounds;[16,38] the small differences being due to the use of slightly different Gaussian basis sets in the periodic and embedded cluster calculations. However, one must advert that the UHF values are by far too small because of the lack of dynamic electron correlation effects.[15,16] Calculated magnetic coupling constants which are in the experimental interval are obtained when the energy difference in Eq. (2) is obtained from difference dedicated configuration interaction (DDCI) calculations.[15,16,42] The DDCI values for the magnetic coupling constants together with those for the hopping integrals are collected in Table II. For $YBa_2Cu_3O_6$ accurate experimental values exist for both J and $J_\perp$. Shamoto *et al.* reported $J=-120\pm20$ meV,[44] whereas Millis and Monien reported $J_\perp=-14$ meV.[37] Both values are well reproduced by the present DCCI embedded cluster calculations. This is in agreement with the trend already found for other cuprates.[16]

The good agreement between predicted and experimental values for J and $J_\perp$ in $YBa_2Cu_3O_6$ reinforces the predictive character of the present *ab initio* calculations and permits one to claim that the remaining effective parameters are realistic. Several conclusions emerge from the analysis of the values on Table II. First, the magnitude of the interplane parameters is significant and should be taken into account in any realistic model of high-T_c superconductivity in multilayered cuprates. Notice that, as a first approach, one gets

TABLE II. Effective parameters (in meV) of an extended *t-J* Hamiltonian for several two-layered high-T_c superconducting cuprates. For $HgBa_2Ca_2Cu_3O_8$ two different values of t and J are given since this compound has two different types of Cu-O planes per cell: the central symmetric (top values) and the two other ones (bottom values).

	t	J	$t_\perp$	$J_\perp$	T_c
$YBa_2Cu_3O_6$	−551	−142	−121	−14	92
$HgBa_2CaCu_2O_6$	−580	−154	−59	−3	128
$HgBa_2Ca_2Cu_3O_8$	−590 −650	−165 −155	−62	−2	133
$LaBa_2CaCu_2O_6$	−558	−143	−91	−4	60

$J_\perp \leqslant 0.1$ J which, for $YBa_2Cu_3O_6$ is in full agreement with the measurements of Millis and Monien.[37] However, it is important to realize that for the other three cuprates $J_\perp$ is found to be substantially smaller than 0.1 J. On the other hand, the $t_\perp \approx 0.25\ t$ relationship indicates a possible cooperative mechanism between the two neighbor CuO_2 planes. However, from the Mermin-Wagner theorem[45] it follows that, to provide a realistic three dimensional model to estimate T_c, this *t-J* model must be complemented with terms between CuO_2 planes in different unit cells. Unfortunately, the calculation of these parameters is not so straightforward because the interaction path is not as clear as in the in-plane or interplane parameters thus making it difficult to define the appropriate cluster model and, also due to the fact that it is likely that the interactions are so small that are within the limit of numerical accuracy of the present approach. Nevertheless, the present results provide additional data for a possible relation between the calculated electronic structure parameters and the increased T_c of the multilayered compounds. However, one could expect that the interaction parameters between layers of different crystal cells are small and similar for all the structures and, hence, one can assume that the nature of the superconducting phase is dominated by stronger interactions. In this sense, the different relative values of J, t, $J_\perp$, and $t_\perp$ parameters for the systems studied in this work may offer some alternative clues about their relative T_c values. As a first observation, note that the in-plane J values correlate with the critical temperature as already suggested in previous work.[15] However, a closer inspection to results in Table II shows that the predicted t and J values for $YBa_2Cu_3O_6$ are very similar to those of $LaBa_2CaCu_2O_6$ and yet the T_c values for these two compounds are significantly different; $T_c=92$ K (Ref. 31) for the former and $T_c=60$ K for the latter.[46] Therefore, the present results suggest that that the difference in T_c cannot be explained by a simple *t-J* model. Moreover, the fact that $J_\perp$ for $YBa_2Cu_3O_6$ is near four times larger than for $LaBa_2CaCu_2O_6$ together with the evidence that T_c grows with J (Ref. 15) seems to indicate that the interplane coupling may be related to observed differences. This supposition is also supported by the results obtained for the two- and trilayered Hg-containing cuprates. Both, two and trilayered Hg-containing cuprates exhibit similar t and J parameters and also similar $t_\perp$ and $J_\perp$ values. This is fully consistent with T_c values for these two compounds which differ by less than 4%. This small difference can be attributed to the simultaneous presence of more interplane interactions. However, for the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ family, notice that the optimum T_c experimental values decrease for the $n>3$.[34]

To summarize, accurate *ab initio* values for the parameters of an extended *t-J* Hamiltonian are reported for four superconducting cuprates having two or three nearby CuO_2 planes in the unit cell. The magnitude of interplane parameters is rather large and hence need to be considered in realistic models of high-T_c superconductivity in multilayered cuprates. From the present results it is also possible to argue that cuprates with similar in-plane t and J values may exhibit large difference in T_c depending on the magnitude of the interplane $t_\perp$ and $J_\perp$ effective parameters. Finally, it is hoped

that the present *ab initio* parameters for an extended *t-J* Hamiltonian may be used to better understand some of the special features appearing in the magnetic and optical spectra of bi- or trilayered cuprates which, with the present *t-J* models for monolayered cuprates, are explained as anomalies.[35–37,47]

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