

## Role of dynamical polarization of the ligand-to-metal charge transfer excitations in *ab initio* determination of effective exchange parameters

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The role of the bridging ligand on the effective Heisenberg coupling parameters is analyzed in detail. This analysis strongly suggests that the ligand-to-metal charge transfer excitations are responsible for a large part of the final value of the magnetic coupling constant. This permits us to suggest a variant of the difference dedicated configuration interaction (DDCI) method, presently one of the most accurate and reliable for the evaluation of magnetic effective interactions. This method treats the bridging ligand orbitals mediating the interaction at the same level than the magnetic orbitals and preserves the high quality of the DDCI results while being much less computationally demanding. The numerical accuracy of the new approach is illustrated on various systems with one or two magnetic electrons per magnetic center. The fact that accurate results can be obtained using a rather reduced configuration interaction space opens the possibility to study more complex systems with many magnetic centers and/or many electrons per center.

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### I. INTRODUCTION

Strongly correlated systems have attracted a lot of attention in the last decade. Indeed, chemists have synthesized a large number of materials and new families of molecular systems which present unusual and fascinating properties directly related to the strongly correlated character of their electronic structure. One can cite as examples the high- $T_c$  superconducting copper oxides,<sup>1</sup> colossal magnetoresistant manganite oxides,<sup>2</sup> photomagnetic polycyanides molecules<sup>3</sup> and materials,<sup>4</sup> molecular magnets,<sup>5</sup> etc.

In all these materials a few electrons (per unit cell) are responsible for their spectacular properties. These electrons are usually unpaired and localized both spatially and energetically near the Fermi level (from now on we will refer to them as magnetically active electrons). Consequently, the electronic wave function of these systems is essentially multiconfigurational and cannot be correctly treated by single-reference based methods such as Hartree-Fock plus perturbation theory or even density functional theory.<sup>6</sup> The description and rationalization of the physical properties of these systems is usually carried out in terms of effective valence-bond (VB) type Hamiltonians describing the interactions between the above defined magnetically active electrons.<sup>7,8</sup> Among the most widely used effective models we quote the Heisenberg<sup>9</sup> model — which describes the effective exchange between unpaired electrons — or the  $t-J$ <sup>10</sup> model — which treats in addition to the exchange phenomenon the hole or electron hopping. Clearly, properties such as the metallic versus insulating character of a given compound, the total magnetization or the magnetic order, depend on the relative amplitudes of the different effective integrals. Therefore, it is of crucial importance to be able to quantify the different effective terms of these models. Unfortunately, experimental data are often unable to determine these effective parameters and, for this purpose, it is necessary to rely on

accurate *ab initio* quantum-chemical calculations.<sup>11</sup>

Here, it is worth to mention that in the recent years a large amount of the quantum chemical calculations has been carried out within the framework of density functional theory (DFT). However, it is well known that these methods badly fail in the treatment of such strongly correlated systems. For instance, DFT fails even to predict the insulating character of NiO.<sup>12</sup> Also, one needs to recall that DFT methods tend to largely overestimate the singlet triplet local excitation energy associated with the magnetic coupling in the high- $T_c$  cuprate superconductors.<sup>13</sup> For the  $\text{La}_2\text{CuO}_4$  compound, the local density approximation (LDA) estimates of the local magnetic exchange range from 600 to 800 meV according to the functional used. The experimental measurements<sup>14</sup> yield  $135 \pm 6$  meV. For such problems it is therefore necessary to rely on wave-function, multireference, *ab initio*, spectroscopy methods such as the difference dedicated configurations interaction<sup>15</sup> (DDCI) which has proved to be able to quantitatively reproduce the magnetic coupling constant of a large family of magnetic systems.<sup>11</sup> The DDCI method uses a configurations interaction expansion of the electronic wave function which is specially designed for the calculation of excitation energies involving essentially open-shell states. This configuration interaction (CI) method is based on the choice of the so-called valence complete active space (CAS), on which a CI expansion is constructed including all possible Slater determinants belonging to the CAS, plus a selection of the single and double excitations out the CAS determinants. This selection is done in order to eliminate from the Hamiltonian matrix all configurations that do not contribute to the considered energy difference at the second order of perturbation theory, that is all double excitations from two inactive orbitals toward two virtual ones.

The DDCI based approaches have been proved to yield very accurate results for the calculation of excitation energies

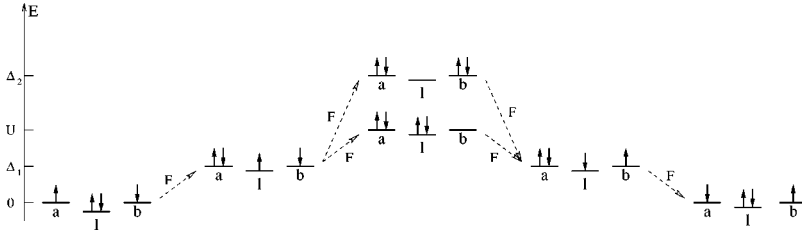


FIG. 1. Through-bridge effective exchange mechanism.

in magnetic systems, both for molecular spectroscopy and local excitations in solids. On top of the results already mentioned,<sup>11</sup> one can cite the remarkable accuracy of the calculation of the singlet-triplet excitation energy in oxalato-bridged Cu(II) binuclear complexes, where the error of the DDCI method is smaller than  $5 \text{ cm}^{-1}$  compared to the experimental data,<sup>16</sup> the prediction of the magnetic exchange in superconductor copper oxides,<sup>17</sup> or the on-rung doublet-doublet excitation on the famous  $\alpha'$ - $\text{NaV}_2\text{O}_5$ .<sup>18</sup>

While the DDCI method offers the possibility of accurate determinations of effective parameters for strongly correlated systems it has a rather serious drawback. This is the dimension of the Hamiltonian matrix to be diagonalized with a concomitant huge numerical cost. This problem may even render the calculation unfeasible for systems with too many open shells arising from several magnetic atoms, several open-shell orbitals per center or too large ligands. Indeed, the dimension of the CI space scales as  $n_{\text{CAS}} \times n_{\text{norb}}^2 \times n_{\text{occ}}$  where  $n_{\text{CAS}}$  is the number of determinants in the complete active space, CAS, used as reference space,  $n_{\text{norb}}$  and  $n_{\text{occ}}$  refer, respectively, to the total number of orbitals and the number of inactive orbitals. It would therefore be highly desirable to determine the key contributions to the energy difference within the DDCI space and hence be able to restrict the diagonalization space to these configurations without significant loss of accuracy. It is clear that such an analysis may be system-type and excitation-type dependent. Nevertheless, a detailed analysis of the different physical contributions strongly suggests that some general rules exist. In this paper we will describe these rules by examining the magnetic coupling parameters of various bridged bimetallic systems, either molecular or embedded cluster models of magnetic materials with localized magnetic moments.

The next section analyzes the physics of the through-bridge effective magnetic exchange related to the singlet-triplet excitation. In view of this analysis, Sec. III describes the physical content of the DDCI wave function, as well as some simplified versions such as DDCI2 and CAS+single and proposes an alternative method to DDCI. Section IV proposes a numerical criterion for the selection of the pertinent ligand orbitals to be included in the alternative method and will present a systematic numerical study of both methods on a series of copper- and nickel-based compounds. Finally Sec. V reports the conclusions and perspectives.

## II. ON THE BRIDGING LIGAND ROLE

The locality of the effective magnetic exchange integrals has been largely discussed in the literature.<sup>7,19,20</sup> It has been shown, both theoretically and numerically, that it can be de-

scribed within a system fragment involving only (i) the two centers supporting the magnetically active electrons (from now on denoted as the magnetic centers), (ii) the bridging ligands, and (iii) the first shell of neighboring closed-shell chemical entities responsible for the screening of the interaction. It is clear that for an analysis of the interactions within the valence shell, only the magnetic centers, associated with their magnetic orbitals supporting the magnetically active electrons, and the bridging ligands need to be considered.

Let us first suppose that each magnetic center supports one unpaired electron. The effective exchange  $\mathcal{J}_{ab}$  between these magnetically active electrons can be analyzed using quasi-degenerated perturbation theory.<sup>8,21</sup> The magnetically active electrons being strongly correlated the most natural model space is composed of the two neutral determinants  $|\Pi_i \varphi_i^2 a \bar{b}\rangle$  and  $|\Pi_i \varphi_i^2 b \bar{a}\rangle$ , where  $a$  and  $b$  are the two magnetic orbitals, respectively, associated with the two magnetic centers  $A$  and  $B$ , and  $\varphi_i$  stands for any of the doubly occupied orbitals. Clearly, the strongly correlated character of this problem necessitates that correlation effects be accounted for in the zeroth-order Hamiltonian, while the delocalization can be described in the perturbative part. For this reason we will assume an Epstein-Nesbet<sup>22</sup> partition of the Hamiltonian and a zeroth-order wave function written in terms of the localized above cited determinants. In addition, the two magnetic centers, being bridged by closed-shell ligands, are separated by a rather large distance. Therefore, the direct interaction between them, such as the direct exchange integral  $K_{ab}$  and the through-space hopping integral  $t_{ab}$  can be considered as negligible in front of the through-bridge interactions. As a consequence the through-space Anderson's superexchange mechanism, that scales as  $4t_{ab}^2/U$  is negligible in such bridged systems. We will consequently consider only the through-bridge interactions in the forthcoming analysis. The leading term of the effective exchange integral thus results from the fourth perturbative order (see Fig. 1) and can be expressed as a function of a bridging-ligand orbital  $l$

$$\mathcal{J}_{ab} = -2 \frac{(F_{al}^{(a)})^2 (F_{al}^{(l)})^2}{(\Delta_1)^2 U} - 4 \frac{(F_{al}^{(a)})^2 (F_{al}^{(b)})^2}{(\Delta_1)^2 \Delta_2}, \quad (1)$$

where  $F$  stands for the appropriate Fock operator and  $H$  for the Hamiltonian. If  $C$  symbolizes the remaining doubly occupied orbitals ( $\Pi_{i \neq l} \varphi_i^2$ ) and  $a$  and  $b$  are supposed symmetry related, one has

$$F_{al}^{(a)} = \langle C a l \bar{l} b | F | C a l \bar{a} b \rangle,$$

$$F_{al}^{(l)} = \langle Cb\bar{b}l\bar{l} | F | Cb\bar{b}l\bar{a} \rangle,$$

$$F_{al}^{(b)} = \langle Cb\bar{b}a\bar{l} | F | Cb\bar{b}a\bar{a} \rangle,$$

$$\Delta_1 = \langle Ca\bar{a}l\bar{b} | H | Ca\bar{a}l\bar{b} \rangle - \langle Cal\bar{b} | H | Cal\bar{b} \rangle,$$

$$U = \langle Ca\bar{a}l\bar{l} | H | Ca\bar{a}l\bar{l} \rangle - \langle Cal\bar{b} | H | Cal\bar{b} \rangle,$$

$$\Delta_2 = \langle Ca\bar{a}b\bar{b} | H | Ca\bar{a}b\bar{b} \rangle - \langle Cal\bar{b} | H | Cal\bar{b} \rangle.$$

In the case of  $S=1$  atoms, such as  $Ni^{2+}$ , the two (quasi-)degenerated  $e_g$ -like orbitals support two ferromagnetically coupled unpaired electrons. The exchange integral then involves the  $|S_z(A)=1; S_z(B)=0\rangle$  and  $|S_z(A)=0; S_z(B)=1\rangle$  configurations. In this case two ligand orbitals have to be involved, respectively coupling the two types of  $e_g$  orbitals [let us say  $e_g(1)$  and  $e_g(2)$ ]. It can be simply shown that (i) the effective exchange integral is still equal to the singlet triplet excitation energy, (ii) the above mechanism is still valid for each of the  $e_g$  orbitals, and (iii) the total exchange can be expressed as  $\mathcal{J}_{ab} = 1/2 \mathcal{J}_{ab}[e_g(1)] + 1/2 \mathcal{J}_{ab}[e_g(2)]$ .

From the above expressions it results that the first order correction to the singlet  $|\psi_0(Sg)\rangle = (|Cl^2a\bar{b}\rangle + |Cl^2b\bar{a}\rangle)/\sqrt{2}$  state is due to the ligand to metal charge transfer configurations, the second order correction resulting from the double ligand-to-metal charge-transfer and the metal-to-metal charge transfer configurations. These first and second order corrections are highly related to the perturbative evaluation of the above effective exchange since

$$\begin{aligned} |\psi_1(Sg)\rangle &= -\sqrt{2} \frac{F_{al}^{(al)}}{\Delta_1} \frac{|Ca^2l\bar{b}\rangle + |Ca^2b\bar{l}\rangle + |Cb^2l\bar{a}\rangle + |Cb^2a\bar{l}\rangle}{2}, \\ |\psi_2(Sg)\rangle &= -2 \frac{F_{al}^{(al)} F_{al}^{(l)}}{\Delta_1 U} \frac{|Cl^2a^2\rangle + |Cl^2b^2\rangle}{\sqrt{2}} \\ &\quad - 2\sqrt{2} \frac{F_{al}^{(al)} F_{al}^{(b)}}{\Delta_1 \Delta_2} |Ca^2b^2\rangle. \end{aligned}$$

The quality of the description of the effective exchange  $\mathcal{J}_{ab}$  will therefore be conditioned by the numerical accuracy of the above effective first and then second order wavefunction coefficients. It is well known that renormalization of these coefficients due to the dynamical polarization and correlation effects are dominated by the screening effects; this is the dynamical repolarization of the different above configurations.<sup>23</sup> One can therefore expect that the dynamical repolarization of ligand-to-metal charge-transfer configurations will be crucial for the accuracy of the effective exchange.

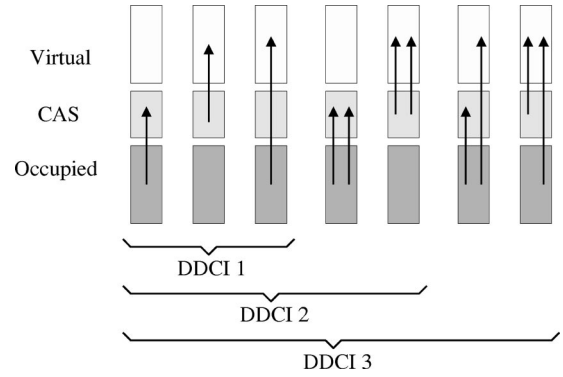


FIG. 2. Schematic representation of the DDCI1, DDCI2, and DDCI3 or DDCI configurations.

### III. ON THE DYNAMICAL REPOLARIZATION OF THE LIGAND-TO-METAL CHARGE-TRANSFER CONFIGURATIONS

The difference dedicated configurations interaction method have been very successful in accurately predicting the effective magnetic exchange integrals. In order to propose a computationally less demanding but equally accurate method, it is of great interest to analyze how the above cited ligand-to-metal charge-transfer and how their corresponding dynamical polarization contributions are accounted for in the DDCI method.

Let us now briefly recall the main principles of the DDCI or DDCI3 and of the DDCI1 and DDCI2 simplified versions. The DDCI starts from a multireference configuration interaction (CI) wave functions containing all single and double excitations that can be constructed from all determinants defining a minimal complete active space (CAS). This minimal CAS does only contains the magnetically active orbitals and electrons and therefore while it includes the superexchange mechanisms it does not account for the through bridge interactions. The DDCI method is based on the restriction of the CI space to all single and double excitations on the CAS determinants which do contribute to the effective exchange integral (or equivalently singlet-triplet excitation energy) at the second order of perturbation (see Fig. 2).

The DDCI (often referred to as DDCI3) space therefore include all double-excitations on the CAS determinants — complemented by the necessary determinants to have spin- and symmetry-adapted configurations — except the two hole two-particle determinants. Hence, the double excitations from two doubly occupied orbitals toward two virtual ones are not included in the DDCI space. The DDCI2 space excludes in addition all two-hole one-particle and one-particle two-hole excitations (see Fig. 2). Finally the DDCI1 space is the configuration space of all single excitations on the CAS — of course, again completed for spin and space symmetry. One immediately sees that the reference determinants involved in  $|\Psi_0(Sg)\rangle$  and  $|\Psi_0(Tp)\rangle$  are included in the CAS, as well as the metal ionic configurations. The ligand-to-metal charge transfer configurations already appear in the DDCI1 space, while the double ligand-to-metal charge transfers appear in the DDCI2 space. The dynamical polarization effects on these configurations correspond precisely to the single

TABLE I. DDCI2 versus DDCI3 evaluation of the effective exchange integrals between copper or nickel atoms (in meV). In the copper compounds the exchange integral as been computed as the singlet-triplet local excitation energy, while for the nickel compounds, due to the spin 1 character of the nickel atoms, the exchange integral has been computed both from the triplet-quintet excitation energy (first line) and from the singlet-triplet excitation energy (second line). It can be noted that both methods yield equivalent results.

| Compound                                         | DDCI1 | DDCI2  | DDCI3  | Exp.     |
|--------------------------------------------------|-------|--------|--------|----------|
| La <sub>2</sub> CuO <sub>4</sub>                 | -91.1 | -96.3  | -145.5 | -135 ± 5 |
| Hg Ba <sub>2</sub> Cu O <sub>4</sub>             | -87.3 | -92.5  | -153.7 |          |
| Sr <sub>2</sub> CuO <sub>2</sub> Cl <sub>2</sub> | -69.3 | -73.3  | -131.0 | -125     |
| Tl Ba <sub>2</sub> Cu O <sub>5</sub>             | -95.6 | -101.4 | -166.7 |          |
| K Ni F <sub>3</sub>                              | -5.09 | -5.38  | -6.82  | -8.2     |
|                                                  | -5.03 | -5.30  | -6.64  |          |
| K <sub>2</sub> Ni F <sub>4</sub>                 | -5.52 | -5.84  | -7.34  | -8.6     |
|                                                  | -5.46 | -5.76  | -7.18  |          |

<sup>a</sup>See Ref. 24.

<sup>b</sup>See Ref. 25.

<sup>c</sup>See Ref. 26.

<sup>d</sup>See Ref. 27.

excitations. Therefore these effects enter at the DDCI1 level for the reference determinants as well as for the metal ionic determinants. The dynamical polarization of the ligand-to-metal charge-transfer configurations are spread over the DDCI1, DDCI2, and DDCI3 (the most numerous) spaces (see Appendix B). Finally, the dynamical polarization of the double ligand-to-metal charge-transfer configurations are not taken into account in the DDCI space. The very good results of the DDCI method, despite the lack of the double transfers screening effects, can be attributed to the fact that these double transfers have usually a negligible contribution to the effective exchange process (their weight is, for instance, smaller than  $2.1 \times 10^{-2}$  in the triplet or singlet wave function in the case of the copper oxide compounds).

Table I details the effective exchange integral on a few copper oxide and nickel fluoride systems as computed using the DDCI2 and DDCI3 methods (see Appendix A for computational details). The difference between the DDCI2 and DDCI3 results range between 30 to 40% of the nominal value of the exchange integral on the copper oxides and around 20% on the nickel fluorides. These large differences are in agreement with the above analysis on the crucial role of the ligand-to-metal charge-transfer repolarization which largest contributions are treated at the DDCI3 level only (see Appendix B).

One can therefore suggest to include the ligand-to-metal charge-transfer configurations already in the CAS. This is simply achieved by adding the bridging ligand orbital to the CAS. In this way the repolarization of the ligand-to-metal charge transfers configurations as well as the repolarization of the ligand-to-metal double charge transfers would be accounted for at the DDCI1 level.

Looking at the CI space sizes, the size of the DDCI1 space scales as  $n_{\text{CAS}} \times n_{\text{orb}} \times n_{\text{occ}} \times n_{\text{virt}}$ , while the DDCI space

TABLE II.  $10^3$  the square of the overlap between the atomic  $3d$  orbital of the magnetic atoms as specified in the second column and the first doubly-occupied orbitals below the Fermi level. Only orbitals belonging to the same irreducible representation as the magnetically active orbitals, namely,  $a_g$  and  $b_{2u}$ , have been considered. The orbitals are ordered in increasing energetic order from left to right within each irreducible representation.

| Compound                                         | AO            | Overlap square $\times 10^3$ |           |           |   |                 |           |           |               |
|--------------------------------------------------|---------------|------------------------------|-----------|-----------|---|-----------------|-----------|-----------|---------------|
|                                                  |               | $a_g$ irrep.                 |           |           |   | $b_{2u}$ irrep. |           |           |               |
| La <sub>2</sub> CuO <sub>4</sub>                 | $d_{x^2-y^2}$ | 1                            | <b>18</b> | 3         | 2 | 1               | <b>31</b> | 1         |               |
| Hg Ba <sub>2</sub> Cu O <sub>4</sub>             | $d_{x^2-y^2}$ | 2                            | <b>28</b> | 3         | 1 | 2               | <b>46</b> | 1         |               |
| Sr <sub>2</sub> CuO <sub>2</sub> Cl <sub>2</sub> | $d_{x^2-y^2}$ | 2                            | <b>23</b> | 4         | 2 | 2               | <b>43</b> | 1         |               |
| Tl Ba <sub>2</sub> CuO <sub>5</sub>              | $d_{x^2-y^2}$ | 5                            | <b>29</b> | 4         | 3 | 19              | <b>41</b> | 0         |               |
| K Ni F <sub>3</sub>                              | $d_{x^2-y^2}$ | 0                            | <b>4</b>  | <b>3</b>  | 1 | 0               | 1         | <b>11</b> | <b>3</b> 0 0  |
|                                                  | $d_{z^2}$     | 0                            | <b>1</b>  | <b>8</b>  | 0 | 0               | 0         | <b>4</b>  | <b>9</b> 0 0  |
| K <sub>2</sub> Ni F <sub>4</sub>                 | $d_{x^2-y^2}$ | 1                            | <b>6</b>  | <b>1</b>  | 0 | 0               | 1         | <b>13</b> | <b>0</b> 0 0  |
|                                                  | $d_{z^2}$     | 0                            | <b>0</b>  | <b>13</b> | 1 | 0               | 1         | <b>0</b>  | <b>17</b> 0 0 |

scales as  $n_{\text{CAS}} \times n_{\text{orb}} \times n_{\text{occ}} \times n_{\text{virt}}$  where  $n_{\text{CAS}}$ ,  $n_{\text{orb}}$  and  $n_{\text{occ}}$  have the same meaning as in the Introduction and  $n_{\text{virt}}$  is the number of virtual orbitals. It immediately follows that in addition to a better treatment of the ligand-to-metal charge transfer excitations, the DDCI1 method built up on an extended CAS will be less computationally demanding despite the increase of the CAS size.

#### IV. RESULTS

The key question is now how to determine a systematic procedure to select, within the doubly occupied orbitals, the pertinent ligand orbital(s) that mediate the effective exchange interactions. This is not an easy task because, although the line of reasoning in the previous section follows a localized orbital scheme, the actual calculations are carried out in a delocalized basis as usual in ab initio calculations.

In the DDCI procedure the orbitals are usually defined using a minimal CASSCF procedure for the high spin state. We will stick on this point and extract from the minimal CAS inactive orbitals the pertinent ligand ones. The magnetically active orbitals are essentially of atomic nature ( $nd$  orbitals of the metal atoms) and thus the ligand orbitals optimally mediating the exchange interaction should (i) exhibit a large overlap with these  $nd$  atomic orbitals [this ensures a large numerator in Eq. (1)], and (ii) be close enough to the Fermi level in order to preserve the perturbative expression [small denominators also in Eq. (1)]. Table II shows the overlap between the copper  $3d_{x^2-y^2}$  (respectively, nickel  $3d_{z^2}$  and  $3d_{x^2-y^2}$ ) atomic orbitals and the highest energy doubly occupied orbitals, those located immediately below the Fermi level.

One immediately notices that in most cases, except for the TlBa<sub>2</sub>Cu O<sub>5</sub> compound, there is one ligand orbital per symmetry that exhibits a non-negligible overlap with each of the considered  $3d$  atomic orbitals. The choice of the bridging ligand orbital to add to the CAS appears thus to be quite unambiguous (two orbitals for the copper compounds and

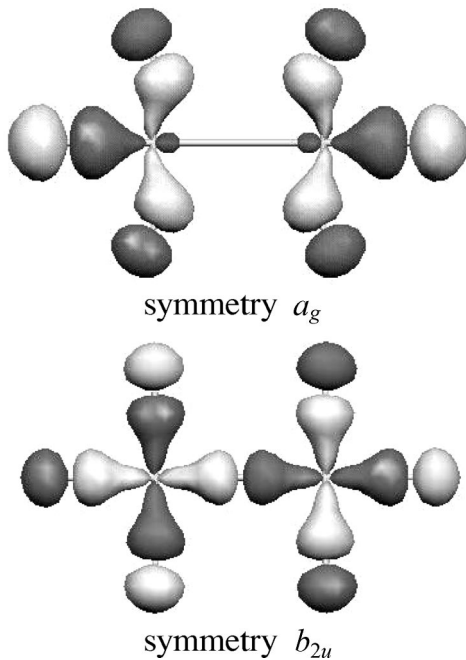


FIG. 3. Ligand orbitals of the copper oxide compounds having a non-negligible overlap with the  $3d$  atomic orbitals of the copper. These orbitals are composed of atomic  $2p$  orbitals of the oxygens, pointing toward the copper atoms

four for the nickel ones). At this point one should notice that, unlike the usual description of the mediated effective exchange, there is not only one bridging orbital that contribute (two for  $S=1$  magnetic atoms) but one per magnetic orbital. For the case of the  $\text{La}_2\text{CuO}_4$  copper oxide compound, these orbitals are represented in Fig. 3. While the  $b_{2u}$  orbital has a large coefficient of the bridging oxygen  $p_x$  orbital, this is not the case for the  $a_g$  orbital that does not have any significant weight on any orbital of the bridging oxygen. Yet, this  $a_g$  orbital has to be considered, since, according to our results, the antiferromagnetism is otherwise strongly overestimated. Indeed, a DDCI2 calculation on the minimal CAS yields an effective exchange integral of  $-86$  meV. The DDCI2 result improves to  $-141$  meV when both ligand  $a_g$  and  $b_{2u}$  orbitals are included in the active space, but deteriorates to  $-196$  meV when solely the ligand  $b_{2u}$  orbital is added and to  $-39$  meV when solely the ligand  $a_g$  orbital is added.

Consequently, DDCI1 calculations have been performed using CAS spaces enlarged to the two ligand orbitals for the copper oxides and the four ligand orbitals for the nickel fluoride (see Appendix A for computational details). Results are reported in Table III and compared with the DDCI3 reference calculations using the minimal CAS.

From the results in Table III, it is clear that DDCI3 using minimal CAS as reference for single and double excitations and the DDCI1 based on the extended CAS reference essentially yield the same results, except for the  $\text{Tl Ba}_2\text{Cu O}_5$  compound. Indeed, in the other copper oxides, the relative error between the two methods is always smaller than 6%, being as weak as 1.3% for the  $\text{Hg Ba}_2\text{Cu O}_4$  compound. These results therefore confirm the previous analysis that the crucial physical effect to be accounted for in the DDCI3

TABLE III. Extended CAS DDCI1 in meV and minimal CAS DDCI3 evaluations of the effective exchange integrals. For the nickel compound the first line corresponds to the effective exchange evaluated from the triplet-quintet excitation energy, while the second line corresponds to the evaluation from the singlet-triplet excitation energy.

| Compound                             | Minimal CAS<br>DDCI 3 | Extended CAS<br>DDCI 1 | Exp.           |
|--------------------------------------|-----------------------|------------------------|----------------|
| $\text{La}_2\text{CuO}_4$            | -145.5                | -148.9                 | $-135.5 \pm 5$ |
| $\text{Hg Ba}_2\text{Cu O}_4$        | -153.7                | -155.8                 |                |
| $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ | -131.0                | -138.7                 | -125           |
| $\text{Tl Ba}_2\text{Cu O}_5$        | -166.7                | -125.2                 |                |
| $\text{K Ni F}_3$                    | -6.82                 | -7.20                  | -8.2           |
|                                      | -6.64                 | -7.08                  |                |
| $\text{K}_2\text{Ni F}_4$            | -7.34                 | -7.62                  | -8.6           |
|                                      | -7.18                 | -7.51                  |                |

wave function is the dynamical repolarization of the ligand-to-metal charge transfer configurations. Nevertheless, it is noticeable that the only case giving lesser quality results is the case for which it was not possible to clearly identify the bridging ligand orbitals.

In the nickel compounds the relative error between the two methods is somewhat larger due to the weakness of the exchange. The absolute error is however only of about half a meV with the DDCI1 results being slightly closer to the experimental values. The improvement can be understood by the fact that the repolarization of the double ligand-to-metal charge transfer is accounted for in the extended-CAS-DDCI1 calculation while it is not in the minimal-CAS-DDCI3 one. It is worth pointing out that in the nickel compounds the fact that four magnetic orbitals and four ligand orbitals are involved increases considerably the number and importance of double ligand-to-metal charge transfer.

## V. CONCLUSION

From a careful analysis of the mechanism of the through-bridge effective exchange interactions between two magnetic atoms, we have shown that one of the crucial effects in the effective exchange mechanism is the ligand to metal charge transfer. From this analysis, it appears that an accurate evaluation of the effective exchange integral (or equivalently of the singlet-triplet excitation energy) requires a proper treatment of the dynamical repolarization on these charge transfer configurations. To this end a method has been proposed for the determination of the bridging ligand orbitals involved in these charge transfer excitations. It is therefore proposed to include these mechanisms already in the zeroth-order wave function. To this end it is enough to include the bridging ligand orbitals in the complete active space (CAS). It is noticeable, that on a rather large series of compounds the evaluation of the effective exchange using the traditional minimal-CAS-DDCI3 method and using the present enlarged-CAS-DDCI1 approach yield almost identical results provided that the bridging ligand orbitals can be determined without ambiguity.

There is a very important practical consequence of the present study. The final dimension of the configuration interaction space in the enlarged-CAS-DDCI1 strategy is considerably smaller than the one corresponding to the traditional minimal-CAS-DDCI3. This permits us to lift the bottleneck encountered in the DDCI method when applied to systems with more magnetic centers or more magnetic orbital and electrons per center, i.e., the very large dimension of the CI space leading to almost intractable diagonalization problems. Indeed, in most systems, the number of single excitations out of the extended CAS are much less numerous than the DDCI space on the minimal CAS. In cases where the double ligand-to-metal charge transfers are non negligible, one can even expect the enlarged-CAS-DDCI1 method to yield better results than the minimal-CAS-DDCI3. Indeed, the repolarization of these double transfer excitations is properly taken into account in the former method while they are totally omitted in the latter.

To conclude, the present study points out the crucial importance of the repolarization of the charge transfer and double charge transfer excitations, in order to accurately determine the effective exchange (or magnetic coupling) constants, and it proposes a simple yet efficient method to include these effects. It is suggested that this new procedure will permit the study of systems with a larger number of magnetic electrons and orbitals such as the technologically relevant  $\text{LaMnO}_3$  related compounds.

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#### APPENDIX A

The  $\text{La}_2\text{CuO}_4$ ,  $\text{HgBa}_2\text{CuO}_4$ ,  $\text{TlBa}_2\text{CuO}_5$ ,  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  compounds are of perovskite geometry. The copper atoms are localized in  $\text{CuO}_2$  planes, responsible for the conduction and supraconduction properties of the systems. These compounds are essentially ionic crystals, the copper being in the  $\text{Cu}^{2+}$  oxidation state with a  $3d^9 4s^0$  configuration. The ligand field splitting results in a magnetic nondegenerated  $3d_{x^2-y^2}$  orbital.

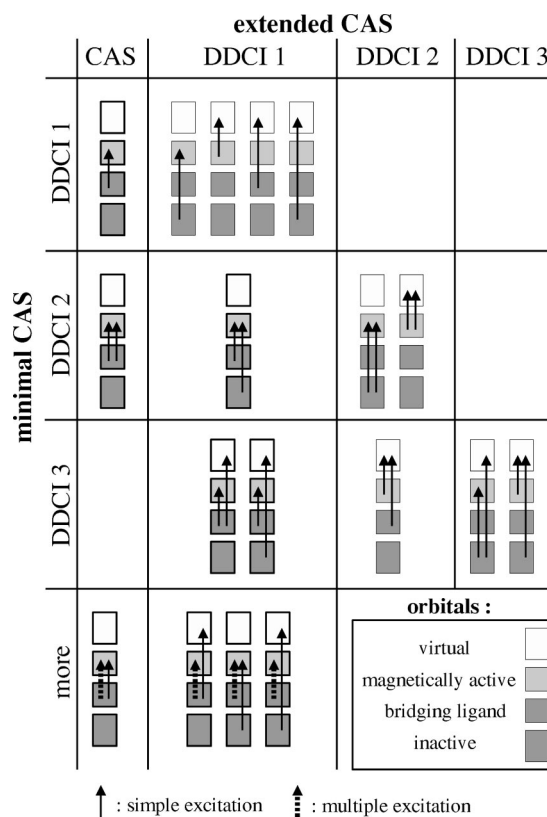


FIG. 4. Decomposition of the enlarged CAS DDCI1, DDCI2, and DDCI3 spaces on their minimal CAS counterparts.

The nickel-based compounds exhibit similar perovskite structure. The nickel atoms exhibit a  $\text{Ni}^{2+}$  oxidation state with a high-spin ( $S=1$ )  $3d^8$  atomic configuration. In this case the magnetic orbitals are the two  $e_g$  orbitals of the  $O_h$  symmetry group.

The geometry of the systems computed here have been extracted from x-ray experimental data.<sup>28</sup> The embedding have been derived in order to account for the major effects of the rest of the crystal on the cluster under consideration, namely the electrostatic potential, the exclusion effects of the electrons of the rest of the crystal on the computed fragment orbitals.

The metal atoms are treated using core pseudo-potentials and valence  $3-\zeta$  quality basis set.<sup>29</sup> The bridging atoms are treated using large ANO basis set<sup>30</sup> and the other ligands using effective core potentials and valence  $3-\zeta$  quality basis set.<sup>31</sup> The CASSCF calculations have been performed using the MOLCAS Version 5.2 package.<sup>32</sup>

#### APPENDIX B

Figure 4 displays the different configurations involved in the enlarged CAS DDCI1, DDCI2, and DDCI3 spaces as a function of the minimal CAS DDCI1, DDCI2, and DDCI3 spaces.

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