

Toward a variational treatment of the magnetic coupling between centers with elevated spin moments

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Abstract

A multireference configuration interaction scheme is presented to calculate electronic structure parameters for systems with an elevated number of unpaired electrons. The paper concentrates on the magnetic coupling but the method can also be applied to other parameters. The reference wave function contains not only the usual configurations contained in the Anderson model but is extended with ligand-to-metal charge transfer configurations. Subsequently a small subset of the complete difference dedicated configuration interaction space is included in the calculation. Different strategies to introduce the charge transfer configurations in the reference wave function are compared. Projected model ligand vectors ensure the optimal inclusion of the charge transfer effects and good agreement with more extensive calculations is obtained at a more reduced computational cost.

Key words: magnetic coupling, *ab initio* calculations, DDCI, spin ladders, high- T_c superconductors, ferrimagnetism

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1 Introduction

The theoretical study of the coupling between localized spin moments in molecules and solids is an emerging field. The constant increase of computer-power and the development of new quantum chemical computational schemes

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allows the (quantum-)chemists to treat larger and more realistic systems with higher accuracy. In the last decade, the density functional theory (DFT) has been widely applied to the study of the magnetic coupling [1–7]. Medium-sized molecules can be treated without the necessity to model any part of the system, such as bulky external ligands. One has, however, to rely on the broken symmetry approach to describe electronic states that cannot be expressed with a single Kohn-Sham determinant [8,9]. Moreover, the mapping of energy expectation values of such symmetry broken states and the eigenvalues of the Heisenberg Hamiltonian is subject of discussion [2,7,10–17].

Alternatively, one can apply wave-function based *ab initio* methodologies. Electronic states with any spin coupling can be defined rigorously and the mapping with the Heisenberg Hamiltonian is unique. Both the difference dedicated configuration interaction (DDCI) [18] and the complete active space second-order perturbation theory (CASPT2) [19,20] have been successfully applied to many systems. Not only, experimental data could be reproduced satisfactorily, but also can one analyze and interpret the magnetic coupling in a direct way [21–34].

The major drawback of the wave-function based methods is the high computational cost in comparison to DFT. DDCI diagonalizes a subset of the multireference singles and doubles CI (MR-SDCI) space. The reduction is based on the understanding that up to second-order quasi-degenerate perturbation theory, the effect of the double excitation from doubly occupied to virtual orbitals cause a uniform shift in the diagonal elements of the CI matrix. Hence, they do not contribute to the energy difference between electronic states and can be left out of the calculation. Since these double excitations are most numerous, the dimension of the DDCI space is largely reduced in comparison to a MR-SDCI calculation. Although total energies lose their meaning and results at different geometries cannot be compared, the method produces very accurate vertical excitation energies. The vast majority of the DDCI studies concerning magnetic systems have been performed for the coupling between two $S=1/2$ magnetic centers. In that case the size of the reference wave function is limited and the treatment of remaining electron correlation effects is straightforward.

The DDCI calculations beyond the $S=1/2$ dimers become more cumbersome. The calculation of the magnetic coupling parameter J between two $S=1$ centers (e.g. in a dinuclear Ni(II) complex) is still possible, but the calculation is rather expensive and external ligands need to be modeled with smaller groups and small basis sets. A further increase of the spin moment or the nuclearity leads to intractable CI expansions.

Because of the perturbational nature of CASPT2, the computational limits for this method are somewhat less rigid. A CASPT2 calculation is still feasible

for a reference wave function constructed with 15 magnetic orbitals and 15 unpaired electrons. This opens the way to an *ab initio* evaluation of the magnetic coupling between elevated spin moments and/or in complexes with more than two magnetic centers. Although, a reference wave function that only includes the magnetic orbitals and unpaired electrons usually gives good estimates of J , it should include part of the ligand to metal charge transfer (LMCT) effects to obtain quantitative agreement with experiment for strongly coupled systems such as copper oxides [35]. Moreover, the method becomes unreliable for couplings smaller than $\sim |8| \text{ cm}^{-1}$ and shows important deviations from the expected Heisenberg splitting between states of different multiplicity in case of elevated spin moments [36].

2 Methodology

From the above discussion, it is clear that an alternative, less expensive strategy is required to extend the applicability of *ab initio* wave function based calculations. One such scheme is based on a further reduction of the determinants in the CI expansion. DDCI2 [37] treats a subset of determinants that imply a change in the occupation of at least two active orbitals [38]. This set of determinants is significantly smaller than the full DDCI set but normally only reproduces about 50% of the experimental coupling. This methodology has been applied for Cr(III) and Ni(II) dimers [39,40] and in the study of the magnetic coupling in $\text{Na}_6\text{Fe}_2\text{S}_6$ [41].

Alternatively, one could reduce the CI expansion by eliminating molecular orbitals (MO's). However, the orbital energies are in general not a good criterion to decide upon the importance of the MO's for the relative energy of the electronic states. Instead, the unitary transformation to dedicated orbitals of the molecular orbitals obtained at a low-level calculation [42] makes it possible to order the orbitals with respect to their contribution to the magnetic coupling and to cut the MO space in a rational way. The computational cost of DDCI is reduced with (almost) no loss of precision down to CI expansions that are only 30% of the complete DDCI space [42].

The importance of LMCT configurations for the magnetic coupling has been recognized in many studies (see Refs [21,24,43–47] and references therein) and is considered as one of the key ingredients of the superexchange. Calzado and co-workers [22] unraveled the relative importance of many more mechanisms in the calculation of J . They classify all determinants external to the CAS by the number of holes (h) in the doubly occupied orbitals and particles (p) in the virtual orbitals with respect to the determinants in the CAS.

It was shown that a CI with the single excitations on top of the CAS (CAS*S)

usually results in $\approx 50\%$ of the full DDCI result. This CAS*S contains the $1h$, the $1p$, and the $1h-1p$ determinants, and hence the LMCT determinants. However the coefficients of these excitations remain rather small. Adding the $2h$ and $2p$ determinants (i. e. the DDCI2 subset) does not significantly affect the results. Hence, it was concluded that the remaining $2h-1p$ and $1h-2p$ determinants play a very important role. Further analysis showed that not all determinants in the latter group contribute equally to J [21]. The most relevant contributions arise from the ligand to metal charge transfer (LMCT) excitations coupled to excitations that account for the polarization of the electron density in reaction to this LMCT process. This polarization increases the weight of the LMCT excitations in the wave function and in general very good agreement with experimental magnetic couplings is obtained for the full DDCI calculation.

By introducing the LMCT determinants in the CAS, the excitations that account for the polarization –i.e. the $2h-1p$ determinants– already appear at the CAS*S level. This observation opens a third possibility to reduce the computational cost of the variational determination of J . This extended CAS*singles method was introduced by Calzado and Malrieu [48,49] in the study of electronic structure parameters in $\text{La}_{(2-x)}\text{Sr}_x\text{CuO}_4$ and recently discussed in more detail by Gellé *et al.* [50]. The central question of the method is the choice of the active space: What ligand orbitals should be included in the active space to obtain the most efficient description of the LMCT process and the polarization of the electron density in response to that? Calzado and Malrieu use the dedicated orbital transformation to identify the most implicated ligand orbitals and add them to the active space. An alternative choice has been presented by Gellé *et al.* Their choice is based on the overlap of the canonical doubly occupied Hartree-Fock orbitals with the atomic basis function that has the highest coefficient in the singly occupied (or magnetic) orbitals of the spin state with highest multiplicity. In both proposals, the active space is extended with as many ligand orbitals as there are magnetic orbitals.

The results of the CI singles calculations with an extended CAS reference wave function (CAS(ext)*S) are certainly encouraging, but several questions remain to be answered. In the first place, the methodology proposed has only been tested for antiferromagnetic interactions in ionic insulators (copper oxides and nickel fluorides) with perovskite structure. No evidence have been presented that the results can be extrapolated to insulators with less symmetric crystal structure or to molecular systems with more complex bridging ligands. Furthermore, it remains unclear from the two previous works why ligand orbitals are added to the active space that do not have any significant contribution from the bridging ligand, but are instead delocalized over the external ligands (see Fig. 4a of Ref. [49] and Fig. 3 of Ref. [50]). This is in contradiction with the usual understanding of the magnetic coupling as a through bridge process where the external ligands only play a minor role.

In the present paper, we will analyze and critically compare the different choices of extending the active space. An orbital transformation will be presented that ensures the optimal inclusion of the LMCT determinants in the active space. Furthermore, we will establish to what extent CAS*S with an extended CAS reference wave function is valid for more complex insulators and molecular complexes. Finally, the method will be applied to estimate the magnetic coupling between centers with elevated spin moments.

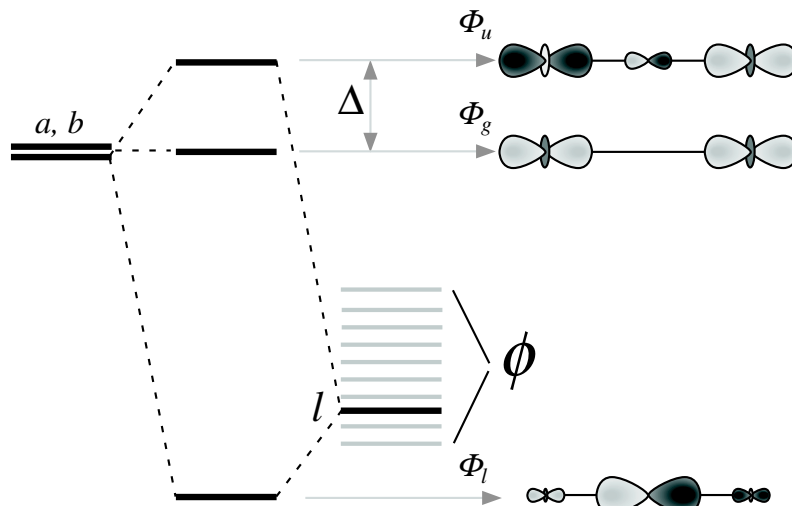


Fig. 1. Molecular orbital diagram showing the interaction between metal centered and ligand-type orbitals. See text for further details.

3 Choice of the ligand orbitals

Figure 1 summarizes schematically the one-electron reasoning of the Anderson model [51] or the Hay-Thibeault-Hoffmann model [52] for antiferromagnetic superexchange. The degenerate orbitals a and b are singly occupied atomic-like orbitals localized on the magnetic centers. On the right side of the diagram, l is one of the ligand orbitals among the whole set of doubly occupied ligand orbitals ϕ . The interaction of l with a and b gives rise to two non-degenerate magnetic orbitals Φ_g and Φ_u and a molecular orbital Φ_l , which is basically localized on the bridging ligand. The splitting Δ between the magnetic orbitals is a measure of the magnetic coupling between the unpaired electrons. To achieve optimal superexchange, l should be localized on the bridge and close in energy to a and b .

The canonical self-consistent field (SCF) orbitals are usually delocalized over the whole system and no guarantee can be given that there exist an orbital

among the doubly occupied that is sufficiently localized on the bridging ligand. Dedicated orbitals are usually determined from a CAS*S calculation with a minimal CAS reference. One of the major effects of such calculations is the drastic reduction of the effective on-site repulsion parameter U , which is a measure of the energy difference between the neutral determinants (n electrons per magnetic site) and the ionic determinants ($n + 1$ or $n - 1$ electrons per magnetic site). Hence, CAS*S dedicated orbitals are actually biased toward the energy lowering of the ionic determinants, which is optimal when orbitals are delocalized over all ligands coordinating the magnetic site and not just the bridging ligands that connect the magnetic sites.

To ensure more control over the shape of the ligand orbital that will be added to the CAS, we perform a unitary transformation of the doubly occupied Hartree-Fock orbitals by the projection of a model vector $|\tilde{l}\rangle$ of pure bridging ligand character onto the inactive space.

$$|l\rangle = \hat{P}|\tilde{l}\rangle = \left[\sum_i^n |i\rangle\langle i| \right] |\tilde{l}\rangle \quad (1)$$

with $|i\rangle$ an inactive canonical Hartree-Fock orbital and n the total number of inactive orbitals. The projected model vector $|l\rangle$ is orthogonal to the active orbitals but not to the inactive orbitals. The inactive orbital with the largest overlap with $|l\rangle$ is eliminated and the remaining orbitals are orthogonalized onto the projected vector by means of the Gram-Schmidt procedure. Afterwards, $|l\rangle$ is added to the active space.

When there are m active orbitals, we construct a maximum of m ligand-type vectors $|\tilde{l}\rangle$ by putting all coefficients in the magnetic orbitals to zero except those corresponding to basis functions centered on the bridging ligand. Only the ligand-type vectors with a norm above a certain threshold are projected onto the inactive space. For example, the ligand-type vector resulting from magnetic orbital Φ_g in Figure 1 does not have any significant contribution from the ligand. By symmetry, only the deep-lying s -type orbital can contribute to this magnetic orbital. However, its contribution is so tiny that the resulting ligand-type vector has a very small norm and is not further concerned.

4 Test calculations

To test the new strategy of constructing the extended CAS reference wave function, J has been calculated for four members of the widely studied perovskite copper oxide family [53,54]. These compounds exhibit large couplings along the linear Cu–O–Cu bonds with marked LMCT effects. The minimal

Table 1

DDCI and CAS(ext)*S magnetic coupling parameters (in meV) of four copper oxides with similar perovskite structure. The last row lists the number of determinants in the CI for the singlet state of $\text{HgBa}_2\text{CuO}_4$.

Compound	DDCI	CAS(ext)*S			Exp.
		Projection	Dedicated	Overlap [50]	
La_2CuO_4	-140	-138	-162	-143	-128 ± 6^a , -134 ± 5^b
$\text{Sr}_2\text{CuO}_2\text{Cl}_2$	-131	-137	-161	-139	-125^c
$\text{TlBa}_2\text{CuO}_5$	-167	-171	-203	-125	
$\text{HgBa}_2\text{CuO}_4$	-159	-155	-196	-154	
Determinants	$5.2 \cdot 10^5$	$1.7 \cdot 10^4$	$3.1 \cdot 10^4$	$3.1 \cdot 10^4$	

^a Ref. [55] ^b Ref. [56] ^c Ref. [57]

active space contains two electrons and two orbitals that transform following the a_g and b_{1u} irreducible representations of the D_{2h} symmetry group. Figure 2 gives a graphical representation of the two active or magnetic orbitals of $\text{HgBa}_2\text{CuO}_4$. These orbitals are representative for the other copper oxide systems.

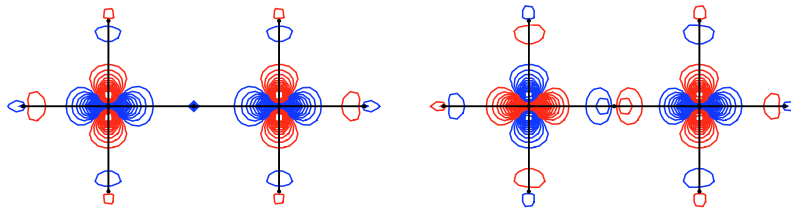


Fig. 2. The a_g (left) and b_{1u} (right) magnetic orbitals for $\text{HgBa}_2\text{CuO}_4$.

DDCI based on such active space accurately reproduces experimental J 's [24,53,54] and will be used as reference data. Table 1 compares the results of CAS(ext)*S calculations with the three different strategies to extend the active space mentioned in the previous section. In the case of extending the active space with the most dedicated orbitals (column 4, Dedicated) or by selecting the ligand orbitals by the overlap criterion (column 5, Overlap), the extended CAS contains four orbitals and six electrons. However, in the new strategy of projection (column 3, Projection), the model vector of a_g symmetry has a very small norm and has been discarded. Hence, the results in column 3 are obtained with an extended CAS of only three orbitals and four electrons.

A first look at Table 1 shows that all J -values calculated with CAS(ext)*S are within 25% of the DDCI value. This is a significant improvement with respect to the CAS*S values based on the minimal active space, which typically

deviate 40-50% from the DDCI values. A closer analysis evidences that the extension of the active space with the most dedicated orbitals systematically overestimates J by about 20%. The Projection and Overlap procedure lead to values in significant better agreement with DDCI, although the CI expansion in the former procedure is smaller. Moreover, the overlap selection criterion is not without shortcomings. The value for $\text{TlBa}_2\text{CuO}_5$ is 25% smaller than the DDCI reference, whereas such deviations are not observed for the projected ligand vectors.

The shape of the projected ligand orbital added to the CAS (see Fig. 3 on the right) has a markedly different character than those added by the other two procedures. The projected orbital of b_{1u} symmetry is highly localized on the bridging oxygen whereas the dedicated and canonical SCF orbitals (see Fig. 4 and 5) are essentially delocalized over the whole cluster. To analyze the apparent contradiction that the addition of different shaped orbitals to the CAS lead to similar magnetic couplings, we performed additional calculations in which either the a_g or b_{1u} ligand orbital is added to the active space. Results are listed in Table 2.

The role of the projected a_g orbital is rather unimportant, which is not unexpected for a deep-lying O-2s orbital. In case of delocalized ligand orbitals, the two orbitals added to the active space act in opposite direction. The a_g orbital introduces strong ferromagnetic interactions and give a J that is much smaller for the minimal CAS. On the contrary, the b_{1u} orbital introduces antiferromagnetic contributions and increases J . For the delocalized b_{1u} orbitals, this effect is largely overestimated and unrealistic J 's are obtained. The fact that good results are obtained with the Overlap selection and reasonable results with dedicated orbitals when both orbitals are added seems to be due to a cancellation of the two effects. Moreover, it can be seen that the ferromagnetic effect introduced by the dedicated a_g orbital is less strong than for the orbital selected by overlap. On the contrary, the antiferromagnetic effect due to the b_{1u} dedicated orbital is significantly larger. As a consequence the sum of the two effects gives too large a J when dedicated orbitals are added to the CAS, whereas (in most cases) the overlap criterion gives better results. Note that the effect of adding the a_g or b_{1u} orbital is not additive and only indicate the tendency in the CI calculation with both orbitals in the CAS.

Remains the question why the Overlap criterion fails to select a good ligand orbital in some cases and does not correctly reproduce the DDCI value. As mentioned before a deviation of 25% is found for $\text{TlBa}_2\text{CuO}_5$. The key to this question can be found in Figs. 5 and 6. Because the a_g orbital is very similar for $\text{HgBa}_2\text{CuO}_4$ and $\text{TlBa}_2\text{CuO}_5$ the addition of this orbital to the CAS introduces an equal amount of ferromagnetic interaction for both compounds. However, the shape of the b_{1u} orbital is markedly different, although the overlap with the atomic orbitals on the magnetic centers are very similar. In the

Table 2

CAS*S magnetic coupling parameters (in meV) of $\text{HgBa}_2\text{CuO}_4$ with different reference wave functions.

Active space	Projection	Dedicated	Overlap
minimal CAS	-87	-87	-87
+ a_g	-99	-35	-11
+ b_{1u}	-155	-273	-253
+ a_g, b_{1u}	-168	-196	-154

case of $\text{TlBa}_2\text{CuO}_5$, the b_{1u} orbital is less localized on the bridging ligand, and hence, not so effective for antiferromagnetism. This leads to a partial compensation only of the ferromagnetic interaction introduced by the a_g orbital and too small a J -value.

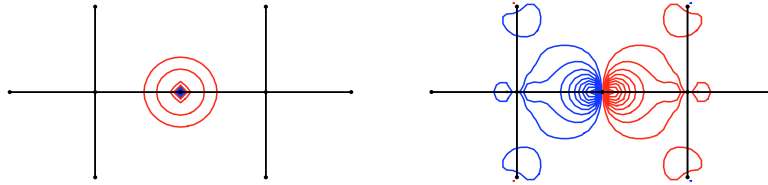


Fig. 3. $\text{HgBa}_2\text{CuO}_4$ projected ligand orbitals of a_g (left) and b_{1u} (right) symmetry. Only the b_{1u} orbital is added to the active space.

Fig. 4. Most dedicated ligand orbitals added to the extended CAS for $\text{HgBa}_2\text{CuO}_4$

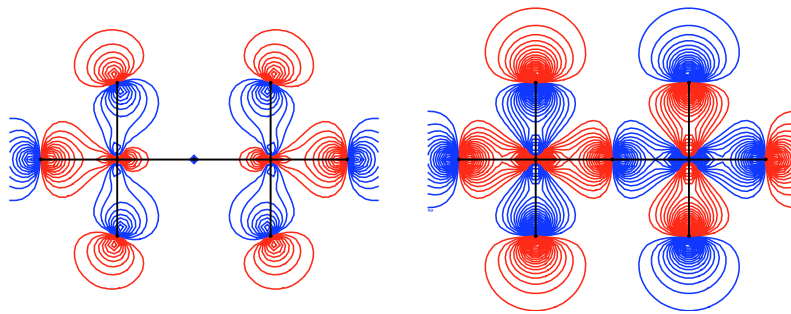


Fig. 5. Canonical SCF ligand orbitals in the extended CAS for $\text{HgBa}_2\text{CuO}_4$ selected by overlap following the procedure outlined in Ref. [50].

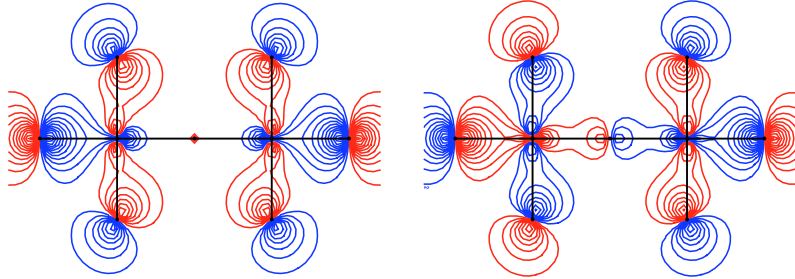


Fig. 6. Canonical SCF ligand orbitals in the extended CAS for $\text{TlBa}_2\text{CuO}_5$ selected by overlap following the procedure outlined in Ref. [50].

5 Spin ladder compounds

In order to establish the validity of the CAS(ext)*S approach, we now turn our attention to less symmetric copper oxide systems. In the next section we will study molecular systems and systems with elevated spin moments. The spin ladder systems SrCu_2O_3 , CaCu_2O_3 and $\text{Sr}_2\text{Cu}_3\text{O}_5$ recently received a lot of attention [58,59] being an interpolation between the quasi one-dimensional spin-1/2 chains and the two-dimensional layered perovskites, discussed in the previous section. These systems exhibit many interesting physical phenomena, although we will restrict the discussion here to magnetic coupling parameters. The Cu^{2+} ions are arranged in quasi isolated spin ladders with two (SrCu_2O_3 and CaCu_2O_3) or three legs ($\text{Sr}_2\text{Cu}_3\text{O}_5$). Magnetic coupling occurs along the legs and the rungs that connect the different legs of the same ladder. The Sr compounds have almost planar ladder planes resulting in similar coupling along rung and leg, whereas the ladder planes in CaCu_2O_3 are strongly distorted and hence, the coupling along the rung is much smaller than along the leg. Additionally, there is a weak interladder coupling in all three compounds.

Table 3 lists the results of CAS(ext)*S calculations and compares them to DDCI values obtained with a minimal active space. For the leg and rung interactions only one ligand orbital has been added to the active space. This orbital is very similar in shape as the b_{1u} depicted in Fig. 3. However, the interladder interaction is mediated by two oxygen ions and hence two ligand-centered O-2p orbitals have to be added to the active space.

The CAS(ext)*S compares less favorable with DDCI than for the simpler perovskites, deviations of about 20 meV are observed and in some cases (e.g. $J_{leg(1)}$ in $\text{Sr}_2\text{Cu}_3\text{O}_5$) even larger differences occur. In almost all cases the interaction is predicted to be too antiferromagnetic (i.e. overestimation for negative J and underestimation for positive J). The behaviour of CAS(ext)*S with dedicated orbitals is even worse, all antiferromagnetic interactions are systematically overestimated by a large amount. The Overlap selection criterion gives in gen-

Table 3

Magnetic coupling parameters (in meV) of the spin ladder compounds SrCu₂O₃, CaCu₂O₃, and Sr₂Cu₃O₅. Projected ligand vectors are added to the active space. The last row lists the number of determinants in the CI for the singlet state used to calculate J_{leg} in SrCu₂O₃.

Compound		DDCI	CAS(ext)*S	CAS(ext)*DDCI2
SrCu ₂ O ₃	leg	-175	-197	-188
	rung	-152	-196	-186
	inter	21	6	5
CaCu ₂ O ₃	leg	-130	-144	-137
	rung	-16	-36	-33
	inter	17	8	6
Sr ₂ Cu ₃ O ₅	leg(1) ^a	-184	-220	-210
	rung	-165	-202	-192
	inter	21	34	25
	leg(2)	-172	-193	-185
Determinants		6.1·10 ⁵	2.2·10 ⁴	4.1·10 ⁴

^a leg(1) refers to the middle leg in the three-legged ladder, leg(2) is the outer leg

eral more reasonable agreement with DDCI, but in some cases the J -value is very different due to the uncontrollable nature of the canonical SCF orbitals.

To improve the performance of the limited CI with an extended CAS, we added the $2h$ and $2p$ excitations to the CI space, i.e. we perform a DDCI2 with an extended CAS. With respect to the leading Cu-3d⁹-O-2p⁶-Cu-3d⁹ configurations, the CI now also contains the $2h$ - $2p$ excitations in which two electrons from the bridging ligand are excited to the virtual space. This type of excitations account (at least partially) for the dynamical correlation effects of the electrons on the bridge. As a consequence, the LMCT state becomes slightly more unfavorable and the interaction with the leading configuration reduces. This leads to a smaller antiferromagnetic coupling. In a one-electron reasoning (see Fig. 1), the introduction of electron correlation on the bridge lowers the orbital energy of the ligand orbital l . This makes the separation with the metal-centered orbitals a and b larger, and the splitting Δ smaller.

CAS(ext)*DDCI2 also introduces the $1h$ - $2p$ type of determinants in the N -electron wave function. These excitations contribute ferromagnetically to the magnetic coupling parameter [22]. and are hence also expected to reduce the overestimation of the negative J 's by CAS(ext)*S.

The last column in Table 3 indeed shows that the antiferromagnetic interac-

Table 4

DDCI, CAS(ext)*S and CAS(ext)*DDCI2 magnetic coupling parameters (in meV) for La_2NiO_4 . The last row lists the number of determinants for the singlet state. $J_{exp} = -31$ meV

	DDCI	CAS(ext)*S		CAS(ext)*DDCI2	
		Projection	Dedicated	Overlap	Projection
$E_S - E_T$	-24.1	-33.3	-38.4	-33.1	-32.0
$\frac{1}{2}(E_T - E_Q)$	-26.3	-36.8	-44.4	-36.9	-35.8
$\frac{1}{3}(E_S - E_Q)$	-25.6	-35.6	-42.4	-35.6	-34.5
Determinants	$7.7 \cdot 10^6$	$2.3 \cdot 10^5$	$1.7 \cdot 10^6$	$1.7 \cdot 10^6$	$4.2 \cdot 10^5$

tions are less antiferromagnetic now and the values are in better agreement with DDCI. On the other hand for the smaller ferromagnetic interactions the situation is less clear. Although the absolute differences are of the same order as the larger antiferromagnetic interactions, the relative error is quite large and it remains unclear whether CAS(ext)*S or CAS(ext)*DDCI2 is a suitable methodology to calculate ferromagnetic interactions.

CAS(ext)*DDCI2 hardly improves the results with dedicated orbitals neither repairs the incidental failures (e.g. for $\text{TlBa}_2\text{CuO}_5$) when canonical orbitals selected by overlap are added to the CAS. This is closely related with the fact that the orbitals added to the CAS in these procedures are delocalized over the whole cluster. The electrons in these orbitals experience much less dynamical correlation effects than electrons in localized orbitals such as the ones obtained by projection. Finally, it is observed that the results with projected orbitals for the cuprates listed in Table 1 are not affected by the inclusion of the 2h and 2p excitations.

6 La_2NiO_4 and molecular complexes

The magnetic coupling in Ni(II) perovskites are in general much smaller than the corresponding Cu(II) compounds. This can be ascribed to the fact that the LMCT energy is higher in the Ni-compounds. La_2NiO_4 still has a sizeable magnetic coupling (experiment: $J = -31$ meV [60]) and is used here as a first test to treat systems with more than two unpaired electrons. The minimal CAS contains four electrons and four orbitals with mainly Ni-3d(x^2-y^2) and Ni-3d($2z^2-x^2-y^2$) character. This active space is extended with one projected ligand orbital of O-2p character, i.e. a CAS(6,5) (6 electrons and 5 orbitals). In the case of selection by overlap or dedicated orbitals, four ligand orbitals have to be added to the minimal CAS, resulting in a CAS(12,8).

The two $S=1$ spin moments on Ni^{2+} couple to quintet, triplet and singlet, and two independent estimates of J can be calculated from the energy differences. The results in Table 4 indicate small deviations of the pure Heisenberg splitting, which can be ascribed to the appearance of biquadratic terms in the magnetic coupling [25]. The ratio $E_T - E_Q/E_S - E_Q$ is 0.686 for DDCI, where the pure Heisenberg splitting gives a ratio of 1/3. This deviation of 3% is significantly larger than the ratio reported by Moreira and co-workers for K_2NiF_4 [25].

Concerning the comparison of the different CAS(ext)*S strategies with DDCI, the general features observed for the copper oxides can also be recognized for the Ni compound. Table 4 shows that CAS(ext)*S slightly overestimates the antiferromagnetic contributions to J in comparison with the DDCI result, although the comparison with the experimental value is as good as for DDCI. This overestimation is largest when the four dedicated orbitals with highest participation number are added to the CAS. Adding one projected ligand orbital or four canonical orbitals selected by overlap give identical results. The CI expansion is however almost ten times longer in the latter case. Adding the 2h and 2p excitations to the CI-space (CAS(ext)*DDCI2) slightly reduces the difference with DDCI as observed before. Note that the number of Slater determinants is still smaller than in the CAS*S calculation with a CAS(12,8) reference wave function.

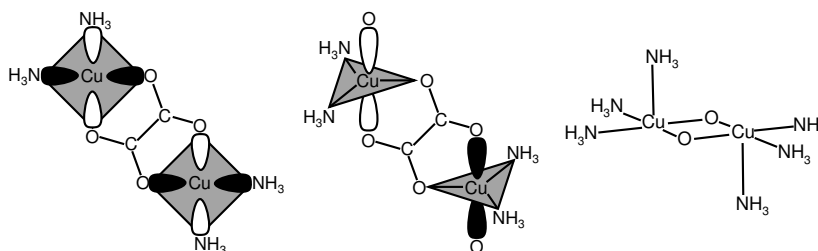


Fig. 7. Schematic representation of the oxalato-bridged Cu(II) complexes with square pyramidal (SPY) (left) and trigonal bipyramidal (TBP) (middle) Cu coordination, and the oxo-bridged Cu(II) complex (right). The axial NH_3 group for Cu_2 -oxalato (SPY) is not shown.

The model systems depicted in Fig. 7 are used to establish the performance for molecular complexes. These model systems have been studied before [1,21,61,62] and exhibit magnetic coupling ranging from moderately antiferromagnetic to rather large ferromagnetic. Only the trigonal bipyramidal Cu(II) oxalato-bridged model (Cu_2 -oxalato (TBP)) represents a real molecule, namely $(\text{Et}_5\text{dien})_2\text{Cu}_2(\mu\text{-C}_2\text{O}_4)$, with $\text{Et}_5\text{dien} = 1,1,4,7,7$ -pentaethyldiethylenetriamine. The experimental magnetic coupling of this molecule is -9.3 meV [63,64]. The other two models are hypothetical molecules.

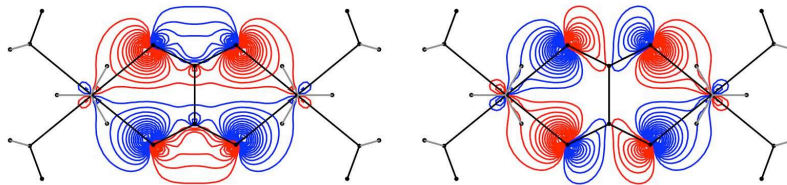


Fig. 8. Cu-oxalato (SPY) projected ligand orbitals.

Table 5

DDCI, CAS(ext)*S and CAS(ext)*DDCI2 magnetic coupling parameters (in meV) for three dinuclear Cu(II) molecular complexes. The last row lists the number of determinants for the singlet state in Cu₂-oxalato (SPY).

Molecule	DDCI	CAS(ext)*S			CAS(ext)*DDCI2
		Projection	Dedicated	Overlap	Projection
Cu ₂ -oxalato (SPY)	-22.4	-21.9	-18.9	-10.0	-20.7
Cu ₂ -oxalato (TBP)	-7.3	-10.4	-2.5	-2.8	-9.7
Cu ₂ -oxo	44	70	101	-92	41
Determinants	1.9·10 ⁶	1.0·10 ⁵	1.0·10 ⁵	1.0·10 ⁵	4.2·10 ⁵

The polyatomic nature of the bridges that connect the two Cu ions in the three complexes makes that there exist valence bridge molecular orbitals with the same symmetry for both magnetic orbitals. The extended CAS contains four orbitals and six electrons. Figure 8 shows the projected ligand orbitals added to the CAS for Cu₂-oxalato (SPY) and Table 5 resumes the results obtained with the different orbital choices to introduce LMCT excitations in the CAS. The projected ligand orbitals can best be described as bonding and anti-bonding linear combinations of oxalato O-2p orbitals with small in-phase contributions of the Cu-3d_{xy} orbital.

Taking the DDCI with minimal CAS as reference values (second column), we observe that CAS(ext)*S behaves reasonably well for the antiferromagnetic systems but overestimates the ferromagnetic coupling in Cu₂-oxo. CAS(ext)*DDCI2 hardly affects the results for the Cu₂-oxalato complexes, but corrects the overestimation of J for Cu₂-oxo. The extension of the CAS with dedicated orbitals gives in general worse results, and the selection of canonical SCF orbitals by overlap is invalidated for these kind of systems. In all three cases the DDCI J -value is not reproduced and in the case of Cu₂-oxo the coupling parameter is completely wrong as strong antiferromagnetic coupling is predicted where a moderate ferromagnetic coupling is expected. The failure is again due to the fact that at least one of the orbitals added to the CAS have negligible contribution of the bridging ligand.

Finally, we report the results of a hetero dinuclear complex, namely the $[(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cr}(\text{C}_2\text{O}_4)\text{Ni}(\text{NH}_3)_3]$ model as described in Ref. [34]. Ni(II) has an electronic configuration $[\text{core}]3d^8$ with two unpaired electrons and Cr(III) is $[\text{core}]3d^3$ with three unpaired electrons. Hence, the minimal CAS contains five magnetic orbitals and five electrons, which leads to a DDCI expansion of $1.56 \cdot 10^8$ determinants. This is obviously too large to be handled and alternative strategies are necessary. The dedicated orbital transformation and subsequent controlled reduction of the MO-space is one possibility, but the CI-space needs to be reduced significantly below the critical value of $\approx 30\%$ and results should be looked at with caution [33].

The calculation of the magnetic coupling constant of the Ni-Cr complex with the CAS(ext)*S methodology involves an active space with 10 orbitals (5 magnetic plus 5 ligand-centered orbitals) and 15 electrons. The CI singles on top of this extended reference wave function leads to a coupling constant of 6.3 cm^{-1} with practically no deviation from the pure Heisenberg splitting. This result is in rather good agreement with the experimental value of 9 cm^{-1} [65]. The number of determinants in this CAS(ext)*S calculation is becoming rather large because of the size of the CAS, however, one could easily reduce the computational cost by using dedicated virtual orbitals in combination with the CAS(ext)*S methodology. This combination opens the way to a variational evaluation of the magnetic coupling constants (and other electronic structure parameters) in systems with even more unpaired electrons.

7 Conclusions

Accurate estimates of the coupling constants between magnetic centers and other electronic structure parameters can be computed from a minimal active space, reduced to the magnetic orbitals and the magnetic electrons, provided that: i) the magnetic orbitals are obtained from a variational calculation, which incorporates an optimal delocalization between the metal and the ligands, and ii) this CASCI calculation is followed by an extensive multireference CI, including all semi active double excitations on the top of the CAS, i.e. a DDCI calculation.

The CAS(ext)*S method is presented as a reasonably accurate alternative to this rather expensive standard DDCI method to variationally determine the magnetic coupling parameter and other electronic structure parameters in magnetic systems. The methodology is based on the understanding that LMCT excitations play a fundamental role in the magnetic coupling provided the N-electron wave function accounts for the dynamical repolarization of the electron charge distribution in response to such processes. DDCI accounts for these effects through the $2h-1p$ excitations, but it can also be accomplished

by performing a CI singles with a reference wave function extended with the LMCT configurations.

Where the active space to construct the reference wave function for DDCI is easily chosen (all magnetic orbitals and the corresponding unpaired electrons), the extended active space is less trivially obtained. It should be ensured that it includes in an optimal way the LMCT effects. Three different procedures to extend the active space are compared and the results show that the projection of a model vector with pure bridging ligand character onto the inactive orbital space provides an efficient scheme to introduce all important LMCT configurations in the reference wave function. Contrary to the other two schemes its final results do not depend on the partial cancelation of two antagonist contributions (cf. Table 2).

For the relatively simple lamellar cuprates, CAS(ext)*S reproduces with great precision the DDCI values, which in turn are in very good agreement with available experimental data. In the less symmetric spin ladder cuprates, the methodology performs less well and tends to overestimate the antiferromagnetic component of the coupling. This overestimation is partially remedied by adding the $2h$ and $2p$ excitations to the CI expansion according to the DDCI2 scheme. The wave function contains now dynamical correlation effects of the electrons in the bridging ligand orbital added to the CAS. This tends to reduce the importance of LMCT excitations. Moreover, the wave function includes $1h-2p$ type of excitations, which have been shown to contribute ferromagnetically to the coupling. The test calculations on the molecular systems reveal that the extension of the CAS with a ligand orbital selected by overlap with the magnetic orbital [50] is not a universal recipe. This procedure badly fails for the three systems considered in this paper. The extension of the active space with the most dedicated orbital is also not a guarantee for good estimates of the magnetic coupling parameter.

Finally, the possibilities are explored of the treatment of systems with elevated spin moments. The coupling between two Ni(II) cations in La_2NiO_4 is correctly reproduced and also for the more challenging Ni-Cr dimer a good variational estimate is obtained. The combination of the CAS(ext)*S or CAS(ext)*DDCI2 with the reduction of the virtual MO-space by means of a dedicated orbital transformation seems to be a very promising way to proceed to even larger systems, either with more magnetic centers or in dimers (and probably trimers) with higher spin moment per magnetic center.

A Computational information

Cu_2O_7 and Ni_2O_{11} cluster models are used to represent the perovskite copper and nickel oxides, respectively. These clusters are embedded in point charges that represent the Madelung potential in the cluster region. To avoid boundary effects, the point charges closest to the cluster are replaced with total ion potentials that account (at least partially) for the short-range attractive and repulsive interactions between the cluster atoms and its nearest neighbours. For the spin ladders, the interaction along rung and leg is also calculated with an embedded Cu_2O_7 cluster, whereas the interladder interaction is derived from a Cu_2O_6 cluster. The cluster geometry is adopted from the experimental structure.

In the perovskite copper oxides systems, the inner electrons of the Cu ions ($1s^2 2s^2 2p^6$) are replaced with the Hay and Wadt pseudopotential. The valence electrons are described with the corresponding basis set of triple- ζ quality [66]. The atomic basis sets for the transition metal centers (Cu, Ni, Cr) in the rest of the systems are of the atomic natural orbitals (ANO) type with a (5s,4p,3d,1f) contraction [67]. The lighter atoms (C and O) bridging the magnetic centers are described with (3s,2p,1d) contracted ANO basis functions [68]. The atoms that form the external ligands are described with (3s,2p) contracted ANO basis functions in all systems but for the perovskite copper oxides. In this case the O-1s electron is replaced with the Durand-Barthelat pseudopotential and the valence electrons are described with the corresponding double- ζ basis set [69].

Defining the Heisenberg Hamiltonian as $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$, the magnetic coupling parameter J is obtained from $E(S) - E(S-1) = SJ$, where $E(S)$ is the energy of the electronic state with spin multiplicity S .

Optimization of the molecular orbitals used in the CI calculations and the transformation of the integrals to the molecular orbital basis have been done with the MOLCAS 5.4 code [70], the subsequent CI calculations have been done with the CASDI code [71].

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