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REGULAR ARTICLE

Extending the active space in multireference configuration interaction calculations of magnetic coupling constants

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Abstract In the last two decades, difference dedicated configuration interaction (DDCI) calculations have been outlined as a rather accurate and a successful approach for the evaluation of magnetic coupling constants *J*. The DDCI space contains all single and double semi-*active* excitations on the top of the complete active space, which is only composed of the magnetic orbitals. The main drawback of the procedure is its computational cost, in particular for systems involving several metallic centres with $S > ½$. To overcome this constraint, an alternative strategy has been proposed in the past which consists in restricting the CI expansion to single excitations on the top of an extended active space, involving a few doubly occupied and in some cases virtual orbitals of ligand character. This strategy reduces considerably the size of the CI matrices, and then makes possible to deal with larger and more complex systems. However, the so obtained *J* values are overestimated compared to the corresponding DDCI and to the experimental values. We analyze here the origin of this behavior in the light of a recent paper where the role of ligand-to-metal charge transfer excitations on the quantitative description of *J* has been re-examined.

Keywords Magnetic coupling constants · Truncated CI calculations · Binuclear compounds

1 Introduction

The work by Bleaney and Bowers in the 1950s about the magnetic susceptibility of copper acetate can be considered as the first step on the research field of molecular magnetism [1]. Since then, a huge effort has been devoted to the understanding of the origin of the magnetic properties of transition metal complexes and the quantitative evaluation of the magnetic coupling constants [2]. Interpretatative models are based on Anderson's mechanism [3, 4], in which the coupling constant, *J*, results from the balance of a ferromagnetic (F) and an antiferromagnetic (AF) term:

$$J = 2K_{ab} - 4{t_{ab}}^2/U = J_F + J_{AF} \tag{1}$$

where K_{ab} represents the direct exchange contribution to the coupling, and the kinetic exchange term, including the hopping integral t_{ab} and the on-site Coulomb repulsion, *U*, takes into account the delocalization effects.

Nowadays, ab initio multireference configuration interaction (MRCI) techniques can be considered as the best tools for obtaining correct descriptions of the electronic configurations of the states involved in the coupling, as well as for

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Dedicated to the memory of Professor Jean-Pierre Daudey, for the broad and stimulating discussions held with him and for the friendly and warm atmosphere he constantly maintained both inside and outside the academic environment. With the present work, we want to stress his role in pioneer ab initio calculations on magnetic coupling in transition metal complexes.

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determining with numerical accuracy the amplitude of the magnetic coupling constants [5–7]. Among them, the difference dedicated CI (DDCI) approach by Miralles et al. [8, 9] has been particularly successful. In this variational method, where the reference space is in general the minimal Complete Active Space (CAS) involving magnetic orbitals and electrons, a truncation of the CI space is performed, based on perturbative arguments. The spectroscopy oriented configuration interaction method (SORCI) [10] proposed by Neese rests on the same logics, but restricts the DDCI treatment to the most interacting determinants, the weakly coupled ones being treated in a perturbative mode, as in the CIPSI method [11]. The main drawback of these approaches is that they are computationally demanding, in particular for systems with large external ligands and more than two transition metal atoms.

For this reason, several strategies have been proposed in the past by us and other authors to reduce the computational cost of the MRCI calculations. They can be classified in two main groups: those aimed to reduce the size of the MOs set and consequently of the DDCI matrices, and those oriented to the rational extension of the minimal CAS (CASext) involving not only the magnetic orbitals but also orbitals centred on the ligands and to perform low cost variational calculations, as single excitations on top of the extended CAS, CASext + *S*.

The key point in all of them is the criterion used to select the MOs, both those to be eliminated in a truncation scheme or those to be included in the active space. Different criteria have been used to select the MOs:

1. The participation in the low spin–high spin energy difference, as in the case of the excitation energy dedicated molecular orbitals [12, 13], to truncate the inactive and/or virtual MOs subsets.
2. The energetics and the overlap with the magnetic orbitals [14], to select ligand-type MOs among the inactive subset.
3. The use of localized orbitals (projected ligand orbitals [15], self-consistent localized orbitals [16, 17]) to generate ligand-type MOs.

While the *J* values provided by DDCI calculations on truncated MOs spaces are in agreement with the reference DDCI ones, the evaluations based on low cost multireference CI calculations on extended CAS are systematically overestimated with respect to DDCI values. The aim of this work is to examine the origin of this behavior in the light of a recent work where the main mechanisms governing the magnetic coupling have been revisited. For this purpose, a set of binuclear Cu(II) and Ni(II) compounds has been considered, their magnetic coupling constants being evaluated by means of CASext + CI calculations. The systems and computational details are described in Sect. 2. The main conclusions of a series of previous works about the role of the ligand-to-metal charge transfer configurations on the magnetic coupling are summarized on Sect. 3 and a detailed analysis of the results is presented in Sect. 4 where advantages and weak points of the procedure are discussed. Finally, Sect. 5 outlines the main conclusions and perspectives.

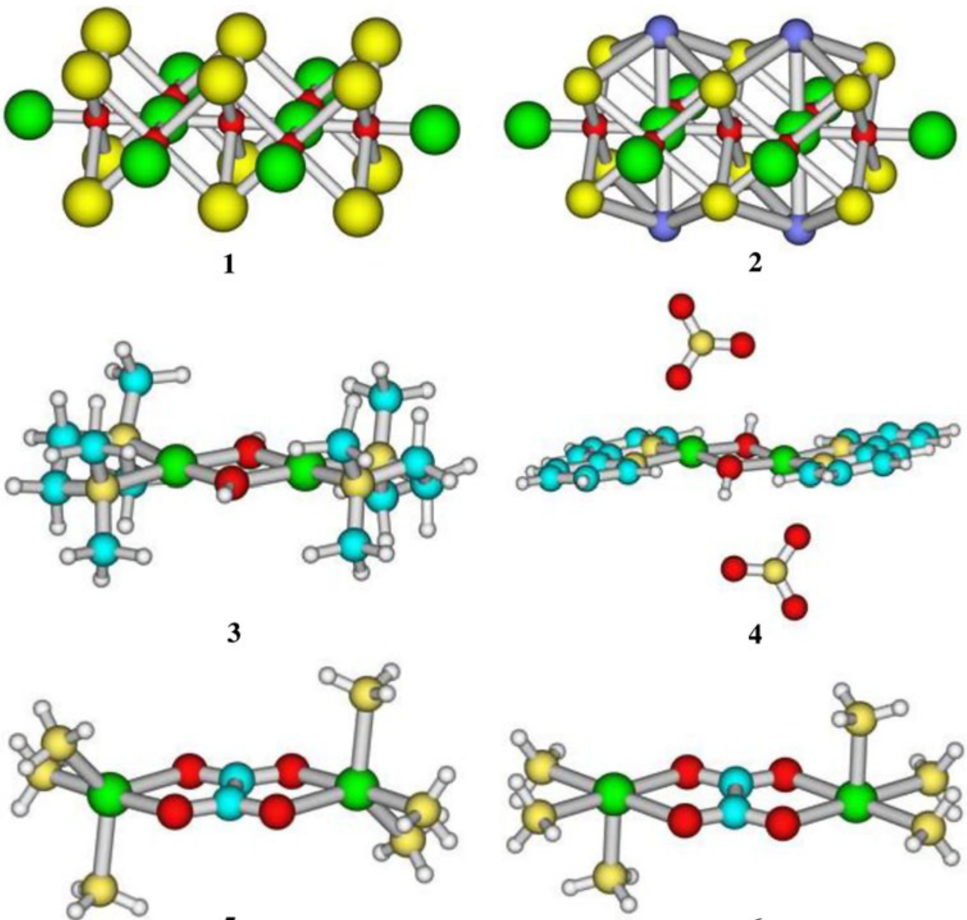
2 Description of the systems and computational details

Two sets of compounds have been considered, corresponding to binuclear Cu(II) and Ni(II) complexes, represented in Figs. 1 and 2, respectively. Regarding Cu(II), six different compounds have been analyzed. Compounds **1** (La_2CuO_4) [18–21] and **2** ($Sr_2CuO_2Cl_2$) [22] correspond to antiferromagnetic cuprates, with experimental coupling constants $J = -1{,}030$, $-1{,}096$ cm^{-1} for **1**, $J = -1{,}008 \pm 48$ cm^{-1} for **2**.

Systems **3** and **4** represent two bis-μ-OH complexes of formula [LCu-$(OH)_2$-CuL], giving AF coupling in **3** [23, 24] with L = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, and F coupling in **4** [25, 26], with L = 2′-bipyridine. Compound **5** is an oxalato-bridged complex of formula [LCu-(C_2O_4)-CuL] with L = 1,1,4,7,7-pentaethyldiethylene-triamine modeled by NH_3 groups with the coordinated N atoms at the experimental position[27]. The same molecular formula but with a model geometry used in previous works corresponds to system **6** [15].

Three binuclear Ni(II) systems have also been considered, where the metallic atoms are hexacoordinated and the bridging ligands are oxalate or chlorine ions. Both oxalato-bridged complexes have the general formula [LL′Ni-(C_2O_4)-NiLL′], with L = diethylenetriamine and L′ = H_2O in **7** and L = L′ = $C_2O_4{}^{2-}$ in **8** and present a weak antiferromagnetic coupling of −28.8 and −22.8 cm^{-1}, respectively [28]. [L_2Ni-Cl_2-NiL_2], with L = ethylenediamine, **9**, is weakly ferromagnetic [29], with $J = 19$ cm^{-1}. DDCI calculations on the whole set of MOs are not technically feasible for these systems, and then here the low-cost CASext + *S* strategy could be particularly interesting.

Geometries from X-Ray crystal structures have been used for all the systems considered. In the case of La_2CuO_4 (**1**) and $Sr_2CuO_2Cl_2$ (**2**) cuprates, binuclear fragments Cu_2O_7 have been used in the calculations, conveniently embedded in a set of point charges and total ion potentials emulating the Madelung potential of the infinite crystal. In all the calculations, core electrons of Cu atoms (up to 3*s*) were replaced with effective core potentials, and the (9*s*6*p*6*d*)/[3*s*3*p*4*d*] set was used for the valence electrons of Cu [30]. For systems **5** and **6**, and for Ni(II) complexes **7**–**9**, metal atoms are represented by means of ANO-type basis functions with contractions (5*s*4*p*3*d*1*f*), based on our previous experience with these systems [31, 32]. ANO-type

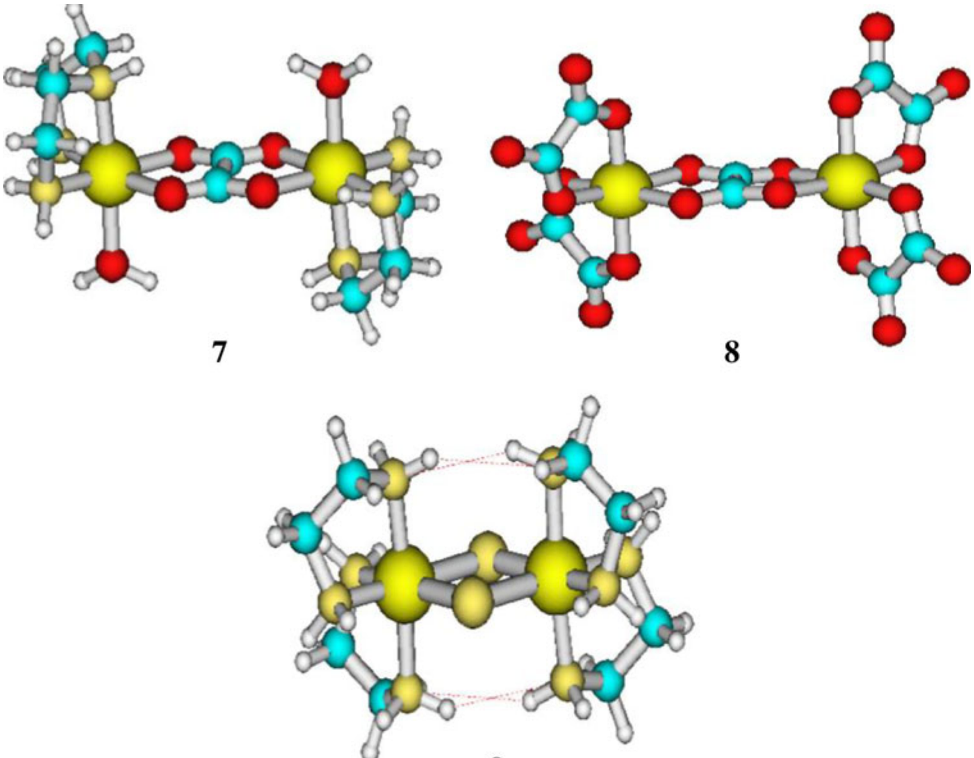


1 2

3 4

5 6

Fig. 1 Structures of the binuclear Cu(II) compounds described in Sect. 2



7 8

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Fig. 2 Structures of the binuclear Ni(II) compounds described in Sect. 2

basis functions are used for the ligands, of different quality depending on the specific position: contractions (3*s*2*p*1*d*) for the atoms in the bridging groups, contractions (3*s*2*p*) for the atoms directly bonded to the metal atoms, and contractions (2*s*1*p*) for the rest. H atoms are represented by means of ANO-type functions with a contraction (2*s*1*p*) when are placed on the bridging ligands, and 2*s* or 1*s* for the remaining atoms [33–35].

CI calculations have been performed with CASDI code [36], starting from the canonical MOs of the single reference high spin state obtained with Molcas 7.0 package [37]. Truncated CI calculations, including specific excitation subspaces have been carried out with an expressly modified version of CASDI code, which provide the natural orbitals to be used on the subsequent extended CAS CI calculations.

3 The role of ligand-to-metal charge transfer excitations on the magnetic coupling

As stated in the Anderson's model, the AF component is driven by the coupling between the valence bond neutral, *N*, and ionic configurations, *I*. These configurations belong to the CAS defined by the magnetic orbitals and the corresponding electrons. The active electron approximation of Kahn and Briat [38] and Hay et al. [39] are based on this model. Regardless of their success to qualitatively explain the main features of the magnetic interactions, it is a fact that magnetic coupling is not simply a phenomenon involving only the unpaired electrons of the system. Neither the nature nor the amplitude of the interaction can be explained solely from the interaction of the active electrons, but it concerns also to a large extent the remaining electrons. Therefore, electron correlation effects must be taken into account to obtain a correct description. In this sense, the work carried out by de Loth et al. [40] in the 1980s can be considered as a milestone in the field, with applications on several dinuclear complexes [41–44] carried out by Daudey and co-workers, and the DDCI method can be considered as its "variational heir". The main idea behind this approach is that the CI matrix is built with only those configurations playing a role on the energy difference of the states involved in the coupling. This approach has provided estimates of *J* in remarkable good agreement with experimental data in the recent past [17, 31, 45–51].

Stimulated by its performance, we have carried out a series of works [52–55] where the physics of the magnetic coupling in binuclear Cu(II) systems has been analyzed, trying to attribute the sign and the magnitude of electron correlation contributions to the coupling constant. The excited configurations are classed depending on the number of electrons promoted from doubly occupied inactive orbitals (holes, *h*) and the number virtual orbitals (particles, *p*) involved in the excitation. The main conclusions of these works can be summarized as follows:

1. The bare CAS at best only takes into account 20% of the whole magnetic coupling constant.
2. Single excitations on the CAS play an important role in the coupling. This 1*h*–1*p* class of excitations introduces spin-polarization effects as well as the polarization of the ionic forms, whose main effects consists in lowering their effective energy. Second order estimations account for these contributions to *J*.
3. The 2*h*–1*p* class of excitations with respect to the CAS plays an important role and gives a significant AF contribution in AF systems and a small F effect in F ones, depending on the weight of the ionic forms in the singlet state. Among this class of determinants, a special impact can attributed to those that can be formally considered as resulting from single excitations on ligand-to-metal charge transfer (*LMCT,* 1*h*) configurations. To have a quantitative effect on the magnetic coupling constant, both the ionic and *LMCT* configurations must be stabilized by the 1*h*–1*p* excitations.
4. The mechanisms responsible for the contribution of 2*h*–1*p* excitations involve their coupling with the ionic forms, mediated by the *LMCT* determinants. Their important effects on *J* are not of second order but of higher-order nature.
5. The 1*h*–2*p* class of excitations produces a damping of the effect of the 2*h*–1*p* one. For F systems, their role is negligible, but they introduce a moderate F effect on AF systems.
6. To reach numerical accuracy, *LMCT*, 1*h*–1*p*, 2*h*–1*p* and 1*h*–2*p* excitations with respect to the CAS must be included in the CI.
7. The correct inclusion of the correlation effects produces an increase of the weight of the ionic configurations on the singlet wave function with respect to the bare CAS one, as well as a non-negligible contribution of the *LMCT* forms, which manifests as a larger delocalization of the active orbitals on their close neighbor ligands.

The role played by the *LMCT* forms suggests that it might be worth to work with an extended CAS, where not only the magnetic metal-centered orbitals are included, but also a few ligand MOs. Then, this extended CAS contains the neutral and ionic valence forms, the dominant *LMCT* configurations (simple and double *LMCT*, if the CAS contains several occupied ligand orbitals), and some of the 1*p* excitations, if virtual orbitals are also included. Since, beyond the polarization of the ionic configurations introduced by 1*h*–1*p* excitations, a large contribution comes from the single excitations of the *LMCT*, it is reasonable to expect that a CI calculation restricted to the single excitations on the top of this extended

CAS can quantitatively reproduce the J value obtained with DDCI calculations on a minimal CAS. This is the key idea behind several works in the recent past, although in most of them, it was not explicitly explained, the driving force being just the significant reduction of computation time and hardware resources (disk, memory).

Figure 3 plots previous CASext + S results on J obtained from different alternatives of extending the CAS, in front of DDCI values calculated from the minimal CAS. A first series shows the results published in the recent past by Gellé et al. [14] for several solid state Cu(II) and Ni(II) magnetic systems, where J is evaluated from binuclear clusters adequately embedded in a set of point charges. The active space is enlarged with two (Cu compounds) or four (Ni compounds) occupied orbitals belonging to the same irreducible representations as the active ones. They have been selected according to their energies (immediately below the Fermi level) and maximum overlap with the magnetic orbitals among the set of canonical MOs of the high spin state. A second series corresponds to the results by Bordas et al. [15] on the same solid state magnetic Cu(II) and Ni(II) binuclear fragments as well as spin-ladder cuprates and molecular magnetic Cu(II) compounds. In this case, the ligand-centered MOs added to the active space have been selected from the projection of a model vector of pure bridging ligand character onto the inactive space of the canonical MOs of the high spin state.

The third series of results in Fig. 3 corresponds to an alternative strategy to select the MOs to be included in the active space, based on their participation on the 1h and 1p excitation processes. When starting from the high spin state HF MOs, there is a non-null interaction between the ionic forms and the 1h and 1p excitation classes [52, 55], i.e. those determinants where one electron is promoted from an occupied inactive orbital to an active one, and those resulting from an excitation from an active orbital to a virtual one. *LMCT* forms are contained in the 1h set and, similarly, the metal to ligand charge transfer, *MLCT*, configurations belong to the 1p set. The diagonalization of the singlet–triplet average density matrix obtained from CAS + 1h CI calculations might define the relevant doubly occupied ligand MOs, as those with occupation number slightly different from 2.0. Likewise, the CAS + 1p CI might define the most relevant virtual MOs, as those with non-zero occupation numbers. Therefore, the natural orbitals resulting from CAS + 1h + 1p CI calculations define the most relevant occupied and virtual orbitals. The so-selected MOs are those with larger participation on the 1h and 1p processes and will be denoted as "1h + 1p" natural MOs hereafter. The CAS is enlarged with these MOs, and the J values obtained at the CASext + S CI level for the set of six Cu(II) magnetic compounds described in Sect. 2 is shown in Fig. 3. The global results show similar nice performances, with good linear behavior between J calculated at the CASext + S and DDCI levels, good regression coefficients and slopes close to 1. As a first conclusion, the CASext + S scheme seems to work correctly, its performance being practically independent on the criteria used to select the MOs included in the active space.

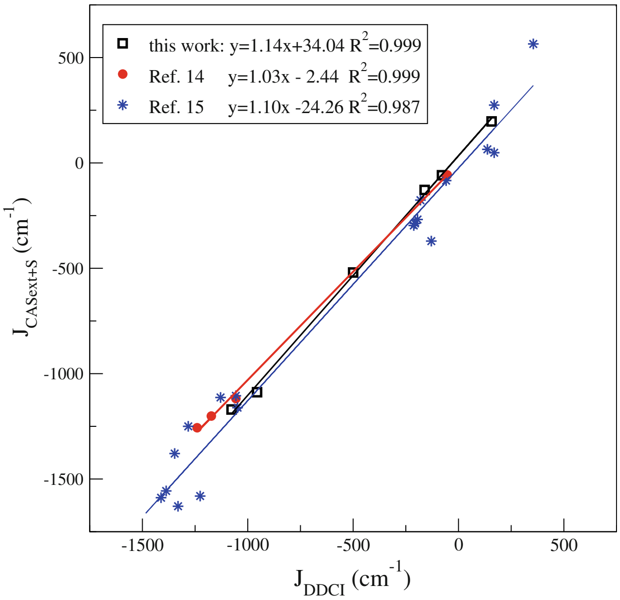


Fig. 3 Plot of CASext + S versus DDCI magnetic coupling constants, J. Active ligand-type MOs proposed by Bordas et al. [15] (*blue star*), Gellé et al. [14] (*red circle*) and this work (*black square*)

4 A closer inspection

A tight inspection of Fig. 3 indicates that all the estimates of J coming from CASext + S calculations are overestimated with respect to DDCI ones. This trend is also evidenced in Table 1, where the J values for systems **1–6** obtained with this strategy and different active spaces have been collected. At zeroth-order, these Cu(II) dimers are described by a CAS(2/2). The performance of the CASext + S strategy is quite independent on the criteria employed to generate the MOs to be included in the active space, as corroborated by the results in Table 2. This table collects the J values for systems **1–6** obtained at the CAS(6/4) + S level, where the two MOs added to the minimal CAS are natural orbitals obtained from the average singlet–triplet density matrix from different truncated CI spaces. The labeled "U" MOs result from CAS + 1h–1p calculations, where the CI space contains all the single excitations involving simultaneously 1h and 1p on the top of the minimal CAS. As mentioned above, these 1h–1p excitations are responsible for the stabilization of the ionic configurations, i.e. for the lowering of U on-site repulsion.

Table 1 Magnetic coupling constants J (cm^{-1}) obtained at different CI levels

CAS (n_e/n_{MO})	CI space	La_2CuO_4 **1**	$Sr_2CuO_2Cl_2$ **2**	[$Cu_2(OH)_2$] **3**	[$Cu_2(OH)_2$] **4**	[$Cu_2(C_2O_4)$] **5**	[$Cu_2(C_2O_4)$] **6**
(2/2)	CASCI	−254	−160	−35	33	−7.3	−13.4
	DDCI	−1,077	−956	−500	157	−78.3	−160.5
(6/4)	CASCI	−310	−193	−51	31	−7.6	−13.7
	CAS + S	−1,169	−1,032	−504	194	−57.3	−126
	DDCI2[a]	−1,242	−1,078	−552	153	−62.8	−139
(6/6)	CASCI	−400	−270	−47	57	−12.3	−22.8
	CAS + S	−1,231	−1,119	−503	220	−65.1	−141.4
Exp.		[−1,030, −1,096] [18–21]	−1,008 [22]	−509 [23, 24]	172 [25, 26]	−75 [27]	Model [15]

For systems **1**–**3**, "1h + 1p" natural orbitals are used in extended CAS, while "U" natural orbitals are used for systems **4**–**6**

[a] DDCI2 includes CAS + S+2h + 2p

Table 2 Comparison of J values obtained from CAS(6/4) + S calculations, where the MOs added to the minimal active space have been selected by different criteria (see text for description)

MOs	La_2CuO_4 **1**	$Sr_2CuO_2Cl_2$ **2**	[$Cu_2(OH)_2$] **3**	[$Cu_2(OH)_2$] **4**	[$Cu_2(C_2O_4)$] **5**	[$Cu_2(C_2O_4)$] **6**
"1h + 1p"	−1,169	−1,032	−504	93	−11.5	−114
"U"	−1,148			194	−57.3	−126
CAS + S	−1,170	−1,088	−520	197	−58.4	−128
Exp.	[−1,030, −1,096] [18–21]	−1,008 [22]	−509 [23, 24]	172 [25, 26]	−75 [27]	Model [15]

The labeled "CAS + S" MOs are the natural MOs of the CI subspace including the whole set of single excitations (1h, 1p and 1h–1p) on top of the minimal CAS.

Let us start by describing the features of the orbitals added to the active space. Figure 4 shows the highest occupied and the lowest virtual "1h + 1p" orbitals of u symmetry for Cu(II) system **2** and Figs. 5 and 6 the highest occupied and the lowest virtual "U" orbitals for systems **4** and **5**, respectively. Since DDCI natural orbitals are expected to concentrate all the relevant electron correlation effects, the corresponding DDCI natural MOs of u symmetry have also been included in these figures for comparison. Both sets of orbitals present similar shapes, the only main difference being the relative weight of the ligand and metal-centered orbitals.

The CAS(6/4) space is obtained by adding two extra occupied orbitals to the active space. For all the considered systems, these orbitals correspond to the in-phase combinations of the active d metal orbitals and orbitals of the first-sphere ligands, with especially large contributions coming from the bridging ligands. The CAS(6/6) space is obtained by adding two virtual orbitals to the CAS (6/4) which present shapes similar to magnetic orbitals ones, with out-of-phase combinations of d metal and ligand orbitals, but large coefficients appear on the diffuse d' metal atomic orbitals.

With respect to the minimal CAS(2/2) space which only contains the neutral and ionic VB forms of Anderson's model, the CAS(6/4) space includes also a reduced number of 1h excitations which correspond to *LMCT* forms, given that the two added occupied orbitals are concentrated on ligands. A few 2h excitations are also contained in this space. Scheme 1 shows the different classes of determinants contained on this extended CAS. The labels identify the excitation with respect to the minimal CAS. The CAS(6/6) includes also 1p and 1h–1p excitations beyond the determinants of CAS(6/4). Scheme 2 shows the additional determinants contained in the CAS(6/6) space with respect to CAS(6/4) one. Due to the diffuse d nature of the added virtual orbitals, the 1p excitations are not *MLCT* excitations, but they take into account part of the relaxation of the magnetic orbitals. This space also contains a reduced number of determinants (~200) which do not belong to the DDCI (2/2) set.

Table 1 reports the J values obtained for systems **1**–**6** at CASCI level with three different CAS: the bare one, which contains only the metal-centered magnetic orbitals, CAS(6/4) and CAS(6/6). As expected, at this level, the magnetic coupling estimates are far from experimental values, but the impact of the extension of the CAS on J values, introducing an AF contribution on AF systems, and F contribution on F systems, is in line with the analysis reported in a recent work [55]:

1. The *LMCT* forms in the CAS(6/4) calculations favor the singlet state, due to their interaction with the ionic VB forms (which do not play any role in the triplet state). This introduces a differential stabilization and consequently an increase of the AF nature of the interaction. For F systems, this effect is negligible.

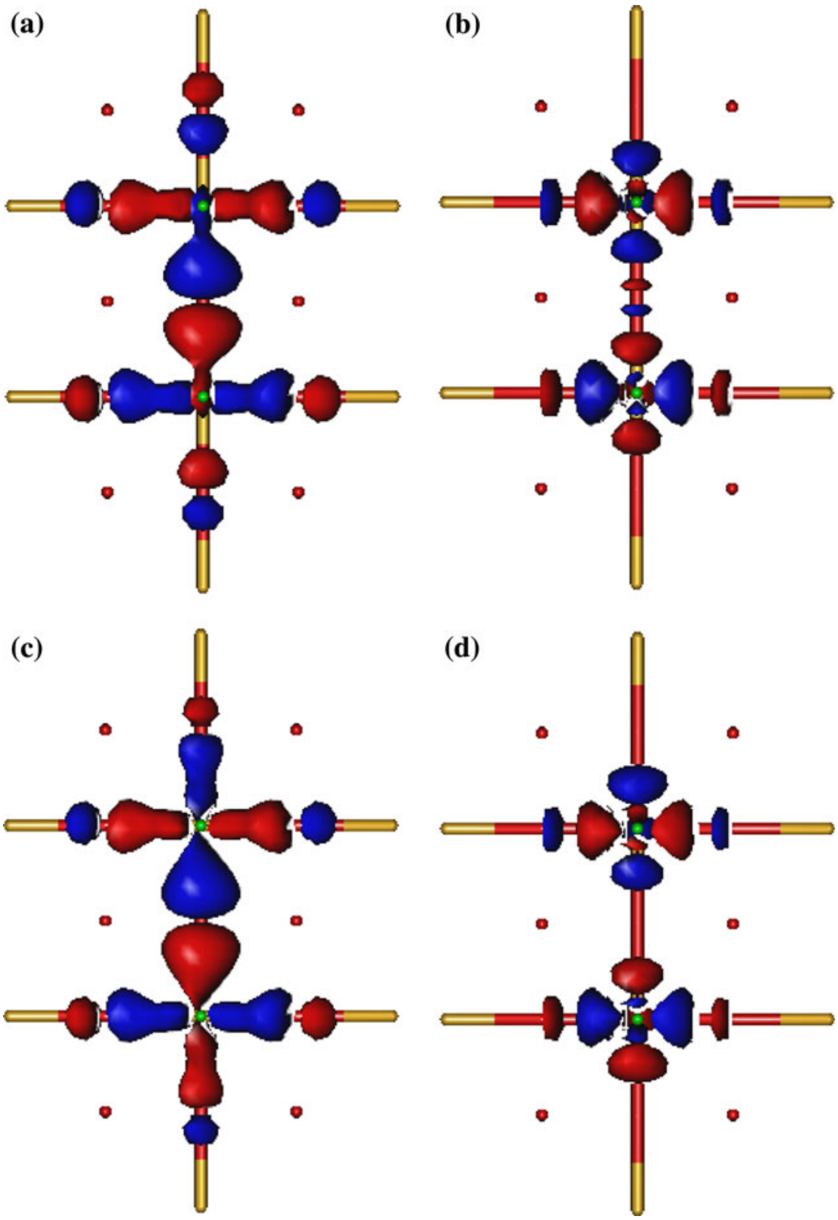


Fig. 4 Natural orbitals of *u* symmetry added to the minimal CAS for system **2**. **a** Occupied and **b** virtual "1*h* + 1*p*" MOs; **c** Occupied and **d** virtual natural orbitals, from DDCI(2/2) singlet–triplet average density matrices, included for comparison

This trend has been observed in previous class-partitioned CI calculations on the top of the minimal CAS, in particular for CAS(2/2) + 1*h*, where all the single excitations from the doubly occupied orbitals to the magnetic ones are taken into account (see Table 3). Notice that the CAS(6/4) space is a part of the CAS(2/2) + 1*h* one. In general, a larger AF contribution is obtained from the diagonalization of the extended CAS than from the inclusion of 1*h* excitations, which can be related to the improvement of the orbitals.

2. In CAS(6/6) calculations, the 1*p* excitations also give an AF contribution, for the same reason as 1*h*. This is corroborated by the CAS(2/2) + 1*p* results in Table 3. The presence of 1*h*–1*p* forms strengthens the AF effect in the case of AF systems, due to the dramatic stabilization of the ionic forms (drop of the on-site Coulomb repulsion, *U*), as indicated by the CAS(2/2) + 1*h*–1*p* values in Table 3. However, 1*p* excitations introduce a F contribution on F systems (see results for system **4** in Table 3), due to spin polarization effects governed by these determinants (without impact on AF systems).

When single excitations are added to these extended spaces, a general overestimation of the *J* absolute value is obtained. Taking into account the opposite effects of 2*h*–1*p* and 1*h*–2*p* classes of excitations in minimal CAS DDCI calculations, the effect of the single excitations on the extended CAS can be explained on the basis of the composition of the resulting CI spaces, as follows:

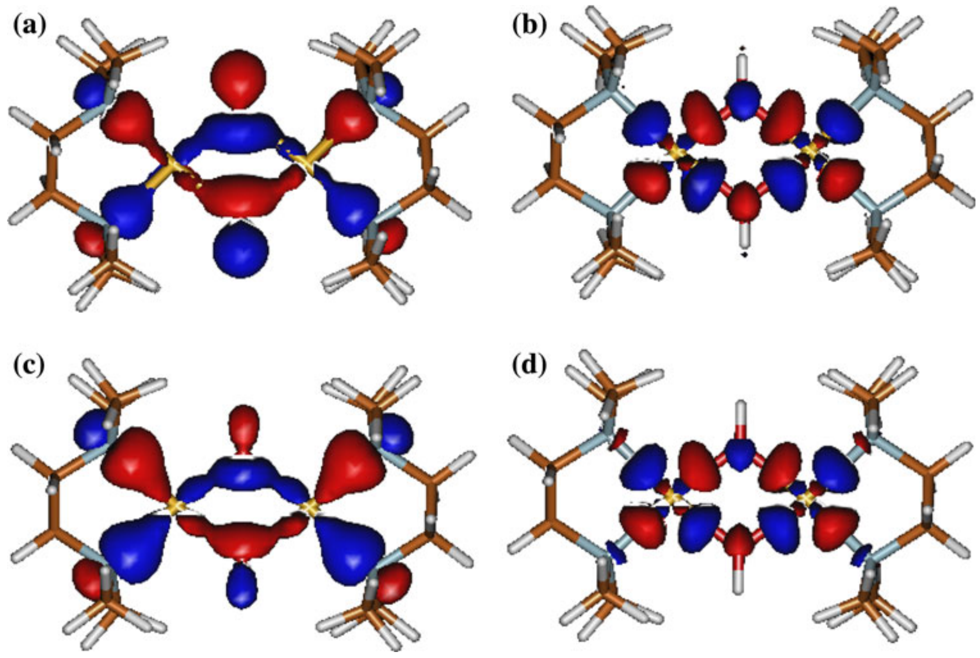


Fig. 5 Natural orbitals of *u* symmetry added to the minimal CAS for system **4**. **a** Occupied and **b** virtual "*U*" MOs; **c** occupied and **d** virtual natural orbitals, from DDCI(2/2) singlet–triplet average density matrices, included for comparison

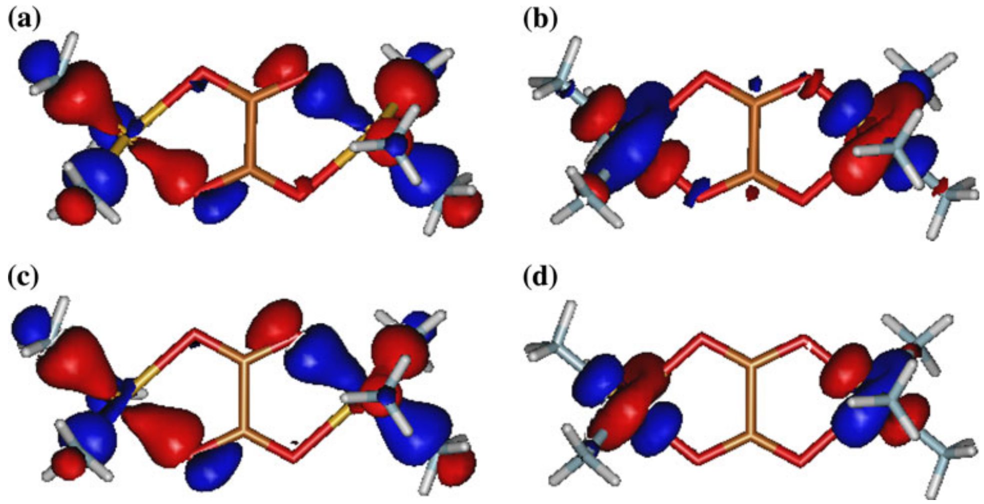
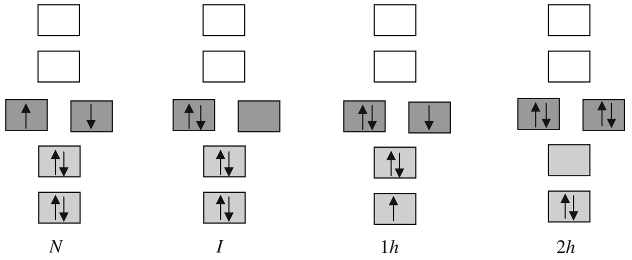
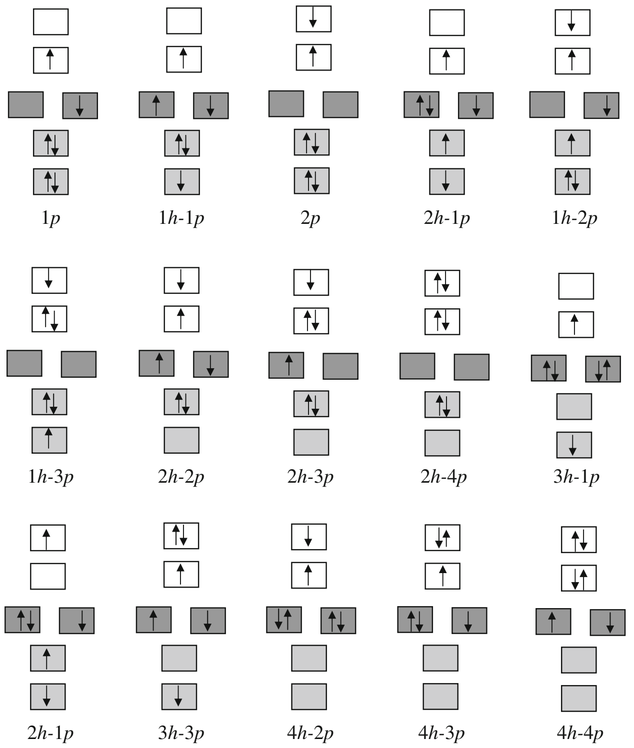


Fig. 6 Natural orbitals of *u* symmetry added to the minimal CAS for system **5**. **a** Occupied and **b** virtual "*U*" MOs"; **c** occupied and **d** virtual natural orbitals, from DDCI(2/2) singlet–triplet average density matrices, included for comparison



Scheme 1 Classes of determinants contained in CAS(6/4) space

1. The CAS(6/4) + S space contains part of the $2h$–$1p$ determinants contained in the DDCI(2/2) space, but not the $1h$–$2p$ excitations. The $2h$–$1p$ determinants participate in two main mechanisms, which introduce opposite contributions to J value. The $2h$–$1p$ determinants and *LMCT* forms mediate the coupling between the ionic and neutral forms, producing a general increase of the effective hopping integral between the magnetic orbitals, t_{ab}. This coupling between configurations *I–LMCT–2h1p–N* has only a significant impact on J when the dynamical polarization effects of the ionic and *LMCT* forms are taken into account, and this requires the presence of the $1h$–$1p$ determinants [55]. This mechanism is important in AF systems, where the ionic forms present non-null coefficients in the singlet wavefunction. For F systems, the interaction between the $2h$–$1p$ and *LMCT* configurations favors the triplet state, which presents a differential stabilization, and consequently produces a large ferromagnetic contribution to J. Since the



Scheme 2 Classes of determinants contained on CAS(6/6) space, in addition to those on CAS(6/4) shown in Scheme 1

CAS(6/4) contains only two doubly occupied orbitals, only a reduced part of the 2*h*–1*p* excitations are included in the CAS(6/4) + *S* space, and consequently the overestimation is lower than in the case of a CAS(2/2) + *S*+2*h*–1*p* space, as evidenced on Table 3.

2. While the CAS(6/6) + *S* additionally introduces those 1*h*–2*p* governed by the two extra virtual orbitals, their damping effect is not observed, probably due to the fact that this contribution is numerically less relevant than the 2*h*–1*p* one, and that the effect of the 1*h*–2*p* determinants cannot be concentrated on a reduced number of virtual orbitals in contrast to the 2*h*–1*p* ones. Consequently, the CAS(6/6) + *S* spaces work differently as the CAS(2/2) + *S*+1*h*–2*p* ones, as shown in Table 3.

Regarding systems with $S > 1/2$, the three explored binuclear Ni(II) compounds show similar behavior, although with practically no overestimation. In these systems, the minimal CAS is composed of four active orbitals, which can be described as the symmetric and antisymmetric combinations of d_{z^2} and $d_{x^2-y^2}$ orbitals of Ni centers. The orbitals included in the extended CAS have been selected from the diagonalization of the average singlet and quintet CAS + *S* density matrices, and correspond to the in-phase combinations of the Ni 3*d* magnetic orbitals and 2*p* ligand orbitals. Figure 7 represents those of symmetry *u* for system **7**. *J* has been obtained from the energy difference between the triplet and quintet states: $J = (E_T - E_Q)/2$, assuming a Landé spacing between the different levels. The complete set of molecular orbitals have been used in the reference DDCI calculations for systems **8** and **9**, while a truncated subset of inactive orbitals obtained from the energy-difference dedicated orbitals transformation [12] has been used for system **7**, due to the size of the full DDCI space for the triplet state, 10^8 determinants, that makes this calculations prohibitive and far from a systematic way to evaluate magnetic coupling constants.

As shown in Table 4, for these systems the *J* values obtained from CASext + *S* calculations are in good agreement with DDCI estimates, with deviations no larger than 1 cm^{-1}. The agreement with experiment is good for the F system **9** [29], while the AF values for **7** and **8** are underestimated by 5–10 cm^{-1} [28].

5 Conclusions

The computation of the magnetic coupling between localized unpaired electrons in organic poly-radicals and magnetic coordination chemistry complexes is not an easy task,

Table 3 Magnetic coupling constant *J* (cm^{-1}) for systems **1–6** obtained from class-partitioned CI and CASext + *S* calculations

CI space	La_2CuO_4 **1**	$Sr_2CuO_2Cl_2$ **2**	$[Cu_2(OH)_2]$ **3**	$[Cu_2(OH)_2]$ **4**	$[Cu_2(C_2O_4)]$ **5**	$[Cu_2(C_2O_4)]$ **6**
CAS(2/2)	−254	−160	−35	33	−7.3	−13.4
CAS(2/2) + 1*h*	−276	−169	−37	33		
CAS(2/2) + 1*p*	−285	−180	−49	34		
CAS(2/2) + *S*+2*h*-1*p*	−1,378	−1,199	−650	248		
CAS(2/2) + *S*+1*h*-2*p*	−542	−372	−94	71		
CAS(6/4)	−310	−193	−51	31	−7.6	−13.7
CAS(6/4) + *S*	−1,169	−1,032	−504	194	−57.3	−126
CAS(6/6)	−400	−270	−47	57	−12.3	−22.8
CAS(6/6) + *S*	−1,231	−1,119	−503	220	−65.1	−141.4
Exp.	[− 1,030, −1,096] [18–21]	−1,008 [22]	−509 [23, 24]	172 [25, 26]	−75 [27]	Model [15]

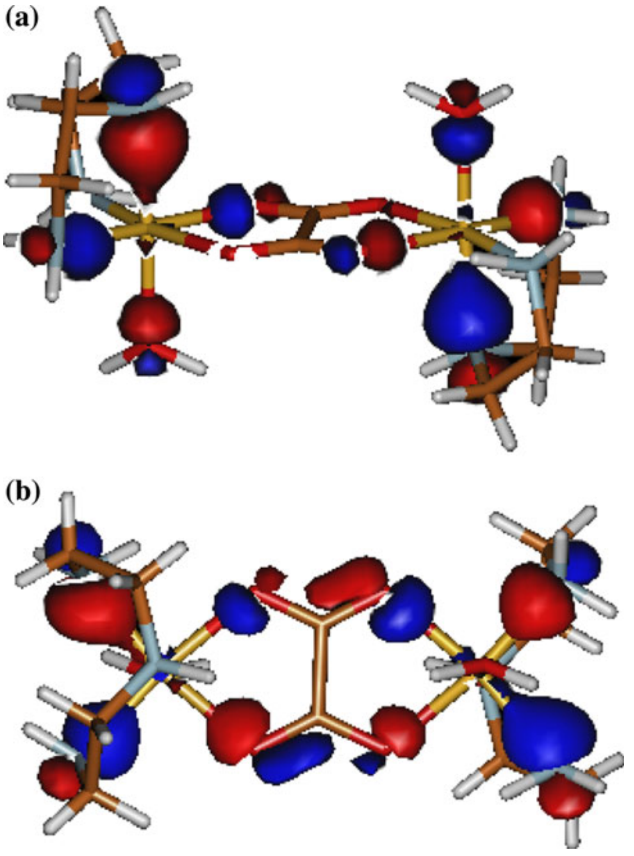


Fig. 7 Occupied CAS + *S* average natural orbitals of *u* symmetry included in the extended CAS for system **7**

Table 4 Magnetic coupling constant *J* (in cm^{-1}) for **7–9** binuclear Ni(II) systems

	Exp.	DDCI	CAS(12/8) + *S*
$[Ni_2(C_2O_4)]$ **7**	−28.8 [28]	−16.0–15.6 [32][a]	−16.6
$[Ni_2(C_2O_4)]$ **8**	−22.8 [28]	−11.3–15.3 [32][a]	−15.4
$[Ni_2(Cl_2)]$ **9**	19 [29]	18.5	17.9

Natural orbitals of the average singlet-quintet CAS(2/2) + *S* density matrix are used in the CASext + *S* calculations. Values reported by Bordas et al. [32] are also included

[a] Energy-difference dedicated MOs have been used to truncate the inactive space and to make feasible the DDCI calculations

since the concerned energy differences are extremely small with respect to the total electronic energy. Independent energy calculations of the various nearly degenerate states of different spin multiplicities can be performed but this procedure faces the risk of numerical uncertainties. The unrestricted DFT calculations that are easily performed at a low computational cost and may be extremely useful belong to this category. Their drawbacks are the sensitivity of the energy splitting to the chosen exchange correlation potential on one hand, and on the other hand, the fact that the calculated solutions for the states of non-maximum spin multiplicities are not spin eigenfunctions, which leads to strong debates. All strict ab initio calculations (i.e. those based on the exact electronic Hamiltonian) identify magnetic orbitals and magnetic electrons defining a minimal CAS, that can be extended to other orbitals and electrons. Some of these calculations are state specific. This is the case for instance of CASPT2, which definitely shows the importance of dynamical correlation effects. The most reliable calculations are variational ones (avoiding problems related to the choice of a zeroth-order Hamiltonian, and any parameter) and start from a common set of MOs, trying to target the energy difference from balanced variational calculations of the spin eigenstates under consideration. The DDCI method defines a truncated CI space from a second order analysis of the energy difference. Its performances are excellent, but its computational cost is high, and this fact limits severely its domain of application.

In the past, several strategies have been considered to reduce its cost and to extend its domain of validity. One consists in treating the most numerous excited determinants in a perturbative manner. This may be done from a selection of the most contributing determinants, as done in SORCI code. A different possibility is to restrict the variational calculation to some classes of excitations, and to treat the 2*h*–1*p* and 1*h*–2*p* excitations, which are the most numerous, with perturbation theory up to second order, but in a recent work, we have shown that their impact on the energy difference is not a second-order one. An alternative solution is based on the Anderson's superexchange model and suggests to extend the CAS to the MOs of the ligand, which transfer the magnetic information between the magnetic centres, and to perform only 1*h*–1*p* excitations on the top of this extended CAS [12, 17]. The present paper has examined the reliability and drawbacks of this strategy. We propose here a very direct and inexpensive way of defining the ligand MOs which should contribute to the super exchange mechanism. The efficiency of this determination is similar to that of previously proposed determinations. While it seems possible to capture the main part of the effect of 2*h*–1*p* excitations by introducing a few appropriately defined ligand-type occupied MOs in the CAS, this approach misses the main part of the damping effect of 1*h*–2*p* excitations and the resulting coupling constant are somewhat overestimated in AF systems. Attempts to introduce virtual MOs in the CAS fail to capture the effect of 1*h*–2*p* excitations. Actually, the most involved virtual MOs obtained from the density matrix diagonalization of the CAS + 1*h* + 1*p* CI do not appear to be ligand-supported but metal centered orbitals. There is no symmetry either between the roles of holes and particles, or between the 1*h*–2*p* and 2*h*–1*p* classes of excitations. A quantitative agreement with experiment, similar to that obtained from minimal CAS and DDCI calculations is not achieved by this strategy. It seems that there exists a significant distinction between the magnetic MOs and those of the ligands, among which a selection of a very limited number of contributing members is not possible.

This situation leads us to the conclusion that the extension of the domain of applicability of the DDCI method has to be searched in a topologically based limitation of the excitation processes of all classes, by employing localized inactive MOs, both occupied and virtual. Some of them may be frozen, since too far from the magnetic centres, and transition distributions between very distant MOs may be neglected, both resulting in a huge reduction of the number of semi active excitations [17, 56].

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