

Improving the calculation of magnetic coupling constants in MRPT methods

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Abstract

The magnetic coupling in transition metal compounds with more than one unpaired electron per magnetic center has been studied with multiconfigurational perturbation theory. The usual shortcomings of these methodologies (severe underestimation of the magnetic coupling) have been overcome by describing the Slater determinants with a set of molecular orbitals that maximally resemble the natural orbitals of a high-level multiconfigurational reference configuration interaction calculation. These orbitals have significant delocalization tails onto the bridging ligands and largely increase the coupling strengths in the perturbative calculation.

Keywords: Magnetic coupling, multiconfigurational perturbation theory, NEVPT2, transition metal complexes, DDCI ■

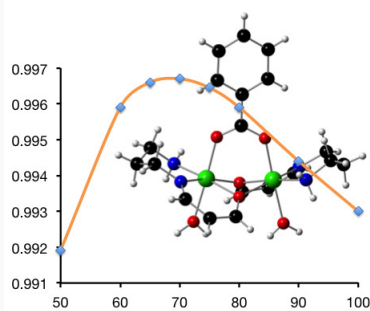
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Taking into account the ionic state in the optimization procedure of the molecular orbitals results in slightly more delocalized magnetic orbitals, and hence, repairs the underestimation of the magnetic coupling commonly observed for multiconfigurational perturbation theory.

Introduction

The calculation of accurate magnetic coupling constants has been a relevant theoretical problem for many years. The smallness of the energy differences and the antagonist physical effects involved in the interaction between spin moments make this a challenging topic for theoreticians. The difference dedicated configuration interaction (DDCI) method^{1,2} has been proven capable to produce coupling strengths in good agreement with the experimental findings for binuclear complexes and, more recently, also for polynuclear systems.³ Due to the variational nature of the method, DDCI can be applied with a minimal complete active space configuration interaction (CASCI) reference wave function, which makes it easy to use and attractive from a conceptual point of view.⁴⁻⁶ However, the high computational cost associated with DDCI calculations makes the method less suitable for systems with large ligands, many magnetic centers, or many unpaired electrons per magnetic center. Several variants of DDCI were developed in order to reduce the computational cost for such large systems, obtaining promising results.⁷⁻¹²

A second family of methods commonly used in the calculation of magnetic couplings are those based on multiconfigurational reference perturbation theory (MRPT). Applied to second order (MRPT2), these methods provide a computationally efficient alternative to DDCI extending the applicability range of the *ab initio* methods to larger systems. Although MRPT2 gives in general a rather reasonable description, there are some points that need to be carefully addressed in order to extract relevant conclusions from the perturbative treatment of the magnetic coupling. In the first place, one should be aware of the possible appearance of intruder states, and special attention in the definition of $\hat{H}^{(0)}$ must be taken. Compared to DDCI, MRPT2 results may show a strong dependence on the size of the active space, usually requiring the inclusion of ligand orbitals and a second set of magnetic orbitals in order to obtain quantitative results.^{13,14} Calculations based on a minimal active space reference wave function tend to underestimate the coupling strength by $\sim 60-80\%$.

A recent study on the role of the magnetic orbitals in the perturbative calculation of the magnetic coupling has identified the origin of the inability of MRPT2 methods to correctly estimate the J value in the nature of the starting MOs and has also proposed a pragmatic

strategy to improve the values on binuclear copper complexes without the necessity of extending the active space.¹⁵ The strategy is based on the observation that the natural DDCI magnetic orbitals are significantly more delocalized than the corresponding ones obtained from the bare CAS description of the system.¹⁶ Using the natural DDCI orbitals to express the minimal active space reference wave function for a perturbative treatment of the dynamic electron correlation greatly improves the calculated magnetic couplings, but such approach is of course not very efficient. The scheme proposed in Ref. 15 describes how one can obtain a set of orbitals that maximally resembles the natural DDCI orbitals without going beyond the minimal active space description. Instead of optimizing the orbitals for the ground state triplet or singlet (or an average of them), the reference wave function is obtained as a state average (SA) of two singlet states. The first one is the ground state singlet dominated by configurations with one unpaired electron per magnetic site (*neutral* singlet), and the second state is the so-called *ionic* singlet, which is dominated by configurations where the unpaired electron of one magnetic site is transferred to the other. Because of the double occupancy of the magnetic orbitals in the ionic singlet, the inclusion of this state in the orbital optimization procedure results in a set of orbitals with a higher degree of delocalization than the standard procedure. The optimal ratio between neutral and ionic states was determined by maximizing the overlap of the SA optimized magnetic orbitals with the natural DDCI orbitals. A ratio of 70% - 30% was found to give maximum overlap in a representative series of binuclear copper complexes and this ratio also turned out to provide accurate magnetic couplings when used in the perturbative treatment of the dynamic electron correlation based on a minimal active space.

The idea of this work is to extend the strategy to systems with more than two unpaired electrons. The main focus is on complexes with two magnetic orbitals per center, giving rise to a local magnetic moment of $S = 1$, but we also report a case with larger local spin moments. The $S = 1$ systems are still tractable with DDCI, and hence, we can establish the validity of the strategy by calculating the overlap with the natural DDCI orbitals. The applicability of the strategy to systems other than the previously tested binuclear copper complexes, is an important step towards a simple and computationally efficient scheme based on a minimal active space description in systems where DDCI cannot be applied anymore.

Molecular complexes and computational details

A simple yet accurate phenomenological Hamiltonian that accounts for the coupling between the local spin angular moments S_i and S_j was first introduced by Heisenberg as

$$\hat{H} = -J\hat{S}_i \cdot \hat{S}_j \quad (1)$$

where $\hat{S}_i$ is the total spin operator of site i and J parametrizes the coupling strength. Negative J -values correspond to antiferromagnetic coupling. In the complexes considered here, each Ni(II) ion has a triplet ground state, giving rise to quintet, triplet and singlet states when coupled to the other Ni(II) ion in the complex. The Heisenberg Hamiltonian predicts a regular energy spacing between these three states, known as the Landé pattern:

$$E(S - 1) - E(S) = JS \quad (2)$$

To investigate the importance of the deviations to the Heisenberg Hamiltonian, we calculated J from the energy difference of singlet and triplet, and triplet and quintet

$$E(S = 0) - E(S = 1) = J \quad (3)$$

$$\frac{1}{2}(E(S = 1) - E(S = 2)) = J \quad (4)$$

When the two J values are equal the states follow the so called "Heisenberg behavior". Otherwise one should either extend the model Hamiltonian with biquadratic interactions terms,^{6,17-19} (which are usually very small^{18,20,21}) or put doubts on the reliability of the computational scheme.¹⁴

As test systems for magnetic coupling between sites with spin angular moments $S = 1$, we selected a series of binuclear Ni(II) systems with different bridges, represented in Figure 1. The structure of the complexes was taken from x-ray crystallographic data and (when necessary) slightly modified to adapt it to a specific symmetric point group. Previous studies suggest that small geometrical changes to symmetrize the structure do not significantly affect the calculated coupling strength.^{22,23}

First, we present two complexes which have a double end-to-end azido bridge between the Ni(II). The general formula is $[\text{Ni}(\mu_{1,3}\text{-N}_3)(\text{R})]_2^{2+}$, where the external ligands are $\text{R} =$

5,5,7,12,12,14-hexamethyltetraazacylotetradecane (**1a**) and 1,2-diaminopropane (**1b**). Both compounds have a strong antiferromagnetic coupling (J) of -75.1 and -114.5 cm^{-1} respectively,^{24,25} and they differ in the dihedral angle between the Ni(II) coordination spheres with respect to the bridge.^{25,26} To facilitate the calculations we have replaced the external ligands with NH_3 groups. As for the symmetrization, this only has a weak influence on the calculated coupling.²³

$[\text{Ni}_2(\text{dien})_2(\text{H}_2\text{O})_2(\text{ox})]^{+2}$ (dien = diethylenetriamine, ox = oxalate) (**2**) with $J = -28.8$ cm^{-1} has an oxalato-bridge.²⁷ More complex bridges are found in the complexes **3-5**. First we consider $[\text{Ni}_2(\text{PHP6Me})\text{Cl}(\text{H}_2\text{O})_4]^{3+}$ (PHP6Me = 1,4-bis((6-methylpyridine-2-carboxaldimino) amino)phthalazine) (**3**)²⁸ with $J = -25.98$ cm^{-1} and $[\text{Ni}_2(\text{ppd})_2(\text{H}_2\text{O})_4]^{4+}$ (ppd = 3,6-bis(1'-pyrazolyl)pyridazine) (**4**)²⁹ with $J = -29.6$ cm^{-1} . The Ni(II) ions in $[\text{Ni}_2\text{L}_2(\text{O}_2\text{CPh})(\text{H}_2\text{O})_2]^{+}$ (L = 2-[(3-Methylamino-propyl imino)-methyl]-phenoxide) (**5**)³⁰ with $J = -16.48$ cm^{-1} are coupled through a triple bridge: one carboxylate group and two alkoxo groups. Finally, the Ni(II) ions in La_2NiO_4 (**6**) are connected by an O^{2-} ion. The linear Ni–O–Ni pathway gives rise to a very strong coupling ($J = -240$ cm^{-1}). The coupling in this extended system was calculated using a Ni_2O_{11} fragment embedded in a set of point charges and total ion potentials simulating the Madelung potential of the infinite crystal and the short-range Coulomb and exchange interactions with the surrounding, respectively.

The orbital optimizations and CASPT2 calculations were performed using MOLCAS.³¹ The CASDI program^{32,33} was used to perform the DDCI calculations and the NEVPT2 results were obtained with the computer code developed at the University of Ferrara.³⁴ Relativistic Atomic Natural Orbitals (ANO-RCC) basis sets were used, contracted to [2s] for H, [3s,2p] for C and N in external ligands, [3s,2p,1d] for O and bridging C and N, [4s,3p,1d] for Cl and [5s,4p,3d] for Ni. The DDCI calculations are at the limit of what is still feasible, especially for the complexes with voluminous ligands. To reduce the number of inactive (virtual) MOs and consequently the size of the DDCI space, we apply the dedicated orbital transformation^{7,35} to order the MOs by decreasing importance for the energy differences.³⁶ The less important MOs were excluded from the generation of the CI expansion. To avoid any bias towards a particular spin state in the DDCI calculations, we used the iterative DDCI scheme.³⁷ The results are made independent of the starting orbital set by constructing average natural

orbitals by diagonalizing the triplet-quintet average DDCI density matrix and perform a new DDCI step with the average orbitals. The process is iterated until the energy difference becomes constant, normally in three or four steps.

The original zeroth-order Hamiltonian³⁸ was used in CASPT2 because this choice has been shown to be more adequate for magnetic couplings than the present zeroth-order Hamiltonian³⁹ based on the IPEA=0.25 Hartree parameter. The zeroth-order Hamiltonian of n -electron valence PT2 (NEVPT2)^{40–43} is based on Dyal’s model Hamiltonian,⁴⁴ which contains all two-electron interactions among the active electrons. We have used both the strongly-contracted (SC) and partially-contracted (PC) variant of NEVPT2.

State average methodology

The reference wave function for the DDCI and MRPT2 calculations was obtained at the CASSCF level. Binuclear Ni(II) compounds present 2 magnetic orbitals and 2 electrons per metal atom. Therefore the minimal active space required has 4 electrons in 4 orbitals, CAS(4,4). The compounds present a C_i symmetry point group, except **4** which has C_{2v} . Figure 2 shows the magnetic orbitals of gerade (g) symmetry, a combination of $3d_{xy}$ (a) and $3d_{z^2}$ (b) Ni orbitals. According to previous studies, the former has a higher contribution to the spin coupling due to the favorable delocalization in the plane containing the nickel and the bridge atoms.¹⁸

To obtain a test set of molecular orbitals with a larger degree of delocalization an excited electronic state with ionic character has to be identified. However, due to the size of the active space, a large number of ionic singlet states appear in the calculation, in contrast to the copper case where at most two ionic states are possible. Moreover, local excited states (d-d transitions) also form part of the CAS space. Therefore, the first step was to identify the states which were relevant for the magnetic coupling under study.

To facilitate the analysis of the electronic states the symmetry adapted magnetic orbitals were transformed to local atomic-like orbitals by a unitary transformation based on the projection of a model vector in the active space.¹⁰ Orbitals localized on the left/right Ni(II) ion are labelled with A and B, respectively. The ground state (1^1A_g) is dominated by

the configuration state functions with one electron in each magnetic orbital arising from the $M_S = 0, \pm 1$ components of the local triplet states. This "neutral" character of the ground state is also present in the first nine excited singlet states. All these states have multiconfigurational character and are dominated by configurations in which an electron is transferred from one magnetic orbitals to the other on the same site. Their energy is in the region between 4 and 10 eV above the ground state. The next excited singlet state is at 26 eV above the ground state at CASSCF level. This ionic state (8^1A_g) is basically a combination of two configurations; one with two electrons in $A_{3d_{xy}}$ and two singlet coupled electrons in $A_{3d_{z^2}}$ and $B_{3d_{xy}}$, and the other with two electrons in $B_{3d_{xy}}$ and two singlet coupled electrons in $A_{3d_{xy}}$ and $B_{3d_{z^2}}$. That is, one of the $3d_{z^2}$ orbitals loses its electron in favor of the other atom's $3d_{xy}$ orbital. Close in energy we found similar ionic states with configurations where the $3d_{z^2}$ orbitals are doubly occupied instead of the $3d_{xy}$ ones. Finally, more than 90 eV above the ground state there are two doubly ionic states with configurations where the 4 electrons belong to a single atom. Taking into account that the $3d_{xy}$ orbitals are more important for the spin coupling than the $3d_{z^2}$ ones, we selected the first ionic gerade state for the SA-CASSCF calculations, obtaining a set of MOs from wave functions with a mixing of 50% 1^1A_g / 50% 8^1A_g ($W = 50\%$) up to 90% 1^1A_g / 10% 8^1A_g ($W = 90\%$) following the recipe applied for the Cu(II) binuclear complexes.¹⁵

The overlap of the magnetic orbitals obtained in the SA-CASSCF with different weights of ionic state (S) with the natural DDCCI orbitals (N) is calculated by

$$ovl(S, N) = \sqrt{\frac{\sum_{i \in S} \sum_{j \in N} | \langle i | j \rangle |^2}{n}} \quad (5)$$

where n is the total number of magnetic orbitals (four in this case) and i and j are the SA-CASSCF and IDDCI magnetic orbitals, respectively. This ensures that the calculated overlap does not depend on the particular representation of the magnetic orbitals (localized-delocalized and redundant orbital rotations in the active space).

Results

Table 1 shows the magnetic coupling constant J for systems **1a**, **2** and **3** using the state specific CASSCF(4,4) molecular orbitals. As stated before, NEVPT2 couplings with these MOs are weaker than the IDDCI result, which in turn is in rather good agreement with experiment. Small differences may arise from the symmetrization, modelling of the external ligands and truncation of the MO space after the dedicated orbital transformation. The CASPT2 estimates of J obtained from E(S)-E(T) are reasonable. If we analyze the deviation from the Heisenberg behavior, we observe that NEVPT2 results nicely fit the Landé pattern, while CASPT2 shows unrealistic deviations. For these systems, the number of determinants in the singlet DDCI functions are rather large ($\approx 1.0 \times 10^8$) and it becomes computationally quite expensive to obtain IDDCI converged energies for the singlets. Hence, we cannot directly access the degree of deviation from Heisenberg at this level of calculation. However, previous theoretical studies on system **1a**²⁶ and related complexes^{14,21} show that the deviations obtained in DDCI are in general small. This suggests that the deviations to the Heisenberg behavior observed with CASPT2 are not physically grounded, as previously concluded for other complexes.^{14,45,46}

To decide on the optimal weight of the ionic state in the SA-CASSCF orbital optimization, we have calculated the overlap of the magnetic orbitals for different weights of the neutral state (W). Table 2 shows how the overlap of the SA-CASSCF and IDDCI natural magnetic orbitals evolves as function of W . The trend is more or less uniform for all the compounds, increasing with the neutral % until reaching a maximum and then decreasing again for smaller weights of the ionic state. This "inverted parabola" shape is consistent with the previous copper study. The maximum is located in the region between $W = 70$ to 80 , with an overlap quite close to 1, as found for the copper complexes.

This is also illustrated in Figure 3, where it can be clearly seen that the singlet state CASSCF $3d_{xy}$ orbital is more compact, more localized on the metals, than the IDDCI natural orbital. As stated before, this difference is crucial when working with MRPT2 methods. We can also see that the SA-CASSCF orbital is quite similar to the IDDCI natural orbital.

In Table 3, we present the NEVPT2 results for systems **1a**, **2** and **3** obtained with the

cited SA-CASSCF MOs, focusing on the optimal range $W = 70 - 80\%$ based on the overlap analysis. As in the case of the Cu(II) dinuclear complexes,¹⁵ a decrease of the neutral weight (W) in the SA orbitals leads to an increase of the antiferromagnetic character of the coupling. The calculated values reach a nearly exact coincidence with the IDDCI estimates around $W = 70\%$; for **1** at slightly larger value and for **2** at somewhat smaller W . This is the same percentage of neutral/ionic mixing found for Cu compounds.

Furthermore, the results in Table 3 show that the Landé pattern for the splitting of the three spin states is maintained for all weights in the NEVPT2 calculations. Using SA-CASSCF orbitals to express the reference wave functions for CASPT2 does not lead to an improved description. The deviations to the Heisenberg behavior remain (become more pronounced) and the calculated J -values are not better than those obtained with state-specific orbitals using the singlet-triplet energy difference to determine J .

Table 4 shows the magnetic coupling constant with state specific and SA-CASSCF MOs ($W = 70-80\%$) for complexes **1b** and **4-6**. In line with the analysis for **1a**, **2** and **3**, the same pattern is observed, that is, (i) too small values for CASCI and NEVPT2 with state specific MOs, (ii) reasonable agreement with IDDCI and experiment for CASPT2 when state-specific orbitals are used only if the singlet-triplet energy difference is considered, (iii) significant improvement when NEVPT2 is applied with SA-CASSCF($W = 70\%$) orbitals, (iv) and non-negligible deviations to Heisenberg in the CASPT2 spectrum. The large coupling between the Ni(II) ions in La_2NiO_4 crystal (**6**) is also reasonably reproduced with NEVPT2 based on SA-CASSCF($W = 70\%$) orbitals. In this case small deviations from the Landé pattern are observed. These deviations were reported for DDCI calculations as well and were ascribed to a non-negligible contribution of biquadratic interactions caused by relatively low-lying local non-Hund states.¹⁸

Finally, we compare the performance of the different methods taking into account the percentage error with the experimental values. Table 5 shows the percentage difference between the calculated and experimental J values. First of all, we can see the good performance of singlet-triplet CASPT2 using state specific MOs, with an average error of 27%. In addition to the methodological drawbacks (possibility of intruder states, choice of zeroth-order Hamiltonian), it is also worth mentioning again that CASPT2 does not follow the Landé

pattern expected from the Heisenberg behavior and in cases with weak coupling the ground state is not always the correct one and one faces serious problems to decide on the nature of the coupling, ferro- or antiferromagnetic.¹⁴ Moreover, it can be anticipated that CASPT2 will be less suitable for antiferromagnetic systems with many unpaired electrons. In these cases, J is only accessible from the energy difference between the states with the highest spin multiplicity due to the size of the active space for low-spin coupled states. However, the large deviations in the Landé pattern for these states observed here makes such approach highly unreliable.

As stated before state specific PC-NEVPT2 performs poorly in our study (average of 70% error) but the use of SA-CASSCF MOs with a 70% of neutral weight greatly improves the results of this method (33% error) and results become comparable to CASPT2 with the advantage of Heisenberg behavior and no appearance of intruder states. Finally, we need to mention the IDDCI performance (24% error) which is slightly bigger than generally obtained with this method in other compounds. The IDDCI results are directly affected by the approximations made in this work, namely a removal of virtual orbitals to reduce the space of determinants to make the calculations of the biggest systems tractable.

Concluding remarks

In this work we expand the study of the role of magnetic orbitals in the calculation of MRPT2 methods. After the cited results on copper, the natural choice was to focus on nickel binuclear complexes as the next step in complexity. The study covers a wide range of antiferromagnetically coupled compounds with different bridge types, which serve as a good testing ground. The results are promising as we show that PC-NEVPT2 can be greatly improved using a set of MOs that are easy to obtain but have the same characteristics as the natural orbitals determined via a computationally expensive scheme. The proposed strategy has an outstanding "accuracy / computational cost" ratio, which might lead this computational scheme to a further wide use.

Concerning the CASPT2 results, we found that reasonable results are obtained using single-state optimized orbitals and no improvement is observed when the SA-CASSCF are

used. However, calculations have to be done with great care since intruder states may appear, a non standard zeroth Hamiltonian has to be employed and last but not least, deviations to the Landé pattern are intrinsic to the method. A second inconvenience of CASPT2 is that for the coupling in binuclear Cu^{2+} complexes the single-state orbitals obtained from a minimal active space does not provide equally good results as observed in the present work for the Ni complexes. To circumvent the drastic increase of the size of the CAS when considering system with more unpaired electrons, it is often recommended to leave behind the concept of a complete active space and rely on restricted active space SCF (RASSCF),⁴⁷ occupation restricted multiple active space (ORMAS)^{48,49} or variants of the generalized active space SCF (GASSCF)^{50,51} approach. This would indeed widen the applicability range of *ab initio* wave function based methods, but the drawbacks lined-out for CASPT2 will also show up for RASPT2, the implementation of MRPT2 with a RASSCF reference wave function.⁵²

Although the complexity of the technique presented in this work increases with the number of unpaired electrons and magnetic centers –there will be more and more roots between the magnetically interesting neutral state and the first ionic state– our future work will be focused on the application to more complex systems, where DDCI calculations are definitely out of the question. A first step in this direction has been taken already. Triggered by the recent study of a binuclear Cr(III) complex by means of the Density Matrix Renormalization Group (DMRG) technique,⁵³ we have further tested our methodology for this model system ($[\text{Cr}_2\text{O}(\text{NH}_3)_{10}]^{4+}$) with 6 unpaired electrons. Following exactly the same strategy as for the Ni complexes, the PC-NEVPT2 result for J is -300 cm^{-1} using SA-CASSCF orbitals with $W = 70\%$, in very good agreement with the DMRG results.⁵⁴ The estimates of the J -value derived from singlet-triplet, triplet-quintet and quintet-heptuplet energy differences are all very similar, no significant deviations from the Landé pattern were observed, in contrast to the DMRG results reported by Harris *et al.*

The work reported here on the dinuclear Ni(II) complexes and the preliminary result for the Cr-complex with six unpaired electrons is of course only a first step in the direction towards a general method applicable to (virtually) any polynuclear complex with localized spin moments. However, the extension of the original proposal –applied only to systems with two $S = \frac{1}{2}$ spin moments– to systems with $S = 1$ (and even higher in the Cr case)

establishes as a general feature that the poor quality of the single-state optimized CASSCF orbitals causes severe underestimations of magnetic coupling strengths with MRPT2, in particular NEVPT2. This failure is largely remedied by using a molecular orbital set that resembles as much as possible IDDCI the natural orbitals, which are slightly more delocalized in nature. This can be considered as the main conclusion of our work and the state-average strategy that we developed to obtain a set of molecular orbital that maximally resembles the IDDCI natural orbitals has been demonstrated to be applicable beyond the previous tested $S = \frac{1}{2}$ -systems. This does not automatically ensure that the same strategy can be applied to any polynuclear system and we recognize that further work has to be done on the strategies to improve the quality of the molecular orbitals that span the reference wave function for the MRPT2 treatment of the electron correlation.

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Figure 1: Structures of the systems of study. Color coding for the atoms: nickel, green; carbon, black; oxygen, red; nitrogen, blue; chlorine, yellow; hydrogen, white; lanthanum, grey.

Figure 2: Symmetry-adapted g magnetic orbitals for system **1b**. (Isovalue = 0.03)

Figure 3: Symmetry-adapted gerade magnetic orbital of $3d_{xy}$ character of complex **1b** for singlet state specific CASSCF (a), SA-CASSCF ($W = 70$) (b) and IDDCI Natural Orbitals (c). (Isovalue = 0.03)

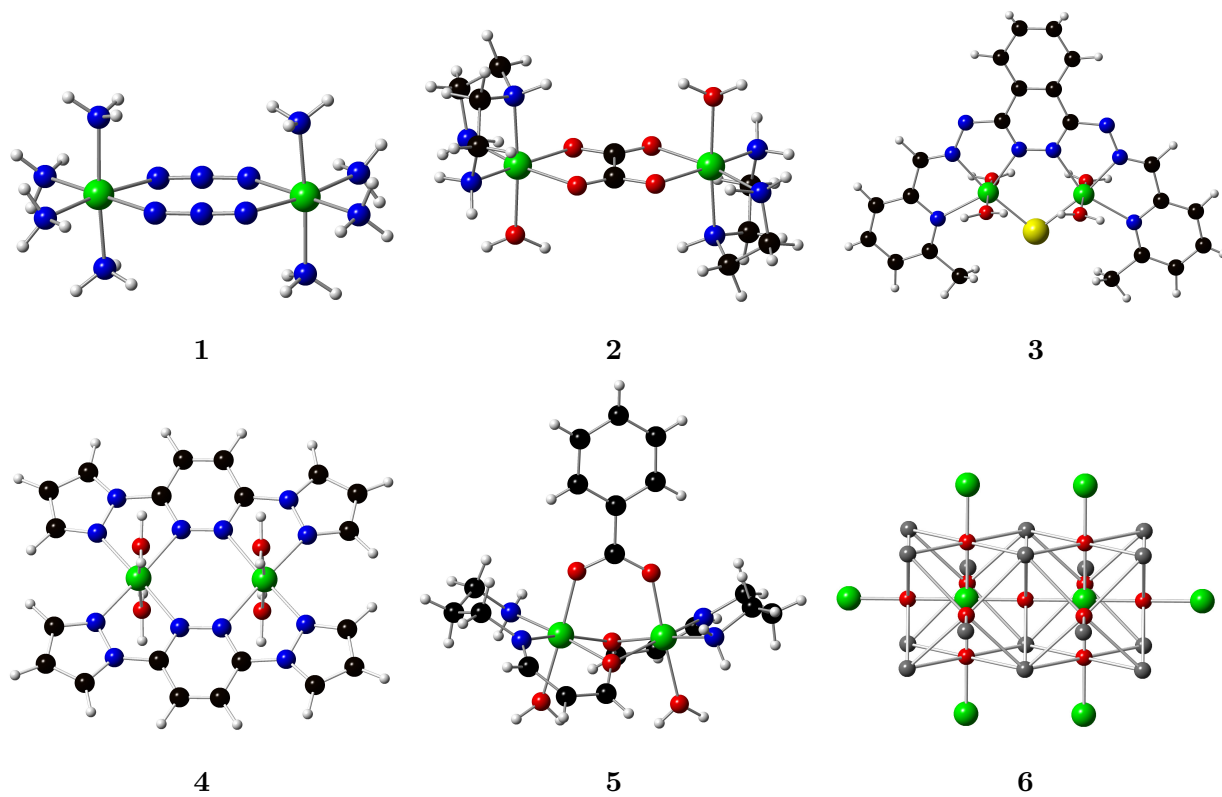


Figure 1
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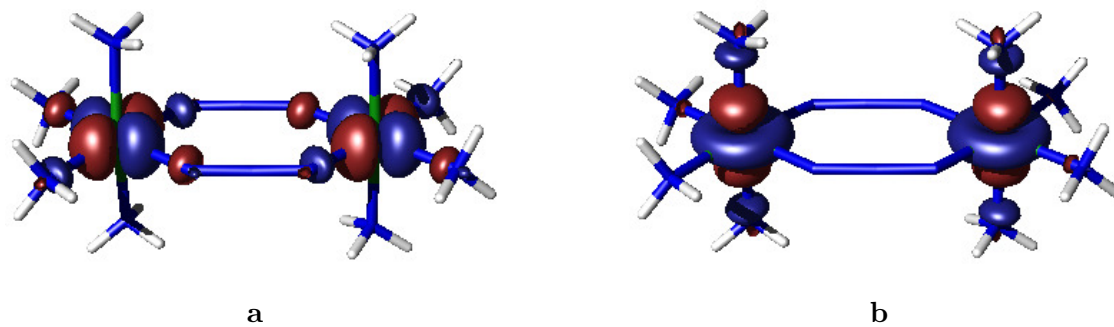


Figure 2
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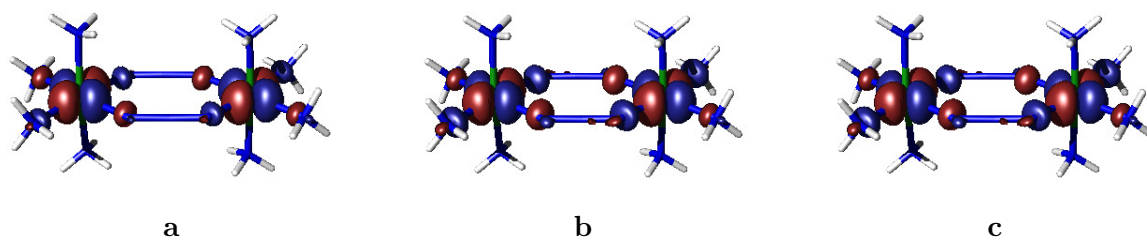


Figure 3
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Table 1: Magnetic coupling constant $J(\text{cm}^{-1})$ calculated using state specific CASSCF(4,4) MOs for complexes **1a**, **2** and **3**. The J-values refer to $E(\text{S})-E(\text{T})$ and $[E(\text{T})-E(\text{Q})]/2$, except for IDDCI where only the latter is reported.

	1a	2	3
CASCI	-10 / -11	-4 / -3	-2 / -2
CASPT2	-62 / -48	-22 / -17	-20 / -13
SC-NEVPT2	-27 / -24	-7 / -6	-6 / -5
PC-NEVPT2	-29 / -26	-7 / -7	-7 / -6
IDDCI	-65	-21	-15
Exp.	-75.1	-28.8	-26

Table 2: Overlap of the magnetic SA-CASSCF and IDDCI natural orbitals for different weights (W , %) of the neutral state used in the orbital optimization. $W = 100\%$ correspond to the singlet ground state MOs. The maximum overlap is marked in bold.

W	1a	1b	2	3	4	5	6
50	0.9675	0.9722	0.9903	0.9905	0.9845	0.9919	0.9891
60	0.9913	0.9914	0.9950	0.9959	0.9947	0.9959	0.9951
65	0.9950	0.9947	0.9959	0.9975	0.9965	0.9966	0.9969
70	0.9962	0.9959	0.9962	0.9984	0.9971	0.9967	0.9981
75	0.9962	0.9961	0.9960	0.9989	0.9968	0.9964	0.9986
80	0.9957	0.9958	0.9956	0.9991	0.9962	0.9960	0.9987
90	0.9938	0.9946	0.9939	0.9987	0.9938	0.9944	0.9977
100	0.9918	0.9929	0.9925	0.9979	0.9919	0.9930	0.9967

Table 3: PC-NEVPT2 magnetic coupling constants J (cm^{-1}) for **1a**, **2** and **3** as function of the weight of the neutral state W (%) used in the SA-CASSCF(4,4) orbital optimization. The values refer to $E(S)-E(T)$ and $[E(T)-E(Q)]/2$.

W	1a	2	3
65	-125 / -126	-21 / -21	-21 / -20
70	-81 / -81	-17 / -17	-15 / -15
75	-56 / -56	-14 / -14	-11 / -11
80	-41 / -41	-12 / -12	-9 / -9
IDDCI	-65	-21	-15

Table 4: Magnetic coupling constant $J(\text{cm}^{-1})$ calculated for systems **1b** and **4-6**. The values refer to $E(S)-E(T)$ and $[E(T)-E(Q)]/2$.

	1b	4	5	6
CASCI	-14 / -13	-5 / -4	1 / 1	-76 / -70
CASPT2	-87 / -68	-23 / -16	-5 / -1	-219 / -206
SC-NEVPT2	-24 / -23	-12 / -11	4 / 2	-162 / -147
PC-NEVPT2	-27 / -27	-13 / -12	1 / 2	-168 / -154
IDDCI	-94	-19	3	-228
W	PC-NEVPT2 with SA-CASSCF MOs			
70	-53 / -52	-21 / -21	-9 / -9	-206 / -214
75	-42 / -42	-17 / -17	-5 / -5	-177 / -183
80	-37 / -36	-14 / -14	-3 / -3	-155 / -160
Exp.	-115	-29.6	-16.5	-242

Table 5: Percentage errors (%) for the different methods used in this work.

	State Specific		State Average ¹	
	CASPT2	PC-NEVPT2	PC-NEVPT2	IDDCI
1a	17	61	8	13
1b	24	76	54	18
2	24	76	41	27
3	23	77	42	42
4	22	59	29	36
5	70	112	45	-
6	10	31	13	6
Average	27 ²	70	33	24