The role of the multiconfigurational character of nitronyl-nitroxide in the singlet-triplet energy gap of its diradicals

Vincenzo Barone [a], Ivo Cacelli [b,c], Alessandro Ferretti [c*]

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a) Scuola Normale Superiore di Pisa, Piazza dei Cavalieri, I-56126 Pisa, Italy
b) Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi 13, I-56124, Pisa, Italy
c) Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), Area della Ricerca, via G. Moruzzi 1, I-56124 Pisa, Italy

Abstract

While technological applications demand for the setup of reliable computational techniques and accurate experiments for the characterization of diradicals, these species are still challenging systems for both theory and experiments. The singlet-triplet energy gap, the J-term of the Heisenberg-Dirac-vanVleck spin Hamiltonian, is the most significant quantity, whose measurement and computational evaluation may serve for understanding and governing magnetism at the molecular scale. In this framework, we report here on a study of three diradicals containing one or two nitronyl-nitroxide species. Using Difference Dedicated Configuration Interaction (DDCI) calculations we investigate on the multiconfigurational character of the O-N-C-N-O fragment of this unit. We find that only through a computational scheme that takes this nature into account, we can be confident of obtaining reliable values of the spin-spin coupling J. In addition, we show that the reduced DDCI2 scheme with a CAS(2,2) reference, apparently able in some cases to reproduce experimental data, provides quite poor results in the present context.

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* corresponding author e-mail: alessandro.ferretti@pi.iccom.cnr.it

Introduction

There is a growing interest in the design and study of magnetic materials, driven by their wide applicability in technological tools and in the improvement of electronic devices [1-18]. At the molecular level, magnetic properties occur in the presence of unpaired electrons, a condition that is well known to be rather common in transition metal complexes (see e.g. ref. [1]) but less frequent in stable organic species. Driven from potential technological applications, much attention has been devoted to poly-radicals, [2, 19-45] where unpaired electrons might operate as spin filters and in devices where spin-dependent transport and/or stable data storage is required. [9, 46] It is recent the study of switchable magnetic species[47], that of the reversible control of charging an open-shell species to a doublet in a three-terminal device [16] and the study of molecular rectification in a diradical species [17].

A systematic experimental effort has brought in the last few years to the synthesis of stable organic poly-radicals [28, 30, 31], while most of the experimental work has been focused with particular attention to diradicals, the smallest member of the series [21, 22, 24, 35, 43, 45], interesting as building blocks for larger multi-spin systems or plugged into Donor-Bridge-Acceptor species. This extensive experimental work (our citation list is far from being complete and we apologize for the many we have not cited) has been accompanied by intense theoretical and computational activity, reviewed in detail in ref. [26] in addition to the articles already cited, carried out with the aim of unraveling the quantities and mechanism controlling the spin-spin interaction, a key point in the mastery of molecular magnets, but also investigating the tailoring of molecular fragments in the search of species with the desired properties [28].

Several models and computational methods have been developed to evaluate the spin-spin interaction [26], beginning with the simplest Heisemberg-Dirac-van Vleck (HDVV) model Hamiltonian, which is still very useful for an evaluation of the coupling terms in multi-spin systems [44, 48, 49], or with the Hubbard Hamiltonian, which can help the interpretation of the magnetic properties of polyradicals. [50, 51] The main objective of quantum chemical computations is the energy gap between eigenstates of different spins, which drives the magnetic properties of the corresponding material.

In the specific case of diradicals, the spin-spin coupling J (with the choice $H=-JS_1 \cdot S_2$) represents the singlet-triplet energy gap ($J=\Delta E_{TS}=E_S-E_T$), a quantity which can be measured with different techniques and compared to theoretical values. Within Density Functional Theory (DFT), broken symmetry (BS) allows to deal with the multi-configurational singlet with one electron on each magnetic moiety at a small computational cost [52-57]. An extension of DFT based on the Spin-Flip [58-61], where the singlet and triplet states with $M_s=0$ are generated by spin flipping operators acting on the $M_s=1$ triplet state, avoids the approximations underlying BS. Wavefunction based methods are theoretically more solid although computationally more expensive and include multi-reference perturbation approaches such as CASPT2, NEVPT2 [62, 63] and MRPT [64], RAS-SF [65-68] and Coupled-Cluster methods such as the spin-flip EOM [37, 69].

Among the various possibility, back in 2008 [70] we have chosen the Difference Dedicated Configuration Interaction (DDCI) approach by Miralles et al. [71, 72], since in our opinion it guarantees a good accuracy at an acceptable computational cost, which is an advantage when dealing with medium-large species as those

available to date. The method has been incorporated in a general theoretical approach we have developed and assembled in a computer code named BALOO [73], which exploits orbital localization, virtual orbital rearrangement and CI calculations, possibly complemented with Multi Reference perturbation theory. DDCI has been applied to some nitroxide and nitronyl nitroxide diradicals [70, 74-81], as well as to triradicals [51] and to a stable tetraradical [82] synthesized in the Rajca group [28, 31]. Beside the singlet-triplet energy gap, DDCI can also successfully be applied to the calculation of the parameters of the spin Hamiltonian [83-85].

Once a minimal CAS space has been defined as a reference, DDCI represents a rational reduction of the CI space generated by all single and double excitations of the Slater determinants (SD) included in the CAS. A natural choice for the CAS space for diradicals is the 4-dimensional CAS(2,2), which is obtained by distributing one electron in each magnetic orbital. This has shown to be a good choice for nitroxides and many other diradicals, either organic or transition metal based (see ref. [26] and references therein). On the other hand, in the case of the nitronyl-nitroxide diradical, known as Ullmann's diradical [86], only DDCI2, a simplified variant of DDCI, is found to fit experimental data [62, 70, 87], whereas the result of the complete DDCI model is only about 1/3 of the experimental value [62] of triplet-singlet energy gap. This apparent failure of DDCI has been interpreted in ref.[62] as due to the defective choice of the reference CAS(2,2), which should take into account that for each nitronyl-nitroxide unit only a 3-site-3-electron (CAS(3,3)) is able to account for the multiconfigurational nature of the wavefunction and, consequently, leads to the correct spin density on the Carbon atom of the O-N-C-N-O fragment bearing the magnetic character.[62, 88, 89] This implies that a CAS(6,6) should be taken as a reference space for the DDCI calculation of ΔE_{TS} in the Ullmann's diradicals, as confirmed by the results of ref. [62].
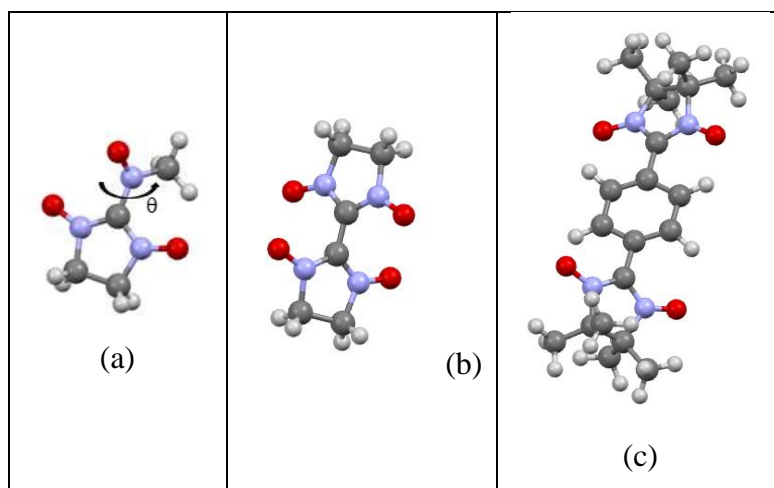

Figure 1 - Structures of the three diradicals (see also text): (a) nitroxide-substituted nitronyl-nitroxide; (b) bis-nitronyl-nitroxide (Ullmann); (c) phenyl-bridged bis-nitronyl-nitroxide, θ is the dihedral angle whose variation modulates the spin-spin coupling.

Here we want to investigate a series of diradicals containing one or two nitronyl-nitroxide magnetic units, with the aim to verify the generality of the above observations, through a systematic comparison of DDCI calculations arising by different levels of the reference CAS. Namely, in the case of one or two nitronyl-nitroxide units the highest level DDCI calculation involves a CAS(4,4) or CAS(6,6) reference, respectively, to

be compared with the DDCI results based on the usual CAS(2,2). We have firstly investigated a nitroxide-substituted nitronyl-nitroxide, which is a simplified version of the system studied by Suzuky et al., [90] including a systematic study of ΔE_{TS} as a function of the torsional angle θ, that modulates the magnetic coupling (Figure 1a). Then the Ullmann's diradical (Figure 1b) and its phenyl-bridged version (Figure 1c) investigated exsperimentally by Caneschi et al. [91] and by us in 2009 using DDCI2, [77] have been considered.

We find that only DDCI based to a reference space accounting for the intrinsic multiconfigurational nature of the nitronyl-nitroxide radical can be considered a reliable computational approach to the calculation of the singlet-triplet energy gap in diradicals. This means that accurate values of J, the parameter of the HDVV Hamiltonian representing the spin-spin coupling, can be obtained by a CAS(4,4)+DDCI for species with one single nitronyl-nitroxide, as those of Figure 1a, or by CAS(6,6)+DDCI, when two of those radicals are present, as for the species of Figure 1b and 1c.

Computational Details

The computation of the singlet-triplet gap ΔE_{TS} by DDCI is based on the idea of including in the variational space those configurations with the largest contribution to the energy gap between states with different spin. Dividing the whole set of MOs into double occupied (core), singly occupied (magnetic) and empty (virtual) MOs, DDCI adds to the minimal CAS(n,n) (n electrons in n "magnetic" MOs) all SDs generated by single and double excitations from the SDs of the CAS, excluding the double excitations which do not involve active orbitals. The DDCI protocol is schematized in Table 1.

Table 1 - The DDCI space in terms of the several classes of configurations expressed with a sequence of three numbers, $N_C.N_M.N_E$, respectively for core, magnetic and empty MOs. The standard notation (see refs. [62, 92]) is reported in the third column.

DDCI	DDCI2		N.n.0	The primary space (includes kinetic exchange)
		1p	N.n-1.1	Single excitations from magnetic orbitals
		1h	N-1.n+1.0	Single excitations from core to magnetic orbitals (related to the superexchange)
		1h1p	N-1.n.1	Single excitations from core to unoccupied orbitals (include spin polarization)
		2p	N.n-2.2	Double excitations from magnetic orbitals
		2h	N-2.n+2.0	Double excitations from core to magnetic orbitals
		1h2p	N-1.n-1.2	Simultaneous excitation from core and magnetic orbitals (not included in DDCI2 scheme)
		2h1p	N-2.n+1.1	Double excitations from core to magnetic and unoccupied orbitals (not included in DDCI2 scheme)

Restricted Open Hartree-Fock (ROHF) MOs were obtained by a HF-SCF calculation for the high spin eigenstate carried out with GAMESS [93, 94], using always the 6-311G* basis set. Magnetic, singly occupied, MOs were localized onto the magnetic sites and an *ad hoc* fragmentation was applied to decrease the dimension of the active MO space. In particular, for the three species of Figure 1, the active space for DDCI only includes the MOs with main component on the molecular pieces of Figure 2. This is justified by the MOs active for the

spin-spin coupling which, as shown in the next section, do not show any significant contribution in the parts that are neglected. We have also frozen the 1s orbitals of the heavy atoms.
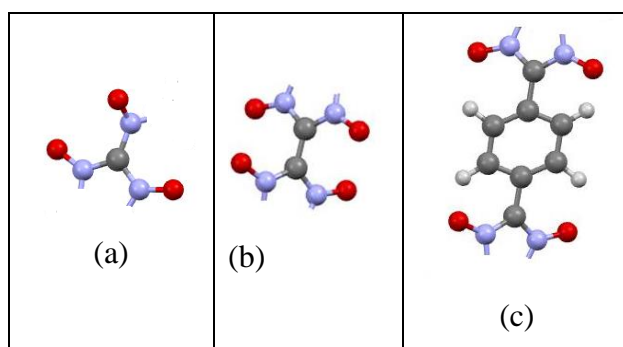

Figure 2 - Fragments of the three diradicals of Figure 1, whose MOs are considered in the construction of the DDCI space.

The corresponding one- and two-electron integrals pertaining to the MOs active for DDCI were then transformed from atomic to molecular basis set for the 3 species of Figure1 and we have then the resulting dimension of the MO space is reported in Table 2.

Table 2 - The dimension of the DDCI (N_{DDCI}) space for the diradicals of Figure 1, fragmented according to Figure 2 (see text). N_D is the number of doubly occupied, N_S that of singly occupied and N_V that of the virtual (empty) MOs.

Fragment	N_D	N_S	N_V	N_{DDCI}
a	19	2	99	120
b	27	2	147	176
c	41	2	241	284

When the dimension of the DDCI space is very large, the calculation of ΔE_{TS} can take advantage from perturbation theory, performing the variational calculation on a reduced space of active MOs and correcting the resulting CI energies by the Complementary Space Perturbative Approach (CSPA), including the perturbative contribution on the remaining MO space [73]. In the present case, this approach was necessary to deal with the species with two nitronyl-nitroxide units, where a CAS(6,6) reference was considered in the DDCI.

Results and Discussion

a) Nitroxide-substituted nitronyl-nitroxide diradical (Figure 1a)

The first species we want to study is a simple system with one single nitronyl-nitroxide unit, such as a nitroxide-substituted nitronyl-nitroxide, which is a simplified version of the species studied by Suzuki et al. [90]. In this diradical, with a triplet ground state, the spin-spin interaction can be modulated by changing the dihedral angle (θ in Figure 1) between the two moieties, allowing a comparison between the DDCI results obtained with a CAS(2,2) and a CAS(4,4) reference at different strengths of the coupling.

In Figure 3 the relevant canonical MOs are reported for θ=70°. In the Figure we can see how the chosen fragmentation of the diradical of Figure 2 is a good approximation, since no significant electron density is present in the neglected parts of the molecule. As the angle θ is changed, the only difference observed in the four MOs of Figure 5 is in a different density distribution without altering their energy order.

DDCI calculations with the CAS(2,2) and CAS(4,4) reference were performed changing the torsional angle θ from 55 to 85°. The results obtained are summarized in Figure 4, along with the values of ΔE_{TS} obtained by CAS without DDCI, the results of CAS(2,2)+DDCI2 and CAS(4,4)+DDCI2 calculations, the simplified method that it was shown to have an acceptable agreement with the experiment for the Ullmann's diradical [62].
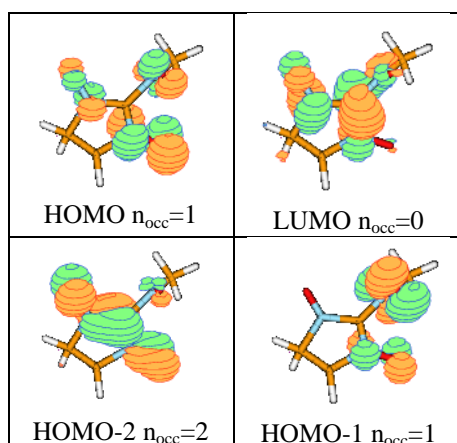

| HOMO $n_{occ}=1$ | LUMO $n_{occ}=0$ |
| HOMO-2 $n_{occ}=2$ | HOMO-1 $n_{occ}=1$ |

Figure 3 – Active orbitals of the nitroxide-substituted nitronyl-nitroxide for the CAS(4,4), n_{occ} is the SCF electronic occupation. CAS(2,2) space is made by the singly occupied HOMO-1 and HOMO only.

At small value of θ, the π orbitals bearing the unpaired electron on each of the two moieties of the diradical, the nitroxide and the nitronyl-nitroxide, are close to each other and one expects a strong spin-spin interaction and, consequently, a significant energy gap. As θ increases, the distance between such orbitals increases as well and the spin-spin interaction and ΔE_{TS} are expected to decrease. This is exactly what we observe in all cases reported in Figure 4. The decrease is always roughly linear with θ, but the steep is different as all energy gaps converge towards a singlet-triplet degeneracy for θ approaching 90°.
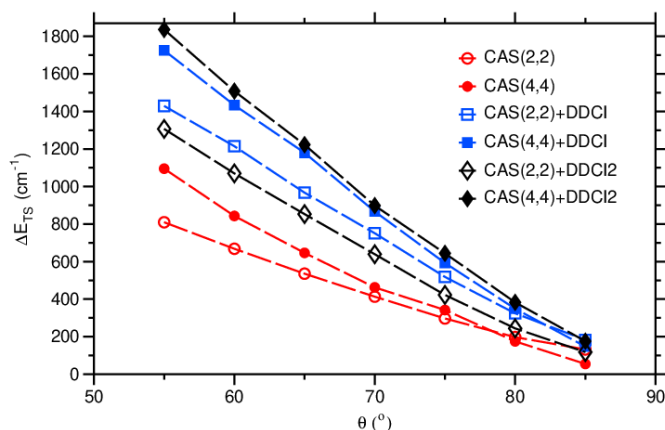
Figure 4 – Singlet-triplet energy gap for the nitroxide-substituted nitronyl-nitroxide as a function of the dihedral angle θ. Empty and filled symbols distinguish calculations with reference CAS(2,2) and CAS (4,4), respectively. The color distinguish the type of calculation and is red for simple CAS, black for CAS+DDCI2 and blue for CAS+DDCI. Lines are only a guide for eyes.

It is clear from the figure that only at small values of the coupling the DDCI based on CAS(2,2) is a good approximation of that based on CAS(4,4). This allow us to conclude that in case of radical species involving nitronyl-nitroxides, the intrinsic multiconfigurational nature of its wavefunction requires a CAS(3,3) level of accuracy. It is evident in Figure 3 that the HOMO-1 and HOMO of the CAS(2,2) do not show any contribution on the Carbon atom in between the two NO, which is instead present in the HOMO-2 and LUMO that complete the CAS(4,4) space. This is in line with the considerations of refs [62, 88]. The simplest 2-orbital-2-electron picture, a good reference space for DDCI in case of nitroxides and other diradicals, seems to be inappropriate for nitronyl-nitroxide moieties, unless the coupling is small enough that CAS(2,2)/DDCI can be seen as a good approximation to the theoretically more sound and accurate CAS(4,4)/DDCI.

Apparently, this property is also observed in different species which keep a multireference character in one of the two magnetic moieties of the diradical. Indeed, replacing the sequence O-N-C-N-O of the nitronyl nitroxide with a H-C-C-N-O, one again can observe that CAS(4,4)/DDCI gives a larger gap than CAS(2,2)/DDCI (see Supporting Information).

A final remark can be made regarding the DDCI2 calculations. With a CAS(2,2) reference, differently from the Ullmann's diradical [62] (see next section), where this approach is found to give a value of ΔE_{TS} in much better agreement with the experiment with respect to the corresponding full DDCI, here we observe that the CAS(2,2)/DDCI2 values are always much smaller than the reference CAS(4,4)/DDCI values. This suggests that CAS(2,2)/DDCI2 can be in general unreliable and the agreement found in the Ullmann's diradical can be considered fortuitous. We also notice that the CAS(22)/DDCI2 gap is always larger than the CAS(2,2) one and there is an increase of about 20% with respect to the CAS(2,2)/1h1p values (not shown). This indicates that the 1h1p excitations stabilize the triplet more than the singlet (i.e. ferromagnetic polarization effects overcome their antiferromagnetic counterpart) at variance with the situation found for singlet ground states, like, e.g. the Ullmann's diradical described in the next section. If we consider a CAS(4,4) as a reference for DDCI2, we can notice that the results are at all angles in very good agreement (less than 10% of difference) with those, computationally much more expensive, yielded by DDCI. In particular, we can notice that the 1h2p and 2h1p excitations, which differentiate the two approaches, decrease the gap acting as antiferromagnetic corrections.

b) Bis-nitronyl-nitroxide (Ullmann) diradical (Figure 1b)

In this section we report the results of the calculations for the Ullmann's diradical, one of the most studied diradical species with a multireference singlet ground state. According to refs. [62, 88], the most appropriate approach for DDCI should consider a CAS(6,6) reference, consistent with the presence of two nitronyl-nitroxide units. At the experimental geometry taken from ref. [62], the six ROHF MOs, relevant for the CAS(6,6)/DDCI are shown in Figure 5, where the singly occupied HOMO-1 and HOMO are the two MOs also involved in the CAS(2,2)/DDCI.

As for the species of the above section, in order to include in the reference the contribution of the π MOs pertaining to the central Carbon atom of the O-N-C-N-O system, we must consider the CAS(6,6), since the HOMO-1 and HOMO do not show any electronic density on it. DDCI calculations, indeed demonstrate the importance of this contribution and confirm what observed in ref. [62]. In Table 3, the results of our series of calculations are summarized.
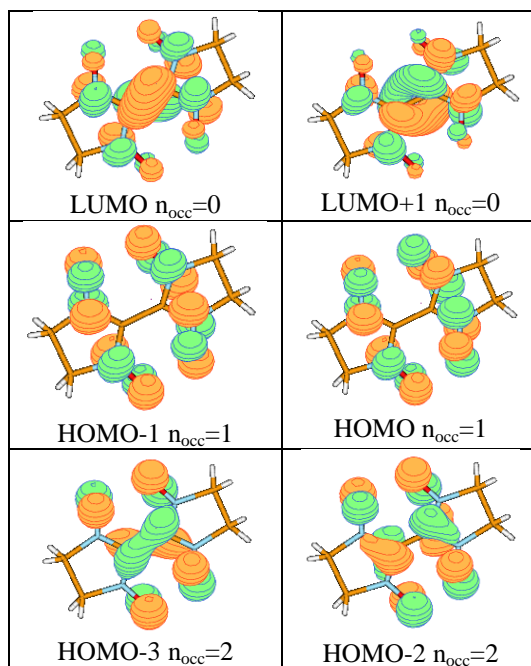

Figure 5 – Active orbitals of the bis- nitronyl-nitroxide (Ullmann) diradical for the CAS(6,6), n_{occ} is the SCF electronic occupation. CAS(2,2) space is made by the singly occupied HOMO-1 and HOMO only.

Already at the CAS level, it is quite apparent that inclusion of two doubly occupied (HOMO-3 and HOMO-2) and two empty (LUMO and LUMO+1) orbitals in the reference strongly affects the value of ΔE_{TS}, which goes from -21 cm^{-1} for the CAS(2,2) to -336 cm^{-1} for the CAS(6,6) computation, the latter result being very close to the experimental value of -311 cm^{-1}.

Table 3 - ΔE_{TS} for the bis-nitronyl-nitroxide diradical computed at different levels of DDCI and with different variational MO spaces (N_{var}) resulting in a N_{dim} dimension of the variational SD space. $\Delta E_{TS}(var)$ is the value obtained by the diagonalization of the variational space without the CSPA correction. $\Delta E_{TS}(MP)$ and $\Delta E_{TS}(EN)$ are the values corrected by Møller-Plesset (MP) and Epstein-Nesbet (EN) CSPA. The N_{var} set includes the 2 singly occupied MOs and N_d doubly occupied. N_{inc} is the number of empty MOs included and N_{ex} the number of those excluded in the CI but considered in the CSPA.

	Nvar	N_d	N_{inc}	N_{ex}	N_{dim}	$\Delta E_{TS}(var)$ (cm^{-1})	$\Delta E_{TS}(EN)$ (cm^{-1})	$\Delta E_{TS}(MP)$ (cm^{-1})
CAS(2,2)						-21.3		
CAS(2,2)/1h1p	176	27	147		39,694	-276.9		
CAS(2,2)/DDCI2	176	27	147		62,728	-278.5		
CAS(2,2)/DDCI	176	27	147		4,190,488	-129.9		
CAS(6,6)						-335.9		
CAS(6,6)/DDCI2	176	27	147		12,082,500	-304.6		
CAS(6,6)/DDCI	78	27	49	98	85,318,940	-308.3	-308.5	-331.1

	103	27	74	73	175,751,065	-309.0	-315.7	-330.6
Experimental [95]	-311							

The CAS(2,2) energy gap is substantially improved by the 1h1p excitations (to -277 cm^{-1}). At variance with the species of the previous section with a triplet ground state, now the 1h1p excitations stabilize the singlet state much more than the triplet state indicating a marked antiferromagnetic spin polarization effect. The same value of ΔE_{TS} is obtained by CAS(2,2)/DDCI2 (-278 cm^{-1}). This means that additional excitations beyond the 1h1p level do not contribute significantly to the gap as a whole, as frequently observed in other diradicals. However, we want to stress again how, in the light of the results obtained for the species of the previous section, the agreement between the observed value of the gap (-311 cm^{-1}) and that computed by CAS(2,2)/DDCI2 (the two differs by roughly 10 %) should not be considered as a demonstration that this computational approach is accurate and reliable. The further addition of 2h1p and 1h2p excitations leading to the CAS(2,2)/DDCI value, results as expected in a substantial decrease of the gap in comparison to the experimental value.

A quantitative agreement with the experiment is instead obtained with the CAS(6,6)/DDCI model (Table 3), which once again confirms that in presence of nitronyl-nitroxide units, the role of the Carbon atom of the O-N-C-N-O system is not negligible and one should include the MOs responsible for its spin density in the reference space, as originally observed in the monoradical. [88] This indeed seems to be confirmed by the CAS(6,6)/DDCI2 results, which, in agreement with what has been observed for the nitroxide-substituted nitronyl-nitroxide, are as good as the CAS(6,6)/DDCI values at a much less computational cost.

c) Phenyl-bridged bis-nitronyl-nitroxide diradical (Figure 1c)

The phenyl-bridged nitronyl-nitroxide diradical was prepared by Caneschi et al. in 1993 [91]. In analogy with the Ullmann's diradical, the unbridged analogue of the previous section, it was found to have a singlet ground state with ΔE_{TS}=-72.3 cm^{-1}, much smaller than the value of the system without the bridge (-311 cm^{-1}). This indicates that, despite its π delocalization, the phenyl bridge acts as a spacer decreasing the through-bond spin-spin interaction.

In the crystal structure, the angle between each of the two nitronyl-nitroxide units and the aromatic ring is ~25°, while the optimized gas phase structure studied by us in 2009 was nearly planar [77]. In order to make significant the comparison with experiment, here we have used the original X-ray structure of Caneschi et al.[91] The active canonical orbitals relevant for the CAS(2,2) and CAS(6,6) models are shown in Figure 4, along with the HF-SCF electronic occupation. The MOs of Figure 4 do not show any significant density in the fragments neglected in the subsequent DDCI calculations and this justifies the fragmentation choice performed as shown in Figure 2. However, as already pointed out in ref. [77], the contribution of the MOs of the phenyl bridge plays a central role and cannot be neglected.
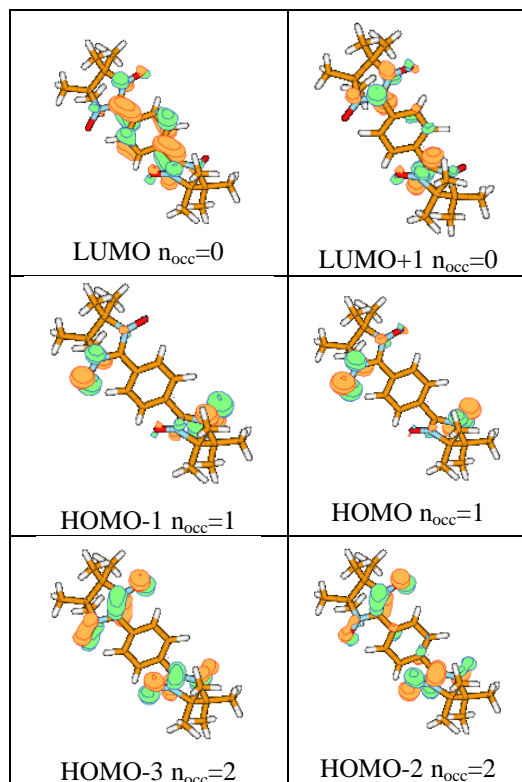
Figure 4 – Active orbitals of the phenyl-bridged-bis- nitronyl-nitroxide [91] for the CAS(6,6), n_{occ} is the SCF electronic occupation. CAS(2,2) space is made by the singly occupied HOMO-1 and HOMO only.

With the CAS(2,2) as a reference, it is nowadays possible to go beyond the small DDCI2 model space we employed in 2009 [77] and to perform accurate DDCI calculations approaching to the full diagonalization in the DDCI space, e.g. with a very small set of MOs considered by CSPA. Using instead the CAS(6,6) model as a reference, the DDCI space grows dramatically and only calculations exploiting quite extensive CSPAs for a large part of the MO space can be carried out. For instance, the heaviest DDCI calculation considered a space of 142 MOs active for CI out of 284 (i. e. the contribution of the excitations involving the highest 142 virtual MOs was added by CSPA) has dimension $5 \cdot 10^8$ (Table 4) and required more than 6 weeks on a 240-CPU-6-TB machine at the Scuola Normale Superiore (SNS), which has also required a setup of the code and a revision of the scripts. The results obtained are summarized in Table 4, where also the convergence with the different spaces of active MOs for DDCI and the dimension of the variational space, are shown.

The first relevant observation concerns with the results of CAS(2,2) and CAS(6,6), that are very different: CAS(2,2) gives, contrary to experiment, a triplet ground state, whereas CAS(6,6) delivers the correct ground state and a ΔE_{TS} of -61 cm^{-1}, not far from the experimental value. CAS(2,2)/DDCI2 performs much better than the CAS(2,2) alone, but the value of ΔE_{TS} is roughly one half of experimental value, confirming that the agreement found for the Ullmann's diradical at the same level of theory is fortuitous. The difference with the value obtained in ref.[77] (>100 cm^{-1}) is due to the smaller dihedral angle between the two nitronyl-nitroxide units. The convergence with the dimension of the space of MOs is very good, since with 74 empty MOs over a total of 241, we obtain a very good approximation of ΔE_{TS} with respect to the full variational value of -35 cm$^-$

[1]. It has also to be noticed that the values of ΔE_{TS} corrected with CSPA according to EN and MP perturbation theory, deliver to the same value.

Table 4 - ΔE_{TS} for the phenyl-bridged nitronyl-nitroxide diradical computed at different levels of DDCI and with different variational MO spaces (N_{var}) resulting in a N_{dim} dimension of the variational SD space. ΔE_{TS}(var) is the value obtained by the diagonalization of the variational space without the CSPA correction. ΔE_{TS}(MP) and ΔE_{TS}(EN) are the values corrected by Moeller-Plesset (MP) and Epstein-Nesbet (EN) CSPA. The N_{var} set includes the 2 singly occupied MOs and N_d doubly occupied. N_{inc} is the number of empty MOs included and N_{ex} the number of those excluded in the CI but considered in the CSPA.

	N_{var}	N_d	N_{inc}	N_{ex}	N_{dim}	ΔE_{TS}(var) (cm^{-1})	ΔE_{TS}(EN) (cm^{-1})	ΔE_{TS}(MP) (cm^{-1})
CAS(2,2)						0.2		
CAS(2,2)/DDCI2	117	41	74	167	37,961	-38.4	-34.7	-35.2
	192	41	149	92	85,736	-38.0	-35.1	-35.1
	242	41	199	42	123,836	-35.4	-35.2	-35.2
	284	41	241		159,704	-35.3		
CAS(2,2)/DDCI	65	24	39	202	361,777	-11.6	-5.2	-5.9
	117	41	74	167	2,119,285	-14.7	-5.4	-6.1
	192	41	149	92	7,025,560	-11.6	-7.2	-7.1
	242	41	199	42	11,840,160	-8.9	-7.9	-8.0
CAS(6,6)						-61.1		
CAS(6,6)/DDCI2	192	41	149	92	15,235,780	-76.3	-77.7	-77.9
	284	41	241		27,273,865	-77.6		
CAS(6,6)/DDCI	65	24	39	202	48,596,325	-49.7	-74.1	-95.3
	117	41	74	167	312,257,785	-87.7	-76.2	-53.2
	142	41	99	142	514,957,660	-89.8	-79.4	-49.7
Experimental [91]					-72.3			

As expected from the results of ref.[62], CAS(2,2)/DDCI does not perform better than the cheaper CAS(2,2)/DDCI2 as ΔE_{TS} drops to -8 cm^{-1}. The full variational calculation was not performed for dimensional reasons, but both EN and MP values with only 42 MOs inactive for the variational space can be considered as accurate as the result of a complete diagonalization.

CAS(6,6)/DDCI calculations are a very hard task, since the dimension of the DDCI space suddenly grows to impracticable values. The two largest calculations, with a CI of $\sim 3 \cdot 10^8$ and half billion of SDs respectively, complemented with CSPA correction, were performed with a 240-CPU-6-TB SGI Ultraviolet 2000 at the SNS. Owing to the small fraction of virtual MOs included in the CI, the three CAS(6,6)/DDCI results reported in Table 4 do not allow performing accurate extrapolation to the full variational energy gap (at N_{ex}=0). However, the three ΔE_{TS} coming from Epstein-Nesbet perturbation, seem to show a noticeable stability around a value quantitatively close to that obtained experimental. Thus we can speculate that the EN results give a reasonable estimate of the correct energy gap, which could be expected in the -70 ÷ -90 cm^{-1} range. The convergence of the Møller-Plesset series are more scattered and seems to converge with a smaller rate.

At a much cheaper computational cost we may consider CAS(6,6,)/DDCI2, which is found to give results in quantitative agreement with the experiments also for the present diradical. We can see in Table 4 that we can

now perform a full variational calculation, which guarantees the maximum accuracy and reliability within the DDCI scheme, although considering smaller variational spaces and exploiting CSPA, gives equivalent results. The results obtained, confirm once more that in presence of nitronyl-nitroxide radical unit the reference CAS(2,2), excellent for the study of nitroxide and other diradicals, fails in accounting for the essential physics of this species, due to the intrinsic multiconfigurational nature of the wavefunction. The absence of π orbitals having a contribution on the Carbon atom of the O-N-C-N-O unit in the MO active space of CAS(2,2) seems to be at the origin of this problem, as suggested by Calzado et. al in ref. [62]. In fact, even in absence of a population analysis, it is rather evident that both the singly occupied MOs forming the CAS(2,2) active space and displayed in Figure 4 do not involve π orbitals of the Carbon atoms bridging the two monoradicals, which instead are shown to contribute at the remaining active MOs of the CAS(6,6).

Conclusions

We have studied three diradicals in which one or both fragments bearing the unpaired electron involve nitronyl-nitroxide moieties, namely a nitroxide-substituted nitronyl-nitroxide biradical, the Ullmann's biradical and its phenyl-bridged version. The main aim of our study is an in depth investigation of the role of the multiconfigurational nature of the nitronyl-nitroxide radical in the spin-spin interaction ruling the observed singlet-triplet energy gap.

In general, the simplest CI basic model for a diradical is a 2-orbital 2-electron system with one orbital *per* magnetic moiety, the two singly occupied MOs of a ROHF calculation of the highest spin state. This model is characterized by one triplet and three singlet states, with two of the singlets describing the two ionic (charge transfer) configurations where both electrons are in the same moiety. This model, quantitatively poor, can be substantially improved by the inclusion of all single and double excited SDs involving at least one of the two magnetic MOs. This approach, proposed by Miralles et al. [71, 72] and known as DDCI, has been found to give values of the singlet-triplet gap in good agreement with the experimental data in nitroxides and many other diradicals, organic and inorganic, but it was proven to fail for the Ullmann's diradical, the nitronyl-nitroxide dimer, where instead its reduced version, DDCI2, seemed to give a correct value.

Few years ago, Calzado et al [62] showed that the CAS(2,2) is insufficient as a reference space for DDCI and a CAS(6,6) should instead be considered. Indeed, the unpaired electron on each moiety is delocalized in the whole O-N-C-N-O fragment which is involved in the magnetic properties of the species [88] and some spin density is observed in the central Carbon atom. This can only be accounted for with CAS(6,6) so that an increased MOs set should be considered in the reference space.

The unanswered question was if this conclusion is general for all radicals containing at least one nitronyl-nitroxide unit or is limited to the Ullmann's diradical, where the two moieties are very close to each other. Furthermore, is the DDCI2 reduced model always able to give singlet-triplet energy gap in agreement with experiments?

In this paper we have shown that DDCI2 is not a reliable approach if an inappropriate reference space is considered. Using a CAS(2,2) reference its agreement with experimental and/or higher level calculations is

random: DDCI2 only delivers an accurate energy gap for the Ullmann's diradical. However, it is apparent that using the proper reference space, that is including all the significant MOs in case of fragments intrinsically of mutireference nature, DDCI2 may also give accurate results saving computational resources.

A robust and reliable DDCI model requires, whenever nitronyl-nitroxide units are present, that at least 1 orbital for each N-O and 1 for the central Carbon of the O-N-C-N-O fragment be included in the reference space, which should then be a CAS(4,4) or a CAS(6,6), when one or t wo units are present. This behaviour is expected to be quite general for diradicals made by species with an intrinsic multiconfigurational character, as demonstrated by the model system H-C-C-N-O analyzed in the Supporting Information.

The applicability of a CAS(2,2) or a CAS (n,n) reference space in DDCI could be judged already at the CAS level, in the sense that only if the gap obtained with a CAS(2,2) and a CAS(n,n) model are sufficiently close to each other, one can be confident that the smaller space is appropriate.

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References

1.   O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.
2.   A. Rajca, *Chem. Rev.*, 1994, **94**, 871 - 893.
3.   J. M. D. Coey, *J. Magn. Magn. Mater.*, 2001, **226**, 2107.
4.   E. Coronado, P. Delhaès, D. Gatteschi and J. S. Milles, *Molecular Magnetism: From Molecular Assemblies to the Devices*, Kluwer Academic Publishers, Dordrecht, 1996.
5.   D. Gatteschi, R. Sessoli and J. Villain, *Molecular nanomagnets*, Oxford University Press, New York, 2006.
6.   S. N. Datta, C. O. Trindle and F. Illas, *Theoretical and Computational Aspects of Magnetic Organic Molecules*, World Scientific Publishing Co. Pte. Ltd., Singapore, 2014.
7.   J. M. Clemente-Juan, E. Coronado and A. Gaita-Arino, *Chem. Soc. Rev.*, 2012, **41**, 7464-7478.
8.   H. Gu, X. Zhang, H. Wei, Y. Huang, S. Wei and Z. Guo, *Chem. Soc. Rev.*, 2013, **42**, 5907-5943.
9.   H. Atsufumi and T. Koki, *J. Phys. D: Applied Physics*, 2014, **47**, 193001.
10.   S. Y. Quek and K. H. Khoo, *Acc. Chem. Res.*, 2014, **47**, 3250-3257.
11.   R. Naaman and D. H. Waldeck, *Annu. Rev. Phys. Chem.*, 2015, **66**, 263-281.
12.   S. Shil, D. Bhattacharya, A. Misra and D. J. Klein, *Phys. Chem. Chem. Phys.*, 2015, **17**, 23378-23383.
13.   S. Sanvito, *Chem. Soc. Rev.*, 2011, **40**, 3336-3355.
14.   M. Nakano and B. Champagne, *J. Chem. Phys. Lett.*, 2015, **6**, 3236-3256.
15.   J. Lee, E. Lee, S. Kim, G. S. Bang, D. A. Shultz, R. D. Schmidt, M. D. E. Forbes and H. Lee, *Angew. Chem. Int. Ed.* , 2011, **50**, 4414-4418.
16.   R. Gaudenzi, J. de Bruijckere, D. Reta, I. d. P. R. Moreira, C. Rovira, J. Veciana, H. S. J. van der Zant and E. Burzurí, *ACS Nano*, 2017, **11**, 5879-5883.
17.   M. L. Kirk, D. A. Shultz, J. Zhang, R. Dangi, L. Ingersol, J. Yang, N. S. Finney, R. D. Sommer and L. Wojtas, *Chemical Science*, 2017, **8**, 5408-5415.
18.   M. Castellano, R. Ruiz-García, J. Cano, J. Ferrando-Soria, E. Pardo, F. R. Fortea-Pérez, S.-E. Stiriba, W. P. Barros, H. O. Stumpf, L. Cañadillas-Delgado, J. Pasán, C. Ruiz-Pérez, G. de Munno, D. Armentano, Y. Journaux, F. Lloret and M. Julve, *Coord. Chem. Rev.*, 2015, **303**, 110-138.
19.   I. d. P. R. Moreira, C. de Graaf and V. Barone, *Theor. Chem. Acc.*, 2000, **104**, 265.
20.   A. I. Krylov, *J. Phys. Chem. A*, 2005, **109**, 10638.
21.   B. D. Koivisto and R. G. Hicks, *Coord. Chem. Rev.*, 2005, **249**, 2612-2630.
22.   T. Itoh, K. Hirai and H. Tornioka, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 138-157.
23.   W. C. Lineberger and T. W. Weston, *Phys. Chem. Chem. Phys.*, 2011, **13**, 11792-11813.
24.   M. Abe, *Chem. Rev.*, 2013, **113**, 7011-7088.
25.   M. Winkler and W. Sander, *Acc. Chem. Res.*, 2014, **47**, 31.
26.   J. P. Malrieu, R. Caballol, C. J. Calzado, C. de Graaf and N. Guihéry, *Chem. Rev.*, 2014, **114**, 429-492.
27.   G. Gryn'ova, M. L. Coote and C. Corminboeuf, *Wiley Interdisciplinary Reviews: Comput. Molec. Science*, 2015, **5**, 440-459.
28.   N. M. Gallagher, A. Olankitwanit and A. Rajca, *J. Org. Chem.*, 2015, **80**, 1291-1298.
29.   A. K. Pal, S. Hansda and S. N. Datta, *J. Phys. Chem. A*, 2015, **119**, 2176-2185.
30.   P. Neuhaus and W. Sander, *Angew. Chem. Int. Ed.* , 2010, **49**, 7277-7280.
31.   A. Rajca, A. Olankitwanit, Y. Wang, P. J. Boratyński, M. Pink and S. Rajca, *J. Am. Chem. Soc.*, 2013, **135**, 18205-18215.
32.   E. Coulaud, D. Hagebaum-Reignier, D. Siri, P. Tordo and N. Ferre, *Phys. Chem. Chem. Phys.*, 2012, **14**, 5504-5511.

33. M. E. Ali, V. Staemmler, F. Illas and P. M. Oppeneer, *J. Chem. Theory Comput.*, 2013, DOI: 10.1021/ct400886w.
34. A. K. Pal, D. R. Mañeru, I. A. Latif, I. de P. R. Moreira, F. Illas and S. N. Datta, *Theor. Chem. Acc.*, 2014, **133**, 1472.
35. A. Olankitwanit, M. Pink, S. Rajca and A. Rajca, *J. Am. Chem. Soc.*, 2014, **136**, 14277-14288.
36. X. Zhu and Y. Aoki, *J. Comput. Chem.*, 2015, **36**, 1232-1239.
37. A. I. Krylov, in *Rev. Comput. Chem.*, eds. A. L. Parril and K. B. Lipkowitz, John Wiley & Sons, Inc., Hoboken, NJ, USAj, 2017, DOI: 10.1002/9781119356059.ch4.
38. D. Bhattacharya, S. Shil, A. Misra, L. Bytautas and D. J. Klein, *J. Phys. Chem. A*, 2016, **120**, 9117-9130.
39. M. Nakano, K. Fukuda and B. Champagne, *J. Phys. chem. C*, 2016, **120**, 1193-1207.
40. T. Steenbock, D. A. Shultz, M. L. Kirk and C. Herrmann, *J. Phys. Chem. A*, 2017, **121**, 216-225.
41. T. Kubo, *Chemistry Letters*, 2015, **44**, 111-122.
42. M. L. Kirk and D. A. Shultz, *Coord. Chem. Rev.*, 2013, **257**, 218-233.
43. S. Kumar, Y. Kumar, S. Keshri and P. Mukhopadhyay, *Magnetochemistry*, 2016, **2**, 42.
44. S. Suzuki, T. Wada, R. Tanimoto, M. Kozaki, D. Shiomi, K. Sugisaki, K. Sato, T. Takui, Y. Miyake, Y. Hosokoshi and K. Okada, *Angew. Chem., Int. Ed.*, 2016, **55**, 10791-10794.
45. N. M. Gallagher, J. J. Bauer, M. Pink, S. Rajca and A. Rajca, *J. Am. Chem. Soc.*, 2016, **138**, 9377-9380.
46. C. Felser, G. H. Fecher and B. Balke, *Angew. Chem. Int. Ed.* , 2007, **46**, 668.
47. S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, N. Suaud, O. Svoboda, R. Bastardis, N. Guihéry and J. J. Palacios, *Chemistry – A European Journal*, 2015, **21**, 763-769.
48. D. Reta, I. d. P. R. Moreira and F. Illas, *J. Chem. Theory Comput.*, 2016, **12**, 3228-3235.
49. D. Reta, I. d. P. R. Moreira and F. Illas, *Phys. Chem. Chem. Phys.*, 2017, **19**, 24264-24270.
50. V. Gopal Chilkuri, G. Trinquier, N. Ben Amor, J.-P. Malrieu and N. Guihéry, *J. Chem. Theory Comput.*, 2013, **9**, 4805-4815.
51. V. Barone, I. Cacelli, A. Ferretti and G. Prampolini, *J. Chem. Phys.*, 2017, **1461**.
52. C. J. Cramer and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10757-10816.
53. A. Bencini and F. Totti, *J. Chem. Theory Comput.*, 2009, **5**, 144-154.
54. F. Neese, *Coord. Chem. Rev.*, 2009, **253**, 526-563.
55. A. Caneschi, D. Gatteschi and F. Totti, *Coord. Chem. Rev.*, 2015, **289–290**, 357-378.
56. J.-P. Malrieu and G. Trinquier, *J. Chem. Phys.*, 2016, **144**, 211101.
57. M. E. Ali and P. M. Oppeneer, *J. Chem. Phys. Lett.*, 2011, **2**, 939-943.
58. Y. Shao, M. Head-Gordon and A. I. Krylov, *J. Chem. Phys.*, 2003, **118**, 4807 - 4818.
59. F. Wang and T. Ziegler, *J. Chem. Phys.*, 2004, **121**, 12191 - 12196.
60. Z. Rinkevicius, O. Vahtras and H. Ågren, *J. Chem. Phys.*, 2010, **133**, 114104

61. Y. A. Bernard, Y. Shao and A. I. Krylov, *J. Chem. Phys.*, 2012, **136**, 204103.
62. C. J. Calzado, C. Angeli, C. de Graaf and R. Caballol, *Theor. Chem. Acc.*, 2011, **128**, 505-519.
63. C. Angeli and C. J. Calzado, *J. Chem. Phys.*, 2012, **137**, 034104.
64. S. Chattopadhyay, U. S. Mahapatra and R. K. Chaudhuri, *Chem. Phys.*, 2012, **401**, 15-26.
65. A. I. Krylov, *Chem. Phys. Lett.*, 2001, **338**, 375 - 384.
66. D. Casanova and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2009, **14**, 9779 - 9790.
67. N. J. Mayhall and M. Head-Gordon, *J. Chem. Theory Comput.*, 2014, **10**, 589 - 599.
68. N. J. Mayhall and M. Head-Gordon, *J. Phys. Chem. Lett.*, 2015, **6**, 1982 - 1988.
69. A. I. Krylov, *Acc. Chem. Res.*, 2006, **39**, 83 - 91.
70. V. Barone, I. Cacelli, A. Ferretti and M. Girlanda, *J. Chem. Phys.*, 2008, **128**, 174303.

71.   J. Miralles, O. Castell, R. Caballol and J.-P. Malrieu, *Chem. Phys.*, 1993, **172**, 33-43.
72.   J. Miralles, J. P. Daudey and R. Caballol, *Chem. Phys. Lett.*, 1992, **198**, 555-562.
73.   I. Cacelli, A. Ferretti, G. Prampolini and V. Barone, *J. Chem. Theory Comput.*, 2015, **11**, 2024-2035.
74.   V. Barone, C. Boilleau, I. Cacelli, A. Ferretti, S. Monti and G. Prampolini, *J. Chem. Theory Comput.*, 2013, **9**, 300-307.
75.   V. Barone, C. Boilleau, I. Cacelli, A. Ferretti and G. Prampolini, *J. Chem. Theory Comput.*, 2013, **9**, 1958-1963.
76.   V. Barone, I. Cacelli, P. Cimino, A. Ferretti, S. Monti and G. Prampolini, *J. Phys. Chem. A*, 2009, **113**, 15150-15155.
77.   V. Barone, I. Cacelli and A. Ferretti, *J. Chem. Phys.*, 2009, **130**, 094306.
78.   V. Barone, I. Cacelli, A. Ferretti, S. Monti and G. Prampolini, *J. Chem. Theory Comput.*, 2011, **7**, 699-706.
79.   V. Barone, I. Cacelli, A. Ferretti, S. Monti and G. Prampolini, *Phys. Chem. Chem. Phys.*, 2011, **13**, 4709-4714.
80.   V. Barone, I. Cacelli, A. Ferretti and G. Prampolini, *J. Chem. Phys.*, 2009, **131**.
81.   V. Barone, I. Cacelli, A. Ferretti and G. Prampolini, *Phys. Chem. Chem. Phys.*, 2009, **11**, 3854-3860.
82.   V. Barone, I. Cacelli, A. Ferretti, G. Prampolini, N. Guihéry, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *Phys. Chem. Chem. Phys.*, 2017, **19**, 9039-9044.
83.   F. Neese, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2017, **8**, e1327.
84.   D. Maganas, J. Krzystek, E. Ferentinos, A. M. Whyte, N. Robertson, V. Psycharis, A. Terzis, F. Neese and P. Kyritsis, *Inorg. Chem.*, 2012, **51**, 7218-7231.
85.   D. Maganas, S. Sottini, P. Kyritsis, E. J. J. Groenen and F. Neese, *Inorg. Chem.*, 2011, **50**, 8741-8754.
86.   E. F. Ullman and D. G. B. Boocock, *J. Chem. Soc. D*, 1969, 1161.
87.   O. Castell, R. Caballol, R. Subra and A. Grand, *J. Phys. Chem.*, 1995, **99**, 154-157.
88.   J. J. Novoa, P. Lafuente, M. Deumal and F. Mota, in *Magnetism: Molecules to Materials IV*, Wiley-VCH Verlag GmbH & Co. KGaA, 2003, DOI: 10.1002/3527600698.ch3, pp. 65-117.
89.   C. Angeli, C. J. Calzado, C. de Graaf and R. Caballol, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14617-14628.
90.   S. Suzuki, T. Furui, M. Kuratsu, M. Kozaki, D. Shiomi, K. Sato, T. Takui and K. Okada, *J. Am. Chem. Soc.*, 2010, **132**, 15908-15910.
91.   A. Caneschi, P. Chiesi, L. David, F. Ferraro, D. Gatteschi and R. Sessoli, *Inorg. Chem.*, 1993, **32**, 1445-1453.
92.   C. J. Calzado, J. Cabrero, J.-P. Malrieu and R. Caballol, *J. Chem. Phys.*, 2002, **116**, 2728.
93.   M. S. Gordon and M. W. Schmidt, in *Theory and Applications of Computational Chemistry: the first forty years*, eds. C. E. Dykstra, G. Frenking, K. S. Kim and G. E. Scuseria, Elsevier, 2005, DOI: citeulike-article-id:3013672, pp. 1167-1189.
94.   M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347-1363.
95.   F. Alies, D. Luneau, J. Laugier and P. Rey, *J. Phys. Chem.*, 1993, **97**, 2922-2925.