

A Strategy to Determine Appropriate Active Orbitals and Accurate Magnetic Couplings in Organic Magnetic Systems

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ABSTRACT: This work addresses the following paradox observed in diradicalar conjugated hydrocarbons: while the natural orbitals occupation numbers clearly indicate only two open-shell orbitals, i.e. two unpaired electrons, the minimal CAS zero-order description fails to reproduce accurately the electronic structures of the lowest states (spin density distribution and singlet–triplet energy gap, i.e., magnetic coupling). We will focus on the question of the optimization of both magnetic and nonmagnetic orbitals for the determination of accurate magnetic interactions in organic compounds. It is analytically demonstrated (in the Appendix) and numerically shown from multireference configuration interaction calculations performed on a series of original organic ferro- and antiferromagnetic compounds that, (i) some double excitations must be considered to obtain reliable magnetic orbitals for the calculation of magnetic couplings, (ii) the account of these excitations results in a larger spatial extent of the magnetic orbitals on the surrounding ligands and hence better drives the interaction between several magnetic centers, and (iii) the reliability of the orbitals is a crucial ingredient for the determination of accurate magnetic couplings. A strategy which optimizes the orbitals at a reasonable computational cost is proposed. It relies on a CAS(2,2) zero-order description and provides orbitals of the same quality as the CAS(full valence π)SCF orbitals. The values of the magnetic couplings computed using the difference dedicated configuration interaction on top of the CAS(2,2) references with the new orbital set are very close to those obtained at the much more computationally demanding CAS(full valence π)PT2 level of treatment.

I. INTRODUCTION

The *ab initio* determination of magnetic coupling has been the subject of many theoretical studies¹ during past decades, as obtaining reliable values happened to be difficult and challenging from most of the wave function theory (WFT) based standard methods. Due to both the intrinsic multiconfigurational character of the lowest-energy wave functions of magnetic systems and the weakness of the magnetic coupling magnitude, both nondynamic and dynamic correlations must be taken into account. Usually complete active space self consistent field (CASSCF) calculations are computed in order to obtain nondynamically correlated zero order wave functions while dynamic correlation is introduced in a second step either perturbatively (CASPT2,^{2,3} NEVPT2⁴) or variationally (MRCI). CASSCF calculations only bring 10% to 20% of the antiferromagnetic values of magnetic couplings in inorganic systems, and the account of dynamic correlation is compulsory in order to achieve sufficient accuracy.

Precise analyses of the physical content of magnetic couplings have permitted the understanding of the role of the different types of excitations in the magnitude and sign of the magnetic coupling in bimetallic complexes.^{5–8} The difference dedicated configuration interaction (DDCI3) method⁹ introduces in the CI space all single excitations and some double excitations on top of the references (see Figure 1). DDCI3 has been shown to provide the most accurate values of magnetic couplings at a reasonable computational cost. Its success has mainly been demonstrated in inorganic systems for which the active space can usually be restricted to the magnetic electrons and their orbitals (and sometimes a few orbitals of the bridging ligand).¹⁰ In most of the complexes in which the magnetic centers are nearest neighbors, accurate values of the magnetic couplings are obtained at the DDCI2 level while the DDCI3 method is compulsory for an accurate treatment of magnetic systems having a bridging

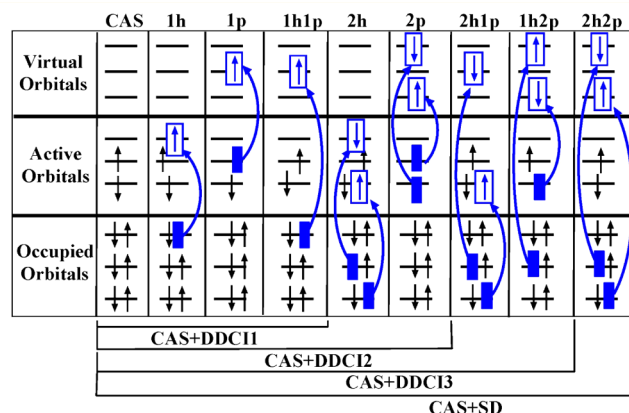


Figure 1. Excitations included in the DDCI1, -2, and -3 and SD CI calculations. 1h stands for one hole, 1p for one particle, and so on.

ligand between the magnetic centers. The important role of ligand-to-metal charge transfer excitations (LMCT) has been rationalized as resulting from the coupling between two-hole, one-particle (2h1p) excitations with the LMCT one-hole (1h) excitations involving the bridging ligand.⁶ The account of these interactions in the variational DDCI3 calculations results in a larger mixing between the ligand orbitals and the magnetic metallic ones.⁶ Indeed, the natural magnetic orbitals calculated from the density matrix of the DDCI wave function of the singlet state are much more delocalized than those of the CASSCF wave function.

While the CASPT2 method does not account for these interactions (which would only appear at the fourth order of

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perturbations), this method has also proved to give reliable values of the magnetic couplings provided that a double shell of d orbitals is introduced in the active space.¹¹ A very recent work¹² has shown that the NEVPT2 method could also provide accurate values of the magnetic couplings provided that appropriate orbitals are used. The procedure of optimization of such reliable magnetic orbitals consists of a state average optimization involving 70% of the magnetic singlet CASSCF state and 30% of the closed-shell singlet ground state. This weighted state-average procedure provides magnetic MOs, which are significantly more delocalized than those of the state specific CASSCF procedure and closer to the natural magnetic MO computed from the correlated DDCI wave functions.

Until recently, the research of magnetic architectures, either molecular or periodic, for instance ferro- or ferri-magnetic lattices, spin crossover systems, and molecular magnets, involved essentially as magnetic centers transition metals or lanthanides and therefore resorted to coordination chemistry. The possible transposition of these successful attempts to organic chemistry raises increasing attention.^{13–20} Conjugated radical or poly-radical conjugated hydrocarbons may play the same role as magnetic ions and may be assembled in a rational way to generate ferromagnetic lattices or bistable architectures. The possibility to start from graphene patches or carved graphenes attracts much interest,²¹ especially in the context of new materials for spintronics. However, the unpaired electrons in such systems are much more delocalized than in coordination chemistry compounds, and this feature raises peculiar difficulties for theoreticians.

Let us consider situations involving unpaired electrons in conjugated hydrocarbons. They may be either ground states of mono- or polyradicals or excited states of systems which are essentially of closed-shell character in their ground state. As well as for inorganic complexes, most of these states are usually represented in terms of a few unpaired electrons, occupying a small number of active MOs, on the top of a closed-shell set of underlying electrons. This is the case for radicals (one unpaired electron) and polyradicals (two or more unpaired electrons), and it is also the case for the excited states of diamagnetic conjugated molecules, where the lowest excited states are usually described as involving one or two unpaired electrons, excited from the highest occupied MO to the lowest empty ones. On the one hand, as will be shown in the following, the diagonalization of the monoelectronic density matrix of the full-CI restricted to the valence π system confirms this simple view: there is a strong contrast between nearly doubly occupied MOs (occupation number close to 2), almost empty virtual MOs (occupation number close to 0), and the expected number of singly occupied MOs, the occupation number of which is close to 1. On the other hand, the minimal CASSCF description which limits the active space to the unpaired electrons in their MO gives very poor agreement with experimental values. And even worse, the treatment of dynamic correlation brought by single and double excitations on top of these few references also provides rather poor descriptions, as will be illustrated below.

This drawback has led several authors to the conclusion that it was compulsory to enlarge the active space²² and even in some cases to extend it to the largest tractable number of π electrons in the same number of π occupied and virtual valence MOs.^{23,24} In this line, we have recently shown²⁵ that in mono- and diradicalar hydrocarbons (i) the singly occupied MOs (SOMOs) optimized using the restricted open shell Hartree–Fock (ROHF) method are too localized, which results in a wrong estimation of the spin densities on the various carbon atoms, and (ii) the Hückel more

delocalized SOMOs are very similar to the CAS(full valence π)SCF optimized MOs having a close-to-one occupation number.

The purpose of the present work is to show that one may avoid this enlargement of the active space, which becomes computationally prohibitive when dynamic correlation is introduced in post-CAS treatments or/and when the number of π electrons increases. The CASSCF active MO obtained from the minimal CAS calculations are exceedingly localized by the energy minimization process, and the improvement of the results relies on the ability to determine accurate active orbitals. A dramatic example concerns the lowest dipolarly allowed excited state of linear polyenes. This state can be considered as resulting from the excitation of one electron from the highest occupied MO (HOMO) to the lowest unoccupied one (LUMO). The CAS(2,2)SCF leads to active MOs which remain localized close to the center of the long polyenic chain.²⁶ Their spatial extension does not change when going to more than $N = 20$ atoms; i.e., they are practically identical for $N = 70$ atoms and $N = 20$ atoms. Consequently, the so-calculated excitation energy rapidly becomes length-independent, in contrast to experimental evidence that establish an N^{-1} decrease of the excitation energy with the chain length. As will be seen, a very convincing picture of the qualitative defect of the minimal CASSCF MO is given by their comparison to the natural MO obtained after a proper treatment of accurate post-CAS or extended CAS correlation effects.

Computational information is presented in section II. Section III exposes the failure of the minimal CASSCF zero order description for the calculation of magnetic couplings in diradicalar conjugated hydrocarbons. The experimentally studied meta-xylylene molecule will be used as a test case, while most of the applications concern larger original model systems, involving two six-membered rings and one or two methylene groups. Section IV proposes an alternative strategy to the CAS(full valence π)SCF calculations which provides accurate orbitals at a reasonable computational cost. The method stands within a minimal CAS zero-order reference but improves the magnetic MO through an iterative CI procedure running on a limited number of valence MOs. The method is first applied to the meta-xylylene molecule for which experimental data are available and which will be studied in detail and then used to calculate the magnetic coupling of several diradicalar compounds. A theoretical analysis of the spatial extent of the magnetic orbitals in organic compounds depending on the method used for their optimization is presented in Appendix A1.

This method is not a pragmatic recipe; it is based on both a knowledge of the qualitative changes brought by the dynamical correlation on the spatial extent of magnetic orbitals in coordination chemistry complexes and on a specific analysis of the problem in highly delocalized conjugated diradicals. For the sake of simplicity this rather long analytic derivation has been given in the Appendix. One may nevertheless schematize its structure as follows. If one considers a system involving two methylene groups CH_2 , bridged by a closed shell aromatic system, such as a benzene ring or a naphthalene frame, a formal evaluation of the delocalization of the SCF magnetic orbitals on the bridge is possible when starting from a strongly localized picture, corresponding to this qualitative view of two localized electrons interacting through a closed shell ligand. A first-order perturbative development, in which the hopping integrals between the outer CH_2 groups and the ring atom to which they are attached act as the perturbation operator, leads to an expression of the magnetic MOs, which now possess tails on the conjugated bridge, through single excitations between the magnetic outer

groups and the “ligand” MOs. These singly excited configurations play the role of the ligand-to-metal and metal-to-ligand charge transfer configurations in coordination chemistry systems. Then the correlation effects are taken into account, in particular, the semiactive double excitations. It is shown that the interaction between these doubly excited determinants and the singly excited ones involving electron transfer between the outer magnetic sites and the conjugated bridge increases the coefficients of the latter configurations with respect to their value in the SCF description. In other terms, we demonstrate, under some reasonable and generally accepted approximations, that the correlation increases the delocalization of the magnetic MOs on the aromatic bridge. Reading of this demonstration is not compulsory to follow either the numerical illustration of this effect or the proposed method which overcomes the defect of the minimal CAS determination of the magnetic orbitals.

II. COMPUTATIONAL INFORMATION

Calculations have been performed on various diradicals which are constituted of two methylene groups connected by several bridges of different lengths. The studied diradicals are the meta-xylylene, two dimethylene naphthalenes, and a para-diphenylene acetylene. The corresponding compounds are respectively labeled 1, 2, 3, and 4. The spin multiplicity of the ground state can be anticipated from Ovchinnikov’s rule²⁷ (also known as the Lieb theorem²⁸), which indicates that the spin of the ground state is equal to the M_s value of the most stable distribution (shown in Figure 2). In diradicals, the nature of the magnetic coupling is

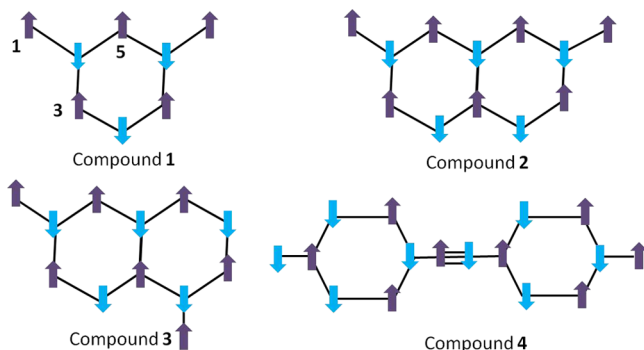


Figure 2. Schematic representation of the different compounds. The most stable spin distribution is indicated.

therefore ferromagnetic or antiferromagnetic depending on the parity of the bridging carbon number in the shortest pathway between the two external CH_2 groups. As a consequence, compounds 1, 2, and 3 ($M_s = 1$) are ferromagnetic while compound 4 ($M_s = 0$) is antiferromagnetic.

Geometries of model systems 2, 3, and 4 have been optimized using the B3LYP unrestricted DFT method implemented in the Gaussian package version 03²⁹ with 6-31G** basis sets. Since obtaining accurate geometries for model systems is not the purpose of the present work, we did not perform any systematic comparison between geometries obtained using different functionals and various basis sets. Moreover, while one may rely on the optimized geometry of the triplet state, the UDFT geometry for the $M_s = 0$ solution is a priori not relevant, since this solution is not an eigenfunction of S^2 . In the case of the real molecule (compound 1), the adiabatic energy difference between the ground state triplet and the excited singlet is available from electron loss experiments.³⁰ In order to check the validity of the

here-proposed computational strategy, we have calculated this adiabatic energy difference taking the more accurate available geometries optimized using the equation of motion spin-flip coupled cluster singles and doubles (EOM-SF-CCSD) method.³¹

CASSCF and CASPT2 calculations have been performed with the Molcas package, version 7.2.³² Both minimal CAS, i.e., only the open shell orbitals and their electrons are included in the active space, and large CAS including all the bonding and antibonding valence π orbitals and their corresponding π electrons in the active space were used. Multireference configuration interactions (MRCI), either DDCI 1, 2, and 3 or SD CI calculations, were performed using the CASDI code.³³ cc-pVDZ Dunning basis sets which consist of 9s4p1d contracted in 3s2p1d for carbon and 4s1p contracted in 2s1p for hydrogen were used.³⁴ The orbitals which are represented are natural orbitals.

III. FAILURE OF THE MINIMAL CASSCF ZERO ORDER DESCRIPTION IN ORGANIC COMPOUNDS AND RECOURSE TO CAS(FULL VALENCE π)SCF CALCULATIONS

Reference 25 compares the spatial extent and Mulliken spin population of the SOMOs obtained at the ROHF and CAS(full valence π)SCF levels for mono- and diradical compounds. It shows that the ROHF SOMOs are exceedingly localized on the methylene groups. Since the spatial extent of the magnetic orbitals may have consequences on the magnetic properties, this section analyzes the dependence of the magnetic coupling of a peculiar diradical (compound 1) to the level of optimization of the orbitals. For this purpose, we have performed several kinds of calculations on the meta-xylylene molecule using different sets of orbitals. Table 1 presents the values of the magnetic couplings

Table 1. Magnetic Couplings in meV of Compound 1 Obtained Using Different Sets of Orbitals Indicated in the Left Column and Different Correlation Treatments Indicated in the First Line^a

	CAS(2,2) CI	CAS(2,2) +DDCI1	CAS(2,2) +DDCI2	CAS(2,2) +DDCI3	CAS(2,2) +SD
triplet MO	342	719	659	459	320
singlet MO	141	631	594	395	162
state specific MO	208	731	693	701	293

^aIn all cases, the zero order description is a minimal CAS(2,2).

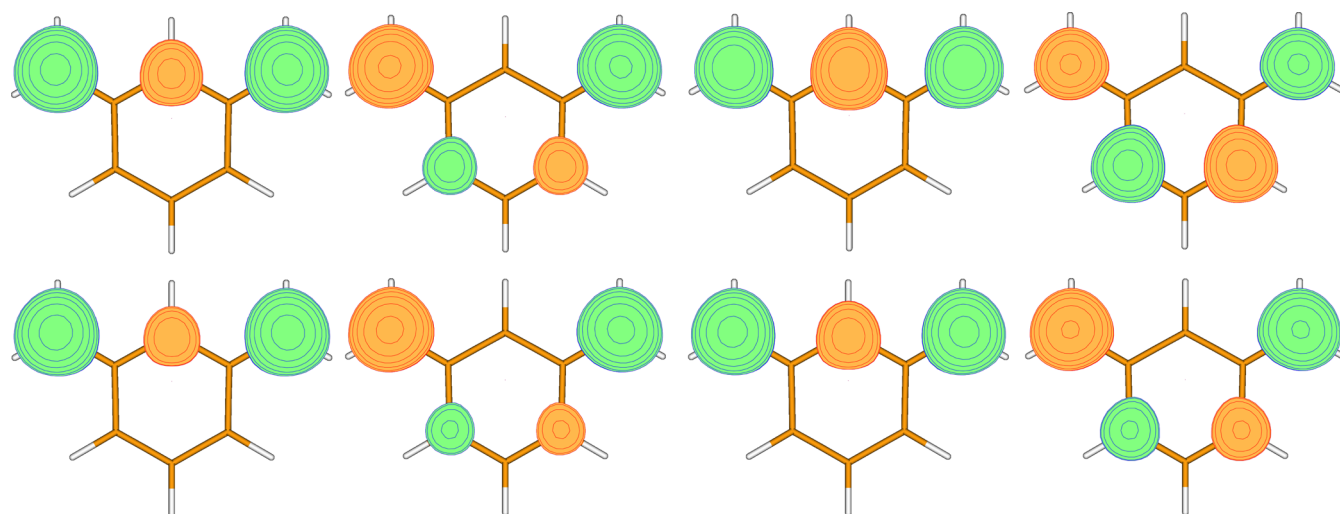
calculated using different correlation treatments but the same CAS(2,2) zero order description. The comparison between the results of the CASCI, CAS+DDCI1, CAS+DDCI2, CAS+DDCI3, and CAS+SD obtained using a single set of CAS(2,2)SCF orbitals (either those of the singlet or those of the triplet) and state specific orbitals shows an important discrepancy. This is in contrast with what is usually observed in inorganic complexes, for which the orbitals of the triplet and those of the singlet are similar and lead to comparable values of the magnetic coupling.⁷ Due to this strong dependence on the orbital set, the strategy which usually provides accurate values of the magnetic couplings in inorganic complexes, i.e., CAS(2,2)+DDCI3 calculations, may fail for the study of organic compounds. One should finally notice the drastic decrease of the values obtained at the SD level of calculation for most of the orbital sets.

We have therefore decided to explore more deeply the dependence on the size of the active space of the magnetic coupling. For this purpose, CAS(full valence π)DDCI, i.e., CAS(8,8)+DDCI, calculations have been carried out. Due to the

Table 2. Magnetic Couplings in meV of Compound 1 Calculated Using Different Sets of Natural Orbitals and Several Levels of Correlation Treatment^a

	CAS(8,8) CI (2450)	CAS(8,8)+DDCI1 (11.4 × 10 ⁶)	CAS(8,8) +DDCI2 (34.4 × 10 ⁶)	CAS(8,8) PT2	CAS(8,16) PT2
triplet MO	737	561	540		
singlet MO	652	541	522		
state sp MO	694	554	537	527	535

^aThe zero order description is always the large active space CAS(8,8). The size of the MRCI calculations matrix is indicated in parentheses.

**Figure 3.** Magnetic orbitals (b_1 and a_2) of compound 1 optimized using the CAS(8,8)SCF method (top) or the CAS(2,2)SCF (bottom) for the singlet (left) or the triplet (right).

large size of the CAS(8,8)+DDCI3 matrix (688×10^6 determinants), this last calculation could not be performed. The results are reported in Table 2. In order to compare the variational and perturbative methods of treatment of dynamic correlation, we have also performed CAS(full valence π)PT2 calculations. The value of the magnetic coupling obtained at the CAS(8,8)PT2 is close to that of the CAS(8,16)PT2 calculation in which the active space has been enlarged to the second shell of p' orbitals dedicated to correlation. As soon as dynamic correlation is taken into account, the values of the magnetic coupling calculated using the CAS(full valence π)SCF orbitals are in reasonable agreement, whatever the level of correlation is, i.e., DDCI1, DDCI2, and PT2. The sensitivity of the results to the state from which the natural orbitals are determined is also considerably reduced. The magnetic orbitals resulting from the minimal and enlarged active spaces are represented in Figure 3. Their different spatial extents over the ligand are visible to the naked eye. It is interesting to note that the occupation numbers of the natural orbitals obtained from the CAS(full valence p)SCF procedure clearly indicate that two orbitals only are essentially singly occupied, the occupation number of the less doubly occupied orbital being 1.90 (1.89) while that of the less empty orbital is 0.10 (0.11) for the singlet (triplet) state.

The Mulliken populations associated with the magnetic orbitals on the different centers are reported in Table 3. The delocalization of the magnetic MO affects the spin population distribution in the triplet state. It is well-known that the spin contact term on the protons, visible in the electron paramagnetic resonance experiments, is directly related to the π spin density on the carbon atom to which the proton is attached. The comparison of the spin densities obtained for the small and large CASSCF calculations shows that the latter introduces negative spin densities in the π system, due to the spin polarization of

Table 3. Atomic Mulliken Population of the Active MO of Compound 1 Computed at the CAS(2,2)SCF and [CASSCF(8,8)] Levels^a

type of MO	atom number	1	3	5
CAS(2,2)SCF [CAS(8,8)SCF]	triplet state	a_2	0.365 [0.232]	0.123 [0.251] 0 [0]
		b_1	0.411 [0.328]	0.001 [0.000] 0.150 [0.312]
	singlet state	a_2	0.416 [0.395]	0.077 [0.097] 0 [0]
		b_1	0.439 [0.419]	0.001 [0.001] 0.100 [0.138]

^aThe irreducible representations of the MO are those of the C_{2v} symmetry point group. The C_2 axis is the Z axis, and the plane of the molecule is the YZ plane. See Figure 2 for the atom numbering.

the doubly occupied π MO. It increases therefore the positive spin populations, but it is interesting to notice that the ratios ρ_3/ρ_1 and ρ_5/ρ_1 are significantly underestimated at the small CAS level, reflecting the excessive localization of the singly occupied MO at this level.

The here-obtained results explain the recourse to enlarged active spaces in previous works.^{23–25} However the computational cost of CAS(full valence π)-based methods becomes prohibitive for larger systems, and an alternative solution is desirable.

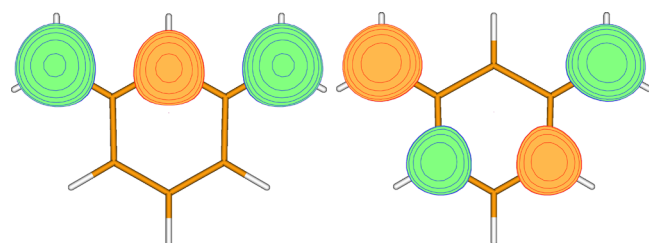
IV. A LOW COMPUTATIONAL COST ALTERNATIVE SOLUTION KEEPING A CAS(2,2) ZERO-ORDER DESCRIPTION

The strategy we propose is based on the following simple idea. Since among all natural orbitals issued from the post-CAS(full-CI valence π) calculation (which is invariant under orbital rotation),

Table 4. Magnetic Couplings in meV for Compound 1 Obtained at Several Levels of the Correlation Treatments and Using the Iterative Procedure Described in the Text^a

	CAS(2,2) CI (2)	CAS(2,2) +DDCI1 (7.6 × 10 ³)	CAS(2,2) +DDCI2 (12.2 × 10 ³)	CAS(2,2) +DDCI3 (441 × 10 ³)	CAS(2,2) +SD (12 × 10 ⁶)
NO1 CI size: 60	524	752	680	508	454
NO2 CI size: 68	574	756	682	519	490
NO3 CI size: 212	660	762	684	540	551
NO4 CI size: 462	614	759	684	529	519
NO5 CI size: 2450	654	762	684	538	547

^aWe recall that the value of the magnetic coupling obtained at the CAS(8,8)PT2 level is 527 meV while that of the CAS(8,16)PT2 level is 535 meV. The size of the CI matrix both in the optimization procedure (first column) and in the correlated calculation (first line) is indicated.

**Figure 4.** Average NO optimized using the CAS(2,2)+DDCI3 restricted to the π orbitals procedure (NO3) in compound 1.**Table 5. Atomic Mulliken Population of the Active NO3 of Compound 1**

type of MO	atom number	1	3	5
NO3	a ₂	0.315	0.171	0
	b ₁	0.375	0.000	0.219

only two orbitals essentially bear a single electron, and it is in principle possible to start from a CAS(2,2) calculation provided that the magnetic orbitals are accurate enough. The method aims to incorporate the main contribution of nondynamic correlations brought by the large active space using an iterative procedure which optimizes the orbitals at a lower computational cost. The iterative procedure consists of using at the iteration $n + 1$ the natural averaged orbitals obtained by diagonalizing the mean density matrix of the triplet and singlet wave functions obtained at iteration n . Ten to fifteen iterations are required to reach convergence of the energies and wave functions. The method proceeds in three steps:

- In order to get an initial guess of reliable valence orbitals, an iterative CAS(2,2)+DDCI1 calculation is first performed. This first step enables us to have accurate valence π^* orbitals for the second step and reliable σ and π occupied orbitals. This first set of orbitals is called NO1.

- In a second step, the valence π orbitals are optimized using an iterative CAS(2,2)+DDCI3 calculation and keeping frozen all the other orbitals obtained in step i. In order to appreciate the dependence of the orbital set to the level of correlation to which the orbitals are optimized, we have performed CAS(2,2)+DDCI2, CAS(2,2)+DDCI3, and CAS(2,2)+SD calculations restricted to the valence π and CAS(full valence π) in the case of compound 1. The so-obtained orbitals are respectively called NO2, NO3, NO4, and NO5. In this second step, we introduce the double excitations which are shown in Appendix A1 to contribute to the spatial delocalization of the orbitals. Note that due to the small size of the truncated CI matrices, the computational cost of this step is negligible in comparison to the dynamically correlated calculation performed at step iii (compare first line and first column of Table 4).
- At convergence of the orbital optimization, minimal-CAS-based dynamically correlated calculations are performed. In these last calculations, of course, none of the orbitals is frozen.

The values of the magnetic coupling are reported in Table 4, and the NO3 set of orbitals is represented in Figure 4. The comparison of the results deserves several comments:

- Looking at the values appearing in each column, one may conclude that the various studied levels of correlation provide consistent values of the magnetic coupling whatever the set of optimized orbitals is.
- Looking at the values appearing in each line, it appears that dynamic correlation still plays an important role when starting from a minimal active space, and it seems compulsory to perform either DDCI3 or SD calculations.
- In comparison to the CAS(2,2)SCF, NO1, and NO2 sets, the reliability of the NO3 and NO4 orbitals for the calculation of magnetic couplings is clearly noticeable. The

Table 6. Magnetic Coupling in meV for Compounds 2, 3, and 4 Computed at Different Levels of Correlation and Using Several Sets of MO^a

		CAS(2,2) CI	CAS(2,2) +DDCI1	CAS(2,2) +DDCI2	CAS(2,2) +DDCI3	CAS(2,2) +SD	CAS(2,2) (SCF) PT2	CAS(Full π) (SCF) PT2
compound 2	triplet CAS(2,2)SCF	131	418	389	232	126	(92) 137	(487) 327
	singlet CAS(2,2)SCF	68	371	351	206	73		
	NO3	410	481	435	325	349		
compound 3	triplet CAS(2,2)SCF	137	369	346	223	130	(88) 113	(432) 291
	singlet CAS(2,2)SCF	62	332	317	192	68		
	NO3	355	402	372	289	308		
compound 4	triplet CAS(2,2)SCF	−33	−175	−181	−155	−39	(−48) −209	(−277) −292
	singlet CAS(2,2)SCF	−71	−200	−210	−187	−76		
	NO3	−249	−296	−317	−305	−254		

^aThe CASSCF (in brackets) and CASPT2 values are given in the two right-most columns (these calculations are performed using state specific MOs).

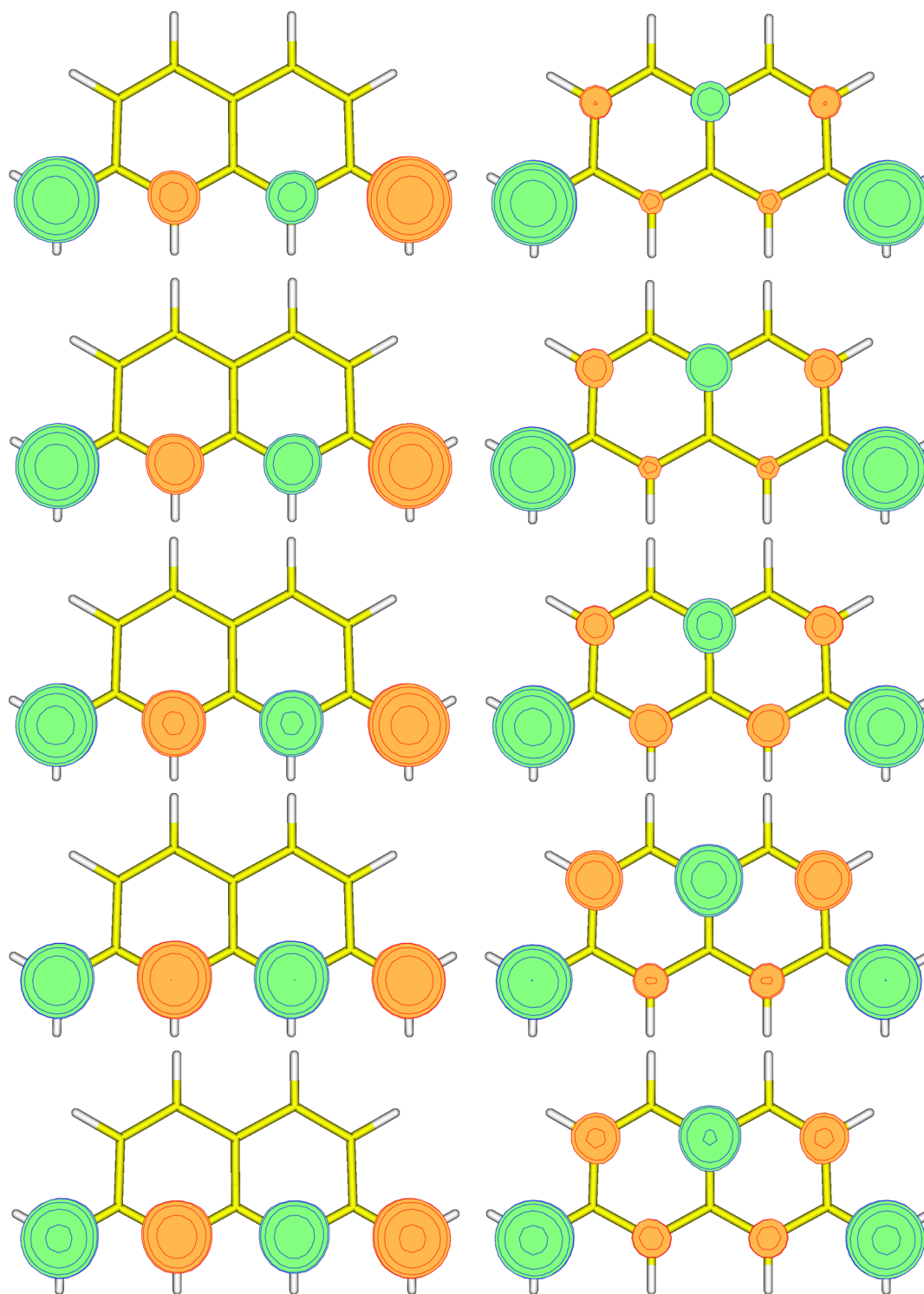


Figure 5. Magnetic orbitals of compound **2** optimized (from top to bottom) at the CAS(2,2)SCF level for the singlet and for the triplet, at the CAS(12,12)SCF level for the singlet and for the triplet, and NO3 magnetic orbitals.

magnetic coupling values calculated using the three sets of orbitals (NO3, NO4, NO5) are in excellent agreement. It is worth noticing that the agreement with the NO5 set is better for the NO3 orbital set than for the NO4 one, probably due to size consistency errors affecting the CAS(2,2)SD calculations.

- iv. Finally, the NO3, NO4, and NO5 magnetic orbitals are indistinguishable to the naked eye (this is the reason why only one set is reported in Figure 4). Comparing these

orbitals with those of both the minimal CASSCF and the CAS(full valence π) SCF calculations (Figure 3), one may note that, as expected, the average orbitals of the NO3 set are more delocalized than those of the minimal CAS and that they are intermediate between those of the singlet and the triplet states optimized using the CAS(full valence π) SCF method.

The Mulliken spin populations associated with the magnetic orbitals on all centers are reported in Table 5 for the NO3

orbitals set. One can check that they are equal to the average values of the CAS(full valence π) SCF Mulliken spin populations of the triplet and singlet states also given Table 3. One should notice that the same accuracy of the NO3 orbital set is observed in monoradicals (see Appendix A2).

Finally, the computed values of CAS(full valence π)PT2, CAS(2,2)+DDCI3, and CAS(2,2)+SD using the average NO3 orbitals predict a vertical triplet to singlet excitation energy around 0.54 eV. This value is higher than the experimental electron loss value (0.45 eV).³⁰ In order to validate our method of calculation, we have calculated the adiabatic transition energy using the singlet and triplet geometries of ref 31 (see Computational Information). The value obtained at the CAS(full valence π)PT2 level is 0.47 eV, in good agreement with the experimental data.

To summarize the procedure, one should mention that the NO3 orbitals set is provided by the natural orbitals of the iterative difference dedicated configuration interaction (IDDCI) procedure using a CAS(2,2) active space and a CAS(2,2)DDCI1 starting orbitals set and then freezing all orbitals other than valence π ones in the iterative process.

In order to show the validity of the previously detailed strategy, it has been applied to compounds 2, 3, and 4. The dependence of the result on the MO set may be appreciated comparing the following MO optimizations: the minimal CAS(2,2)SCF for the triplet and the singlet and average NO3. The CAS(2,2)PT2 and CAS(full valence π)PT2 values of the magnetic couplings are also reported in Table 6. The same conclusions as those given in the detailed study of compound 1 can be formulated, comparing the values of the magnetic couplings computed at several levels of correlation. One should again notice the proximity of the CAS(full valence π)PT2 results and the CAS(2,2)+DDCI3 using the NO3 orbital set while the computational costs in the case of the larger compound 4 between the here-proposed procedure and the CAS(full valence π)PT2 are very different: the size of the matrix of the DDCI3 calculation including all orbitals (the largest calculation which is performed to get reliable values of the magnetic coupling in our strategy) is 1.1×10^6 , while the size of the CAS(full valence π) matrix is 41.4×10^6 , which only gives a correct zero-order description; i.e., the CAS(full valence π)PT2 value should still differ from the CAS(full valence π)SCF one.

The magnetic orbitals of compound 2 optimized using the CAS(2,2)SCF and CAS(full valence π)SCF are represented in Figure 5. As for the meta-xylylene, the NO3 average magnetic orbitals are intermediate between those of the singlet and triplet states optimized using the CAS(full valence π) SCF orbitals, while the CAS(2,2)SCF orbitals are exceedingly localized.

V. CONCLUSION

This paper solves the following contradiction: according to the chemical intuition diradicals, organic compounds are usually seen as bearing two unpaired electrons while the CAS(2,2)SCF provides very poor values of the magnetic couplings. Even sophisticated methods of treatment of dynamic correlation applied on top of the two references fail to reproduce the correct values when using the corresponding CAS(2,2)SCF orbitals. This has led people to start from large (and full valence π when possible) CASSCF zero-order descriptions which rapidly become computationally prohibitive when the size of the conjugated system increases. However, the occupation numbers of the natural orbitals clearly indicate that only two orbitals bear a single electron. The smallest occupation number of the essentially doubly occupied natural NOs is 1.85, in all the series of compounds, while the largest occupation number of the

essentially empty NOs is 0.16. These systems must definitely be seen as diradicals. The present work has shown that the main problem concerning the calculation of the singlet–triplet energy splitting arises from the poor quality of the CAS(2,2)SCF orbitals, which are exceedingly localized. In order to reach improved active orbitals, we have proposed a new strategy which optimizes iteratively the orbitals keeping a CAS(2,2) zero-order description and a treatment of dynamic correlation limited to the π electrons. We have shown the following:

The excessive localization of the CAS(2,2)SCF orbitals, which even if of lesser extent also occurs in transition metal complexes,³⁵ has been rationalized using a theoretical derivation which shows that doubly excited determinants play a crucial role in the delocalization of the magnetic orbitals (see Appendix A1).

The quality of the iterated orbitals optimized at the average NO CAS(2,2)+DDCI3 restricted to the valence π orbitals (set NO3) is similar to that of the CAS(full valence π)SCF average NO (set NO5). They are even better than those obtained at the CAS(2,2)+SD level where the valence π orbitals were restricted (set NO4) due to larger size consistency errors affecting the latter. Actually, the iterative DDCI3 procedure introduces the effect of higher excitations such as the 2h-2p (introduced via the iterative procedure), which are expected to play a role in the delocalization character of the orbitals.

The use of improved MOs leads to values of the magnetic couplings very close to those of the much more computationally demanding CAS(full valence π)PT2, while keeping a minimal active space. In the case of the meta-xylylene for which an experimental value is available, the adiabatic energy difference between the singlet and the triplet states calculated using the CAS(full valence π)PT2 method is in good agreement with the electron loss measured value.

As already shown in previous papers (see for instance ref 7), not only the simplest contributions to the magnetic exchange (Anderson mechanism) such as the direct exchange (ferromagnetic) and the kinetic exchange (antiferromagnetic) vary with the spatial extent of the magnetic orbitals but also the contributions of the bridging ligand (generalized Anderson mechanism).

The computational cost is dramatically reduced in comparison to the CAS(full valence π)SCF optimization. For instance, in the case of compound 4, the size of the matrix to be diagonalized at the CAS(2,2)+DDCI3 level restricted to the valence π orbitals is only 1230 determinants, while the size of the matrix of the CAS(full valence π) is 41×10^6 . The size of the CAS(2,2)+DDCI3 matrix on the full orbital set is only 1.1×10^6 , while the CAS(full valence π)+DDCI3 on the full orbital set would be impossible to perform.

Finally, the here-proposed optimization process provides reliable values of the magnetic couplings whatever the nature, either ferromagnetic or antiferromagnetic, of the magnetic couplings is.

The study essentially concentrated on diradical conjugated hydrocarbons. The here-proposed methodology might eventually be tested on other problems, in particular in the treatment of the lowest singly excited states of closed-shell conjugated systems. Of course, as mentioned in the Introduction, the problem of the excessive localization of the magnetic orbitals on the metal ions is a well-known problem in coordination chemistry. Even if it has a lesser impact on the values of the magnetic couplings, some failures have also been encountered in inorganic complexes.³⁶ Our strategy should be applied to such problematic systems in the future, in particular in cases where there is not such a clear σ separation. It will require identifying

the reasonable subset of ligand MOs surrounding the metal ions which would play the role of the π valence MO in the present work. The iterated DDCI3 procedure applied to this limited subset should introduce the correct ligand/metal delocalization in the magnetic MO while the full and expansive DDCI3 calculation involving the full orbital set would introduce the dynamic correlation at the final step.

APPENDIX

A1. Theoretical Analysis of the Origin of the Excessive Localization of the CASSCF Active MO in Conjugated Systems

1. Spatial Extent of the Magnetic Orbital in Monoradical Compounds. This section addresses theoretically the question of the exceeding localization of magnetic orbitals observed in organic compounds. We shall first start with monoradicals since this peculiarity has already been observed²⁵ in methylene benzene and methylene naphthalene. One should also mention that this exceeding localization had also been noted in inorganic complexes even if of lesser extent.³⁵ The derivation generalizes the arguments given in a paper⁵ devoted to the magnetic coupling in inorganic bimetallic compounds. It will first concern the simpler case of a monoradical and then will be developed for diradical compounds. Hereafter, we shall concentrate on alternant (or bipartite) hydrocarbons. These systems do not present odd-membered rings. As a consequence, they are such that the carbon atoms may be partitioned in two sets, to which one may attach a “color”, such that the nearest neighbor of an atom of one set is chemically linked to atoms belonging to the other set. The nearest neighbors of a carbon bearing a “blue arrow” bears a “purple arrow” and vice versa. Some useful theorems have been established for such graphs from the Hückel model Hamiltonian, in particular the “mirror theorem”.³⁷ This theorem says that to each bonding canonical MO i one may associate an antibonding canonical MO i^* , and the absolute values of the coefficients of these pairs of MOs on the various sites p, q, r, \dots are equal. Actually, one may show that the signs of the coefficients are identical for the atoms of one color and opposite for the atoms of the other color:

$$\begin{aligned} C_{i^*p} &= C_{ip} \text{ if } p \text{ bears, say, a blue arrow, and} \\ C_{i^*p} &= -C_{ip} \text{ if } p \text{ bears a purple arrow.} \end{aligned}$$

This correspondence between the bonding and antibonding valence MOs remains approximately satisfied when considering more sophisticated Hamiltonians, even *ab initio* ones.

Let us consider a $\text{CH}_2\text{-Ar}$ radical, where Ar represents a conjugated closed-shell aromatic system, such as benzene or naphthalene. In a localized zero order picture, one may consider the unpaired electron as localized on the CH_2 group, in an orbital labeled a' . The doubly occupied MO of the aromatic rings, labeled i', j', \dots , and their unoccupied antibonding counterparts i'^*, j'^*, \dots are assumed to be orthogonal and localized on the Ar group. We start from a single determinantal strongly localized description $\Phi_0' = | \dots i' \bar{i}' j' \bar{j}' a' |$. This function is obtained from a constrained SCF procedure in which the MO a' is frozen on the π orbital of the external CH_2 group. This solution defines a Fock operator \hat{F}' which exhibits off-diagonal matrix elements between the MOs i', j' , and a' as well as between a' and i'^* or j'^* and zero elements between the beforehand optimized SCF MO of the aromatic part. The delocalization between the magnetic site and the aromatic system can be introduced by a proper rotation between the orbitals a' and $i', j', \dots, i'^*, j'^*, \dots$ to

obtain an SCF determinant:

$$\Phi_0 = | \dots i' \bar{i}' j' \bar{j}' a | \quad (1)$$

where the self-consistent MOs, i, j , and a , now exhibit delocalization tails between the CH_2 group and the aromatic ring. At the first-order of perturbations, the SCF MO can be written as

$$i = i' + \frac{\langle i' | \hat{F}' | a' \rangle}{\langle i' | \hat{F}' | i' \rangle - \langle a' | \hat{F}' | a' \rangle} a' = i' + \lambda_{ia} a' \quad (2)$$

and

$$a = a' - \frac{\langle i' | \hat{F}' | a' \rangle}{\langle i' | \hat{F}' | i' \rangle - \langle a' | \hat{F}' | a' \rangle} i' = a' - \lambda_{ia} i' \quad (3)$$

The energies of the bonding MO i' are lower than the energy of the nonbonding MO a' , so that the energy denominator is negative. Let us call p the π atomic orbital on the carbon atom P of Ar which is connected to the CH_2 group. Then one may approximate

$$\langle i' | \hat{F}' | a' \rangle = \langle p | \hat{F}' | a' \rangle c_{i'p} \quad (4)$$

where $c_{i'p}$ is the coefficient of the atomic orbital p in the MO i' .

If the coefficients of a' and p in the MO i' have the same sign (which does not represent a restriction), the numerator is negative (as are the hopping integrals of the Hückel Hamiltonian between orbitals presenting a positive overlap). The coefficients λ_{ia} are positive

$$\lambda_{ia} > 0 \quad (5)$$

the MOs i and j take an in-phase tail on the CH_2 group, while the singly occupied MO (SOMO) takes out-of-phase tails on the aromatic rings bonding MO. One should as well consider delocalization processes between the SOMO and the antibonding MO i'^* :

$$i^* = i'^* + \frac{\langle i'^* | \hat{F}' | a' \rangle}{\langle i'^* | \hat{F}' | i'^* \rangle - \langle a' | \hat{F}' | a' \rangle} a' = i'^* + \lambda_{i^*a} a' \quad (6)$$

On the contrary, if the coefficient of the MO i'^* on the atomic orbital p is chosen positive (which is also a matter of convention), the mixing coefficient λ_{i^*a} is negative, and opposite to λ_{ia} . According to the mirror theorem relating the amplitudes of the bonding and antibonding MO in alternant hydrocarbons, $0 > \lambda_{i^*a} = -\lambda_{ia}$. Finally, the singly occupied MO is

$$a = a' - \sum_{i'} (\lambda_{ia} i' + \lambda_{i^*a} i'^*) = a + \sum_{i'} \lambda_{ia} (i'^* - i') \quad (7)$$

In view of the preceding remark concerning the mirror theorem, one may notice that the coefficient of the SCF MO a on the atom P will be zero. Actually the delocalization tail of the SOMO on the conjugated system only concerns the atoms of the opposite “color” of the atom to which the CH_2 group is attached. In other words

$$\begin{aligned} C_{ap} &= 0 = C_{ar} \text{ if } r \text{ is of the same color as } p, \\ C_{aq} &= -\sum_{i'} 2\lambda_{ia} \text{ if } q \text{ is of another color than } p \end{aligned} \quad (8)$$

This result coincides with the well-known feature of the SOMOs in Hückel or RO-SCF descriptions, namely the fact they have zero coefficients on the sites of minor color.

Our thesis is that this SCF SOMO is unduly localized, and dynamic correlation should lead to more delocalized natural

MOs. Perturbing the MOs under the effect of the single excitations to the first order cancels the matrix elements of the Fock operator to the second order. Actually, the new SCF description defines a new Fock operator \hat{F} which satisfies Brillouin's theorem:

$$\langle i|\hat{F}|a\rangle = 0 \quad (9)$$

At the first order of perturbation, the singly excited charge transfer determinants $\Phi_{\bar{i}\rightarrow\bar{a}} = a_{\bar{a}}^+ a_i \Phi_0$ or $\Phi_{a\rightarrow i^*} = a_{i^*}^+ a_a \Phi_0$ between the magnetic group and the aromatic rings have zero coefficients, due to the Brillouin's theorem. This will no longer be the case in the second-order wave function, since these determinants have strong interactions with some doubly excited determinants. The largest interaction will concern the coupling between the determinants $\Phi_{\bar{i}\rightarrow\bar{a}}$ with the doubly excited determinant $\Phi_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}} = a_{k^*}^+ a_{\bar{a}}^+ a_j \Phi_0$ and the coupling between $\Phi_{a\rightarrow i^*} = a_{i^*}^+ a_a \Phi_0$ with the doubly excited determinants $\Phi_{j\rightarrow k^*, a\rightarrow i^*} = a_{k^*}^+ a_{i^*}^+ a_a \Phi_0$. In these determinants the excitation from j to k^* may be of both spins. Let us consider for instance the second mechanism. The first-order coefficient of the determinant $\Phi_{j\rightarrow k^*, a\rightarrow i^*}$ is given by

$$C_{j\rightarrow k^*, a\rightarrow i^*} = -\frac{\langle \Phi_{j\rightarrow k^*, a\rightarrow i^*} | \hat{H} | \Phi_0 \rangle}{\Delta E_{j\rightarrow k^*, a\rightarrow i^*}} = -\frac{\langle jk^*, ai^* \rangle}{\Delta E_{j\rightarrow k^*, a\rightarrow i^*}} \quad (10)$$

The denominator is a positive excitation energy, and the bielectronic integral in the numerator can be estimated by expressing the distribution ai^* from the strongly localized atomic orbitals a' and i'^* , keeping the largest charge distributions, $i'^*i'^*$ and $a'a'$, in the multipolar expansion of this distribution:

$$ai^* = a'i'^* - \lambda_{i^*a}(i'^*i'^* - a'a') \approx -\lambda_{i^*a}(i'^*i'^* - a'a') \quad (11)$$

where the intersite overlap distribution has been neglected. The product ai^* may be seen as a dipole which will interact with the transition dipole jk^* on the aromatic rings.

$$\begin{aligned} \langle jk^*, ai^* \rangle &= -\lambda_{i^*a}(\langle jk^*, i'^*i'^* \rangle - \langle jk^*, a'a' \rangle) \\ &= -\lambda_{i^*a}(\langle j|J_{i'^*} - J_a|k^* \rangle) \end{aligned} \quad (12)$$

Now, the leading second-order coefficient of the singly excited configuration $\Phi_{a\rightarrow i^*}$ will be given by

$$C_{a\rightarrow i^*} = \sum_{j,k^*} \frac{\langle \Phi_{a\rightarrow i^*} | \hat{H} | \Phi_{j\rightarrow k^*, a\rightarrow i^*} \rangle}{\Delta E_{a\rightarrow i^*}} \frac{\langle \Phi_{j\rightarrow k^*, a\rightarrow i^*} | H | \Phi_0 \rangle}{\Delta E_{j\rightarrow k^*, a\rightarrow i^*}} \quad (13)$$

Since $\langle \Phi_{a\rightarrow i^*} | H | \Phi_{j\rightarrow k^*, a\rightarrow i^*} \rangle = \langle j|J_{i^*} - J_a|k^* \rangle$, one may write

$$\begin{aligned} C_{a\rightarrow i^*} &= \sum_{j,k^*} -\lambda_{i^*a} \frac{\langle j|J_{i^*} - J_a|k^* \rangle}{\Delta E_{a\rightarrow i^*}} \frac{\langle j|J_{i^*} - J_a|k^* \rangle}{\Delta E_{j\rightarrow k^*, a\rightarrow i^*}} \\ &\approx \sum_{j,k^*} -\lambda_{i^*a} \frac{\langle j|J_{i^*} - J_a|k^* \rangle^2}{\Delta E_{a\rightarrow i^*} \Delta E_{j\rightarrow k^*, a\rightarrow i^*}} \\ &= \lambda_{ia} \chi_i \end{aligned} \quad (14)$$

and since we have seen that λ_{i^*a} is negative, the coefficient $C_{a\rightarrow i^*}$ is positive. So is the quantity χ_i .

Actually the demonstration has to be performed as well on the ring to methyl excitations $\Phi_{\bar{i}\rightarrow\bar{a}}$. It proceeds according to the same logic. The first order wave function involves the determinants $\Phi_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}}$ the coefficients of which are given by

$$\begin{aligned} C_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}} &= -\frac{\langle \Phi_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}} | \hat{H} | \Phi_0 \rangle}{\Delta E_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}}} \\ &= -\frac{\langle jk^*, ai \rangle}{\Delta E_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}}} \\ &\approx \lambda_{ia} \frac{\langle j|J_{i'} - J_a|k^* \rangle}{\Delta E_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}}} \end{aligned} \quad (15)$$

Since

$$C_{\bar{i}\rightarrow\bar{a}} = \sum_{j,k^*} \frac{\langle \Phi_{\bar{i}\rightarrow\bar{a}} | \hat{H} | \Phi_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}} \rangle}{\Delta E_{\bar{i}\rightarrow\bar{a}}} \frac{\langle \Phi_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}} | H | \Phi_0 \rangle}{\Delta E_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}}} \quad (16)$$

and since the coefficient of the singly excited determinant

$$C_{\bar{i}\rightarrow\bar{a}} = \lambda_{ia} \sum_{j,k^*} \frac{\langle j|J_{i'} - J_a|k^* \rangle^2}{\Delta E_{\bar{i}\rightarrow\bar{a}} \Delta E_{j\rightarrow k^*, \bar{i}\rightarrow\bar{a}}} = \lambda_{ia} \chi_i' \quad (17)$$

is positive, the quantity χ_i' is also positive. This means that the natural doubly occupied MO i''

$$i'' = i + C_{\bar{i}\rightarrow\bar{a}} a \quad (18)$$

takes a larger in-phase tail on the CH_2 group. Finally, the natural SOMO will be written as

$$a'' = a + \sum_{i^*} C_{a\rightarrow i^*} i^* - C_{\bar{i}\rightarrow\bar{a}} i \quad (19)$$

Looking at the equations, and due to the mirror theorem, the operators J_i and J_{i^*} may be considered as equal, since the ii and i^*i^* distributions may be developed, neglecting interatomic differential overlap distributions, as usual in the popular and efficient Pariser–Parr–Pople (PPP) and complete neglect of differential overlap (CNDO) treatments of conjugated systems, as

$$ii = \sum_t C_{it}^2 tt \quad (20)$$

$$i^*i^* = \sum_t C_{i^*t}^2 tt \quad (21)$$

and since $C_{i^*t}^2 = C_{it}^2$, according to the mirror theorem. Consequently

$$\langle j|J_a - J_{i^*}|k^* \rangle^2 = \langle j|J_{i^*} - J_a|k^* \rangle^2 \quad (22)$$

$\chi_i' = \chi_i$ and $C_{a\rightarrow i^*} = C_{\bar{i}\rightarrow\bar{a}}$. Finally,

$$a'' = a + \sum_i C_{a\rightarrow i^*} i^* - C_{\bar{i}\rightarrow\bar{a}} i = a + \sum_i \lambda_{ai} \chi_i (i^* - i) \quad (23)$$

Remembering the expression of a in terms of the strongly localized MOs a' , i' , and i'^* (see eq 7), and that the MOs i and i^* only differ from the MOs i' and i'^* by a first-order of perturbations treatment, the natural SOMO can be written as

$$a'' = a + \sum_i \lambda_{ai} \chi_i (i^* - i) = a' + \sum_i \lambda_{ai} (1 + \chi_i) (i'^* - i') \quad (24)$$

Since the quantities χ_i are positive, the delocalization tails of the SOMO on the aromatic part of the molecule have been increased. As expected, the correlation expands these tails while

keeping the nodes on the atoms of the same color as the atom of attachment of the CH₂ group.

2. Spatial Extent of Magnetic Orbitals in Diradicals. Let us consider diradicals obtained by attaching two CH₂ groups on an aromatic ring. The logic of the demonstration remains the same and will not be repeated. One must however notice that we focus here on the effect of the so-called 2h-1p and 1h-2p double excitations, which in inorganic complexes brings the major contribution to the delocalization of the metal transition ion magnetic orbitals on the surrounding ligands. Actually, the general expression of the singly excited charge transfer configurations coefficients at the second order of perturbation is

$$C_{\bar{i} \rightarrow \bar{a}} = \sum_{j,h,k^*} \frac{\langle \Phi_{\bar{i} \rightarrow \bar{a}} | H | \Phi_{h \rightarrow k^*, \bar{j} \rightarrow \bar{a}} \rangle \langle \Phi_{h \rightarrow k^*, \bar{j} \rightarrow \bar{a}} | H | \Phi_0 \rangle}{\Delta E_{\bar{i} \rightarrow \bar{a}} \Delta E_{h\bar{j} \rightarrow k^* \bar{a}}} + \sum_{r,h,k^*} \frac{\langle \Phi_{\bar{i} \rightarrow \bar{a}} | H | \Phi_{h \rightarrow k^*, \bar{i} \rightarrow \bar{r}} \rangle \langle \Phi_{h \rightarrow k^*, \bar{i} \rightarrow \bar{r}} | H | \Phi_0 \rangle}{\Delta E_{\bar{i} \rightarrow \bar{a}} \Delta E_{h\bar{i} \rightarrow k^* \bar{r}}} \quad (25)$$

where, in the second sum, r may either be a virtual MO or the SOMO a . This may be expressed as

$$C_{\bar{i} \rightarrow \bar{a}} = \sum_{j,h,k^*} - \frac{\langle hj || k^* i \rangle \langle k^* a || hj \rangle}{(\Delta E_{\bar{i} \rightarrow \bar{a}})(\Delta E_{h\bar{j} \rightarrow k^* \bar{a}})} + \sum_{a,h,k^*} \frac{\langle hallk^* a \rangle \langle ak^* || hi \rangle}{(\Delta E_{\bar{i} \rightarrow \bar{a}})(\Delta E_{h\bar{i} \rightarrow k^* \bar{a}})} + \sum_{l^*,h,k^*} \frac{\langle hallk^* l^* \rangle \langle l^* k^* || hi \rangle}{(\Delta E_{\bar{i} \rightarrow \bar{a}})(\Delta E_{h\bar{i} \rightarrow k^* l^*})} \quad (26)$$

One recognizes that this expression incorporates the previously discussed mechanism, which is brought by the special cases $j = i$ in the first sum and by the second one. Nevertheless, the third sum runs over 2h-2p configurations, which are not considered in the DDCI space. Similarly, regarding the excitations from the SOMO to the antibonding MO of the aromatic system,

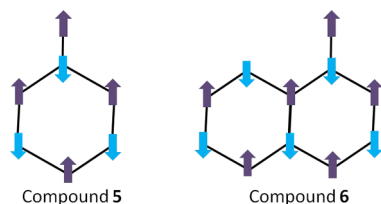


Figure 6. Schematic representation of the methylene benzene compound 5 and methylene naphthalene compound 6.

$$C_{a \rightarrow i^*} = \sum_{j,h,k^*} \frac{\langle \Phi_{a \rightarrow i^*} | H | \Phi_{j \rightarrow k^*, h \rightarrow i^*} \rangle \langle \Phi_{j \rightarrow k^*, h \rightarrow i^*} | H | \Phi_0 \rangle}{\Delta E_{a \rightarrow i^*} \Delta E_{jh \rightarrow k^* i^*}} + \sum_{l^*,h,k^*} \frac{\langle \Phi_{a \rightarrow i^*} | H | \Phi_{j \rightarrow k^*, a \rightarrow l^*} \rangle \langle \Phi_{j \rightarrow k^*, a \rightarrow l^*} | H | \Phi_0 \rangle}{\Delta E_{a \rightarrow i^*} \Delta E_{ja \rightarrow k^* l^*}} \quad (27)$$

which can be expressed as

$$C_{a \rightarrow i^*} = - \sum_{j,k^*} \frac{\langle jallk^* a \rangle \langle k^* i^* || ja \rangle}{\Delta E_{a \rightarrow i^*} \Delta E_{aj \rightarrow i^* k^*}} - \sum_{j,h,k^*} \frac{\langle jallk^* h \rangle \langle k^* i^* || jh \rangle}{\Delta E_{a \rightarrow i^*} \Delta E_{jh \rightarrow k^* i^*}} + \sum_{l^*,j,k^*} \frac{\langle ji^* || k^* l^* \rangle \langle k^* l^* || ja \rangle}{\Delta E_{a \rightarrow i^*} \Delta E_{ja \rightarrow k^* l^*}} \quad (28)$$

The first and the third sums run over 1h-2p excitations, the second one over 2h-2p excitations. Notice that adding to the first sum the specific contribution $l^* = i^*$ in the third sum, one gets the previously analyzed correction of eq 17.

It may be worth looking at the possible role the 2h-2p excitations in the delocalization of the active MO a . In coordination chemistry, their role is minor. In conjugated radicals or diradicals, they may contribute significantly. Looking for instance at the second sum in the above eq 28, one sees that if j, h, i^* , and k^* have large amplitudes on the site bearing the CH₂ group, both integrals $\langle jallk^* h \rangle$ and $\langle k^* i^* || jh \rangle$ may be important. A similar conclusion may be obtained regarding the third sum of eq 26. The 2h-2p excitations are in general not important in coordination chemistry because the ligands usually present lone pairs toward the metal ion. The main delocalization effect concerns the LMCT excitations $i \rightarrow a$ rather than the MLCT ones. The 2h-2p contribution to the delocalization is only important when the ligand presents both valence occupied and virtual MOs close to the metal ion. This is not usually the case, and this explains why the natural MOs of the DDCI calculations, which omit the 2h-2p excitations, are in general satisfactory. As an exception, one may quote the azido ligands, which present both occupied and virtual MOs close to the magnetic centers.⁸ Numerical calculations have shown that in such a case the enlargement of the active space to these ligand MOs was necessary to obtain reasonable values of the magnetic couplings. A similar situation may be found in dinitroxides.¹⁰

The above analysis explains why obtaining appropriate active MOs in conjugated radicals can rely neither on minimal CASSCF calculation nor on the DDCI calculations starting from a zero order CASSCF description: the CASSCF MOs are always

Table 7. Mulliken Spin Population of the Magnetic Orbitals Optimized at the ROHF Level and CAS(Full Valence p)SCF Level and Using the Proposed Procedure Leading to the NO3 Orbital Set for the Methylene Benzene and Methylene Naphthalene Compounds 5 and 6, Respectively

	atom number	1	2	3	4	5	6	7	8	9	10	11
compound 5	Hückel	0.571	0.000	0.143	0.000	0.143	0.000	0.143				
	ROHF	0.803	0.006	0.062	0.002	0.050	0.002	0.062				
	NO3	0.574	0.014	0.120	0.005	0.152	0.005	0.120				
	CAS(7,7) SCF	0.591	0.013	0.117	0.005	0.142	0.005	0.117				
compound 6	Hückel	0.530	0.000	0.059	0.000	0.059	0.000	0.235	0.000	0.059	0.000	0.059
	ROHF	0.791	0.012	0.026	0.002	0.027	0.004	0.110	0.001	0.016	0.001	0.012
	NO3	0.568	0.020	0.026	0.003	0.055	0.008	0.243	0.003	0.043	0.002	0.031
	CAS(11,11) SCF	0.529	0.019	0.033	0.003	0.070	0.008	0.242	0.003	0.053	0.002	0.036

exceedingly localized, but in contrast with coordination chemistry magnetic problems the 2h-1p and 1h-2p excitations are not sufficient to restore a correct delocalization of the magnetic MOs. As will be shown, this statement does not imply that the CASSCF calculation and the post-CASSCF calculations have to concern all the π electrons in all the π MOs. For the quality of the NO3 orbital set for monoradicals, see Figure 6 and Table 7).

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Notes

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