

# THE DIFFERENCE-DEDICATED CONFIGURATION INTERACTION METHOD: AN ACCURATE PROCEDURE TO CALCULATE ENERGY TRANSITIONS

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**Abstract:** The Difference Dedicated Configuration Interaction method is described and its performance illustrated by applications on electronic transitions, singlet-triplet separations and magnetic exchange coupling.

**Keywords:** *ab initio*, Configuration Interaction, optical transition, magnetic coupling.

## 1. INTRODUCTION

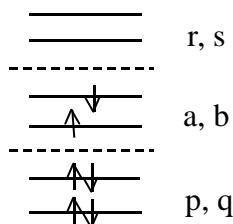
Nowadays, a large variety of spectroscopic techniques can provide very accurate energy transitions. Theoreticians usually determine these energy differences from the independent calculation of several roots of the Schrödinger equation, evaluated at a given level of approximation. Although the variational principle gives a reference criterion to evaluate the quality of the approximate wavefunction, the importance of getting as low as possible absolute energies is often over-emphasized. This criterion does not necessarily imply the minimum error in the calculated transition since the correlation energy included by the truncated expansion of the wavefunction may be very different for each state. Moreover, single-reference wavefunctions do not provide in general good descriptions of excited states. The consequence is that the error may be very different for each energy evaluated and that it is difficult to obtain reliable energy transitions from independent calculations, even performed at a high level of accuracy. The problem becomes particularly dramatic for very small energy differences such as those found between the different spin multiplets in magnetic systems, very often lower than  $100\text{ cm}^{-1}$  ( $\sim 5 \cdot 10^{-4}$  hartree).

Different formalisms have been proposed to evaluate energy differences. Single reference<sup>1,2,3,4,5,6,7</sup> or multireference<sup>8,9,10</sup> Green's functions formalisms have been used to determine ionization potentials, electron affinities or electronic spectra. Equation of Motion (EOM)<sup>11,12,13,14</sup> and Random Phase Approximation (RPA)<sup>15,16</sup> have been used coupled to single reference<sup>17,18,19,20</sup> or multireference Coupled Cluster (CC) methods<sup>21,22,23,24,25</sup>. Among Configuration Interaction (CI) methods, Goddard and collaborators have proposed the Correlation Consistent CI (CCCI)<sup>26,27</sup>, useful for singlet-triplet energy gaps in carbenic systems, and the Dissociation Consistent CI (DCCI)<sup>28,29</sup>, well adapted to calculate dissociation energies. The Difference Dedicated Configuration Interaction (DDCI)<sup>30</sup> method is a variational method specifically designed to calculate energy differences such as ionization potentials, electron affinity, optical transitions, magnetic exchange coupling, etc. An iterative procedure (IDDCI)<sup>31</sup> has been implemented to ensure the independence of the results of the molecular orbital (MO) set. Many examples, especially in magnetic systems, have shown the performance of the method that is described in the next section.

## 2. THE DDCI METHOD TO EVALUATE ENERGY DIFFERENCES

The CI space used in the DDCI procedure is selected from second-order Perturbation Theory considerations. Perturbation Theory is however only used formally to truncate the CI space, to include only the contributions that are relevant for the energy difference(s) of interest.

Grounded on the early perturbative calculations of singlet-triplet (S-T) gaps in biradicalar systems by De Loth *et al.*<sup>32</sup>, DDCI allows to evaluate variationally any type of vertical energy difference<sup>30</sup> from a common set of MOs for all states. The first step in the scheme is the definition of a minimal model space  $S$ , that gives a zero-order description of the transition(s) to be calculated. For this purpose the MO set is partitioned in three subsets, namely doubly occupied,  $p, q$ , active,  $a, b$ , and virtual,  $r, s$ , as shown in the scheme:



In the most general case, the model space is taken as the minimal Complete Active Space (CAS) including the orbitals that describe the transition at the single electron level. If the transition has a strongly mixed character, other orbitals have to be added to the active space. Some examples will help us to illustrate how this minimal CAS is chosen.

- i) Optical transitions may often be described with two active orbitals. Nevertheless, there are important exceptions such as the strong valence-Rydberg mixing occurring in some unsaturated hydrocarbon excited states: the  ${}^1A_g \rightarrow {}^1B_{1u}$  transition in ethylene presents such a problem. To take into account this mixed character, Rydberg orbitals of the correct symmetry have to be added to the active space<sup>33</sup>. The active space is thus defined from the configurations generated with two electrons and three active MOs: the occupied and the virtual ones implicated in the transition,  $b_{2u}$ ,  $b_{3g}$ , and a Rydberg orbital of the same symmetry,  $R_{b3g}$ .
- ii) Ionization Potentials (IP) and Electron Affinities (EA) may as well be calculated by the same procedure. Taking potassium<sup>34</sup> as an example, for the

first IP,  ${}^2\text{S}(\text{K}) \rightarrow {}^1\text{S}(\text{K}^+)$ , the active space is defined by one electron and one orbital, 4s, plus a fictitious orbital of low energy (1s), situated at  $r \rightarrow \infty$ , in order to keep constant the number of electrons; in the same way, for the EA  ${}^1\text{S}(\text{K}^-) \rightarrow {}^2\text{S}(\text{K})$ , the active orbitals are the 4s and 4p atomic orbitals, and the CAS is generated by two electrons in four orbitals (plus the 1s orbital at  $r \rightarrow \infty$ ).

- iii) The exchange coupling constant in bicentric magnetic systems is proportional to the energy difference between different multiplicity states. The active space is generated by the number of magnetic orbitals and of unpaired electrons of the system: two electrons and two orbitals for diradicalar systems<sup>35,36</sup> such as Cu(II) dinuclear complexes, four electrons and four orbitals in Ni(II) dimers<sup>37</sup>, six electrons and six orbitals in Cr(III) dimers<sup>38</sup>, etc. The active molecular orbitals in these weakly interacting systems are bonding and antibonding molecular orbitals occupied by the unpaired d electrons of the metal centers.

Once the model space (namely the CAS) is defined, the external correlation is included up to the second-order in the framework of the quasi-degenerate perturbation theory. At this level of theory, the elements of the effective Hamiltonian built on the previously defined model space are, for  $|\Phi_I\rangle, |\Phi_J\rangle \in S$  :

$$\langle \Phi_I | \hat{H}_{\text{eff}}^{(2)} | \Phi_J \rangle = \langle \Phi_I | \hat{H} | \Phi_J \rangle + \sum_{\Phi_\alpha \notin S} \frac{\langle \Phi_I | \hat{V} | \Phi_\alpha \rangle \langle \Phi_\alpha | \hat{V} | \Phi_J \rangle}{E_J^{(0)} - E_\alpha^{(0)}} \quad [1]$$

where  $\hat{V}$  is the perturbation operator and  $E_J^{(0)}$  and  $E_\alpha^{(0)}$  are the zero-order energies of the determinants  $|\Phi_J\rangle$  and  $|\Phi_\alpha\rangle$ , respectively.

From the Slater rules it is easy to demonstrate that the purely inactive  $\{|\Phi_\alpha\rangle = |D_{pq,rs}^+ \Phi_I\rangle\}$  double excitations, *i.e.* those involving two electrons from the doubly occupied MOs to virtual ones, do not give any contribution to the off-diagonal elements,

$$\langle D_{pq,rs}^+ \Phi_I | \hat{H} | \Phi_J \rangle = 0 \quad \text{for } I \neq J \quad [2]$$

These purely inactive double excitations give very important contributions to the correlation energy, but at the Møller-Plesset level only shift by the same value the diagonal elements of the effective Hamiltonian:

$$\sum_{D_{pq,rs}^+ \Phi_I} \frac{\langle \Phi_I | \hat{V} | D_{pq,rs}^+ \Phi_I \rangle \langle D_{pq,rs}^+ \Phi_I | \hat{V} | \Phi_J \rangle}{E_J^{(0)} - E_{D_{pq,rs}^+ \Phi_I}^{(0)}} = \sum_{p,q,r,s} \frac{|\langle pq || rs \rangle|^2}{\Delta_{pq \rightarrow rs}} \quad [3]$$

where the denominator is a difference of orbital energies:

$$\Delta_{pq \rightarrow rs} = \epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s \quad [4]$$

and thus do not contribute to the spectrum.

To include higher orders of perturbation as well as to avoid intruder states, a well-known problem of perturbative effective Hamiltonians, the above perturbative arguments are extrapolated to build a CI space that includes all the second-order excitations that are significant in the spectrum evaluation. It means that the same contributors to the perturbative calculation are included in a CI space, which is then treated variationally. In that way, interactions between double excitations are automatically allowed. Hence, the CI subspace includes the CAS and single and double excitations on them involving at least one active orbital. Figure 1 schematizes the type of determinants included and excluded of the CI, when compared to the ‘full’ CAS Single Double CI (CAS\*SDCI).

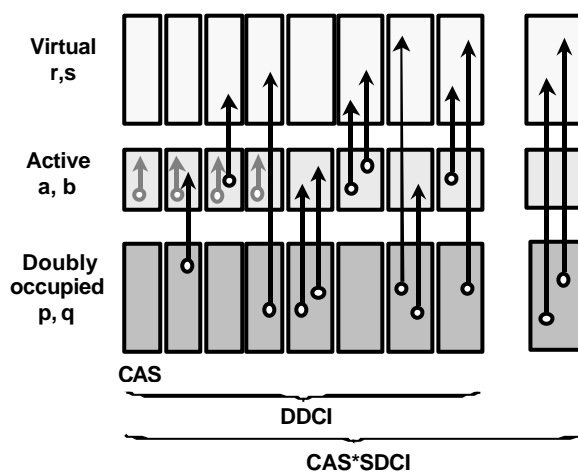


Figure 1. Schematic representation of the contributions to the DDCI space

Because DDCI is entirely variational, it is an uncontracted method and therefore allows the external correlation to modify the coefficients of the zero-order CAS wavefunction. This is an advantage over CAS + perturbative calculations such as CASPT2<sup>39</sup>, which can only overcome this difficulty by sufficiently enlarging the CAS. When compared with CAS\*SDCI calculations, the DDCI subspace has several advantages. The first one is the computational cost, since DDCI dimension scales as  $\text{dim}[\text{CAS}] * N^3$ , where  $N$  is the size of the orbital set, instead of  $\text{dim}[\text{CAS}] * N^4$ . The second one arises from the fact that the purely inactive double excitations, responsible of the major part of electron correlation, are not included and thus the calculated correlation energy is only a small part of the total one, avoiding large size-consistency errors, at least for a small number of active electrons. The counterpart is of course that DDCI cannot give good absolute energies.

DDCI gives thus energy differences from purely variational calculations. A DDCI space is generated for each desired symmetry and the energies and wavefunctions for all the searched states are obtained by diagonalization.

An important point is the choice of the MOs since the results are dependent on them. An iterative improvement in the active orbitals (IDDCI)<sup>31</sup> has been proposed to avoid this difficulty. The DDCI wavefunction for each state,

$$\Psi_i = \sum_k c_{ki} \Phi_k \quad i = 1, n \quad [5]$$

gives the first order density matrix,  $R_i$ ,

$$R_i = \langle \Psi_i | \hat{R} | \Psi_i \rangle \quad [6]$$

and an average density matrix may be obtained:

$$\bar{R} = \sum_i R_i / n \quad [7]$$

which after diagonalization gives average natural orbitals (NOs) adapted to the different states. The procedure is iterated to self-consistency and gives energy differences independent of the starting MOs. The improvement of the active orbitals is shown by the weight of the CAS projection of the wavefunction that increases along the iterative procedure. Furthermore, the analysis of the NO occupation numbers gives a criterion on the quality of the CAS which may be

revised. The main advantage of the IDDCI procedure over other cheaper methods to obtain average orbitals, such as state average CASSCF calculations, is that it allows to mix states belonging to different irreducible representations without any difficulty.

The arguments that lead to the DDCI selected space are only strictly correct for vertical transitions, but the method may as well be applied to calculate adiabatic transitions. The contributions of the neglected double excitations to the correlation energy of each state vary with the geometry and their effect must be evaluated and added to the results of the DDCI calculations. In previous works we proposed that this correction should be estimated at the MP2 level: in substituted carbenes<sup>40</sup>, where there are significant differences between the geometries of the singlet and the triplet state, this correction contributes about 10% to the gap. When the perturbative estimation is not accurate enough, a previous good knowledge of the ground state potential energy surface is needed. This can either be obtained from independent accurate calculations or from experimental information. The transition(s) between the ground state and the excited state(s), calculated at the DDCI level for each geometry is (are) then added to the energy of the ground state. The controversial ground state of tetramethyleneethane<sup>41</sup> – triplet or singlet, depending on the experimental data origin – could be rationalized by this procedure. Very accurate potential energy curves for  $K_2$  excited states were as well calculated in this way<sup>34</sup>.

The ROHF molecular orbitals have been obtained by using the MOLCAS 4.1 package<sup>42</sup>. The CASDI<sup>43</sup> and the DDCI-SCIEL<sup>44</sup> programs have been used in the CI calculations and in the determination of the natural MOs.

### 3. COMPARISON WITH SOME FULL CI BENCHMARKS

The performance of DDCI has been quoted with the current state-of-the-art methods to calculate optical transitions, especially with Coupled Cluster methods such as EOM-CCSD<sup>45</sup>, including the effect of triple excitations such as CCSDT-3<sup>46</sup> and CC3<sup>47</sup> or the Self-Consistent Size-Consistent ( $SC^2$ ) CI method<sup>48</sup>. Full CI calculations on small systems as Be,  $CH^+$ , BH, and  $CH_2$ <sup>49,50,51</sup> have been used as benchmarks by several authors<sup>49,52,53,54,55,56</sup>. IDDCI has also been applied to these molecules<sup>57</sup> with the same basis sets and geometries. For Be<sup>50</sup>, sixteen states have been calculated, the lowest  $^1S$ ,  $^1P^0$  and  $^1D$  states, giving DDCI spaces with around 10000 determinants in all cases. For  $CH^+$ <sup>51</sup> the first excited  $^1\Sigma^+$ ,  $^1\Pi$  and  $^1\Delta$  states were calculated, with CI spaces including around 2000 determinants. For BH<sup>49</sup> three  $^1\Sigma^+$ , three  $^1\Pi$  and the first  $^1\Delta$  states were calculated. Finally, for  $CH_2$ <sup>49</sup> ten states of  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$  symmetries were calculated. For these two last

molecules, the CI spaces ranged from 8000 to 20000 determinants, depending on the symmetry.

Figure 2 summarizes the results on these series of calculations by representing the mean absolute deviations from FCI obtained by the different methods: Coupled Cluster Singles and Doubles, different levels of application of EOM treatment, such as EOM-CCSD or CCSDT-3, or the Linear Response (LR) approach, such as CC3. Results obtained with the size-consistent self-consistent SDCl technique, (SC)<sup>2</sup>SDCl, are also available. The general trend is that IDDCI results compare advantageously with the other methods. The mean absolute error is always lower than 0.1 eV: 0.008 eV for Be, 0.03 for BH, 0.05 for CH<sub>2</sub> and 0.09 for CH<sup>+</sup>. When comparing the results for this last molecule with the impressive quality of the MCLR<sup>51</sup> calculation, it should be pointed out that the latter includes more than 200000 determinants in the active space, *i.e.* 13% of the whole CI space, in front of the 0.2 % used in the IDDCI calculation.

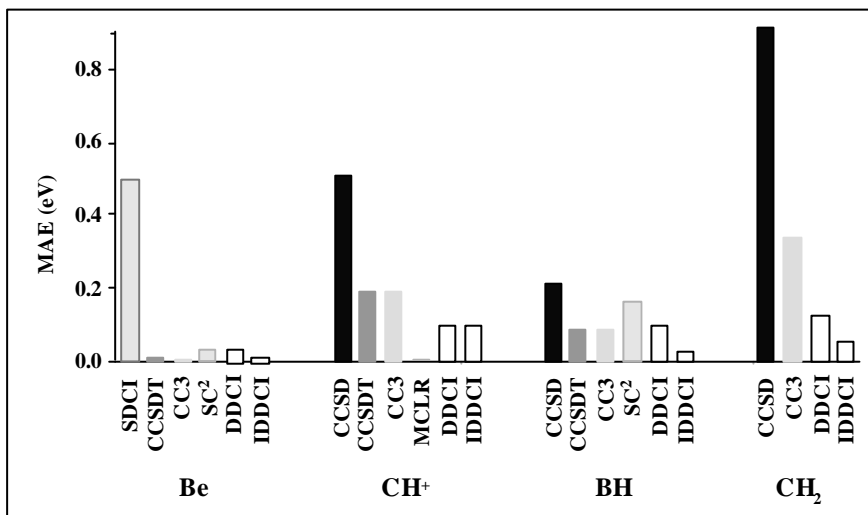


Figure 2. Mean absolute error with respect to FCI calculations

Another observation is that the error range of IDDCI transitions is quite similar for all the transitions of a given system. It is particularly relevant since transitions with a predominant biphotonic character are obtained with the same accuracy while single-reference methods give very large errors, even by including the effects of triples as CC3 or CCSDT-3.



## 4. THE VERTICAL SPECTRUM OF ETHYLENE

Several systems have been studied to test the capability of the DDCI method to reproduce the experimental spectra. In particular, the lowest vertical transitions of ethylene<sup>33</sup> have been calculated. A large Atomic Natural Orbitals (ANO) basis set has been used in this case for carbon and diffuse s and d functions centered on the C-C bond have been added to correctly describe the Rydberg character when necessary. The active space includes two electrons and three active orbitals (the  $\pi$ , the  $\pi^*$  and a Rydberg orbital of the appropriate symmetry) for all the states. The DDCI spaces include around 40000 determinants for all the symmetries. The results reported in Table 1 show that in general the agreement with the experiment is quite good, and that the performance is in general better than with CASPT2, which is nowadays accepted to give small errors for a large series of compounds. Among the results, the  ${}^1A_g \rightarrow {}^1B_{1u}$  transition deserves a special comment, since the  ${}^1B_{1u}$  state presents a strong mixing between a valence ionic  $\pi \rightarrow \pi^*$  and a Rydberg  $\pi \rightarrow 3d_\pi$  component. The variational character of DDCI allows the relaxation of the CAS contributions under the dynamic correlation effects and the transition is quite well reproduced, unlike the CASPT2 method which has an error of 0.4 eV for this transition.

Table 1. Vertical transitions (eV) in ethylene

Excited state	IDDCI	CASPT2 <sup>58</sup>	Experiment
$1^1B_{3u}$ (3s)	7.09	7.17	7.11 <sup>59,60,61,62</sup>
$1^1B_{1g}$ (3p $\sigma$ )	7.76	7.85	7.80 <sup>63,64</sup>
$1^1B_{2g}$ (3p $\sigma$ )	7.96	7.95	7.90 <sup>64</sup>
$1^1B_{1u}$ (V)	7.90	8.40	8.0 <sup>65, a)</sup>
$2^1A_g$ (3p $\pi$ )	8.33	8.40	8.28 <sup>64</sup>
$2^1B_{3u}$ (3d $\sigma$ )	8.59	8.66	8.62 <sup>59,60,61,66</sup>
$1^1A_u$ (3d $\pi$ )	9.12	8.94	
$1^1B_{2u}$ (3d $\delta$ )	9.10	9.18	9.05 <sup>59,66</sup>
$2^1B_{1u}$ (3d $\pi$ )	9.35	9.31	9.33 <sup>67,68</sup>
$1^3B_{1u}$ (V)	4.58	4.39	4.36 – 4.60 <sup>67,68</sup>
$1^3B_{3u}$ (3s)	6.95	7.05	6.98 <sup>60</sup>
$1^3B_{1g}$ (3p $\sigma$ )	7.83	7.80	7.79 <sup>60</sup>
$1^3B_{2g}$ (3p $\sigma$ )	7.92	7.90	
$2^3A_g$ (3p $\pi$ )	8.19	8.26	8.15 <sup>60</sup>
$2^3B_{3u}$ (3d $\sigma$ )	8.56	8.57	8.57 <sup>60</sup>
$1^3A_u$ (3d $\pi$ )	9.13	8.94	
$1^3B_{2u}$ (3d $\delta$ )	9.05	9.09	
$2^3B_{1u}$ (3d $\pi$ )	9.16	9.07	

<sup>a)</sup> from theoretical estimations

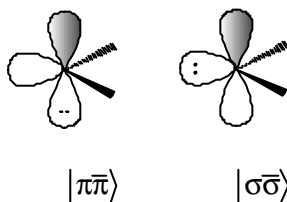
## 5. ADIABATIC TRANSITIONS

Adiabatic transitions can also be studied provided that the effects of the neglected purely inactive double excitations are taken into account. Several types of systems have been studied and in many cases it has been shown that it is enough to include the effect of double excitations at the second-order perturbation theory level to reach good energy separations. This is the case for first row atoms systems but not for systems with highly polarizable cores. An accurate description of the ground state is needed in this case.

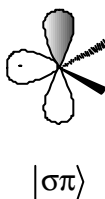
### 5.1. Singlet-triplet gap in substituted carbenes and silylenes

The first application was the calculation of the singlet-triplet gap in singly and doubly halogeno-substituted carbenes and silylenes<sup>40</sup>. In the unsubstituted molecules of this series,  $\text{CH}_2$  and  $\text{SiH}_2$ , the singlet state can be described at zero-order as a combination of the  $\sigma^2$  and the  $\pi^2$  configurations:

$$\Psi(1^1 A_1) = \lambda |[\text{core}] \sigma \bar{\sigma}\rangle - \mu |[\text{core}] \pi \bar{\pi}\rangle$$



and the triplet as the configuration  $\Psi(1^3 B_1) = |[\text{core}] \sigma \pi\rangle$



Therefore, the active space is generated by two orbitals and two electrons.

Large basis sets including two d and one f functions are needed at the carbenic center to obtain accurate values of the singlet-triplet gap. Since triplet bond angle is about 25-30° larger for all the molecules, the differential contribution of the inactive double excitations is included at the MP2 level. This correction ranges between 0.3 and 2.4 kcal mol<sup>-1</sup>. The zero point energy correction has also been added. Table 2 reports the results for this series, which are in an excellent agreement with the experimental ones, within the chemical precision. Only CH<sub>2</sub> has a triplet ground state and the degree of substitution tends to stabilize the singlet state. The values are quite comparable with the results of Goddard *et al.* obtained with DCCI, which includes a very similar part of the correlation. In view of this excellent agreement it may be predicted that trifluoromethylcarbene, CHCF<sub>3</sub>, with a calculated gap of 11.1 kcal mol<sup>-1</sup>, has a triplet ground state like CH<sub>2</sub>.

Table 2. Singlet-triplet gap (kcal mol<sup>-1</sup>) in carbenes and silylenes.

	DDCI	DCCI <sup>69,a)</sup>	MP4 <sup>70,a)</sup>	MRCI+Q <sup>71</sup>	LDA <sup>72</sup>	LDA/NL <sup>72</sup>	EXP
CH <sub>2</sub>	9.5	10.0	12.9	9.5	12.2	7.2	9.1 <sup>73</sup>
CF <sub>2</sub>	-56.3	-57.1	-57.6		-55.8	-55.6	-56.7 <sup>74</sup>
CCl <sub>2</sub>	-19.7	-20.5	-20.5		-21.9	-23.8	
CBr <sub>2</sub>	-15.6		-16.5		-20.9	-22.4	
CHF	-15.1	-14.7	-14.3				-14.6 <sup>75</sup>
CHCl	-5.8	-5.1	-4.8				>-11.4 <sup>75</sup>
CHBr	-5.3		-4.4				>-9 <sup>75</sup>
SiH <sub>2</sub>	-19.7	-21.5		-20.2			-21.0,-18.0 <sup>76</sup>
SiHF	-40.0	-41.3					
SiF <sub>2</sub>	-75.9	-76.6			-75.9	-76.3	-75.2, -77.2 <sup>77</sup>
CHCF <sub>3</sub>	11.1						

a) Zero point energy included

## 5.2. Systems with highly polarizable cores

In systems with highly polarizable cores the inter-shell correlation, namely the core-valence correlation, plays an important role in the description of the spectroscopy and of the dissociation energy. To treat these systems, large core basis sets including internal polarization functions and very large CI are to be used implying high computational costs and possible size-extensivity errors. Alternatively, effective core potentials (ECP) are also used, which try to simulate the effect of the static and dynamical polarization of the core by the valence electrons. ECP results are in general accurate but some empirical parameters and some cut-off radii are needed and the core-polarizability is assumed to remain constant, even with variable occupation of the valence orbitals in the different

states.

As a third possibility that avoids external parameters but has a relatively low computational cost, IDDCI has been applied to alkaline atoms, alkaline hydrides and  $K_2$ <sup>34</sup>. Large basis sets have been used in all cases and a relativistic small [Ar3d<sup>10</sup>] core pseudopotential has been used for Rb<sup>78</sup>. The active spaces depend on the symmetry and on the dissociation products. The largest DDCI space in all these calculations includes around 90000 determinants.

Ionization potentials, electron affinities and the lowest electronic transitions of K and Rb have been calculated. The largest error with respect to the experiment found in all these energies has been 0.08 eV. In the diatomic systems, the equilibrium distance is very different for different states and therefore the geometry relaxation has to be included in the calculation. Dissociation and adiabatic transition energies calculated at the IDDCI level without the contribution of the inactive double excitations are in general underestimated. However, when the effect of the inactive double excitations is included at the MP2 level, as shown in Table 3, all the spectroscopic constants are in very good agreement with the experimental ones, and in general closer to experiment than ECP ones. The largest error found for the equilibrium distances is 0.04 Å. The performance is particularly good for the energetic parameters, dissociation energies or adiabatic excitation energies, where the largest deviation is 0.05 eV.

Table 3. Spectroscopic constants for the ground and the lowest excited singlet states of KH and RbH. IDDCI: DDCI potential energy curve with iteratively optimized MOs including the MP2 contribution of inactive double excitations.  $R_e$ , equilibrium distance;  $D_e$ , dissociation energy;  $w_e$ , vibrational constant;  $T_e$ , adiabatic excitation energy.

		<b>X <sup>1</sup>S<sup>+</sup></b>			<b>A <sup>1</sup>S<sup>+</sup></b>		
		<b>IDDCI</b>	<b>ECP<sup>79</sup></b>	<b>Exp<sup>80</sup></b>	<b>IDDCI</b>	<b>ECP<sup>81</sup></b>	<b>Exp<sup>80</sup></b>
<b>KH</b>	$R_e$ (Å)	2.27	2.24	2.24	3.68	3.80	3.68
	$D_e$ (eV)	1.96	1.81	1.92	1.19	1.08	1.18
	$w_e$ (cm <sup>-1</sup> )	987	1022	984	246	288	228
	$T_e$ (eV)				2.37	2.16	2.36
<b>RbH</b>	$R_e$ (Å)	2.38	2.36	2.37	3.66		3.70
	$D_e$ (eV)	1.76	1.81	1.77	1.08		1.04
	$w_e$ (cm <sup>-1</sup> )	971	950	938	232		245
	$T_e$ (eV)				2.25		2.30

For  $K_2$ , dispersion effects that correspond to double excitations of core

electrons in both atoms do not belong to the DDCI space and this affects the shape of the potential energy curves. This fraction of the correlation energy of the core electrons cannot be isolated when symmetry-adapted MOs are used and the MP2 calculation of the excluded effects does not ensure sufficient precision in this case and gives up to 0.4 eV error in  $D_e$ . However, there is very precise experimental information about the  $1^1\Sigma_g^+$  ground state potential energy curve of  $K_2$ <sup>82</sup> and the potential curves of the excited states may be calculated by adding the vertical transition between the ground state and the excited states to each point of the experimental  $1^1\Sigma_g^+$  curve.

Table 4. Spectroscopic constants for some low excited states of  $K_2$ . IDDCI: IDDCI vertical energy difference to the  $1^1\Sigma_g^+$  ground state added to the experimental potential energy curve<sup>82</sup>.  $R_e$ , equilibrium distance;  $D_e$ , dissociation energy;  $T_e$ , adiabatic excitation energy;  $w_e$ , vibrational constant.

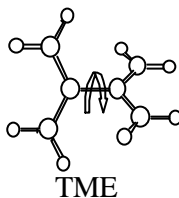
		$R_e$ (Å)	$D_e$ (eV)	$T_e$ (eV)	$w_e$ (cm <sup>-1</sup> )
$1^1S_u^+$	IDDCI	4.55	0.774	1.366	69.82
	CCSD <sup>86</sup>	4.57	0.760	1.318	72.28
	ECP <sup>83</sup>	4.53	0.781	1.365	70.42
	Exp <sup>84</sup>	4.55	0.785	1.377	70.55
$1^3S_u^+$	IDDCI	5.29	0.038	0.510	28.14
	CCSD <sup>86</sup>	5.29	0.011	0.520	28.65
	ECP <sup>83</sup>	5.73	0.029	0.503	20.81
	Exp <sup>85</sup>	5.77	0.032	0.520	21.63
$1^1P_u$	IDDCI	4.25	0.241	1.911	74.58
	CCSD <sup>86</sup>	4.30	0.131	1.948	73.54
	ECP <sup>83</sup>	4.24	0.234	1.912	74.05
	Exp <sup>82</sup>	4.24	0.223	1.906	74.89
$1^3P_u$	IDDCI	3.91	0.938	1.213	92.43
	CCSD <sup>86</sup>	3.91	0.928	1.150	91.82
	ECP <sup>83</sup>	3.88	0.928	1.218	94.80
	Exp <sup>84</sup>	3.88	0.933	1.229	91.54

As shown in Table 4, the results are in excellent agreement with experimental data, within 0.02 eV error range, and with accurate ECP calculations and of better quality than CCSD<sup>86</sup> calculations. The only exception is the

equilibrium distance for the  $1^3\Sigma_u^+$  state because of the very flat potential curve of this state, which gives a dissociation energy lower than 0.04 eV.

### 5.3. Tetramethyleneethane

The controversial ground state of the tetramethyleneethane (TME) biradical<sup>41</sup>, schematically represented below, can also be explained from the same type of calculation, by adding the vertical IDDCI energy differences to an accurate calculation of the ground state, at the CAS(2,2)\*SDCI level, including ACPF corrections. A triplet or a singlet ground state has been alternatively proposed as ground state, depending on the experimental source.



The torsion angle is different at the equilibrium geometries of both states ( $90^\circ$  for the singlet,  $45^\circ$  for the triplet). In our calculations, the singlet state is found more stable than the triplet one for any conformation, but only 0.3 kcal mol<sup>-1</sup> below the triplet state at the triplet minimum geometry. At this geometry, the singlet and triplet states can therefore be considered almost degenerate. The spin-orbit coupling of these states has been determined to be negligible by Michl<sup>87</sup>. If the mechanism of the reaction that produces the TME diradical leads to triplet products, the decay from the triplet to the singlet must be slow. Therefore, the triplet state can be populated and consequently experimentally observed. In any case, the S-T energy difference is tuned by the torsion coordinate, to the extent that the ground state can be modified when the TME is incorporated in a larger structure that constrains rotationally the diradical.

## 6. MAGNETIC SYSTEMS

### 6.1. General aspects

In transition metal polynuclear complexes where the metallic centers are bridged by large diamagnetic ligands, the weak interaction between the metallic

centers is dominated by the spin coupling between the unpaired electrons of the metal through the bridge ligand. This type of interaction may lead to high spin or low spin ground states, but in general the separation of the different spin multiplets is very small. The phenomenon is observed in molecular systems as well as in periodic solids such as cuprates. A lot of bridged metal binuclear compounds with a wide variety of bridging ligands have been described. Among the metals, Cu(II) is one of the most frequent and there is a large variety of bridges of different structural complexity, among which chloro<sup>88</sup>, azido<sup>89</sup>, oxo, hydroxo<sup>90</sup>, oxalato<sup>91</sup>, etc., are the most simple ones. In general, there is a strong relationship between the magnetic behaviour and the structural factors such as the metal coordination, the nature of the external ligands, the geometrical structure of the metal-bridge-metal unity, etc.

In the early 1970s successful qualitative interpretations<sup>92,93</sup> of the magneto-structural correlations were established for dimeric Cu(II) systems. In the 1980s, the first quantitative approaches to evaluate the exchange coupling constant also dealt with copper binuclear complexes. Among these methods, the second-order perturbative treatment by de Loth *et al.* for biradicals<sup>32</sup> gave reasonable agreement with experiment for a number of systems. Noodleman's broken symmetry approach<sup>94</sup> was also applied to a number of systems.

The coupling constant is 'experimentally' obtained by fitting the experimental data (magnetic susceptibility, EPR or other) to the microscopic expression of the observable. The spectrum needed in the partition function is obtained from the phenomenological Heisenberg Hamiltonian, which expression for a two center systems is:

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 \quad [8]$$

where  $\hat{S}_1$  and  $\hat{S}_2$  are the local spin operators and  $J$  is the exchange coupling constant. The energy difference between two states of  $S$  and  $S-1$  total spin is given by:

$$E(S-1) - E(S) = 2JS \quad [9]$$

In this formulation, a negative value of the coupling constant indicates antiferromagnetic coupling (low spin ground state), usually interpreted through Anderson's<sup>95</sup> superexchange mechanism. Other terms may be added to [8] to obtain better data fitting but only when the contribution of these additional terms becomes important, i.e., when the energy transitions significantly deviate from expression [9].

A consequence of the indirect extraction of  $J$  is that, although great precision is got in the experimental data, the final value depends on the model adopted to fit the data to and also of the quality of the fitting. This makes it difficult to precise its error range.

The theoretical estimation of  $J$  consists thus in evaluating the energy difference between states of different multiplicity. The magnetic interaction in diradicals such as Cu (II) ( $d^9$ ) binuclear complexes leads to two possible states, a triplet (T) and a singlet (S), and the separation is:

$$E_S - E_T = 2J \quad [10]$$

Parallely, for Ni (II) ( $d^8$ ) dimers, the triplet-quintet (Q) difference is given by:

$$E_T - E_Q = 4J \quad [11]$$

DDCI has been applied to a large number of magnetic systems, from the molecular as well as from the solid state fields. The magneto-structural dependence of the  $[L_3Cu(\mu-C_2O_4)CuL_3]^{2+}$  and  $[L_4Ni(\mu-C_2O_4)NiL_4]^{2+}$  complexes are among the recent applications.

## 6.2. Oxalato-bridged copper and nickel binuclear complexes

Oxalato-bridged Cu(II) binuclear complexes constitute a very rich family since there is a wide variety of compounds with different external ligands<sup>91,96,97,98,99,100</sup>. Most frequently, copper is pentacoordinated<sup>96-100</sup>, in complexes with  $[(L_3)_2(\mu-C_2O_4)Cu_2]^{2+}$  generic formula where  $L_3$  stands for external ligands, from three monodentate to a single tridentate ligand, usually coordinated by nitrogen or oxygen centers. In parallel with the volume of experimental information, theoreticians have also paid attention to the  $\mu$ -oxalato Cu(II) binuclear complexes applying different levels of theory and rationalizing the magneto-structural dependence.<sup>92,101,102,103</sup>

Pentacoordination is compatible with a large flexibility of the geometry of the coordinated copper cation. All the structures found are intermediate between three limit structures, represented in Figure 3. Different types of interaction are found between the oxalato bridge and the metal centers. The NNOO structure, Fig. 3a), is a square basis pyramid with two oxygen atoms of the ligand coordinated to the metal; in the TBP trigonal bipyramid structure, Fig. 3b), and the NNNO square basis pyramid, Fig. 3c), only one oxygen atom is coordinated to the metal. The  $\alpha$  angle allows to summarize the structural differences in a single parameter.



Several complexes with saturated N-coordinated ligands have been crystallographically and magnetically characterized<sup>96-99</sup>. It is accepted that the external ligands play a limited role in the magnitude of the coupling, provided that the electronegativity of the ligand and the type of coordination are preserved. Because of the large size of the external ligands, the DDCI calculations have been performed<sup>36</sup> on a model in which all the nitrogen coordinated ligands are substituted by  $\text{NH}_3$  groups,  $[(\text{NH}_3)_6(\mu\text{-C}_2\text{O}_4)\text{Cu}_2]^{2+}$ , and the remaining crystallographic parameters are used. Several centrosymmetric experimental structures have been considered, and the three limit geometries, represented in Figure 3, have been added since they have been discussed previously<sup>102,104</sup> in the analysis of the magnetic trends of this family.

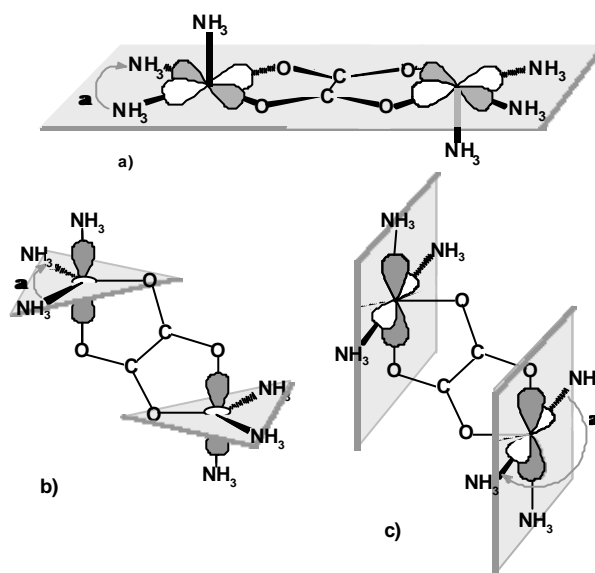


Figure 3. Schematic representation of  $[(\text{NH}_3)_6(\mu\text{-C}_2\text{O}_4)\text{Cu}_2]^{2+}$  structure, in the three limit structures: a) square basis pyramid, NNOO; b) trigonal bipyramid, TBP; c) square basis pyramid NNNO.

The basis set includes 2d and 1f functions for the metal, DZP basis set for the oxalato ligand and DZ basis set for the external ligands. The active space is generated by two electron and two active orbitals, the symmetry combinations of the magnetic orbitals.

Table 5 reports the DDCI results obtained for this family. The NNOO coordination, with  $\alpha = 90^\circ$ , presents the strongest antiferromagnetic coupling and the NNNO coordination, with  $\alpha = 180^\circ$  the weakest one. For the experimental structures, the coupling constant has intermediate values, according to  $\alpha$ . This trend has been justified in previous rationalizations based on one electron arguments<sup>102,104</sup>, such as the overlap between the oxygen pair orbitals and the metal magnetic d orbitals, as shown in Figure 3.

Table 5. Structural dependence of the magnetic exchange coupling constant,  $J$  ( $\text{cm}^{-1}$ ), in  $[(L_3)_2(\mathbf{m}\text{-C}_2\text{O}_4)\text{Cu}_2]^{2+}$  complexes. For the definition of  $\mathbf{a}$ , see Figure 3. DDCI calculations performed on the  $[(\text{NH}_3)_6(\mathbf{m}\text{-C}_2\text{O}_4)\text{Cu}_2]^{2+}$  model.

Structure	$\mathbf{a} (^\circ)$	$J_{\text{DDCI}}$	$J_{\text{B3LYP}}$	$J_{\text{exp}}$
NNOO	90	-139		
TBP	120	-72		
NNNO	180	-2		
$[(\text{Et}_5\text{dien})_2(\mu\text{-C}_2\text{O}_4)\text{Cu}_2](\text{BPh}_4)_2^{\text{a}}$	130	-38	-81 <sup>103, b)</sup>	-37 <sup>96,98</sup>
$[(\text{Et}_5\text{dien})_2(\mu\text{-C}_2\text{O}_4)\text{Cu}_2](\text{PF}_6)_2^{\text{a}}$	153	-13		-10 <sup>96,98</sup>
$[(\text{tmen}, 2\text{-MeIm})_2(\mu\text{-C}_2\text{O}_4)\text{Cu}_2](\text{PF}_6)_2^{\text{a}}$	153	-7		-7 <sup>99</sup>
$[(\text{dien})_2(\mu\text{-C}_2\text{O}_4)\text{Cu}_2](\text{ClO}_4)_2^{\text{a}}$	160	-2		< -1 <sup>97</sup>

<sup>a)</sup> dien = diethylenetriamine, Et<sub>5</sub>dien = 1,1,4,7,7-pentaethyldiethylenetriamine, tmen = N,N,N',N'-tetramethylethylenediamine, 2-MeIm = 2-methylimidazole

<sup>b)</sup> Calculated with Noodleman's<sup>94</sup> unrestricted broken symmetry method, with  $J = E_{\text{BS}} - E_{\text{T}}$ , where BS stands for the broken-symmetry state.

DFT calculations have also been performed<sup>103</sup> on a series of complexes of the same family, with the B3LYP<sup>105</sup> functional and the Noodleman's expression. When taking into account that the broken symmetry state is approximately midway between the true singlet and the triplet states, B3LYP overestimates  $J$  by a factor of 2. Although the trends are in agreement with the experimental ones, it is a general fact that DFT methods tend to overestimate the antiferromagnetic coupling because of the tendency of these methods to overestimate delocalization effects. This trend is related to a strong delocalization of the spin density, as demonstrated from the comparison with FCI on models<sup>106</sup>. Polarized neutron diffraction experiments on oxamato and oxamido bridged Mn(II)-Cu(II) compounds<sup>107</sup> have given evidence that DFT predicts too low spin densities on the metal.

The role of the external ligands is a matter of discussion. From one-electron considerations<sup>108</sup> and DFT calculations<sup>103</sup>, it has been argued that an

increase of the  $\sigma$  donor character of the ligands gives rise to a stronger antiferromagnetic character. The apical nitrogen coordinated group can be substituted by  $\text{H}_2\text{O}$  in near NNOO coordination structures in  $[(\text{L}_2, \text{H}_2\text{O})_2(\mu\text{-C}_2\text{O}_4)\text{Cu}_2]^{2+}$  complexes<sup>99,109</sup>. Since it is not possible to find equivalent structures with only a different apical ligand and, as shown previously, the magnetic coupling is extremely sensible to small geometrical differences, DDCI calculations have been performed on the NNOO model (see Figure 3) with a  $\text{H}_2\text{O}$  ligand in the apical position. From the above discussion, a weaker antiferromagnetic coupling was expected for the  $[(\text{NH}_3)_4(\text{H}_2\text{O})_2(\mu\text{-C}_2\text{O}_4)\text{Cu}_2]^{2+}$  complex since  $\text{H}_2\text{O}$  is a more electronegative ligand. However, the DDCI coupling constant,  $J = -141 \text{ cm}^{-1}$ , does not confirm this hypothesis, and shows that one electron arguments, although often very useful, have to be used prudently in problems with complex correlation mechanisms.

Two structures corresponding to crystallographically<sup>99,109</sup> characterized complexes were as well calculated. The influence of the pyramidalization of the complex in the coupling, schematized in Figure 4 is shown in Table 6.

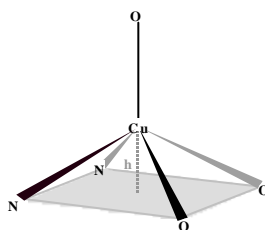


Figure 4. Schematic representation of the pyramidalization distortion in the  $[(\text{NH}_3)_4(\text{H}_2\text{O})_2(\mu\text{-C}_2\text{O}_4)\text{Cu}_2]^{2+}$  model

The first result reported in the table is in a reasonable agreement with the experimental value. As shown by the precedent results with nitrogen coordinated external ligands, distortions from the square basis NNOO coordination tend to give weaker antiferromagnetic coupling, which is in agreement with the trend shown in this case. The B3LYP results is overestimated as previously discussed.

The Ni(II) homologues have less versatile structures because of the almost octahedral coordination of the metal. Two hexacoordinated complexes have also been calculated, on the  $[(\text{NH}_3)_8(\mu\text{-C}_2\text{O}_4)\text{Ni}_2]^{2+}$  and  $[(\text{NH}_3)_6(\text{H}_2\text{O})_2(\mu\text{-C}_2\text{O}_4)\text{Ni}_2]^{2+}$  models, following experimental structures<sup>108,110</sup>. The DDCI active space is generated by the magnetic orbitals, *i.e.* by four electrons in four orbitals. Table 7 shows that the results are of the same quality as for copper complexes.

Table 6. Influence of pyramidalization on the magnetic exchange coupling constant,  $J$  ( $\text{cm}^{-1}$ ), in  $[(L_2, H_2O)_2(\mathbf{m}\text{-C}_2\text{O}_4)\text{Cu}_2]^{2+}$  complexes. For the definition of  $h$ , see Figure 4. DDCI calculations performed on the  $[(\text{NH}_3)_4(\text{H}_2\text{O})_2(\mathbf{m}\text{-C}_2\text{O}_4)\text{Cu}_2]^{2+}$  model.

Structure	$h$ (Å)	$J_{\text{DDCI}}$	$J_{\text{B3LYP}}$	$J_{\text{exp}}$
$[(\text{tmen}, \text{H}_2\text{O})_2(\mu\text{-C}_2\text{O}_4)\text{Cu}_2](\text{ClO}_4)_2^{\text{a)}}$	0.182	-163	-338 <sup>103, b)</sup>	-193 <sup>99</sup>
$[(\text{tmen}, \text{H}_2\text{O})_2(\mu\text{-C}_2\text{O}_4)\text{Cu}_2](\text{PF}_6)_2^{109, \text{a)}}$	0.208	-143		

<sup>a)</sup> tmen = N,N,N',N'-tetramethylethylenediamine

<sup>b)</sup> Calculated with Noodleman's<sup>94</sup> unrestricted broken symmetry method, with  $J = E_{\text{BS}} - E_{\text{T}}$ , where BS stands for the broken-symmetry state.

Table 7. Exchange coupling constant,  $J$  ( $\text{cm}^{-1}$ ), in  $[(L_3, H_2O)_2(\mathbf{m}\text{-C}_2\text{O}_4)\text{Ni}_2]^{2+}$  complexes. DDCI calculations performed on the  $[(\text{NH}_3)_8(\mathbf{m}\text{-C}_2\text{O}_4)\text{Ni}_2]^{2+}$  and the  $[(\text{NH}_3)_6(\text{H}_2\text{O})_2(\mathbf{m}\text{-C}_2\text{O}_4)\text{Ni}_2]^{2+}$  models.

Structure	$J_{\text{DDCI}}$	$J_{\text{exp}}$
$[(\text{Me}_2\text{ciclen})_2(\mu\text{-C}_2\text{O}_4)\text{Ni}_2](\text{ClO}_4)_2$	-11	-17 <sup>110</sup>
$[(\text{dien}_2, \text{H}_2\text{O})_2(\mu\text{-C}_2\text{O}_4)\text{Ni}_2]\text{Cl}_2^{\text{a)}}$	-10	-14 <sup>108</sup>

<sup>a)</sup> Me<sub>2</sub>ciclen = 1,7-dimethyl-1,4,7,10-tetraazacyclododecane, dien = diethylenetriamine

Many other magnetic systems have been calculated with DDCI. Particularly interesting results have been obtained by F. Illas *et al.*<sup>111,112,113,114,115</sup> in ionic solids. Since magnetic coupling is a local phenomenon<sup>116,117</sup>, solids can be treated with the same level of complexity as molecules by using cluster models, where the Madelung field of the periodic lattice is conveniently simulated. The agreement with experiment follows the same trend of accuracy as presented here.

## 7. CONCLUSIONS AND PERSPECTIVES

As illustrated by the preceding applications, many types of energy differences can be calculated with DDCI within the highest level of accuracy obtained at present by quantum chemistry methods that include high level treatments of correlation. The basic feature of the method consists in including in a variational CI only the part of the correlation energy that contributes to the energy difference from a second-order perturbative analysis. Optical vertical and adiabatic transitions, singlet-triplet gaps and exchange magnetic coupling constants are obtained with small deviations from experiment. It gives the possibility of using the method to predict with reliability the behaviour of new systems. In particular,

magnetic interactions and charge transfer in new materials offer a large field of applications. Examples of the predictive capacity have been given recently<sup>113,114</sup>.

Many systems of technological interest have a complex structure and need very large computation requirements. The active spaces increase very quickly with the number of active electrons and the dimension of the CI space becomes unmanageable. Although techniques as Dedicated MOs<sup>118</sup> have been proven to be efficient to truncate the MO set, many systems go beyond the present possibilities. Different strategies may be explored. One possibility is the selection of the most relevant configurations of the CAS. This largely reduces the multireference model spaces and consequently the total space. Another way is to combine variational and perturbative methods in the DDCI scheme through effective Hamiltonian techniques. These strategies do not rule out each other. Work is in progress in both directions.

Finally, although size extensivity error is much smaller than in methods including a larger part of the correlation energy, it may become significant when a large number of active electrons are correlated and size-consistency corrections can probably become very important. The development of new multireference size-extensive corrections is another important goal to obtain accurate results in electronically complex systems.

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