

# Application of the iterative difference-dedicated configuration interaction method to the determination of excitation energies in some benchmark systems: Be, CH<sup>+</sup>, BH and CH<sub>2</sub>

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**Abstract.** The iterative difference-dedicated CI method (IDDCI) has been applied to determine excitation energies in small systems for which benchmark FCI and other high-level calculations exist. Transitions to excited singlet and triplet states in Be and vertical transitions in CH<sup>+</sup>, BH and CH<sub>2</sub> are reported. The deviations from FCI results are lower than 0.1 eV and compare advantageously with SDCI including size-consistency corrections, (SC)<sup>2</sup>SDCI, and with coupled cluster calculations including the effect of triples, especially for the states which have a predominant double excitation character. The IDDCI procedure has been speeded up by using smaller subspaces for optimizing the molecular orbitals.

**Key words:** Transitions in atomic Be – Vertical transitions in BH, CH<sup>+</sup>, CH<sub>2</sub> – Benchmark calculations – Difference dedicated CI – Orbital improvement

## 1 Introduction

There are various methods available nowadays for determining the molecular properties of the ground state, all of which give results which are very close to the FCI ones. Among them, several coupled cluster methods (CC), which include the effect of triples, have been described [1–4]. Results of similar quality may also be obtained by dressing the singles and doubles CI (SDCI) matrix with corrections that enable size-consistency to be restored by means of the (SC)<sup>2</sup> technique [5, 6]. However, the accurate treatment of excited states is a more difficult problem. Both types of procedures have been extended to calculate excitation energies. Of the CC procedures, the CCSDT level for the reference state has led to different accurate approximations in the equation of motion (EOM) treatment [7–9], such as CCSDT-3 and CCSD( $\bar{T}$ ) [9], or in the linear response (LR) approach, such as CC3 [10]. In the (SC)<sup>2</sup> framework,

recent works [11, 12] have proved that excitation energies can be determined from the higher roots obtained from diagonalizing the dressed SDCI or MR-SDCI matrix built for the ground state. The results of both types of calculations are in general very good, although some discrepancies appear. This is the case in the above-mentioned CC3 or CCSD( $\bar{T}$ ) methods, which render excellent agreement with FCI results when the excited state is dominated by a single excitation, but a considerable error when the excited state has a large double excitation character. The (SC)<sup>2</sup> method applied to a single reference SDCI, (SC)<sup>2</sup>SDCI, or to a small multireference CI, (SC)<sup>2</sup>MRCI, overcomes most of this problem but the results are dependent on the orbitals used in the calculation.

Among the multireference methods, widely used methods such as CASPT2 [13] give very good results for a large number of systems [14–18]. However, in spite of this general high quality, significant errors may appear in some particular cases, when there is a non-negligible mixture between states of different character, e.g. valence and Rydberg, in other words, when the reference and the outer space are not sharply separated. The contracted character of the method does not allow the external correlation to modify the coefficients of the complete active space (CAS) since it does not contribute in first-order perturbation theory.

In order to solve these problems, we have described the difference-dedicated configuration interaction method (DDCI) [19], which consists of a CI built only with a small reference space and in the subspace of the singles and the doubles which contribute to the energy difference on the grounds of second-order perturbation considerations, i.e. the CASSDCI subspace defined by that CAS, all singles, and the doubles which involve at least one active orbital. The most important feature of the method is that the role of the dynamic correlation on the CAS is explicitly considered in the variational calculation. An iterative version of the method, IDDCI [20], has recently been proposed that allows the results to be independent of the starting molecular orbitals (MOs), since they are iteratively optimized. The results obtained up to now have been excellent, but because of the

iterative procedure for obtaining the MOs, it may be objected that the successive diagonalizations make the method expensive. This problem has been recently solved, since the MOs can be optimized with just a small subspace of the complete DDCI space. In this paper, we present the results obtained using this procedure on some FCI benchmarks such as Be,  $\text{CH}^+$ , BH and  $\text{CH}_2$  for which results with CCSD [21], CCSDT-3 [9], CC3 [10, 22, 23] or  $(\text{SC})^2$  [11] also exist, so the performance of the different methods can be compared. After a brief reminder of the IDDCI method, the transitions to different excited singlet and triplet states of these systems are presented.

## 2 Method

### 2.1 Selection of the differential space

In previous papers [19, 20, 24, 25], we proposed a specific configuration interaction for the direct evaluation of energy differences, the DDCI method. This method is based on a zero-order description of the transitions given by a small CAS, with  $n$  electrons (two in most cases) and  $m$  active orbitals, which include valence occupied and unoccupied as well as Rydberg orbitals to describe the diffuse states or states of a valence-Rydberg mixed character when necessary.

Once the model space has been defined by the CAS, an effective Hamiltonian can be built from a second-order expansion in the framework of the quasi-degenerate perturbation theory, (QDPT [26]). At this level, it is easy to demonstrate [19] that the double excitations from two inactive occupied MOs,  $p$  and  $q$ , to two unoccupied MOs,  $i$  and  $j$ ,  $pq \rightarrow ij$ , do not contribute to the off-diagonal elements of the effective Hamiltonian and, since the effect of these determinants is to shift the same value over all diagonal elements, these excitations are not relevant to the evaluation of excitation energies. This information gives a criterion for building a selected CI space, the DDCI space, which includes all the single and double excitations with at least one active MO. This space is treated variationally so the intruder state problem is avoided and the weight of the CAS determinants in the wave function is modified by the effect of the dynamic correlation.

The main characteristics of the DDCI method may be summarized in four points:

1. DDCI is a variational method.
2. It is an uncontracted method, which may be crucial if excited states are to be accurately described, since the external correlation may substantially modify the coefficients of the CAS since it is included at infinite order.
3. The DDCI matrix is invariant under rotation of the MOs in the doubly occupied or virtual subsets.
4. By avoiding the most numerous double excitations, those implying two inactive double occupied and two inactive virtual orbitals,  $pq \rightarrow ij$ , the size of the DDCI space [19] increases only with the third power of the basis set dimension,  $N^3$ , where  $N$  is the number

of orbitals, while the MR\*SDCI space increases with  $N^4$ . This last feature and the fact that the CAS taken as model space is quite small makes DDCI especially advantageous when compared with other CI methods. On the other hand, the comparison with the CC3 iterative procedure is even more favourable, since its computation time scales as  $N^7$ , while the SDCI scales as  $N^6$ . On top of this, for CC3 and related methods, the cost of the iterations must be added. On the other hand, the  $(\text{SC})^2\text{SDCI}$  method scales as  $N^6$ , but needs iterative diagonalizations to reach self-consistency.

### 2.2 Choice of the molecular orbitals

The main problem of DDCI, as well as other truncated CI procedures, is the fact that the results depend on the choice of the starting molecular orbitals. In general, the canonical orbitals are a good choice for describing valence states [24], but poor results are obtained if diffuse Rydberg states are to be calculated. In order to avoid this lack of accuracy an iterative improvement in the active orbitals has recently been proposed [20].

Let us suppose that we are interested in the energy gap between the ground state and several excited states. An initial DDCI calculation gives the DDCI wave function for the  $n$  lowest states. From here the associated one-particle density matrices can be calculated for each state in the initial basis set of MOs. We can now define a new density matrix  $\mathbf{R}$  as the average of the density matrices of all these states. By diagonalizing this average density matrix, a new set of MOs is obtained. Their occupation numbers give useful information for classifying the MOs in the three sub-sets, inactive doubly occupied, virtual and active MOs. Thus, when the occupation number is close to two the MO is an inactive core orbital, and when close to zero, a virtual orbital. Intermediate occupations correspond to active orbitals. The new set of MOs is used to perform a new DDCI, and the procedure is iterated until the self-consistency of the wavefunctions and energies of the different states is attained. This iterative procedure for improving the MOs is expected to increase the projection on the CAS of the DDCI eigenvectors.

The main problem of this iterative procedure, which we have called IDDCI, is the high computational cost for large DDCI spaces, since the molecular integrals must be calculated, the DDCI matrix diagonalized and the density matrix built for each state at each iteration, typically four times before the self-consistency is reached. To avoid this inconvenience, the whole iterative procedure may be shortened using a smaller subspace of DDCI. Since only the single excitations are directly coupled to the determinants of the CAS through the single particle density operator,  $\mathbf{R}$ :

$$\langle \Phi_1 | \mathbf{R} | \Phi_\alpha \rangle = 0, \quad \text{if } |\Phi_1\rangle \in \text{CAS}, \text{ and } |\Phi_\alpha\rangle = \mathbf{D}^+_\alpha |\Phi_1\rangle;$$

where  $\mathbf{D}^+_\alpha$  is a double excitation operator, a very fast iterative procedure may be performed using only the determinants obtained by single excitations over the CAS, the CAS\*S space, in such a way that the space

remains very small. Once the self-consistency has been reached and a new set of orbitals specially adapted to the calculation of the excitation energy has been obtained, only one diagonalization is performed with the whole DDCI space. Up to now, the orbitals obtained with this procedure are very close to those obtained with the initially described IDDCI procedure [20], which used the whole DDCI space throughout the procedure.

The above procedure is not the only way of obtaining mean natural orbitals: state-averaged CASSCF calculations can also provide active orbitals well suited for determining electronic transitions. Some tests on the benchmark systems presented in the next section have proved a similar efficiency when different states of the same symmetry are considered. However, the advantage of the IDDCI procedure is that it allows us without any difficulty to mix states belonging to different irreducible representations.

### 3 Results

The IDDCI method was applied to different benchmark systems: Be, CH<sup>+</sup>, BH and CH<sub>2</sub>, for which FCI [23, 27, 28], EOM-CCSD [21], CC3 [10, 22, 23], CCSDT-3, CCSD( $\bar{T}$ ) [9] or (SC)<sup>2</sup> [11] results exist. All the calculations start with the choice of the initial orbitals and of a small CAS. The orbitals are optimized through the IDDCI procedure, which also gives information about the quality of the CAS at each step. The excitation energies are calculated as the difference between the roots of the DDCI space once the self-consistency of the orbitals is reached.

#### 3.1 Be electronic transitions

The lowest singlet and triplet states, <sup>1,3</sup>S, <sup>1,3</sup>P<sup>0</sup> and <sup>1,3</sup>D of the beryllium atom were calculated using a (15*s*9*p*5*d*/9*s*9*p*5*d*) basis set of which FCI results [27] are available.

To describe these states, we define different CAS, all of which have two electrons and six active orbitals. The 2*s* and 2*p* valence orbitals belong in all cases to the active space, the 2*p* orbitals being included to describe the important 2*s*<sup>2</sup>→2*p*<sup>2</sup> polarization effect in the ground state. Two orbitals are added to describe the excited states: 3*s* and 4*s* for the <sup>1,3</sup>S states, 3*p*<sub>z</sub> and 4*p*<sub>z</sub> for the <sup>1,3</sup>P<sup>0</sup> states and 3*d*<sub>z</sub> and 4*d*<sub>z</sub> for the <sup>1,3</sup>D states.

The calculation was started with the orbitals of the Be<sup>2+</sup> dication, which concentrate the diffuse functions and therefore reproduce the excited states better. Table 1 shows the dimension of the CAS, CAS\*S and DDCI spaces for each irreducible representation, and it can be seen that the dimension of the single excitation subspace (CAS\*S) used in the iterative procedure is only 10% of the complete DDCI subspace

Table 2 shows the deviations from the FCI calculations when determining the excitation energies to several excited singlet and triplet states. Although the results obtained with the orbitals of the dication are generally good (DDCI column in the table), their quality is not homogeneous even for the same symmetry, as shown, for instance, by the <sup>3</sup>D states: the deviations from the FCI transitions go from −0.016 eV for the <sup>1</sup><sup>3</sup>D to 0.091 eV for the <sup>2</sup><sup>3</sup>D. It may also be verified that the results depend on the type of MOs used in the

**Table 1.** The difference-dedicated CI (DDCI) space dimension for Be

Transition	Symmetry	CAS	CAS*S	DDCI
X <sup>1</sup> S → <sup>1,3</sup> S				
	S	12	1158	11037
X <sup>1</sup> S → <sup>1,3</sup> P <sup>0</sup>				
	S	12	1066	10261
	P	6	1010	10420
X <sup>1</sup> S → <sup>1,3</sup> D				
	S	8	886	9713
	D	6	942	9546

**Table 2.** Be excitation energies to singlet and triplet states. FCI results and deviations from FCI, in eV (MAE, mean absolute error)

State	EOMCCSD <sup>a</sup>	CCSDT-3 <sup>b</sup>	CC3 <sup>c</sup>	SDCI <sup>d</sup>	(SC) <sup>2</sup> CI <sup>d</sup>	DDCI <sup>e</sup>	IDDCI <sup>e</sup>	FCI <sup>f</sup>
Singlet								
1 <sup>1</sup> P <sup>0</sup>		0.001	0.000	0.668	0.011	−0.010	0.003	5.318
1 <sup>1</sup> S		0.002	0.001	0.615	0.015	0.000	−0.005	6.765
1 <sup>1</sup> D		0.008	0.012	0.621	0.046	−0.006	0.003	7.089
2 <sup>1</sup> P <sup>0</sup>		0.001	0.000	0.632	0.016	−0.012	−0.005	7.462
2 <sup>1</sup> D		0.003	0.004	0.616	0.027	−0.008	−0.008	8.034
2 <sup>1</sup> S		0.002	0.001	0.621	0.016	0.077	−0.006	8.076
3 <sup>1</sup> P <sup>0</sup>		0.001	0.001	0.286	0.018	0.076	−0.007	8.302
3 <sup>1</sup> D		0.002	0.002			0.088	−0.010	8.536
MAE		0.003	0.003	0.580	0.021	0.035	0.006	
Triplet								
1 <sup>3</sup> P <sup>0</sup>	−0.004			0.652	−0.007	−0.012	−0.006	2.733
1 <sup>3</sup> S	0.003			0.612	0.006	−0.003	−0.005	6.444
2 <sup>3</sup> P <sup>0</sup>	0.006			0.647	0.018	−0.018	−0.009	7.295
1 <sup>3</sup> D	0.007			0.315	0.015	−0.016	−0.010	7.741
2 <sup>3</sup> S	0.006			0.619	0.013	0.051	−0.007	7.985
3 <sup>3</sup> P <sup>0</sup>	0.006			0.090	0.018	0.067	−0.010	8.272
2 <sup>3</sup> D	0.007			0.116	0.015	0.091	−0.011	8.449
MAE	0.006			0.436	0.013	0.037	0.008	

<sup>a</sup> Ref. [21]

<sup>b</sup> Ref. [9]

<sup>c</sup> Ref. [22]

<sup>d</sup> Ref. [11]

<sup>e</sup> This work

<sup>f</sup> Ref. [27]

calculation. The iterative improvement in the MOs avoids both difficulties. In this case the mean error on the transitions decreases from 0.037 eV in the first iteration to 0.008 eV at the convergence of the procedure and the error range gets much narrower since it does not exceed 0.011 eV.

Table 2 also shows the results obtained with other high-level calculations for excited states, such as EOM-CCSD [21], CCSDT-3 [9], CC3 [22] or SDCI with and without size-consistency corrections [11]. The values obtained with the IDDCI iterative procedure compare advantageously with the SDCI type methods, since IDDCI gives a smaller mean deviation from the FCI results: 0.006 eV for the singlets and 0.008 eV for the triplets, compared with 0.021 and 0.013 eV for the (SC)<sup>2</sup>SDCI method, which is a clear improvement on the crude SDCI results. Although slightly higher, the singlet states mean error compares well with the equation of motion CCSDT-3 and linear response CC3 mean deviation of 0.003 eV. The same can be said for the triplets, where the available EOM-CCSD calculations give a mean error of 0.006 eV.

As previously discussed, the main advantage of the IDDCI method is the size of the CI space and its scaling with the basis set dimension. For Be, the FCI spaces for singlet excited states are formed by around 400 000 determinants, while as shown in Table 1 the IDDCI spaces contain less than 3% of this number. In spite of this, errors are always lower than 0.01 eV. The (SC)<sup>2</sup>CI shows good results with only 2877 determinants, since this particular case has very high symmetry and the calculation is performed with a single reference SDCI.

All the excited states presented in this section are dominated by single replacement excitations relative to the reference state. In order to check the response of our method when describing states which are dominated by double replacement excitations, calculations were performed on CH<sup>+</sup>, BH and CH<sub>2</sub>.

### 3.2 CH<sup>+</sup>

Calculations were carried out on the lowest valence states of CH<sup>+</sup> using a (10s6p1d/5s3p1d) basis set for carbon and a (5s1p/3s1p) for hydrogen set [28]. The internuclear distance was fixed at 2.13713 a.u. The active space includes two electrons and a variable number of active orbitals, depending on the symmetry of the excited

state. For the states of  $\Sigma^+$  and  $\Delta$  symmetry, three active orbitals are necessary, one  $\sigma^+$  and two  $\pi$  orbitals. For the state of  $\Pi$  symmetry, one  $\sigma^+$  and one  $\pi$  orbital are needed. Canonical orbitals were used to start the iterative procedure.

Table 3 shows the dimensions of the spaces used to calculate the excitation energies. The dimensions must then be compared with that of the FCI space, formed by 1 729 600 determinants. Table 4 shows the results obtained with our procedure as well as with other methods. When they are compared with FCI data [28], the poorest results are given by the CCSD calculations [10] (mean error 0.505 eV) which include a complete treatment of single and double excitations. When the effect of the triples is included in an approximate way in the CC3 method [10], the results are systematically improved although the mean error, of 0.187 eV, is still important. The reason is that these methods do not calculate all the transitions with the same accuracy. For the excitation to the <sup>1</sup> $\Pi$  state, which is dominated by a single replacement configuration, the mean errors are 0.031 eV for CCSD, 0.014 eV for CCSDT-3 [9] and 0.012 eV for CC3, while the errors for the excitations dominated by a double replacement configuration (<sup>1</sup> $\Sigma^+$  and <sup>1</sup> $\Delta$  transitions) are much larger, of several tenths of eV. For the DDCI and IDDCI calculations the mean error is 0.1 eV and of the same order for every transition.

MCLR [28] results are also shown in Table 4. Although their quality is impressive, it should be pointed out that they were obtained using a very large MCSCF reference state, 9 $\sigma$  4 $\pi$  and 1 $\delta$  active MOs, with 235 633 determinants in the active space. This is 13% of the FCI space, a big percentage when compared with the 0.2% used in the DDCI calculation. In fact, when MCLR uses a number of determinants as DDCI, the error reaches 0.3 eV.

**Table 3.** DDCI space dimension for CH<sup>+</sup>

Transition	Symmetry	CAS	CAS*S	DDCI
X <sup>1</sup> $\Sigma^+ \rightarrow$ <sup>1</sup> $\Sigma^+$				
X <sup>1</sup> $\Sigma^+ \rightarrow$ <sup>1</sup> $\Pi$	$\Sigma$	3	289	2903
	$\Pi$	2	172	2013
X <sup>1</sup> $\Sigma^+ \rightarrow$ <sup>1</sup> $\Delta$	$\Pi$	2	200	1972
	$\Sigma$	3	289	2903
	$\Delta$	2	272	2344

**Table 4.** CH<sup>+</sup> excitation energies to singlet states. FCI results and deviations from FCI, in eV (MAE, mean absolute error)

State	CCSD <sup>a</sup>	CCSDT-3 <sup>b</sup>	CC3 <sup>a</sup>	MCLR <sup>c</sup>	DDCI <sup>d</sup>	IDDCI <sup>d</sup>	FCI <sup>c</sup>
<sup>1</sup> $\Sigma^+$	0.560	0.233	0.230	0.012	-0.144	-0.134	8.549
<sup>1</sup> $\Pi$	0.031	0.014	0.012	0.000	0.076	0.086	3.230
<sup>1</sup> $\Delta$	0.924	0.315	0.318	0.003	-0.055	-0.068	6.964
MAE	0.505	0.187	0.187	0.005	0.092	0.096	

<sup>a</sup> Ref. [10]

<sup>b</sup> Ref. [9]

<sup>c</sup> Ref. [28]

<sup>d</sup> This work

### 3.3 BH

The lowest singlet excitations of the BH molecule were calculated with the same basis set used in the FCI calculation [23]: a  $(19s6p3d/5s4p3d)$  basis set for borine and a  $(6s3p/4s3p)$  basis set for hydrogen. The internuclear distance was fixed at 2.3289 a.u. The active space includes two electrons in all cases. For the  $^1\Sigma^+$  states five active orbitals are necessary: three  $\sigma^+$  and two  $\pi$  ones, the almost localized  $2p_x$  and the  $2p_y$  orbitals of borine. The CAS for the  $^1\Pi$  states includes four orbitals, one  $\sigma^+$  and three  $\pi$  which are essentially of  $p_x$  character. For the  $^1\Delta$  state, there are three active orbitals in the CAS: one  $\sigma^+$  and two  $\pi$  orbitals, the almost localized  $2p_x$  and  $2p_y$  orbitals of borine. The calculations were started with the  $\text{BH}^{2+}$  dication MOs because in this case it was impossible to give a good description of the excited states with the canonical ones. In this academic case, because of the small basis set and the high symmetry, for some irreducible representations quasi null or strictly null density matrices may appear when only single excitations are considered. Consequently, it is not possible to get the natural orbitals from these density matrices. To avoid this problem, which appeared in the determination of the transitions to the  $^1\Pi$  y  $^1\Delta$  states, the orbitals of these symmetries were not optimized. Table 5 shows the size of the CAS, CAS\*S and DDCI spaces.

Table 6 gives the results for the transitions to singlet states. The mean errors for CCSD [23], CCSDT-3 [9] and CC3 [23] methods in comparison with FCI results are 0.217 eV, 0.09 eV and 0.085 eV, respectively. As in the previous  $\text{CH}^+$  calculations, the accuracy of these results is not homogeneous. For the states dominated by double replacement configurations, the  $C^1\Delta$  and  $C^1\Sigma^+$  transitions, the mean errors are 0.59 eV at the CCSD level and 0.25 eV at the CC3 level.

**Table 5.** DDCI space dimension for BH

Transition	Symmetry	CAS*S	CAS	DDCI
$X^1\Sigma^+ \rightarrow B^1\Sigma^+, C^1\Sigma^+, D^1\Sigma^+$	$\Sigma$	1845	11	20127
$X^1\Sigma^+ \rightarrow A^1\Pi, D^1\Pi, G^1\Pi$	$\Sigma$	1454	10	14133
	$\Pi$	886	6	15912
$X^1\Sigma^+ \rightarrow C^1\Delta$	$\Sigma$	641	3	9981
	$\Delta$	548	2	8546

**Table 6.** BH excitation energies to singlet states. FCI results and deviations from FCI, in eV (MAE, mean absolute error)

State	CCSD <sup>a</sup>	CCSDT-3 <sup>b</sup>	CC3 <sup>a</sup>	(SC) <sup>2</sup> CI <sup>c</sup>	DDCI <sup>d</sup>	IDDCI <sup>d</sup>	FCI <sup>a</sup>
$A^1\Pi$	0.022	0.02	0.008	-0.177	0.084	0.030	2.944
$C^1\Delta$	0.795	0.32	0.310	0.547	0.024	0.019	5.880
$B^1\Sigma^+$	0.041	0.02	0.016	-0.030	0.022	-0.022	6.378
$C^1\Sigma^+$	0.392	0.18	0.180	0.264	0.030	-0.090	6.996
$D^1\Pi$	0.035	0.03	0.014	0.000	0.152	0.008	7.466
$E^1\Sigma^+$	0.193	0.06	0.052	0.093	0.286	-0.022	7.559
$G^1\Pi$	0.038	0.02	0.016	-0.008	0.054	-0.010	8.239
MAE	0.217	0.09	0.085	0.160	0.093	0.029	

<sup>a</sup> Ref. [23]

<sup>b</sup> Ref. [9]

<sup>c</sup> Ref. [11]

<sup>d</sup> This work

The (SC)<sup>2</sup>SDCI results of Heully et al. [11] show a mean error of 0.16 eV. The error is not homogeneous in this case either. For example, for the  $C^1\Delta$  transition it is 0.547 eV. In order to improve this result, the authors performed a (SC)<sup>2</sup>MRCI calculation, but the result still differs from the FCI value by 0.4 eV. The authors believe that this is because the ground state orbitals are not adequate to describe the double excited state  $C^1\Delta$ . This argument is also supported by the DDCI and IDDCI results, since the mean error decreases from 0.09 eV, when using the dication MOs, to 0.03 eV when the transition dedicated orbitals are used, which justifies our iterative procedure of improving the MOs. This accuracy is reached after only four iterations.

### 3.4 CH<sub>2</sub>

Calculations were carried out for the lowest transitions to  $^1A_1$ ,  $^1A_2$ ,  $^1B_1$  and  $^1B_2$  singlet states in  $\text{CH}_2$  using a  $(18s4p1d/4s2p1d)$  basis set for carbon and  $(5s1p/3s1p)$  for hydrogen [23]. The geometry was fixed at  $d_{\text{C-H}} = 2.11 \text{ \AA}$  and  $\alpha_{\text{HCH}} = 75.86^\circ$ . The size of the active space is different for each symmetry. The active space for the  $^1A_1$  and  $^1B_2$  states includes two electrons and four active orbitals, three  $a_1$  and one  $b_2$ . In the remaining symmetries, for both  $^1A_2$  and  $^1B_1$  states there was a problem with the size of the active space. For the  $^1B_1$  state the starting active space included two electrons and three active orbitals of  $a_1$ ,  $b_2$  and  $b_1$  symmetry. When the iterative IDDCI procedure was used to improve the orbitals, a pseudonatural occupation of 1.73 was found for an orbital, which did not belong to the initially defined active space. This result proved that the definition of the active space was not suitable and that this orbital should also have been included in the active space. This example shows how the IDDCI method can help to define the active space. Finally, the new active space for the  $^1A_2$  and  $^1B_1$  states includes four electrons and four active orbitals, one  $a_1$ , one  $b_2$  and two  $b_1$  orbitals for the  $^1B_1$  state, and four orbitals of  $a_1$ ,  $b_2$ ,  $b_1$  and  $a_2$  symmetry for the  $^1A_2$  state. Table 7 gives the dimension of the different spaces. The iterative procedure was performed within the single excitation subspace. The starting orbitals were those of the restricted open-shell (OSRHF) calculation of the first triplet state, the  $^3B_2$ .

Table 8 shows the excitation energies to the lowest singlet states in  $\text{CH}_2$ . The mean error when using

**Table 7.** DDCI space dimension for CH<sub>2</sub>

Transition	Symmetry	CAS	CAS*S	DDCI
1 <sup>1</sup> A <sub>1</sub> → 2 <sup>1</sup> A <sub>1</sub> , 3 <sup>1</sup> A <sub>1</sub> , 4 <sup>1</sup> A <sub>1</sub>	A <sub>1</sub>	10	854	7990
1 <sup>1</sup> A <sub>1</sub> → 1 <sup>1</sup> B <sub>2</sub> , 2 <sup>1</sup> B <sub>2</sub> , 3 <sup>1</sup> B <sub>2</sub>	A <sub>1</sub>	10	854	7990
	B <sub>2</sub>	6	710	7044
1 <sup>1</sup> A <sub>1</sub> → 1 <sup>1</sup> B <sub>1</sub> , 2 <sup>1</sup> B <sub>1</sub>	A <sub>1</sub>	10	1342	21536
	B <sub>1</sub>	8	1324	21516
1 <sup>1</sup> A <sub>1</sub> → 1 <sup>1</sup> A <sub>2</sub> , 2 <sup>1</sup> A <sub>2</sub>	A <sub>1</sub>	10	1326	21550
	A <sub>2</sub>	10	1438	21590

**Table 8.** CH<sub>2</sub> excitation energies to singlet states. FCI results and deviations from FCI, in eV (MAE, mean absolute error)

State	CCSD <sup>a</sup>	CC3 <sup>a</sup>	DDCI <sup>b</sup>	IDDCI <sup>b</sup>	FCI <sup>a</sup>
2 <sup>1</sup> A <sub>1</sub>	1.456	0.471	-0.150	-0.112	4.656
3 <sup>1</sup> A <sub>1</sub>	-0.005	-0.005	-0.114	-0.033	6.514
4 <sup>1</sup> A <sub>1</sub>	-0.019	-0.005	-0.109	-0.027	8.479
1 <sup>1</sup> B <sub>2</sub>	-0.014	-0.005	-0.005	0.041	1.793
2 <sup>1</sup> B <sub>2</sub>	1.799	0.571	-0.161	-0.076	8.906
3 <sup>1</sup> B <sub>2</sub>	1.823	0.615	-0.044	0.044	10.552
1 <sup>1</sup> B <sub>1</sub>	0.011	0.016	0.022	-0.027	7.703
2 <sup>1</sup> B <sub>1</sub>	1.603	0.517	0.044	0.044	8.016
1 <sup>1</sup> A <sub>2</sub>	0.005	0.005	0.120	0.098	5.853
2 <sup>1</sup> A <sub>2</sub>	2.416	1.173	0.479	0.019	9.409
MAE	0.914	0.338	0.125	0.051	

<sup>a</sup> Ref. [23]<sup>b</sup> This work

OSRHF orbitals is 0.12 eV and decreases to 0.05 eV with the final iterated active orbitals. In this case, comparison with coupled-cluster approximations is quite favourable to IDDCI, since the mean error of CCSD and CC3 [23] results is 0.9 eV and 0.3 eV, respectively. A more detailed analysis shows that the mean error at the CC3 level for the states dominated by single replacement excitations is only 0.008 eV. However, the description of states dominated by a double excitation is rather incorrect, since the mean error increases to 1.69 eV at the CCSD level and 0.55 eV at the CC3 level. On the other hand, the (SC)<sup>2</sup>MRSDCI procedure of Heully et al. [11], who used a slightly different basis set, gave very good results for the transitions to the 2<sup>1</sup>A<sub>1</sub> state, which is dominated by double replacement excitations, and to the 3<sup>1</sup>A<sub>1</sub> and 4<sup>1</sup>A<sub>1</sub> states, which are essentially described by a single excitation. The three transitions only deviate from their FCI values by 0.04 eV, 0.01 and 0.01 eV, respectively. The size of the (SC)<sup>2</sup>MRSDCI matrix is, in this case, around 5000 determinants and the quality and the computational requirements are quite similar to IDDCI.

## 4 Conclusions

Comparison with FCI results confirms the accuracy of the results obtained by using a small model space and the iterative procedure for improving the MOs. This leads to

two positive conclusions. The first is that the dimension of the DDCI space, which is defined by all the determinants obtained by single excitations and double excitations involving at least one active MO, remains tractable. The second is that the zero-order description gives a simple physical model of the electronic transitions.

It has also been shown that the inexpensive technique of using the small subspace formed by single excitations only in the iterative procedure of improving the molecular orbitals and the full DDCI space just at the end of the procedure is highly effective. Moreover, this iterative procedure gives a rational way of modifying the active space when necessary, as shown by the transitions to <sup>1</sup>B<sub>1</sub> and <sup>1</sup>A<sub>2</sub> states in methylene. Exceptions may be found, if the dynamic correlation strongly modifies the weight of the determinants of the CAS in the wavefunction. In these cases, the use of the CAS\*S function to optimize the orbitals is not sufficient. We found an example of this behaviour in the determination of <sup>1</sup>B<sub>1u</sub> in ethylene, because of the strong mixture of valence and Rydberg character. The problem may be easily detected by analyzing the projections on the CAS, which do not reach convergence.

An important advantage of the IDDCI method is that the quality of the results is maintained for different types of excitations, those which are essentially described by a single excitation process as well as those with the main weight on a double replacement. On the contrary, other methods like the CC3 coupled-cluster method of Jørgensen et al. give excellent results for the first type of transition but very poor results for transitions dominated by double excitations.

The independence of the results from the starting MOs is an important characteristic of the IDDCI method. The iterative procedure of optimization of MOs through the mixing of the density matrices of the states involved in the transition has shown its good performance. This technique could as well be used with other accurate CI procedures such as the dressing (SC)<sup>2</sup> technique which generally gives quite accurate results but fails in some cases because of the inadequacy of the canonical MOs to describe the excited states with few references. However, the dressing (SC)<sup>2</sup> procedure uses full SDCI spaces and needs to iterate the diagonalization of the CI space to self-consistency which increases the computational cost.

A final comment concerns the use of the method on potential curves. Since the reference space is the CAS and the CI space is preserved along the geometry variation, the curves are perfectly smooth, as has been shown in the potential curves of different excited states of KH and K<sub>2</sub> [29].

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