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## Direct selected multireference configuration interaction calculations for large systems using localized orbitals

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A selected multireference configuration interaction (CI) method and the corresponding code are presented. It is based on a procedure of localization that permits to obtain well localized occupied and virtual orbitals. Due to the local character of the electron correlation, using local orbitals allows one to neglect long range interactions. In a first step, three topological matrices are constructed, which determine whether two orbitals must be considered as interacting or not. Two of them concern the truncation of the determinant basis, one for occupied/virtual, the second one for dispersive interactions. The third one concerns the truncation of the list of two electron integrals. This approach permits a fine analysis of each kind of approximation and induces a huge reduction of the CI size and of the computational time. The procedure is tested on linear polyene aldehyde chains, dissociation potential energy curve, and reaction energy of a pesticide-Ca<sup>2+</sup> complex and finally on transition energies of a large iron system presenting a light-induced excited spin-state trapping effect. © 2011 American Institute of Physics. [doi:10.1063/1.3600351]

### I. INTRODUCTION

The multireference configuration interaction (MRCI) method is well suited to address problems where the physics is not described by a single reference wave function. This includes many studies concerning spectroscopy and also molecules in which the ground state is of multireference character, such as magnetic systems. Compared to perturbative approaches such as complete active space perturbation theory at second order (CASPT2), MR-single and double CI (MR-SDCI) additionally takes into account the effect of the non-active orbitals on the CAS wave function and their interaction between themselves at all perturbation orders. The lack of size extensivity due to the truncation of the CI is a great problem especially for large systems, but several efficient corrections to this error have been proposed, such as - for multireference CI - coupled electron pair (MR-CEPA(0)),<sup>1</sup> MR-CEPA,<sup>2</sup> average coupled pair functional (MR-ACPF),<sup>1,3</sup> average quadratic coupled cluster (MR-AQCC),<sup>4</sup> and others, such as class dressed correction.<sup>5</sup> MR-CEPA(0), MR-CEPA, and class dressed corrections have already been implemented in the presented MR-SDCI code.<sup>5</sup>

In the most popular MRCI approach, a full CI (FCI) is performed in a reduced space of active orbitals, namely, the complete active space and all single and double excitations from the CAS (CAS+SD) are added, as justified by the presence of at most two-body operators in the Hamiltonian. Several codes have been written for some tens of years, such as

the MR-DCI of Buenker and Peyerimhoff,<sup>6,7</sup> the MELDF program of Davidson and co-workers,<sup>8</sup> the CASDI developed in our group,<sup>9</sup> or the MRCI included in the COLUMBUS<sup>10</sup> and MOLCAS<sup>11</sup> packages. The size of the CAS space grows exponentially with the number of active orbitals so that the number of active electrons and active orbitals is hardly larger than (16/16). The computational cost of the non-active part grows as  $N^6$ , where  $N$  is the number of orbitals. As a consequence, without further approximations, the MRCI methods are restricted to rather small systems.

A large number of approaches have been proposed to reduce the cost of the method. For example, Werner and Knowles<sup>12</sup> proposed the internally contracted MRCI. In this method, all configurations with one electron in the external space are generated as in a non-contracted CI but, for double excitations – the most numerous ones –, pair excitation operators are applied to the reference wave function (corresponding to the CAS part) as a whole. Compared to the non-contracted MRCI, where the pair excitation operators are applied to each determinant of the CAS space, the size of the CI matrix is smaller by a factor equal to the dimension of the CAS space. The dependence on the number  $N$  of orbitals remains  $N^6$ , but the prefactor is dramatically reduced, even if the calculation cost of the CI matrix is higher compared with a non-contracted CI matrix of the same size. Another way to reduce the computational cost is the approach of Bytautas and Ruedenberg that proposed a procedure of extrapolation of the FCI expansion.<sup>13,14</sup>

Another possibility is to reduce the size of the CI matrix by keeping only the most important configurations or determinants. Indeed, in a MRCI calculation, CAS+SD, for

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example, the large majority of them correspond to improbable situations that have a very small weight in the wave function. The important determinants can be chosen one by one on physical criteria, but an automated choice is preferred. This can be obtained by using a perturbative step as in the configuration interaction through perturbation and selected iterations (CIPSI)<sup>15</sup> and ORCA<sup>16</sup> codes. Starting from a set of one or some reference determinants, a perturbative calculation generates all the determinants simply and doubly excited with respect to these references and calculates their energy contribution. One defines a threshold, and the most important determinants are added to the variational space. The process can be iterative.

More recently, the reduction of the computational time has been obtained by the use of localized orbitals, as in the recent works of Bories *et al.*<sup>17</sup> or Chwee *et al.*<sup>18–21</sup> This approach allows one to neglect long range interactions, thanks to the fact that electron correlation is a local phenomenon.<sup>22–25</sup> As a consequence, the proportion of determinants that have a small weight in the wave function is even smaller. This approach leads to a “linear scaling” behavior. A method is said to be linear scaling when its computational cost grows as  $N$ , the particle number of the system. Several such methods have been implemented, for example self consistent field (SCF), second order Moller–Plesset (MP2), coupled cluster CCSD(T), or MP2 gradient.<sup>18,26–33</sup> One must notice that, compared to other approaches, only the use of localized orbitals can yield linear scaling calculations.

As soon as one intends to neglect small interactions, one or several thresholds must be introduced to decide what should be taken into account and what can be neglected. The choice of thresholds or parameters is always delicate. A first methodological part of this paper presents a discussion about what quantities can be neglected, according to which criterion, and what was already investigated on this subject in the past. In a second step, the effect of the various ways to reduce the computational cost is successively analyzed using calculations on a series of linear polyene aldehydes  $C_nH_{n+1}O$ . The goal of this work is to produce a selected MRSDCI method and a code that gives complete MRSDCI results, but the size-consistency error of the original MRSDCI method is an important problem as noticed above. In general, a simple Davidson correction is applied. As this correction depends on the correlation energy and coefficients of the wave function, we have discussed the effect of the threshold on this correction. Thereafter, we have investigated the dissociation of the  $[Ca^{2+}$  – atrazine model pesticide] complex as a possible discontinuity along the potential energy curve can occur when using thresholds. The accuracy of the method on reaction energies has been analyzed on the same complex. Finally, a spectroscopic study of the 2,6 di-(pyrazol-1-yl) pyridine]<sub>2</sub>-Fe<sup>II</sup> complex presenting a light induced spin state trapping (LIESST) effect has been performed.

## II. METHOD

### A. Computational cost of a CI calculation

The CI matrix is diagonalized using the iterative Davidson<sup>34,35</sup> algorithm. At iteration  $n$ , the coefficient  $C_i^n$  of

the current trial vector  $\Psi_n$  is updated as follows (Eq. (1)):

$$\delta C_i^n = \frac{E^n C_i^n - \sigma_i^n}{H_{ii} - E^n}; \quad \sigma_i^n = \sum_j H_{ij} C_j^n. \quad (1)$$

The most time consuming part is by far the product  $\sigma^n = H\Psi^n$ , where  $H$  is the Hamiltonian matrix and  $\Psi^n$  is the current CI vector. Three quantities are concerned in the calculation of the product: two vectors  $\sigma^n$  and  $\Psi^n$ , and the matrix elements of  $H$  that are essentially two electron repulsion integrals. During the computation of the product, two of them are usually kept in memory, and it is possible to read sequentially the third one from disk.

The question of storing in memory both vectors or one vector and the integrals has no definitive answer. The most relevant choice is to read from disk the largest file. In general, the integrals are more numerous, since their number grows as  $N^4$ , while the number of determinants grows only as  $N_{oc}^2 N_v^2$ , where  $N_{oc}$  and  $N_v$  are, respectively, the numbers of occupied, and virtual orbitals. Furthermore, for very large systems, the size of the vectors can be reduced by performing a lower level CI (CI of single excitations or difference dedicated CI (DDCI), where all two hole two particle excitations are excluded,<sup>36</sup> for example), while the number of integrals can hardly be reduced. However, the prefactor corresponding to the dimension of the CAS space can be large. In the preceding code<sup>17</sup> and in its new version presented in this study, the two vectors are stored in memory and the integrals are sequentially read from disk during the direct CI calculation.

To reduce the computational cost, it is convenient to eliminate some integrals as well as to truncate the determinant basis, i.e., the size of the CI matrix. Actually, it is more important to reduce the number of determinants than the number of integrals. If there are many integrals and if they are read from disk, the calculation will be time-consuming, since the program is “integral driven” (the external loop consists in reading them) and the computational time is therefore proportional to their number. However, in theory, the calculation remains always possible. On the contrary, if the matrix dimension is too big, it will be impossible for reasons of memory storage.

### B. Reducing the scaling by using localized orbitals

The recently developed methods that intend to reduce the computational cost of a CI calculation are based on the use of localized orbitals, which takes benefit of the local character of the electron correlation. Some years ago we have proposed a method of *a priori* localization of molecular orbitals,<sup>37–39</sup> which yields well localized core, valence, and even virtual orbitals. In the standard localization methods, SCF or CASSCF orbitals are first obtained and then localized by rotations in each one of the occupied, active and virtual subspaces. In our *a priori* approach, a set of local orbitals (LO) is build as a first step. Each one of these LOs is spanned by only the neighbor atomic orbitals. For example, a LO corresponding to a bond between atoms A and B is a linear combination of the atomic orbitals of these two atoms. These LOs are of poor quality, i.e., the determinant in which all LOs are occupied by two electrons up to the Fermi level has a

very high energy compared to the Hartree-Fock solution. In a second step, these orbitals are “optimized” to reach a SCF or CASSCF quality. Two approaches are possible. One can project the LOs onto delocalized canonical SCF or CASSCF orbitals, or use a super-CI like procedure, which improve the orbitals through successive rotations that maintain their local character (see Ref. 37). One may notice that it is possible to obtain well localized orbitals even for delocalized systems as polyene chains, for example.<sup>40</sup> In this case, localized  $\pi$  orbitals on the double bonds have been obtained as in a Lewis picture, and the relatively high  $\pi$  electron density on the single bonds of these kinds of molecules is obtained by the tails of the neighbor double ones. It is sometimes impossible to get localized orbitals. For example, again in the example of a polyene – but for the first excited  $\pi \rightarrow \pi^*$  state – if one chooses to have only two active orbitals and two active electrons, these orbitals will be the  $\pi$  and  $\pi^*$  HOMO and LUMO. As each of them is unique in its symmetry, their shapes are completely imposed by the CASSCF calculation. If, in the standard CASSCF solution, they are not localized – and actually, they are not – it is impossible to localize them with any method.

As we have a complete set of localized (occupied and virtual) orbitals, all of them will be treated in the same way. The procedure of selected MRCI starts with the construction of a topological matrix, which determines if two local orbitals must be considered as “interacting” (they are in the same region of space) or not. A first problem is to choose a criterion to build the topological matrix. It would be possible to use a distance criterion. Beyond a certain distance  $d$  between two orbitals, their interaction would no more be taken into account. A drawback of this simple criterion is that it does not distinguish between different type of orbitals, core, valence, virtual, or diffuse,  $\sigma$  or  $\pi$ , and so on. Some preliminary tests have shown that it yields poor results. Choosing the exchange integral  $K_{ij}$  as cut off criterion is quite relevant to decide whether two local orbitals  $i$  and  $j$  must be considered as in interaction or not. If  $K_{ij}$  is lower than a given threshold  $Th$ , the interaction is neglected.  $K_{ij}$  has the advantage to be always positive and, contrary to the overlap, it is never zero for symmetry reasons. It decreases exponentially, much faster than the coulomb integral, which makes easier the definition of a distance cut off.

Moreover, using it in various situations seems to witness that it has a real physical content. We have verified that, in a polyene, for example, the distance of interaction (i.e., the distance between  $i$  and  $j$  for which  $K_{ij}$  is larger than the threshold) is larger for the  $\pi$  than for the  $\sigma$  orbitals, which is quite satisfactory.

The  $K_{ij}$  exchange integral is also chosen as an interaction criterion, for example, in the Cholesky decomposition<sup>41,42</sup> used in the MOLCAS package<sup>43–45</sup> or by Whitten.<sup>46</sup>

The time consuming product  $\sigma^n = H\Psi^n$  can be decomposed in a series of elementary products  $c_{\mu'} = H_{\mu\nu}c_{\nu}$ , where  $c_{\mu'}$ ,  $c_{\nu}$  are, respectively, coefficients of  $\sigma^n$ ,  $\Psi^n$  and  $H_{\mu\nu}$  is in most cases a two-electron integral. The most time consuming product occurs when determinants  $\mu$  and  $\nu$  are doubly excited. They are described by double excitations  $ij \rightarrow ab$  and  $kl \rightarrow cd$ . Among the 8 indices, only 6 can be different if the determinants interact, for example,  $ij \rightarrow ab$  and  $ij \rightarrow cd$ . In

this case, the two-electron integral connecting the two determinants is  $(ac|bd)$ . There are 6 different and independent indices, and this is the reason why the computational cost of the product  $\sigma^n = H\Psi^n$  grows as  $N^6$ .

If some indices are not independent from the others, the scaling decreases. For example, the integral  $(ac|bd)$  is small if the pairs  $(a, c)$  and  $(b, d)$  are not interacting pairs and can be eliminated (let us recall that the pair  $(a, c)$  is not considered as an “interacting pair” according to a distance criterion, but according to the fact that  $K_{ij}$  is larger than the  $Th$  threshold). Therefore, one can consider that  $a$  and  $b$  vary from 1 to  $N$  while  $c$  varies from 1 to  $N_{Na}$ , number of neighbors of  $a$  (the local orbitals interacting with  $a$ ) and  $d$  varies from 1 to  $N_{Nb}$ . The scaling is now  $N_N^2 N^4$ , where  $N_N$  is the average number of neighbors of a localized orbital and does not depend on the size of the molecule. Finally, a linear scaling behavior is obtained if one imposes the six orbitals to be in the same region of space.

### C. Truncating the basis of determinants and the list of integrals

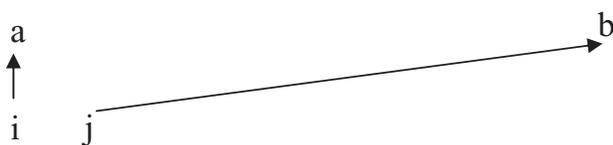
In this part, we shall present the rules for the elimination of singly and doubly excited determinants of the CI matrix basis and the way to truncate the list of two electron integrals.

The approach presented in this paper differs from what can be found in the literature, especially in Refs. 18–21 for what concerns the manner to reduce the size of the CI and the number of two electron integrals. Saebo and Pulay<sup>25,47–51</sup> proposed various localized treatment of electron correlation. They obtain occupied localized orbitals (OLO) using the Boys<sup>52</sup> or Pipek-Mezey<sup>53</sup> methods. As it is difficult to localize virtuals with these techniques, they built a local basis set around each OLO starting from the OLO and the atomic orbitals that are in the vicinity. In these works, but also in the recent proposals of Chwee and Carter,<sup>18–21</sup> the truncation of the determinant or configuration state functions basis is obtained through the weak pair approximation (WP)– interaction between OLOs and the truncation of virtuals (TOV)– interaction between occupied and virtual orbitals, while the reduction of the number of integrals results from the application of pre-screening techniques.<sup>28,54,55</sup>

#### 1. Reducing the determinant basis

A first condition is to keep spin symmetry in the wave function (the final eigenvectors must be eigenfunctions of  $S^2$ ). This is simply obtained by observing the following condition. If a given determinant  $D = [\text{CAS}] ij \rightarrow ab$  is kept in the basis, where [CAS] represents the distribution of electrons on the active orbitals, all its spin equivalent determinants, i.e., those obtained from  $D$  by all spin permutations on singly occupied orbitals, will also be kept. As a consequence, spin is never considered in the topological matrix that defines the orbital interactions.

A first possibility to reduce the CI size is to keep only the double excitations  $ij \rightarrow ab$  for which  $(i,a)$  and  $(j,b)$  [or  $(i,b)$  and  $(j,a)$ ] are interacting pairs according to the topological



SCHEME 1.

interaction, which corresponds to the above referred TOV approximation. The corresponding exchange integrals between an occupied and a virtual orbital are  $K_{ia}$  and  $K_{jb}$  [or  $K_{ib}$  and  $K_{ja}$ ], and the determinant is kept if both exchange integrals are larger than a given threshold  $Th_1$ . This is equivalent to state that, in the  $ij \rightarrow ab$  determinant, no orbital should be isolated, as for example, in the following case (Scheme 1).

This criterion keeps all determinants whose orbitals are in the same region of space but also those composed of two occupied/virtual pairs, such as presented in Scheme 2.

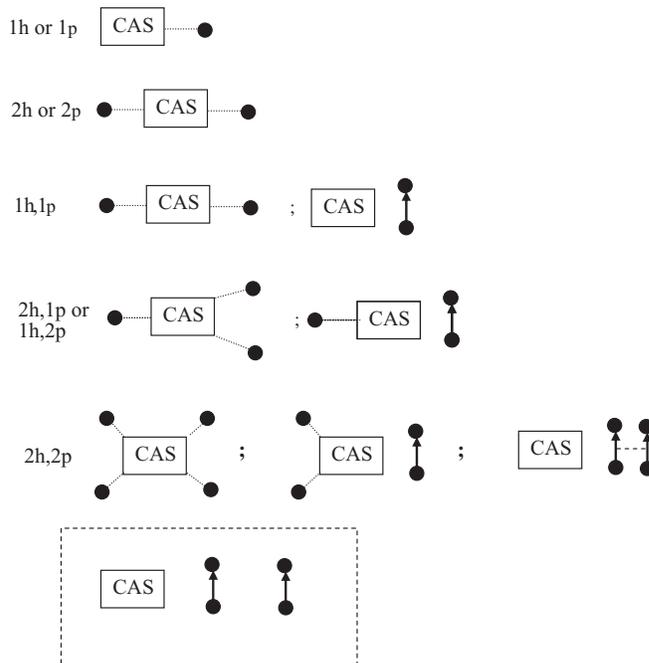
The latter determinants are responsible for the dispersive interactions. Depending on the system under study, they can also be eliminated by using a second criterion similar to the WP approximation. The criterion chosen in this work is to enforce that at least one orbital of the  $(i,a)$  pair must interact with one of  $(j,b)$ , i.e., at least one of the exchange integrals  $K_{ib}$ ,  $K_{ij}$ ,  $K_{ja}$ , or  $K_{ab}$  is larger than the second threshold  $Th_2$  (notice that, in this example, we have already  $K_{ia} > Th_1$  and  $K_{jb} > Th_1$ ). Contrarily to the case of  $Th_1$ , all kinds of exchange integrals (occupied/occupied, occupied/virtual, and virtual/virtual) are concerned. Giving  $Th_1 \neq 0$  and  $Th_2 \neq 0$  ensures that all orbitals of the determinant are in the same region of space, since only one index can be chosen without constraint and the size of the CI matrix grows as  $N$ .

Generally, the dispersive interactions are small, and then the determinants eliminated by  $Th_2$  are expected to play a minor role. However, in some cases, the latter determinants should not be ignored. Thus, two different topological matrices have been used, in order to keep the possibility to partly neglect or not the dispersive effects. In the following,  $Th_1$  and  $Th_2$  will be called “general” and “dispersion” thresholds, respectively.

The active orbitals, which span the CAS, deserve a special treatment. As they play an important role in the physics of the problem, it has been decided that all of them should be in interaction between themselves. Finally, one defines another topological matrix describing the interaction of the active and non-active spaces. According to this criterion, a non-active orbital interacts with the CAS if, using the general threshold  $Th_1$ , it interacts with at least one active orbital.



SCHEME 2.



SCHEME 3. The scheme gathers all criteria used in the code to keep a determinant.

Finally, the action of  $Th_1$  and  $Th_2$  are resumed on Scheme 3, where all different situations are shown for all numbers of holes (h) and particles (p). To be kept, a determinant has to belong to one of the cases in Scheme 3.

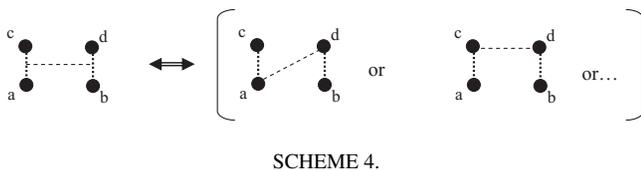
The dot lines represent the interactions between a non-active orbital and an active one, the arrows the interaction between two non-active orbitals, while the dashed lines depict the interaction between pairs (we recall here that two pairs interact if at least one orbital of pair 1 interacts with one orbital of pair 2).

For example, the conditions for a 2-hole/1-particle determinant may be found in the line “2h, 1p or 1h, 2p.” A 2h, 1p determinant corresponds to an excitation  $CAS \rightarrow p$  and one  $h \rightarrow p$ . There are two possibilities to keep the determinant. Either all non-active orbitals interact with the CAS or only one hole, but in this case the other hole and the particle must interact one with each other. The last case (dashed square) corresponds to the situation where the determinant is eliminated if  $Th_2$  is non-zero.

This approach allows one to truncate also less excited CIs, such as, for example, DDCI or single excitation CI.

## 2. Reducing the number of two-electron repulsion integrals

The rules to eliminate small integrals are similar to those that shorten the list of determinants. Here again, topological matrices are used. A two-electron integral  $\langle ac | 1/r_{12} | bd \rangle$  represents the interaction between the  $ac$  and  $bd$  distributions ( $a$ ,  $b$ ,  $c$ , and  $d$  are any orbitals). If  $a$  and  $c$  (or  $b$  and  $d$ ) are localized orbitals and are spatially distant, the value of the integral is small. It is therefore convenient to consider only the integrals for which  $c$  is a neighbor of  $a$  and  $d$  is a neighbor of  $b$ .



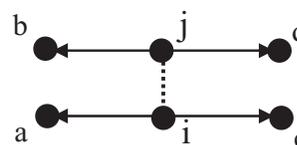
Their number grows as  $N^2$ , since only  $a$  and  $b$  are independent.

To reach a  $N$ -scaling behaviour, it is necessary to introduce additional approximations. The sole possibility is to eliminate also interactions between pairs  $(a,c)$  and  $(b,d)$  when this interaction is weak, which will happen when the pairs are distant one from another. In their recent papers, Chwee *et al.*<sup>18–21</sup> evaluate an upper bond of the integral value by using the Cauchy-Schwartz approach and test densities, according to the work of Schütz *et al.*,<sup>28,31</sup> which allows them to achieve linear scaling. We have preferred to use the criterion based on the values of exchange integrals described above. To check the interaction between  $(a,c)$  and  $(b,d)$  pairs, one must consider the four exchange integrals  $K_{ab}$ ,  $K_{ad}$ ,  $K_{cb}$ , and  $K_{cd}$ , in which each index belongs to a different pair. The condition to keep an integral  $(a, c, b, d)$  is then that all  $a, c, b$ , and  $d$  localized orbitals must be directly or indirectly connected, i.e., every one of them has an exchange integral larger than a given threshold  $Th_i$  with at least one other index, as in the example of Scheme 4.

The value of the integral  $(ac|bd)$  decreases exponentially with the distances  $a-c$  and  $b-d$ . It decreases only as  $1/r$  with the distance between the  $(a,c)$  and  $(b,d)$  pairs. However, only one threshold is used for both kinds of interactions. One must notice that the use of the upper bond of Schütz *et al.*<sup>31</sup> does not guarantee by itself a linear scaling behaviour. The test eliminates small integrals, and it appears that the number of remaining integrals grows as  $N$ . The reason for this linear growing should be that, due to distance considerations, integrals  $(ac|bd)$  vanish when the  $(a,c)$  and  $(b,d)$  pairs are distant.

One may notice that the elimination of determinants on one hand and of integrals on the other hand are not independent. Indeed, considering the interaction between two determinants  $ij \rightarrow ab$  and  $ij \rightarrow cd$  through the integral  $(ac|bd)$ , the linear scaling is obtained when all six orbitals are in the same region of space. If  $Th_1$  and  $Th_2$  are larger than zero, all orbitals describing each determinant ( $i, j, a, b$  and  $i, j, c, d$ ) must be close to one another and as a consequence, also  $a, b, c, d$ .  $Th_i$  seems then to be unnecessary. However, it is relevant to introduce three conditions, because a larger number of small integrals would be kept in the calculation.

Indeed, using  $Th_i$ , one keeps the integral  $(ac|bd)$  by considering the value of the corresponding exchange integrals and, thus, each index  $a, b, c$ , and  $d$  interacts with another index of the same list. Using only the determinant thresholds is less demanding, since it keeps the case where two indices interact only through  $i$  or  $j$ , and not necessarily directly (see Scheme 5). This is not equivalent, even if linear scaling would also be obtained, but with larger sizes. In the same way,



SCHEME 5. Using only  $Th_1$  and  $Th_2$  thresholds,  $(ij \rightarrow ab|H|ij \rightarrow cd)$  is computed. However, the introduction of  $Th_i$  eliminates it if  $(a,b)$  does not interact with  $(c,d)$ , since it eliminates the integral.

giving  $Th_1$  and  $Th_i$  non-zero values should be sufficient to ensure linear scaling.

### III. TESTS

The effects of the three thresholds (general  $Th_1$ , dispersion  $Th_2$  and integral  $Th_i$ ) will be successively studied. In a first step,  $Th_2 = Th_i = 0$  and the dependence of the correlation and transition energies on  $Th_1$  is analyzed for small chains of  $C_nH_{n+1}O$  aldehyde molecules ( $n = 3$  to 9). The influence on the reference weights ( $\sum_{I \in \text{CAS}} C_I^2$ ) and the Davidson correction to the energy are also discussed.

In a second step, the effects of the other thresholds are analyzed.  $Th_1$ ,  $Th_i$ , and  $Th_2$  are successively introduced in the calculation of the transition energies of a series of aldehyde molecules  $C_nH_{n+1}O$  ( $n = 3$  to  $n = 25$ ).

A time dependence of the calculations is finally presented.

The complex of a model of the atrazine pesticide molecule with  $Ca^{2+}$ , a soil abundant cation, is studied using various sets of thresholds. On the one hand, we investigate the behaviour of the dissociation potential energy curve, plotted as a function of the distance. On the other hand, the complexation energy is computed. In this case, the problem of the size-consistency is pointed.

The last example study is devoted to a large iron-containing system. It concerns the metal centered spectroscopy of the  $[2,6\text{-di}(\text{pyrazol-1-yl})\text{pyridine}]_2 \text{Fe}^{\text{II}}$  complex.

#### A. Aldehyde molecules $C_nH_{n+1}O$

##### 1. Computational details

The calculations were based on atomic natural orbitals-relativistic correlation consistent (ANO-S)<sup>56</sup> basis sets with the following contraction scheme: for C a  $(10s6p3d)$  set contracted to  $[3s2p1d]$  and for H a  $(7s3p)$  set contracted to  $[2s1p]$ . The starting MOs for MRCI calculations are localized MOs of SCF quality. The electronic ground and  $n \rightarrow \pi^*$  singlet excited states have been calculated with 2 electrons correlated in 2 active orbitals. This active space includes the  $n$  lone pair and the  $\pi$  anti-bonding orbital of the CO group, which corresponds to 4 determinants. Idealized structures have been used, with  $d_{C=O} = 1.22 \text{ \AA}$ ,  $d_{C-C} = 1.45 \text{ \AA}$ ,  $d_{C=C} = 1.35 \text{ \AA}$ , and  $d_{C-H} = 1.1 \text{ \AA}$ . All angles are identical and equal to  $120^\circ$ . The symmetry group is Cs.

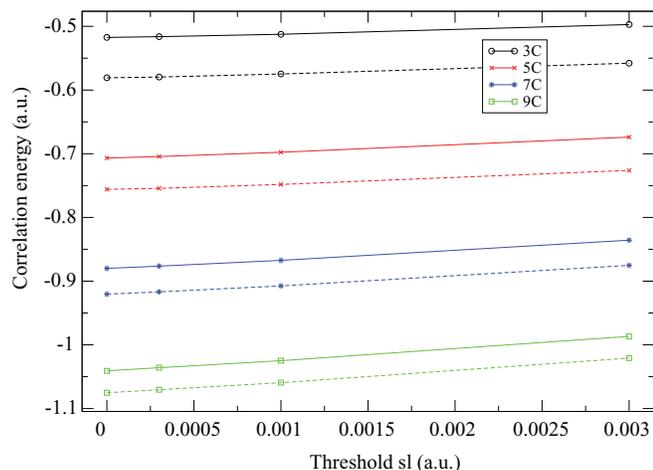


FIG. 1. Correlation energies of ground (straight line) and  $n \rightarrow \pi^*$  singlet excited (dashed line) states for the  $C_nH_{n+1}O$  molecules ( $n = 3$  to  $9$ ).

## 2. Evolution of the correlation energy and reference weights as a function of the general $Th_1$ threshold for the $C_nH_{n+1}O$ molecules ( $n = 3$ to $9$ )

In Table I, we present the variation of the correlation energies when  $Th_1$  increases, compared with the reference CAS-SDCI values for both ground and  $n \rightarrow \pi^*$  states. For the smallest 0.0003 a.u. value of  $Th_1$ , the percentage of the recovered correlation energy is about 99.8% for  $C_3H_4O$ . Both percentages are found to be similar for the ground and excited states and decrease slowly when the size of the molecule increases. The error on transition energies is less than 0.005 eV with this threshold. With the largest value (0.003 a.u.), the percentage of correlation energy is lesser, around 96% but still similar for ground and excited states. The error introduced on the calculated transition energy is found reasonable, from

0.07 eV for the smallest chain until 0.02 eV for larger chains. When  $n$  varies from 3 to 9, the difference on the transition energies introduced by the truncation diminishes. This is due to the fact that, in this example, the correlation energies of the ground and excited states are closer in the larger systems (Figure 1). One may also notice that the correlation energy curves have very similar slopes.

The truncated CI methods are known to present dramatic size-consistency error. The easiest solution is to apply the well-known Davidson correction to the total energy, while more sophisticated diagonal energy corrections such as MR-CEPA(0),<sup>1</sup> MR-ACPF,<sup>1,3</sup> MR-AQCC,<sup>4</sup> or class dressed<sup>5</sup> also modify the wave-function. The Davidson correction of the size-inconsistency consists in modifying the correlation energy by a factor depending on the coefficients of the references in the wave function<sup>57</sup> (Eq. (2)),

$$E^{\text{SDCI+Q}} = E_0 + E_c \left( 2 - \sum_{I \in \text{CAS}} C_I^2 \right). \quad (2)$$

The correlation energy ( $E_c$ ) is the energy brought by the excitations from the CAS.  $E$  being the energy resulting from the MRSDCI diagonalization,  $E_c = E - \langle \Psi_0 | H | \Psi_0 \rangle$ , where  $\Psi_0$  is the eigenfunction of the CASCI. We note  $E_0$  the reference CASCI energy.

Table II presents the reference weights of ground and  $n \rightarrow \pi^*$  excited states. The reference weight of the excited state is slightly more affected than the ground state by the increase of the threshold. As expected, the reference weights are higher for largest thresholds while the percentage of correlation energy is lower. These two tendencies act in the same direction on the corrected Davidson energy: since the threshold augments as this energy increases. Table III presents the Davidson corrected total and transition energies. The transition energies obtained at complete SDCI level ( $Th_1 = 0.0$  a.u.) are

TABLE I. Evolution of the correlation energy as a function of the general threshold  $Th_1$  for the  $C_nH_{n+1}O$  molecules ( $n = 3$  to  $9$ ).

$Th_1$ (a.u.)	Reference $E_0$ and correlation $E_c$ energies and % $E_c$ for the ground state	Reference $E_0$ and Correlation $E_c$ energies and % $E_c$ for the $n \rightarrow \pi^*$ state	Transition energy $n \rightarrow \pi^*$ (eV)
$C_3H_4O$	$E_0 = -190.794182$ a.u.	$E_0 = -190.529107$ a.u.	5.49
	$E_c = -0.517339$ a.u.	$E_c = -0.580722$ a.u.	
	0.0000	99.79%	
	0.0003	99.80%	
	0.0010	98.98%	
$C_5H_6O$	$E_0 = -267.695371$ a.u.	$E_0 = -267.426281$ a.u.	5.52
	$E_c = -0.706763$ a.u.	$E_c = -0.755907$ a.u.	
	0.0000	99.67%	
	0.0003	99.80%	
	0.0010	98.98%	
$C_7H_8O$	$E_0 = -344.595265$ a.u.	$E_0 = -344.324861$ a.u.	6.00
	$E_c = -0.879937$ a.u.	$E_c = -0.920389$ a.u.	
	0.0000	99.60%	
	0.0003	99.61%	
	0.0010	98.60%	
$C_9H_{10}O$	$E_0 = -421.494771$ a.u.	$E_0 = -421.223808$ a.u.	6.26
	$E_c = -1.040769$ a.u.	$E_c = -1.075227$ a.u.	
	0.0000	99.53%	
	0.0003	99.56%	
	0.0010	98.53%	
$C_3H_4O$	$E_0 = -190.794182$ a.u.	$E_0 = -190.529107$ a.u.	5.56
	$E_c = -0.517339$ a.u.	$E_c = -0.580722$ a.u.	
	0.0000	99.79%	
	0.0003	99.80%	
	0.0010	98.98%	
$C_5H_6O$	$E_0 = -267.695371$ a.u.	$E_0 = -267.426281$ a.u.	6.04
	$E_c = -0.706763$ a.u.	$E_c = -0.755907$ a.u.	
	0.0000	99.67%	
	0.0003	99.80%	
	0.0010	98.98%	
$C_7H_8O$	$E_0 = -344.595265$ a.u.	$E_0 = -344.324861$ a.u.	6.26
	$E_c = -0.879937$ a.u.	$E_c = -0.920389$ a.u.	
	0.0000	99.60%	
	0.0003	99.61%	
	0.0010	98.60%	
$C_9H_{10}O$	$E_0 = -421.494771$ a.u.	$E_0 = -421.223808$ a.u.	6.28
	$E_c = -1.040769$ a.u.	$E_c = -1.075227$ a.u.	
	0.0000	99.53%	
	0.0003	99.56%	
	0.0010	98.53%	
$C_3H_4O$	$E_0 = -190.794182$ a.u.	$E_0 = -190.529107$ a.u.	6.43
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$C_7H_8O$	$E_0 = -344.595265$ a.u.	$E_0 = -344.324861$ a.u.	6.45
	$E_c = -0.879937$ a.u.	$E_c = -0.920389$ a.u.	
	0.0000	99.60%	
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$C_9H_{10}O$	$E_0 = -421.494771$ a.u.	$E_0 = -421.223808$ a.u.	6.45
	$E_c = -1.040769$ a.u.	$E_c = -1.075227$ a.u.	
	0.0000	99.53%	
	0.0003	99.56%	
	0.0010	98.53%	

TABLE II. Evolution of the reference weights  $\sum_{I \in \text{CAS}} C_I^2$  as a function of the general threshold  $Th_1$  for the  $C_nH_{n+1}O$  molecules ( $n = 3$  to 9).

	$Th_1$ (a.u.)	CAS-SDCI	CAS-SDCI	CAS-SDCI	CAS-SDCI
		0.0	0.0003	0.001	0.003
$C_3H_4O$	GS	0.85786	0.85819	0.85939	0.86269
	$n \rightarrow \pi^*$	0.78159	0.78248	0.78674	0.79396
$C_5H_6O$	GS	0.82559	0.82610	0.82778	0.83182
	$n \rightarrow \pi^*$	0.78485	0.78582	0.78832	0.79455
$C_7H_8O$	GS	0.80127	0.80183	0.80370	0.80823
	$n \rightarrow \pi^*$	0.77572	0.77653	0.77873	0.78388
$C_9H_{10}O$	GS	0.78215	0.78263	0.78456	0.78922
	$n \rightarrow \pi^*$	0.76425	0.76511	0.76706	0.77194

dramatically changed by the Davidson correction particularly for the smallest chains. The error on the transition energies computed at the selected SDCI level is larger when the Davidson correction is applied and increases with the threshold  $Th_1$  (from 0.02 eV with  $Th_1 = 0.0003$  a.u. until 0.25 eV with  $Th_1 = 0.003$  a.u. for  $C_3H_4O$ ). This is partly due to the difference on the excited state's reference weight. Similarly to the SDCI results, when the system becomes larger, the Davidson correction and the effect of the thresholds are less important since the correlation energies and the reference weights of the ground and excited states are closer in the larger systems.

### 3. Dimensions and time dependence of the calculations as a function of the various thresholds for the $C_nH_{n+1}O$ molecules ( $n = 3$ to 25)

a. General Threshold  $Th_1$  Table IV gives the number of determinants in the CI, the time per iteration and the transition

energies from the ground state to the  $n \rightarrow \pi^*$  excited state for  $C_nH_{n+1}O$  molecules ( $n = 3$  to 25) as a function of  $Th_1$ .

For systems larger than  $n = 9$ , the complete CAS-SDCI could not be performed. However, satisfactory reference values could be obtained as described below. Indeed, the 0.0003 a.u.  $Th_1$  threshold gives an error on the transition energy smaller than 0.01 eV for  $n = 3$  to 9. Thus, we have assumed that, beyond  $n = 9$ , the results obtained with this threshold can be taken as reference values.  $Th_1 = 0.0003$  a.u. can be used up to the  $C_{15}H_{16}O$  chain. For larger systems, the calculation becomes unfeasible, and a similar procedure will be applied with a greater value of  $Th_1$ .

Using larger values of  $Th_1$  affects more the transition energies of the small chains. Compared with the new reference  $Th_1 = 0.0003$  a.u., (i) for  $C_3H_4O$  molecule, the transition energy error is 0.03 eV for  $Th_1 = 0.001$  a.u., up to 0.07 eV for  $Th_1 = 0.003$  a.u.; (ii) for  $C_5H_6O$  molecule, this discrepancy is smaller: 0.01 eV to 0.05 eV; (iii) reliable results are obtained with the 0.003 a.u. threshold from the  $C_7H_8O$  molecule, with an error of 0.02 eV while finally, (iv) the error is smaller than 0.01 eV for  $n = 13$  and  $n = 15$ . As the error decreases with the size of the system, the  $Th_1 = 0.003$  a.u. value will be taken as new reference values for  $n \geq 13$ .

When the system becomes larger, the sizes of the calculations are dramatically decreased, if one compares with the  $Th_1 = 0$  a.u. For  $C_7H_8O$ , the dimension of the complete CI calculation is  $48 \times 10^6$  determinants. With the largest threshold ( $Th_1 = 0.003$  a.u.), this size is reduced to 10%. For  $C_{19}H_{20}O$ , the same threshold generates around 1% of the determinants. In addition to the reduced disk space, the consequence is that it saves a considerable amount of time. For  $C_7H_8O$ , 36 850 seconds per iteration are necessary for the complete

TABLE III. Total and transition energies obtained at MR-SDCI and MR-SDCI+Q (Davidson correction) levels as a function of the general threshold  $Th_1$  for the  $C_nH_{n+1}O$  molecules ( $n = 3$  to 9).

$Th_1$ (a.u.)	Total energy (a.u.) of the ground state		Total energy (a.u.) of the $n \rightarrow \pi^*$ state		$n \rightarrow \pi^*$ (eV)		
	SDCI	SDCI+Q	SDCI	SDCI+Q	SDCI	SDCI+Q	
$C_3H_4O$	<b>0.0000</b>	-191.311522	-191.385057	-191.109829	-191.236666	<b>5.49</b>	<b>4.04</b>
	0.0003	-191.310416	-191.383624	-191.108650	-191.234710	5.49	4.05
	0.0010	-191.306603	-191.378670	-191.103883	-191.226581	5.52	4.14
	0.0030	-191.291413	-191.359687	-191.086975	-191.201919	5.56	4.29
	<b>0.0000</b>	-268.402134	-268.525404	-268.182188	-268.344825	<b>5.99</b>	<b>4.91</b>
$C_5H_6O$	0.0003	-268.399799	-268.522296	-268.179663	-268.341021	5.99	4.93
	0.0010	-268.393121	-268.513397	-268.172463	-268.330476	6.00	4.98
	0.0030	-268.369297	-268.482634	-268.147444	-268.295608	6.04	5.09
	<b>0.0000</b>	-345.475202	-345.650072	-345.245250	-345.451671	<b>6.26</b>	<b>5.40</b>
	0.0003	-345.471681	-345.645358	-345.241616	-345.446484	6.26	5.41
$C_7H_8O$	0.0010	-345.462596	-345.633021	-345.232368	-345.433271	6.26	5.44
	0.0030	-345.430921	-345.591179	-345.200054	-345.389203	6.28	5.50
	<b>0.0000</b>	-422.535349	-422.762080	-422.299035	-422.552517	<b>6.43</b>	<b>5.70</b>
	0.0003	-422.530685	-422.755861	-422.294307	-422.545762	6.43	5.72
	0.0010	-422.519644	-422.740676	-422.283240	-422.530161	6.45	5.73
$C_9H_{10}O$	0.0030	-422.481552	-422.689549	-422.244599	-422.477397	6.45	5.77

TABLE IV. Influence of the general threshold ( $Th_1$ ) on the transition energy, on the number of determinants (Ndet), and on the central processing unit (cpu) time per iteration for the  $C_nH_{n+1}O$  molecules ( $n = 3$  to 25).

$Th_1$ (a.u.)	0.0000			0.0003			0.001			0.003		
	n	Ndet	cpu/it (s)	$\Delta E$ (eV)	Ndet	cpu/it (s)	$\Delta E$ (eV)	Ndet	cpu/it (s)	$\Delta E$ (eV)	Ndet	cpu/it (s)
3	3 014 784	200	5.49	2 231 727	135	5.49	1 580 881	60	5.52	728 639	25	5.56
5	15 359 724	2960	5.99	7 540 710	765	5.99	4 677 247	270	6.00	1 861 211	70	6.04
7	48 703 616	36850	6.26	16 296 029	3560	6.26	9 462 412	705	6.26	3 490 663	230	6.28
9	119 142 900	X <sup>a</sup>	6.43	28 544 009	4490	6.43	15 897 206	1415	6.43	5 652 906	305	6.45
11	247 386 816			44 276 307	9240	6.55	24 088 120	2505	6.55	8 369 850	580	6.56
13	458 757 404			63 334 747	15160	6.64	34 071 310	4125	6.64	11 515 128	745	6.64
15	783 189 504			86 079 605	20580	6.71	45 946 192	6220	6.71	15 250 250	1185	6.71
17	1 255 230 756			112 249 091			59 487 722	8980	6.76	19 509 650	2285	6.76
19	1 914 041 600			142 168 877			74 781 304			24 293 316	3165	6.81
21	2 803 395 276			175 539 609			91 827 218			29 516 980	3620	6.85
25	5 471 888 084			252 615 781			131 175 220			41 589 140	6600	6.90

<sup>a</sup>For  $n = 9$ , the calculation was so computationally demanding that we used the classical MRCI code (CASDI<sup>9</sup>), which takes more benefit of the symmetry  $C_s$  group.

CAS-SDCI calculation, while it only takes 230 seconds for the 0.003 a.u. threshold. This makes possible the calculation of a large molecule as  $C_{25}H_{26}O$ , with reliable results for only  $41 \times 10^6$  determinants instead of  $5 \times 10^9$ .

#### b. Integral Threshold $Th_i$ . Scaling of the number of integrals

In a second step, we have introduced an integral threshold  $Th_i$ , keeping the general  $Th_1$  threshold fixed to 0.003 a.u. The results are presented in Table V and Figure 2. With respect to  $Th_i = 0$  a.u., the largest value of the integral threshold ( $Th_i = 0.003$  a.u.) presents a maximal error on the transition energy of 0.02 eV, while it reduces the number of integrals by a factor thousand and the time by a factor 10 for the  $C_{25}H_{26}O$  molecule. One must notice that this discrepancy 1000/10 is not surprising, since, with  $Th_1 \neq 0$ , a lot of integrals are in the list but are not involved in any  $\sigma^n = H\Psi^n$  product.

The  $Th_i$  threshold on the  $(ac|bd)$  integrals imposes the four orbitals  $a, b, c, d$  to be in the same region of space. As a consequence, when  $Th_i$  is not equal to zero, the number of integrals grows linearly with the size of the system, as shown on Figure 2. However, one may notice that the con-

dition  $Th_i \neq 0$  does not guarantee by itself the linear scaling for the computational time. Indeed, if we consider the interaction of two determinants  $ij \rightarrow ab$  and  $ij \rightarrow cd$  through the  $(ac|bd)$  integral, (i) the  $Th_i$  threshold on the integrals imposes the four orbitals  $a, b, c, d$  to be in the same region of space, but does not impose any condition on  $i$  and  $j$ . (ii) The conditions  $Th_1 \neq 0$  and  $Th_i \neq 0$  impose the four orbitals  $i, j, a, b$  and also  $i, j, c, d$  to be in the same region of space. Then, all determinants involve connected orbitals and the dependence should be linear. For  $Th_1 = 0$ , the dependence is  $N^3$ .

#### c. Dispersion Threshold $Th_2$ . Scaling of the number of determinants

Finally, the third threshold named dispersion threshold ( $Th_2$ ) is introduced, keeping the preceding validated 0.003 a.u. value for  $Th_1$ . In order to analyse the dispersive effects, we have reset  $Th_i$  to zero. In Table VI, one can notice the very small effect of these dispersion determinants on the transition energy between the ground and the  $n \rightarrow \pi^*$  excited state in aldehydes: a maximal deviation of 0.03 eV is found when  $Th_2 = 0.003$  a.u. As can be seen in Figure 3, the number of determinants grows linearly with  $n$ .

TABLE V. Influence of the integral threshold ( $Th_i$ ) on the transition energy ( $\Delta E$ ) and on the dimensions of the calculation with  $Th_1 = 0.003$  a.u. Nint is the number of integrals for the  $C_nH_{n+1}O$  molecules ( $n = 3$  to 25).

$Th_i$ (a.u.)	0.000			0.0003			0.003		
	n	Nint	cpu/it (s)	$\Delta E$ (eV)	Nint	cpu/it (s)	$\Delta E$ (eV)	Nint	cpu/it (s)
3	3 086 370	25	5.56	2 622 981	25	5.56	630 594	10	5.55
5	16 077 285	70	6.04	9 015 105	55	6.04	1 137 297	23	6.02
7	51 536 628	230	6.28	17 785 848	130	6.28	1 622 127	42	6.27
9	126 890 415	305	6.45	27 062 781	205	6.45	2 109 078	69	6.43
11	264 603 510	580	6.56	36 544 479	270	6.56	2 578 194	128	6.55
13	492 179 625	745	6.64	45 892 659	330	6.64	3 051 750	176	6.63
15	842 161 320	1185	6.71	55 425 315	400	6.71	3 537 267	238	6.70
17	1 352 130 003	2285	6.76	64 996 539	730	6.76	4 018 164	314	6.75
19	2 064 705 930	3165	6.81	74 572 395	855	6.81	4 499 979	360	6.80
21	3 027 548 205	3620	6.85	84 120 105	960	6.85	4 975 506	471	6.84
25	5 919 862 455	6600	6.90	102 659 277	1450	6.90	5 930 955	680	6.89

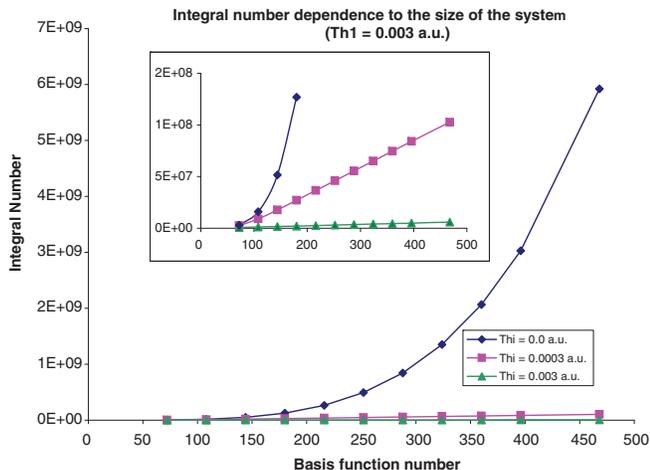


FIG. 2. Scaling of the number of integrals number with the number of basis functions for the  $C_nH_{n+1}O$  molecules ( $n = 3$  to 25).

TABLE VI. Influence of the dispersion threshold ( $Th_2$ ) on the transition energy ( $\Delta E$ ) and on the dimensions of the calculation with  $Th_1 = 0.003$  a.u. and  $Th_i = 0.0$  a.u. for the  $C_nH_{n+1}O$  molecules ( $n = 3$  to 25).

$Th_2$ (a.u.)	0.000			0.003		
	Ndet	cpu/it (s)	$\Delta E$ (eV)	Ndet	cpu/it (s)	$\Delta E$ (eV)
3	728 639	25	5.56	476 243	14	5.55
5	1 861 211	70	6.04	882 963	36	6.02
7	3 490 663	235	6.28	1 266 247	62	6.26
9	5 652 906	305	6.45	1 665 006	103	6.42
11	8 369 850	585	6.56	2 080 906	160	6.54
13	11 515 128	745	6.64	2 457 704	236	6.62
15	15 250 250	1170	6.71	2 864 762	344	6.69
17	19 509 650	2270	6.76	3 268 866	483	6.74
19	24 293 316	3165	6.81	3 675 732	660	6.79
21	29 516 980	3655	6.85	4 060 132	880	6.83
25	41 589 140	6555	6.90	4 848 260	1460	6.89

TABLE VII. Influence of all thresholds on the transition energy  $\Delta E$  and on the dimensions of the calculation for the  $C_nH_{n+1}O$  molecules ( $n = 3$  to 25).

$Th_1 = Th_i = Th_2$ (a.u.)	0.000				0.003			
	Ndet	Nint	cpu/it (s)	$\Delta E$ (eV)	Ndet	Nint	cpu/it (s)	$\Delta E$ (eV)
3	3 014 784	3 086 370	200	5.49	476 243	630 594	8	5.55
5	15 359 724	16 077 285	2960	5.99	882 963	1 137 297	14	6.01
7	48 703 616	51 536 628	36 850	6.26	1 266 247	1 622 127	21	6.26
9	119 142 900	126 890 415	X	6.43	1 665 006	2 109 078	29	6.43
11	247 386 816	264 603 510			2 080 906	2 578 194	47	6.54
13	458 757 404	492 179 625			2 457 704	3 051 750	59	6.62
15	783 189 504	842 161 320			2 864 762	3 537 267	72	6.69
17	1 255 230 756	1 352 130 003			3 268 866	4 018 164	86	6.75
19	1 914 041 600	2 064 705 930			3 675 732	4 499 979	102	6.79
21	2 803 395 276	3 027 548 205			4 060 132	4 975 506	119	6.83
25	5 471 888 084	5 919 862 455			4 848 260	5 930 955	180	6.89

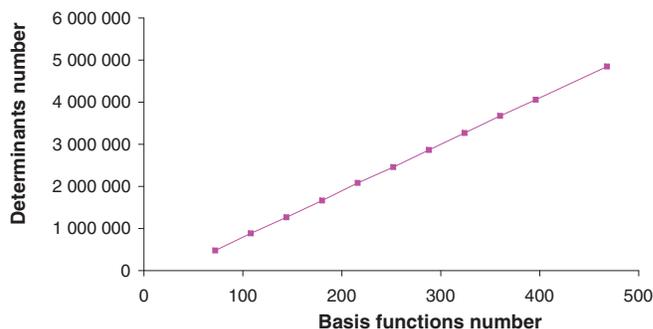


FIG. 3. Scaling of the determinant number with the number of basis functions for the  $C_nH_{n+1}O$  molecules ( $n = 3$  to 25).  $Th_1 = 0.003$  a.u. and  $Th_2 = 0.003$  a.u.

*d. Scaling of the computational time with the size of the system* Finally, the three thresholds are introduced at the same time. As we can see in Table VII, a good agreement is obtained for transition energies (maximum error of 0.06 eV); the number of determinants and the number of integrals are lowered until 0.1% for the more extended system while the time per iteration is now around 0.06% for  $C_7H_8O$ .

The accuracy of the MRCI transition energies obtained with non-zero thresholds is comparable with the same calculations without any approximation, in particular when the molecule is extended.

The scaling of the computational time is represented on Figure 4. Two curves are represented: one with  $Th_1 = Th_2 = Th_i = 0.003$  a.u., the other one with  $Th_1 = Th_2 = Th_i = 0.001$  a.u. Despite that the number of integrals and of determinants grows linearly with the size of the system, there is a deviation from linearity. Several reasons may be mentioned:

- Some not time consuming processes do not grow linearly with  $N$  during the calculation. In particular, concerning the truncation of the list of integrals, all those that have at least two equal indices are kept. In particular,  $(ij|il)$  integrals appearing in the interaction of two determinants that differ with only one excitation are kept whatever the values of the exchange integrals  $K_{ij}$ ,  $K_{il}$ ,

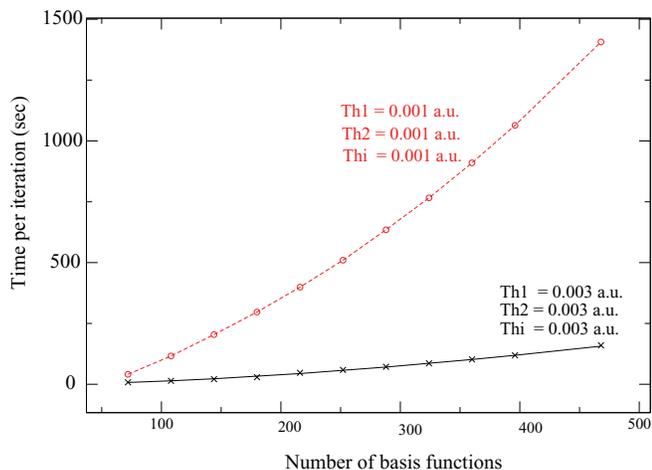
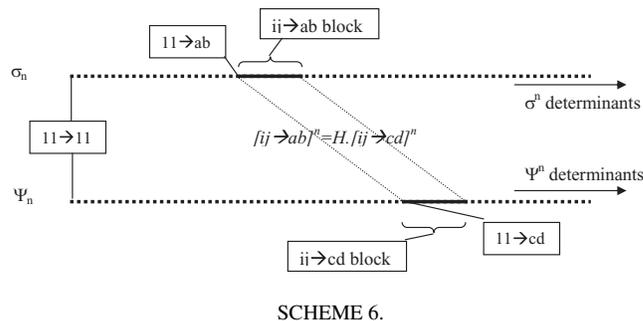


FIG. 4. Time dependence to the number of basis functions.

and  $K_{jl}$ . In the same way, some determinants corresponding to distant excitations are kept in the basis even when applying  $Th_2$  such as, in Scheme 3, the second cases of the last two lines (“2h1p or 1h2p”, “2h2p”). There would be no technical difficulty in applying the same truncation rules as defined before, but it deteriorates the results for a small saving of computational time.

- Another reason for the non-linear scaling of the computational time has perhaps a more technical origin. In a CAS+SDCI code without any truncation, it is easy to code the  $\sigma^n = H\Psi^n$  product in such a way that many coefficients of  $\sigma^n$  and  $\Psi^n$  that appear sequentially in the operation are contiguous in the memory of the computer. For example, if one considers the case  $[ij \rightarrow ab]^n = H.[ij \rightarrow cd]^n$ , the determinants  $ij \rightarrow ab$  and  $ij \rightarrow cd$  can be addressed by blocks beginning at  $(1,1,a,b)$  and  $(1,1,c,d)$  the lengths of which are the number of possible values of the pair  $(i,j)$ , as illustrated in Scheme 6. In the present code, the determinants are no more addressed according to their indices  $i, j, a$ , and  $b$ , but according to the pairs  $(i,a)$ ,  $(j,b)$  to guarantee a list without lacking determinant. As a consequence, the above product no more concerns quantities that are stored in memory in a contiguous way. When the size  $N$  of the CI is large, the cost of the product grows with a scaling slightly larger than  $N$  if the coefficients appear in a random order.



SCHEME 6.

## B. Complexation reaction of an atrazine metabolite with $\text{Ca}^{2+}$

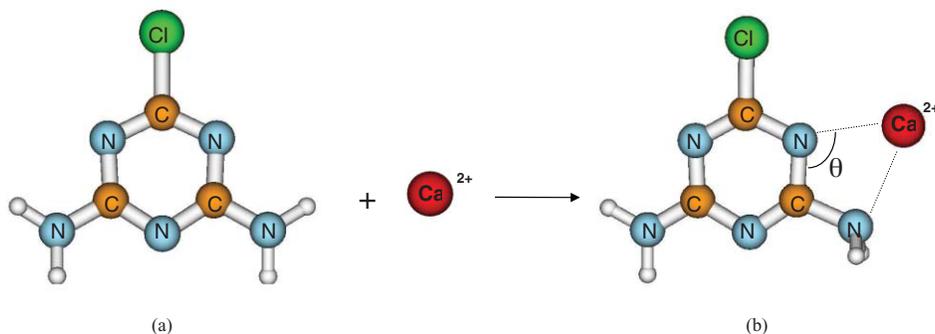
The 2-chloro-1,3,5-triazine-4,6-diamine molecule denoted AtrMod thereafter (see Figure 5(a)) is a metabolite of the well-known atrazine pesticide. To understand the adsorption and desorption processes of pesticide in soil, the study of their complexes with soil abundant cations is interesting. To evaluate the ability of selected SDCI calculations to compute energy pathways, the lowest complex of AtrMod with  $\text{Ca}^{2+}$  has been chosen for its large complexation energy.<sup>58</sup> Figure 5 shows the complexation reaction of AtrMod (Figure 5(a)) with  $\text{Ca}^{2+}$  which leads to the AtrMod- $\text{Ca}^{2+}$  complex (Figure 5(b)).

### 1. Computational details

The computations have been performed using geometries optimized with the GAUSSIAN 03 package<sup>59</sup> at the B3LYP hybrid functional<sup>60–62</sup> level with the standard Pople 6–31G\* basis set for C, N, H, and the corresponding Francl for Cl<sup>63</sup> and Blaudeau for Ca.<sup>64</sup> This double-zeta plus polarisation (DZP) basis set has also been used for the dissociation potential energy curve. However, an extended triple-zeta plus polarisation (TZP) basis set such as the 6–311+G(2d, 2p) is necessary to compute accurate complexation energy. This standard basis set was used for the first row atoms, the corresponding basis sets of MacLean-Chandler for Cl<sup>65</sup> and Blaudeau for Ca (Ref. 64) were used in this case.

### 2. The dissociation potential energy curve

The dissociation potential energy curve has been plotted on Figure 6 as a function of the AtrMod- $\text{Ca}^{2+}$

FIG. 5. Complexation of (a) AtrMod. (b) AtrMod- $\text{Ca}^{2+}$ .

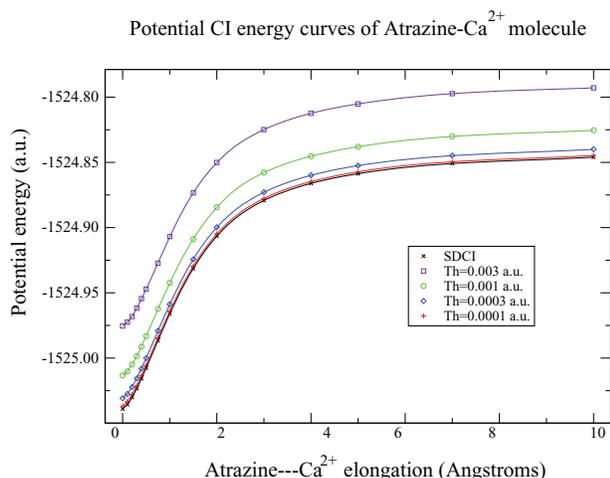


FIG. 6. Potential energy curves of AtrMod-Ca<sup>2+</sup> at selected and complete SDCI levels.

distance at the SDCI/DZP level using various sets of thresholds (with  $Th_1 = Th_2 = Th_i$ ). For these sets of equal thresholds, we will use the  $Th$  denomination thereafter. From the lowest AtrMod-Ca<sup>2+</sup> minimum, the Ca<sup>2+</sup> cation has been moved away from AtrMod. The distance has been varied from the equilibrium situation (2.372 Å to the closest cycle nitrogen) to 12.372 Å, which corresponds to a total elongation of 10 Å, keeping the  $\theta$  angle constant (see Figure 5(b)). When thresholds  $Th$  of 0.0001 a.u. are used, the number of determinants (Ndet) is divided by three and the results are about as accurate as with the SDCI performed without thresholds. On Figure 7, the relative error to the SDCI results (without thresholds) is represented for each set of thresholds.

With  $Th = 0.0001$  a.u., the largest error is of 0.5 kcal/mol, which is lower than the expected precision of the calculation. Using  $Th$  of 0.0003 a.u. also gives accurate results with a maximum error of 1.3 kcal/mol. The other sets of thresholds ( $Th = 0.001$  and 0.003 a.u.) lead to larger maximum error (3.1 and 6.5 kcal/mol, respectively).

Far from the equilibrium region, the error in the interaction energy is expected to be very small for any threshold, since dispersion (Scheme 7(c)) and double excitation charge

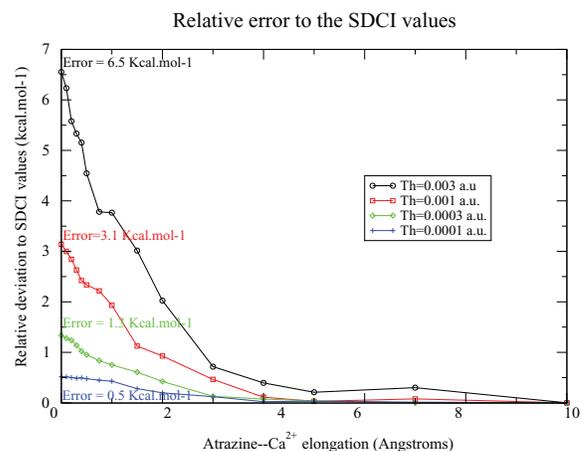


FIG. 7. Relative errors of the selected SDCI to the complete SDCI energies for AtrMod-Ca<sup>2+</sup>.

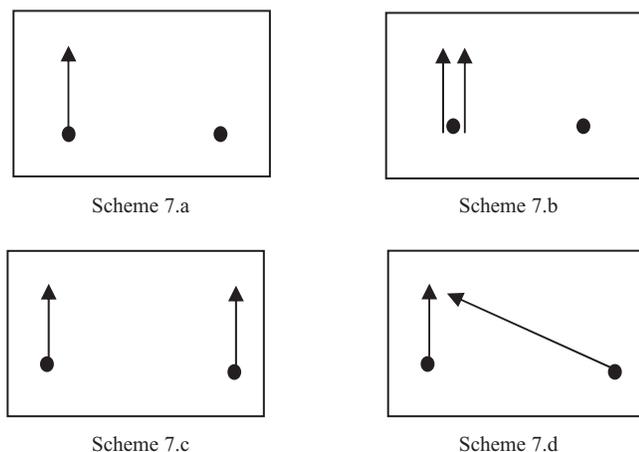
transfer (Scheme 7(d)) involving the Ca<sup>2+</sup> ion should vanish. Indeed, all curves are parallel but do not superimpose (Figure 6), since local single and double excitations (Schemes 7(a) and 7(b)) are taken into account on each fragment with an increasing error on total energy for the AtrMod fragment. As a consequence, the asymptotic value of the curves of Figure 6 is lower for smaller thresholds.

In the schemes 7, the two points represent AtrMod and Ca<sup>2+</sup> and the arrows intra- or inter molecular excitations.

During the Ca<sup>2+</sup> approach to AtrMod, the error increases up to the equilibrium distance.

The behaviour for intermediate distances shows that the intersystem contributions to the energy appear for an elongation around 3 to 4 Å.

Some discontinuities in the potential energy curve of selected SDCI method can be observed. However, for the two smallest thresholds, this phenomenon is quite weak and as no consequence for the shape of the curve. Even for  $Th = 0.003$  a.u., the result can be considered as not satisfactory, not because of the noise on the curve, but because of the error of 6.5 kcal mol<sup>-1</sup> on the interaction energy. To avoid this phenomenon, a solution would be to have the same topological interaction matrix for all distances, for example, by transferring the matrix of the equilibrium to the other distances.



SCHEME 7.

### 3. Complexation energy calculations

The complexation energy  $E_{\text{comp}}$  of AtrMod with Ca<sup>2+</sup> has been computed at the SDCI/TZP level using various sets of thresholds from the largest  $Th = 0.003$  a.u. to the smallest 0.0001 a.u. The reference SDCI/TZP computation has been performed without threshold. To be comparable to the already computed CCSD(T)/TZP results,<sup>58</sup> each complexation energy has been corrected from size-consistency error with the Davidson correction (see SDCI+Q energies in Table VIII). The reference SDCI+Q/TZP complexation energy is in good agreement with the CCSD(T)/TZP value (+0.7 kcal/mol). The largest thresholds results are far from the expected value (+7.7 kcal/mol to the complete SDCI+Q). At the contrary, the  $Th = 0.0001$  a.u. set of thresholds gives

TABLE VIII. Complexation energies of AtraMod-Ca<sup>2+</sup> in kcal mol<sup>-1</sup> at the CCSD(T)/TZP, SDCI/TZP, and SDCI+Q/TZP levels. Reference results (obtained without thresholds) are given in bold. The number of determinants (Ndet) is given for the selected and complete SDCI calculations.

$Th_1 = Th_2$ = $Th_i$ (a.u.)	0.003	0.001	0.0003	0.0001	<b>0</b>
CCSD(T)/TZP					<b>-91.6</b>
SDCI/TZP	-69.1	-68.1	-70.7	-72.5	<b>-73.4</b>
SDCI+Q/TZP	-83.3	-83.2	-87.0	-89.6	<b>-90.9</b>
Ndet	1 146 303	4 459 744	17 278 731	36 666 784	<b>99 662 193</b>

reasonable results when compared to the reference SDCI and SDCI+Q complexation energies (+0.9 and +1.3 kcal/mol, respectively), while it corresponds to a quite important reduction of the number of determinants.

As a conclusion of Sec. II B, the complexation energy computed with Davidson size-consistency correction is nearly as accurate as the CCSD(T)/TZP value when using  $Th = 0.0001$  a.u. Moreover, the dissociation energy curve of AtraMod-Ca<sup>2+</sup> is perfectly described when using thresholds  $Th$  of 0.0001 a.u. and correctly reproduced with  $Th = 0.0003$  a.u. In these two cases, the small discontinuities can hardly be detected.

Compared with the above study on transition energies, smaller thresholds have to be used in order to get results of similar quality. Indeed, as the number of interacting entities grows, an increasing number of intersystem interactions are neglected when thresholds are applied.

One can also notice another interesting use of the thresholds. It permits to identify the elongation distance for which the dispersive effects begin to be non-negligible in the association process of Ca<sup>2+</sup> with AtraMod.

### C. d-d spectroscopy of a metal transition complex

The [2,6 di-(pyrazol-1-yl)pyridine]<sub>2</sub>-Fe<sup>II</sup> complex (Figure 8, hydrogen atoms are not shown) presents a LIEST effect. At low temperature, the ground state is low spin. The spin state transition occurs at 260 K. In the x-ray structure<sup>66</sup>,

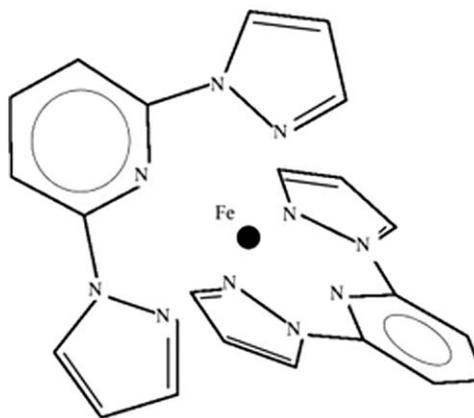


FIG. 8. [2,6 di-(pyrazol-1-yl) pyridine]<sub>2</sub>-Fe<sup>II</sup>.

the two ligand geometries deviated slightly from the C<sub>2v</sub> symmetry.

In this example, we studied the *d-d* spectroscopy of the low spin complex in the C<sub>2v</sub> “symmetrized” geometry. A Barandiaran effective core potential (ECP) with the associated basis set (9s6p6d3f contracted to [3s3p4d1f]) is used for Fe (14 valence electrons)<sup>67</sup> and ANO-L<sup>68</sup> basis sets were employed for C (14s9p4d3f)/[3s2p], N (14s9p4d3f)/[3s2p1d] and H (8s4p3d)/[2s].

In order to study *d-d* transitions, the active space was composed of the 6 *d*-electrons and the 5 *d*-orbitals of the iron generating 100 determinants in the reference space. The seven lowest states have been calculated: the a<sup>1</sup>A<sub>1</sub> ground state, three quintets (a<sup>5</sup>B<sub>1</sub>, a<sup>5</sup>B<sub>2</sub>, a<sup>5</sup>A<sub>2</sub>) and three triplets (a<sup>3</sup>B<sub>1</sub>, a<sup>3</sup>B<sub>2</sub>, a<sup>3</sup>A<sub>2</sub>). The localized ground state CASSCF molecular orbitals were used to start all the calculations performed at the SDCI level (Table IX).

The dimension of a complete CAS-SDCI without any threshold is 68 × 10<sup>9</sup>, while the CAS-SDCI with the three thresholds set to 0.003 a.u. generates 272 × 10<sup>6</sup> determinants. In order to test the validity of this level of approximation, we have reduced the active space to multireference determinants for which the coefficients are greater than 0.05 in the CI wave functions, keeping spin eigenfunctions. Thus, the weight of the CAS references is very slightly modified (less

TABLE IX. d-d transition energies of [2,6 di-(pyrazol-1-yl) pyridine]<sub>2</sub>-Fe<sup>II</sup> complex obtained at SDCI level (in eV).

	CAS-SDCI (CAS-SDCI+Q)	MR-SDCI	MR-SDCI	MR-SDCI	MR-SDCI	MR-SDCI
$Th_1$	0.003	0.003	0.001	0.0005	0.003	0.001
$Th_i$	0.003	0.003	0.003	0.003	0.001	0.001
$Th_2$	0.003	0.003	0.003	0.003	0.003	0.001
a <sup>1</sup> A <sub>1</sub>	0.00	0.00	0.00	0.00	0.00	0.00
a <sup>5</sup> B <sub>1</sub>	0.42 (0.53)	0.40	0.42	0.43	0.39	0.41
a <sup>5</sup> B <sub>2</sub>	0.43 (0.54)	0.41	0.43	0.44	0.40	0.42
a <sup>5</sup> A <sub>2</sub>	0.69 (0.79)	0.67	0.68	0.70	0.66	0.68
a <sup>3</sup> B <sub>1</sub>	1.17 (1.21)	1.22	1.23	1.24	1.22	1.23
a <sup>3</sup> B <sub>2</sub>	1.08 (1.13)	1.13	1.14	1.14	1.13	1.14
a <sup>3</sup> A <sub>2</sub>	0.69 (0.74)	0.74	0.73	0.74	0.73	0.73
cpu/it/root (s)	10 900	1800	10 000	35 000	3100	13 730
Ndet (millions)	272	70	200	486	70	268

than  $10^{-3}$ ), while the largest reference space is reduced by a factor 5 (19 determinants). This allows one to lower the values of the thresholds and therefore to test the stability of the results. This approximation introduces a small deviation of 0.02 eV for the singlet-quintets excitation energies and until 0.05 eV for the singlet-triplets ones. Then, the general  $Th_1$  threshold has been decreased to 0.001 a.u. and 0.0005 a.u. The transition energies are very slightly modified (at most 0.03 eV) while the number of determinants is considerably augmented (from  $70 \times 10^6$  until 486). The integral threshold as well as the dispersion one does not change the results when there are lowered to 0.001 a.u., respectively, for a reasonable supplementary computational cost. Finally, the results are very stable and the largest thresholds are already satisfactory.

Concerning the size-consistency error, as the coefficients are very similar for each set of quintet or triplet states whatever thresholds are concerned, the Davidson correction has also very similar effect on the transition energies: between 0.09 eV and 0.11 eV on the transition energies of the quintet states and between 0.03 and 0.05 eV for the triplet ones. So, only one set of Davidson corrected transition energies are reported in Table IX (values between parentheses given in column 2).

#### IV. CONCLUSION

A MRCI procedure using localized orbitals in order to reduce the size of the CI matrix has been proposed. Thank to the introduction of two parameters ( $Th_1$  and  $Th_2$ ) to reduce the number of determinants and a third one ( $Th_i$ ) to shorten the list of repulsion integrals, a quasi-linear scaling behaviour is obtained.

The reductions of the size of the CI matrix and of the number of two electron repulsion integrals are based on topological considerations. Two localized orbitals  $i$  and  $j$  are considered as interacting, if the corresponding exchange integral  $K_{ij}$  is larger than a given threshold. The code lets the possibility to use different thresholds for the integrals ( $Th_i$ ) and for the determinants. In the latter case, two thresholds are available: a first one ( $Th_1$ ) concerns the occupied/virtual interactions and a second one ( $Th_2$ ) can be used to reduce even more the number of determinants by neglecting some dispersive effects.  $Th_1$  and  $Th_2$  can also be considered as analyzing tools. Concerning the repulsion integrals, a second parameter  $Th_{ij}$  could be introduced to distinguish, in the integral  $(ij|1/r_{12}|kl)$ , what concerns the overlap between  $i$  and  $j$  (respectively  $k$  and  $l$ ) and the interaction between the  $ij$  and  $kl$  distributions.

The various studied applications show that the choice of the thresholds seems to depend on what is under consideration (transition energy, reaction energy, etc. . .) and – as for the size of the atomic basis sets – has to be converged to guarantee quality of the results.

This approach permits a huge reduction of the CI size and of the computational time, which makes possible to perform CI calculations for the ground and excited states of large molecules. The dependence of the computational time to the number of basis function is not strictly linear. But one must notice that, in the examples presented in this work, the re-

duction of the computational cost was large enough so that the CI is no more the bottleneck of the calculation. The parts corresponding to the calculation of atomic integrals and the integral transformation are by far more demanding steps. In the study of the  $C_{25}H_{26}O$  molecule, the atomic integrals calculation, the SCF step and the integral transformation (MOLCAS package<sup>11</sup>, without using the Cholesky decomposition) took respectively 2h20, 0h30, and 1h40 of computational time while the CI step needed only 0h55 ( $Th_1 = Th_2 = Th_i = 0.003$  a.u.). All calculations have been performed on an Intel Xeon 2.66 GHz computer. Work is in progress to use Cholesky decomposition<sup>41,42</sup> in the integral transformation to obtain an efficient code at all steps of the calculation.

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