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Multireference perturbation CI IV. Selection procedure for one-electron properties

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Abstract. We present in this paper a modification of the selection procedure, within the CIPSI algorithm, specifically intended for the calculation of one-electron properties. In this new procedure the determinants are selected following their contribution to a certain one-electron property. As test cases we report the calculation of the electric dipole of carbon monoxide and of the hyperfine coupling constants of the CH_3 radical.

Key words: Multireference CI – Perturbation CI – CIPSI – One-electron properties

Introduction

In the last decades a large effort has been devoted to the development of post Hartree-Fock methods for the accurate calculation of electronic energies and wavefunctions. Different criteria are used to evaluate the accuracy of the wavefunction such as, for instance, the energy variational principle for variational calculations or the norm of the perturbation correction to the wavefunction in perturbation calculations. These criteria are the basis for the construction of iterative strategies which allow a progressive improvement of the accuracy of the calculation, as in the case of the MRDCI [1] and CIPSI [2] methods. Once the wavefunction is known, the physical properties can be calculated as the mean value of the associated operator on the wavefunction. We shall consider here only one-electron properties. Following this approach it is quite difficult to control the accuracy of the value obtained for the physical property. Indeed it is not guaranteed that determinants (or configurations) which give large contributions to the energy (or to large changes in the wavefunction) do the same for a certain one-electron property. A limiting case can be conceived, where the determinantal space can be divided in two different sets: the first containing the determinants which contribute to the energy with a negligible contribution to the one-electron property and the complementary space containing the determinants needed to correctly describe the one-electron property. In this case, in order to have an accurate value of the property, one should approach the full CI (FCI) limit for the energy and thus perform very large CI calculations. Usually the situation is not so dramatic, but a slow convergence of the properties with respect to the number of determinants used in the CI is often observed. We present in the next section the basis of a new selection procedure within the frame of the CIPSI [2, 3, 4, 5] algorithm which allows the determinants giving a large contribution to the description of the one-electron property to be identified. In order to test the new approach and to compare it with the selection procedure used for the energy calculation which, in its original formulation [2] as well as in successive reelaborations [6, 7], is based on the contributions to the wavefunction, we report below two test cases: the electric dipole of CO and the hyperfine coupling constants of CH_3.

Method

In recent papers [6, 7] (parts I and II of this series) we have revised the original CIPSI algorithm. Briefly one identifies a variational space called S which contains the most important determinants describing the electronic states under investigation. The Hamiltonian projected onto S is diagonalized and the eigenstates are taken as zero-order descriptions of the true wavefunctions

$$\hat{\mathrm{P}}\mathscr{H}\hat{\mathrm{P}}\left|\Psi_m^{(0)}\right\rangle = E_m^{(MR)}\left|\Psi_m^{(0)}\right\rangle \tag{1}$$

$$\hat{\mathrm{P}} = \sum_{N\in S}|N\rangle\langle N| \quad \left|\Psi_m^{(0)}\right\rangle = \sum_{N\in S} C_N^m|N\rangle \tag{2}$$

The contributions of the determinants not belonging to S are evaluated by a second-order Rayleigh-

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Schrödinger treatment. Two different partitions of the Hamiltonian ($\hat{\mathscr{H}} = \hat{\mathscr{H}}_0 + \hat{\mathscr{V}}$) are implemented: the Epstein-Nesbet (EN) and the Møller-Plesset barycentric (MPB) procedures. The second-order energy correction is

$$E_m^{(2)} = -\sum_{I \notin S} \frac{\left| \left\langle I \middle| \hat{\mathscr{V}} \middle| \Psi_m^{(0)} \right\rangle \right|^2}{E_I - E_m^{(0)}} \tag{3}$$

and the first-order correction to the wavefunction is

$$\left| \Psi_m^{(1)} \right\rangle = -\sum_{I \notin S} |I\rangle \frac{\left\langle I \middle| \hat{\mathscr{V}} \middle| \Psi_m^{(0)} \right\rangle}{E_I - E_m^{(MR)}} = \sum_{I \notin S} C_{I,m} |I\rangle \tag{4}$$

In the CIPSI algorithm the S space is iteratively enlarged to include new determinants. In refs. [6, 7] we have proposed some new improvements to the original algorithm. In particular we have devised a new selection procedure, called "*aimed* selection", which ensures a balanced description of different states at different nuclear geometries. Both in the original (Ψ-selection) and in the *aimed* selection, the aim is to choose from the determinants treated by perturbation at step n, a set of determinants to be added to S in order to obtain the variation space for step $n + 1$. The determinants are ranked following their perturbative contribution to the first order correction to the wavefunction. The two selection procedures differ only in the algorithm used to decide where the determinant list has to be truncated.

While this approach has been shown to provide high quality results for potential energy surfaces of ground and excited states for medium size molecules, difficulties may be met for some one-electron properties. A recent implementation of a fast diagrammatic algorithm for the evaluation of the first-order correction to the one-particle density matrices [8] (part III of this series) has allowed us to exploit rather large S spaces in the calculation of one-electron properties. These calculations have pointed out a general slow convergence of the obtained values with respect to the dimension of the S space. The convergence can be speeded up in some cases with an appropriate choice of the molecular orbital set (as for instance with pseudo-natural orbitals).

In order to devise a general algorithm able to improve the convergence, we have reconsidered the criterion used to rank the determinants before selection. For the sake of simplicity we consider hereafter only state properties (for the transition ones the results can be easily generalized). First of all, let us write the expression of a one-electron property (indicated with **O**) in terms of the one-particle density matrix:

$$\mathbf{O} = \sum_{ij}^{N} O_{ij} \rho_{ij} \tag{5}$$

where N is the dimension of the one-electron basis set,

$$\rho_{ij} = \left\langle \Psi \middle| a_j^+ a_i \middle| \Psi \right\rangle \tag{6}$$

is the one-electron density matrix and

$$O_{ij} = \left\langle \varphi_i \middle| \hat{O} \middle| \varphi_j \right\rangle \tag{7}$$

is the matrix element between spin-orbitals φ_i and φ_j of the operator $\hat{O}$ associated to **O**.

In a perturbation scheme ρ is expanded in orders of perturbation

$$\rho = \rho^{(0)} + \rho^{(1)} + \ldots \tag{8}$$

The property **O** will accordingly have the expression

$$\begin{array}{lll} \mathbf{O} & = & \mathbf{O}^{(0)} + \mathbf{O}^{(1)} + \ldots \\ & = & \sum_{ij}^{N} O_{ij} \rho_{ij}^{(0)} + \sum_{ij}^{N} O_{ij} \rho_{ij}^{(1)} + \ldots \end{array} \tag{9}$$

The zero- and first-order terms are

$$\rho_{ij}^{(0)} = \left\langle \Psi^{(0)} \middle| a_j^+ a_i \middle| \Psi^{(0)} \right\rangle \tag{10}$$

$$\rho_{ij}^{(1)} = \left\langle \Psi^{(0)} \middle| a_j^+ a_i \middle| \Psi^{(1)} \right\rangle + \left\langle \Psi^{(1)} \middle| a_j^+ a_i \middle| \Psi^{(0)} \right\rangle \tag{11}$$

Using expression (4) for $\Psi^{(1)}$, $\rho_{ij}^{(1)}$ can be written as

$$\rho_{ij}^{(1)} = \sum_{I \notin S} C_I \left\{ \left\langle \Psi^{(0)} \middle| a_j^+ a_i \middle| I \right\rangle + \left\langle I \middle| a_j^+ a_i \middle| \Psi^{(0)} \right\rangle \right\} \tag{12}$$

Therefore the first-order correction to **O** is

$$\mathbf{O}^{(1)} = \sum_{I \notin S} C_I \sum_{ij} \mathbf{O}_{ij} \left\{ \left\langle \Psi^{(0)} \middle| a_j^+ a_i \middle| I \right\rangle + \left\langle I \middle| a_j^+ a_i \middle| \Psi^{(0)} \right\rangle \right\} \tag{13}$$

and we can identify the contribution of the determinant $|I\rangle$ to $\mathbf{O}^{(1)}$ as

$$\mathbf{O}_I^{(1)} = C_I \sum_{ij} \mathbf{O}_{ij} \left\{ \left\langle \Psi^{(0)} \middle| a_j^+ a_i \middle| I \right\rangle + \left\langle I \middle| a_j^+ a_i \middle| \Psi^{(0)} \right\rangle \right\} \tag{14}$$

We can therefore use $\mathbf{O}_I^{(1)}$ as a criterion to rank the determinants and select the ones to be added to the S space for the next step using a threshold η

$$|I\rangle \rightarrow S \quad \text{if} \quad \left| \mathbf{O}_I^{(1)} \right| \geq \eta \tag{15}$$

This new selection procedure is called hereafter "*property* selection". Note that from Eq. (12) for $\rho_{ij}^{(1)}$, only determinants $|I\rangle$ which are a single excitation with respect to some determinant in S can be selected in this way. Remembering that single excitations usually give small contributions to the energy (the largest contributions coming from double excitations), this consideration immediately shows that the two ranking criteria can strongly differ. Finally let us note that doubly excited determinants may contribute to the one-electron property: their contributions appear in the second-order correction to the density matrix and are simply not considered here.

In the next section we present the results obtained following this approach in two test cases.

Test case: the electric dipole of CO

The calculation of the electric dipole moment of CO (μ) in its ground state has represented a challenge for theoretical chemistry for a long time. For a short review and a clear illustration of the origins of such difficulties, the reader is referred to ref. [9]. As we are concerned essentially with the convergence trend with the dimension of the CI space, we report here only calculations at the experimental equilibrium geometry ($R_e = 2.132$ au) and with the ANO basis set of Widmark and collaborators [10], which consists of a (14*s*9*p*4*d*3*f*) contracted to [7*s*7*p*4*d*3*f*] (138 basis functions). Work is in progress in our laboratory for a complete study on CO (transition dipole moments as function of *R* and the importance of the basis set composition). The orbitals are the natural orbitals of a CASSCF calculation: the active space contains ten electrons and is defined by the orbitals derived from the eight 2*s* and 2*p* valence atomic orbitals (10 electrons in 8 orbitals, 328 configurations of A_g symmetry in the D_{2h} group). The CASSCF calculations have been carried out using the DALTON suite of programs [11].

In Fig. 1 we report μ as a function of the dimension of the *S* space in the case of the wavefunction-driven (*aimed*) selection procedure. In the first step the *S* space contains only one closed shell determinant with the seven doubly occupied orbitals having occupation numbers close to two in the CAS wavefunction. It is evident that the *property* selection procedure must be applied to a wavefunction which already includes electron correlation to a good level. Actually, a purely property-driven selection scheme would keep the wavefunction seriously lacking from the point of view of correlation. Therefore the *aimed* selection calculation is compared with a calculation where a few steps are performed using the wavefunction-driven method, followed by a *property* selection procedure. The results of such a calculation are reported in Fig. 2. We note that the *property* selection can be applied to an *S* space of larger dimension than in the case of the *aimed* selection because in the former only single excitations are generated and therefore *S* spaces of several thousands of determinants are easily accessible. The results presented in Fig. 2 clearly show the advantage of the *property* selection: the inclusion of a few hundreds of determinants selected in this way gives practically the limit values for the electric dipole and therefore the convergence behavior is strongly improved. Moreover the variational and perturbation results are very close to one other.

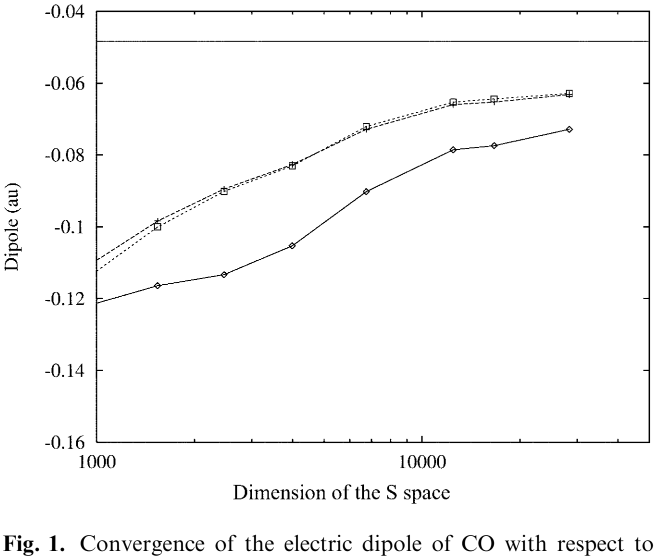

Fig. 1. Convergence of the electric dipole of CO with respect to the dimension of the *S* space using the *aimed* selection procedure. *Full line* → variational results, *dashed line* → EN perturbation results, *dotted line* → MPB perturbation results. *Horizontal full line* → experimental value (–0.0484 au [12])

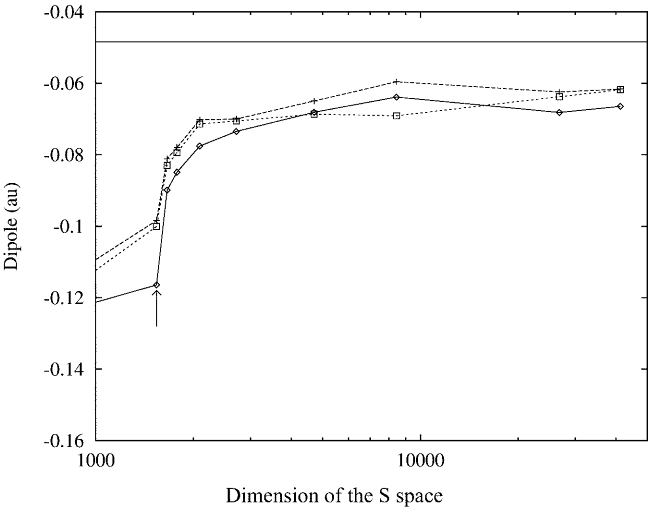

Fig. 2. The same as Fig. 1 but using the *aimed* selection for the first few steps and the *property* selection for the subsequent steps. The arrow indicates the "correlated wavefunction" expanded on 1540 determinants from which the *property* selection starts (see text)

Test case: the hyperfine coupling constants of CH_3

The calculation of hyperfine coupling constants (a_N, with N designating the nucleus) involves the accurate calculation of the total spin density of the electrons on the nuclei (for a recent review see, for instance, ref. [13]). In order to gain the correct behavior of the wavefunction at the nuclei the basis set must be sufficiently flexible for the core electrons: in particular the basis functions describing the 1*s* orbitals of second row atoms must be, at least partially, decontracted. In our calculation we use a modification of the cc-pvtz basis set [14]. The set of primitive *s* functions has been modified and a different contraction scheme has been considered [15]. This basis has been shown to give both correct energies and good EPR parameters in QCISD calculations [15]. The exponents and the contraction coefficients used in the present work are reported in Table 1.

It is well known that in order to compare theoretical and experimental values of a_N for CH_3, the effect of vibration must be considered, as has been shown by Barone and coworkers [18]. The static (i.e., calculated at the planar equilibrium geometry) values of $a_C = 27.8$ Gauss and $a_H = -24.6$ Gauss are seen to produce dynamic values (i.e., including the vibrational average) which agree well with experimental values.

As in the test case of the CO electric dipole, we are here only interested in the convergence behavior of

Table 1. The cc-pvtz basis set [14] modification [15] used in this work

Exponents	Contraction coefficients						
HYDROGEN							
s-type functions							
1500.00000	0.000050	0	0	0			
225.00000	0.000430	0	0	0			
33.87000	0.005610	0	0	0			
5.09500	0.045760	0	0	0			
1.15900	0.202472	1	0	0			
0.32580	0.504290	0	1	0			
0.10270	0.383130	0	0	1			
p-type functions							
1.4070	1	0					
0.3880	0	1					
CARBON							
s-type functions							
8236.0000	0.000531	−0.000113	0	0	0	0	0
1235.0000	0.004108	−0.000878	0	0	0	0	0
280.8000	0.021087	−0.004540	0	0	0	0	0
79.2700	0.081853	−0.018133	0	0	0	0	0
25.5900	0.234817	−0.055760	0	0	0	0	0
11.8760	0.000000	0.000000	1	0	0	0	0
8.9970	0.434401	−0.126895	0	0	0	0	0
4.2920	0.000000	0.000000	0	1	0	0	0
3.3190	0.346129	−0.170352	0	0	0	0	0
0.9059	0.039378	0.140382	0	0	1	0	0
0.3643	−0.008983	0.598684	0	0	0	0	0
0.1285	0.002385	0.395389	0	0	0	1	0
0.0469	0.000000	0.000000	0	0	0	0	1
p-type functions							
18.7100	0.014031	0	0				
4.1330	0.086866	0	0				
1.2000	0.290216	0	0				
0.3827	0.501008	1	0				
0.1209	0.343406	0	1				
d-type functions							
1.0970	1	0					
0.3180	0	1					
f-type functions							
0.7610	1						

the properties: therefore we shall consider only the experimental planar equilibrium geometry (R_e(C-H) = 1.079 Å [17]) and our reference "experimental" values are $a_C = 28$ Gauss and $a_H = -25$ Gauss. In a future work we shall apply the *property* selection procedure to a set of different small radicals and we shall discuss this kind of calculations at more length. We only note here that hyperfine coupling constants are usually computed using unrestricted formalisms (UHF, UMP2, etc.) where the spin polarization is easily described at the orbital level but such methods present problems when the (dynamic) electron correlation is important or the wavefunction has a multireference nature. On the contrary, the calculation of a_N is a difficult task in a restricted formalism because the spin polarization is introduced at the CI level, but there are standard procedures for the inclusion of static and dynamic electron correlations.

We report in Figs. 3 and 4 the convergence behavior for a_C using the *aimed* selection (Fig. 3) and some steps with the *aimed* selection (until S contains 1138 determinants) followed by other steps with the *property* selection (Fig. 4). The same calculations are reported in Figs. 5 and 6 for a_H. The comments of the previous section are still valid for this test case. The *property* selection procedure starting from a fairly well correlated wavefunction is able to increase the convergence of the computed properties with respect to the *aimed* selection procedure. In the case of hyperfine coupling constants, the ability of the new approach to correctly describe the property of interest is particularly noteworthy.

Conclusions

We have presented a modification of the selection procedure used in the CIPSI algorithm which is specifically devised for the calculation of one-electron properties. The new procedure has been applied in two test cases for two different properties. We have found that the convergence of the property as a function of the dimension of the S space is substantially improved with respect to the original procedure. We think that our novel approach is particularly well suited for the

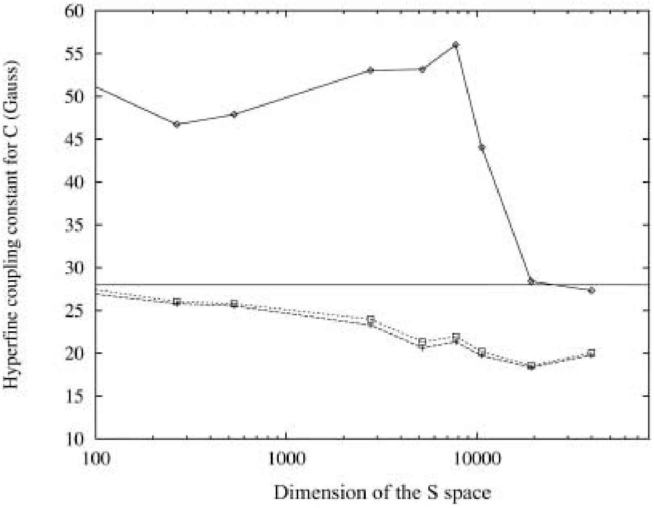

Fig. 3. Convergence of the hyperfine coupling constant of C with respect of the dimension of the *S* space selected using the *aimed* selection procedure. *Full line* → variational results, *dashed line* → EN perturbation results, *dotted line* → MPB perturbation results. *Horizontal full line* → "experimental" value (28 Gauss [16], see text)

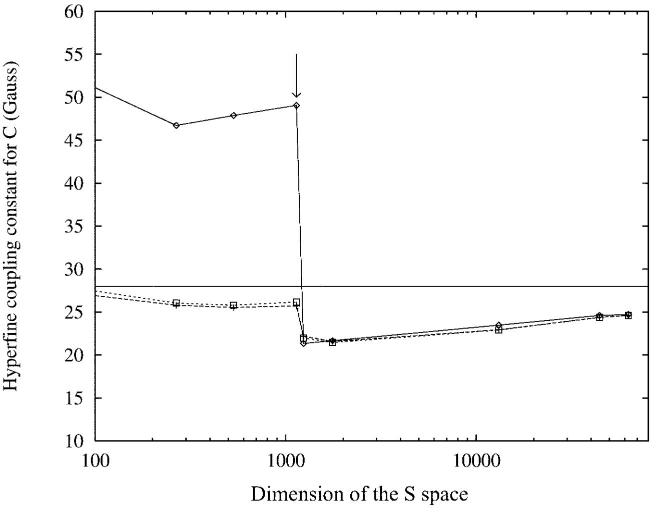

Fig. 4. The same as Fig. 3 but with the *aimed* + *property* selection procedure. The arrow indicates the "correlated wavefunction" expanded on 1138 determinants from which the *property* selection starts (see text)

calculation of hyperfine coupling constants in systems where the importance of electron correlation would make difficult the use of unrestricted methods. Further applications will be presented in the near future.

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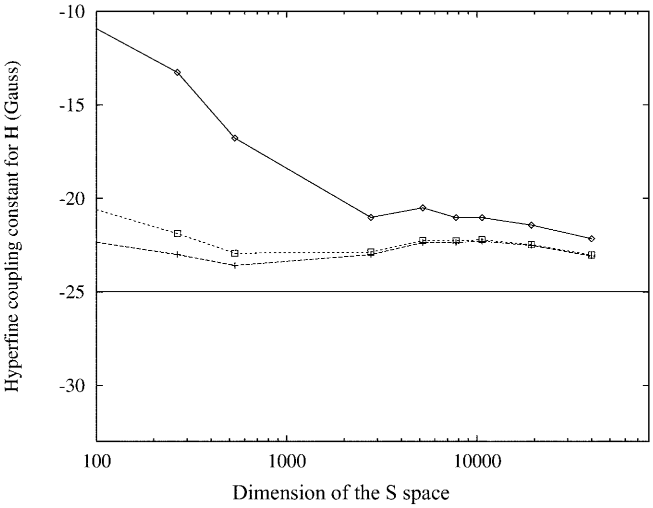

Fig. 5. The same as Fig. 3 but for the hyperfine coupling constant of H

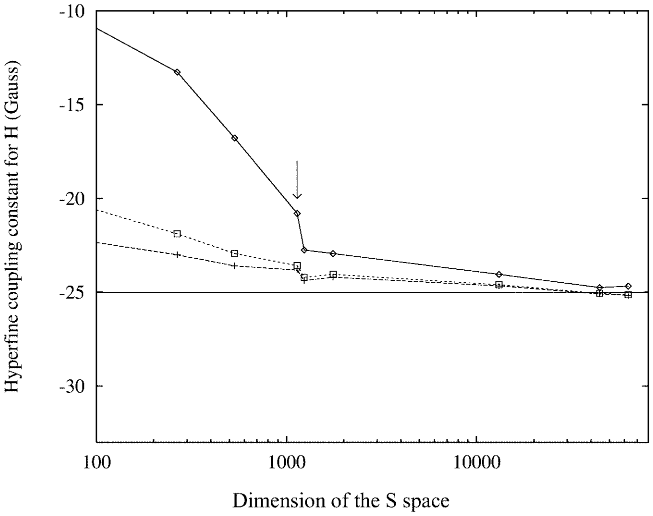

Fig. 6. The same as Fig. 4 but for the hyperfine coupling constant of H

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