

Size-consistent selected configuration interaction calculations. A few tests of efficiency

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As recently shown, size extensivity of any truncated or selected CI may be obtained by a self-consistent dressing of the determinant energies. This dressing has been implemented in two direct CI algorithms and its efficiency is illustrated on a series of eight-electron problems for which full-CI results are known (HF, H₂O, NH₃ in DZP basis sets). The dressing has been applied to CIs defined by single and double excitations on complete active spaces, single and double substitutions on selected reference spaces or by iterative double threshold selection. In most cases the dressing reduces the error by at least a factor of two to three and in selected CIs it makes it possible to save about one order of magnitude in the size of the CI. The best results are obtained from iteratively selected CIs, the error being lower than 5×10^{-4} hartree for 2×10^5 determinant CIs.

1. Introduction

Direct full configuration interaction (FCI) algorithms have been proposed and improved during the last ten years [1–3], making it possible to deal with up to 10^9 determinants [4]. However, this limit is already obtained in small molecular problems (few electrons, small basis sets). Since, in general, highly excited configurations have small coefficients in the wavefunctions, selected CIs may be interesting. And actually in many problems, 1% of the configurations are sufficient to reach 99% of the correlation energy. In that spirit, two different direct selected CI algorithms have been proposed by the present authors, one [5] written in a hole-particle formalism, the other [6] based on the string formalism. The two programs appear to have similar efficiencies.

Selected CIs face a major drawback, namely their size inconsistency or bad behaviour when the number of particles increases. The popular Davidson's type corrections [7] which were initially proposed for the single and double CI (SDCI), are not reliable when some double excitations become of large amplitude and have an unsatisfactory behaviour when

the number of particles becomes large [8]. The generalizations to multireference singles and doubles CI (MRSDCI) are not strongly grounded [9–11].

This problem has recently been solved in its full generality – at least for the ground state – by one of us (JPM) and co-workers [12]. Any selected or truncated CI may be made size extensive – and strictly separable when localized MOs are used – by an appropriate self-consistent dressing of the energies of the single determinants. This dressing is easy to compute, as recalled in section 2 and its practical efficiency has already been demonstrated on a few numerical tests, for cases where the selected CIs include up to quadrupole excitations. It was important to implement the dressing in a fully general scheme, and especially to combine it with direct selected CI algorithms. This has been done in the present work.

The efficiency of the self-consistent size-consistent CI ((SC)²CI) is studied here on three different cases:

(1) single and double substitutions on a complete active space (CAS-SDCI), the complete active space being essentially of valence character;

(2) single and double substituents on a selected multireference space (MR-SDCI);

(3) selected CIs coming from a two-step two-threshold iterative procedure.

The numerical tests concern three problems in double zeta plus polarization basis set, for which full-CI results are available, namely

– HF [13] at three interatomic distances, typical of a single bond breaking;

– H₂O [14] at three OH interatomic distances, the breaking of two single bonds leading to high components on a quadruply excited configuration;

– NH₃ [4] in its equilibrium geometry.

The results are presented and discussed in section 3.

2. Brief formulation of the method

The principle of the self-consistent size-consistent configuration interactions has been derived and explained elsewhere [12,15]. It rests on the theory of intermediate effective Hamiltonians [16,17]. The set of selected determinants is considered as a model space on which a modified (dressed) Hamiltonian will be built. In that model space the ground state determinant ϕ_0 plays a special role (it defines the main model space) since only one root is searched. As previously discussed, one exact eigenenergy and the projection onto the model space of the corresponding exact eigenvector may be obtained from a truncated Hamiltonian matrix, if one proceeds to an appropriate dressing of this matrix, and the simplest dressing consists in a change of the diagonal energies of the single determinants of the model space. It has been shown that the size extensively and, more precisely, the cancelation of any unlinked contribution may be obtained if the dressing is given by the following expression, for each determinant ϕ_i :

$$\langle \phi_i | \Delta | \phi_i \rangle = \sum_j c_j \langle \phi_0 | H | \phi_j \rangle, \quad (1)$$

$D_j^+ \phi_i \neq 0$
and $D_j^+ \phi_i \notin S$

where D_j^+ is a double excitation operator, S is the selected space, and c_j is the coefficient of the doubly excited determinant $\phi_j = D_j^+ \phi_0$ in the eigenvector in the intermediate normalization,

$$\psi = \phi_0 + \sum_j c_j \phi_j. \quad (2)$$

The dressing may be written differently by introducing the searched correlation energy

$$E = \sum_j c_j \langle \phi_0 | H | \phi_j \rangle, \quad (3)$$

as

$$\langle \phi_i | \Delta | \phi_i \rangle = E - \sum_{\substack{j \\ D_j^+ \phi_i = 0 \\ \text{or } D_j^+ \phi_i \in S}} c_j \langle \phi_0 | H | \phi_j \rangle. \quad (4)$$

The dressing is a function of the eigenenergy and of the eigenvector of the dressed matrix, so that the problem

$$[H + \Delta(E, C) - E]C = 0 \quad (5)$$

is self-consistent and must be treated iteratively. In eq. (4), the summation is shorter than that of eq. (1) since it only sums over

(i) the double excitations which are impossible on ϕ_i , D_j^+ involving at least one hole or one particle occurring in the creation of ϕ_i from ϕ_0 . This part of the summation deals with the exclusion principle violating (EPV) contribution. From a previous work [18] concerning the infinite summation of EPV diagrams, we have introduced one-, two- and three-index arrays making the calculation of the EPV part of the dressing absolutely straightforward, without any supplementary loop;

(ii) the double excitations which do not take out from the selected space, $D_j^+ \phi_i$ belonging to S space. The implementation of that condition is a bit more difficult. One first performs a full dressing by

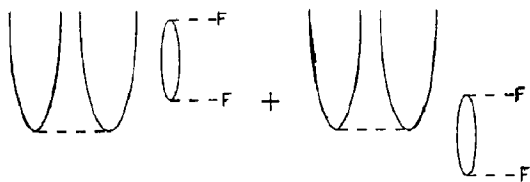
$$\langle \phi_i | \Delta' | \phi_i \rangle = E - \sum_{D_j^+ \phi_i = 0} c_j \langle \phi_0 | H | \phi_j \rangle \quad (6)$$

and later on one considers the de-excitations $(D_j^+)^{-1}$. If $\phi_k = D_j^+ \phi_i$ then $(D_j^+)^{-1} \phi_k = \phi_i$ and one proceeds to an undressing of the element $\langle \phi_i | \Delta' | \phi_i \rangle$ by the quantity $-c_j \langle \phi_0 | H | \phi_j \rangle$. This undressing step is done within the multiplication of H by C, and is not time-consuming.

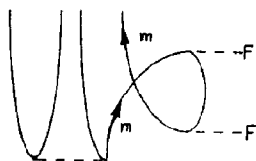
Two remarks must be formulated:

(i) If ϕ_0 is not the Hartree-Fock solution, for instance, if one starts the CI from a preliminary multiconfigurational (or CAS) SCF calculation, the Brillouin theorem does not hold and in eqs. (1) and (4) ϕ_j may be a singly excited state as well. This modification has been taken into account in the

present work although it does not bring much change. This inclusion cancels all the unlinked effects of the types



Of course the corresponding EPV diagrams are considered



(ii) The dressing might be incorporated into the diagonalization process itself and work is in progress to do that. But the convergence of the self-consistent dressing is achieved in a few iterations (typically three to obtain five to six significant decimals in hartrees), and the Davidson's diagonalization of the dressed matrix starting from the eigenvector of the undressed or previously dressed CI matrices are rapid, so that the inclusion of the size-consistent self-consistent correction only multiplies the cost of the CI by a factor of two.

3. Results

3.1. Singles and doubles on a CAS

Two calculations have been performed on the water molecule in a DZP basis set, for which FCI is available [14], one starting from a four electrons in four molecular orbitals CAS (i.e. OH bonding and anti-bonding MOs) which only counts 20 determinants ("small CAS"), the other also adding the two electrons of the π lone pair and a virtual MO of the same symmetry, the number of determinants for this six electrons in six MOs CAS being 112 ("big CAS"). The single and double substitutions lead to CIs of 20004 and 95666 determinants, respectively. The results of the corresponding undressed and dressed CIs

appear on table 1, together with the result of SDCI and of the dressed (SC)²SDCI. The dressing of the SDCI only reduced the error by about 40%, and the error increases when the bonds are lengthened; for $r=r_e$, the error is only reduced from 2.1 to 1.1 eV by the dressing.

As soon as the $(\sigma \rightarrow \sigma^*)^2$ valence double excitations are incorporated to the CAS, the CAS(S+D)CI results become rather accurate, the error being smaller and less distance dependent (from 0.0051 to 0.0039 hartree for the small CAS, and from 0.0026 to 0.0019 hartree for the big CAS). The dressing reduces the errors by a factor two to three; 0.0021 hartree for the small CAS, 0.0009 hartree for the big one, and this error becomes distance-independent (within 10^{-4} hartree, i.e. 0.06 kcal mol⁻¹), so that the same accuracy is preserved along the curve. This behaviour compares advantageously with the errors of CCSD (0.00179, 0.00559 and 0.00933 hartree at r_e , $1.5r_e$ and $2r_e$) [19].

When comparing with results obtained by using the generalized Davidson's correction, one finds errors of the same order of magnitude, but of opposite signs (the Davidson's corrections going below the exact energy). It should be noted that our dressing simply consists in the exact cancellation of unlinked contribution, which the Davidson's correction tries to achieve in an approximate manner. In this eight-electron problem, this approximation overestimates this effect, while it underestimates it when the number of electrons is large [7,8]. This is due to the neglect of the EPV contributions, which are of opposite sign and play an important role when the number of particles is small.

3.2. Multireference singles and doubles CI

Instead of starting from a CAS as reference space, one may start from a selected reference space, i.e. from a set of determinants which have been selected from their contribution to the energy or to the eigenvector of the considered state. The popular MRDCI [20,21] or CIPSI [22,23] schemes belong to that strategy, the selection being based on the energy in the first scheme, in the coefficient in the second one. Both try to approach the exact MRSDCI energy, which is not size consistent. The implemen-

Table 1

Correlation energy of the H₂O molecule in a DZP basis set, calculated from CASSDCI (in hartree) and errors to FCI [14] in parentheses, for three interatomic distances

	SDCI (2349 dets)		CAS ₁ SDCI ^{a)} (24004 dets)		CAS ₂ SDCI ^{b)} (95666 dets)	
	before dressing	after dressing	before dressing	after dressing	before dressing	after dressing
r_e	-0.2033 (0.0128)	-0.2089 (0.0072)	-0.2110 (0.0051)	-0.2139 (0.0022)	-0.2135 (0.0026)	-0.2152 (0.0009)
$1.5r_e$	-0.2405 (0.0304)	-0.2532 (0.0177)	-0.2663 (0.0046)	-0.2688 (0.0021)	-0.2688 (0.0023)	-0.2701 (0.0010)
$2.0r_e$	-0.2943 (0.0757)	-0.3283 (0.0417)	-0.3661 (0.0039)	-0.3679 (0.0021)	-0.3681 (0.0019)	-0.3691 (0.0009)

^{a)} Valence CAS with four electrons in four molecular orbitals.

^{b)} Full valence CAS with six electrons in six molecular orbitals.

tation of the size extensive correction seems to be an interesting goal.

Two problems have been studied with selected reference spaces, namely the H₂O molecule again and the HF molecule for which FCI is also available [13], both at three interatomic distances.

For the HF molecule (cf. table 2) the results are not spectacular, the dressing does not reduce the error by a factor of two, specially for large CIs. This means that the error of MRSDCI is not essentially due to its unlinked contributions. It is interesting to see that the generalized Davidson's corrections are

much larger than the dressing due to the neglect of the EPV terms (which play an important role in such a small eight-electron problem). The generalized Davidson's correction sometimes overshoots and sometimes underestimates the correlation energy, depending on the characteristics of the CI, as explained in section 4.

Nevertheless it is worth comparing our results with the most refined coupled cluster results [19]. At equilibrium bond length, our results are one order of magnitude better than CCSD, and comparable to CCSDT. When the bond is lengthened to $2r_e$, due to

Table 2

Correlation energy of the HF molecule in a DZP basis set, from MRSDCI calculations (in hartree) and errors to FCI [13], for three interatomic distances

	Ref CI		MRSDCI				Errors to FCI (10^{-3} hartree)			
	No. ref	ΔE_0	No. det (10^3)	undressed	dressed	dressing effect	Davidson correction	this work	CCSD	CCSDT
r_e	164	-0.146895	82	-0.203450	-0.203636	-0.000186	-0.000593	0.246	3.01	0.266
	234	-0.162498	102	-0.203544	-0.203648	-0.000104	-0.000317	0.234		
	308	-0.172812	119	-0.203625	-0.203689	-0.000064	-0.000169	0.193		
	376	-0.179614	130	-0.203636	-0.203689	-0.000053	-0.000099	0.193		
$1.5r_e$	212	-0.185648	97	-0.226832	-0.226951	-0.000119	-0.000355	0.213	5.10	0.646
	244	-0.191255	105	-0.226854	-0.226953	-0.000099	-0.000263	0.211		
	294	-0.197058	116	-0.226879	-0.226960	-0.000081	-0.000171	0.204		
	353	-0.202014	126	-0.226927	-0.226998	-0.000071	-0.000114	0.166		
$2.0r_e$	209	-0.219708	96	-0.263134	-0.263295	-0.000161	-0.000393	0.241	10.18	1.125
	245	-0.226753	108	-0.263178	-0.263309	-0.000131	-0.000274	0.227		
	295	-0.252581	125	-0.263294	-0.263381	-0.000087	-0.000188	0.155		
	363	-0.237240	139	-0.263352	-0.263422	-0.000070	-0.000129	0.114		

the multiconfigurational character of the reference, the present results are much better by two orders of magnitude than CCSD and one order of magnitude than CCSDT, the error being only two times larger than CCSDTQ (0.062×10^{-3} hartree) [24] which is much more expensive.

For the water molecule, the results are reported in table 3, at the lines $\tau=0$. The interest of using a selected reference set of determinants appears by comparing, for $r=r_e$, the CASSDCI (112 reference determinants) with the MRSDCI (121 reference determinants), the variational errors being 2.6×10^{-3} and 1.6×10^{-3} hartree, respectively. On the other hand, when comparing the different selected spaces, the dressing is efficient, always reducing the error by a factor of three to two. One sees that a dressed calculation with 131×10^3 determinants (from 121 reference determinants) gives a lower energy than an undressed calculation involving 275×10^3 determinants (from 323 references), which costs between five to eight times more.

One may compare the results obtained for the three distances (r_e , $1.5r_e$ and $2r_e$) using similar selections with about 300 references. The errors are almost the

same ($(0.35 \pm 0.05) \times 10^{-3}$ hartree) for the three distances and three times smaller than from the dressed CASSDCI. It is worth to compare with the errors of CCSD (1.79 , 5.59 and 9.33×10^{-3} hartree at r_e , $1.5r_e$ and $2r_e$) and of CCSDT (0.434 , 1.473 and -2.211×10^{-3} hartree) [19]. Our errors are about three times larger than those of CCSDTQ at $2r_e$ (0.108×10^{-3} hartree) [24].

3.3. Flexibly selected CIs

Instead of performing MRSDCI where one considers *all* the double substitutions on a selected set of reference determinants, a two-threshold selection may be used. The reference determinants ϕ_i may be selected as those having a coefficient larger than a first threshold η ,

$$|c_i| > \eta \Rightarrow \phi_i \text{ belongs to the reference space} \quad (7)$$

and then one may restrict the CI to the determinants obtained from the multireference wavefunction

$$\psi = \sum_{i=1, n_R} c_i \phi_i \quad (8)$$

Table 3

Correlation energy of the H₂O molecule in a DZP basis set, from MRSDCI calculations ($\tau=0$) and two-threshold selected CIs (in hartree), and errors to FCI [14], for three interatomic distances

	Ref CI			Selected CI						
	η	No. ref	ΔE_0	$\tau \times 10^5$	No. det	without dressing (error)		after dressing (error)		Davidson correction
r_e	0.010	121	-0.106170	5	31746	-0.212945	(0.003113)	-0.215028	(0.001054)	(+0.00058)
				2	63671	-0.213975	(0.002107)	-0.215339	(0.000743)	(-0.00052)
				0	131681	-0.214461	(0.001621)	-0.215483	(0.000599)	(-0.00105)
	0.008	169	-0.120483	5	34166	-0.213160	(0.002922)	-0.215166	(0.000916)	(+0.00070)
				2	73422	-0.214299	(0.001783)	-0.215479	(0.000603)	(-0.00052)
				0	177321	-0.214948	(0.001134)	-0.215660	(0.000422)	(-0.00122)
	0.007	224	-0.131954	5	37417	-0.213407	(0.002675)	-0.215305	(0.000777)	(+0.00077)
				2	81134	-0.214548	(0.001534)	-0.215610	(0.000472)	(-0.00044)
				0	217733	-0.215288	(0.000794)	-0.215723	(0.000359)	(-0.00118)
0.006	323	-0.149234	5	43884	-0.213740	(0.002342)	-0.215475	(0.000607)		
			2	90683	-0.214795	(0.001287)	-0.215758	(0.000324)		
			0	215426	-0.215474	(0.000608)	-0.215770	(0.000312)		
$1.5r_e$	298	-0.211659	5	38731	-0.268809	(0.002102)	-0.270250	(0.000661)		
			2	74291	-0.269602	(0.001309)	-0.270436	(0.000475)		
			0	260884	-0.270219	(0.000692)	-0.270513	(0.000398)		
$2.0r_e$	313	-0.308551	5	32175	-0.368359	(0.001624)	-0.369440	(0.000543)		
			2	57965	-0.368939	(0.001044)	-0.369580	(0.000403)		
			0	281587	-0.369386	(0.000597)	-0.369672	(0.000311)		

by a single or double substitution and such that the perturbative estimate of its coefficient

$$\left| c_k = \frac{\langle \psi | H | \phi_k \rangle}{E_0 - E_k} \right| > \tau \quad (9)$$

is larger than a second threshold τ . Of course $\tau < \eta$. This is the procedure used in the three-class CIPSI algorithm [23]. For $\tau=0$ the results are those of MRSDCI. The intrinsic efficiency of the double selection appears from tables 3 and 4. Even before dressing, it is better to work with 91×10^3 determinants selected from 323 references than to consider the 132×10^3 determinants representing all single and double substitutions from 121 determinants, the error being lower for a twice lower cost. After dressing, the advantage is even more marked since the error is 3×10^{-4} hartree in the small calculation instead of 6×10^{-4} hartree in the big one. After dressing, a computation with 44×10^3 determinants ($\tau=$

5×10^{-4}) from 323 references is as efficient as the dressed MRSDCI ($\tau=0$) from 121 references, which involves 132×10^3 determinants, i.e. a three times larger dimension of the CI. The combined use of double selection and dressing saves more than one order of magnitude in the computational cost.

The same considerations may be formulated when comparing differently selected CIs, since the same energy is obtained from 37×10^3 determinants selected from a subspace of 224 reference determinants as from 63×10^3 determinants selected from 121 references. Anyway, as is apparent from fig. 1, the efficiency of the dressing to approach the exact energy is dramatic; the dressed energies are much more stable than the undressed ones, the slope of the energy curves $E=f(\tau)$ being reduced by a factor of 10 by the dressing.

As a final case, the NH_3 molecule has been studied and the results are reported in table 4 and fig. 2. In that problem we have not performed full MRSDCIs

Table 4

Correlation energy of the NH_3 molecule in a DZP basis set for various selected CIs (see the text). The estimate of the full CI energy is -0.2099 hartree [4]

Ref. space		Selected CI space			
$\eta \times 10^3$	No. ref	$\tau \times 10^5$	No. det $\times 10^{-3}$	before dressing	after dressing
8	141	5	35	-0.205340	-0.208470
		4	47	-0.205861	-0.208697
		3	66	-0.206477	-0.208946
		5	105	-0.207185	-0.209203
		1	189	-0.207936	-0.209487
7	163	5	38	-0.205470	-0.208547
		4	49	-0.205976	-0.208769
		3	70	-0.206597	-0.209026
		2	110	-0.207333	-0.209296
		1	203	-0.208103	-0.209560
6	232	5	43	-0.205774	-0.208753
		4	55	-0.206271	-0.208976
		3	77	-0.206870	-0.209227
		2	121	-0.207602	-0.209484
		1	232	-0.208425	-0.209709
5	355	5	51	-0.206179	-0.208978
		4	66	-0.206665	-0.209183
		3	90	-0.207225	-0.209414
		2	136	-0.207899	-0.209661
		1	266	-0.208733	-0.209864
4	504	1	293	-0.208937	-0.209976
2	1412	0.2	934	-0.209812	-0.210126

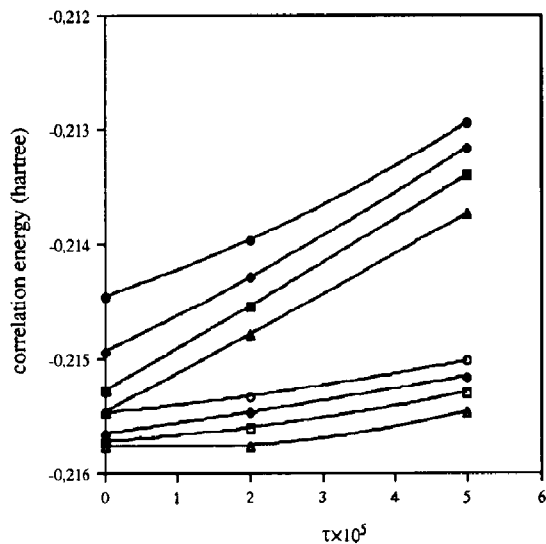


Fig. 1. Correlation energy for the H_2O molecule in a DZP basis set at τ_c ; convergence of two-threshold selected CIs. Dimension of the multireference spaces: (\bullet) $\eta=0.010$ (121 determinants); (\blacklozenge) $\eta=0.008$ (169 determinants); (\blacksquare) $\eta=0.007$ (224 determinants); (\blacktriangle) $\eta=0.006$ (323 determinants). τ is the second threshold (see the text), the open signs concern the results of the same CIs after self-consistent dressing.

($\tau=0$), but doubly selected CIs. The conclusions are almost the same as for H_2O . A dressed calculation from 43×10^3 determinants (from 232 selected reference determinants) gives the same energy as our largest undressed calculation, involving 266×10^3 determinants; the dressing saves a factor six in the size of the CI matrix, i.e. between one and two orders of magnitude in the computational cost. Again, it is better to proceed to the second selection from a larger number of references even if, as shown in fig. 2, this effect is considerably reduced by the dressing.

One may notice that we obtained the same energy (-0.20986 hartree) from 266×10^3 determinants after dressing as Handy and Knowles from their selected-truncated vector of 665×10^3 determinants [4]. Larger CIs (until 935×10^3 determinants, see table 4) have been performed. The largest one gives a variational energy of -0.209813 hartree, i.e. identical to the lowest value obtained by Handy and Knowles with a vector truncated to 665×10^3 most contributing determinants. The dressing is not yet negligible -0.210126 . Since our dressing has never overshoot below the exact energy, we believe that the exact correlation energy of NH_3 should be somewhat

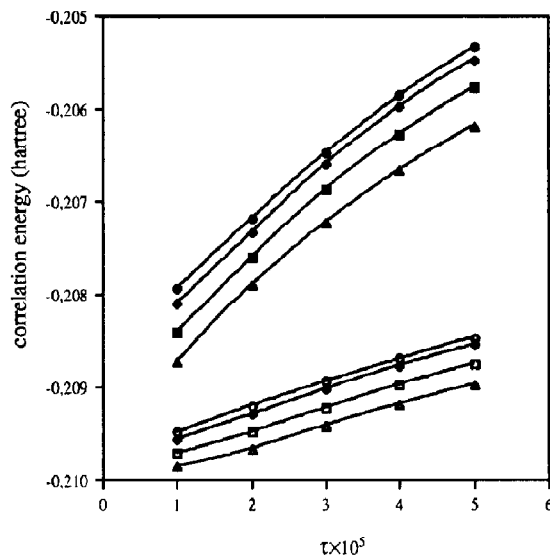


Fig. 2. Correlation energy for the NH_3 molecule in a DZP basis set; convergence of two-threshold selected CIs. Dimension of the multireference spaces: (\bullet) $\eta=0.008$ (141 determinants); (\blacklozenge) $\eta=0.007$ (163 determinants); (\blacksquare) $\eta=0.006$ (232 determinants); (\blacktriangle) $\eta=0.005$ (355 determinants). τ is the second threshold (see the text), the open signs concern the results of the same CIs after self-consistent dressing.

below -0.2100 au. In view of that uncertainty, we have not reported errors in table 4.

4. Discussion

The self-consistent size-consistent single and double CI may be considered as the most elaborate (and exact) CEPA (coupled electron pair approximation) algorithm. It cannot compete with coupled cluster on singles and doubles, CCSD, since it only includes the unlinked corrections of triples and quadrupoles (and higher degrees of excitation) to cancel them strictly. It does not incorporate the linked corrections going through triples and quadrupoles. A recent work [25] has added these corrections to the (SC)²SDCI energies, giving accurate results, but the complete incorporation of this effects is rather costly. The present work, taking benefit of the full generality of our self-consistent size-consistent dressing, essentially incorporates the leading linked corrections going through quadruple and more highly ex-

cited determinants by treating them variationally in the dressed CI matrix.

The CAS(S+D)CI had only been studied on a two configuration CAS problem [12], the F_2 molecule. Its application to a multiple bond breaking on H_2O is efficient since the error ranges between 1 and 2 mhartree, and is distance independent; its application to bonds of higher multiplicity should not present any problem and is under work.

However, it is clear that for the same price it is better to perform selected MRSDCI; in other words, it is more important to incorporate some non-valence doubly or quadruply excited determinants in the reference space rather than to include *all* valence exotic determinants. Since the dressing procedure ensures the size consistency, the size consistency of the reference space is not crucial, as clearly demonstrated on the dissociation of the water molecule from selected MRSDCI.

In MRSDCI where all double excitations have been performed on a limited set of reference determinants, essentially doubly excited ones, all doubly excited configurations belong to the MRSDCI space, but not all the quadruples, since one only generates determinants of the form $\phi(i_j^a b c d)$, where $\phi(i_j^a b)$ is a reference determinant. This means that one only treats part of the linked 4th order corrections going through the quadruples. Two consequences arise:

– One is the fortuitous character of the small errors that are sometimes obtained by applying the generalized Davidson correction to the MRSDCI results. This is due to a cancellation of errors between the neglect of EPV terms which are positive corrections, and the neglect of the linked corrections going through the quadruples not incorporated in the CI.

– The other concerns the interest of considering a sufficiently large number of doubly excited references before selecting the quadruples. It is much more interesting to have quadruples which are products of doubles of mean amplitudes than to include *all* the quadruples obtained from a limited number of large doubles.

This suggestion is confirmed by the high accuracy of our self-consistently dressed selected CIs when the selection was performed with two thresholds, one for the selection of the reference determinants, another one for the selection of the most important double substitutions on these references. The deviation to

FCI values of these dressed CIs of moderate size (8×10^4 determinants for HF and H_2O) is similar to the error of CCSDT at equilibrium geometries, and (in contrast to CCSDT) does not increase when bonds are broken, since the rational selection insures the same quality to the wavefunction. The dressing greatly improves the stability of the evaluations of the correlation energy as a function of the selection criteria. After dressing, the error decreases to that of an undressed CI of three to six times larger size, so that the dressing saves more than one order of magnitude in the computational effort. Finally with a number of rationally selected determinants close to 2×10^5 , the error to the FCI energies is below 0.4 mhartree in these eight valence electron problems, whatever the interatomic distances are. We think that the recently proposed self-consistent dressing of CI matrices, ensuring their size consistency, opens a wide domain of applications to the selected CI algorithms.

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