

CONVERGENCE OF AN IMPROVED CIPSI ALGORITHM

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Received 2 August 1982; in final form 24 November 1982

The configuration interaction CIPSI algorithm defines three classes of determinants of decreasing importance: the most important ones (< 100) are generators, the mean class ($\approx 10^3$) is treated variationally or to the fourth order, while the less important ones ($\approx 10^5$) are treated to the second order only. The accuracy of the result is studied as a function of the borders between the classes in the case of H_2O (double-zeta basis set), where the exact solution is known, and for the nearly degenerate CN^+ problem.

1. Introduction

Since full configuration interaction (CI) is not achievable for molecules involving many electrons and/or large basis sets, quantum chemists are forced to use approximate schemes, such as truncations to a certain level of excitation [single + double CI for instance (SDCI)], freezing of some MOs, cluster expansions, etc. In order to avoid incorrect dependence of truncated CIs on the number of particles, one may follow the perturbative approach which treats the correlation potential as a perturbation operator. This way, opened a long time ago by Møller and Plesset [1], leads to the important results of the many-body perturbation theory (linked cluster theorem [2,3], diagrammatic representations [2,3]). However, its convergence rests upon the quality of the zeroth-order wavefunctions, and while the expansion may be convergent from the ground state Hartree–Fock determinant in most cases, the convergence may be slow, and may disappear for excited states. In many cases near degeneracy between important configurations requires the use of a multiconfigurational zeroth-order wavefunction or zeroth-order space. One may use the quasi-degenerate perturbation theory [4–8] (QDPT) in one of its numerous versions, which leads to the perturbative construction of an effective hamiltonian. For ac-

tual CI problems this approach is poorly convergent since it faces the recurrent problem of the so-called “intruder states” (see for instance, refs. [9,10]). An alternative solution consists in perturbing a multiconfigurational wavefunction resulting from a preliminary variational treatment of the CI matrix reduced to the most important determinants. This is the way followed by Whitten and Hackmeyer [11] or by the CIPSI algorithm [10,12,13]. The latter approach (which has been widely used for ground and excited state studies, see, for instance, refs. [14–18]) consists in an iterative selection of a first class of determinants $\{S\}$, the weight of which in the exact wavefunction Ψ_m is larger than a certain threshold η

$$\Phi_K \text{ belongs to } \{S\} \quad \text{if} \quad |\langle \Psi_m | \Phi_K \rangle| > \eta.$$

This first class of determinants is treated variationally

$$P_S = \sum_{K \in \{S\}} |\Phi_K\rangle \langle \Phi_K|. \quad (1)$$

$$P_S H P_S |\Psi_m^0\rangle = \epsilon_m^{(0)} |\Psi_m^0\rangle, \quad (2)$$

the resulting multiconfigurational wavefunction

$$\Psi_m^0 = \sum_K C_{mK} \Phi_K$$

is then perturbed to the second order by the other

determinants which do not belong to $\{S\}$

$$\epsilon_m^{(2)} = \sum_{I \in \{S\}} \frac{\langle \Psi_m^0 | H | \Phi_I \rangle^2}{E_m^0 - E_I^0}. \quad (3)$$

In practice the definition of $\{S\}$ is iterative; starting from an initial guess of $\{S\}$ one selects the most important determinants of the first-order correction to the wavefunction. At the k th iteration if the first-order coefficient of Φ_I is larger than η^k

$$\left| \frac{\langle \Psi_m^0 | H | \Phi_I \rangle}{\Delta E} \right| > \eta^k.$$

Φ_I is added to $\{S\}$ and the process may be repeated by decreasing η^k to $\eta^{k+1} < \eta^k$. In such a case there is no a priori selection of the multireference space $\{S\}$, the quality of which is progressively increased.

The present paper (i) first presents an improved version of the CIPSI algorithm, by introducing an intermediate class of determinants which is treated to a higher order of perturbation, (ii) tests the convergence of the CIPSI algorithm on two well-defined problems. The first one concerns the ground state energy of the water molecule calculated in a double-zeta basis set for which the exact solution has been reached recently by Saxe et al. [19]. As a second example the CN^+ ($1\Sigma^+, 3\Pi$) lowest states have been treated since this is a highly degenerate problem [20–22], already studied by several authors using different CI schemes.

This new version of the CIPSI algorithm presents common features with the MRD CI scheme of Buenker and Peyerimhoff [23] which has been used with success in spectroscopic studies [24–27] and potential surfaces analysis [28]. Differences between the two methods will be discussed in section 8.

2. The improved (three classes) CIPSI algorithm

In its original version [12], the accuracy of the CIPSI algorithm can only be improved by enlarging the zeroth-order subspace $\{S\}$. Referring to eq. (2) it is clear that as the number n_{cf} of determinants belonging to S increases, the number of generated determinants in the second-order expansion

increases rapidly, since

$$\langle \Psi_m | H | \Phi_I \rangle = \sum_{K \in \{S\}} C_{mK} \langle \Phi_K | H | \Phi_I \rangle, \quad (4)$$

when a determinant Φ_K is included in $\{S\}$ it brings all its doubly substituted determinants Φ_I . The number of determinants generated in the perturbation expansion in principle should increase as $n_{cf} n_{oc}^2 n_v^2$, where n_{oc} and n_v are the number of occupied and virtual MOs, respectively. For each new determinant Φ_I one must calculate all $\langle \Phi_K | H | \Phi_I \rangle$ in order to test whether Φ_I has not already been considered and to calculate $\langle \Psi_m | H | \Phi_I \rangle$, thus the computation time should increase as $n_{cf}^2 n_{oc}^2 n_v^2$. As a consequence n_{cf} must keep limited values (≈ 40 – 200 determinants) for most of the problems. Then the accuracy of the method is limited by the very low order of perturbation to which the other determinants are treated.

As an improvement, one may define a third (intermediate) class of determinants $\{M\}$, the weight of which in the wavefunction appears to be smaller than those of the generators belonging to $\{S\}$ but larger than a second threshold τ

$$\begin{aligned} \Phi_K &\in \{S\}, & \text{if } \eta < |\langle \Psi | \Phi_K \rangle|, \\ \Phi_J &\in \{M\}, & \text{if } \tau < |\langle \Psi | \Phi_J \rangle| < \eta, \\ \Phi_I &\in \{S\}, & \text{if } |\langle \Psi | \Phi_I \rangle| < \tau. \end{aligned}$$

This improved CIPSI method is now characterized by two parameters (τ, η) , the former version corresponding to the particular case $(\tau = \eta, \eta)$. The intermediate class $\{M\}$ may be treated to a higher order of perturbation theory than the lower one $\{s\}$, or may be treated variationally. For instance, one may go to the fourth order in $\{S + M\}$.

If one defines a zeroth-order energy E_m^0 for the zeroth-order wavefunction Ψ_m^0 resulting from the preliminary diagonalization of $P_S H P_S$

$$E_{m\{M+S\}} = E_m^0 + \epsilon_m^{(1)} + \epsilon_{m\{M\}}^{(2)} + \epsilon_{m\{M\}}^{(3)} + \epsilon_{m\{S+M\}}^{(4)}, \quad (5)$$

where

$$\epsilon_m^{(1)} = \epsilon_m^{(0)} - E_m^0, \quad (6)$$

$$\epsilon_{m\{M\}}^{(2)} = \sum_{I \in \{M\}} \frac{\langle \Psi_m^0 | H | \Phi_I \rangle^2}{E_m^0 - E_I^0}, \quad (7)$$

$$\epsilon_{m,\{M\}}^{(3)} = \sum_{J,K \in \{M\}} \left[\frac{\langle \Psi_m^{(0)} | H | \Phi_J \rangle \langle \Phi_J | H | \Phi_K \rangle}{E_m^0 - E_J^0} \right. \\ \left. \times \frac{\langle \Phi_K | H | \Psi_m^{(0)} \rangle}{E^0 - E_K^0} \right] - \epsilon_m^{(1)} \langle \Psi_{m,\{M\}}^{(1)} | \Psi_{m,\{M\}}^{(1)} \rangle. \quad (8)$$

$$\epsilon_{m,\{M+S\}}^{(4)} = \sum_{J,K,L \in \{M\}} \left[\frac{\langle \Psi_m^{(0)} | H | \Phi_J \rangle \langle \Phi_J | H | \Phi_K \rangle}{E_m^0 - E_J^0} \right. \\ \left. \times \frac{\langle \Phi_K | H | \Phi_L \rangle \langle \Phi_L | H | \Psi_m^{(0)} \rangle}{(E_m^0 - E_K^0)(E_m^0 - E_L^0)} \right] \\ + \sum_{J,K \in \{M\}} \sum_{I \in \{S\}} \left[\frac{\langle \Psi_m^{(0)} | H | \Phi_J \rangle \langle \Phi_J | H | \Psi_I^{(0)} \rangle}{E_m^0 - E_J^0} \right. \\ \left. \times \frac{\langle \Psi_I^{(0)} | H | \Phi_K \rangle \langle \Phi_K | H | \Psi_m^{(0)} \rangle}{(E_m^0 - E_I^0)(E_m^0 - E_K^0)} \right] \\ - \epsilon_m^{(1)} (\langle \Psi_{m,\{M\}}^{(1)} | \Psi_{m,\{M\}}^{(2)} \rangle + \langle \Psi_{m,\{M\}}^{(2)} | \Psi_{m,\{M\}}^{(1)} \rangle) \\ - \epsilon_{m,\{M\}}^{(2)} (\langle \Psi_{m,\{M\}}^{(1)} | \Psi_{m,\{M\}}^{(1)} \rangle), \quad (9)$$

with

$$|\Psi_{m,\{M\}}^{(1)}\rangle = \sum_{I \in \{M\}} \frac{\langle \Psi_m^{(0)} | H | \Phi_I \rangle}{E_m^0 - E_I^0} |\Phi_I\rangle, \quad (10)$$

$$|\Psi_{m,\{M\}}^{(2)}\rangle = \sum_{I,J \in \{M\}} \frac{\langle \Psi_m^{(0)} | H | \Phi_I \rangle \langle \Phi_I | H | \Phi_J \rangle}{(E_m^0 - E_I^0)(E_m^0 - E_J^0)} |\Phi_J\rangle. \quad (11)$$

The final energy will be approximated by adding the second-order effect of the determinants I belonging to $\{S\}$

$${}^{(4)}E_m = \epsilon_{m,\{S+M\}}^{(4)} + \epsilon_{m,\{S\}}^{(2)}. \quad (12)$$

$$\epsilon_{m,\{S\}}^{(2)} = \sum_{I \in \{S\}} \frac{\langle \Psi_m^{(0)} | H | \Phi_I \rangle^2}{E_m^0 - E_I^0}. \quad (13)$$

The process may be viewed as a differential multiple perturbation expansion in powers of various operators, defined by

$$V_1 = \sum_{I \in \{S\}} \langle \Psi_I | V | \Psi_I \rangle |\Psi_I\rangle \langle \Psi_I| \\ + \sum_{J,K \in \{M\}} \langle \Phi_J | V | \Phi_K \rangle |\Phi_J\rangle \langle \Phi_K|. \quad (14)$$

$$V_2 = \sum_{I \in \{S\}} \sum_{I \in \{S\}} \langle \Psi_I | V | \Phi_I \rangle |\Psi_I\rangle \langle \Phi_I|, \quad (15)$$

$$V_3 = \sum_{J \in \{S+M\}} \sum_{I \in \{S\}} \langle \Phi_I | V | \Phi_J \rangle |\Phi_I\rangle \langle \Phi_J|. \quad (16)$$

and pictured in fig. 1. The process consists in perturbing V_1 to the fourth order and V_2 to the second order (V_3 would only occur first through $V_2 V_3 V_2$ or $V_1 V_3 V_2$ contributions). One may perturb V_1 to infinite orders as well, i.e. diagonalize $\{S+M\}$. In such a case

$$E_m = \epsilon_{m,\{S+M\}}^{(0)} + \epsilon_{m,\{S\}}^{(2)}, \quad (17)$$

with

$$P_{\{S+M\}} = \sum_{K \in \{S+M\}} |\Phi_K\rangle \langle \Phi_K|. \quad (18)$$

$$P_{\{S+M\}} H P_{\{S+M\}} |\Psi_{m,\{S+M\}}^{(0)}\rangle = \epsilon_{m,\{S+M\}} |\Psi_{m,\{S+M\}}^{(0)}\rangle. \quad (19)$$

In practice $\epsilon_{m,\{S\}}^{(2)}$ is calculated as the difference

$$\epsilon_{m,\{S\}}^{(2)} = \epsilon_m^{(2)} - \epsilon_{m,\{M\}}^{(2)}$$

The computation time of the second-order perturbation correction remains proportional to $n_{cf}^2 n_{oc}^2 n_c^2$, and the diagonalization of $\{S+M\}$ requires a time proportional to $(n_{cf} + n_m)^2$ if n_m is the number of determinant of the middle-class $\{M\}$. One may hope that an equivalent accuracy may be achieved in the three-class procedure with a smaller number of generators, i.e. starting with $n_{cf}^{(1)}$ generators and treating variationally $a(n_{cf}^{(1)} + n_m)$ matrix (with a large enough value for n_m) will give as accurate a result as the second-order perturbation from $n_{cf}^{(2)}$ generators with $n_{cf}^{(2)} \gg n_{cf}^{(1)}$. Speaking in terms of thresholds, one may hope that the three-class procedure will allow us to use larger values of η by considering a small enough value for the threshold τ . Of course one must find

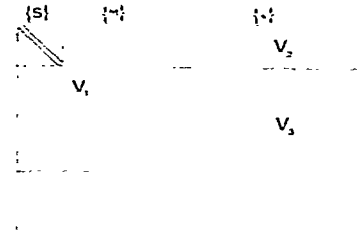


Fig. 1. Partitioning of the CI matrix.

a balance between the two time-consuming steps (second-order perturbation and diagonalization) limiting both the size of the diagonalized matrix and the length of the second-order expansion.

3. Size dependence

Of course the diagonalization of the $\{S+M\}$ matrix introduces some spurious normalization effects resulting in a bad N dependence [3]. One may apply one of the corrections which intend to cancel the normalization effects and ensure the correct N dependence. (For a discussion of the N dependence of multireference CI techniques see ref. [13].) One may use either Davidson's correction [30] multiplying $\epsilon_{m, \{S+M\}}^{(0)} - \epsilon_{m, S}^{(0)}$ by $2 - (C_m^0)^2$, where C_m^0 is the coefficient of the zeroth-order wavefunction Ψ_m^0 in the eigenvector of $P_{\{S+M\}}HP_{\{S+M\}}$, by $(C_m^0)^{-2}$ (Siegbahn's correction [31]), or by $[1 - (C_m^0)^2]^{-1}$ (Silver-Davidson's correction [32]).

If one uses the perturbation expansion in $\{S+M\}$ the same defect appears. As well-known from the single reference case (perturbation of a single determinant), the unlinked bubble diagrams in the third-order cancel with $\epsilon^{(1)}\langle\Psi^{(1)}|\Psi^{(1)}\rangle$ and the fourth-order ones cancel with contribution from $-\epsilon^{(2)}(\langle\Psi^{(1)}|\Psi^{(2)}\rangle + \langle\Psi^{(2)}|\Psi^{(1)}\rangle)$. On the contrary, most of the positive quantity $-\epsilon^{(2)}\langle\Psi^{(1)}|\Psi^{(1)}\rangle$ should cancel with unlinked corrections in the fourth-order general summation which involves higher levels of excitations, outside of $\{S+M\}$. To correct this defect, one may be tempted to disregard $\epsilon^{(2)}\langle\Psi^{(1)}|\Psi^{(1)}\rangle$ i.e. replace $\epsilon_{m, \{S+M\}}^{(4)}$ by

$$\epsilon_{m, \{S+M\}}^{(4)} = \epsilon_{m, \{S+M\}}^{(4)} + \epsilon_{m, M}^{(2)}\langle\Psi_{m, M}^{(1)}|\Psi_{m, M}^{(1)}\rangle. \quad (20)$$

However, $\epsilon_{m, M}^{(2)}\langle\Psi_{m, M}^{(1)}|\Psi_{m, M}^{(1)}\rangle$ also involves some contributions which do not cancel and generate the so-called exclusion principle violating linked diagrams the contribution of which is positive at this order. Therefore if one uses $\epsilon_{m, \{S+M\}}^{(4)}$ one should get an upper bond to the energy, while if one uses $\epsilon_{m, \{S+M\}}^{(4)}$ the resulting energy may go below the exact one.

4. Choice of H_0

The definition of the unperturbed hamiltonians H_0 remains rather arbitrary [33]. Four definitions

have been proposed previously, derived from the case of a single determinant zeroth-order wavefunction for which two basic H_0 may be proposed. For the single determinants outside of $\{S\}$, one may use either the Møller–Plesset definition [1] (hereafter labelled MP)

$$H_0^{\text{MP}}|\Phi_I\rangle = \left(\sum_i \epsilon_i a_i^\dagger a_i\right)|\Phi_I\rangle, \quad (21)$$

or the Epstein–Nesbet definition [34,35] (hereafter labelled EN)

$$H_0^{\text{EN}}|\Phi_I\rangle = \langle\Phi_I|H|\Phi_I\rangle|\Phi_I\rangle. \quad (22)$$

For the subspace $\{S\}$ one may use either the eigenvalues of P_SHP_S ,

$$H_0|\Psi_m^{(0)}\rangle = \epsilon_m^{(0)}|\Psi_m^{(0)}\rangle, \quad (23)$$

or a barycentric definition.

$$H_0|\Psi_m^{(0)}\rangle = \left(\sum_{K \in \{S\}} \langle\Phi_K|H_0|\Phi_K\rangle C_{mK}^2\right)|\Psi_m^0\rangle, \quad (24)$$

where H_0 may be the Møller–Plesset or Epstein–Nesbet zeroth-order hamiltonians for the single determinant cases. The barycentric H_0 has been shown [12] to satisfy the physical separability criterion up to the fourth order, namely it ensures that if one treats two non-interacting subsystems A and B as a supersystem (at infinite distance for instance), the excitations on system B have no influence on the transition energies of system A. This would not be necessarily the case when the eigenvalues of P_SHP_S are taken as zeroth-order energies of the multiconfigurational wavefunctions belonging to $\{S\}$.

5. Summary of the various estimates of the energy

One may summarize the various evaluations of the energy which appeared in the preceding discussion and which have been actually calculated in the numerical tests.

Variational values

$\epsilon_m^{(0)}(\tau, (\eta = \tau))$, variational energy obtained from the diagonalization of P_SHP_S , mean energy of Ψ_m^0 , P_S selecting all determinants which have a component larger than τ .

$\epsilon_m^{(0)}(\tau, \eta)$, variational energy obtained from the

diagonalization of $P_{\{S+M\}}HP_{\{S+M\}}$, where M selects all the determinants having a component lower than τ and larger than η .

Corrected variational value

$\epsilon_m^{(0)DS}(\tau, \eta) = \epsilon_m^0(\tau, \eta) / [C_m^0(\tau, \eta)]^2$, is the Davidson–Siegbahn corrected variational energy. C_m^0 being the weight of $|\Psi_m^0\rangle$ in the wavefunction resulting from the diagonalization of $P_{\{S+M\}} \times HP_{\{S+M\}}$.

Variation + perturbation final energies

${}^{(4)}E_m^{\text{MP}}$, given by eq. (12), with the MP definition of H^0 for the determinants outside of $\{S\}$, and the corresponding barycentric definition [cf. eq. (22)] of the zeroth-order energy for the multiconfigurational functions $\Psi_I \in \{S\}$.

${}^{(4)}E_m^{\text{EN}}$, given by eq. (12), with the EN definition of H^0 for the determinants outside of $\{S\}$ and $E^0 = \langle \Psi^0 | H | \Psi^0 \rangle$ for the multiconfigurational functions $\Psi_I \in \{S\}$ (i.e. the eigenvalues of $P_S HP_S$).

$${}^{(4)}E_m^{\text{C.MP}} = {}^{(4)}E_m^{\text{MP}} + \epsilon_{m,M}^{(2)\text{MP}} \langle \Psi_{m,M}^{(1)\text{MP}} | \Psi_{m,M}^{(1)\text{MP}} \rangle. \quad (25)$$

$${}^{(4)}E_m^{\text{C.EN}} = {}^{(4)}E_m^{\text{EN}} + \epsilon_{m,M}^{(2)\text{EN}} \langle \Psi_{m,M}^{(1)\text{EN}} | \Psi_{m,M}^{(1)\text{EN}} \rangle. \quad (26)$$

to correct the preceding values in order to get a correct size consistence of the energy.

$$E_m^{\text{VMP}} = \epsilon_{m,\{S+M\}}^{(0)} + \epsilon_{m,s}^{(2)\text{MP}}, \quad (27)$$

[cf. eqs. (13) and (19)] adding the second-order MP correction by the determinants belonging to $\{s\}$ to $\epsilon_{m,\{S+M\}}^{(0)}$.

$$E_m^{\text{VEN}} = \epsilon_{m,\{S+M\}}^{(0)} + \epsilon_{m,s}^{(2)\text{EN}}, \quad (28)$$

adding the second-order EN correction by the determinants belonging to $\{s\}$ to $\epsilon_{m,\{S+M\}}^{(0)}$.

$$E_m^{\text{VDS.MP}} = \epsilon_{m,\{S+M\}}^{(0)DS} + \epsilon_{m,\{s\}}^{(2)\text{MP}}, \quad (29)$$

$$E_m^{\text{VDS.EN}} = \epsilon_{m,\{S+M\}}^{(0)DS} + \epsilon_{m,\{s\}}^{(2)\text{EN}}, \quad (30)$$

replace the variational eigenvalue $\epsilon_{m,\{S+M\}}^{(0)}$ by its Davidson–Siegbahn corrected estimate in the preceding expressions.

6. Numerical calculations

6.1. H_2O in a double zeta basis set

Since the exact solution of this problem is known [19], the results may be expressed in terms of

absolute energy errors. The exact correlation energy is -0.14803 au, the (single + double)CI error is 0.00855 au (when corrected by the Davidson formula), while the (single–double–triple–quadruple)CI is only in error by 0.00026 au.

Sixteen calculations have been performed corresponding to various values of the two threshold parameters (η and τ). The characteristics of these calculations are reported in table 1. The first columns of tables 1–5 correspond to the original two-class CIPSI algorithm ($\tau = \eta$, no middle class). As previously discussed [10], the MP values slowly converge by upper values when the size of $\{S\}$ (i.e. the quality of the wavefunction) is increased, but the error remains important when 82 determinants are involved in $\{S\}$. The EN values converge from below, but the excellent agreement obtained from the largest $\{S\}$ subspace diagonalizations is certainly partly fortuitous.

The zeroth-order subspace $\{S\}$ progressively includes the most important doubly excited determinants. The best zeroth-order wavefunction contributes for $\approx 56\%$ of the total correlation energy. The size of the $\{S+M\}$ matrices as reported in table 1 remains very limited, but quite surprisingly, the energy obtained from these limited CIs, involving the most important quadruple excita-

Table 1

Characteristics of the H_2O calculations. For each value of η and τ , one finds the variational energy $\epsilon_m^{(0)}$ (in au), the weight of $\Psi_m^{(0)}$ in the corresponding eigenvector of $\{S+M\}$, and the size of the $\{S+M\}$ CI matrix. The exact energy is taken as a conventional zero

η	$\tau = \eta$ (original CIPSI)	$\tau = 0.01$	$\tau = 0.002$	$\tau = 0.0005$
0.060	0.14802	0.03474	0.01075	0.00929
	1.0	0.963	0.959	0.959
	(1)	(135)	(304)	(413)
0.040	0.11481	0.03364	0.00961	0.00610
	1.0	0.973	0.968	0.967
	(10)	(142)	(333)	(657)
0.025	0.09500	0.03444	0.00866	0.00394
	1.0	0.980	0.976	0.975
	(31)	(139)	(374)	(798)
0.015	0.06325	0.03585	0.00819	0.00430
	1.0	0.990	0.985	0.984
	(82)	(143)	(403)	(1129)

Table 2

Energy error on the correlation energy of H₂O, as estimated from the perturbative estimates ⁽⁴⁾E^{MP} (MP) and ⁽⁴⁾E^{EN} (EN) (au) [4]

η	$\tau = \eta$		$\tau = 0.01$		$\tau = 0.002$		$\tau = 0.0005$	
	MP	EN	MP	EN	MP	EN	MP	EN
0.060	0.00855	-0.03523	0.00938	0.00310	0.00975	0.00754	0.00977	0.00758
0.040	0.01253	-0.01350	0.00726	0.00209	0.00666	0.00490	0.00525	0.00324
0.025	0.01191	-0.00509	0.00496	0.00014	0.00518	0.00502	0.00394	0.00272
0.015	0.00900	-0.00060	0.00422	-0.00052	0.00324	0.00230	0.00265	0.00184

tions. quickly goes below the canonical SDCI result (cf. the errors for $\tau = 0.0005$, when $\eta = 0.040$, 0.025 or 0.015). This first result illustrates the interest of using a rationally chosen multiconfigurational zeroth-order wavefunction, followed by a rational selection of the most important determinants, as compared to an a priori truncation of the CI matrix in terms of excitation levels. The CIPSI process may be viewed as a progressive selection of the most important perturbation contributions.

In table 2, the middle-class $\{M\}$ effect is taken into account to fourth order [eq. (12)], the remainder $\{s\}$ being treated to second order only. For the best calculations ($\eta = 0.025$, 0.015, $\tau = 0.002$ or 0.0005), the error is about one half to one fourth of the SDCI error. As expected the Epstein–Nesbet definition of H_0 gives better values, and the normalization defect makes the error positive. When one tries to eliminate this normalization defect by adding the $\epsilon^2 \langle \Psi^{(1)} | \Psi^{(1)} \rangle$ term [cf. eq. (20)], the error (cf. table 3) is reduced to one fourth to one tenth of the SDCI error, and may become negative. The difference between the MP and EN results essentially comes from the second-order treatment of the remainder $\{s\}$. The fourth-

order values for the treatment of $\{S + M\}$ are almost identical to the diagonalization results.

This statement appears clearly by comparing tables 2 and 4. Table 4 reports the results of $E_m^{V,MP}$ (respectively EN) [eq. (27), respectively (28)] adding the second-order effect of $\{s\}$ to the eigenvalues of $\{S + M\}$. Table 5 includes the Davidson–Siegbahn correction to avoid the normalization defect of the diagonalization of $\{S + M\}$ [eqs. (29) and (30)]. The error is drastically reduced by a factor of one third in the MP treatment, and the Epstein–Nesbet values are in a fascinating agreement with the exact result. The comparison between figs. 2 and 3 illustrates the efficiency of the Davidson–Siegbahn correction in this multireference case. However, the agreement with the exact energy cannot be attributed only to this (de)normalization correction since the error on the Davidson corrected SDCI (0.00169 au) is much larger than the present errors for $\tau = 0.005$. For this last value, the error is not larger than the SDTQ CI one (resulting from the diagonalization of a 17×10^3 configurations matrix), at a much smaller computational effort. This agreement shows the advantage of the CIPSI hierarchical selection of

Table 3

Energy error on the correlation energy of H₂O, as estimated from the corrected perturbative estimates [eqs. (25) (MP) and (26) (EN)] (au)

η	$\tau = \eta$		$\tau = 0.01$		$\tau = 0.002$		$\tau = 0.0005$	
	MP	EN	MP	EN	MP	EN	MP	EN
0.060	0.00855	-0.03523	0.00512	-0.00748	0.00407	-0.00618	0.00402	-0.00628
0.040	0.01253	-0.01350	0.00542	-0.00190	0.00389	-0.00097	0.00239	-0.00278
0.025	0.01191	-0.00509	0.00420	-0.00135	0.00369	0.00215	0.00239	-0.00026
0.015	0.00900	-0.00060	0.00406	-0.00080	0.00266	0.00130	0.00201	0.00072

Table 4

Energy error on the correlation energy of H₂O, as calculated from eqs. (27) (MP) and (28) (EN) (without Davidson correction) (au)

η	$\tau = \eta$		$\tau = 0.01$		$\tau = 0.002$		$\tau = 0.0005$	
	MP	EN	MP	EN	MP	EN	MP	EN
0.060	0.00855	-0.03523	0.00870	0.00408	0.00863	0.00851	0.00863	0.00860
0.040	0.01253	-0.01350	0.00721	0.00285	0.00644	0.00604	0.00504	0.00494
0.025	0.01191	-0.00509	0.00510	0.00027	0.00512	0.00466	0.00388	0.00373
0.015	0.00900	-0.00060	0.00426	-0.00053	0.00327	0.00251	0.00265	0.00245

determinants. Since the Davidson–Siegbahn corrected results of eqs. (29) and (30) are much better and more stable than the corrected fourth-order values of eqs. (19) and (20), the purely perturbative treatment of $\{S + M\}$ will not be discussed for the CN⁺ problem.

6.2. The CN⁺ near degeneracy problem

The calculation is performed in a (double-zeta + polarization) basis set proposed by Bruna et al. [21] and for their suggested R_c values. Our calculation differs from the basis of their MRD CI treatment (reported extensively in ref. [21]) by the lack of f functions in the middle of the bond and the use of five components for d functions. In that problem, the SCF calculations predict the $^3\Pi$ to be lower in energy than the $^1\Sigma^+$ configuration by ≈ 0.1 au.

Table 6 gives the main characteristics of the calculations, τ and η values, size of the multireference space and of the $\{S + M\}$ matrices, zeroth-order energies, and eigenvalues of $\{S + M\}$. The zero of energy is taken as the $^1\Sigma^+$ SCF determinant energy (-91.6265 au). One may notice that the $\{S + M\}$ diagonalizations selected on the same

grounds (same τ and η thresholds) tend to give a constant splitting of -0.020 au, between the two states (in favour of $^3\Pi$).

Tables 7 and 8 reproduce the total energies according to eqs. (29) and (30) (second-order correction by the remainder $\{s\}$ added to the Davidson–Siegbahn corrected eigenvalue of $\{S + M\}$) which appeared to give the most reliable values from the test study of H₂O. From the lowest right corner of this table the Møller–Plesset values seem to converge from above and the Epstein–Nesbet values seem to converge from below. There is still some important difference (≈ 0.009 au) between these two estimates, the Epstein–Nesbet one certainly being more reliable.

The calculation of exact energies is usually less important than the knowledge of energy variations, from one geometry to another or from one state to another. The most important question in this precise problem is the energy difference between the $^1\Sigma^-$ and the $^3\Pi$ states. Table 9 gives the $E(^1\Sigma^-) - E(^3\Pi)$ energy difference as a function of η and τ for both definitions of the perturbation expansion. The uncertainty in the energy difference seems to be significantly less than the fluctuation of the energy of each state. In view of

Table 5

Energy error on the correlation energy of H₂O, as calculated from eqs. (29) (MP) and (30) (EN) (including Davidson correction) (au)

η	$\tau = \eta$		$\tau = 0.01$		$\tau = 0.002$		$\tau = 0.0005$	
	MP	EN	MP	EN	MP	EN	MP	EN
0.060	0.00855	-0.03523	0.00436	-0.00026	0.00281	0.00268	0.00273	0.00270
0.040	0.01253	-0.01350	0.00397	-0.00038	0.00188	0.00148	0.00019	0.00008
0.025	0.01191	-0.00509	0.00277	-0.00206	0.00165	0.00119	0.00016	0.00001
0.015	0.00900	-0.00060	0.00309	-0.00171	0.00111	0.00036	0.00031	0.00011

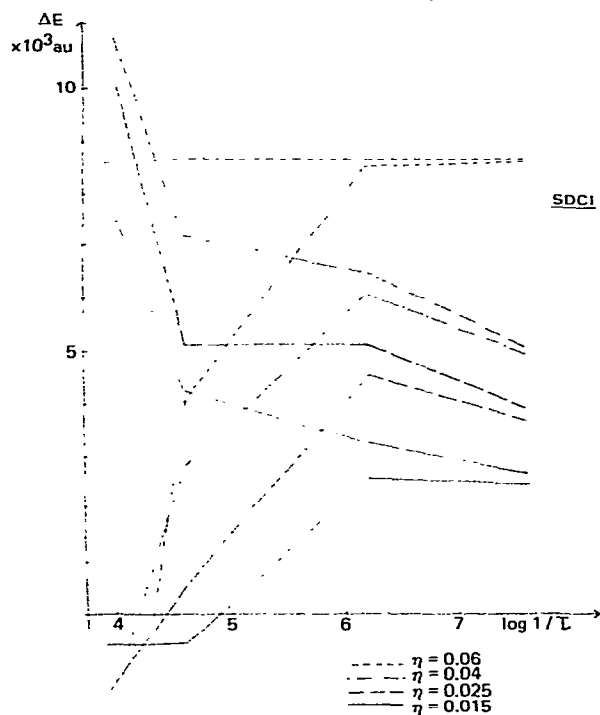


Fig. 2. Convergence of the CIPSI algorithm for the H_2O ground state correlation energy. The reference energy corresponds to the exact calculation in the same basis set (ref. [19]). The parameters η and τ correspond to the selection thresholds for the primary (S) and intermediate (M) spaces. For a given value of η , the upper (respectively lower) curve corresponds to the Møller–Plesset [eq. (27)] (respectively Epstein–Nesbet; eq. (28)) partition.

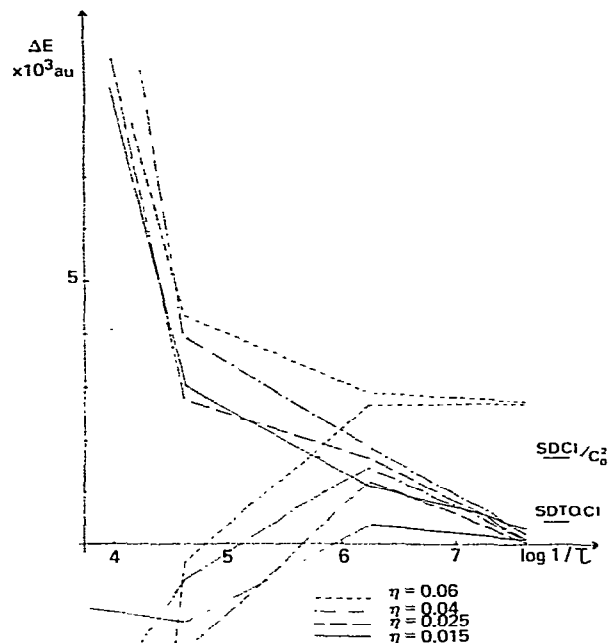


Fig. 3. Same quantities as in fig. 2 when the Davidson–Siegbahn correction is applied to the variational result, eqs. (29) and (30).

Table 6

Characteristics of the CN^- calculations. For each value of η and τ , one finds the variational energy $\epsilon_{\{S^0, M\}}^{(0)}$ (in au), the weight of $\Psi_m^{(0)}$ in the corresponding eigenvector, and the size of the ($S+M$) CI matrix. The SCF ($^1\Sigma_g^+$) energy (-91.6265 au) is taken as zero of energy

η	$^1\Sigma^-$				η	$^3\Pi$				
	$\tau = \eta$	$\tau = 0.01$	$\tau = 0.005$	$\tau = 0.0035$		$\tau = \eta$	$\tau = 0.01$	$\tau = 0.005$	$\tau = 0.0035$	
0.15	-0.0501	-0.2515	-0.2997	-0.3169	0.15	0.1043	-0.1968	-0.3262	-0.3419	
	1.0	0.866	0.867	0.867		1.0	0.907	0.903	0.903	
	(4)	(282)	(771)	(1210)		(1)	(254)	(707)	(1047)	
0.055	-0.1473	-0.2470	-0.3001	-0.3242	0.075	-0.161	-0.2731	-0.3281	-0.3463	
	1.0	0.951	0.941	0.935		1.0	0.944	0.935	0.931	
	(26)	(246)	(675)	(1185)		(12)	(216)	(671)	(1045)	
0.035	-0.1770	-0.2483	-0.3034	-0.3260	0.030	-0.1867	-0.2720	-0.3261	-0.3462	
	1.0	0.966	0.953	0.949		1.0	0.961	0.950	0.946	
	(40)	(246)	(676)	(1171)		(29)	(212)	(640)	(1047)	
	-0.1923	-0.2476	-0.3027	-0.3253		0.025	-0.2088	-0.2707	-0.3250	-0.3458
	1.0	0.975	0.961	0.956			1.0	0.973	0.960	0.955
(75)	(231)	(661)	(1163)	(45)	(199)	(617)	(1022)			

Table 7

$^1\Sigma^+$ energy estimates from eqs. (29) MP and (30) EN, including the Davidson–Siegbahn corrected variational energies and MP and EN second-order contribution (au)

η	$\tau = \eta$		$\tau = 0.01$		$\tau = 0.005$		$\tau = 0.0035$	
	MP	EN	MP	EN	MP	EN	MP	EN
0.15	-92.0378	-92.1860	-92.0545	-92.0791	-92.0526	-92.0650	-92.0518	-92.0599
0.075	-92.0326	-92.1043	-92.0406	-92.0637	-92.0426	-92.0563	-92.0458	-92.0553
0.035	-92.0354	-92.0692	-92.0428	-92.0600	-92.0472	-92.0599	-92.0480	-92.0574
0.025	-92.0364	-92.0642	-92.0422	-92.0619	-92.0462	-92.0587	-92.0474	-92.0566

the four best calculations (last two values of η and τ) one finds that the energy difference lies between 0.009 and 0.003 au (i.e. 0.3 and 0.1 eV) the lowest state being the $^3\Pi$ state.

Two calculations on the same system have been performed with the MRD CI method. Bruna et al. [36] using a basis set similar to ours also suggest that $E(^1\Sigma^+) > E(^3\Pi)$ by 0.05 eV. Adding f functions in the basis (see ref. [21]) seems to favour the $^1\Sigma^+$ state which is found to be the stablest state by 0.1 eV. The result obtained in ref. [22] with the CAS SCF method is difficult to compare since it uses a set of two d functions in each atom.

7. Discussion

The proposed algorithm implies three levels of approximation:

- progressive choice of a multireference zeroth-order variational wavefunction, which does not necessarily give an important part of the correlation energy but allows us to include the most important changes of the wavefunction, which are likely to slow down the convergence of the perturbation expansion, and to reach the most important triple and quadruple excited configurations. This zeroth-order wavefunction may include up to 200 determinants.

Table 8

$^3\Pi$ energy estimates from eqs. (29) (MP) and (30) (EN) (au)

η	$\tau = \eta$		$\tau = 0.01$		$\tau = 0.005$		$\tau = 0.0035$	
	MP	EN	MP	EN	MP	EN	MP	EN
0.15	-92.0516	-92.1497	-92.0600	-92.0779	-92.0605	-92.0682	-92.0605	-92.0655
0.075	-92.0406	-92.0778	-92.0560	-92.0736	-92.0594	-92.0677	-92.0604	-92.0662
0.035	-92.0403	-92.0712	-92.0525	-92.0683	-92.0556	-92.0640	-92.0568	-92.0626
0.025	-92.0380	-92.0589	-92.0487	-92.0635	-92.0537	-92.0620	-92.0556	-92.0615

Table 9

Energy difference between the two nearly degenerate states [$E(^1\Sigma^+) - E(^3\Pi)$] from eqs. (29) (MP) and (30) (EN) (au)

η	$\tau = \eta$		$\tau = 0.01$		$\tau = 0.005$		$\tau = 0.0035$	
	MP	EN	MP	EN	MP	EN	MP	EN
0.15	0.0138	0.0383	0.0055	-0.0012	0.0079	0.0032	0.0087	0.0056
0.075	0.080	0.0265	0.0154	0.0099	0.0168	0.0114	0.0146	0.0109
0.035	0.049	0.0020	0.0097	0.0083	0.0084	0.0041	0.0088	0.0052
0.025	0.0016	-0.0053	0.0065	0.0014	0.0075	0.0033	0.0081	0.0049

– selection of the most important determinants obtained through single and double substitution on the multiconfigurational zeroth-order wavefunction, and diagonalization of the resulting matrix, which may have the size of 1 to 5×10^3 determinants.

– the other singly and doubly substituted determinants are treated by a second-order perturbation. Their number may be huge (10^6) but the low order of perturbation allows a rapid calculation.

These three levels of approximation define clearly the main difficulties of the procedure. One may hope that starting from a refined zeroth-order wavefunction, the perturbation expansion is rapidly convergent (as appears from the fact that the fourth-order corrected energy does not differ from the variational value in $\langle S + M \rangle$). However, the $\langle S + M \rangle$ variational treatment introduces a first error which is due to the normalization of the wavefunction. This error may be corrected through the Davidson–Siegbahn formulas, which appear to be very efficient for this multireference case, in view of the H_2O test. Then the second-order treatment of the remainder introduces a last and more important error. It is likely that $\epsilon^{(2)\text{MP}}$ is underestimated, while $\epsilon^{(2)\text{EN}}$ may be slightly overestimated.

The error on $\epsilon^{(2)\text{MP}}$ and $\epsilon^{(2)\text{EN}}$ may be evaluated by considering two successive iterations $\tau_1 > \tau_2$ for a given value of η . Then some determinants, which were treated in a perturbative mode in the first iteration are treated variationally in the second one, and from the comparison of the variational and perturbative corrections

$$\left[\epsilon^{(0)\text{DS}}(\tau, \eta_1) + \epsilon^{(0)\text{DS}}(\tau, \eta_2) \right] \times \left[\epsilon^{(2)}(\tau, \eta_1) - \epsilon^{(2)}(\tau, \eta_2) \right]^{-1} = \lambda, \quad (31)$$

one may try to obtain the λ^{MP} and λ^{EN} correction parameters which should allow us to correct the last perturbation correction and guess some improved estimate ($\tau \rightarrow 0$), closer to the exact solution. Such an analysis has been performed and we obtained

$$\begin{aligned} \lambda^{\text{MP}} &= 1.05 \pm 0.02, \\ \lambda^{\text{EN}} &= 0.95 \pm 0.04, \quad \text{for } {}^1\Sigma^+; \\ \lambda^{\text{MP}} &= 1.07 \pm 0.03, \end{aligned}$$

$$\lambda^{\text{EN}} = 0.96 \pm 0.03, \quad \text{for } {}^3\Pi;$$

when applied to the best calculations, these corrections suggest (in au)

$$E({}^3\Pi) = -92.0601 \text{ (MP) or } -92.0587 \text{ (EN)},$$

$$E({}^1\Sigma^+) = -92.0514 \text{ (MP) or } -92.0521 \text{ (EN)},$$

$$\Delta E = 0.0087 \text{ (MP) or } 0.0066 \text{ (EN)}.$$

The discrepancy between the MP and EN absolute values of each state is of course reduced and the energy difference between the two states is somewhat stabilized with respect to our previous estimates. This procedure may be thought as an attempt to reach the final variational DCI from a given multireference space, i.e. the limit $\tau = 0$ for a given value of η . This is an alternative solution along the way followed by the MRD CI scheme (at its first extrapolation step).

As another extrapolation technique, one may consider the surface $E = f(\tau, \eta)$ and rather than finding the $f(0, \eta)$ limiting curve which requires a further extrapolation for $\eta \rightarrow 0$, one may try to find directly an estimate of $E(\tau = 0, \eta = 0)$, from the few points calculated on the surface. Considering two calculations which imply a consistent improvement in η and τ , i.e. two calculations (τ_1, η_1) and (τ_2, η_2) such that

$$\tau_1/\eta_1 = \tau_2/\eta_2 = a \quad (a < 1), \quad (\tau_2 < \tau_1),$$

they belong to a line $\tau = a\eta$ which goes through the origin $\tau = \eta = 0$. Then assuming a constant energy variation along this line one may try to estimate $E(\tau = 0, \eta = 0)$ from the best calculation τ_2, η_2 and the local slope of the energy curve

$$E(0, 0) = E(\tau_2, \eta_2) + \frac{E(\tau_2, \eta_2) - E(\tau_1, \eta_1)}{\tau_2 - \tau_1} \tau_2. \quad (32)$$

This may be done independently on both the MP and EN surfaces, the agreement between the two independent estimates gives an indication upon the reliability of the extrapolation procedure. When applied to the CN^+ problem, this procedure gives:

$$E({}^3\Pi) = -92.0556 \text{ (MP) or } -92.0553 \text{ (EN)},$$

$$E({}^1\Sigma^+) = -92.0480 \text{ (MP) or } -92.0484 \text{ (EN)},$$

$$\Delta E = 0.0076 \text{ (MP) or } 0.0069 \text{ (EN)}.$$

These extrapolated values are somewhat higher (by ≈ 0.0040 au) than the previous ones but they are surprisingly consistent, and the energy difference is confirmed to lie around 0.0070 au (0.2 eV) with an increased certitude. The later extrapolation technique seems more reliable since it handles simultaneously τ and η , while the former one only deals with the dependence of the energy on the parameter τ .

8. Comparison with MRD CI

At this stage one may be tempted to compare our procedure with the improved MRD CI scheme [21], which also handles three classes of determinants in a very similar way. Besides some differences in the relative sizes of $\{S\}$ and $\{M\}$, the main differences concern:

(i) The use of Brillouin–Wigner type of estimate $\epsilon_{\{s\}}^{\text{BW}}$ for the remainder $\{s\}$ instead of the MP and EN Rayleigh–Schrödinger estimates $\epsilon_{\{s\}}^{(2)\text{MP(or EN)}}$.

(ii) The place where the Davidson correction is performed. The MRD CI method tries to make first an extrapolation procedure to guess the variational result of the SD multireference CI, determining λ such that

$$\epsilon_{\{S+M\}}^{\text{var}} + \lambda \epsilon_{\{s\}}^{\text{BW}} = \epsilon_{\{S+M+s\}}^{\text{var}}.$$

Then the Davidson correction is applied to this extrapolated value. (notice that at this stage the evaluation of C^0 becomes difficult, since it should be extrapolated; the fact that our extrapolated energies [$E(^3\Pi) \approx -92.0555$ au, $E(^1\Sigma^+) \approx -92.0482$ au] are lower than the limits proposed in ref. [21], despite the use of a slightly larger basis set in ref. [21], may be related to an underestimation of the Davidson correction for $\tau = 0$.)

(iii) The quality of the zeroth-order wavefunction is improved by enlarging $\{S\}$ and the extrapolated and Davidson-corrected results are plotted as functions of the quality of the zeroth-order wavefunction $(C^0)^2 = |\langle \Psi_m^0 | \Psi_m \rangle|^2$ which should tend toward 1 and a new extrapolation is performed for $C^0 \rightarrow 1$.

In the present procedure, we do prefer to apply the Davidson correction to the variational part

only and we accept the uncertainty on the second-order remainder. The previously defined extrapolated λ correction [eq. (31)] for the second-order $\epsilon^{(2)}$ values may be performed, or, preferably an extrapolation of the energy along a line $\tau = a\eta$ ($a \ll 1$) [eq. (32)], but our objective is to reach first some stability in the results before further extrapolations. It actually appears from the four best calculations in table 7 that a certain stability (< 0.003 au, i.e. 0.1 eV) has been obtained for each state and that the energy ordering between the two states is not affected by the remaining uncertainty (for a given choice of H_0): for instance, for the four best calculations, the highest estimate of $E(^3\Pi)$ (-92.054 au for MP, -92.061 au for EN) is always lower than the lowest estimate of $E(^1\Sigma^+)$ (-92.049 for MP, -92.069 for EN), without any extrapolation or corrective factor. Our point of view is that a sufficient stability of the results for small values of τ and η would be preferable to hardly controlled extrapolation techniques. Of course the energy stabilization of $E(\tau, \eta)$ in a certain region ($\eta_1 < \eta < \eta_2$, $\tau_1 < \tau < \tau_2$) of the parameters may be fortuitous, but such a local stabilization would prevent any reliable extrapolation as well.

9. Conclusion

The improved CIPSI algorithm proposed in the present work defines three classes of determinants for each state:

- the largest ones $S(\text{strong})$ are generators and define a multiconfigurational zeroth-order wavefunction, which will be perturbed by allowing all single and double substitutions.

- the mean ones $M(\text{middle})$ ($\approx 10^3$) are perturbed to all orders, and the normalization defect is corrected through the Davidson–Siegbahn formulas,

- the most numerous smallest ones (s) ($\approx 10^6$) are only included through their second-order correction. Two threshold parameters η and τ define the borders of the classes, and are progressively decreased for a rational selection of the classes and for a study of the stability of the results.

Several states may be calculated simulta-

neously, provided that $S = S_1 \cup S_2$, $M = M_1 \cup M_2 - (M_1 \cup M_2) \cap S$ and $s = s_1 \cup s_2 - (s_1 \cup s_2) \cap (M \cup S)$.

The numerical tests of the exactly resolved H_2O problem showed a very good convergence and accuracy (especially with the Epstein–Nesbet definition of H_0); the error is of the same order as from the SDTQ CI diagonalization at a much smaller computational expense. For the nearly degenerate CN^+ problem, the process indicates ${}^3\Pi < {}^1\Sigma^+$, with a great stability the energy difference being between 0.1 and 0.3 eV. A direct extrapolation technique has been suggested to correct the second-order contributions. The proposed algorithm has been compared with the parent MRD CI scheme which essentially differs by the fact that the Davidson correction is applied after a first extrapolation, and followed by a second extrapolation.

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