

Recent Advances in Multireference Second Order Perturbation CI: The CIPSI Method Revisited

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The evolution of the CIPSI method, with the latest modifications recently implemented in our laboratory, is described. A new version, based on a diagrammatic technique, is presented. Test calculations which have been run on water, ethylene, and transacrolein, show that the new method is a powerful tool for the study of medium-size molecular systems.

INTRODUCTION

CIPSI (Configuration Interaction by Perturbation with multiconfigurational zeroth-order wave functions Selected by Iterative process) is a variation-perturbation method for the determination of correlated electronic wave functions and energies. It was first developed in 1973 by Huron, Malrieu, and Rancurel¹ and has been widely employed² since as a valuable tool, also for accurate studies of excited states and potential energy surfaces. In the course of the years, until very recently, CIPSI has undergone extensions and improvements, due both to the research group of Toulouse and to ours.^{2d,3-9} Therefore, we think it useful to expose once more the method, with all the recent extensions and options with which it is endowed and to give some details about its implementation in the version currently in use in our laboratory.

The last section of the article will be devoted to the discussion of some test calculations on two well known benchmarks, H₂O¹⁰ and C₂H₄,¹¹ as well as on a larger system, transacrolein.

THE CIPSI METHOD

Full CI calculations involve overwhelmingly large numbers of configurations even for molecular systems and basis sets of modest size. The necessity of truncating the configurational basis has led to devise different methods for partitioning the CI space in classes, each

corresponding to a different level of approximation in the treatment.

The CIPSI method is essentially based on a partition of the CI space in two subspaces. The Slater determinants $|J\rangle$ which are most important for the description of the electronic states of interest are contained in the subspace S . The CI Hamiltonian in such a basis set is diagonalized:

$$\hat{P}\hat{H}\hat{P}|\Phi_m^{(0)}\rangle = E_m^{(0)}|\Phi_m^{(0)}\rangle \quad (1)$$

where $\hat{P} = \sum_{J \in S} |J\rangle \langle J|$ is the projection operator in S . The solution of the full CI problem is approximated by taking into account all the other configurations by a perturbation treatment based on the zeroth order wave functions $\Phi_m^{(0)}$. Up to the second-order in perturbation theory, the only nonvanishing contributions are provided by those determinants which differ by one or two spin-orbitals from at least one $|J\rangle \in S$. The second-order correction to the correlation energy is given by:

$$E_m^{(2)} = - \sum_{K \in S} \frac{|\langle \Phi_m^{(0)} | H | K \rangle|^2}{E_K - E_m^{(0)}} \quad (3)$$

where E_K is the mean value of the Hamiltonian for the Slater determinant $|K\rangle$. Equation (3) refers to the Epstein-Nesbet partition (EN) of the electronic Hamiltonian^{10,11}, but other choices are possible; the most frequently employed is the Møller-Plesset baricentric¹² (MPB) partition, according to which E_K is replaced by a sum of Hartree-Fock energies of the spin-orbitals i occupied in the Slater determinant $|K\rangle$:

$$E_k = \sum_{i=1}^{n_{el}} \epsilon_i \quad (4)$$

The ϵ_i depend on the orbital occupation pattern of a reference (usually SCF) determinant¹³; a balanced choice of the Møller-Plesset zeroth order energies inside the S space consists in the so-called "baricentric" energy,¹ which replaces $E_m^{(0)}$ in eq. (3):

$$E_m^{(MPB)} = - \sum_{J \in S} c_{mJ}^2 E_J \quad (5)$$

(here c_{mJ} is the coefficient of $|J\rangle$ in $|\Phi_m^{(0)}\rangle$). The first-order correction of the wave function consistent with eq. (3) is:

$$|\Phi_m^{(1)}\rangle = - \sum_{K \in S} |K\rangle \frac{\langle K|H|\Phi_m^{(0)}\rangle}{E_k - E_m^{(0)}} \quad (6)$$

Improving the Efficiency of the Perturbation Calculation

The most time consuming part of a CIPSI calculation consists in evaluating the perturbation energy, eq. (3). (We have employed different versions of the CIPSI program on IBM computers of the 370 series and on a GOULD-SEL CONCEPT 32/87 mini-computer.) In the original version of the program, this required that all single and double spin-orbital substitutions should be applied to all the determinants belonging to S . The generated determinant $|K'\rangle$ is then compared with each $|K\rangle \in S$, in order to: (i) check that $|K'\rangle \in S$; (ii) check that $|K'\rangle$ has not already been generated; (iii) calculate the $\langle K|H|K'\rangle$ matrix element. The number of operations needed in this calculation is roughly proportional to $N_{occ}^2 N_{virt}^2 N_s^2$, where N_{occ} , N_{virt} , and N_s are the dimensions of the occupied MO space, of the virtual MO space and of the S determinantal space.

This large number of operations could in principle be reduced by setting up a code based on spin-adapted functions, instead of Slater determinants, as in the SPIN-CIPSI program of Gouyet and Prat.¹⁴ An efficient alternative was provided by Pelissier,³ who worked out the relationships between the contributions to summation (3), due to determinants connected by spin and/or space symmetry transformations: this feature, when implemented, shortened the calculation time by at least a factor of 2 (considerably more for diatomic molecules), also depending on the S subspace employed.

In a typical CIPSI run, the generation of the orbital indices of valid single and double excitations and the comparison of determinants consume more CPU time than the floating-point arithmetics needed in evaluating and summing up the perturbation contributions. On the other hand, two CIPSI calculations with the same S subspace go through the same operations concerning orbital, integral, and determinantal indices, and only differ in the floating-point operations involving the bielectronic integrals. We have thus implemented a "tape perturbation CI", which consists in stocking on a disk file all the necessary information about the determinants which can be generated by single and double excitations applied to the S subspace, and their relationships with the determinants belonging to S . The CPU time required by any subsequent calculation, taking advantage of the information already stocked on disk, is reduced by a factor which increases with the dimension of the S space, typically from 3 to 10. This feature is particularly useful for the scanning of potential energy surfaces and for coordinate optimization: notice that, at least in the latter case, it is highly recommendable to employ the same S subspace, suitably selected from exploratory calculations performed at some representative geometries.^{2d}

A very large gain in efficiency, not depending on previous storage of information, has been realized by implementing a completely new perturbation program, based on the explicit diagrammatic formulation of all the interactions connecting each couple of determinants of S to the second-order of perturbation.⁹ The CPU time required with this method contains a component proportional to $N_{occ}^2 N_{virt}^2 N_s$, and another one proportional to $N_{occ} N_{virt} (N_{occ} + N_{virt}) N_s^2$ for the most unfavorable distribution of orbital differences; also here the spin symmetry is exploited to reduce the total number of operations. Our rather limited experience shows that the diagrammatic program is faster than the traditional one about 10–20 times for large number of electrons and dimensions of the MO and determinantal bases. For reasons which will be clear in the following and because it takes more time to evaluate EN energies than MP, we have only implemented the MPB option in the diagrammatic program.

Questions of Convergence

A typical application of the CIPSI method consists of two to four runs, with progressively enlarged S spaces: all the determinants contributing to the perturbed wave function with a coefficient [eq. (6)] larger than a given threshold η will be included in the S space for the next step of the calculation. As the diagrammatic method does not generate the individual excited determinants involved in the perturbation, we use the original program to select the determinants; only in the last step, the most time consuming, the diagrammatic method is employed. In principle the result of this procedure tends to the full CI limit. There are two kinds of approximation which improve by enlarging the S space: (i) the truncation of the total CI space considered in the calculation, S + single excitations + double excitations; (ii) the usage of a second-order perturbation formula instead of the exact diagonalization of the CI matrix; the error implied in the latter approximation becomes less and less important as the determinants which are closest in energy to the sought-for CI roots (giving the largest perturbation contributions) are progressively included in the S subspace, compatibly with the increasing cost of the calculation. According to a wide experience in the application of the CIPSI method, the second source of error often remains more important than the first, especially when dealing with problems connected with spectroscopy or chemical reactivity, because in such cases the degree of near-degeneracy of the determinants can vary to a considerable extent depending upon the electronic state and/or the nuclear geometry.

Resorting to the third-order of perturbation theory might contribute to solve this problem; this seems to be feasible in the framework of diagrammatic perturbation theory, without a significant loss of generality in the definition of the S subspace.

Another way to improve the CIPSI method under this respect has been suggested by Evangelisti, Daudey, and Malrieu⁵ in analogy with other hierarchical partitions of the CI space.^{15,16} The basic idea is to introduce an intermediate class of determinants, not to be considered as generators of excited determinants for the perturbation calculation, the contribution of which is taken into account to

infinite order by diagonalization. We shall set out our implementation of the three-class method, which slightly differs from that of ref. 5.

We set up a zeroth-order space S and a subspace G of generators, on the basis of two selection thresholds η_S and η_G ($\eta_S \leq \eta_G$) and of the perturbation coefficients [eq. (6)] obtained in a preceding, less extended, calculation. The CI matrix built upon the S space is diagonalized and all the singly and doubly substituted determinants [Q space in Fig. 1(a)] are generated from the subspace G . The CI matrix takes on the aspect shown in Figure 1(b): only a few eigenvectors, usually the lowest of a given symmetry, are calculated by the Davidson technique¹⁷; the wave functions $\Phi_m^{(0)}$ and the energies $E_m^{(0)}$ thus obtained [eq. (1)] represent the zeroth-order description of the electronic states of interest. The second-order perturbation theory then operates as already specified by eqs. (2)–(6). A considerable amount of computation is saved by the optional approximation of neglecting the B matrix [Fig. 1(a)] in building the matrix elements C [Fig. 1(b)] between the excited determinants belonging to Q and the zeroth-order eigenvectors; this is justified because the interaction between the determinant $|K\rangle EQ$ and the nongenerator $|J\rangle ES$ should be multiplied by the presumably small coefficients of J in the zeroth-order wave functions. In the diagrammatic approach we have adopted this last approximation because we found it too laborious to recognize whether a given diagram, connecting two nongenerator determinants M , NES , corresponds or not to an excited determinant which might be generated from the G subspace. In this case, the diagrammatic calculation is formally identi-

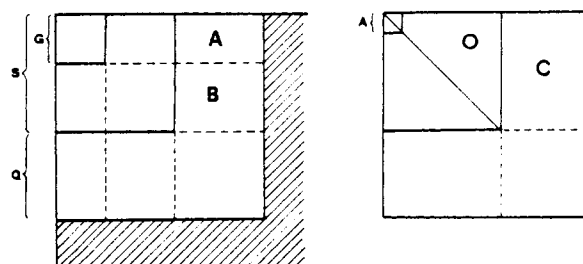


Figure 1. Partition of the CI space in the three class CIPSI algorithm, before (a) and after (b) the diagonalization in the S subspace: G , generators; S , zeroth order; Q , single and double excitations from G ; A , zeroth-order eigenvectors of interest.

cal to that carried out by taking only G as the zeroth-order space and in practice it requires little more computing time. Our implementation (either with or without the afore-said approximation) differs from the original proposal by Evangelisti, Daudey, and Malrieu⁵ in that the zeroth-order wave functions they employ in the perturbation calculation are obtained by diagonalization in the G space; the eigenvalues relative to the S space serve only to correct the final energy results; this procedure and ours may behave rather differently in some cases, for instance in the neighborhood of conical intersections, when a problem of identification of the eigenvectors in the S space with those in the G space may arise.

In the framework of the three-class algorithm, one might introduce a further correction to the computed correlation energy, of the type proposed by Siegbahn,¹⁸ as in the work of Evangelisti, Daudey, and Malrieu.⁵ In the same spirit (as suggested by one of the referees), one might renormalize the projection of $\Phi_m^{(0)}$ in the G space, which amounts to dividing the perturbation correction by the square norm. These proposals deserve further investigation, also in connection with the size consistence problem.¹⁹

Additional Features

Both the diagrammatic and the original versions of CIPSI allow a Quasi Degenerate Perturbation Theory calculation^{4,8,20} to be performed, still adopting the CI eigenvectors in the S space as zeroth-order wave functions, instead of single determinants as in the standard formulation of QDPT.²¹ This implementation of QDPT preserves a basic advantage of the CIPSI method, consisting in avoiding the occurrence of quasidegeneracies at the border between the zeroth-order and the perturbation spaces. The QDPT calculation is most valuable in the case of close lying electronic potential energy surfaces.⁶ For the treatment of avoided crossings and conical intersections, the QDPT can be employed in conjunction with a procedure which transforms the adiabatic zeroth-order basis in a quasidiabatic one,^{7,8,22} without resorting to a preliminary calculation of the nonadiabatic coupling matrix elements. A separate program calculates spinless one-particle (one-

state or transition) density matrices to the zeroth- and first-order of perturbation theory [eq. (6)]; the matrix elements corresponding to the α , β molecular orbitals are given by:

$$[P_{mn}^{(0)}]_{\alpha\beta} = \langle \Phi_m^{(0)} | a_\alpha^\dagger a_\beta | \Phi_n^{(0)} \rangle \quad (7)$$

$$[P_{mn}^{(1)}]_{\alpha\beta} = \langle \Phi_m^{(0)} | a_\alpha^\dagger a_\beta | \Phi_n^{(1)} \rangle + \langle \Phi_m^{(1)} | a_\alpha^\dagger a_\beta | \Phi_n^{(0)} \rangle \quad (8)$$

where a_α^\dagger , a_β are the pertinent creation and annihilation operators.

All the features and options illustrated in this section and in the preceding ones are compatible with one another (MPB or EN partitions, intermediate class of nongenerators belonging to S , QDPT, quasidiabatic states, evaluation of density matrices). All the programs can treat systems with even or odd number of electrons, with any spin multiplicity, starting from an arbitrary MO basis. The S space may include determinants with up to 6 excitations with respect to a reference closed shell. The dimension of S is limited to 2000 determinants, of which at most 400 are generators. The MO set is confined to 70 basis functions; with the present limitations imposed by the architecture of our GOULD SEL CONCEPT 32/87 minicomputer, i.e., about 1.8 Mbytes of internal storage, the largest symmetry block cannot exceed 47 MOs.

TEST CALCULATIONS

We have performed test calculations on two famous benchmarks for the CI, water,²³ and ethylene²⁴ with a double- ζ atomic basis set, and on a larger system, transacrolein, where the performance of the method is better assessed.

Water

Saxe, Schaefer, and Handy²³ performed a full CI calculation on the ground state of H_2O , with a double- ζ basis set; their variational energy, obtained with a 256473 configurations wave function, is -76.157866 a.u. This is, of course, an ideal benchmark for approximate methods aiming to obtain accurate results on small systems. The three-class CIPSI method was already tested against double- ζ H_2O by Evangelisti, Daudey, and Malrieu.⁵ Our versions of the program have been likewise submitted to this test; we used the same geometry and basis set as Saxe,

Schaefer, and Handy²³ and we obtained an identical SCF energy, to the first ten significant digits. Our results are shown in Figure 2 and Table I. They bear a strong similarity with those of Evangelisti, Daudey, and Malrieu,⁵ both with regard to the dependence on the thresholds η_G and η_s , and in the closest approximation obtained of the full CI limit. Obviously, our employing larger G spaces allows a better accuracy to be reached. We have carried out three-class calculations with and without neglect of the B submatrix in the CI Hamiltonian (see Fig. 1); the exact results are consistently slightly better than the approximate ones; it is not surprising that the latter resemble more closely those of Evangelisti and co-workers because they neglect the same class of interactions between determinants, contained in the B matrix. We only report the CPU times required on the GOULD SEL minicomputer with the largest G and S spaces ($N_G = 392$, $N_s = 1940$): 1600 sec for the exact CIPSI calculation, 1200 sec. for the approximate one, 390 sec with the diagrammatic version.

Ethylene

Saxe and co-workers²⁴ performed also an extensive SD-GUGA calculation for the ethylene molecule, with a double- ζ basis sup-

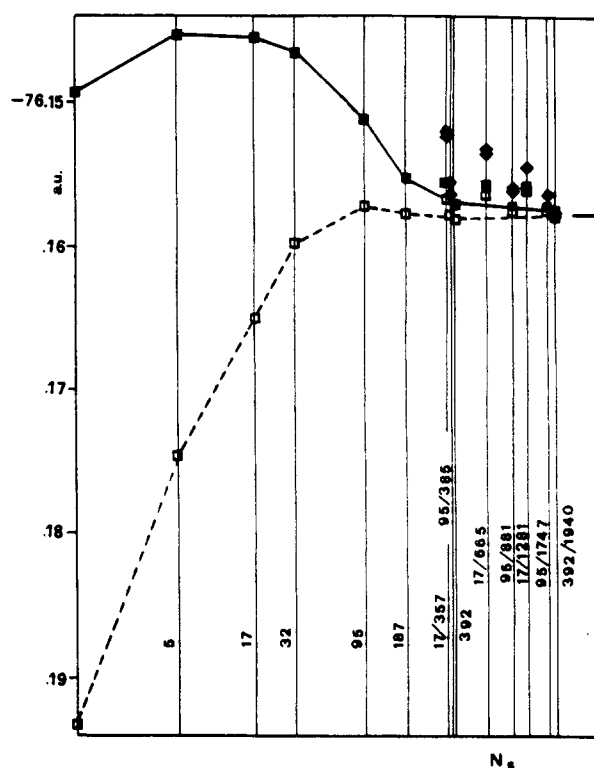


Figure 2. CIPSI results for water. Total energy in hartrees versus number of determinants in the S space (logarithmic scale). ■, Møller-Plesset baricentric partition; □, Epstein-Nesbet; ♦ and ◇, MPB and EN calculations with neglect of the B matrix elements. The numbers labelling the vertical lines give N , for each calculation, or N_G and N_s , when $G \neq S$. On the right margin the variational limit of ref. 23 is shown.

plemented with six polarization d functions on the carbon atoms. Their calculation was

Table I. CIPSI results for H_2O . Energy differences in hartrees, with respect to the full CI limit, -76.157866 .

η_G	η_s	N_G	N_s	$\Delta E(\text{VAR})$	$\Delta E(\text{MPB})$	$\Delta E(\text{EN})$	$ \langle \Phi \Phi \rangle ^a$
—	—	1	1	+0.148028	+0.008551	-0.035232	0.0759
0.0500	0.0500	5	5	+0.122381	+0.012481	-0.016755	0.0535
0.0300	0.0300	17	17	+0.097244	+0.012347	-0.007001	0.0358
0.0300	0.0020	17	357	+0.009021	+0.002372	+0.001301	0.0014
0.0300 ^b	0.0020	17	357	+0.009021	+0.005839	+0.005516	0.0004
0.0300	0.0006	17	665	+0.005882	+0.002206	+0.001610	0.0008
0.0300 ^b	0.0006	17	665	+0.005882	+0.004531	+0.004418	0.0001
0.0300	0.0003	17	1281	+0.003944	+0.002008	+0.001685	0.0004
0.0300 ^b	0.0003	17	1281	+0.003944	+0.003389	+0.003344	0.0001
0.0200	0.0200	32	32	+0.077343	+0.011385	-0.001914	0.0256
0.0120	0.0120	95	95	+0.045613	+0.006758	+0.000668	0.0106
0.0120	0.0020	95	385	+0.008231	+0.001147	+0.000064	0.0013
0.0120 ^b	0.0020	95	385	+0.008231	+0.002383	+0.001552	0.0011
0.0120	0.0008	95	881	+0.005051	+0.000892	+0.000311	0.0007
0.0120 ^b	0.0008	95	881	+0.005051	+0.001993	+0.001634	0.0004
0.0120	0.0004	95	1747	+0.002926	+0.000691	+0.000384	0.0003
0.0120 ^b	0.0004	95	1747	+0.002926	+0.001484	+0.001335	0.0002
0.0060	0.0060	187	187	+0.018061	+0.002672	+0.000146	0.0038
0.0018	0.0018	392	392	+0.008004	+0.000957	-0.000097	0.0013
0.0018	0.00045	392	1940	+0.002584	+0.000359	+0.000093	0.0003
0.0018 ^b	0.00045	392	1940	+0.002584	+0.000313	+0.000035	0.0003

^aEpstein-Nesbet partition.

^bApproximate evaluation of perturbation.

based on a set of approximate NOs obtained from a variational wave function including all singles and doubles. The final wave function included all the 5057 single and double excitations with respect to the closed-shell ground state, plus a selection of triples and quadruples, for a total of 1046758 configurations; no excitation from the $1s$ ($1a_g$ and $1b_u$) orbitals of the carbon atoms was allowed. The variational energy thus obtained was $E_{\text{var}} = -78.35451$ a.u. As the atomic integrals package we use (a modification of HONDO IV²⁵) only provides a set of five pure d functions, we replaced the $x^2 + y^2 + z^2$ linear combination with one s function for each carbon atom, having the same Gaussian exponent. The SCF energy thus obtained exactly reproduced that given by Saxe, Schaefer, and Handy with seven significant digits, -78.05053 , therefore enabling us to proceed to meaningful comparisons between our CIPSI results and the variational one.

Figure 3 and Table II show the convergence of two sets of CIPSI calculations, using two different MO bases: canonical SCF MOs and approximate Natural Orbitals obtained by diagonalizing the one-particle density matrix relating to a variational wave function built upon 1951 determinants. In the best SCF-MO-CIPSI calculations we performed ($N_s = 360, N_G = 1951$), about 3440000 determinants were generated. The energies thus obtained are all slightly higher than the variational result by Saxe, Schaefer, and Handy, E_{var} ; if we consider the last two steps in the CIPSI procedure, with the passage from the two-class to the three-class algorithm, the best stability is obtained with the EN partition,

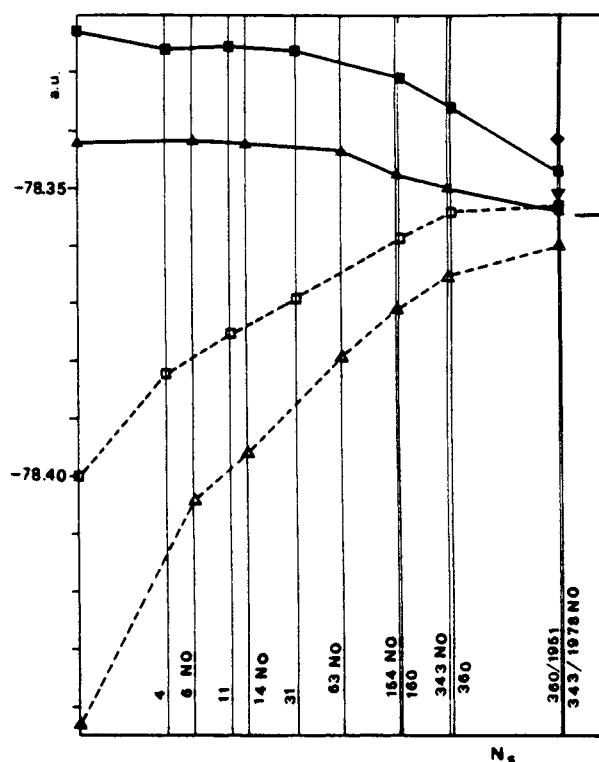


Figure 3. CIPSI results for ethylene, total energy in hartrees versus number of determinants in the S space (logarithmic scale). ■, and □, ◆ as in Figure 2; ▲ and ▽, MPB and EN calculations with Natural Orbitals; ▼, approximate MPB calculations with NOs. The numbers labelling the vertical lines give N_s for each calculation, or N_G and N_s , when $G \neq S$. On the right margin the variational limit of ref. 24 is shown.

eventually yielding an energy difference $\Delta E = E_{\text{CIPSI}} - E_{\text{var}} = +1.6$ mH. The approximation of neglecting the B Hamiltonian submatrix (Fig. 1) yields a higher energy ($\Delta E = +13$ mH). The NO-CIPSI calculations show a better convergence trend, according to various indicators: the zeroth-order variational energies, the square norm of the first-

Table II(a). CIPSI results for ethylene, with SCF MOs. Energies in hartrees. CPU times in seconds. Best variational result: -78.35451 (ref. 11).

η_G	η_s	N_G	N_s	$E(\text{VAR})$	$E(\text{MPB})$	$E(\text{EN})$	$ \langle\Phi \Phi\rangle ^*$	CPU time
—	—	1	1	-78.05053	-78.32299	-78.40025	0.1815	7
0.0500	0.0500	4	4	.07461	.32590	.38214	0.1319	13
0.0300	0.0300	11	11	.08651	.32565	.37536	0.1190	34
0.0200	0.0200	31	31	.10112	.32616	.36904	0.1046	160
0.0120	0.0120	160	160	.14339	.33072	.35857	0.0725	2280
0.0080	0.0080	360	360	.18342	.33584	.35418	0.0526	10100 (640 ^b)
0.0080	0.0030	360	1951	.27283	.34700	.35294	0.0193	50200
0.0080 ^c	0.0030	360	1951	.27283	.34134	—	0.0154 ^d	700 ^b

*Epstein-Nesbet partition, if not indicated otherwise.

^bDiagrammatic calculation.

^cApproximate evaluation of perturbation.

^dMøller-Plesset partition.

Table II(b). CIPSI results for ethylene, with Natural Orbitals. Energies in hartrees. CPU times in seconds. Best variational energy: -78.35451 (ref. 11).

η_G	η_s	N_G	N_s	$E(\text{VAR})$	$E(\text{MPB})$	$E(\text{EN})$	$ \langle\Phi \Phi\rangle ^a$	CPU time
—	—	1	1	-78.04981	-78.34206	-78.44312	0.2175	7
0.0500	0.0500	6	6	.09041	.34163	.40426	0.1346	19
0.0300	0.0300	14	14	.10729	.34216	.39597	0.1195	56
0.0200	0.0200	63	63	.14869	.34352	.37922	0.0844	470
0.0120	0.0120	154	154	.18764	.34753	.37102	0.0608	2250
0.0080	0.0080	343	343	.22434	.34989	.36525	0.0420	9040
0.0080	0.0025	343	1978	.29667	.35375	.35975	0.0152	49100
0.0080 ^b	0.0025	343	1978	.29667	.35117	—	0.0122 ^c	710 ^d

^aEpstein-Nesbet partition, if not indicated otherwise.^bApproximate evaluation of perturbation.^cMøller-Plesset partition.^dDiagrammatic calculation.

order correction to the wave function, the number of determinants selected for the same threshold η ; the difference between EN and MPB as well as between "rigorous" and "approximate" results (see Fig. 3 and Table II). The NO-CIPSI results are also closer to E_{var} ($\Delta E(\text{EN}) = -5.2$ mH, $\Delta E(\text{MPB}) = +0.8$ mH, and $\Delta E(\text{MPB}, "B = 0" \text{ approx.}) = +3.3$ mH). The best EN and MPB results, together with the convergence trends shown in Figure 3, would place the total energy between -78.354 and -78.360 , with an uncertainty of $\pm 1\%$ on the correlation energy. In comparing these results with those of Saxe, Schaefer, and Handy one should consider that in the largest NO-CIPSI calculation about 3260000 determinants were generated, whereas the variational wave function of ref. 24 consists of 1046758 configurations, or 4241550 determinants: the latter could be thought of as single and double excitations originating from all the singles and doubles within the valence space.²⁴ The size of our perturbation space is, therefore, slightly smaller than the variational space of ref. 24, but the criterion with which it is built up allows a somewhat greater flexibility: in fact, the G space in our calculation included many excitations outside the valence space (mostly doubles).

Transacrolein

We have also tested our program on a larger system, where the variational calculations cannot reach an accuracy comparable to that obtained for H_2O or C_2H_4 . We have

chosen the molecule of transacrolein, where there are several low lying excited states which can be reasonably described by means of a split-valence atomic basis set. The experimental ground-state equilibrium geometry²⁶ was adopted for all the states. In the SCF calculation we made use of semilocal pseudopotentials for the C and O atoms²⁷⁻²⁹ and of a double- ζ basis set.²⁹ The SCF energy was -34.416734 a.u. We performed CIPSI calculations with $22 e^-/40$ MO for the $^1A'$ ground state and the first $^{1,3}A''$ excited states. We also determined approximate Natural Orbitals for the ground and the lowest $^1A''$ state, from variational wave functions including, respectively, 1490 and 678 determinants. Figure 4 shows the total energy for the ground state and the transition energies, obtained by means of MO and NO-CIPSI calculations.

The total ground-state energy evaluated by means of the MPB partition appears to be more stable, with respect to increments in size of the G and S subspaces, than the EN results, both in the MO and NO calculations. The correlation energy can be estimated in 0.383 ± 0.005 a.u. The square norm of the first-order correction to the wave function is 0.095 and 0.082, respectively, for the largest MO and NO calculations. In the first case we have $N_G = 296$, $N_s = 1967$, and 17,340,000 generated determinants for three A' states, in the latter $N_G = 95$, $N_s = 927$ and 6,440,000 generated determinants for one state.

Also for the transition energies the MPB partition generally seems to give more stable results. The description of the $^1A'$ state manifestly improves when using NOs instead of the SCF-MOs of the ground state.

CONCLUDING REMARKS

The level of accuracy and the associated computer requirements deserve some more comments, which can be drawn from the test calculations on H_2O (10 e-/14 MO), C_2H_4 (12 e-/50 MO), and $\text{C}_3\text{H}_4\text{O}$ (22 e-/40 MO). As the difficulty of finding a good zeroth-order description increases along with the complexity of the molecular system, two trends manifest themselves: (i) The use of the EN partition seems to be advisable only for very accurate calculations, whereas the MPB partition gives more stable results for larger systems; this can be related to the smaller absolute values of the MPB correlation energies with respect to EN and is due to the difference in the denominators of eq. (3): they are normally larger in the MPB partition than in EN, thus damping the most dramatical oscillations due to the truncation of the perturbation series. (ii) As already observed, the computer times increase with the number of electrons and orbitals, much faster when using the original version of CIPSI than with the diagrammatic program; therefore,

the speed ratio between the two algorithms goes from about 1 for a 6 e-/61 MO calculation (BH^{30}), to 20–50 for three-class calculations on large systems.

The range of situations where the storage of determinantal and orbital indices on disk is most effective is about reversed: for BH with $N_Q = 396$, $N_s = 1059$ the first calculation takes 13800 sec, whereas all the successive runs need only 1230 sec; for larger systems, according to our experience, the efficiency factor oscillates around 3.

In conclusion the CIPSI method, in the versions presented here, shows a great flexibility as to the kind and size of the systems to which it can be applied, to the level of accuracy which can be reached and to the optional features now available.

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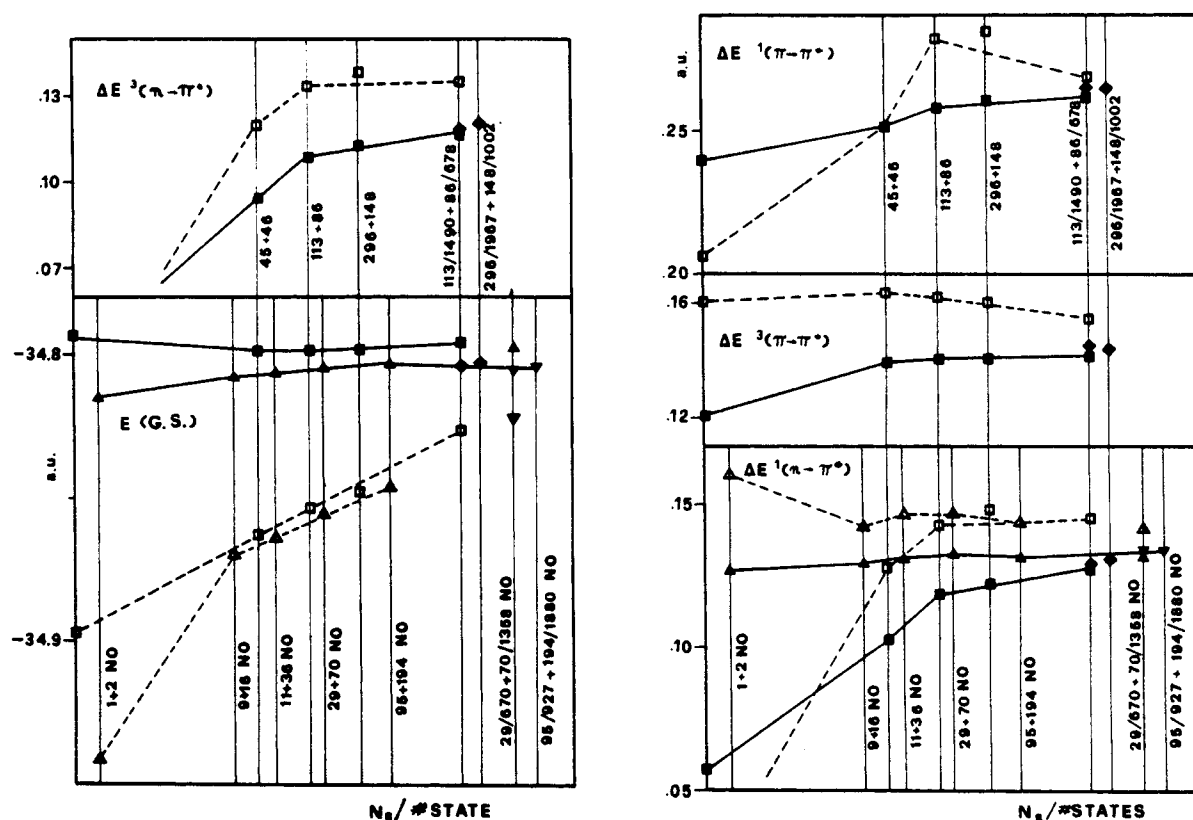


Figure 4. CIPSI results for transacrolein. Total and transition energies in hartrees versus N_s /(number of states). Same symbols as in Figures 2 and 3. The numbers labelling the vertical lines give N_s for each calculation, or N_G and N_s when $G \neq S$, for the A' and the A'' states separately.

References

1. B. Huron, J.-P. Malrieu, and P. Rancurel, *J. Chem. Phys.*, **58**, 5745 (1973).
2. See for instance: (a) G.-H. Jeung, J.-P. Daudey, and J.-P. Malrieu, *Chem. Phys. Lett.*, **94**, 300 (1983); (b) G.-H. Jeung, F. Spiegelmann, J.-P. Daudey, and J.-P. Malrieu, *J. Phys. B*, **16**, 2659 (1983); (c) F. X. Gadea, F. Spiegelmann, M. C. Castex, and M. Morlais, *J. Chem. Phys.*, **78**, 7270 (1983); (d) R. Cimiraglia, M. Persico, and J. Tomasi, *J. Am. Chem. Soc.*, **107**, 1617 (1985).
3. M. Pélissier, Thèse d'état, Université Paul Sabatier, Toulouse, 1980.
4. J.-P. Daudey and J.-P. Malrieu, in *Current Aspects of Quantum Chemistry 1981*, R. Carbo, Ed., Elsevier, Amsterdam, 1982, p. 35.
5. S. Evangelisti, J.-P. Daudey, and J.-P. Malrieu, *Chem. Phys.*, **75**, 91 (1983).
6. F. Spiegelmann and J.-P. Malrieu, *J. Phys. B*, **17**, 1235 (1984).
7. F. Spiegelmann and J.-P. Malrieu, *J. Phys. B*, **17**, 1259 (1984).
8. R. Cimiraglia, J.-P. Malrieu, M. Persico, and F. Spiegelmann, *J. Phys. B*, **18**, 3073 (1985).
9. R. Cimiraglia, *J. Chem. Phys.*, **83**, 1746 (1985).
10. P. S. Epstein, *Phys. Rev.*, **28**, 695 (1926).
11. R. K. Nesbet, *Proc. Roy. Soc. A*, **230**, 312, 322 (1955).
12. C. Møller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934).
13. R. K. Nesbet, *Rev. Mod. Phys.*, **35**, 552 (1963).
14. J. F. Gouyet and M. T. Prat, *J. Chem. Phys.*, **64**, 946 (1976).
15. R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, *Mol. Phys.*, **35**, 771 (1978).
16. R. J. Buenker, S. D. Peyerimhoff, and P. J. Bruna, in *Computational Theoretical Organic Chemistry*, NATO ASI C67, I. G. Csizmadia and R. Daudel, Eds., Reidel, Dordrecht, 1981.
17. E. R. Davidson, *J. Comp. Phys.*, **17**, 87 (1975).
18. P. E. M. Siegbahn, *Chem. Phys. Lett.*, **55**, 386 (1978).
19. J.-P. Malrieu, *Theoret. Chim. Acta (Berl.)*, **62**, 175 (1982).
20. M. G. Sheppard, B. I. Schneider, and R. L. Martin, *J. Chem. Phys.*, **79**, 1364 (1983).
21. See for instance: I. Shavitt and R. Redmon, *J. Chem. Phys.*, **73**, 5711 (1980).
22. M. Persico, in *Spectral Line Shapes*, Vol. 3, F. Ros-tas, Ed., de Gruyter, Berlin, 1985, p. 587.
23. P. Saxe, H. F. Schaefer, III, and N. C. Handy, *Chem. Phys. Lett.*, **79**, 202 (1981).
24. P. Saxe, D. J. Fox, H. F. Schaefer, III, and N. C. Handy, *J. Chem. Phys.*, **77**, 5584 (1982).
25. HONDO IV, H. Dupuis, J. Rys, and H. F. King, *QCPE* **12**, 336 (1977); *J. Chem. Phys.*, **65**, 111 (1976); PSONDO, modified version by J.-P. Daudey.
26. A. E. Cherniak and C. C. Costain, *J. Chem. Phys.*, **45**, 104 (1966).
27. P. Durand and J.-C. Barthelat, *Theoret. Chim. Acta (Berl.)*, **38**, 283 (1975).
28. J.-C. Barthelat, P. Durand, and A. Serafini, *Mol. Phys.*, **33**, 159 (1977).
29. Laboratoire de Physique Quantique, Université Paul Sabatier, Internal Technical Report, Toulouse (1981).
30. R. Cimiraglia, M. Persico, and F. Spiegelmann, unpublished results.