

Regular article

Multireference perturbation configuration interaction V. Third-order energy contributions in the Møller–Plesset and Epstein–Nesbet partitions

Celestino Angeli, Renzo Cimiraglia

Dipartimento di Chimica, Università di Ferrara, Via Borsari 46, 44100 Ferrara, Italy

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Abstract. A simple implementation of third-order perturbation theory applied to a multireference zero-order wavefunction is presented. Two different partitions of the Hamiltonian (Møller–Plesset baricentric and Epstein–Nesbet) are considered. Two test cases, CH₂ and N₂, are examined. The third-order results are shown to be in good agreement in either partition and are generally an improvement with respect to the second-order results. The phenomenon of intruder states, absent in Epstein–Nesbet, appears to be magnified in the Møller–Plesset partition.

Key words: Multireference configuration interaction – Perturbation configuration interaction – CIPSI – Third order

1 Introduction

Møller–Plesset perturbation theory MPPT [1] is one of the most widely used methods to address the correlation problem in quantum chemistry, drawing its conceptual value from the diagrammatic representation and the linked cluster theorem [2]. Besides, MPPT represents an effective computational tool so that nowadays even high-order perturbation contributions can be routinely calculated [3]. MPPT is based on a zero-order wavefunction consisting of a single Slater determinant built on molecular spin orbitals ψ_i obtained by solving the Hartree–Fock equations and, accordingly, is well suited to describe molecules with a closed-shell ground state. If one wishes to describe a large portion of the potential-energy surface involving the breakage of chemical bonds or if one wants to properly describe the electronically excited states of molecules or open-shell states, it is usually inappropriate to restrict the calculation to a single-determinant-based treatment and one is forced to

resort to a multireference approach. Multireference perturbation theory (MRPT) is based on the description of the zero-order wavefunction through the diagonalization of the electronic Hamiltonian in a properly chosen determinantal space, S , and on the evaluation of the remaining correlation energy through perturbation theory. The choice of the reference space, S , is usually done either on the basis of a complete active space (CAS) [4], or on the imposition of a given excitation level, such as a singles and doubles configuration interaction [5] or on a selection criterion to build up the determinantal space, such as in the CIPSI technique [6].

The previous articles in the series published by our group [7, 8, 9, 10] were involved with the second-order treatment of the energy, either by proposing an extrapolation technique suitable for large zero-order spaces [7], by improving the selection criteria in the CIPSI algorithm [8, 10] or by adopting diagrammatic techniques [11, 12] for the calculation of the first-order one-particle density matrix [9].

The zero-order Hamiltonian, H_0 , of MRPT is often chosen to be of one-electron type so that it reduces to the Fock operator in the case of a single reference space, but different choices based on a two-electron zero-order H_0 are possible and have recently been shown to be viable and promising [13, 14]. MRPT is usually carried out to second order in the energy, higher orders being deemed unnecessary if a good zero-order wavefunction has been chosen. However, in an important article Werner [15] showed that third-order MRPT is feasible without prohibitive costs and provided a number of test calculations useful to judge the convergence of the perturbation series. Another implementation of third-order MRPT has been recently provided by Havenith et al. [16]. In the present work we present a simple implementation of the third-order MRPT which has been adapted to the CIPSI suite of programs [6, 17, 8]. Two different partitions of the Hamiltonian are considered, the Møller–Plesset baricentric (MPB) and the diagonal bielectronic Epstein–Nesbet (EN). The convergence properties of the two partitions are examined in some test cases.

Correspondence to: R. Cimiraglia

2 Theory

Starting from the usual series expansion of Rayleigh–Schrodinger perturbation theory

$$\Psi_m = \Psi_m^{(0)} + \Psi_m^{(1)} + \dots, \\ E_m = E_m^{(0)} + E_m^{(1)} + E_m^{(2)} + E_m^{(3)} + \dots,$$

where $H_0\Psi_m^{(0)} = E_m^{(0)}\Psi_m^{(0)}$ and $H = H_0 + V$, the following results for first-, second- and third-order corrections to the energy are well known:

$$E_m^{(1)} = \langle \Psi_m^{(0)} | V | \Psi_m^{(0)} \rangle, \\ E_m^{(2)} = \langle \Psi_m^{(1)} | V | \Psi_m^{(0)} \rangle, \\ E_m^{(3)} = \langle \Psi_m^{(1)} | V | \Psi_m^{(1)} \rangle - E_m^{(1)} \|\Psi_m^{(1)}\|^2.$$

In MRPT the zero-order wavefunction solves a variational eigenvalue equation $P_S H P_S \Psi_m^{(0)} = E_m^{\text{var}} \Psi_m^{(0)}$, where P_S is the projection operator onto a given determinantal space S , $P_S = \sum_{M \in S} |M\rangle\langle M|$. We introduce the auxiliary projectors

$$P_m = |\Psi_m^{(0)}\rangle\langle \Psi_m^{(0)}| \quad P_S = \sum_{m'} P_{m'},$$

$$Q = \sum_{K \notin S} |K\rangle\langle K|.$$

The MPB zero-order Hamiltonian is based on the introduction of a diagonal Fock operator $F = \sum_r \epsilon_r a_r^\dagger a_r$, where ϵ_r designate suitably defined orbital energies. We assume that the spin orbitals upon which the Slater determinants are built diagonalize the one-particle density matrix obtained by $\Psi_m^{(0)}$ (natural spin orbitals) and that the orbital energies are conveniently defined as $\epsilon_r = h_{rr} + \sum_s n_s \langle rs || rs \rangle$, where n_s designates the occupation number of spin orbital ψ_s . The definition of the MPB zero-order Hamiltonian is then:

$$H_0^{\text{MPB}} = \sum_{m'} P_{m'} F P_{m'} + Q F Q.$$

The EN partition [6] is used with

$$H_0^{\text{EN}} = P_S H P_S + \sum_{K \notin S} |K\rangle\langle K | H | K\rangle\langle K|.$$

The zero-order energies in the MPB partition are thus

$$E_m^{(0)} = \langle \Psi_m^{(0)} | F | \Psi_m^{(0)} \rangle, \\ E_K^{(0)} = \sum_{r \in K} \epsilon_r \quad (\psi_r \text{ occupied in } |K\rangle), \\ E_m^{(0)} + E_m^{(1)} = E_m^{\text{var}},$$

whereas in the EN partition

$$E_m^{(0)} = E_m^{\text{var}} \quad E_K^{(0)} = \langle K | H | K \rangle.$$

The first-order correction to the wavefunction reads

$$\Psi_m^{(1)} = \sum_{K \notin S} C_{K,m}^{(1)} |K\rangle \quad C_{K,m}^{(1)} = - \frac{\langle \Psi_m^{(0)} | V | K \rangle}{E_K^{(0)} - E_m^{(0)}}.$$

The perturbation scheme that has been presented can be classified as an uncontracted treatment because the full dimensionality of the interacting space defined by the projector Q is used. In other treatments, such as the CASPT2 [4, 18], an internally contracted scheme is adopted where a subset of the interacting space is defined through the application of all the double substitutions to $\Psi_m^{(0)}$. Other promising contraction schemes have been proposed recently [13, 14].

The third-order contribution to the energy can be easily obtained once the coefficients $C_{K,m}^{(1)}$ are available. The evaluation of $E_m^{(3)}$ was performed by first calculating the second-order contribution $E_m^{(2)}$ with storage of the coefficients $C_{K,m}^{(1)}$ and then by retrieving the coefficients and carrying out the summation

$$\sum_{K,L \notin S} C_{K,m}^{(1)} C_{L,m}^{(1)} \langle K | V | L \rangle.$$

The renormalization term needs only to be introduced for the MPB partition which has a nonvanishing first-order contribution to the energy. The CIPSI program [6] with the modifications introduced in our laboratory [17, 8, 7] was employed for the calculation of $E_m^{(2)}$ and $C_{K,m}^{(1)}$. Further modifications were introduced in the code, allowing for the use of configuration state functions (eigenfunctions of S^2 and S_z) instead of simple determinants.

Being based on the CIPSI procedure, which takes directly into account the generation of configurations stemming from the zero-order space, S , our third-order program suffers from the same limitations inherent in the CIPSI code, i.e. mainly a severe dependence on the dimensions of S . Moreover the storage and subsequent retrieval of the coefficients $C_{K,m}^{(1)}$ can involve rather large allocation of computer memory as well as disk space. We have verified that the imposition of a small threshold on the coefficients to be stored is very effective in speeding up the calculation without any significant loss of accuracy. Also, the computer code is very easily parallelizable and we have realized a version of the program, suited to a cluster of personal computers, in a “server–client” approach, with the “server” program “listening” and distributing the calculation to the “client” programs.

3 Test calculations

3.1 CH_2

A series of calculations was carried out on the 1A_1 and 3B_2 electronic states of CH_2 , where both the full configuration interaction results of Bauschlicher and Taylor [19] and the CASPT3 results of Werner [15] are available. We adopted the double zeta plus polarization basis set and geometrical parameters provided in Ref. [19] and carried out perturbation calculations starting from CAS–Self-consistent-field (SCF) zero-order wavefunctions as defined in Ref. [15]. The DALTON suite of programs [20] was utilized to produce the CAS–SCF wavefunctions. The results referring to a CAS space obtained by distributing the six valence electrons on the six valence orbitals are given in Table 1. The second-order perturbation theory

results for the ${}^3B_2 - {}^1A_1$ separation are too high both for the MPB and the EN partition, but the third-order contribution is seen to produce a substantial correction, bringing also the MPB and EN values closer to one another. Our results are similar to those reported by Werner [15]. Table 1 also contains the results for large CAS spaces with six electrons on either eight or 14 orbitals, respectively. Improving the zero-order wavefunction clearly shows better convergence properties and attenuates the discrepancies between MPB and EN. It is to be remarked that our third-order results for the MPB and EN partitions produce total energies close to each other even in the smallest CAS space.

3.2 N_2

As a second test calculation we chose the ground state of the N_2 molecule, which constitutes a rather severe case for post-SCF procedures due to the difficulties in properly describing the dissociation process for a triple bond. Being a symmetrical system, it is well known [21] that the EN partition meets with particular difficulties in the description of the dissociative part of the potential-energy curve.

On the other hand, the MPB partition, albeit substantially exempt from the size-consistency problem,

Table 1. Energies obtained with the second- and third-order procedures compared to the full configuration interaction results

| Method | 1A_1 energy (au) | 3B_2 energy (au) | ΔE (K _{cal} mol ⁻¹) |
|--------------------------------|-----------------------|-----------------------|--|
| 3210 active space ^a | | | |
| CAS-SCF | -38.945529 | -38.965954 | 12.82 |
| CAS-PT2 ^b | -39.013092 | -39.037695 | 15.44 |
| CAS-PT3 ^b | -39.023374 | -39.043766 | 12.80 |
| MPB2 ^c | -39.011695 | -39.036885 | 15.81 |
| EN2 ^c | -39.024854 | -39.048424 | 14.79 |
| MPB3 ^c | -39.021887 | -39.042750 | 13.09 |
| EN3 ^c | -39.023624 | -39.043291 | 12.34 |
| 4220 active space ^a | | | |
| CAS-SCF | -38.968726 | -38.982788 | 8.82 |
| CAS-PT2 ^b | -39.017120 | -39.038707 | 13.54 |
| CAS-PT3 ^b | -39.024593 | -39.044195 | 12.30 |
| MPB2 ^c | -39.016396 | -39.038139 | 13.64 |
| EN2 ^c | -39.024499 | -39.046250 | 12.47 |
| MPB3 ^c | -39.023789 | -39.044005 | 12.69 |
| EN3 ^c | -39.025216 | -39.044839 | 12.31 |
| 7331 active space ^a | | | |
| CAS-SCF | -39.009906 | -39.029672 | 12.40 |
| CAS-PT2 ^b | -39.023760 | -39.043345 | 12.29 |
| CAS-PT3 ^b | -39.025954 | -39.045359 | 12.18 |
| MPB2 ^c | -39.024489 | -39.044125 | 12.32 |
| EN2 ^c | -39.026107 | -39.045722 | 12.31 |
| MPB3 ^c | -39.025951 | -39.045521 | 12.28 |
| EN3 ^c | -39.026187 | -39.045699 | 12.24 |
| FCI ^d | -39.027284 | -39.046348 | 11.96 |

^a Partition of the active space orbitals in the A_1 , B_1 , B_2 and A_2 symmetries

^b Ref. [15]

^c This work

^d Ref [19]

may be affected by the presence of occasional “intruder states” which deteriorate the calculation, as has been reported by Roos and Andersson [22] in the study of the ${}^3\Sigma_u^+$ state of N_2 . In the present calculation use was made of the atomic natural orbital basis set of Widmark et al. [23], which consists of $14s\ 9p\ 4d\ 3f$ contracted to $7s\ 7p\ 4d\ 3f$ (138 basis functions). Starting from a CAS-SCF calculation involving six electrons distributed over the six valence p orbitals, the dynamical correlation energy was evaluated with second- and third-order perturbation theory in both the MPB and EN partitions.

The spectroscopic properties calculated at the various perturbation orders are set out in Table 2. The energy profiles for the EN case are shown in Fig. 1. As can be seen, the corrections brought by the third order are very small in the region of the minimum but become pronounced in the dissociative part of the curve, causing the dissociation energy, D_e , to drop from 10.93 eV for EN2 to 9.75 eV for EN3, in good agreement with the experimental value of 9.91 eV [24]. The curves for the MPB partition are reported in Fig. 2. Here opposite behaviour is found with respect to the EN results, the third-order correction being rather sizable close to the minimum and small in the dissociation region. For MPB partition D_e is calculated as 9.12 eV in MPB2 and 9.39 eV in MPB3. Also, the phenomenon of the intruder states becomes apparent in MPB3 for a couple of points (at $r = 3.6$ and 4.2 au) even though no divergence is noted in MPB2.

The squared norm of the first-order correction to the wavefunction, which shows a quadratic dependence on the energy denominators as in the third-order energy correction, is reported for both partitions in Fig. 3.

Table 2. Spectroscopic properties of the ${}^1\Sigma_g^+$ ground state of N_2

| Method | r_e (Å) | D_e (eV) | ω_e (cm ⁻¹) | $x_e\omega_e$ (cm ⁻¹) |
|----------|-----------|------------|--------------------------------|-----------------------------------|
| MPB2 | 1.101 | 9.115 | 2325.1 | 15.5 |
| En2 | 1.097 | 10.927 | 2376.3 | 14.7 |
| MPB3 | 1.099 | 9.387 | 2354.0 | 14.9 |
| EN3 | 1.099 | 9.745 | 2348.1 | 14.9 |
| Exp.[24] | 1.098 | 9.906 | 2358.6 | 14.3 |

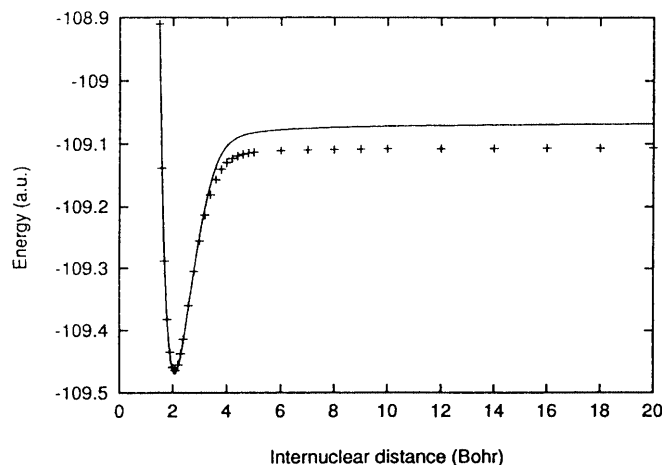


Fig. 1. Potential-energy curve for the N_2 molecule. Full line: Epstein–Nesbet (EN) second order; +: EN third order

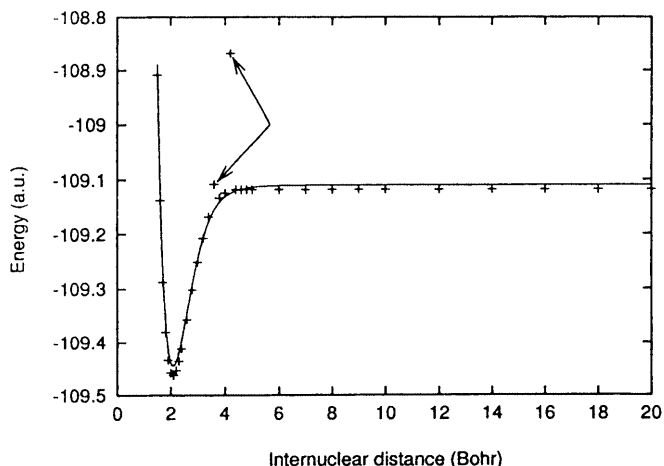


Fig. 2. Potential-energy curve for the N_2 molecule. *Full line:* Møller–Plesset baricentric (MPB) second order; *+*: MPB third order. The *arrows* indicate the points affected by the intruder state problem (see text)

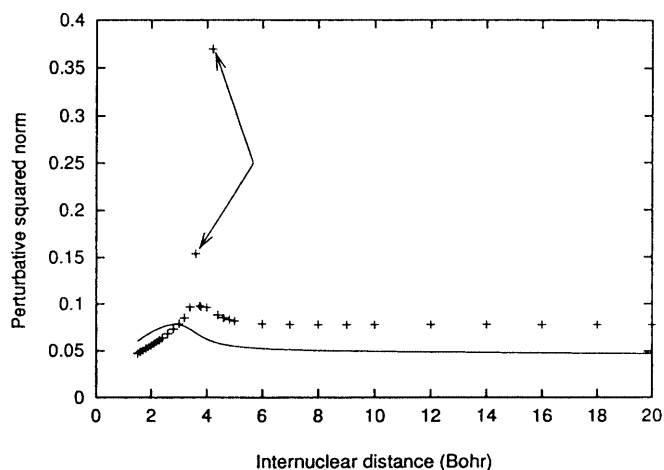


Fig. 3. Squared norms of the first-order correction to the wavefunction for the N_2 molecule. *Full line:* EN; *+*: MPB. The *arrows* indicate the points affected by the intruder state problem (see text)

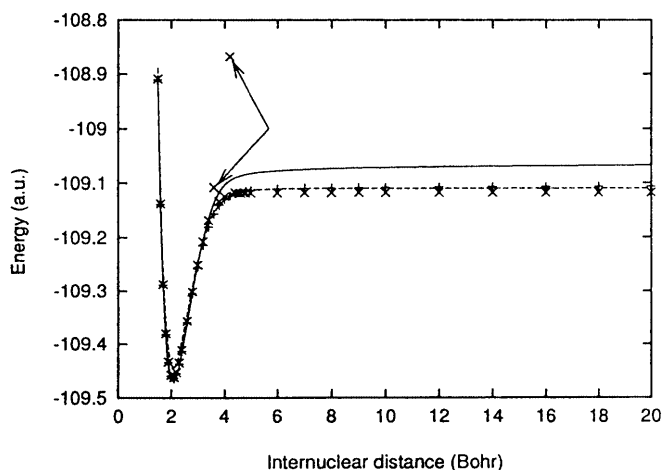


Fig. 4. Comparison of EN and MPB second- and third-order energy curves for N_2 . *Full line:* EN2; *dashed line:* MPB2; *+*: EN3; *x*: MPB3. The *arrows* indicate the points affected by the intruder state problem (see text)

Again, the appearance of the intruder states is manifest for the MPB partition. Finally, in Fig. 4 all the energy curves are reported together, with a view to showing the levelling off of the EN3 and MPB3 results.

4 Conclusions

We have shown a simple implementation of the third-order energy contribution calculation for the MPB and EN partitions. The main purpose of the present work was to ascertain whether both partitions manifest a convergence trend beyond second order and we have seen through a few numerical examples that this appears to be actually the case. We have also noted the preoccupying tendency to magnify the intruder state phenomenon on the part of the Møller–Plesset partition and we suspect that this behaviour could be common to all Møller–Plesset–based third-order treatments. Such a problem could possibly be solved by means of some form of level-shift technique [22, 25] to make third-order corrections usable.

Third-order calculations can be useful to assess the validity of specific assumptions introduced in the zero-order Hamiltonian, such as the introduction of one- and two-body denominator shifts [26], whose influence can be properly appreciated starting from third order.

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