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An application of second-order *n*-electron valence state perturbation theory to the calculation of excited states

Celestino Angeli, Stefano Borini, Renzo Cimiraglia

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

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Abstract. *n*–electron valence state perturbation theory (NEVPT) is a form of multireference perturbation theory where all the zero-order wave functions are of multireference nature, being generated as eigenfunctions of a two–electron model Hamiltonian. The absence of intruder states makes NEVPT an interesting choice for the calculation of electronically excited states. Test calculations have been performed on several valence and Rydberg transitions for the formaldehyde and acetone molecules; the results are in good accordance with the best calculations and with the existing experimental data.

Keywords: Multireference configuration interaction – Perturbation configuration interaction – *n*-electron valence state perturbation theory – Excited states

1 Introduction

Most molecules in their ground state near the equilibrium geometry have a closed-shell nature and can be successfully described by a single Slater determinant at the Hartree–Fock level of theory. A good portion of the correlation energy can then be effectively gained at a low computational cost by applying Møller–Plesset perturbation theory [1], usually at the second order level (MP2). In a great deal of chemically interesting circumstances, though, the description based on a single-reference determinant becomes defective, as, for instance, in molecular geometries far from equilibrium during the course of a chemical reaction or in excited electronic states. In such cases it is essential to provide a zero-order description where all the determinants (configurations) that play an important rôle in the electronic wave function are explicitly taken into account. Multireference perturbation theory (MRPT), where the zero-order wave function is variationally built upon a configuration interaction (CI) involving the most important determinants is a natural extension of the single–determinant Møller–Plesset perturbation theory. We shall not review here the more than 30-year-old history of MRPT, confining ourselves to recalling that the most successful treatments are based on a zero-order reference of complete-active-space self–consistent-field (CAS–SCF) type [2,3], where the first–order perturbation correction to the wave function is built in terms of contracted excitations applied to the zero-order wave function [4]. The CASPT2 technique of Roos and collaborators stands out as a particularly efficient method for the treatment of correlation energy in a multireference–based description of molecular systems. Recently a variant of CAS–based MRPT, called *n*–electron valence state perturbation theory (NEVPT), has been proposed [5,6,7], where particular care has been addressed to complying with some important formal requirements, among which we quote (1) strict separability (size consistence), ensuring that the energy of a system made of noninteracting parts be equal to the sum of the energies of the isolated parts calculated with the same method and (2) absence of "intruder states", requiring that the energies of the zero-order wave functions belonging to the outer space be well separated from the energy of the reference state, thus averting divergences in the perturbation summation. The latter requirement assumes particular relevance in the treatment of electronically excited states, where the appearance of intruders can most easily manifest itself.

This paper is addressed to the description of electronically excited states with the NEVPT at the second order level (NEVPT2) technique in a couple of test molecules, formaldehyde and acetone. The principal aim of this work is not to solve the still open questions of the interpretation of the electronic spectra of the molecules studied but, rather, to verify the ability of NEVPT2 to provide a viable means of calculation of excited states.

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Correspondence to: R. Cimiraglia
e-mail: cim@dns.unife.it

The rest of the paper is organized as follows: a brief summary of the NEVPT2 method is provided in Sect. 2; Sect. 3 is dedicated to the description of various electronic transitions in the formaldehyde and acetone molecules; Sect. 4 contains concluding remarks.

2 Summary of the NEVPT2 method

NEVPT2 has been formulated in different variants, according to the type of zero-order Hamiltonian adopted and to the degree of contraction employed in the definition of the zero-order wave functions, referred to as the "perturbers" in the following. In all the NEVPT variants the perturbers exhibit multireference nature and are obtained as eigenfunctions of a two–electron model Hamiltonian. The state of interest Ψ_m is approximated at zero-order by a CAS–CI wave function $\Psi_m^{(0)}$ (usually CAS–SCF) obtained by diagonalizing the Hamiltonian matrix built on a given CAS space. The spatial orbitals utilized are subdivided into the three usual CAS classes: core, with occupation numbers always equal to 2, active, with all possible occupations (0,1,2), and virtual, with occupation always zero in all the determinants of the CAS. The zero-order wave functions other than the variational $\Psi_m^{(0)}$ (the perturbers) also belong to CAS–CI spaces characterized by well-defined occupation patterns of the inactive (core and virtual) orbitals. A generic perturber is designated as $\Psi_{l,\mu}^{(k)}$ and the CAS–CI space to which it belongs as $S_l^{(k)}$, where k is the number of electrons promoted to (if positive) or removed from (if negative) the active space ($-2 \leq k \leq 2$), l denotes the fixed occupation pattern of the inactive orbitals and μ enumerates the various perturbers in $S_l^{(k)}$. The number of types of CAS–CI spaces which play a rôle in second–order perturbation theory is restricted to eight: there are two possible types with $k = 0$ according to whether two or one core electron is transferred to the virtual orbital space; for $k = +1$ (-1) two types are also possible, the first implying a transfer of two core electrons to one virtual orbital and to the active space (from one core electron and one active space electron to two virtual orbitals), the second involving the passage of only one electron to (from) the active space; lastly, the case $k = +2$ (-2) generates only one type of space with two electrons passing from the core to the active space (from the active to the virtual space). The different variants of NEVPT2 are defined according to the number of perturbers that are chosen from the $S_l^{(k)}$ spaces. In the "strongly contracted" approach only one function is chosen, by projecting the action of the electronic Hamiltonian to the reference function onto the $S_l^{(k)}$ space: $\Psi_l^{(k)} = P_{S_l^{(k)}} H \Psi_m^{(0)}$, whereas in the "partially contracted" approach the $\Psi_{l,\mu}^{(k)}$ perturbers belong to the subspace $\bar{S}_l^{(k)}$ of $S_l^{(k)}$ generated by the double-excitation operators which map $\Psi_m^{(0)}$ onto $S_l^{(k)}$. The energies of the perturbers are evaluated through the use of a model Hamiltonian, H^D, by the following prescription:

1. For the strongly contracted approach

$$E_l^{(k)} = \frac{\left\langle \Psi_l^{(k)} | H^{\mathrm{D}} | \Psi_l^{(k)} \right\rangle}{\left\langle \Psi_l^{(k)} | \Psi_l^{(k)} \right\rangle} \quad .$$

2. For the partially contracted variant the perturbers and their energies are provided by the diagonalization of the H^{D} operator in the $\bar{S}_l^{(k)}$ subspaces:

$$P_{\bar{S}_l^{(k)}} H^{\mathrm{D}} P_{\bar{S}_l^{(k)}} \Psi_{l,\mu}^{(k)} = E_{l,\mu}^{(k)} \Psi_{l,\mu}^{(k)} \quad .$$

From the computational point of view, a particularly convenient choice of the model Hamiltonian is provided by Dyall's operator [8],

$$H^{\mathrm{D}} = H_i + H_v \quad , \tag{1}$$

$$H_i = \sum_i^{\mathrm{core}} \epsilon_i E_{ii} + \sum_r^{\mathrm{virt}} \epsilon_r E_{rr} + C \quad , \tag{2}$$

$$H_v = \sum_{ab}^{\mathrm{act}} h_{ab}^{\mathrm{eff}} E_{ab} + \frac{1}{2} \sum_{abcd}^{\mathrm{act}} \langle ab|cd \rangle (E_{ac}E_{bd} - \delta_{bc}E_{ad}) \quad , \tag{3}$$

where ϵ_i and ϵ_r are suitable orbital energies [9], $E_{xy} = a_{x\alpha}^+ a_{y\alpha} + a_{x\beta}^+ a_{y\beta}$ is the spin–traced excitation operator [10], h_{ab}^{eff} is a modified one–electron matrix taking into account the interaction with the core electrons, $h_{ab}^{\mathrm{eff}} = h_{ab} + \sum_j^{\mathrm{core}} (2\langle aj|bj \rangle - \langle aj|jb \rangle)$, and C is a constant ensuring the equivalence of H^{D} with H within the CAS space.

The form of the operator H^{D} in Eqs. (1),(2) and (3) only ensures that the resulting first-order perturbation correction to the wave function is invariant under unitary transformations of orbitals belonging to the active space. It is an easy task to extend the H^{D} definition so that invariance is guaranteed under unitary transformations within each of the three orbital classes (core, active, virtual) by modifying the inactive one–electron component, H_i, into the following:

$$H_i = \sum_{i,j}^{\mathrm{core}} f_{ij} E_{ij} + \sum_{r,s}^{\mathrm{virt}} f_{rs} E_{rs} + C \quad , \tag{4}$$

with

$$f_{ij} = -\left\langle a_i \Psi_m^{(0)} | H | a_j \Psi_m^{(0)} \right\rangle + \delta_{ij} E_m^{(0)} \tag{5}$$

and

$$f_{rs} = \left\langle a_r^+ \Psi_m^{(0)} | H | a_s^+ \Psi_m^{(0)} \right\rangle - \delta_{rs} E_m^{(0)} \quad . \tag{6}$$

Diagonalization of the two **f** matrices leads then to the adoption of so-called canonical core and virtual orbitals, a practice that we shall tacitly assume in the calculations reported in the next sections.

As shown in Ref. [7], all the relevant quantities which are necessary for the second-order correction to the energy, i.e. the interaction of the reference $\Psi_m^{(0)}$ function with the perturbers and the energy denominators, can be easily calculated with the help of auxiliary quantities which need the knowledge of the zero-order density matrices of particle rank not higher than 4, with indices only spanning the active orbital space. In the case of the partially contracted approach, the use of Dyall's Hamiltonian is particularly beneficial because each of the eight typologies of $\bar{S}_l^{(k)}$ subspaces only necessitates one diagonalization which is then valid for all the various $\bar{S}_l^{(k)}$ instances. Thus the partially contracted approach, albeit involving many more perturber functions than the strongly contracted case, only needs a small computational overhead when compared with the strongly contracted case. The two forms of NEVPT2, though, show very similar results in the second–order correction to the energy, as shown in Ref. [7], demonstrating that the strongly contracted approach is built on an effective averaging process.

A final remark concerns the issue of the occurrence of possible small denominators (intruder states) in the perturbation summation: the most critical case can present itself in the $S_r^{(-1)}$ spaces, which involve the passage of one electron from the active space to a virtual orbital (r), accompanied by an excitation within the active space. In such a case the energy denominators can be expressed as the difference between the energy of a virtual orbital (ϵ_r) and that associated with a ionization potential in the valence shell. If the virtual orbital is very diffuse, as happens when introducing Rydberg orbitals in the basis set, ϵ_r is close to zero and the energy denominator reduces to the valence ionization, which is anyway never zero. So NEVPT2 should be applicable to the study of valence excited states, the energies of which are well separated from the first ionization potential.

3 Applications

3.1 Formaldehyde

The vertical spectrum of the formaldehyde molecule was computed at the ground-state experimental geometry [11] [R(CO) = 1.208 Å, R(CH) = 1.116 Å and θ(HCH) = 116.5°]. The molecule belongs to the C_{2v} point group symmetry and lies in the yz-plane with the C and O atoms on the z-axis. The atomic natural orbital

(ANO) basis set of Widmark et al. [12] was used with two different contraction schemes: the smaller, indicated by ANO(S), is C,O [4s3p1d]/H[2s1p] and the larger, ANO(L), is C,O [6s5p3d2f]/H[4s3p2d]. These valence basis sets were augmented with diffuse functions in order to properly describe the diffuse orbitals involved in the Rydberg states. These basis functions are obtained by contraction of a set of 8s8p8d Gaussian primitives whose exponents were generated using the procedure proposed by Kaufmann et al. [13]. The contraction coefficients were computed following the procedure developed by Roos et al. [14] and two contraction schemes were considered: [1s1p1d], Ryd(S), and [3s3p3d], Ryd(L). In order to directly compare our results with the CASPT2 and the size-consistent self-consistent CI calculations of Merchán and Roos [15] and of Pitarch-Ruiz et al. [16], respectively, we used in the calculations the combinations ANO(S)-Ryd(S) and ANO(L)-Ryd(L).

The molecular orbitals were obtained from average CAS-SCF calculations which involve the lowest states of a given symmetry. The active spaces, together with the number and the nature of the states considered in the averaging procedure are reported in Table 1 and are taken from Ref. [15]. The number of orbitals for each irreducible representation was chosen by the authors so that all the states of interest could be correctly described. In some cases the active space was enlarged in order to minimize the effect of the intruder-states problem in the CASPT2 calculations. Given that our perturbation treatment is not affected by the intruder-states problem, in our calculations a reduction of the active space should be possible but the comparison of our results with those of Refs. [15, 16] would be in this case less clear.

The energies of the states were computed in a state-specific multireference perturbation scheme. The zero-order description of each state was obtained from a CAS-CI calculation using the average CAS–SCF active orbitals. The inactive orbitals were transformed in order to diagonalize the state-specific Fock matrices defined in Eqs. (5) and (6). A second-order correction to the energy was computed using the strongly contracted (SC) and partially contracted (PC) variants of the NEVPT method. All orbitals and electrons were included in the perturbation treatment. The excitation energies were computed with respect to the same ground-state energy, which was evaluated as the second-order correction to the energy with the reference energy and wave function obtained from a state-specific CAS–SCF calculation with four electrons in two b_1 ($\pi + \pi^*$) and two b_2 (n_y + virtual) orbitals. This approach for the calculation of the excitation energies differs from that used in the CASPT2 [15] calculation, where a different ground-state energy was used for each irreducible representation. The vertical excitation energies obtained in our calculations are reported in Table 2 for the Rydberg states and in Table 3 for the valence states, together with the results of previous theoretical calculations and with some experimental results.

In Tables 4 and 5 we show the comparison between our results and those of Pitarch-Ruiz et al. [16], which can be considered a good reference since they involve the whole single plus double excitations space on top of a CAS at a variational level with a size-consistency correction. We remark that the mean absolute error of our results is always small, with the worst case being represented by the SC-NEVPT in the ANO(L) + Ryd(L) basis (0.15 eV). The small errors appearing in Tables 4 and 5 bear out the reliability of NEVPT2, which can yield results of good accuracy, comparable with much more refined calculations, but at a much lesser computational cost.

For the case of the smaller basis [ANO(S) + Ryd(S)] the CASPT2 results are also available [15] and are reported in Table 4 for comparison. It can be remarked that NEVPT2 and CASPT2 appear to be of the same quality, with the former showing in all cases a small squared norm of the wave function perturbation correction (see Tables 2, 3), thus getting over the intruder state problem.

As to the comparison with the experimental data, beyond a satisfactory general agreement with our theoretical results we can make the following observations:

- In accordance with most theoretical calculations, our vertical 2 $^1A_1$ and 1 $^1B_2$ Rydberg transitions appear in inverted order with respect to experimental adiabatic transitions [22]: a more stringent comparison would require the calculation of adiabatic transition with due allowance for the zero-point-energy correction.
- The calculation of the $^1A_1$ Rydberg states with the larger basis set introduces one more Rydberg state ($n_y \rightarrow \pi^*$) below the valence $\pi \rightarrow \pi^*$; such a state was ignored in the average CAS–SCF since we were interested in transitions involving Rydberg orbitals not exceeding the quantum number $n = 3$.
- Mixing between Rydberg and valence character may occur in both the $^1A_1$ and the $^1B_1$ transitions [15, 18]. For a correct treatment of such states a quasi–degenerate treatment would be required [27, 28]. We expect to introduce such corrections in NEVPT2 in the near future.

Table 1. Active spaces and number of states used in the average complete-active-space self-consistent-field (*CAS-SCF*) calculations for the formaldehyde molecule (in all cases four active electrons)

Number of MOs[a]	Symmetry and nature of states	Number of states[b]
(0340)	$^1A_1$ (GS;$n_y \rightarrow 3p_y, 3d_{yz}; \pi \rightarrow \pi^*$)	4
(2200)	$^1B_1$ ($\sigma \rightarrow \pi^*$)	1
(0211)	$^1B_1$ ($n_y \rightarrow 3d_{xy}$)	1
(4210)	$^1B_2$ ($n_y \rightarrow 3s, 3p_z, 3d_{x^2-y^2}, 3d_{z^2}$)	4
(0410)	$^1A_2$ ($n_y \rightarrow \pi^*$, $3p_x$, $3d_{xz}$)	3

[a] Number of molecular orbitals in the active space for the four irreducible representations (a_1, b_1, b_2, a_2)

[b] number of states used in the averaging procedure

Table 2. Vertical excitation energies (eV) for the Rydberg states of the formaldehyde molecule. The numbers in *parentheses* are the squared norms of the first-order corrections to the wave function. The squared norm for the ground state is 0.075 (n-electron valence state perturbation theory *NEVPT*, strongly contracted *SC*), 0.076 (NEVPT, partially contracted *PC*), 0.091 (NEVPT SC) and 0.097 (NEVPT PC): the former two values were obtained with the atomic natural orbital (*ANO*) basis with contraction [4s3p1d/2s1p] + 1s1p1d, ANO(S) + Ryd(S), while the latter two values were obtained with the ANO basis set with contraction [6s5p3d2f/4s3p2d] + 3s3p3d, ANO(L) + Ryd(L)

Method	2 A_1 ($3p_y$)	3 A_1 ($3d_{yz}$)	1 B_2 ($3s$)	2 B_2 ($3p_z$)	3 B_2 ($3d_{x^2-y^2}$)	4 B_2 ($3d_{z^2}$)	2 A_2 ($3p_x$)	3 A_2 ($3d_{xz}$)	2 B_1 ($3d_{xy}$)
CAS–SCF[a,b]	8.07	9.18	7.37	8.15	9.08	9.21	8.84	9.78	9.16
CAS–SCF[a,c]	8.04	9.12	7.29	8.08	8.99	9.12	8.81	9.72	9.12
SC-NEVPT[a,b]	8.27	9.42	7.28	8.11	9.13	9.30	8.33	9.34	9.26
	(0.077)	(0.076)	(0.092)	(0.090)	(0.083)	(0.082)	(0.080)	(0.079)	(0.079)
SC-NEVPT[a,c]	8.39	9.56	7.32	8.16	9.17	9.37	8.46	9.48	9.39
	(0.084)	(0.083)	(0.090)	(0.090)	(0.087)	(0.086)	(0.099)	(0.097)	(0.086)
PC-NEVPT[a,b]	8.20	9.34	7.28	8.12	9.14	9.31	8.33	9.34	9.27
	(0.084)	(0.084)	(0.095)	(0.093)	(0.085)	(0.084)	(0.082)	(0.081)	(0.081)
PC-NEVPT[a,c]	8.31	9.49	7.33	8.17	9.17	9.38	8.45	9.48	9.39
	(0.092)	(0.090)	(0.092)	(0.092)	(0.089)	(0.088)	(0.103)	(0.100)	(0.087)
CASPT2 [15]	8.12	9.24	7.30	8.09	9.13	9.31	8.32	9.31	9.23
MC/BMP [17]	7.95	9.11	6.90	7.77	8.95	9.11	8.46	8.82	9.06
$(SC)^2$ CAS + SD[b] [16]	8.14	9.26	7.17	7.96	9.00	9.19	8.30	9.28	9.12
$(SC)^2$ MR + SD[c] [16]	8.27	9.31	7.12	7.95	8.96	9.18	8.36	9.34	9.36
CCR(3)[b] [16]	8.01	9.16	7.11	7.91	8.99	9.21	8.25	9.26	9.12
CCR(3)[c] [16]	8.14	9.27	7.16	7.99	9.04	9.27	8.38	9.40	9.25
MRD-CI [18]	8.10	9.25	7.15	8.05	9.05	9.25	8.32	9.34	9.32
MR-CISD + Q [19]	8.13	9.28	7.27	8.10	9.15	9.30	8.34	9.36	9.26
MR-AQCC [19]	8.24	9.38	7.21	8.03	9.09	9.24	8.46	9.49	9.37
EOM-CCSD [20]	7.99	10.16	6.99	7.93	9.25	9.98	8.45	10.67	9.84
EOM-CCSD [21]	7.98	9.13	7.04	7.88	8.94	9.12	8.21	9.29	10.89
Exp [22]	7.97		7.11	8.14	8.88		8.37		
Exp [23]									9.22
Exp [24,25]			7.09						

[a] This work

[b] ANO basis set with contraction [4s3p1d/2s1p] + 1s1p1d, ANO(S) + Ryd(S)

[c] ANO basis set with contraction [6s5p3d2f/4s3p2d] + 3s3p3d, ANO(L) + Ryd(L)

Table 3. Vertical excitation energies (eV) for the valence states of the formaldehyde molecule. The numbers in *parentheses* are the squared norms of the first-order corrections to the wave function. The squared norm for the ground state is 0.075 (NEVPT SC), 0.076 (NEVPT PC), 0.091 (NEVPT SC) and 0.097 (NEVPT PC): the former two values were obtained with the ANO(S) + Ryd(S) basis (see text), while the latter two values were obtained with the ANO(L) + Ryd(L) basis (see text)

Method	4 A_1 ($\pi \rightarrow \pi^*$)	1 A_2 ($n_y \rightarrow \pi^*$)	1 B_1 ($\sigma \rightarrow \pi^*$)
CAS–SCF[a,b]	10.59	5.28	9.89
CAS–SCF[a,c]	10.47	5.27	9.82
SC-NEVPT[a,b]	10.09	4.04	9.53
	(0.087)	(0.105)	(0.081)
SC-NEVPT[a,c]	9.97	3.93	9.37
	(0.095)	(0.113)	(0.091)
PC-NEVPT[a,b]	9.94	4.03	9.45
	(0.100)	(0.109)	(0.088)
PC-NEVPT[a,c]	9.80	3.91	9.28
	(0.112)	(0.118)	(0.097)
CASPT2 [15]	9.77	3.91	9.09
MC/BMP [17]	10.37	3.83	13.69
$(SC)^2$ CAS + SD[b] [16]	9.89	4.15	9.35
$(SC)^2$ MR + SD[c] [16]	9.74	4.04	9.33
CCR(3)[b] [16]	9.80	4.01	9.29
CCR(3)[c] [16]	9.64	3.97	9.25
MRD-CI [18]	9.60	4.05	9.35
MR-CISD + Q [19]	9.80	4.07	9.40
MR-AQCC [19]	9.84	4.04	9.37
EOM-CCSD [20]	9.47	3.98	9.33
EOM-CCSD [21]	9.37	4.04	9.43
Exp [22]		4.07	
Exp [26]		3.79	

[a] This work

[b] ANO(S) + Ryd(S) basis (see text)

[c] ANO(L) + Ryd(L) basis (see text)

Table 4. Energy differences (eV) between the perturbation and the size-consistent [$(SC)^2$] CAS + single and double excitations (SD) results of Ref. [16]

	PC-NEVPT[a]	SC-NEVPT[a]	CASPT2[b]
2 A_1	0.06	0.13	−0.02
3 A_1	0.08	0.16	−0.02
4 A_1	0.05	0.20	−0.12
1 B_2	0.11	0.11	0.13
2 B_2	0.16	0.15	0.13
3 B_2	0.14	0.13	0.13
4 B_2	0.12	0.11	0.12
1 A_2	−0.12	−0.11	−0.24
2 A_2	0.03	0.03	0.02
3 A_2	0.06	0.06	0.03
1 B_1	0.10	0.18	-0.26
2 B_1	0.15	0.14	0.11
Mean absolute error	0.10	0.13	0.11

[a] This work

[b] Ref. [15]

Table 5. Energy differences (eV) between the perturbation and the $(SC)^2$ multireference + SD results of Ref. [16]

	PC-NEVPT[a]	SC-NEVPT[a]
2 A_1	0.04	0.12
3 A_1	0.18	0.25
4 A_1	0.06	0.23
1 B_2	0.21	0.20
2 B_2	0.22	0.21
3 B_2	0.21	0.21
4 B_2	0.20	0.19
1 A_2	−0.13	−0.11
2 A_2	0.09	0.10
3 A_2	0.14	0.14
1 B_1	−0.05	0.04
2 B_1	0.03	0.03
Mean absolute error	0.13	0.15

[a] This work

3.2 Acetone

The computational strategy used for acetone closely follows the one applied to formaldehyde. The vertical spectrum was computed at the ground-state experimental geometry [11]. The molecule belongs to the C_{2v} point group symmetry with the OCCC skeleton in the *yz*-plane (C and O atoms on the *z*-axis and with an orientation of the CH_3 groups that place the two H atoms lying in the *yz*-plane as far as possible). For acetone, we only consider the C,O[4s3p1d]/H[2s1p] contraction of the ANO basis set of Widmark et al. [12].

The Rydberg states are described using a set of 8s8p8d diffuse functions [13] contracted to [1s1p1d] following the procedure described in Ref. [14].

As in formaldehyde, average CAS-SCF calculations provide the molecular orbitals: the active spaces and the number and the nature of the states considered in the averaging procedure are reported in Table 6 and are taken from Ref. [29]. With respect to formaldehyde, the active space was modified by adding the two CO σ and σ^* orbitals and the two CO σ electrons, except for the A_1 symmetry, where three virtual orbitals (one of b_1 and two of b_2 symmetry) were removed. In Ref. [29] the CO σ and σ^* orbitals were added to the active space in order to correctly describe the adiabatic electronic transitions for the valence states, in which an elongation of the CO bond is observed owing to the promotion of an electron to the π^* orbital.

Table 6. Active spaces and number of states used in the average CAS-SCF calculations for the acetone molecule (always six active electrons, except in the case of the $^1B_1$ ($\sigma \rightarrow \pi^*$), which is computed with four active electrons

Number of MOs[a]	Symmetry and nature of states	Number of states[b]
(2230)	$^1A_1$ (GS;$n_y \rightarrow 3p_y$,$3d_{yz}$;$\pi \rightarrow \pi^*$)	4
(2200)	$^1B_1$ ($\sigma \rightarrow \pi^*$)	1
(2211)	$^1B_1$ ($n_y \rightarrow 3d_{xy}$)	1
(6210)	$^1B_2$ ($n_y \rightarrow 3s$, $3p_z$, $3d_{x^2-y^2}$, $3d_{z^2}$)	4
(2410)	$^1A_2$ ($n_y \rightarrow \pi^*$,$3p_x$,$3d_{xz}$)	3

[a] Number of molecular orbitals in the active space for the four irreducible representations (a_1,b_1,b_2,a_2)

[b] Number of states used in the averaging procedure

Given that we present here only results for the vertical transitions, also in the case of acetone a reduction of the active space used in Ref. [29] would have been possible, but we chose to maintain the same active space in order to have a meaningful comparison with the CASPT2 data.

The energies of the states were computed following the strategy outlined for formaldehyde and the transition energies are reported in Table 7 for the Rydberg states and in Table 8 for the valence states, together with the results of other theoretical calculations and with some experimental results.

We note that our PC-NEVPT2 results compare very well with the CASPT2 ones. We also remark that in two of the valence transitions (4 $^1A_1$, $\pi \rightarrow \pi^*$ and 1 $^1A_2$, $n_y \rightarrow \pi^*$) the difference between SC and PC NEVPT appears to be unusually large (0.59 and 0.20 eV, respectively); we think that this is justification for the zero-order wave function to necessitate significant improvement.

4 Concluding remarks

Among the formal requirements satisfied by NEVPT (Sect. 2), the absence of intruder states appears particularly interesting for the application to the calculation of electronically excited states. The results shown in the preceding section for the vertical transitions of formaldehyde and acetone are of good quality and exhibit good agreement with the best calculations performed so far as well as with the existing experimental data. Our calculations were carried out starting from rather modestly sized CAS–SCF wave functions. The computational overhead involved in the two forms of NEVPT (SC and PC) amounts to only a small fraction of the CAS–SCF calculation for such small active orbital spaces and this favorable situation is not expected to drastically change when passing to larger molecules,

Table 7. Vertical excitation energies (eV) for the Rydberg states of the acetone molecule. The numbers in *parentheses* are the squared norms of the first-order corrections to the wave function. The squared norm for the ground state is 0.164 (NEV-PT SC) and 0.167 (NEV-PT PC)

Method	2 A_1 ($3p_y$)	3 A_1 ($3d_{yz}$)	1 B_2 ($3s$)	2 B_2 ($3p_z$)	3 B_2 ($3d_{x^2-y^2}$)	4 B_2 ($3d_{z^2}$)	2 A_2 ($3p_x$)	3 A_2 ($3d_{xz}$)	2 B_1 ($3d_{xy}$)
CAS–SCF[a]	7.91	8.46	6.02	6.75	7.30	7.39	7.29	7.99	7.38
SC-NEVPT[a]	7.40	8.03	6.75	7.67	8.25	8.37	7.48	8.24	8.36
	(0.182)	(0.179)	(0.159)	(0.155)	(0.154)	(0.153)	(0.168)	(0.166)	(0.154)
PC-NEVPT[a]	7.27	7.91	6.71	7.64	8.22	8.34	7.39	8.17	8.35
	(0.195)	(0.192)	(0.166)	(0.161)	(0.160)	(0.158)	(0.177)	(0.175)	(0.158)
CASPT2 [29]	7.26	7.91	6.58	7.48	8.04	8.18	7.34	8.09	8.20
EOM-CCSD [20]	7.45	8.23	6.39	7.51	7.95	8.48	7.41	8.44	8.43
EOM-CCSD [21]	7.41	8.02	6.42	7.39	7.82	8.10	7.31	8.04	8.11
Exp [29]		7.8			8.09				8.17
Exp [30]			6.35						
Exp [22]			6.36				7.45		
Exp [31]	7.41			7.45			7.36		

[a] This work

Table 8. Vertical excitation energies (eV) for the valence states of the acetone molecule. The numbers in *parentheses* are the squared norms of the first-order corrections to the wave function. The squared norm for the ground state is 0.164 (NEV-PT SC) and 0.167 (NEV-PT PC)

Method	4 A_1 ($\pi\rightarrow\pi^*$)	1 A_2 ($n_y \rightarrow \pi^*$)	1 B_1 ($\sigma\rightarrow\pi^*$)
CAS–SCF[a]	11.60	5.57	10.38
SC-NEVPT[a]	9.60	4.42	9.29
	(0.204)	(0.189)	(0.182)
PC-NEVPT[a]	9.01	4.22	9.23
	(0.293)	(0.207)	(0.190)
CASPT2 [29]	9.16	4.18	9.10
EOM-CC [20]	9.15	4.48	9.30
EOM-CC [21]	8.52	4.47	8.87
Exp [26]		4.38	
Exp [22]		4.43	

[a] This work

provided that the active space can be kept within manageable dimensions (10 or less, say).

No evidence of divergences or misbehavior in the perturbation summation was found in the calculation of the Rydberg states, which are particularly prone to exhibiting the appearance of intruder states. We are confident that NEVPT2 can be successfully adopted as a standard tool for the exploration of electronically excited states of medium–sized molecules.

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