

Second-order perturbation theory using correlated orbitals. II. A coupled MCSCF perturbation strategy for electronic spectra and its applications to ethylene, formaldehyde and vinylidene

O. Parisel ^{*}, Y. Ellinger

Equipe d'Astrochimie Quantique, Laboratoire de Radioastronomie Millimétrique, ENS et Observatoire de Paris, 24, rue Lhomond, F-75231 Paris Cedex 05, France

Received 14 August 1995; revised 1 December 1995

Abstract

In this second paper, the philosophy of coupling multiconfigurational variational wave functions to perturbation treatments (MC/P methodology) is extended to the calculation of electronic spectra. The corresponding methodology is presented with emphasis on its flexibility and an overview of other available approaches is given. The contracted MC/P scheme is then applied to ethylene $\text{H}_2\text{C}=\text{CH}_2$, formaldehyde $\text{H}_2\text{C}=\text{O}$ and vinylidene $\text{H}_2\text{C}=\text{C}$. It is shown that combining well-designed averaged zeroth-order MCSCF wave functions to a barycentric Møller–Plesset (BMP) partition of the electronic Hamiltonian provides accurate spectra, contrary to Epstein–Nesbet partitions. The MC/BMP transition energies compare with experimental data within a few hundreds of cm^{-1} . These results have been obtained using a polarized double-zeta quality basis set augmented by a set of semi-diffuse functions ($6\text{-}31 + \text{G}^*$) and by an extra set of diffuse orbitals to account for Rydberg states. Since non-dynamic correlation effects that are important for a proper description of the manifold of the excited states of interest are included in the MCSCF zeroth-order space while all remaining correlation effects (non-dynamic and dynamic) are treated at the perturbation level, the present study lets anticipate applications of the MC/P methodology to medium size systems without much computational trouble.

1. Introduction

1.1. Pure variation or perturbation approaches

Despite continuous efforts over many decades, the determination of accurate wave functions and energies for excited states of polyatomic systems remains a challenging problem to quantum chemistry. As

quoted out by McWeeny and Pickup as soon as in 1980 [1], new theories are still required but are not enough: aiming at the “chemical accuracy” from the viewpoint of ab initio quantum chemistry also requires a highly efficient computational implementation of new formalisms and algorithms. Although carefully designed implementations of various codes and developments in parallel computational chemistry allow now for calculations that were unrealistic even a few years ago, the evaluation of correlation energies and the determination of highly correlated wave functions, that are both necessary to properly

^{*} Corresponding author. E-mail: parisel@vega.ens.fr.

describe excited states or potential energy surfaces, remains in most cases a tremendous task which can hardly be performed routinely and rigorously for large systems when one aims to quantitative results.

At the present day, configuration interactions (CI), that will be widely discussed in the forthcoming parts of this contribution, and the many-body perturbation theory (MBPT) approaches are the most widely used methods to deal with the correlation problem from the computational chemistry point of view (for the corresponding detailed formalisms and philosophies, see, for example, Ref. [2] and references therein). CI or MBPT approaches are not, however, the only methodologies available to treat those phenomena that need consideration of the molecular electronic correlation. At this point, one should mention the coupled cluster (CC) treatments, either as formulated in Refs. [3–8] or in the equation of motion approach (for a recent application, see Ref. [9] and references therein for details). As another technique is the density functional theory (DFT) whose applications to excited states are beginning to be investigated (see, for example, Refs. [10,11] and references therein). Both these methodologies benefit from an increasing interest for accurate studies on excited states but, though very promising, they have not yet however reached the widespread recognition of the CI and MBPT methods.

Coming back to the perturbation methodologies, it is worth noting that the MBPT approach based on an HF-SCF (Hartree–Fock self-consistent field) single-reference taking RHF (restricted Hartree–Fock) or UHF (unrestricted Hartree–Fock) orbitals has been particularly developed, at various order of perturbation n , leading to the widespread MP_n or UMP_n treatments when a Møller–Plesset (MP) partition of the electronic Hamiltonian is considered. If the full configuration interaction (FCI) wave function is known, it is even possible to obtain the perturbation energy of a molecular system at any order of perturbation [12]. The implementation of MBPT approaches in the Rayleigh–Schrödinger–Møller–Plesset formulation in various codes and the large distribution of some of them make the MP_n theories an easy way to include correlation effects in the calculations. Such approaches benefit from a wide number of applications that proved reliable *when applied to relevant problems*.

It is however too often forgotten that the usual single-reference MBPT is relevant only for structures that are already well-described by a single determinant: a second-order perturbation treatment on a closed-shell molecule using HF orbitals and the SCF determinant as zeroth-order wave function will be relevant only if this function dominates the exact wave function of the system [13]. It follows that using standard MP_n approaches for the determination of potential energy surfaces (PES) which invoke distorted geometries, breakings of chemical bonds or state crossings, or for the description of molecules involving holes in their valence shells (as transition metal complexes for example) should be considered with an extreme critical mind. This point is even more crucial for excited states where appropriate perturbative excitonic treatments are necessary as shown in pioneering works [14–18]. Moreover, there is no method currently and widely available to perform efficient MP_n calculations on open-shell systems described by a spin-clean single ROHF determinant (restricted open Hartree–Fock) although this problem has been intensely reconsidered in the last years [19–32]. To our knowledge, these methods have not been applied to a wide enough series of problems at the present day so that it is difficult to judge their capabilities. Due to the lack of easy open-shell perturbation theories based on a ROHF single determinant, UHF orbitals instead are used when dealing with unpaired electrons, which sometimes leads to the well-known drawbacks of a spin contamination fluctuating between excited states or along a PES (for an extreme example, see Ref. [33]). Poor convergence [34,35] and even dramatic failures have been found [36–39] either in the energetics or in the molecular properties. The advantages of MP_n perturbation treatments are however clear from both the theoretical and computational points of view. For example, size consistency is ensured, analytical gradients and Hessians are available, parallelization of the codes is easy to implement.

Most of the previous advantages are lost in the variational CI approaches: getting upper-bound energies has to be paid for and despite numerous and ingenious implementations using a large variety of algorithms, large-scale CI are not easily tractable. The cost–effectiveness argument leads either to carefully design ad hoc CI spaces or to arbitrary truncate

the FCI space in order to accommodate the storage limitations of modern computers. The single-reference SDCI (singles and doubles configuration interaction) approach is an example of such a truncation which is known to give an unbalanced description of the correlation energy between the ground and excited states [40] and thus unable to predict reliable transition energies. Even the inclusion of tri- and quadri-excited configuration state functions (CSF) in the so-called SDTQ-CI calculations appears to be insufficient, especially as soon as the single reference does not dominate the exact wave function by a large margin. The lack of size consistency in such truncated one-reference CIs ([41] and references therein) is also a well-known inconvenient. The partition of the correlation effects in non-dynamic and dynamic contributions [42,43] was however a major improvement that first led to the multiconfigurational approach (MCSCF) and then to complete active space SCF (CASSCF) treatment of non-dynamic correlation effects [2], while dynamic contributions have been reached using multi-reference CI (MRCI) [44,45]. In any case, a careful choice of the configurations included in the multiconfiguration MCSCF space has to be made in order to avoid both the inflation of the forthcoming MRCI expansions and the lack of some potentially important configurations needed for a proper description of the phenomenon under investigation. But even carefully truncated variational spaces or carefully selected reference CSFs in MRCI calculations also may lead to deceptive results when dealing with excited states in which correlation effects, both non-dynamic and dynamic, are of essential importance and not always easily predictable from the pure chemical viewpoint.

It is seen that neither the MBPT nor the CI approaches are the panacea: variational methods suffer from computational restrictions, and single-reference perturbation schemes usually suffer from the intrinsic poor quality of the reference zeroth-order wave function.

1.2. *Coupling variation and perturbation treatments*

The idea of coupling variational and perturbation methods is nowadays gaining wider and wider accep-

tance in the quantum chemistry community. The background philosophy is to realize the best blend of a well-defined theoretical plateau provided by the application of the variational principle with the computational efficiency of the perturbation techniques [8,20,26,27,30,31,46–64]: in that sense, the aim of these approaches is to improve a limited variational multi-reference wave function by a perturbation treatment. It is however deceptive that, apart from a few outstanding exceptions, most of the quoted approaches were only devoted to academic benchmark applications at the present day.

One of these exception is now more than 20 years old and led to the so-called CIPSI (configuration interaction by perturbation with multiconfigurational zeroth-order wave function selected iteratively) method whose basic idea is to progressively include the most important correlation terms in the variational space to be improved by a forthcoming second-order perturbation treatment [46,65–67]. The selection of the configurations to be included in the variational zeroth-order space is made according to a user-fixed numerical threshold based either on the contribution of these terms to the perturbed wave function, as in the original CI-3I approaches, or on their energetic contribution to the total energy [50,68]. The pitfalls to avoid when using such iterative algorithms are now well-established: in particular, extreme caution must be taken to ensure an homogeneous treatment of correlation energies along a reaction path or between excited states. Furthermore, such an iterative determination of the zeroth-order space leads to the admixture of contributions accounting for non-dynamic correlation in the variational part but also for contributions describing dynamic correlation as well: the chemical interpretation of the zeroth-order wave function is thus at least partially lost and distinguishing between non-dynamic and dynamic effects is difficult.

To our knowledge, the CIPSI methodology, which has been recently reviewed in Ref. [64], has however been the first widely used multi-reference perturbation theory, and the first to be applied to a large variety of problems of physical chemistry that spread from the pioneering works on H_2 [46] to chemisorption cluster model calculations [69] which, for the first time, applied a complete zeroth-order space to a non-academic benchmark. It was also applied to the

determination of accurate potential energy surfaces (for a recent example, see Ref. [70]), spin-orbit couplings in the *ab initio* scheme [71] or zero-field splitting parameters in a semi-empirical framework [72]. It was furthermore recently extended to semi-empirical electronic Hamiltonians (PPP or CS/INDO), using zeroth-order spaces designed to deal with the optical spectra of large conjugated systems or related ions [73–78].

Another attractive approach which has been proposed as soon as 1981 [79], has been widely developed and has now stood the test of time: the CASPT2 (complete active space second-order perturbation theory) method [53,80] takes a CASSCF [2] *ab initio* wave function as reference for a MP-like perturbation. Several studies on various molecules or atoms have been performed with this method; the agreement between experimental and theoretical results for the electronic spectra is spectacular: the CASPT2 approach, with the use of atomic natural orbitals (ANO) basis sets, can be considered as the first general successful *ab initio* treatment of excited states, and applies to the treatment of potential energy surfaces as well (for a review of CASPT2 applications, see Refs. [81–83] and references therein). Improvements of the CASPT2 formalism by slightly modifying the partition of the zeroth-order Hamiltonian are in progress [81] but the slight inconvenient of CASPT2 remains that one has to build the zeroth-order wave functions as CASSCF wave functions: the formal completeness of the variational part of the CASPT2 methodology has then to be paid for by a large expansion of the variational zeroth-order references. As an example, a CAS space generated by 6 electrons in 6 active orbitals (for the benzene molecule C_6H_6 for example) includes up to 12 excited CSFs relative to the closed-shell RHF determinants: such high-level excitations are usually of very limited importance on the behavior of the CASSCF wave function and will furthermore generate 14 excited terms in the forthcoming perturbation treatment, which will have so small contributions on the second-order energy that they could be neglected in the whole treatment without loss of confidence.

Parallel and independently, an analogous method known as GMP n (generalized Møller–Plesset) was proposed [51,52,84,85] that has not been applied to the determination of electronic spectra to our knowl-

edge. It can be considered as equivalent to CASPT2 except in the choice of the configurations included in the perturbation: GMP2 applies the single and double excitation operators towards the external space on each configuration involved in the reference wave function while CASPT2 applies these operators on the reference wave function as a whole. It follows that CASPT2 requires a reorthogonalization of the perturbative space in order to avoid problems due to linear (or near-linear) dependences, giving slight complications in the perturbation treatment. Furthermore, as formulated in Refs. [53,80], the CASPT2 approach widely uses the facts that the zeroth-order space is complete and that the CASSCF orbitals used in the perturbation have been optimized relative to that space (either using several orbital sets for different electronic states or using one set of averaged orbitals for several electronic states of the same symmetry): as a consequence, the formulation is simplified by the application of the extended Brillouin theorem [86] which allows for the automatic exclusion, in the perturbation treatment, of all the singly-excited wave functions generated by the application of the single-excitation operators on the converged CASSCF reference wave function. It is however clear that CASPT2 could be generalized without difficulties to break itself of these restrictions.

Finally, the very recent method developed by Hirao et al. [26,27,54,59], also appears very promising in view of the very good results obtained on the electronic spectrum of the benzene or ozone molecules [63,87]: the formalism developed in the so-called MRMP approach is by far simpler than that needed in the CASPT2 approach and is closely related to that is used in our MC/P methodology as will be described below.

The fact that, in some cases, chemical accuracy was only obtained by using zeroth-order spaces larger than those supported by some “chemical intuition” [52,53], by extending the perturbation to the third order [51,52], or by involving some correction functions with no clear physical or chemical meaning [30–32] prompted us to investigate some aspects of the variation–perturbation coupling in more details (different perturbation schemes as well as different sets of correlated orbitals). The limitation we imposed to that study was *to restrict the zeroth-order*

space to the only components assumed necessary to properly account for the chemistry of the problem under investigation [60].

It is the aim of the present contribution to point out that it is possible to systematically remedy some of the previous drawbacks in the treatment of excited states. Following the conclusions of our previous investigations and the philosophy of our so-called MC/P method, we emphasize that the zeroth-order wave function has to be qualitatively correct and thus requires a variational treatment (MCSCF wave function) that accounts for non-dynamic effects.

In this spirit, the iterative construction of the zeroth-order space (as in the CIPSI methodology) is no longer relevant and the zeroth-order space is constructed once for all as a whole entity that include all the physical chemistry of the problem at hand. Furthermore, this space is carefully fractionated into a product of smaller MCSCF, CASSCF or GVB spaces in order to get free from the computational restrictions that appear when one has to use strict CASSCF spaces as reference: in our treatment, strict completeness is lost but chemical completeness is retained. Such a way, semi-quantitative results are obtained that are brought up to chemical accuracy by the inclusion of the remaining correlation effects (dynamic and remaining non-dynamic) through a forthcoming perturbation on the previously determined variational zeroth-order wave function.

The MC/P strategy developed along these lines allows thus to go beyond the MCSCF level and at the same time preserves a large flexibility either in the choice of the zeroth-order wave functions, zeroth-order Hamiltonians or in the choice of the orbitals. The present paper will report the philosophy adopted for the determination of accurate electronic spectra and will illustrate it on three small size molecules: C_2H_4 , H_2CO and H_2CC . Ethylene will be studied as a first academic benchmark, the excited states of formaldehyde will then be revisited. A final application will be given as the determination of the electronic spectrum of the vinylidene molecule.

Variational calculations were performed using the Alchemy II package [88] while the further perturbation calculations used the MC/P code developed in our group [60].

In order to estimate the quality of our results, it will sometimes be referred to a “quadratic

deviation”. Given two sets of N data $\{x'_i\}$ and $\{x''_i\}$, this quantity has been defined as

$$\Delta x = \sqrt{\sum_{i=1}^N \frac{1}{N} (x'_i - x''_i)^2}.$$

What we furthermore will call “dispersion” is

$$\Delta \sigma = \sqrt{\sum_{i=1}^N \frac{1}{N} (|x'_i - x''_i| - \Delta x)^2}.$$

The only aim of such a use of statistics is to have an efficient way to compare our results either to experimental data or to other computed quantities: the simplest determination of the largest absolute error is by far a too crude criterium to test the reliability of any quantum chemistry strategy that aims at giving accurate results on a large range of energies.

2. The MC/P formalism and philosophy

2.1. The spectral decomposition of the Hamiltonian

Let S be the space spanned by a set of orthogonal CSFs (or, ultimately Slater determinants) referred to as I . Strategies for choosing S according to relevant chemical criteria will be developed in Section 2.3.

Let $|i\rangle$ be a variational wave function, obtained through a CI calculation in the S space (using a given set of *orthogonal* orbitals) and using the exact electronic Hamiltonian H :

$$|i\rangle = \sum_{I \in S} c_I^i |I\rangle, \quad (1)$$

$$H|i\rangle = E_i^S |i\rangle. \quad (2)$$

Let now P be the space of the Slater determinants J spanned by applying one- and two-electron excitation operators on each I included in S : P is thus spanned by singly and doubly excited Slater determinants relative to those spanning S . This way, *orthogonality* of any two K and L , each belonging either to S or to P , is ensured.

Having S as a zeroth-order variational space, and P as a perturbation space (which is unambiguously defined as generated from S), the second-order perturbation theory makes it, a priori, possible to obtain a corrected value E_i for the zeroth-order E_i^S as

$$E_i = E_i^0 + E_i^1 + E_i^2. \quad (3)$$

Owing to our choices for the S and P spaces, and the definition of the one-particle space employed to build the determinants on, all requirements are fulfilled which allows to express the first- and second-order corrections to the energy in their simplest forms according to the Rayleigh–Schrödinger formulation of perturbation theory. Splitting H into a zeroth-order Hamiltonian H^0 and its perturbation part V , one gets

$$E_i^0 = \langle i | H^0 | i \rangle, \quad (4)$$

$$E_i^1 = \langle i | V | i \rangle, \quad (5)$$

$$E_i^2 = \sum_{J \in P} \frac{|\langle i | V | J \rangle|^2}{E_J - E_i^0}. \quad (6)$$

We point out that in the implementation used here, and contrary to the CASPT2 [53,80] or MRMP approaches [26], the zeroth-order wave function is not necessarily supposed to satisfy the generalized Brillouin theorem [86]: this means that the orbitals that can be used are not necessarily those obtained at a converged MCSCF calculation in the S space (examples are shown in Ref. [60]), provided they are orthogonal. Moreover, the S space may not necessarily be the same as that used for the determination of the orbitals. This flexibility allows to efficiently deal with the so-called intruder states (Section 2.2.4).

As shown in Ref. [46], the zeroth-order Hamiltonian of the system can be taken in a spectral form as

$$H^0 = \sum_{I \in S} E_I |I\rangle \langle I| + \sum_{J \in P} E_J |J\rangle \langle J|. \quad (7)$$

This points out that H^0 is unambiguously defined by giving the energies E_I and E_J respectively in the variational space S and in the perturbation space P. Furthermore, this Hamiltonian is diagonal: $\langle I | H^0 | J \rangle = 0$ since $\langle I | J \rangle = 0$. Such a formulation of H^0 leads to the so-called “barycentric partitions”, as will be described in the following.

2.2. The partitions of the Hamiltonian

2.2.1. The barycentric Møller–Plesset partition (BMP) [89]

In the Møller–Plesset partition, the diagonal matrix elements of H^0 are defined as

$$E_K = \langle K | F | K \rangle \quad (K \in S \text{ or } P), \quad (8)$$

where F should be a one-electron operator for the perturbation theory to be computationally efficient

since in this case diagrammatic series and linked cluster theorem can be used [66].

For a multi-reference zeroth-order wave function, Eq. (7) gives the zeroth-order energy E_i^0 as a barycentric quantity:

$$E_i^0 = \sum_{I \in S} |c_i^I|^2 E_I. \quad (9)$$

If the reference wave function is a MCSCF wave function, then, the “natural” choice for F comes from the expression of the generalized Fock operators:

$$F_\nu^{\text{MCSCF}} = f_\nu h + \sum_\mu a_{\nu\mu} J_\mu - b_{\nu\mu} K_\mu, \quad (10)$$

where f_ν are the halves of the diagonal components of the one-electron density matrix, $a_{\nu\mu}$ and $b_{\nu\mu}$ the energy coefficients and, finally, J_μ and K_μ the usual Coulomb and exchange operators. So doing, we lost some simplicity in the choice of the operator. It is however possible to define a one-electron operator very analogous to the more familiar closed-shell Fock operator [26,60]:

$$F = h + \sum_j f_j (2J_j - K_j). \quad (11)$$

In that case, F has to be seen as an effective operator (of Longuet-Higgins-type, for example, see Ref. [90]) in which orbital occupancies are explicitly considered. It is clear that this operator is not diagonal in general, but it can be transformed to a diagonal form as shown in Ref. [26]. The occupation numbers can be chosen for each electronic state under investigation or can be given the values of the natural orbital occupation numbers provided by an averaged MCSCF calculation. More generally, given a set of orbitals, it is always possible to define a (non-local) one-electron operator having these orbitals and energies as eigenvectors and eigenvalues [91]. Such a possibility which amounts to extending relation (11) will not be developed further here, but allows the use of various types of orbitals in the perturbations. Among others, the natural orbitals (NOs) of a multiconfigurational treatment are known to improve the recovering of the electronic correlation calculations [60,92–94]. The variational spaces can moreover always be designed to remove any arbitrariness in the expansion of the zeroth-order

wave function if expressed in terms of the corresponding NOs and CSFs.

This approach, hereafter referred to as “barycentric Møller–Plesset” (BMP) perturbation theory is an extension of the usual MP single-reference approach and gives back the usual MP2 or UMP2 methods if RHF or UHF orbitals are used (all $f_p = 1$ in both cases, which necessarily implies a single-reference approach).

2.2.2. The barycentric Epstein–Nesbet (BEN) partition [46,95–98]

In the Epstein–Nesbet partition, H^0 is taken as the diagonal part of the exact Hamiltonian in the $S \cup P$ space, and V as its extra-diagonal part.

$$E_K = \langle K | H | K \rangle \quad (K \in S \text{ or } P). \quad (12)$$

Eq. (9) still applies in getting the zeroth-order energy for $|i\rangle$.

Using the BMP or the BEN partitions in the determination of electronic spectra will be discussed in Sections 3.2 and 4.2.2.

2.2.3. Eigenvalue partitions

One may wonder whether it would not be simpler to put

$$E_i^0 = E_i^S \quad (13)$$

in the definition of the zeroth-order energy instead of Eq. (9). So doing an eigenvalue Møller–Plesset (EMP) partition is obtained when coupling Eq. (13) with Eq. (8) or an eigenvalue Epstein–Nesbet partition when coupled with Eq. (12). As shown in Refs. [46,64], both these approaches lead to unphysical behaviors of transition energies when dealing with the spectroscopy of one of the two A and B components of an intermolecular system $A \cdots B$, where A and B do not interact.

Barycentric partitions are thus by far superior to eigenvalue ones. In this paper, however, EEN transition energies will also be reported as a numerical illustration of a theoretically established failure.

2.2.4. The intruder state problem

A state J whose energy E_J falls close to the zeroth-order energy E_i^0 will have the second-order energy correction diverged, according to Eq. (6). Such intruder states are not uncommon when dealing

with excited states or even with potential energy surfaces (for an extreme example, see Ref. [99]). The probability of encountering intruder states in a multi-reference perturbation calculation increases with the S space. This is especially true with those approaches that use complete valence spaces as S spaces: as the zeroth-order expansion grows, i.e. the level of the excitations considered at the variational level increases, the energy gap between those excited states, described as eigenvectors of the S space, and those remaining determinants spanning the perturbation space P decreases. It is worth mentioning that such intruder states usually interact only weakly with the eigenvectors of S , either through H or V .

As discussed in Ref. [64] and in references therein, this problem is readily and confidently solved by applying a level shift (LS) on the denominator of Eq. (6): such a viewpoint has been used recently to extend the CASPT2 methodology to the so-called LSCAPT2 [100].

The other strategy is to include these intruder states in the S space. Such an approach however is hazardous in perturbation treatments based on complete configuration spaces (full-valence CI spaces, for example): adding those orbitals and excitation levels needed to describe the intruder states may result in an untractable increase of the zeroth-order configuration space (and at the same time strongly affects its chemical sense). When no formal completeness restriction is imposed for the multi-reference zeroth-order space, which is the case in the MC/ P approach, the intruder states can be *individually* added to S .

2.2.5. Contracted and decontracted perturbations

If both $|i\rangle$ and $|j\rangle$ are eigenvectors of H in the S space, then $\langle i | H | j \rangle = 0$. Due to the formalism of the second-order perturbation theory in its simplest formulation, the second-order coupling between $|i\rangle$ and $|j\rangle$ induced by the perturbation determinant J are not taken into account, i.e. one neglects the possible role of energetic contributions such as

$$\sum_{J \in P} \frac{\langle i | H | J \rangle \langle J | H | j \rangle}{E_J - \frac{1}{2} [E_i^0 + E_j^0]} \quad (14)$$

so that the perturbation is called “contracted” [64]. Such indirect couplings within the S space can be important when dealing with excited states that are

strong admixtures of valence, Rydberg and ionic characters. The relative influence of the dynamic correlation on each of them (which is recovered in the perturbation) being different explains why some excited states are difficult to properly describe using a contracted multi-reference perturbation theory like CASPT2 or the present version of MC/P: a contracted perturbation can poorly describe the polarizations of the electronic densities induced by the second-order couplings in the S space. A (partially) decontracted scheme has to be used in those cases to improve transition energies: this can be done using the quasi-degenerate perturbation theory (QDPT) ([64,66,67,101] and references therein), for example. Such an improvement is currently under development in the MC/P approach and the results will be presented in a forthcoming contribution.

2.3. The “chemical” choice for the zeroth-order wave function

There is no general recipe to choose the “best” zeroth-order wave function. However, to avoid large variational expansions or to be sure not to miss some important effects by a too drastic truncation, it may be wise to keep some rules in mind in order to design, at least, a “good” zeroth-order wave function.

First of all, the wave function has to contain the necessary ingredients to properly describe the phenomenon under investigation: for example, when dealing with electronic spectra, it has to contain every CSFs needed for the qualitative description of the excited states. The zeroth-order wave function has then to include a number of monoexcitations from the ground state occupied orbitals to some virtual orbitals. In that sense, the choice of a single CI wave function (SCI) as proposed by Foresman et al. [8,56] in their CIS/MP2 treatment of electronic spectra represents the smallest zeroth-order space that can be considered.

However, the restriction of this space to monoexcited configurations wrongly sweeps away the complexity of excited state wave functions [40] and the CIS/MP2 is not able to provide reliable absolute transition energies and is not reliable even when simply dealing with the ordering of the excited states (see the dramatic example of the formaldehyde

molecule in Section 4). In particular, such a truncated SCI space lacks all the CSFs that account for non-dynamic correlation effects (especially pair excitations) on the ground and excited states as well as any zeroth-order description of doubly excited states. These important contributions are poorly recovered by any subsequent second-order perturbation while being essential in the description of either electronic spectra or potential energy surfaces. In those cases, a wave function generated by a specific configuration interaction is necessary. The structure of the corresponding multiconfiguration reference space must however be carefully designed if one does not want to handle large expansions that might include useless CSFs. The “chemical” intuition can help in designing the most relevant CI space as will be shown below. In particular, CAS spaces which are often used to build zeroth-order wave functions before performing large-scale CI can be split into products of smaller CAS or GVB [102] spaces without loss of accuracy: the formal completeness of the treatment may sometimes be lost, but the saving in the computing time is always considerable. At all events, the Lewis structures are correctly represented so that “chemical completeness” is achieved.

It is furthermore logical to use a set of orbitals that is coherent with the design of the zeroth-order space: the natural orbitals issued from well-designed MCSCF treatments are unique and therefore attractive candidates for building the configurations necessary to the perturbation development.

Finally, in order to ensure an homogeneous treatment of all excited states at the variational level, the MCSCF calculation should be averaged over the states under investigation. The lowest eigenfunctions of the MCSCF Hamiltonian will provide the zeroth-order wave functions to build the perturbation on. They account for the chemical aspect of the system by considering only those electrons expected to be responsible for the properties being studied. The zeroth-order level of wave function will thus provide a semi-quantitative answer.

Following these lines, it is clear that only part of the non-dynamic correlation effects involved in the description of the excited states will be included in the MCSCF treatment. The remaining effects that are considered of less essential importance will be recovered at the perturbation level as well as dynamic

correlation effects. The perturbation will thus give the final quantitative answer.

It is now well-established that extended one-particle spaces have to be considered to describe diffuse excited states (Rydberg states for example), as well as for a proper account of dynamic correlation effects. As a consequence, it is legitimate to consider large basis set expansions if one aims at predicting accurate values of transition energies. However, the inclusion of high-momentum correlating orbitals to account for angular correlation or the consideration of high-zeta basis sets to account for radial correlation leads to such large expansions of the first-order perturbation correction to the variational zeroth-order initial wave function that such high-quality treatments for large molecular systems are unfortunately untractable. It is our opinion that using large basis sets requires even larger post-SCF treatments to be relevant, especially when dealing with excited states. One might expect, however, that using smaller, but well-balanced basis sets coupled to appropriate post-SCF treatments will result in a balanced description of the dynamic correlation effects. The forthcoming calculations, performed using a polarized double-zeta quality basis set, expanded by a first set of semi-diffuse functions and a second set of Rydberg atomic orbitals, will illustrate this point.

2.4. General philosophy and flexibility of the MC / P methodology

As developed from the beginning of this contribution, the general philosophy of the MC/P methodology is to replace the strict completeness of the variational zeroth-order space, as used in CASPT2, by the chemical completeness together with maintaining a strict separation between non-dynamic (variational level) and dynamic (perturbation level) correlation effects.

So doing, an analysis of the electronic structure in terms of Lewis-localized orbitals is essential in order to discard from the zeroth-order space electronic excitations of poor impact for the properties under investigation.

The MC/P methodology has furthermore been implemented in such a way that a very attractive flexibility has been retained.

- * Choice of the zeroth-order space S:

- any product of MCSCF spaces (chosen on chemical criteria or not),
- any space formed by additions of individually selected CSFs to the precedent space (especially intruder states).
 - * Choice of the orbitals:
 - any set of orthogonal orbitals,
 - closely related to the zeroth-order space S or not.
 - * Zeroth-order Hamiltonian:
 - Møller–Plesset,
 - Epstein–Nesbet,
 - barycentric or eigenvalue formulations.
 - * Active electrons or orbitals:
 - user-defined, at each of the variational and/or perturbation steps.
 - * Generating space for the perturbation:
 - any restriction of the S space,
 - the S space as a whole.
 - * Intruder states:
 - individual inclusion in the S space.

3. Ethylene

Ethylene C_2H_4 has been intensely studied for many years, on both the experimental and theoretical points of view. A number of reviews of interesting results dealing with the electronic structures of the ground and excited states can be found in the literature [56,103–105].

3.1. Computational details

The geometry reported in Ref. [105]: $CC = 1.339$ Å, $CH = 1.086$ Å and $\angle HCC = 117.6^\circ$, in D_{2h} point group, is used. The molecule is supposed to lie in the xy plane; the x axis corresponds to the C_2 axis, as in Fig. 1a.

The MCSCF and the following perturbation calculations were done using the standard 6-31 + G* basis set [106] expanded by a set of spd Rydberg functions. Exponents of this additional Gaussians were: 0.023, 0.021 and 0.015; the final corresponding basis set will be referred to as 6-31 + G* R.

3.1.1. The active space for C_2H_4

The MCSCF calculations were performed within the CASSCF framework using the configuration

space that includes all the spin and symmetry adapted CSFs arising from the electronic distributions presented in Table 1. Only the π system of the molecule is considered at this zeroth-order level of wave function: all contributions originating from the core, the σ_{CC} and σ_{CH} electrons will be recovered at the perturbation level. Some of the Rydberg orbitals ("R"), which were selected by preliminary investigations, are explicitly included in the CASSCF space in order not to overcorrelate valence states relative to Rydberg states. The state averaging was done for a number of states of same space and spin symmetry as detailed in Table 1. Except the difference in the choice of the basis set, the CASSCF wave functions are of same nature as those used for the recent CASPT2 treatment of ethylene [105].

3.2. Results and discussion

The CASSCF and MC/P results are presented in Table 2 together with the CASPT2F [105] values, the CIS/MP2 results cited in Ref. [8] and some available experimental data. It is immediately seen that the CASSCF, the MC/BEN and the MC/EEN levels of calculation fail to correctly reproduce the experimental spectrum. On the contrary, the MC/BMP calculation matches the experiment at least as closely as CASPT2.

One among the reasons why the CASSCF approach fails in reproducing the experimental spectrum probably comes from the lack of the σ skeleton in the CASSCF space: a better zeroth-order wave function would have the σ_{CC} bond and its corre-

sponding anti-bonding orbital included in the active space to account for the related non-dynamic correlation effects.

We note that all CASSCF transitions energies are smaller than experimental ones with the exception of an excellent match for the transition from the ground state to the 1^1B_{1u} and 1^3B_{1u} valence excited states. The location of the 1^1B_{1u} state $^1(\pi\pi^*)$ is a case study in quantum chemistry and has been widely discussed (see references quoted in Ref. [105]): it is now recognized that this so-called V state presents a strong mixture of valence and Rydberg character so that its location will be very dependent on the methodology used to describe it. In a recent study [107] it was proved that the expectation $\langle z^2 \rangle$ decreases with the size of MRCI expansions: as a consequence, it can be expected that CASSCF calculations will not be able to properly describe it and that the good match obtained in this work at this level of calculation might be fortuitous. Inspection of the CASSCF wave function shows however a weight of 74% for the $^1(\pi\pi^*)$ CSF, which indicates a dominant valence character although strongly contaminated by Rydberg terms. Transitions to Rydberg states are uniformly underestimated by about 0.59 eV with a 0.23 eV dispersion. Since the averaged CASSCF wave functions are build using a CASSCF space that allows for the mixing of valence and Rydberg orbitals, we expect the valence states to be somewhat too diffuse while the Rydberg states are lowered in energy due to a coupling with the valence. Transition energies are thus anticipated to be too small for excited Rydberg states which is effectively observed.

When dynamic correlation effects are considered, it is seen (Table 2) that only the MC/BMP development provides accurate transition energies. We point out that the averaged increase in the transition energies when going from the CASSCF level of calculation to the MC/BMP approach is 0.60 eV with a small dispersion of 0.22 eV, which illustrates a well-balanced perturbation treatment. The deviation relative to the experimental values is only 0.13 eV on the whole excited state manifold, which is less than a CH stretching vibration. No larger discrepancy than 0.27 eV occurs, which means an error of less than 4% when reported to the corresponding transition energy. The dispersion is 0.08 eV. The

Table 1
Configuration space for MCSCF calculations on C_2H_4

Symmetry	Set 1 (frozen)	Set 2	Averaging
a_g	$1s_C^+ \sigma_{CC} \sigma_{CH}$	R R R	2S/1T
b_{1u}	$1s_C^- \sigma_{CH}$	R	2S/2T
b_{2u}	σ_{CH}	R	1S/1T
b_{3g}	σ_{CH}	R	none
b_{3u}		π R	3S/3T
b_{2g}		π^* R	1S/1T
b_{1g}		R	1S/1T
a_u			1S/1T
Electronic distribution			
	14	2	

CASPT2F method is directly comparable to the MC/BMP approach because of a very close partition of the electronic Hamiltonians in both theories: it gives a deviation of 0.13 eV, with no discrepancy larger than 0.40 eV, and a dispersion by 0.10 eV. This largest deviation of 0.40 eV is observed for the $1^1B_{1u}(\pi\pi^*)$ state and is reduced to 0.20 eV in our MC/BMP calculation: as discussed above, this state is a strong mixture of valence, ionic and Rydberg characters and would require the use of decontracted multi-reference perturbation to be more accurately

accounted for. It is thus to be concluded that the excellent results given by the two methods rest on the combination of variational and perturbation treatments. Even if better absolute energies can be obtained for individual states by using larger atomic expansions, it is seen that a well-balanced basis set of moderate size is able to provide accurate energy differences. We note that, in the case of the ethylene molecule, CIS/MP2 gives a deviation of 0.19 eV for the singlet manifold: the largest discrepancy is 0.35 eV, which is in error by 4.9% when compared to the

Table 2
CASSCF and MC/P transition energies (eV) for the ethylene molecule

	CASSCF	MC/BEN	MC/EEN	MC/BMP	Experiment	CASPT2F ^a	CIS/MP2 ^l
singlet states							
$1^1B_{1u}(\pi\pi^*)$	7.92	9.15	8.91	8.20	8.00 ^b	8.40	8.39
$1^1B_{3u}(3\sigma)$	6.55	7.79	7.57	7.05	7.11 ^c	7.17	7.52
$1^1B_{1g}(3p\sigma)$	7.18	8.33	8.07	7.56	7.80 ^d	7.85	8.14
$1^1B_{2g}(3p\sigma)$	7.20	8.39	8.14	7.63	7.90 ^e	7.95	8.12
$2^1A_g(3p\pi)$	7.86	8.64	8.91	8.37	8.28 ^f	8.40	8.42
$2^1B_{3u}(3d\sigma)$	8.01	9.41	9.14	8.61	8.62 ^g	8.66	8.92
$2^1B_{1u}(3d\pi)$	8.97	10.01	9.63	9.10	9.33 ^h	9.31	9.38
$1^1A_u(3d\pi)$	8.12	9.71	9.45	8.84		8.94	9.00
$3^1B_{3u}(3d\delta)$	8.15	9.60	9.30	8.78	8.90 ⁱ	9.03	9.14
$1^1B_{2u}(3d\delta)$	8.19	10.14	9.87	9.10	9.05 ^j	9.18	
triplet states							
$1^3B_{1u}(\pi\pi^*)$	4.29	4.89	4.79	4.22	4.18 ^m 4.36 ^h	4.39	
$1^3B_{3u}(3s)$	6.46	7.77	7.56	7.04	6.98 ^k	7.05	
$1^3B_{1g}(3p\sigma)$	7.15	8.49	8.25	7.77	7.79 ^k	7.80	
$1^3B_{2g}(3p\sigma)$	7.13	8.49	8.24	7.74	7.79 ^k	7.90	
$1^3A_g(3p\pi)$	7.35	9.07	8.81	8.16	8.15 ^k	8.26	
$2^3B_{3u}(3d\sigma)$	7.99	9.46	9.18	8.68	8.57 ^k	8.57	
$2^3B_{1u}(3d\pi)$	8.44	9.64	9.23	8.87		9.07	
$1^3A_u(3d\pi)$	8.11	9.74	9.48	8.87		8.94	
$1^3B_{2u}(3d\delta)$	8.18	10.05	9.78	9.01		9.09	
$3^3B_{3u}(3d\delta)$	8.11	9.64	9.35	8.83		8.97	
deviation	0.59	0.77	0.55	0.13	0.00	0.13	0.19
dispersion	0.23	0.19	0.19	0.08	0.00	0.10	0.12

^a [105].

^b Vertical value estimated from Refs. [103,107,146–148].

^c [103,149–152].

^d [153–155].

^e [152,156].

^f [154,155].

^g [149–152,156].

^h [153,157].

ⁱ [149–152,158].

^j [149,150,156].

^k [151] (adiabatic).

^l As cited in Ref. [8].

^m Most recent value [159].

corresponding experimental value. The dispersion for this series of computed values is 0.12 eV.

Contrary to the barycentric Møller–Plesset perturbation scheme that ensures an excellent agreement with the experimental results, the Epstein–Nesbet partitions fail to produce any accurate result: both overestimate the transition energies. Discrepancies are seen to be as high as 1.15 eV in the MC/EEN approach, while being slightly reduced to 0.91 eV at the MC/BEN level of calculation. Although the deviation from the experiments is by far larger using these two partitions than it was using a BMP partition (MC/EEN: 0.77 eV, MC/BEN: 0.55 eV, MC/BMP: 0.13 eV), it is interesting to point out that both of the former partitions present a small dispersion (MC/EEN: 0.19 eV, MC/BEN: 0.19 eV, MC/BMP: 0.08 eV), which means that these perturbation treatments still remain balanced between different states.

The behavior of the MC/EEN calculations, that show large discrepancies and deviations to experimental values, illustrates an aspect of the failure of EEN partitions to account for transition energies; it is the major reason why barycentric partitions were initially introduced [46].

Table 3 reports the shifts between the MC/EEN and MC/BEN transition energies with respect to the computed MC/BMP corresponding values. It is seen that, for a given partition, these shifts are almost insensitive to the transition considered. They average at 0.81 eV for the EEN partition and at 0.54 eV in the case of the BEN partition with respective dispersions of 0.16 and 0.10 eV. Applying these shifts on the computed transition energies in order to get corrected Epstein–Nesbet energies leads to values that closely match the MC/BMP values and the experimental values, as seen in the last columns of Table 3. The corrected deviation and dispersion are

Table 3

Corrected MC/EEN and MC/BMP transition energies (eV) for the ethylene molecule

	MC/BMP	$\Delta E(\text{MC/BEN})^1$	$\Delta E(\text{MC/EEN})^1$	MC/BEN ²	MC/EEN ²	Experiment
singlet states						
1 ¹ B _{1u} ($\pi\pi^*$)	8.20	0.95	0.71	8.34	8.35	8.00 ^b
1 ¹ B _{3u} (3s)	7.05	0.74	0.52	6.98	7.01	7.11 ^c
1 ¹ B _{1g} (3p σ)	7.56	0.77	0.51	7.52	7.51	7.80 ^d
1 ¹ B _{2g} (3p σ)	7.63	0.76	0.51	7.58	7.58	7.90 ^e
2 ¹ A _g (3p π)	8.37	0.27	0.54	8.10	8.08	8.28 ^f
2 ¹ B _{3u} (3d σ)	8.61	0.80	0.53	8.60	8.58	8.62 ^g
2 ¹ B _{1u} (3d π)	9.10	0.91	0.53	9.20	9.07	9.33 ^h
1 ¹ A _u (3d π)	8.84	0.87	0.61	8.90	8.89	
3 ¹ B _{3u} (3d δ)	8.78	0.82	0.52	8.79	8.74	8.90 ⁱ
1 ¹ B _{2u} (3d δ)	9.10	1.04	0.77	9.33	9.31	9.05 ^j
triplet states						
1 ³ B _{1u} ($\pi\pi^*$)	4.22	0.67	0.57	4.08	4.23	4.36 ^h
1 ³ B _{3u} (3s)	7.04	0.73	0.52	6.96	7.00	6.98 ^k
1 ³ B _{1g} (3p σ)	7.77	0.72	0.46	7.68	7.67	7.79 ^k
1 ³ B _{2g} (3p σ)	7.74	0.75	0.50	7.68	7.68	7.79 ^k
1 ³ A _g (3p π)	8.16	0.91	0.65	8.26	8.25	8.15 ^k
2 ³ B _{3u} (3d σ)	8.68	0.78	0.50	8.65	8.62	8.57 ^k
2 ³ B _{1u} (3d π)	8.87	0.77	0.36	8.83	8.67	
1 ³ A _u (3d π)	8.87	0.87	0.61	8.93	8.92	
1 ³ B _{2u} (3d δ)	9.01	1.04	0.77	9.24	9.22	
3 ³ B _{3u} (3d δ)	8.83	0.81	0.52	8.83	8.79	
deviation	0.13 ³	0.81 ⁴	0.56 ⁴	0.19 ³	0.19 ³	0.00
dispersion	0.08 ³	0.16 ⁴	0.10 ⁴	0.10 ³	0.10 ³	0.00

^a –^m See Table 2.

¹ Shifts relative to the MC/BMP transition energies.

² Corrected values.

³ Relative to the experimental values.

⁴ Relative to the MC/BMP series.

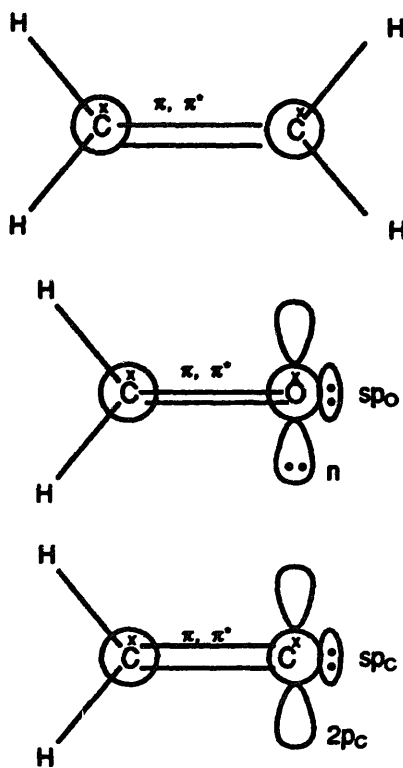


Fig. 1. Lewis structures of ethylene, formaldehyde and vinylidene.

reduced to 0.19 and 0.10 eV for both the Epstein–Nesbet partitions.

The fact that the discrepancies between the Møller–Plesset and the Epstein–Nesbet values remain constant when going from one state to another points out that the Epstein–Nesbet perturbation still ensure a balanced description of excited states. The origin of these shifts can be explained remembering that the Epstein–Nesbet partitions involve, at the second-order of perturbation, some terms that would appear only at higher orders in the Møller–Plesset approach [46,98,108]. Inspection of absolute energies shows that all states are overcorrelated using EN partitions relative to the BMP partition. As an example, the CASSCF energy of the X^1A_g ground state is lowered by 7.47 eV in the BMP calculation, while being lowered by 9.03 and 9.30 eV respectively when using the EEN and BEN partitions. The supplementary correlation recovered for the ground state when going from MC/BMP to MC/EEN is then 1.56 eV; it is 1.83 eV when going to MC/BEN. If we now consider an excited state, the 1^1B_{1u} for example, the supplementary correlation relative to the MC/BMP absolute energy is found to be 0.85

eV (MC/EEN) and 0.88 eV (MC/BEN). Effects of the same order of magnitude are found for the remaining excited states. It follows that these supplementary correlation effects will affect the transition energies by about 0.71 eV (MC/EEN) or 0.95 eV (MC/BEN) which is close to the averaged values (0.60 and 0.80 eV) reported before. As a consequence, the whole spectrum is shifted toward larger energies, relative to the MC/BMP spectrum, as seen in Table 2.

The previous calculations unambiguously show that the MC/BMP/6-31 + G* R level of calculation is relevant for the determination of the transition energies in the ethylene molecule, contrary to uncorrected MC/BEN or MC/EEN approaches. It reproduces the experimental data as well as the high-level CASPT2F/ANO calculation. The results given by the CIS/MP2 method are found to be of similar accuracy. We point out that any of the perturbation treatment reported in Table 2 and Table 3 provides two quasi-degenerate states about the experimental feature at 7.79 eV that might in fact be a superposition of two different excited states (1^3B_{1g} , 1^3B_{2g}).

4. Formaldehyde

A number of experimental and theoretical studies were performed on the carbonyl group [109–112] following the pioneering work of Burawoy [113]. A complete survey is beyond the scope of this paper (for early works see Refs. [114–116]). We will only mention a few of them that we consider of particular importance for a comprehensive coverage of the electronic spectrum of formaldehyde for both the theoretical and experimental points of view. Recently, Chutjian recorded the electron impact excitation spectrum of formaldehyde [117,118] and reported transition energies that are taken as reference values in many other works. So are the experimental values compiled by Robin [119] and Brint et al. [120], the latter pointing out a number of well-defined Rydberg series, of special importance for theoretical benchmarks.

On the theoretical hand, calculations have been performed as soon as in the 1950s [104,114] since formaldehyde represents the smallest member of the carbonyl series. References to early works are avail-

able in the compilation by Davidson and McMurchie [121] and in Refs. [104,114–116]. Of particular interest for a comprehensive assignment of the experimental transitions are the very fine and accurate calculations by Harding and Goddard using their GVB-CI method [118,122], as well as the very recent work by Hachey et al. [123] who included up to *f* orbitals in a MRCI devoted to the vertical excitation energies: their results are in excellent agreement with experimental data but their method is however unlikely to be extended to larger system owing to obvious computational limitations. EOM-CC methodology also has been used [9], but the study was restricted to singlet states: the agreement with experimental data is however fairly good for the lower states. Finally, 5 excited states have been determined using the MROPT methodologies developed in Davidson's group [30], whose transition energies are in good agreement with experiment if using the MROPT1 scheme, but dramatically inaccurate using the MROPT2 approach.

4.1. Computational details

The MP2/6-311 + + G** C_{2v} geometry [56] was used for H₂CO in the present calculations (CO = 1.2122 Å, CH = 1.1044 Å, HCO = 121.94°). It is very close to the experimental geometry [124]. The molecule is supposed to lie in the *yz* plane; the *z* axis corresponds to the C₂ axis, as in Fig. 1b.

The MCSCF and the subsequent perturbations were done using the standard 6-31 + G* basis set [106] expanded by a set of spd Rydberg functions. Exponents of this additional Gaussians were: 0.032 and 0.028 for the *s* and *p* shells of the oxygen atom, and 0.023 and 0.021 for the carbon atom. For the *d* functions, a common value of 0.015 was chosen for both heavy atoms. The final corresponding basis set will be referred to as 6-31 + G*R.

4.1.1. The active space for H₂CO

The configuration space used in the calculation is presented in Table 4. Orbitals are distributed into several sets, and ordered by symmetry. They are

Table 4
Variational space for the formaldehyde molecule (see text for details)

Symmetry	Orbital repartitions ^a							
	set 1	set 2	set 3	set 4	set 5	set 6	set 7	set 8
a ₁	σ _{CO}	σ _{CO} *	sp _O	sp _O *				10 R
b ₁							π π*	4 R
b ₂					n	n*		4 R
a ₂								2 R
Electronic distributions								
A	2	0	2	0	2	0	2	0
A	0	2	2	0	2	0	2	0
A	2	0	0	2	2	0	2	0
A	2	0	2	0	0	2	2	0
A	1	1	2	0	2	0	2	0
B	2	0	2	0	1	0	3	0
B	0	2	2	0	1	0	3	0
B	2	0	0	2	1	0	3	0
B	1	1	2	0	1	0	3	0
C	2	0	2	0	2	0	1	1
C	0	2	2	0	2	0	1	1
C	1	1	2	0	2	0	1	1
C	2	0	0	2	2	0	1	1
C	2	0	2	0	0	2	1	1
D	2	0	2	0	1	0	2	1
D	0	2	2	0	1	0	2	1
D	2	0	0	2	1	0	2	1
D	1	1	2	0	1	0	2	1

^a 2K shells are doubly occupied in all CSFs.

denoted in terms of localized orbitals in order to emphasize their “chemical” meaning: Table 4 presents the various distributions of the correlated electrons into these sets, with “R” standing for Rydberg orbitals or Rydberg states.

For the description of the vertical spectrum of H_2CO , it is necessary to account for $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \text{R}$ and $n \rightarrow \text{R}$ transitions, so that the MCSCF space has been built as a product of smaller MCSCF spaces as follows:

class A: Two electrons in the $(\pi\pi^*)$ set describing both the ground state and the excited $\pi \rightarrow \pi^*$ states using a CAS space.

class B: Three electrons in the $(\pi\pi^*)$ set and only one in the (n) set describing the excited $n \rightarrow \pi^*$ states using a MCSCF space (in fact a CASSCF space due to symmetry restriction).

class C: One electron in the $(\pi\pi^*)$ set and one in the (R) set describing the excited $\pi \rightarrow \text{R}$ states using a MCSCF space.

class D: One electron in the (n) set and one in the (R) set describing the excited $n \rightarrow \text{R}$ states using a MCSCF space.

We emphasize that the Rydberg states are included in the variational MCSCF treatment to avoid a possible undercorrelation relative to the valence states. However, in order to maintain a balanced treatment between the valence and the Rydberg states, only single excitations to the R set were allowed. Contrary to the calculation on the ethylene molecule that considered only selected Rydberg orbitals in the variational space, all Rydberg orbitals were included in the space presented in Table 4. Furthermore, it is seen that all the previous distributions are coupled to diexcitations from the σ_{CO} to the σ_{CO}^* orbital: that way, we account for the non-dynamic repolarization of the polar σ_{CO} bond in a GVB-like approach and for the coupling between the π_{CO} and σ_{CO} dipoles as well.

Finally, we also account for an explicit relaxation of both lone pairs of H_2CO by the inclusion of corresponding correlating orbitals [125] and treat them at a GVB-like level so that these lone pairs are now treated at the same non-dynamical correlation level as the bonding electron pairs considered in the variational calculation. In fact, all attempts to reproduce the experimental values without these correlating orbitals considered in the active space failed.

The final space spanned by these distributions can then roughly be seen as a product of CAS, GVB and MCSCF spaces. It accounts for all effects supposed to be essential to get a good zeroth-order description of the ground and the excited valence and Rydberg states. Part of the dynamic correlation of the 8 electrons included in this variational treatment will be recovered, in the ground state and in the excited states, with the perturbation; so will the correlation energy arising from the core and from the σ_{CH} remaining electrons. The perturbation will also account for any coupling not explicitly included in the distributions presented in Table 4. The state averaging included the number of states reported in Tables 5–8.

4.2. Results and discussion

4.2.1. CASSCF and MC/BMP transition energies

The CASSCF and MC/BMP transition energies from the ground state to the lowest 60 vertical excited states considered in this study are reported in Table 5 (30 singlets) and in Table 7 (30 triplets) where they are compared to the available experimental results and to some previous theoretical calculations [56,118,122,126].

The analysis of the variational MCSCF wave functions clearly shows admixtures of valence and Rydberg characters in many states, either at the orbital level or at the CI level. Most transitions to Rydberg states are accordingly underestimated relative to experiment, while transition energies to valence excited states are overestimated (1^1A_2 , 1^3A_2 , 1^3A_1). Only the valence 5^1A_1 state $^1(\pi\pi^*)$ is underestimated, but a careful inspection of the corresponding MCSCF wave function shows that the weight of the valence configuration, although being the dominant CSF, is only 41% which suggests a dramatic coupling with diffuse states as already seen for the 1^1B_{1u} state $^1(\pi\pi^*)$ of ethylene: a decontracted perturbation scheme should be preferable to properly describe this state.

The Epstein–Nesbet partitions suffer the same limitations as those pointed out in the case of C_2H_4 , and will be discussed in Section 4.2.2. On the contrary, the MC/BMP partition of the Hamiltonian provides a remarkable spectrum for both the valence and the Rydberg states. The averaged deviation rela-

tive to the MCSCF series is 1.12 eV. This is about twice the value computed for the ethylene molecule. The discrepancies from experimental data vary from 0.00 to 0.40 eV for the largest of them. An exact value of the deviation is however difficult to obtain due to both the experimental band widths and the fact that many observed transitions are not necessary vertical so that structural effects and vibrational shifts are involved. However, the calculated root-mean-square deviation of the computed values from their

experimental assignment is found to be, for the whole spectrum, less than 3000 cm^{-1} which corresponds to a CH stretching vibration. To our knowledge, there has been no report, whatever might have been the theoretical method used, of such a small deviation between theory and experiment when dealing with so many excited states together.

Within a few exceptions, all singlet states can be correlated to an observed experimental feature. Especially, the high density of states around 11.8 and

Table 5

Transition energies (eV) to singlet states of formaldehyde (see text for details)

State	MCSCF	MC/BMP	Experiments	HG ^h	HFW ⁱ	FHGPF ^j
X ¹ A ₁	0.00	0.00	0.00	0.00	0.00	0.00
2 ¹ A ₁	7.20	7.95 nR3p _y	7.91 ^{a,b} 7.97 ^c 8.05 ^d 8.14 ^{e,f} 8.15 ^g	8.09 nR3p _y	8.47 nR3p _y	8.06 nR3p _y
3 ¹ A ₁	8.29	9.11 nR3dπ	9.03 ^e 9.07 ^g 8.88 ^q	9.23 nR3d _{yz}	8.75 nR4d _{yz}	
4 ¹ A ₁	9.04	9.88 nR3dπ	9.85 ^d			
5 ¹ A ₁	9.60	10.37 ππ*	10.70 ^g	10.77 ππ*	9.19 ππ*	9.63 ππ*
6 ¹ A ₁	10.53	11.63 πR3p _x	11.60--11.90 ^g	12.00 πR3p _x		
7 ¹ A ₁	11.23	11.84 πR3p _x	11.60--11.90 ^g			
1 ¹ B ₁	7.95	9.06 nR3dδ	9.22 ⁿ	9.21 nR3d _{xy}		
2 ¹ B ₁	8.78	9.90 nR3dδ	10.25 ^d		9.97 sp ₀ π* ^k	9.97 sp ₀ π* ^k
3 ¹ B ₁	9.32	10.68 πR3s	10.7 ^g	10.70 πR3s	10.84 πR3s	
4 ¹ B ₁	10.22	11.65 πR3p _z	11.60--11.90 ^g 11.46 ^p	11.66 πR3p _z	11.84 πR3p _z	
5 ¹ B ₁	11.17	12.66 πR3dσ	12.50--12.80 ^g 12.48 ^p	12.58 πRd _{yz}		
6 ¹ B ₁	11.26	12.78 πR3dδ	12.50--12.80 ^g	12.70 πR3d		
1 ¹ B ₂	5.88	6.90 nR3s	7.13 ^l 7.11 ^m 7.09 ^{c,d,e}	7.16 nR3s	6.85 nR3s	6.60 nR3s
2 ¹ B ₂	6.70	7.77 nR3p _z	7.97 ^e 8.00 ^l 8.14 ^c 8.13 ^d	8.08 nR3p _z	7.66 nR3p _z	7.52 nR3p _z
3 ¹ B ₂	7.66	8.80 nR3s	8.88 ^{d,e} 8.92 ^g	9.05 nR3d _{yz}	8.46 nR3d	
4 ¹ B ₂	7.76	8.95 nRb ₂	8.88 ^{d,e} 8.92 ^g		8.94 nRa ₁	
5 ¹ B ₂	7.97	9.11 nRb ₂	9.26 ^{c,d}	9.17 nR3d	8.96 nR3d	
6 ¹ B ₂	8.26	9.39 nRb ₂	9.63 ^{c,d}		9.19 nR3ds	
7 ¹ B ₂	8.62	9.82 nRb ₂	9.85 ^d			
8 ¹ B ₂	8.65	9.84 nRb ₂	9.97 ^d			
9 ¹ B ₂	9.22	10.35 nRb ₂	10.39 ^d			
10 ¹ B ₂	11.51	12.83 πR3d	12.50--12.80 ^g	12.58 πR3d _{xy}		
1 ¹ A ₂	4.66	3.83 nπ*	> 3.81 ^l 4.0 ^f 4.07 ^m 4.1 ^g 4.2 ^o	4.09 nπ*	4.58 nπ*	4.58 nπ*
2 ¹ A ₂	7.51	8.46 nR3p _x	8.37 ⁿ	8.32 nR3p _x	7.83 nR3p _x	
3 ¹ A ₂	8.29	8.82 nRa ₂	8.88 ^{d,e} 8.92 ^g	9.24 nR3d _{xz}		
4 ¹ A ₂	8.97	9.88 nRa ₂	9.59 ^d		10.08 nR3d	
5 ¹ A ₂	9.53	10.44 nR3p _x	10.13 ^d		10.13 nR4p _x	
6 ¹ A ₂	10.41	11.83 πR3p _y	11.60--11.90 ^g	11.78 πR3p _y	11.63 πR3p _y	
7 ¹ A ₂	11.52	13.01 πR3d	12.50--12.80 ^g	12.88 πR3d _{yz}		

12.7 eV is compatible with the observation of unresolved broad peaks in the 11.6–11.9 and 12.5–12.8 eV spectral intervals [118]. Unfortunately, the lack of spectroscopic resolution makes any unambiguous one-to-one assignment impossible in these regions.

The situation is more favorable at lower energies: up to about 11 eV, each calculated singlet state correlates unambiguously to a well-resolved experimental line, and the deviation from the experiment does not exceed 0.35 eV, which is the largest discrepancy observed, and that represents only a 3.5% error when reported to the corresponding transition energy. Moreover, this discrepancy is obtained for the valence–Rydberg mixed $5^1A_1-1(\pi\pi^*)$ state whose experimental feature appears to be very large. Compared to the calculations by Harding and Goddard [118], the agreement between both methods is excellent. Each state reported by these authors is found in our calculations. In addition, we report some new singlet states of Rydberg character whose description has been made possible essentially because of the larger flexibility of both our MCSCF calculation and one-particle space (basis set including semi-diffuse orbitals that were not in Ref. [118]). Our calculations provide a clear-cut assignment for the 4^1A_1 , 7^1A_1 , 2^1B_1 , 6^1B_2 , 7^1B_2 , 8^1B_2 , 9^1B_2 , 4^1A_2 , and 5^1A_2 states which were not reported previously. It is important to notice that most of these new states correlate to the recent experimental results obtained in the study by Brint and Sommer

[120] which is devoted to the Rydberg series. It is worth to emphasize that all their lower terms of the ns (3 states), np (6 states) and nd (4 terms) series can be related to a calculated state. Getting a correct description of the higher terms of these series would however require the inclusion of a Rydberg orbital progression in the basis set [127], as well as the consideration of f functions [120,123].

The same comments apply to the triplet states, although comparison to experiments is more difficult due to the lack of experimental determinations, even in the low energy region. However, as seen in Table 7, the agreement with available data is excellent, and shows the same quality as for the singlet manifold. So is the correlation with the results by Harding and Goddard [118]. In the triplet manifold, as in the singlet one, the largest flexibility of the present method allows for more states to be found: as an example, we tentatively assign the 6^3B_2 or the 4^3A_2 state, missing in Ref. [118], to a peak reported at 9.59 eV [128].

The comparison to the results obtained using the CIS/MP2 approach [56,126] leads to unquestionable conclusions: not only the CIS/MP2 method does not provide acceptable transition energies for the lowest valence and Rydberg states but it misses some of them and does not provide any good energetical ordering of the excited states. Even if this method presents interesting computational advantages, it can only provide an approximate electronic spectrum, as

Notes to Table 5:

^a [160].

^b [114].

^c [116].

^d [120].

^e [161,162].

^f [163].

^g Cited in Ref. [118] as unpublished results by Chutjian.

^h [118,122].

ⁱ [126].

^j [56].

^k The $sp_O \rightarrow \pi^*$ transition was found to lie at 13.69 eV in our work.

^l [117].

^m [119].

ⁿ [128].

^o [164].

^p [165].

^q [166].

anticipated in Section 2.3, outlined in Ref. [40] and recently admitted [8].

4.2.2. MC/EEN and MC/BEN transition energies

Table 6 and Table 8 report the computed MC/EEN and the MC/BEN transition energies and their discrepancies relative to the MC/BMP values. In order to refine the analysis performed in the case of the ethylene molecule, the deviations and the dispersions relative to the MC/BMP series of calcu-

lation have been evaluated according to each spin and spatial symmetry.

As for ethylene, all Epstein–Nesbet transition energies are overestimated relative to the Møller–Plesset values. Moreover, the MC/BEN values are larger than the MC/EEN ones which was also observed in the case of C_2H_4 .

The overestimation relative to the MC/BMP calculations that match the experimental spectrum is however unfortunately seen to be a function of the

Table 6

Uncorrected Epstein–Nesbet transition energies (eV) to singlet states of formaldehyde (see text for details)

State	MC/BMP	MC/EEN	MC/BEN	$\Delta E(\text{MC/EEN})^a$	$\Delta E(\text{MC/BEN})^a$
X 1A_1	0.00	0.00	0.00	0.00	0.00
2 1A_1	7.95	8.31	8.51	0.36	0.56
3 1A_1	9.11	9.42	9.69	0.31	0.58
4 1A_1	9.88	10.21	10.47	0.33	0.59
5 1A_1	10.37	10.62	10.93	0.25	0.56
6 1A_1	11.63	12.01	12.34	0.38	0.71
7 1A_1	11.84	12.27	12.62	0.43	0.78
deviation	0.00	0.35	0.64	0.35	0.64
dispersion	0.00	0.06	0.09	0.06	0.09
1 1B_1	9.06	9.67	9.88	0.61	0.82
2 1B_1	9.90	10.49	10.72	0.59	0.82
3 1B_1	0.68	11.21	11.50	0.53	0.82
4 1B_1	11.65	12.20	12.45	0.55	0.80
5 1B_1	12.66	13.18	13.52	0.52	0.86
6 1B_1	12.78	13.25	13.66	0.47	0.88
deviation	0.00	0.55	0.83	0.55	0.83
dispersion	0.00	0.05	0.03	0.05	0.03
1 1B_2	6.90	7.53	7.68	0.63	0.88
2 1B_2	7.77	8.40	8.59	0.63	0.82
3 1B_2	8.80	9.45	9.65	0.65	0.85
4 1B_2	8.95	9.55	9.83	0.60	0.88
5 1B_2	9.11	9.76	9.96	0.65	0.85
6 1B_2	9.39	10.07	10.23	0.68	0.84
7 1B_2	9.82	10.44	10.70	0.62	0.88
8 1B_2	9.84	10.48	10.71	0.64	0.87
9 1B_2	10.35	10.92	11.19	0.57	0.84
10 1B_2	12.83	13.40	13.74	0.57	0.91
deviation	0.00	0.62	0.86	0.62	0.86
dispersion	0.00	0.03	0.03	0.03	0.03
1 1A_2	3.83	3.80	3.88	−0.03	0.05
2 1A_2	8.46	8.39	8.43	−0.07	−0.03
3 1A_2	8.82	9.36	9.57	0.54	0.75
4 1A_2	9.88	10.21	10.48	0.33	0.60
5 1A_2	10.44	10.69	11.04	0.25	0.60
6 1A_2	11.83	12.20	12.61	0.37	0.78
7 1A_2	13.01	13.35	13.82	0.34	0.81
deviation	0.00	0.32	0.60	0.32	0.60
dispersion	0.00	0.17	0.32	0.17	0.32

^a The shifts are relative to the MC/BMP transition energies, as well as the deviation and the dispersion.

spatial symmetry. As shown in both Table 6 and Table 8, it is to be about 0.35 eV (MC/EEN) or 0.65 eV (MC/BEN) for A states (either singlet or triplet), but it raises to 0.67 eV (MC/EEN) or 0.84 eV (MC/BEN) for B states. It is clear that applying

these shifts to the Epstein–Nesbet transitions would result, as found for ethylene, in corrected energies that match the experimental values as well as the MC/BMP do. However, the dependence of these shifts upon the spatial symmetry of the excited states

Table 7
Transition energies (eV) to triplet states of formaldehyde (see text for details)

State	MCSCF	MC/BMP	Experiments	HG ^h	HFW ⁱ	FHGPF ^j
1 ³ A ₁	6.25	5.86 $\pi\pi^*$	5.60–6.20 ^a 5.86 ^b 6.0 ^{a,c}	5.95 $\pi\pi^*$	6.72 $\pi\pi^*$	6.81 $\pi\pi^*$
2 ³ A ₁	6.99	7.86 nR3p _y	7.96 ^b 8.11 ^c	8.05 nR3p _y	7.78 nR3p _y	7.61 nR3p _y
3 ³ A ₁	8.06	9.01 nR3d		9.17 nR3d _{yz}		
4 ³ A ₁	8.86	9.83 nR				
5 ³ A ₁	9.37	10.29 nR				
6 ³ A ₁	10.52	11.91 nR	11.60–11.90 ^c	11.77 π R3p _x		
7 ³ A ₁	11.50	12.99 π R	12.50–12.80 ^c	12.76 π R3d _{xz}		
1 ³ B ₁	7.95	9.03 nR3d δ		9.21 nR3d _{xy}	9.97 sp _O π^* ^d	
2 ³ B ₁	8.78	9.87 nR3d δ				
3 ³ B ₁	9.28	10.59 π R3s	10.70 ^c	10.68 π R3s		
4 ³ B ₁	10.13	11.48 π R3p _z	11.60–11.90 ^c	11.57 π R3p _z		
5 ³ B ₁	11.17	12.61 π R3d σ	12.50–12.80 ^c	12.57 π R3d		
6 ³ B ₁	11.24	12.73 π R3d δ	12.50–12.80 ^c	12.68 π R3d		
1 ³ B ₂	5.84	6.82 nR3s	7.09 ^{a,c} 6.83 ^b	7.08 nR3s	6.97 nR3s	6.79 nR3s
2 ³ B ₂	6.64	7.72 nR3p _z	7.92 ^c 7.79 ^b	7.99 nR3p _z	7.75 nR3p _z	7.59 nR3p _z
3 ³ B ₂	7.65	8.80 nR3s			8.67 nR3d	
4 ³ B ₂	7.77	8.97 nRb ₂		9.01 nR3d _{y²}		
5 ³ B ₂	7.96	9.12 nRb ₂		9.16 nR3d		
6 ³ B ₂	8.22	9.37 nRb ₂	9.59 ^e			
7 ³ B ₂	8.62	9.85 nRb ₂				
8 ³ B ₂	8.65	9.87 nRb ₂				
9 ³ B ₂	9.20	10.35 nRb ₂				
10 ³ B ₂	11.50	12.88 π R3d	12.50–12.80 ^c	12.75 π R3d _{xy}		
1 ³ A ₂	4.16	3.41 n π^*	3.3–3.6 ^a 3.2 ^a 3.3 ^{a,f,g} 3.5 ^{c,b,f} 3.35 ^{a,k} 3.19 ^k	3.68 n π^*	4.15 n π^*	4.16 n π^*
2 ³ A ₂	7.53	8.43 nR3p _x	8.31 ^c	8.31 nR3p _x	8.16 nR3p _x	
3 ³ A ₂	8.27	8.72 nRa ₂		9.23 nR3d _{xz}	9.12 nR3p _x	
4 ³ A ₂	8.94	9.89 nRa ₂	9.59 ^e			
5 ³ A ₂	9.49	10.43 nR3p _x			10.52 nR3d	
6 ³ A ₂	10.40	11.81 π R3p _y	11.60–11.90 ^c	11.63 π R3p _y		
7 ³ A ₂	11.52	12.56 π R3d	12.50–12.80 ^c	12.74 π R3d _{yz}		

^a [117].

^b [119].

^c Cited as unpublished results by Chutjian in Ref. [118].

^d The sp_O → π^* transition was found to lie at 14.31 eV in our work.

^e [128].

^f [167].

^g [168].

^h [118,122].

ⁱ [126].

^j [56].

^k [169].

precludes any attempt to get a reliable correction to be applied on MC/EEN or MC/BEN transition energies. One cannot expect transition energies of higher accuracy than those given by the Møller–Plesset partition.

The fact that the absolute energy values given by an Epstein–Nesbet partition are not invariant relative to any rotation of the virtual orbitals [129] could lead to the consideration of other sets of orbitals for

performing the MC/P-EN perturbations. However, it might be difficult to ensure a well-balanced description of the excited states at the variational zeroth-order of calculations by using other orbitals than the natural averaged MCSCF orbitals. As observed in many calculations and as pointed out in Ref. [52], the possible troubles due to the role of the virtual orbitals might be offset using larger zeroth-order spaces. This would however increase the computing

Table 8

Uncorrected Epstein–Nesbet transition energies (eV) to triplet states of formaldehyde (see text for details)

State	MC/BMP	MC/EEN	MC/BEN	$\Delta E(\text{MC/EEN})^a$	$\Delta E(\text{MC/BEN})^a$
1 3A_1	5.86	5.85	6.18	−0.01	0.32
2 3A_1	7.86	8.26	8.43	0.40	0.57
3 3A_1	9.01	9.36	9.59	0.35	0.58
4 3A_1	9.83	10.20	10.43	0.37	0.60
5 3A_1	10.29	10.60	10.87	0.31	0.58
6 3A_1	11.91	12.26	12.65	0.35	0.74
7 3A_1	12.99	13.33	13.79	0.34	0.80
deviation	0.00	0.33	0.62	0.33	0.62
dispersion	0.00	0.13	0.14	0.13	0.14
1 3B_1	9.03	9.67	9.87	0.63	0.84
2 3B_1	9.87	10.47	10.71	0.60	0.84
3 3B_1	10.59	11.12	11.41	0.53	0.82
4 3B_1	11.48	12.05	12.28	0.57	0.80
5 3B_1	12.61	13.17	13.48	0.56	0.87
6 3B_1	12.73	13.74	13.61	1.01	0.88
deviation	0.00	0.67	0.84	0.67	0.84
dispersion	0.00	0.17	0.03	0.17	0.03
1 3B_2	6.82	7.47	7.63	0.65	0.81
2 3B_2	7.72	8.32	8.51	0.60	0.79
3 3B_2	8.80	9.43	9.63	0.63	0.83
4 3B_2	8.97	9.56	9.83	0.59	0.86
5 3B_2	9.12	9.75	9.95	0.63	0.83
6 3B_2	9.37	10.03	10.19	0.66	0.82
7 3B_2	9.85	10.45	10.71	0.60	0.86
8 3B_2	9.87	10.49	10.73	0.62	0.86
9 3B_2	10.35	10.91	11.18	0.56	0.83
10 3B_2	12.88	13.37	13.79	0.49	0.91
deviation	0.00	0.60	0.84	0.60	0.84
dispersion	0.00	0.05	0.03	0.05	0.03
1 3A_2	3.41	3.41	3.50	0.00	0.09
2 3A_2	8.43	8.45	8.53	0.02	0.10
3 3A_2	8.72	9.38	9.57	0.66	0.85
4 3A_2	9.89	10.24	10.50	0.35	0.61
5 3A_2	10.43	10.71	11.05	0.28	0.62
6 3A_2	11.81	12.19	12.59	0.38	0.78
7 3A_2	12.56	13.35	13.82	0.79	1.26
deviation	0.00	0.45	0.73	0.45	0.73
dispersion	0.00	0.23	0.40	0.23	0.40

^a The shifts are relative to the MC/BMP transition energies, as well as the deviation and the dispersion.

times and result in a loss of chemical meaning for the zeroth-order MCSCF space, which runs counter the MC/P philosophy.

5. Vinylidene

As seen in the previous sections, the determination of the electronic spectra of two well-known small size molecules, ethylene and formaldehyde, provides a clear-cut illustration of the validity of the MC/BMP approach. The last part of this paper will apply this methodology to the predictive evaluation of the electronic transition energies of the carbenic vinylidene H_2CC .

Vinylidene, which was first observed in gas phase in 1983 [130] in its singlet ground state, is the lower-lying isomer of the acetylene molecule and has consequently been the subject of numerous studies, especially devoted to its isomerization process to acetylene [131–136]. As the simplest unsaturated carbene [137,138], it has been supposed and demonstrated to be a short-lived intermediate in chemical or photochemical reactions [139]. Moreover, it is the first (elusive) term of the H_2CC_n cumulene series whose $n = 2$ and $n = 3$ terms have been identified in laboratory and in the interstellar medium a short time after [140–142] as the second and the third carbene molecules present in space, following the identification of cyclopropenylidene $\text{c-C}_3\text{H}_2$ [143].

To our knowledge, there are very little data available regarding H_2CC excited states. On the experimental point of view, Ervin et al. [139] reported the observation of the $X^1\text{A}_1$, 1^3B_2 and 1^3A_2 states by applying photoelectron spectroscopy techniques to the negative species H_2C_2^- . Apart from a very fine GVB-CI work [144], no systematic study on the excited electronic states of vinylidene have been reported, although various studies are available that deal with the geometries and infrared signatures of the ground and those excited states that standard quantum chemistry techniques have been able to catch [139].

Compared to ethylene and formaldehyde, vinylidene may be seen as an intermediate case: on the MC/P point of view, the variational treatment of 6 valence electrons is expected to give a well-balanced zeroth-order wave function while 2 and 8 electrons

were to be considered for ethylene and formaldehyde. Since the MC/P approach succeeded for both these compounds, it is expected that the computed spectrum of vinylidene will be of equivalent accuracy.

5.1. Computational details

The geometry of the $X^1\text{A}_1$ ground state of H_2C_2 was optimized at the MP4/6-311++G** level of theory using the GAUSSIAN92 code [145] assuming C_{2v} symmetry. The following structural parameters were obtained: $\text{CC} = 1.313 \text{ \AA}$, $\text{CH} = 1.091 \text{ \AA}$, and $\text{HCH} = 119.72^\circ$. This geometry is in agreement with those reported previously using different methods [139]. The molecule is supposed to lie in the yz plane; the z axis corresponds to the C_2 axis, as in Fig. 1c. The MCSCF and the subsequent perturbations were done using the standard 6-31+G* basis set [106] expanded by a set of spd Rydberg functions. Exponents of this additional Gaussians were 0.023 and 0.021 for the carbon atom. For the d functions, a common value of 0.015 was chosen for both heavy atoms. This basis set will be referred to as 6-31+G*R.

5.1.1. The active spaces for H_2C_2

The configuration spaces used in the calculation are presented in Tables 9–11 in which orbitals are distributed into several sets, and ordered by symmetry. As for H_2CO , they are denoted in terms of localized orbitals in order to emphasize their “chemical” significance. Three different spaces were used

Table 9
MCSCF1 variational space for the vinylidene molecule ^a (see text for details)

Symmetry	Orbital repartitions	
	set 1	set 2
a_1	sp_C	2R
b_1	$\pi \pi^*$	4R
b_2	$2p_\text{C}$	2R
a_2	Electronic distributions	
	4	0
	3	1

^a 2K shells are doubly occupied in all CSFs.

Table 10
MCSCF2 variational space for the vinylidene molecule ^a (see text for details)

Symmetry	Orbital repartitions		
	set 1	set 2	set 3
a ₁	σ _{CC} σ _{CC} [*]	sp _C	2R
b ₁		π π [*]	4R
b ₂		2p _C	2R
a ₂	Electronic distributions		
	2	4	0
	2	3	1

^a 2K shells are doubly occupied in all CSFs.

at the MCSCF level of calculation, all of them freezing the σ_{CH} skeleton in addition to the 1s core orbitals. Tables 9 and 10 and Table 11 present the corresponding electronic distributions of the correlated electrons, with “R” standing for Rydberg orbitals or Rydberg states.

The first space (Table 9) has 4 active electrons which correspond to the p and the sp_C electrons in the ground state. All excitations involving these electrons in the (π π^{*} 2p_C sp_C) set of orbitals are allowed, as well as those involving one excitation to the Rydberg set. Calculations based on this space will thereafter be referred to as MCSCF1 and MC/BMP1 calculations.

It has been known for a long time that the dipole moment of the X ¹A₁ state of the vinylidene molecule

is relatively high (2.23 D) while that of the 1³B₂ state is by far smaller (0.55 D) [144]. Such a variation draws the attention to the possible role of the repolarization of the σ_{CC} bond upon excitations. As a consequence, a second MCSCF space has been considered that can be seen as the product of the MCSCF1 space by a GVB space accounting for such a repolarization effect (Table 10) and that furthermore accounts for the couplings between the σ_{CC} and π_{CC} dipoles, as in the case of formaldehyde. Such calculations are of essential interest for further applications to the H₂(CC)_n cumulene series since the need for the explicit inclusion of the σ_{CC} skeleton in the zeroth-order space would dramatically increase the size of the (MCSCF2 and MC/BMP2) computations.

A third series of calculations (MCSCF3 and MC/BMP3) aimed to investigate the possible influence of a correlating orbital for the axial sp_C lone pair. Table 11 shows the corresponding electronic distributions used to generate the CSFs. It is expected that this correlating orbital will have a less crucial role than in the formaldehyde molecule: more or less artificially, the empty 2p_C orbital can act as such a relaxation orbital which was not the case in H₂CO where the 2p_O corresponding orbital was doubly occupied. No correlation orbital was introduced to allow for the spatial relaxation of the 2p_C orbital, since it is found to be either empty or singly occupied in the excited states, at least for the lowest ones.

Table 11
MCSCF3 variational space for the vinylidene molecule ^a (see text for details)

Symmetry	Orbital repartitions			
	set 1	set 2	set 3	set 4
a ₁	σ _{CC} σ _{CC} [*]	sp _C sp _C [*]		2R
b ₁			π π [*]	4R
b ₂			2p _C	2R
a ₂	Electronic distributions			
	2	2	2	0
	2	1	3	0
	2	0	4	0
	1	2	3	0
	2	1	2	1
	2	0	3	1
	2	2	1	1

^a 2K shells are doubly occupied in all CSFs.

5.2. Results and discussion

The results of the MCSCF and MC/P calculations are collected in Table 12, together with the previous GVB/CI calculations by Davis et al. [144]. The only experimental results available for comparison are the adiabatic transition energies to the 1^3B_2 (2.06 eV) and the 1^3A_2 (2.75 eV) states [139]. Following the previous discussion, Epstein–Nesbet MC/P calculations which give transition energies overestimated by at least 0.40 eV when compared to the MC/BMP calculations are not reported.

Inspection of Table 12 shows that there are no qualitative difference when going from the MCSCF1 space to the larger spaces 2 or 3: all report the same states with the same energetical ordering. The variations in the transition energies between the MCSCF1 and MCSCF2 are relatively small and do not exceed 0.16 eV, which shows that the consideration of the polarization of the σ_{CC} bond is not essential at this level of calculation. Going from MCSCF2 to MCSCF3 does not lead to any quantitative modifications of the previous results; we just remark a systematic decrease (by less than 0.25 eV) in the transition

energies relative to MCSCF1 and MCSCF2 calculations.

The situation is somewhat different when applying the Møller–Plesset perturbation: as an example, the transition energy to the 2^1B_1 state is reduced by 0.50 eV when going from MC/BMP1 to MC/BMP2 and by 0.20 eV going from MC/BMP1 to MC/BMP3. The deviations between the MCSCF and MC/BMP calculations are found to be 0.40 eV for MCSCF1, 0.55 eV for MCSCF2 and 0.50 eV for MCSCF3: these values are comparable to those determined previously for the ethylene molecule. It can be seen that the MC/BMP3 calculations give transition energies in between those given at the MC/BMP1 and MC/BMP2 levels of theory. There are unfortunately too few experimental data to decide which of the calculations is the most accurate. However, it is our opinion that MC/BMP3 calculations are those of higher quality since MCSCF3 is the parallel to the zeroth-order space retained for our best calculations on H_2CO . Besides, it is this space which provides results that matches the more closely the GVB/CI calculations [144] that also gave very accurate results for the formaldehyde system. The

Table 12
CASSCF and MC/P transition energies (eV) for the vinylidene molecule

	MCSCF1	MCSCF2	MCSCF3	MC/BMP1	MC/BMP2	MC/BMP3	GVB/CI
singlet states							
$2^1A_1 \text{ sp}_C \rightarrow R$	8.13	8.29	8.27	7.95	7.91	7.95	
$3^1A_1 \text{ sp}_C \rightarrow R$	8.66	8.82	8.72	8.70	8.53	8.69	
$4^1A_1 \pi \rightarrow R$	8.92	9.10	9.02	8.78	8.79	8.82	
$5^1A_1 \pi \rightarrow R$	9.23	9.38	9.23	8.83	8.79	8.86	
$1^1B_1 \text{ sp}_C^1 \pi^1 2p_C^2$	7.00	6.99	6.93	6.65	6.05	6.45	
$2^1B_1 \text{ sp}_C \rightarrow \pi^*$	7.99	7.95	7.86	7.31	6.82	7.15	
$3^1B_1 \pi \rightarrow R$	8.20	8.24	8.02	8.10	7.76	7.80	
$1^1B_2 \text{ sp}_C \rightarrow 2p_C$	4.14	4.00	3.75	4.55	4.34	4.58	4.64
$1^1A_2 \pi \rightarrow 2p_C$	2.77	2.75	2.69	3.43	3.66	3.49	3.54
triplet states							
$1^3A_1 \pi \rightarrow \pi^*$	4.76	4.87	4.83	4.80	5.02	5.13	5.14
$2^3A_1 \pi \rightarrow R$	8.37	8.51	8.39	8.85	8.84	8.94	
$1^3B_1 \text{ sp}_C \rightarrow \pi^*$	5.98	6.00	5.94	5.70	5.47	5.62	
$2^3B_1 \text{ sp}_C^1 \pi^1 2p_C^2$	6.79	6.81	6.76	6.10	6.23	6.15	
$3^3B_1 \pi \rightarrow R$	7.86	8.10	7.88	7.93	7.64	7.81	
$1^3B_2 \text{ sp}_C \rightarrow 2p_C$	1.60	1.56	1.45	2.15	1.89	2.02 ^a	1.99
$2^3B_2 \text{ sp}_C^1 \pi^1 2p_C^1 \pi^* 1$	7.68	7.81	7.76	8.33	8.11	8.32	
$1^3A_2 \pi \rightarrow 2p_C$	2.52	2.50	2.45	2.60	2.86	2.80 ^a	3.15
$2^3A_2 \pi \rightarrow R$	8.22	8.35	8.22	8.58	8.84	8.70	
quintet states							
$1^5B_2 \text{ sp}_C^1 \pi^1 2p_C^1 \pi^* 1$	5.58	6.00	5.44	5.77	5.96	5.91	5.53

^a Experimental values: 1^3B_2 : 2.06 eV; 1^3A_2 : 2.75 eV.

following discussion will therefore focus on the MC/BMP3 results.

The first excited state of the vinylidene molecule is found to be of 3B_2 symmetry and is computed at 2.02 eV from the ground state. This state has been observed at 2.06 eV using photoelectron spectroscopy techniques applied to the anion $H_2C_2^-$, and is computed at 1.99 eV at the GVB/CI level of theory: it corresponds to a single excitation from the axial lone pair to the non-bonding in-plane $2p_C$ orbital. A second triplet state is predicted at 2.80 eV (1^3A_2): it is obtained by the excitation of a π electron to the $2p_C$ orbital and has been detected at 2.75 eV and computed at 3.15 eV by Davis et al. [144]. The third excited state is the singlet counterpart of the 1^3A_2 state: it is found to lie at 3.49 eV. The singlet counterpart of the 1^3B_2 state lies at 4.58 eV and is the fourth excited state of the vinylidene molecule. Both these singlets have MC/BMP3 transition energies that closely match the GVB/CI values. The 1^3A_1 state, that corresponds to the $\pi-\pi^*$ transition appears at 5.13 eV, about 0.70 eV higher than the corresponding transition energy for the ethylene, and 0.70 eV lower than the same transition in the formaldehyde molecule. The related $^1(\pi\pi^*)$ state is not found in our calculations, which means that, either it lies higher in energy than 8.80 eV, or that it is so strongly mixed to some Rydberg and thus not well described using a contracted multi-reference perturbation scheme. The next valence states appear at 6.45 eV (1^1B_1), 7.11 eV (2^1B_1), 5.62 eV (1^3B_1), 6.15 eV (2^3B_1) and 8.32 eV (2^3B_2). The 1^1B_1 and 2^3B_1 states are described by a double excitation from both the π and the lone pair sp_C orbitals to the in-plane $2p_C$ orbital. The 2^3B_2 has four open shells and one electron in each of the sp_C , π , π^* and $2p_C$ orbitals. The quintet state having this orbital occupancy lies at 5.91 eV according to the MC/BMP3 calculation, about 0.40 eV higher than the value computed using the GVB/CI. As was the case in the ethylene and formaldehyde molecules, the remaining excited states are of diffuse Rydberg character either of π or sp_C type and they appear above 7.80 eV.

6. Conclusion

In this paper, we have extended our MC/P strategy, in its present contracted scheme, that couples

MCSCF and second-order perturbation treatments, to the calculation of electronic spectra and developed the philosophy and the flexibility of this approach.

It has been shown possible to split zeroth-order complete valence spaces into a product of smaller MCSCF spaces (CASSCF, MCSCF, or GVB subspaces): the formal completeness of a valence CASSCF space has been switched into a “chemical completeness”. The three examples reported (ethylene, formaldehyde and vinylidene) show that combining a well-designed averaged zeroth-order MCSCF wave functions to a barycentric Møller–Plesset partition of the electronic Hamiltonian provides accurate spectra that compare with experimental data within a few hundreds of cm^{-1} . These results have been obtained using polarized double-zeta quality basis sets augmented by semi-diffuse and diffuse functions to account for Rydberg states. The limited dimension of such basis sets lets anticipate applications of the MC/P methodology to medium size systems without much computational trouble. Of essential interest for the study of such species is the choice of the zeroth-order MCSCF space that has to include only those non-dynamic correlation effects that are important for a proper description of the manifold of states considered; all remaining correlation effects (non-dynamic and dynamic) can be treated at the perturbation level.

The choice of the partition of the Hamiltonian used to perform the perturbation is of critical importance: it was found that Epstein–Nesbet partitions give transition energies that are systematically shifted relative to the experimental and MC/BMP values. As seen in the cases of ethylene and formaldehyde, this shift is unfortunately not transferable from one molecule to another, and is furthermore a function of the spatial symmetry of the excited states. This rules out any simple extrapolation on the computed MC/EN transition energies to have them as accurate as the MC/BMP values.

Acknowledgements

Part of the calculations presented in this contribution were supported by the CNRS Institut du Développement et des Ressources en Informatique Scientifique (IDRIS) supercomputing center.

References

- [1] R. McWeeny and B.T. Pickup, *Rep. Prog. Phys.* 43 (1980) 1065.
- [2] B.O. Roos, *Lecture Notes in Quantum Chemistry I*, Vol. 58 (Springer, Berlin, 1992).
- [3] W.D. Laidig, P. Saxe and R.J. Bartlett, *Chem. Phys. Letters* 86 (1987) 867.
- [4] R.J. Bartlett, *J. Phys. Chem.* 93 (1989) 1697.
- [5] M. Barysz, M. Rittby and R.J. Bartlett, *Chem. Phys. Letters* 193 (1992) 373.
- [6] R.J. Rico and M. Head-Gordon, *Chem. Phys. Letters* 213 (1993) 24.
- [7] K. Jankowski, K. Kowalski and P. Jankowski, *Chem. Phys. Letters* 222 (1994) 608.
- [8] M. Head-Gordon, R.J. Rico, M. Oumi and T.J. Lee, *Chem. Phys. Letters* 219 (1994) 21.
- [9] S.R. Gwaltney and R.J. Bartlett, *Chem. Phys. Letters* 241 (1995) 26.
- [10] C. Daul, *Intern. J. Quantum Chem.* 52 (1994) 867.
- [11] G. Gardet, F. Rogemond and H. Chermette, *Theoret. Chim. Acta* 91 (1995) 249.
- [12] N.C. Handy, P.J. Knowles and K. Somasundram, *Theoret. Chim. Acta* 68 (1985) 87.
- [13] A. Masson, B. Lévy and J.-P. Malrieu, *Theoret. Chim. Acta* 18 (1970) 193.
- [14] G. Berthier, Y.A. Meyer and L. Praud, *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity, The Jerusalem Symposia on Quantum Chemistry and Biochemistry III* (Jerusalem, 1971).
- [15] F. Pauzat, J. Ridard and B. Lévy, *Mol. Phys.* 23 (1972) 1163.
- [16] F. Pauzat, J. Ridard and P. Millié, *Mol. Phys.* 24 (1972) 1039.
- [17] B. Lévy and J. Ridard, *Chem. Phys. Letters* 15 (1972) 49.
- [18] L. Praud, B. Lévy, P. Millié and G. Berthier, *Intern. J. Quantum Chem. Symp.* 7 (1973) 185.
- [19] I. Hubac and P. Carsky, *Phys. Rev. A* 22 (1980) 2392.
- [20] K. Wolinski, H.L. Sellers and P. Pulay, *Chem. Phys. Letters* 140 (1987) 225.
- [21] J.S. Andrews, D. Jayatilaka, R.G.A. Bone, N.C. Handy and R.D. Amos, *Chem. Phys. Letters* 183 (1991) 423.
- [22] R.D. Amos, J.S. Andrews and N.C. Handy, *Chem. Phys. Letters* 185 (1991) 256.
- [23] W.J. Lauderdale, J.F. Stanton, J. Gauss, J.D. Watts and R.J. Bartlett, *Chem. Phys. Letters* 187 (1991) 21.
- [24] P.J. Knowles, J.S. Andrews, R.D. Amos, N.C. Handy and J.A. Pople, *Chem. Phys. Letters* 186 (1991) 130.
- [25] C. Murray and E.R. Davidson, *Chem. Phys. Letters* 187 (1991) 451.
- [26] K. Hirao, *Chem. Phys. Letters* 190 (1992) 374.
- [27] K. Hirao, *Chem. Phys. Letters* 196 (1992) 397.
- [28] T.J. Lee and D. Jayatilaka, *Chem. Phys. Letters* 201 (1993) 1.
- [29] T.J. Lee, A.P. Rendell, K.G. Dyall and D. Jayatilaka, *J. Chem. Phys.* 100 (1994) 7400.
- [30] P.M. Kozłowski and E.R. Davidson, *J. Chem. Phys.* 100 (1994) 3672.
- [31] P.M. Kozłowski and E.R. Davidson, *Chem. Phys. Letters* 222 (1994) 615.
- [32] E.R. Davidson, *Chem. Phys. Letters* 241 (1995) 432.
- [33] S. Bell, *J. Chem. Soc. Faraday Trans. II* 77 (1981) 321.
- [34] P.M.W. Gill and L. Radom, *Chem. Phys. Letters* 132 (1986) 16.
- [35] M.B. Lepetit, M. Pélissier and J.-P. Malrieu, *J. Chem. Phys.* 89 (1988) 998.
- [36] R.H. Nobes, D. Moncrieff, M.W. Wong, L. Radom, P.M.W. Gill and J.A. Pople, *Chem. Phys. Letters* 182 (1991) 216.
- [37] R.P. Messmer and C.H. Patterson, *Chem. Phys. Letters* 192 (1992) 277.
- [38] N.L. Ma, B.J. Smith and L. Radom, *Chem. Phys. Letters* 193 (1992) 386.
- [39] N.L. Ma, S.S. Wong, M.N. Paddon-Row and W.-K. Li, *Chem. Phys. Letters* 213 (1993) 189.
- [40] B.O. Roos, K. Andersson and M.P. Fülscher, *Chem. Phys. Letters* 192 (1992) 5.
- [41] S. Wilson, *Electron correlation in molecules* (Clarendon Press, Oxford, 1984).
- [42] E. Callen, *J. Chem. Phys.* 23 (1955) 360.
- [43] O. Sinanoglu, *Advan. Chem. Phys.* 6 (1964) 315.
- [44] P.S. Bagus, B. Liu, A.D. McLean and M. Yoshimine, in: *Wave mechanics: the first fifty years, Application of wave mechanics to the electronic structure of molecules through configuration interaction*, eds. W.C. Price, S.S. Chissick and T. Ravensdale (Butterworth, London, 1973) p. 99.
- [45] R.J. Buenker, S.D. Peyerimhoff and W. Butscher, *Mol. Phys.* 35 (1978) 771.
- [46] B. Huron, J.-P. Malrieu and P. Rancurel, *J. Chem. Phys.* 58 (1973) 5745.
- [47] J.-P. Malrieu, P. Durand and J.-P. Daudey, *J. Phys. A* 18 (1985) 809.
- [48] J.J.W. McDouall, K. Peasley and M.A. Robb, *Chem. Phys. Letters* 148 (1988) 183.
- [49] M. Merchán, R. Gonzalez-Luque and I. Nebot-Gil, *J. Chem. Phys.* 93 (1990) 495.
- [50] R.J. Harrison, *J. Chem. Phys.* 94 (1991) 5021.
- [51] R.B. Murphy and R.P. Messmer, *Chem. Phys. Letters* 183 (1991) 443.
- [52] R.B. Murphy and R.P. Messmer, *J. Chem. Phys.* 97 (1992) 4170.
- [53] K. Andersson, P.-A. Malmqvist and B.O. Roos, *J. Chem. Phys.* 96 (1992) 1218.
- [54] K. Hirao, *Intern. J. Quantum Chem.* S 26 (1992) 517.
- [55] M.R. Hoffmann, *Chem. Phys. Letters* 195 (1992) 127.
- [56] J.B. Foresman, M. Head-Gordon, J.A. Pople and M.J. Frisch, *J. Phys. Chem.* 96 (1992) 135.
- [57] J. Miralles, O. Castell, R. Caballol and J.P. Malrieu, *Chem. Phys.* 172 (1993) 33.

- [58] H. Nakano, *J. Chem. Phys.* 99 (1993) 7983.
- [59] K. Hirao, *Chem. Phys. Letters* 201 (1993) 59.
- [60] O. Parisel and Y. Ellinger, *Chem. Phys.* 189 (1994) 1.
- [61] J. Meller, J.L. Heully and J.P. Malrieu, *Chem. Phys. Letters* 218 (1994) 276.
- [62] J.-P. Malrieu, I. Nebot-Gil and J. Sanchez-Marin, *J. Chem. Phys.* 100 (1994) 1440.
- [63] K. Hirao, H. Nakano and T. Hashimoto, *Chem. Phys. Letters* 235 (1995) 430.
- [64] J.P. Malrieu, J.L. Heully and A. Zaitsevskii, *Theoret. Chim. Acta* 90 (1995) 167.
- [65] S. Evangelisti, J.-P. Daudey and J.-P. Malrieu, *Chem. Phys.* 75 (1983) 91.
- [66] R. Cimiraglia, *J. Chem. Phys.* 83 (1985) 1746.
- [67] R. Cimiraglia and M. Persico, *J. Comput. Chem.* 8 (1987) 39.
- [68] Z. Gershgorin and I. Shavitt, *Intern. J. Quantum Chem.* 2 (1968) 751.
- [69] F. Illas, J. Rubio and J.M. Ricart, *J. Chem. Phys.* 88 (1988) 260.
- [70] D. Duflo, J.-M. Robbe and J.-P. Flament, *J. Chem. Phys.* 100 (1994) 1236.
- [71] M. Tadjeddine, J.P. Flament and C. Teichteil, *J. Mol. Struct. THEOCHEM* 166 (1988) 147.
- [72] A. Després, V. Lejeune, E. Migirdicyan, A. Admasu, M.S. Platz, G. Berthier, J.P. Flament, O. Parisel, I. Baraldi and F. Momicchioli, *J. Phys. Chem.* 97 (1993) 13358.
- [73] O. Parisel, G. Berthier and Y. Ellinger, *Astronom. Astrophys.* 266 (1992) L1.
- [74] O. Parisel and Y. Ellinger, *Molecules and Grains in Space: 50th International Meeting of Physical Chemistry (Mont Ste Odile (France), 1994)*.
- [75] O. Parisel and Y. Ellinger, *The diffuse interstellar bands*, ed. A.G.G.M. Tielens, NASA Conf. Publ. 1814; 1994, p. 91.
- [76] O. Parisel, G. Berthier and E. Migirdicyan, *Can. J. Chem.* 73 (1995) 1869.
- [77] M. Vala, J. Szczepanski, O. Parisel, F. Pauzat, D. Tali and Y. Ellinger, *J. Phys. Chem.* 98 (1994) 9187.
- [78] J. Szczepanski, M. Vala, D. Talbi, O. Parisel and Y. Ellinger, *J. Chem. Phys.* 98 (1993) 4494.
- [79] B.O. Roos, P. Linse, P.E.M. Siegbahn and M.R.A. Blomberg, *Chem. Phys.* 66 (1981) 197.
- [80] K. Andersson, P.-A. Malmqvist, B.O. Roos, A.J. Sadlej and K. Wolinski, *J. Phys. Chem.* 94 (1990) 5483.
- [81] K. Andersson, *Theoret. Chim. Acta* 91 (1995) 31.
- [82] K. Andersson and B.O. Roos, in: *Modern electronic structure theory, Multiconfigurational second-order perturbation theory*, ed. D.R. Yarkony (World Scientific Publishing, New York, 1994).
- [83] B.O. Roos, M.P. Fulscher, P.A. Malmqvist, P.L. Serrano-Andres and M. Merchán, in: *Quantum mechanical electronic structure calculations with chemical accuracy, Theoretical studies of the electronic spectra of organic molecules*, ed. S. Langhoff (Kluwer, Dordrecht, 1994).
- [84] R.B. Murphy and R.P. Messmer, *J. Chem. Phys.* 97 (1992) 4974.
- [85] R.B. Murphy and R.P. Messmer, *J. Chem. Phys.* 98 (1993) 10102.
- [86] B. Lévy and G. Berthier, *Intern. J. Quantum Chem.* 2 (1968) 307.
- [87] T. Tsuneda, H. Nakano and K. Hirao, *J. Chem. Phys.* 103 (1995) 6520.
- [88] A.D. McLean, M. Yoshimine, B.H. Lengsfeld, P.S. Bagus and B. Liu, *ALCHEMY II, MOTECC-90* (1990).
- [89] C. Møller and M.S. Plesset, *Phys. Rev.* 46 (1934) 618.
- [90] H.C. Longuet-Higgins and J.A. Pople, *Proc. Roy. Soc. (London)* A 68 (1955) 591.
- [91] E. Steiner, *J. Chem. Phys.* 46 (1967) 1727.
- [92] G. Berthier, A. Daoudi and J.-P. Flament, *J. Mol. Struct. THEOCHEM* 166 (1988) 81.
- [93] G. Berthier, A. Daoudi, G. Del Re and J.-P. Flament, *J. Mol. Struct. THEOCHEM* 210 (1990) 133.
- [94] F. Illas, J. Rubio and J.M. Ricart, *J. Chem. Phys.* 89 (1988) 6376.
- [95] P.S. Epstein, *Phys. Rev.* 28 (1926) 695.
- [96] R.K. Nesbet, *Proc. Roy. Soc. (London)* A 230 (1955) 322.
- [97] R.K. Nesbet, *Proc. Roy. Soc. (London)* A 230 (1955) 312.
- [98] P. Claverie, S. Diner and J.-P. Malrieu, *Intern. J. Quantum Chem.* 1 (1967) 751.
- [99] K. Andersson, B.O. Roos, P.A. Malmqvist and P.O. Widmark, *Chem. Phys. Letters* 230 (1994) 391.
- [100] B.O. Roos and K. Andersson, *Chem. Phys. Letters* 245 (1995) 215.
- [101] F. Spiegelmann and J.P. Malrieu, *J. Phys. B.* 17 (1984) 1259.
- [102] W.J. Hunt, P.J. Hay and W.A. Goddard, *J. Chem. Phys.* 57 (1972) 738.
- [103] A.J. Merer and R.S. Mulliken, *Chem. Rev.* 69 (1969) 69.
- [104] R.S. Mulliken and W.C. Ermler, *Polyatomic molecules. Results of ab initio calculations* (Academic Press, New York, 1981).
- [105] L. Serrano-Andrés, M. Merchán, I. Nebot-Gil, R. Lindh and B.O. Roos, *J. Chem. Phys.* 98 (1993) 3151.
- [106] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees and J.A. Pople, *J. Chem. Phys.* 77 (1982) 3654.
- [107] R. Lindh and B.O. Roos, *Intern. J. Quantum Chem.* 35 (1989) 813.
- [108] V. Kvasnicka, *Chem. Phys. Letters* 43 (1976) 377.
- [109] H.L. McMurry and R.S. Mulliken, *Proc. Natl. Acad. Sci. USA* 26 (1940) 312.
- [110] H.L. McMurry, *J. Chem. Phys.* 9 (1941) 231.
- [111] M. Kasha, in: *Comparative effects of radiations, Ultraviolet radiation effects: molecular photochemistry*, ed. M. Burton, J.S. Kirby-Smith and J.L. Magee (Wiley, New York, 1960) p. 72.
- [112] H.M. McConnell, *J. Chem. Phys.* 20 (1952) 700.
- [113] A. Burawoy, *Chem. Ber.* 63 (1930) 3155.
- [114] M. Sender and G. Berthier, *J. Chim. Phys.* 53 (1958) 384.
- [115] G. Berthier and J. Serre, in: *The chemistry of the carbonyl group, General and theoretical aspects of the carbonyl group*, ed. S. Patai (Interscience, 1966) p. 1.
- [116] D.C. Moule and A.D. Walsh, *Chem. Rev.* 75 (1975) 67.

- [117] A. Chutjian, *J. Chem. Phys.* 61 (1974) 4279.
- [118] L.B. Harding and W.A. Goddard III, *J. Am. Chem. Soc.* 99 (1977) 677.
- [119] M.B. Robin, *Higher excited states of polyatomic molecules* (Academic Press, New York, 1985).
- [120] P. Brint and K. Sommer, *J. Chem. Soc. Faraday Trans. II* 81 (1985) 1643.
- [121] E.R. Davidson and L.E. McMurchie, *Excited states*, Vol. 5 (Academic Press, New York, 1982).
- [122] L.B. Harding and W.A. Goddard III, *J. Am. Chem. Soc.* 97 (1975) 6293.
- [123] M.R.J. Hachey, P.J. Bruna and F. Grein, *J. Phys. Chem.* 99 (1995) 8050.
- [124] K.T. Takagi and T. Oka, *J. Phys. Soc. Japan* 18 (1963) 1174.
- [125] A.D. McLean, B.H. Lengsfeld, J. Pacansky and Y. Ellinger, *J. Chem. Phys.* 83 (1985) 3567.
- [126] C.M. Hadad, J.B. Foresman and K.B. Wiberg, *J. Phys. Chem.* 97 (1993) 4293.
- [127] R.S. Mulliken, *J. Am. Chem. Soc.* 86 (1964) 3183.
- [128] S. Taylor, D.G. Wilden and J. Comer, *Chem. Phys.* 70 (1982) 291.
- [129] J.-P. Malrieu and F. Spiegelmann, *Theoret. Chim. Acta* 52 (1979) 55.
- [130] S.M. Burnett, A.E. Stevens, C.S. Feigerle and W.C. Lineberg, *Chem. Phys. Letters* 100 (1983) 124.
- [131] C.E. Dykstra and H.F. Schaefer III, *J. Am. Chem. Soc.* 100 (1978) 1378.
- [132] M.P. Conrad and H.F. Schaefer III, *J. Am. Chem. Soc.* 100 (1978) 7820.
- [133] Y. Osamura, H.F. Schaefer III, S.K. Gray and W.H. Miller, *J. Am. Chem. Soc.* 103 (1981) 1904.
- [134] R. Krishnan, M.J. Frish, J.A. Pople and P. von Rague Schleyer, *Chem. Phys. Letters* 79 (1981) 408.
- [135] Y. Osamura and H.F. Schaefer III, *Chem. Phys. Letters* 79 (1981) 412.
- [136] J.S. Binkley, *J. Am. Chem. Soc.* 106 (1984) 603.
- [137] P.J. Stang, *Chem. Rev.* 78 (1978) 383.
- [138] J.W. Kenney III, J. Simons, G.D. Purvis and R.J. Bartlett, *J. Am. Chem. Soc.* 100 (1978) 6930.
- [139] K.M. Ervin, J. Ho and W.C. Lineberg, *J. Chem. Phys.* 91 (1989) 5974.
- [140] D.L. Cooper and S.C. Murphy, *Astrophys. J.* 333 (1988) 482.
- [141] J.M. Vrtilek, C.A. Gottlieb, T.C. Killian, P. Thaddeus, J. Cernicharo, M. Guélin and G. Paubert, in: *Astrochemistry of cosmic phenomena, Cumulene carbenes in space and laboratory*, ed. P.D. Singh (IAU, 1992) p. 23.
- [142] P. Thaddeus, C.A. Gottlieb, R. Mollaaghababa and J.M. Vrtilek, *J. Chem. Soc. Faraday Trans.* 89 (1993) 2125.
- [143] P. Thaddeus, J.M. Vrtilek and C.A. Gottlieb, *Astrophys. J.* 299 (1985) L 2.
- [144] J.H. Davis, W.A. Goddard III and L.B. Harding, *J. Am. Chem. Soc.* 99 (1977) 2919.
- [145] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart and J.A. Pople, *GAUSSIAN 92 (revision B)* (Gaussian Inc., Pittsburgh, PA, 1992).
- [146] C. Petrongolo, R.J. Buenker and S.D. Peyerimhoff, *J. Chem. Phys.* 76 (1982) 3655.
- [147] L.E. McMurchie and R.E. Davidson, *J. Chem. Phys.* 67 (1977) 5613.
- [148] M. Zelickoff and K. Watanabe, *J. Opt. Soc. Chem.* 43 (1953) 756.
- [149] R.S. Mulliken, *J. Chem. Phys.* 66 (1977) 2448.
- [150] P.G. Wilkinson, *Can. J. Phys.* 34 (1956) 643.
- [151] D.G. Wilden and J. Comer, *J. Phys. B* 13 (1980) 1009.
- [152] R. McDiarmid, *J. Phys. Chem.* 84 (1980) 64.
- [153] E.H. van Veen, *Chem. Phys. Letters* 41 (1976) 540.
- [154] A. Gedanken, N.A. Kuebler and M.S. Robin, *J. Chem. Phys.* 76 (1982) 46.
- [155] B.A. Williams and T.A. Cool, *J. Chem. Phys.* 94 (1991) 6358.
- [156] K.E. Johnson, D.B. Johnston and S. Lipsky, *J. Chem. Phys.* 70 (1979) 3844.
- [157] W.H. Flicker, O.A. Mosher and A. Kupperman, *Chem. Phys. Letters* 36 (1975) 56.
- [158] P.A. Snyder, P.N. Schatz and E.W. Rowe, *Chem. Phys. Letters* 110 (1984) 508.
- [159] D.E. Love and K.D. Jordan, *Chem. Phys. Letters* 235 (1995) 479.
- [160] A.D. Walsh, *J. Chem. Soc.* (1953) 2306.
- [161] E.P. Gentieu and J.E. Mentall, *Science* 169 (1970) 681.
- [162] J.E. Mentall, E.D. Gentieu, M. Krauss and D.J. Neumann, *J. Chem. Phys.* 55 (1971) 5471.
- [163] M.J. Weiss, C.E. Kuyatt and S. Mielczarek, *J. Chem. Phys.* 54 (1971) 4147.
- [164] J.G. Calvert and J.N. Pitts, *Photochemistry* (Wiley, New York, 1966).
- [165] P.M. Guyon, W.A. Chupka and J. Berkowitz, *J. Chem. Phys.* 64 (1976) 1419.
- [166] W.C.J. Price, *J. Chem. Phys.* 3 (1935) 256.
- [167] J.C.D. Brand, *J. Chem. Soc. (London)* (1956) 858.
- [168] A.D. Cohen and C. Reid, *J. Chem. Phys.* 24 (1956) 85.
- [169] G.W. Robinson and V.E. DiGiorgio, *Can. J. Chem.* 36 (1958) 31.