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REGULAR ARTICLE

Theoretical investigation of excited states of molecules. An application on the nitrogen molecule

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Abstract Diverse existing lines for the calculation of excited states are exposed, with an emphasis on those methods that consider both types of correlation energy: the dynamic and the non-dynamic one. We analyze the possibility of to calculate the dynamic correlation energy using a correlation energy density functional applied to a multi-determinantal wavefunction, which would include the non-dynamic correlation energy, versus the use of mono-determinantal wavefunctions, which are not able to include the long-range correlation energy, and versus the use of variational or perturbative calculations from multi-determinantal wavefunctions, with their excessive computational cost. The results obtained with several methods are compared.

Keywords Excited states · Correlation energy · DFT · Multi-referencial wavefunctions

1 Introduction

The study of the ground and excited states of atoms and molecules is the fundamental challenge for theoretical chemistry and physics. The main purpose is to search for electronic structure methods capable of providing "chemical accuracy" for such states.

In this direction, Prof. Fraga has carried out extensive research, which has led, amongst other things, to the precise calculation of the atomic structures. A good example of this research are the tables with HF-limits results for atoms and their ions [1], their developments and expressions for the relativistic corrections, whose results are, and will continue to be, very useful to the scientific community [2], as well as the incorporation of relativist corrections to the study of the hyperfine structure of the atomic systems [3].

Arriving at such level of precision, with feasible calculations, continues to be a great challenge for molecular systems, although such is not the purpose of this paper. The relativist effects shall not be dealt with here, because for systems of chemical interest, there are some effects, such as the correct consideration of the correlation energy, that have not been yet completely resolved.

The need to include the dynamic (non-static, short-range) and non-dynamic (static or long-range) correlation effects, in order to correctly describe the hypersurface of potential energy curves (PEC), has caused the development of innumerable methods to obtain them.

The goal of this paper is to show the methods that are being used, or that are being developed, for the calculation of the PEC of ground and excited states, and to apply some of them to the nitrogen molecule, analyzing its behaviour, showing its problems and limitations and proposing improvements in its applications.

In the following section, an outline is made of the methods used for the calculation of excited states, focusing on the type of correlation energy included, and analyzing if its applicability includes the PEC calculations. In Sect. 3, details are given of our calculations on N_2, showing the excitation energies and the PECs for the ground and seven lower excited states. In the last section, the results are summarized and some concluding remarks are given.

Contribution to the Serafin Fraga Memorial Issue.

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2 Methodology

The classic approach to the problem of the calculation of the different states for atomic and molecular systems, is the use of configuration interaction methods (CI). However, only the Full-CI using a sufficient large basis set would yield exact results. Such method, though simple to understand, is very difficulty to apply, and at present it is not viable for most problems of chemical interest, in spite of the technological advances in the calculation systems (see the review [4] and for the N_2 molecule, the ref. [5]).

There are a great number of methods making it possible to obtain the energies of the ground and excited states with greater or smaller precision. However, there are few that can be used in a wide range of internuclear distances, for the PEC calculations.

We will distribute these methods in two great groups: on the one hand, those based in mono- or multi-determinantal wavefunctions, optimized for the ground state, and without modifying it, obtaining the energies of the excited states; and on the other, those that consider optimized multi-determinantal wavefunctions for each state in consideration.

The mono-determinantal wavefunctions allow for the obtention of some excited states, but only those that present a different symmetry from that of the ground state; therefore, the application is a very limited one. Within this model, mention must be made of the Hartree–Fock calculations (HF) of the density functional theory (DFT), since they include, with greater or smaller success, the correlation energy.

A first group of methods making it possible to obtain any excited state can be included under the propagator approach denomination (see ref. [6–8]): the random-phase approximation methods (RPA) [9] or the time-dependent applied to HF or DFT approach (TDHF, TFDFT) methods, including the single CI ones (CIS) [10], perturbative corrections of second order [11], and within the TDDFT, several treatments to correct the potentials, optimized effective potentials (OEP), statistical average of orbital potentials (SAOP), asymptotic corrections (AC), etc. [12–18].

Another group is those that apply the equations of motion method to a coupled-cluster (CC) wavefunction type to calculate the excited states. There are several approaches (from the inclusion of simple and double excitations (CCSD) to triple, considered in perturbative or variational form (CCSD(T), CCSDT) [19–22]).

These methods present problems regarding applicability to the calculation of PECs or potential energy surfaces of excited states. Although they have demonstrated greater or smaller precision in the calculation of vertical excitation energies, and the equilibrium position-related properties, they are not able to correctly consider the static effects of the electron correlation.

In order to obtain a correct description of the PEC, resort must be made to multi-reference or multi-configurational wavefunction (MR). The most successful within the MR method is the complete active space self-consistent field approach (CASSCF) [23,24]. This approach includes a large contribution of the long-range correlation energy, and, depending on the specific window of the active space, some of the short-range (dynamic or non-static) correlation energy. Therefore, the remaining non-static correlation energy must be added. A solution is to do a configuration interaction or apply the coupled cluster methods to the MR wavefunction, but their excessive cost and practical problems make these methods almost nonviable (see ref. [25]).

More practical is the use of perturbative methods. There are several within this category, usually based on second-order Moller–Plesset perturbation theory applied to this wavefunction, such as the popular CASPT2, and its extensions by Roos [26,27], the MRMP2 [28], the MROPTn [29] and the multi-configurational quasi-degenerate perturbative theory (MCQDPT) [30,31]. A review of these methods is available in ref. [32].

Currently, the application of DFT methods to a MD wavefunction remains an open issue. The main problem is to correctly consider the fraction of correlation energy not included by MD wavefunction, fundamentally short-range, dynamic, correlation energy. A way to solve this problem is to include a dependence on the natural orbitals; thus, Lie and Clementi (LC) [33,34] scale the correlation energy according to this criterion. Malcolm and McDouall use the notion of an average correlation energy per electron to scale the correlation energy when they use multi-determinantal wavefunctions [35–38], and Gräfenstein and Cremer [39] list the problems and solutions for the combination of density functional theory with multi-reference methods, proposing the inclusion of the on-top pair density by using Khon–Sham (KS) functionals [40,41], the utilization of a correlation functional with pair density dependence, and the inclusion of a correction factor relative to active space used in the multi-referencial calculation, as Miehlich et al. [42] suggest.

We have proposed the calculation of the short-range correlation energy not included in the multi-referential wavefunction, by applying to a self-consistent wavefunction (in this case CASSCF) a correlation energy with an adapted functional, via a perturbative procedure. (A variational-SCF procedure has been applied in other papers [43–45], using several functionals and corrections). These correlation functionals must be sensible to the type of wavefunction used, and this happens with those depending on the occupation number, or on the two-body density. The LC correlation functional is little sensible to the type of wave function; other KS-type functionals, where ρ_α and ρ_β have been replaced by an expression that includes on-top to pair density, suffer from the same problem, and only those that show a direct dependency on ρ_2, seem to be sufficiently sensible to the type of wavefunction [46]. A study of the application of several two-body matrix density functionals has been made, and due to its simplicity and wide use, we chose the Colle and Salvetti (CSq) method [47,48]. We will only use the expression that has a value constant of q, since the dependent expression of a density of reference, presents size-consistency problems.

3 Computational details

This study covers the ground state ($X^1\Sigma_g^+$) and seven excited states, three singlets and four triplets. They are, in increasing order with respect to their vertical excitation energy: $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $a^1\Pi_g$, $B'^3\Sigma_u^-$, $a'^1\Sigma_u^-$ and $w^1\Delta_u$.

The wave functions have been obtained using the Gaussian-03 package [49] or the GAMESS package [50], modified in order to evaluate the correlation energy in a post-SCF procedure by numerical integration [51]. The augmented, correlation-consistent, polarized valence triple zeta (aug-cc-pVTZ) Dunning basis sets [52] were used. To study excited states, very large basis sets should be used, but since only the first excited states will be dealt with here, we believe that these basis sets should suffice.

The MCSCF calculations are CASSCF type [23], with an active space that describes correctly the breaking of the molecular bonds of the states considered. Thus, the CASSCF wave functions are composed of two core molecular orbitals (MOs) and an active space formed by five doubly occupied MOs and three empty MOs (2,5,0,3) for the singlets and an active space of four doubly occupied MOs, two semi-occupied and two empty MOs (2,4,2,2) for the triplets.

The CE is calculated using several CE functionals with a post-SCF procedure, but for simplicity and coherence, only the results of the Colle–Salvetti functional are shown, with a $\beta = q\rho^{1/3}$ [53].

The vertical excitation energy has been evaluated, using a large set of methods: TDDFT, with B3LYP [54–56] (TD-B3LYP) and HCTH407 [57] (TD-HCTD) functionals; CIS (with two frozen core MOs); the CASSCF as has been indicated previously; a perturbative CASSCF (MCQDPT) with the same active space; and EOM-CCSD, for the singlet states (the only ones for which this method is implemented in GAMESS), considering the D_{2h} symmetry group, and an active space of eight MOs and two frozen core ones.

The last column shows the results of the post-SCF consideration of correlation energy, for the CASSCF wavefunction (CASSCF-CSq). These results are similar to those which would be obtained in a SCF procedure [43,58].

Together with the vertical excitation energies, the potential energy curves to dissociation are shown, but only with those methods based in multi-determinantal wavefunction.

The spectroscopic constants were obtained by fitting a large number of calculated points of the PECs, to a polynomial of the $\frac{1}{R}$ variable, where R is the internuclear distance. The experimental data were obtained from ref. [59] for the vertical excitation energies, and ref. [60] for the rest.

4 Results

In Table 1, it can be observed that for the calculation of the vertical excitation energy all methods give qualitatively correct results, with the exception of the CIS method (see also ref. [61]). However, it can be seen that the ones based on a mono-determinantal wavefunction, like the TD methods, are incapable of distinguishing between the $B'^3\Sigma_u^-$ and the $a'^1\Sigma_u^-$ excited states (in ref. [61–64] similar results are obtained).

On the other hand, the multi-determinantal methods correct that deficiency, but the CASSCF results show that it is necessary to include the rest of short-range correlation energy, to arrive at quantitatively precise results. This is not

Table 1 Vertical excitation energy for nitrogen molecule, in eV

State	Exp[a]	TD-B3LYP	TD-HCTH	CIS	EOM-CCSD	CASCF	MCQDPT	CASCF + CSq
$A^3\Sigma_u^+$	7.75	7.10	7.19	6.23		8.22	7.48	8.48
$B^3\Pi_g$	8.04	7.58	7.52	7.30		8.77	7.75	8.76
$W^3\Delta_u$	8.88	7.97	8.50	11.74		9.70	9.70	9.72
$a^1\Pi_g$	9.31	9.27	9.14	9.04	9.45	10.03	9.06	9.86
$B'^3\Sigma_u^-$	9.67	9.33	9.74	8.50		10.41	9.51	10.15
$a'^1\Sigma_u^-$	9.92	9.33	9.74	8.50	10.05	10.98	9.63	10.78
$w^1\Delta_u$	10.27	9.72	10.09	13.60	10.49	11.26	9.73	10.86
$< \lvert\varepsilon\rvert >$		0.51	0.29	1.62		0.79	0.37	0.68
$\varepsilon_{\max}$		−0.91	−0.56	3.33		1.06	0.82	0.86

[a] Values fitted in ref. [65] to experimental spectroscopic constants

only shown in columns 5 and 7, but in other calculations in the literature [6,65,66].

These methods have a calculation, time and memory cost which increases remarkably as the size of the system is greater. This increased need for calculation capacity is not so great when calculations of type DFT to multi-determinantal wavefunctions are made, such as, for example, CASSCF + CSq calculations. However, it is necessary to find a better functional, since, although the CSq functional is sensible to the type of wavefunction used, and its qualitative behavior is the correct one, neither the beta expression used in these calculations, ($\beta = q\rho^{1/3}$) nor the proposal by the authors to even further reduce the short-range correlation energy, provide correct quantitative results, as can be seen in the mean absolute error or in the root mean squared error.

In the study of CASSCF PECs, the various states studied can be classified as follows, according to the dissociation products:

$$\begin{aligned} X^1\Sigma_g^+, A^3\Sigma_u^+ &\longrightarrow {}^4S + {}^4S \\ B^3\Pi_g, W^3\Delta_u &\longrightarrow {}^4S + {}^2D \\ B'^3\Sigma_u^- &\longrightarrow {}^4S + {}^2P \\ a'^1\Sigma_u^-, a^1\Pi_g, w^1\Delta_u &\longrightarrow {}^2D + {}^2D \end{aligned}$$

For all studied states, the CASSCF method produces a qualitatively correct dissociation, and shows its size-consistent character, since the energy of the dissociated molecule is the sum of the energy of the corresponding dissociation products.

Figure 1 contains the results for the fundamental state, and along with the CASSCF results, the PECs obtained with MCQDPT and CASSCF + CSq methods are shown. Also, and by comparing, we plot the PECs obtained with unrestricted-DFT calculations, using only the exchange Becke functional, and with the exchange-correlation B3LYP functional. For all of them a qualitatively correct behavior is obtained, although at the cost of breaking the symmetry in the unrestricted calculations.

It can be seen that the CASSCF wavefunction introduces a part of the short-range correlation energy, and the parallelism is remarkable between the curves that include this short-range correlation energy (partially, (MCQDPT) or totally (CASSCF + CSq, B3LYP)). In Fig. 1, it can be observed that the application of the functional CSq to the CASSCF wavefunction introduces more correlation energy than the pure DFT methods, for geometries next to the bond equilibrium distances.

Figures 2 and 3 show the PECs of the triplet and singlet excited states, respectively. The U-Becke PECs and the

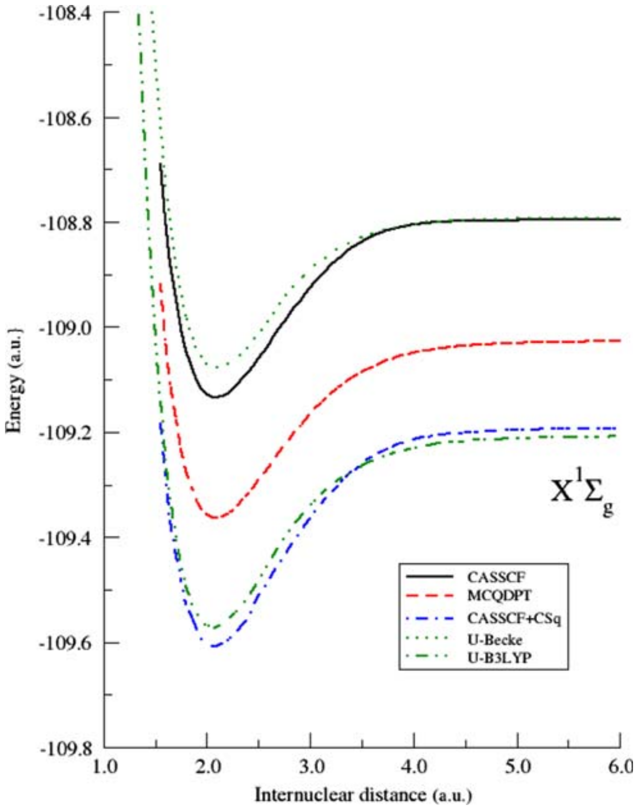

Fig. 1 Potential energy curves of the $X^1\Sigma_g^+$ state of N_2

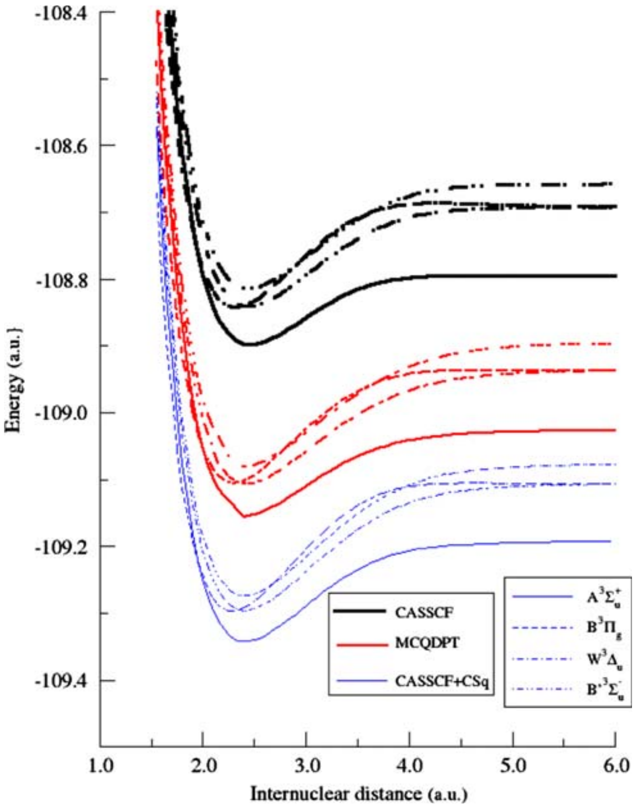

Fig. 2 Potential energy curves of the $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$ and $B'^3\Sigma_u^-$ states of N_2

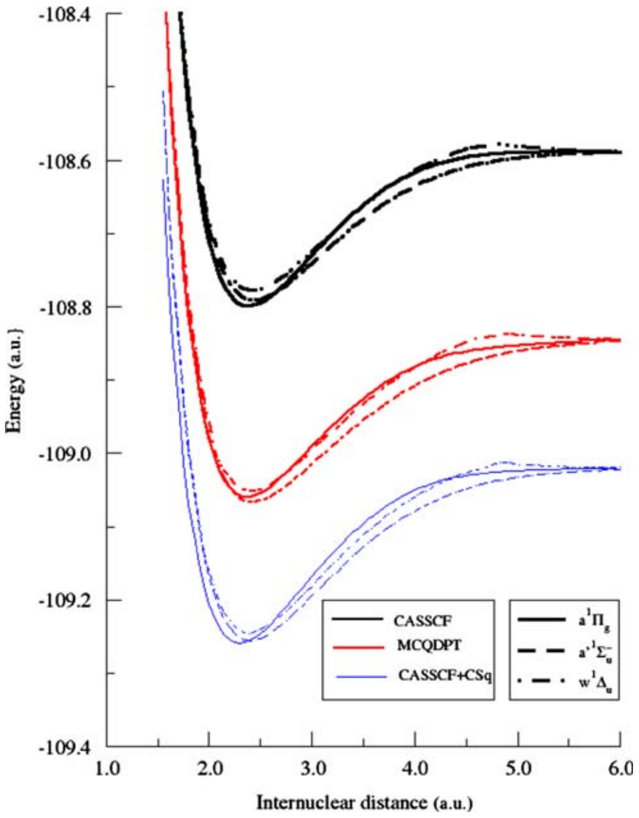

Fig. 3 Potential energy curves of the $a^1\Pi_g$, $a'^1\Sigma_u^-$ and $w^1\Delta_u$ states of N_2

U-B3LYP PECs do not appear, because they cannot be calculated. It can be seen that the perturbative method on the CASSCF wavefunction (MCQDPT), as the CASSCF + CSq, provides a correct dissociation of the different excited states in its corresponding products. The MCQDPT method introduces less correlation energy than the CSq method applied to the CASSCF wavefunction. Finally, the values obtained for spectroscopic constants (bond equilibrium distances R_e, harmonic vibrational frequencies ω_e and dissociation energies D_e) are shown in Table 2. The CASSCF calculations provide good results; however, they improve with the inclusion of the correlation energy, both by the perturbative calculations and the electronic density ones.

5 Conclusions

From the results, it can be inferred that, in order to make calculations for distances next to equilibrium configuration of the fundamental state, any one of the methods indicated provides acceptable results. Due to their simplicity and economy, the TDDFT methods are a great choice, although any other method provides similar results with slightly superior costs.

Table 2 Equilibrium bond distances (R_e) in a.u., harmonic vibrational frequencies (ω_e) in cm^{-1} and dissociation energies (D_e) in eV, for several states of N_2 molecule

State	Exp	CASSCF	MCQDPT	CASSCF + CSq
R_e (a.u.)				
$X^1\Sigma_g$	2.074	2.086	2.091	2.070
$A^3\Sigma_u^+$	2.431	2.465	2.455	2.420
$B^3\Pi_g$	2.291	2.325	2.308	2.292
$W^3\Delta_u$	2.418	2.450	2.435	2.410
$a^1\Pi_g$	2.306	2.383	2.375	2.301
$B'^3\Sigma_u^-$	2.416	2.450	2.448	2.409
$a'^1\Sigma_u^-$	2.410	2.435	2.422	2.400
$w^1\Delta_u$	2.398	2.414	2.395	2.380
$<\lvert\varepsilon\rvert>$		0.033	0.025	0.009
ε_{max}		0.080	0.070	−0.020
ω_e (cm^{-1})				
$X^1\Sigma_g$	2,359	2,299	2,295	2,473
$A^3\Sigma_u^+$	1,461	1,429	1,435	1,524
$B^3\Pi_g$	1,733	1,655	1,670	1,729
$W^3\Delta_u$	1,507	1,462	1,504	1,542
$a^1\Pi_g$	1,694	1,661	1,655	1,741
$B'^3\Sigma_u^-$	1,517	1,459	1,506	1,526
$a'^1\Sigma_u^-$	1,530	1,493	1,495	1,568
$w^1\Delta_u$	1,559	1,526	1,592	1,602
$<\lvert\varepsilon\rvert>$		47	34	44
ε_{max}		−78	−64	114
D_e (eV)				
$X^1\Sigma_g$	9.90	9.18	9.18	11.24
$A^3\Sigma_u^+$	3.68	2.78	3.43	4.09
$B^3\Pi_g$	4.90	4.09	4.60	5.20
$W^3\Delta_u$	4.87	4.03	4.63	5.15
$a^1\Pi_g$	6.08	5.72	5.83	6.42
$B'^3\Sigma_u^-$	5.26	4.26	4.97	5.34
$a'^1\Sigma_u^-$	6.22	5.48	5.98	6.34
$w^1\Delta_u$	5.73	5.15	5.65	6.10
$<\lvert\varepsilon\rvert>$		0.74	0.30	0.41
ε_{max}		0.90	0.72	1.34

The problems arise when carrying out calculations of the PECs, since a multi-determinantal wavefunction is required to correctly describe the dissociation products. In order to apply a correlation density functional, this must be sensible to the type of wavefunction used. The use of a correlation functional of this type entails a great economy of calculation, with respect to other methods based on expansions of the configurations from the multi-determinantal function, which, besides their higher calculation cost, show oscillations throughout the calculation of PECs, which must be evaluated individually and manually.

Nevertheless, it is necessary to emphasize the need to improve the dependency of the correlation functionals of the electronic density, with respect to the type of wavefunction used. We shall continue to work in this area.

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