

Regular article

A study with a complete-active-space self-consistent-field plus density functional theory combination: The low-lying bound states of N₂

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Abstract. The use of a large set of correlation energy functionals, in a post-self-consistent-field procedure, is analyzed for the calculation of the potential-energy curves of the ground state and some excited states in the case of the N₂ molecule. The results show the improvement of the molecular properties, such as dissociation energies, equilibrium bond distances and harmonic vibrational frequencies, (when some of the tested functionals are used), together with the problems that the use of density functional theory functionals applied to multideterminantal wave functions implies.

Keywords: Multiconfigurational self-consistent field – Density functional theory – Correlation energy – Potential-energy curves – Excited states

1 Introduction

The accurate computational description of ground and excited states in molecules is still an objective in computational chemistry. In this paper we show an alternative to the calculation of potential-energy surfaces, for the ground state as well as excited states. For this purpose, we use the N₂ molecule, which has been a challenge for electronic structure method problem (see Ref. [1] for the ground state).

For potential-energy curve (PEC) calculations, we need to consider multideterminantal (MD) wave functions [2] to get a good description of bond breaking. This MD wave function should include, at least, the number of configurations needed to describe the dissociation products, which is, in general, a low number [3]. So, these types of wave functions are one of the classical ways to obtain the excited states. However, a MD wave function includes the dynamical correlation energy (CE),

(the relative to the conformational description of the system into the configurational space), but only considers a small, and variable, amount of the nondynamical correlation energy through the PEC. These effects, not included for the MD wave function, are essential to the accuracy of the calculations of the PECs.

Traditional ab initio methods, such as full configuration interaction, multireference configuration interaction including singles and doubles excitation, CASPT2, and multireference coupled cluster, can achieve the accuracy needed to calculate PECs and spectroscopic properties. However, a high number of configurations have to be included in the calculations, resulting in an expensive computational cost.

Density functional theory (DFT) [4] has become a great tool to incorporate the nondynamical correlation energy of the ground states with a low cost. However, a lot of DFT functionals are based on the Kohn–Sham approach [5], in which a wave function given by a single Slater determinant is introduced for the purpose of representing the density in terms of orbital contributions, and therefore the DFT calculations give poor results for states inherently multiconfigurational, such as degenerate or quasi-degenerate states.

The use of perturbative methods to DFT solutions [6], or the time-dependent DFT [7,8] provide good results for excitation energies, but the potentials used are those obtained for the ground state and they do not have the correct asymptotic behavior, giving bad and unexpected results in some cases [9].

Moreover, there is not a unique and exact time-independent DFT formulation to the calculations of pure excited states, unlike the Kohn–Sham method for the ground state, except for the calculation of the states of lowest energy with symmetries different from that of the ground state. Furthermore, the universal density functional for the energy of the rest of the electronic states can be explicitly dependent of the densities of the lower states [10].

The application of DFT methods to a MD wave function is an open question. In this context the use of CE functionals with a dependence on the natural orbitals

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or on the reduced density matrix, which are applicable to MD wave functions [11, 12, 13, 14, 15, 16, 17] has been analyzed. So, there are procedures to apply the usual DFT functionals to MD wave functions [18], solving the problems for states inherently multi-configurational and so, recently, we have applied this procedure to the study of atomic excited states using a complete-active-space-self-consistent-field (CASSCF) wave function, together with some correlation energy functionals to include the fraction of the the correlation energy not included in the CASSCF wave function [19].

In this paper, this methodology is applied to the ground state and several excited states of the N_2 molecule. The goal is to study the application of several CE functionals in PEC calculations of excited states, to analyze the behavior of these functionals in these calculations, to show their problems, and to propose improvements in their application.

2 Methodology

The MD calculations are of the multiconfigurational SCF (CASSCF) [20] type, with an active space used such that the breaking of ground state and first excited state molecular bonds are described correctly. We have considered two core molecular orbitals (MOs) and eight active MOs [e.g., the $X^1\Sigma_g^+$ state (nitrogen molecule ground state) CASSCF wave function is composed of two core MOs and an active space formed by five doubly occupied MOs and three empty MOs (2, 5, 3)]. For comparative purposes, we made calculations with a CASSCF wave function using four core MOs and six active MOs.

In a post-SCF procedure we calculated the CE using several CE functionals, which can be divided in two types:

1. Standard DFT correlation energy functionals modified by the inclusion of two-body density matrix, $\Gamma_2(\mathbf{R})$, dependence proposed by Moscardó and San-Fabián [18].

$$\rho_\alpha(\mathbf{R}) = \frac{\rho(\mathbf{R}) + \sqrt{\rho(\mathbf{R})^2 - 2\Gamma_2(\mathbf{R})}}{2}, \quad (1)$$

$$\rho_\beta(\mathbf{R}) = \frac{\rho(\mathbf{R}) - \sqrt{\rho(\mathbf{R})^2 - 2\Gamma_2(\mathbf{R})}}{2}. \quad (2)$$

In this group, we employed a local spin density functional, the Vosko–Will–Nussair functional [21] with self-interaction correction (SIC)[22] (VWN-2), three generalized gradient approximation functionals, the Becke 88 (B88-2) functional [23], the Wilson and Levy one (WL-2) [24] and the Lee, Yang and Parr one (LYP-2) [25]. We also used these functionals without the $\Gamma_2(\mathbf{R})$ dependence for comparative purposes.

2. Two-body density matrix dependent functionals: Two versions of the Colle-Salvetti functional [12] and the Moscardó–San-Fabián [26] one were used. The first with

$$\beta = q\rho^{1/3}, \quad (3)$$

(CS-q and MSF-q respectively) and the second with β defined as in Eq. (8) of Ref. [12]:

$$\beta = q \left[1 + \frac{v}{2} \left(\frac{(\nabla_1^2 + \nabla_2^2)\Gamma_{\text{cl}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)}{\Gamma_{\text{cl}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)} - \frac{(\nabla_1^2 + \nabla_2^2)\Gamma_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)}{\Gamma_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)} \right) \right]_{\substack{\mathbf{r}'_1=\mathbf{r}_1 \\ \mathbf{r}'_2=\mathbf{r}_2 \\ \mathbf{r}'_2=0}} \rho(\mathbf{R})^{1/3}, \quad (4)$$

(CS and MSF). The q and v values are in Refs. [12, 26]. In addition to these, the Moscardó–Pérez-Jiménez functional, at level 5, (MPJ5) [27] was used. The $\Gamma_{2\text{HF}}$ of Eq. (4) are calculated including all determinants with a big contribution to the wave function. This modification of the conventional CS functional is used to avoid the discontinuity of the PECs caused by choosing the determinant used in the calculation of $\Gamma_{2\text{HF}}$. This modification was proposed in Ref.[19] (CS-m), where we showed that it improves the CS results for the excited atomic states when several determinants have a big contribution to the wave function.

3 Calculations

The PECs of the following states of the N_2 molecule were calculated:

- Singlet states: $X^1\Sigma_g^+$, $a^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$,
- Triplet states: $A^3\Sigma_u^+$, $W^3\Delta_u$, $B^3\Pi_g$, $B^3\Sigma_u^-$, $G^3\Delta_g$.

The augmented correlation-consistent polarized-valence quintuple-zeta Dunning basis sets [28] were used. The basis functions with symmetry higher than f (g - and h -shell type) were suppressed, because our numerical integration program does not support them yet, but their inclusion is not relevant for our purpose. The role of the basis set in the excited-state calculations is very important and needs many diffuse basis functions in order to obtain correct results.

All the multiconfigurational SCF wave functions were obtained with the GAMESS package[29], and the CE was evaluated by numerical integration [30, 31] as a post-SCF procedure. This post-SCF step can be done because the CE is a small perturbation compared with the total energy of the system. Calculations in a SCF fashion for a generalized valence bond perfect pair (GVB-PP) wave function can be seen in Ref. [32, 33] when the correlation energy obtained in a SCF procedure (correlation potential is included in the GVB-PP equations) is similar to that obtained in a post-SCF one, where the correlation functional is applied to the MD density. Then, we can make the following approximation:

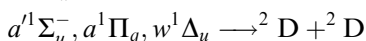
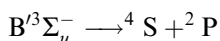
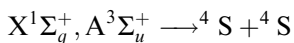
$$E_{\text{c,MD}}^{\text{SCF}} \approx E_{\text{c}}[\rho_{\text{MD}}].$$

The spectroscopic constants were obtained for a large number of calculated points of the potential PECs which were fitted to a polynomial of the $\frac{1}{R}$ variable, where R is

the internuclear distance. The experimental data were obtained from Muller et al. [34].

4 Results and discussion

The CASSCF PECs of the nitrogen molecule are shown in Fig.1. The dissociation products of the states studied can be grouped into the next scheme:



The CASSCF method shows that all the states with equal dissociation products have the same energy at large distances. This energy is the sum of the energy of the corresponding dissociation products, showing their size-consistent character.

4.1 Dissociation behavior

First, we concentrate on the comparative analysis of the energy at large distances when we include the CE calculated with the functionals of Sect. 2. In this analysis, we found that not all the functionals employed in the CASSCF plus DFT method give the same energies for the different states that give the same dissociation products.

The CS and MSF functionals depend on a reference configuration, so, as is shown in Fig. 2, they do not give

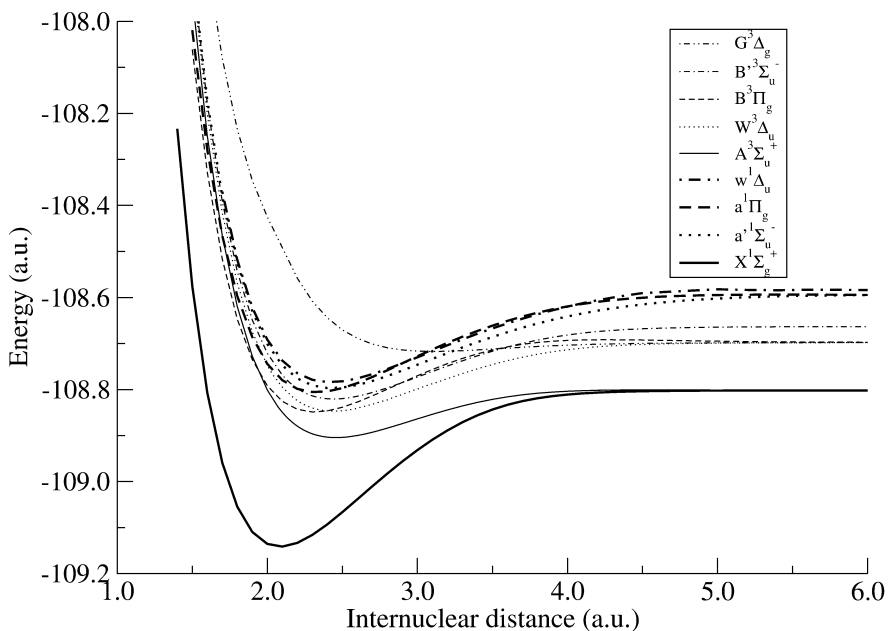


Fig. 1. Multiconfigurational self-consistent-field (MC-SCF) potential-energy curves of the N_2 molecule

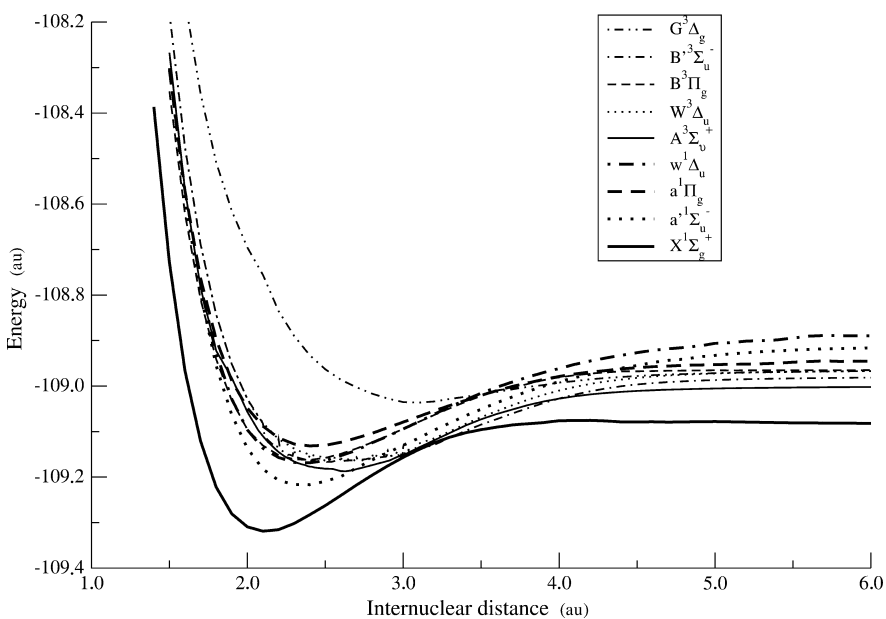


Fig. 2. MC-SCF + CS potential-energy curves of the N_2 molecule

equal energy at the dissociation distance to equal dissociation fragments. The reason for this behavior is the calculation of the reference two-body density matrix of the β expression. So, in this work the reference two-body density matrix is calculated for the determinants of large weights in the MD wave function. Although, this implementation gives accurate approximations to the CE of the excited states of the atoms [19] it is not easy to choose the number of determinants at all distances of the PEC, owing to practical problems. So, this effect gives an incorrect crossing on the PEC of the states which dissociate to $(^4S) + (^2D)$ and the one that dissociates to the $(^4S) + (^2P)$ states. For this reason, the CS and MSF functionals with the β expression of Eq. (4) present problems for the calculation of the PEC in the way that it has been implemented by us.

This problem can be solved by using a β which only depends on the total density, in the CSq and MSFq methods (Fig. 3), whose PECs show the correct behavior, as in the other two-body density-dependent method, the MPJ5. This correct behavior is a direct consequence of the wave function behavior of these $\Gamma_2(\mathbf{R})$ dependent functionals.

With respect to the modified standard DFT methods we are going to analyze when the molecular states that dissociate into the same products are of different multiplicities, the DFT functionals without modification give different CEs for these states of different multiplicity, at the dissociation distances. These deficiencies are removed, for the cases studied, the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, when the modification of ρ_α and ρ_β in the function of $\Gamma_2(\mathbf{R})$ is applied to DFT functionals not dependent on the density gradients, the VWN functional. This fact is shown in Fig. 4. This is an essential improvement of the modified DFT functionals to include the two-body density matrix dependence over the conventional DFT functionals.

The other modified DFT methods, which depend on $\nabla\rho_\alpha$ and $\nabla\rho_\beta$ (B88-2, WL-2 and LYP-2) show a strong dependence on the state multiplicity. This happens

because the inclusion of the two-body density matrix dependence is done for ρ_α and ρ_β and we did not change the gradient. However, this fact can not be observed for the LYP-2 functional, although something similar could be expected in principle. The reason for this behavior is the compensation in the variation of these gradient-dependent terms.

4.2 Size-consistency

Another question is the size-consistency of these calculations. The comparison of our results with the atomic calculations for the different states of nitrogen atom [19] shows that only the CSq is strictly size-consistent, and the LYP-2, by a fortuitous cancellation of errors, is practically size-consistent. The rest of the methods show a strong difference in the energy calculated for the two states of the nitrogen atom and the molecule quasi-dissociated in these states.

The VWN-2 method is size-consistent when the PEC dissociates into two nitrogen atoms in the 4S state, but it is not size-consistent when the dissociation products are different. The reason for this behavior is that the 4S state of nitrogen is described by a monodeterminantal wave function with the active space used in this paper and the rest of the excited states are described by several configurations.

The remaining modified DFT functionals are not size-consistent. The reason can be that not including the modification in the $\nabla\rho_\alpha$ and $\nabla\rho_\beta$ terms or that the defined modification of ρ_α and ρ_β (only exact for a Hartree-Fock wave-function) do not allow the size-consistency.

Finally, the MSFq and MPJ5 functionals are not size-consistent for the known problem of the dependence on the electron number. In order to get the size-consistency it is necessary to implement a correct modification for the expressions of these functionals.

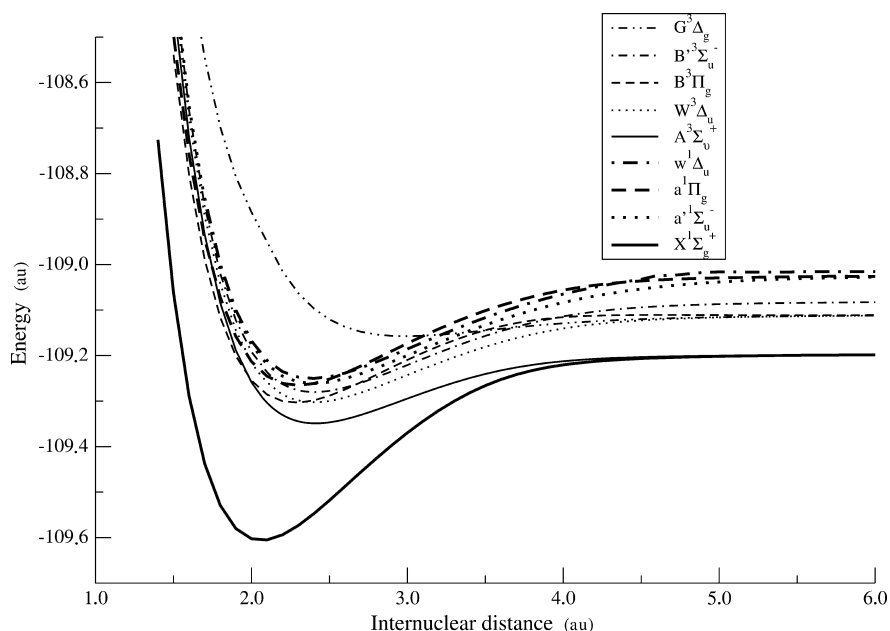


Fig. 3. MC-SCF + CSq potential-energy curves of the N_2 molecule

4.3 Double count of the CE

Next, we are going to analyze the problem of the double count of the correlation energy for the CE functionals employed. All the two-body density matrix dependent functionals and the modified DFT ones consider that a fraction of the dynamical CE is already included in the multireference wave function calculation. Unfortunately, this wave function behaviour is not exact and this fact results in the CE obtained having some of the dynamical CE already included in the multireference wave function. For this reason, the problem of the double count of the CE appears at all internuclear distances of the PEC. However, when this double count is similar at all internuclear distances the spectroscopic properties will be not affected by this double count.

The extent of this double count error depends on the dominant configurational space of the calculation. So, a greater error in the CE calculation corresponds to a greater configurational space. If we analyze the different configurational space [3] for these states at quasidissociated and equilibrium distances, we can see that for the $X^1\Sigma_g^+$ state these are large differences between the dominant configurations at quasidissociation internuclear distances and those at equilibrium internuclear distances. For this state, there are five occupied and three empty MOs at the equilibrium distance, but there are no empty orbitals at the quasidissociated distance. However, for the excited states, they will have six occupied and only two empty MOs near the equilibrium distance, and there are still one or two empty MOs, except for the $A^3\Sigma_u^+$ state, at quasidissociation distances. This fact suggest

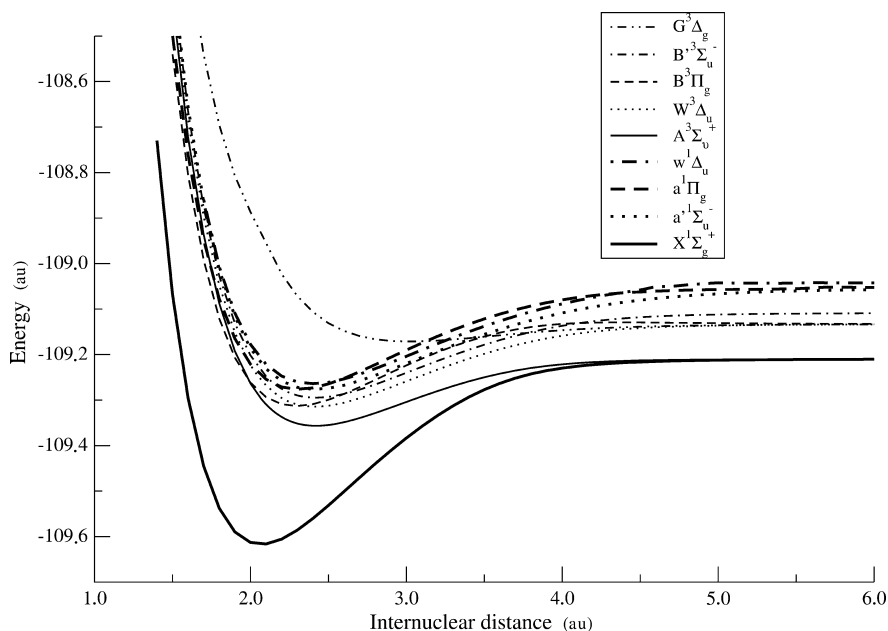


Fig. 4. MC-SCF + VWN-2 potential-energy curves of N_2 molecule

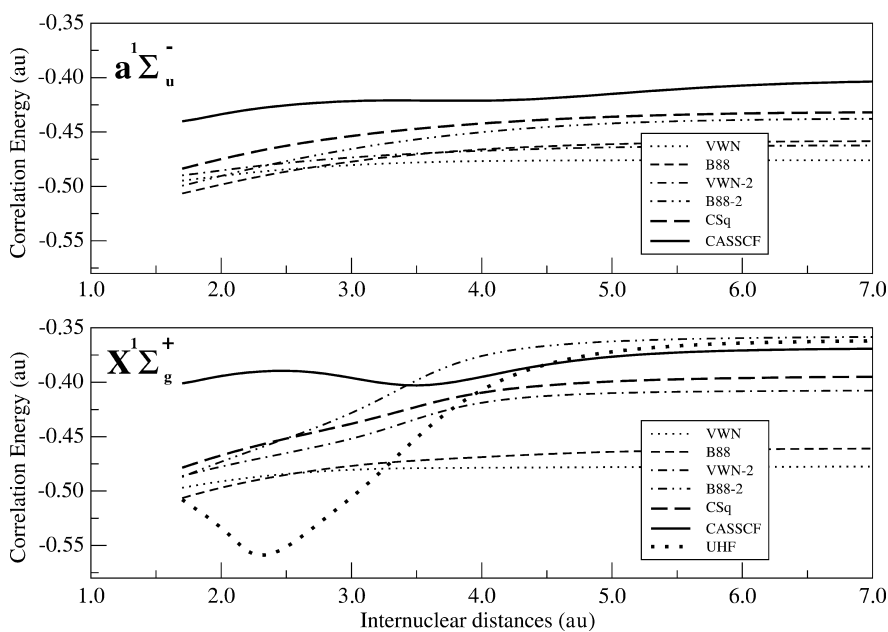


Fig. 5. Correlation energies for $X^1\Sigma_g^+$ and $a^1\Sigma_u^-$ states of the N_2 molecule, calculated with the complete-active-space SCF (CASSCF) densities, and the exact correlation energy for the CASSCF wavefunction. The exact unrestricted Hartree-Fork correlation energy is shown for the $X^1\Sigma_g^+$ state

that the difference in the double count of the CE, through the PEC, must be larger for the ground state than for the excited states, as can see in Fig. 5.

In Fig. 5, the CE calculated with some DFT methods, using the CASSCF density together with the “exact” (taking the experimental energy given by the Hulbert–Hirschfelder potential [35, 36] minus the SCF energy) CASSCF correlation energy is shown. For the ground state the “exact” unrestricted Hartree–Fock CEs are also shown for reference. So, as indicated in Ref. [37] some correction to the ground state will be useful, being unnecessary for the rest of the states studied here, which is the objective of this paper.

To analyze the effect of considering $\Gamma_2(\mathbf{R})$ in the standard DFT methods, in Table 1 we show the average relative error of the CE calculated with these CASSCF plus DFT methods for the molecular states studied at large distances (10 au) and in the equilibrium distance of each state (Table 2). For the excited states, these values correspond to the expression:

$$\frac{1}{n} \sum_j \left| \frac{E_c^j(F) - E_c^j(\text{exp})}{E_c^j(\text{exp})} \right|, \quad (5)$$

where n is the number of excited states studied, $E_c^j(F)$ is the CE calculated for the state j with the F functional, and $E_c^j(\text{exp})$ is the difference between the “experimental” and the calculated energies. The “experimental” ones are the nonrelativistic atomic energies for the quasidissociated system, and the previous energies plus the experimental dissociation energies, D_e for the equilibrium distances. The CS-q method is included for comparison.

As can be seen in this table, although the double count of the CE occurs at all the distances of the PECs, when incorporating $\Gamma_2(\mathbf{R})$ into standard DFT functionals the error decreases, both for the quasidissociated system and for the equilibrium distance. However, as is

to the expected, his increase is better for large internuclear distances than equilibrium nuclear positions, because the nondynamic CE considered by the CASSCF wave function must be smaller in the first case.

So, the double count is greatly diminished when we use the modified DFT functionals, showing a behavior similar to the CSq functional. The MPJ5 and MSFq functionals give an excessive CE; however, this fact is only for the size-consistency problem of these functionals that affects all the points of the PECs.

The WL functional has a particular behavior, overestimating the CE more CE at the equilibrium distance than at the dissociation geometry, which is opposite to the rest of functionals (VWN, B88 and LYP) in that they give a larger overestimation at dissociation than at the equilibrium energy.

4.4 Molecular properties

The values obtained for the bond equilibrium distances, R_e , harmonic vibrational frequencies, ω_e , and D_e are shown in Tables 2, 3, and 4 together with their average errors for excited states.

The CASSCF with two core MOs and eight MOs in the active space is a good approximation to the exact solution, so the results give an absolute error of 0.021 au for R_e , 39 cm^{-1} for ω_e and 0.71 eV for D_e . These good results indicate that this CASSCF wave function has all the Slater determinants required for the description of the dynamical CE of these states. However, the CASSCF gives D_e and ω_e values lower than experiment and R_e values higher than experiment, which suggests the need to include the rest of the CE.

As expected (see Ref. [38]), the CASSCF plus DFT method increases the D_e of the CASSCF one, decreases the R_e , and increases the ω_e . Then, for VWN-2, LYP-2,

Table 1. Correlation energy relative errors (Eq. 5), for several states of quasidissociated and equilibrium internuclear distances of the N_2 molecule

Method	VWN	VWN-2	B88	B88-2	WL	WL-2	LYP	LYP-2	CSq
Ground state									
$r = \infty$	29.5 %	10.5 %	24.9 %	-2.91 %	22.3 %	-17.1 %	21.8 %	3.92 %	7.03 %
$r = r_e$	24.6 %	21.0 %	25.9 %	19.5 %	34.9 %	24.2 %	23.1 %	19.6 %	18.2 %
Excited states									
$r = \infty$	22.2 %	13.7 %	18.0 %	6.79 %	14.9 %	4.70 %	15.2 %	7.44 %	7.83 %
$r = r_e$	15.5 %	12.6 %	16.3 %	12.0 %	20.8 %	13.6 %	13.2 %	10.4 %	9.68 %

Table 2. Equilibrium bond distances, r_e , for several states of the N_2 molecule (in au)

State	MC	VWN-2	B88-2	WL-2	LYP-2	CSq	CS	MSFq	MSF	MPJ5	Exp.
$X^1\Sigma_g^+$	2.083	2.064	2.052	2.042	2.057	2.060	2.111	2.060	2.121	2.057	2.074
$a^1\Sigma_u^-$	2.430	2.411	2.391	2.367	2.397	2.396	2.340	2.408	2.386	2.403	2.410
$a^1\Pi_g$	2.330	2.307	2.285	2.250	2.294	2.295	2.423	2.302	2.353	2.298	2.306
$w^1\Delta_u$	2.418	2.400	2.382	2.360	2.387	2.388	2.356	2.399	2.377	2.394	2.398
$A^3\Sigma_u^+$	2.460	2.423	2.401	2.370	2.410	2.415	2.561	2.415	–	2.409	2.431
$B^3\Pi_g$	2.323	2.300	2.281	2.243	2.287	2.290	2.374	2.296	2.337	2.291	2.291
$W^3\Delta_u$	2.440	2.415	2.397	2.372	2.401	2.402	–	2.410	–	2.405	2.418
$B^3\Sigma_u^-$	2.444	2.420	2.400	2.375	2.405	2.405	2.538	2.415	2.460	2.409	2.416
$G^3\Delta_g$	3.053	2.981	2.933	2.879	2.958	2.955	3.073	2.964	3.030	2.951	3.044
$\langle \epsilon \rangle$	0.023	0.011	0.030	0.062	0.022	0.021	0.085	0.015	0.032	0.019	
$\langle \epsilon_{\text{Rel}} \rangle$	0.959	0.410	1.150	2.426	0.816	0.776	3.521	0.519	1.355	0.698	

CSq, MSFq and MPJ5 the D_e results are improved, the R_e results are better than or similar to the CASSCF results and the ω_e results are slightly worse than the CASSCF results because the CASSCF results are pretty near the experimental results. The functionals with a dependence of the $\nabla\rho_\alpha$ and $\nabla\rho_\beta$ do not give good results. For this reason, an analysis of the modification of these terms to include the $\Gamma_2(\mathbf{r})$ dependence is needed. And the CS and MSF results are poor owing to the reference state dependence in the β expression.

The effect of the size of the active space of the CASSCF calculation on the CASSCF plus DFT methods can be analyzed by the comparative analysis between the calculations with two core MOs and eight active MOs with multiconfigurational SCF calculations and another calculation with four core MOs and six active MOs. Although we cannot expect that this subspace (4,6)

correctly describes the breaking of a triple bond over the entire range of internuclear separations [39], these wave functions may have a lower double count of the CE, so the results for the ground state must be worse for the CASSCF wave function and better for the CASSCF plus DFT one, as shown in the comparative analysis of D_e in Tables 4 and 5 and as discussed in Sect. 4.3.

5 Conclusions

We can conclude that the inclusion of the CE via DFT in the MD wave function is an easy and computationally cheap way to improve MD results especially when a low number of configurations can be used to obtain qualitative results. However, a better understanding of the double count of the CE and the development of new Γ_2

Table 3. Harmonic vibrational frequencies, ω_e , for several states of the N_2 molecule (cm^{-1})

State	MC	VWN-2	B88-2	WL-2	LYP-2	CSq	CS	MSFq	MSF	MPJ5	Exp
$X^1\Sigma_g^+$	2292	2381	2438	2540	2412	2396	2155	2405	2066	2420	2359
$a^1\Sigma_u^-$	1505	1538	1576	1673	1569	1573	1813	1545	1664	1559	1530
$a^1\Pi_g$	1666	1719	1775	1927	1755	1751	1455	1731	1620	1747	1694
$w^1\Delta_u$	1583	1597	1637	1727	1631	1635	1601	1579	1651	1594	1559
$A^3\Sigma_u^+$	1431	1515	1571	1684	1544	1531	1434	1538	–	1555	1461
$B^3\Pi_g$	1665	1709	1759	1909	1742	1739	1548	1718	1629	1733	1733
$W^3\Delta_u$	1484	1534	1580	1679	1567	1565	–	1546	–	1561	1507
$B^3\Sigma_u^-$	1469	1520	1568	1677	1553	1553	1053	1533	1391	1549	1517
$G^3\Delta_g$	732	854	950	1089	896	896	975	887	940	911	766
$\langle \varepsilon \rangle$	34	34	82	200	62	60	207	43	117	56	
$\langle \varepsilon_{Rel} \rangle$	2.44	2.92	6.82	15.5	5.08	4.99	15.1	3.81	9.35	4.86	

Table 4. Dissociation energies, D_e , for several states of the N_2 molecule (eV)

State	MC	VWN-2	B88-2	WL-2	LYP-2	CSq	CS	MSFq	MSF	MPJ5	Exp.
$X^1\Sigma_g^+$	9.22	11.08	12.28	14.22	11.60	11.13	6.49	11.7	7.55	11.91	9.90
$a^1\Sigma_u^-$	5.48	6.08	6.78	7.81	6.54	6.41	8.46	6.14	7.17	6.26	6.22
$a^1\Pi_g$	5.72	6.06	6.66	7.66	6.58	6.51	4.98	6.05	5.53	6.16	6.08
$w^1\Delta_u$	5.45	6.03	6.74	7.78	6.47	6.41	7.58	6.27	6.95	6.40	5.73
$A^3\Sigma_u^+$	2.80	4.01	4.77	6.01	4.41	4.15	5.17	4.41	–	4.56	3.68
$B^3\Pi_g$	4.10	4.89	5.68	7.01	5.39	5.24	5.40	5.14	5.39	5.27	4.90
$W^3\Delta_u$	4.05	4.94	5.64	7.84	5.35	5.22	–	5.23	–	5.37	4.87
$B^3\Sigma_u^-$	4.29	5.07	5.75	6.88	5.49	5.42	5.12	5.33	5.17	5.47	5.26
$G^3\Delta_g$	0.55	1.08	1.55	2.17	1.35	1.32	1.85	1.26	1.55	1.34	1.39
$\langle \varepsilon \rangle$	0.71	0.17	0.68	1.88	0.44	0.34	1.11	0.27	1.37	0.35	
$\langle \varepsilon_{Rel} \rangle$	19.9	5.56	14.8	42.8	9.10	7.15	24.7	6.74	27.9	7.77	

Table 5. D_e for several states of the N_2 molecule, using a multiconfigurational self-consistent-field wave function with four core molecular orbitals (eV)

State	MC	VWN-2	B88-2	WL-2	LYP-2	CSq	CS	MSFq	MSF	MPJ5	Exp.
$X^1\Sigma_g^+$	8.89	10.79	12.03	14.02	11.3	10.85	13.42	11.44	12.83	11.66	9.90
$a^1\Sigma_u^-$	5.31	5.83	6.52	7.52	6.28	6.26	7.08	5.98	6.38	6.11	6.22
$a^1\Pi_g$	3.67	4.20	4.89	6.10	4.68	4.65	4.94	4.35	4.57	4.47	6.08
$A^3\Sigma_u^+$	2.50	3.75	4.52	5.78	4.15	3.90	5.72	4.16	5.18	4.31	3.68
$B^3\Pi_g$	2.44	3.37	4.17	5.69	3.84	3.71	6.34	3.68	4.90	3.83	4.90
$W^3\Delta_u$	4.36	4.45	5.08	6.09	4.87	4.72	5.86	4.66	5.22	4.78	4.87
$B^3\Sigma_u^-$	3.79	4.71	5.41	6.57	5.12	5.00	6.59	5.02	5.88	5.16	5.26
$G^3\Delta_g$	0.40	0.93	1.39	2.02	1.20	1.17	1.98	1.12	1.56	1.20	1.39
$\langle \varepsilon \rangle$	1.42	0.76	0.49	1.05	0.48	0.50	1.20	0.63	0.62	0.54	
$\langle \varepsilon_{Rel} \rangle$	35.2	17.5	9.88	27.0	10.7	11.2	29.4	14.0	14.2	12.1	

dependent functionals are needed when the number of configurations is high as in the case of N_2 .

Summarizing, a CASSCF calculation with an estimation of the CE with the CSq method or the more economics VWN-SIC corrected by Eqs. (1) and (2) can be used for the calculation of excited states PECs, the MSFq and MPJ5 methods need one correction in order to eliminate the N-dependent character, and the search for new expressions for ρ_α and ρ_β in the function of $\Gamma_2(\mathbf{R})$ is needed to improve the CASSCF plus DFT results. We are currently pursuing the application of these methods to other diatomic molecules.

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