

Relationship between singlet–triplet excitation energies and the Kohn–Sham orbitals obtained with potentials that exhibit a wrong asymptotic behavior

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Abstract

A linear relationship was found between the singlet–triplet excitation energy and the energy difference presented by the Kohn–Sham frontier molecular orbitals, independently of the used exchange–correlation functional and of the basis set functions quality. The relationship was explored in three different situations: (a) when the number of carbons is increased in an all-*trans* acetylene family; (b) rotation of the *trans*-butadiene around the single bond; (c) dissociation process of the molecules H₂ and FH. Additionally, it was found a strong relationship between the vertical singlet–triplet excitation energy obtained with the B3LYP and the multiconfiguration-self consistent methods.

1. Introduction

Recently a great interest has been manifested to predict excitation energies in several kinds of systems by using the time-dependent density functional theory (TDDFT) [1]. The principal motivation to use such an approach is that this method contains exchange–correlation effects with a similar computational effort to the random phase approximation. Furthermore when the TDDFT is used with exchange–correlation Kohn–Sham (KS) potentials that exhibit the correct asymptotic behavior the prediction is better [2]. Additionally to TDDFT approach, interesting relations between excitation energies and the energy gap of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been found, if and only if, these orbital energies are

obtained from exchange–correlation potentials that exhibit a correct asymptotic behavior [3]. We should mention that such exchange–correlation potentials can be obtained if the KS equations are inverted [4], or if the optimized effective potential [5,6] is applied with the exact exchange energy [7] or with the self-interaction correction [8]. Also these potentials can be obtained with the constrained search approach [9] or with potentials built ad-hoc to get the correct behavior of the exchange–correlation potential [10]. For all of them large basis sets functions are required. Currently, all of these methods to obtain exchange–correlation potentials with the correct asymptotic behavior are not widely used, instead the chemistry community uses the local density approximation (LDA), the generalized gradient approximation (GGA), or the hybrid methods within the KS approach [11]. Thus, it is interesting to explore if there is a relationship between the HOMO–LUMO gap obtained with common exchange–correlation potentials and excitation energies, in particular the singlet–triplet

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excitation energy, using basis set functions of moderate size. For many reasons the singlet–triplet excitation energy is interesting, for example, it has been recently found that this excitation energy is involved in the photosynthesis process [12]. The reason to be interested in limited basis set functions is related with the fact that in systems of medium or large size is prohibitive to use extended basis set functions.

The aim of this work is to explore the relationship between the gap and the singlet–triplet excitation energies, obtained with widely used exchange–correlation functionals and limited basis set functions, in three different situations: (1) A family of linear polyene chains. (2) Rotation around the single bond in the *trans*-butadiene molecule. (3) Dissociation process of two diatomic molecules; H₂ and FH.

2. Methods

Ten conjugate polyenes were considered, C_{2n}H_{2n+2} with $n = 1, 2, \dots, 10$. All of these systems were studied with the generalized gradient approximation, BLYP [13,14], and with a hybrid method, B3LYP [15]. Optimized geometries were obtained for the systems at singlet state and the total energy was evaluated for the triplet state on the singlet geometry, such that vertical singlet–triplet excitation energies were computed. For the *trans*-butadiene molecule a rotation around of the single bond was made from the *trans* to the *cis* conformer, each 30°, and the vertical singlet–triplet excitation energy was evaluated on each point. For these calculations four basis sets functions were employed; STO-3G [16], 6-311G** [17], DZVP/A1 and

TZVP/A2 [18]. In this way basis set functions of moderate size were tested, also we decided to use auxiliary basis sets to see how is the performance of the fitting approach in conjugate systems when the two-electron Coulomb integrals are approximated. On another side, the dissociation process for the molecules H₂ and FH was studied. For these systems, the B3LYP method was used with the aug-cc-pVTZ basis set [19] without an auxiliary basis set. For the FH molecule the singlet–triplet excitation energy was estimated with the complete active space SCF (CASSCF) method [20], using 10 active orbitals and eight active electrons and the aug-cc-pVTZ basis set. All calculations were done with the NWChem v4.5 program [21].

3. Results and discussion

3.1. Vertical singlet–triplet excitation energy in conjugate polyenes

Several works have shown the performance of TDDFT and DFT in the description of excitation energies in conjugate polyenes, in this work we explore the performance of GGA and hybrid methods in the prediction of the vertical singlet–triplet excitation energy. In Table 1, we are listing the vertical singlet–triplet excitation energies for a set of conjugate polyenes where experimental data are available [22–25]. Also estimations with several theoretical methods, as PT2F and PT2D, are included in Table 1 [26–28]. From this table, it is evident that the PT2F method gives the best comparison with respect to the experimental singlet–triplet excitation energy. However the performance of the

Table 1
Vertical singlet–triplet excitation energy estimated with several methods

Method	Number of carbons			
	2	4	6	8
BLYP/STO-3G	5.12 (17.4)	3.56 (10.6)	2.71 (3.8)	2.21 (5.2)
BLYP/6-311G**	4.60 (5.5)	3.20 (0.6)	2.44 (6.5)	1.98 (5.7)
BLYP/DZVP/A1	4.53 (3.9)	3.18 (1.2)	2.44 (6.5)	1.98 (5.7)
BLYP/TZVP/A2	4.53 (3.9)	3.18 (1.2)	2.44 (6.5)	1.98 (5.7)
B3LYP/STO-3G	5.05 (15.8)	3.73 (15.8)	2.92 (11.9)	2.47 (17.6)
B3LYP/6-311G**	4.54 (4.1)	3.30 (2.5)	2.58 (1.1)	2.15 (2.4)
B3LYP/DZVP/A1	4.51 (3.4)	3.31 (2.8)	2.60 (0.4)	2.17 (3.3)
B3LYP/TZVP/A2	4.48 (2.8)	3.29 (2.2)	2.58 (1.1)	2.16 (2.9)
BLYPTDDFT/6-31++G**		3.04 ^a (5.6)	2.32 ^a (11.1)	1.90 ^a (9.5)
B3LYPTDDFT/6-31++G**		2.83 ^a (12.1)	2.10 ^a (19.5)	1.68 ^a (20.0)
CASSCF/C(4s3p2d), H(3s2p)	4.65 ^b (6.7)	3.39 ^b (5.3)	2.70 ^b (3.4)	2.54 ^c (21.0)
PT2D/C(6s3p1d), H(2s1p)	3.97 ^b (8.9)	3.14 ^b (2.5)	2.55 ^b (2.3)	–
PT2F/C(6s3p1d), H(2s1p)	4.39 ^b (0.7)	3.20 ^b (0.6)	–	2.17 ^c (3.3)
Exp	4.36 ^d	3.22 ^e	2.61 ^f	2.10 ^g

All quantities are in eV. Relative percent error with respect to experimental values is in parentheses.

^a Ref. [28]. For this case the 6-311(2+,2+)G** basis set was used.

^b Ref. [27].

^c Ref. [26].

^d Ref. [22].

^e Ref. [23].

^f Ref. [24].

^g Ref. [25].

B3LYP/TZVP/A2 method also is remarkable, considering that this is computationally cheaper than PT2F method, since we are using an auxiliary basis set for the B3LYP calculation. This performance is slightly modified when the DZVP/A1 basis set is used. The result of B3LYP with the basis set 6-311G** is between the B3LYP/DZVP/A1 and B3LYP/TZVP/A2 methods, although for 6-311G** basis set there is no auxiliary basis set and consequently it is computationally more expensive since the fitting approach reduce the time to compute the Coulomb two-electron integrals. As it was expected the minimal basis set gives the worst estimation for the excitation energies.

With respect to the BLYP/TZVP/A2 method, it is clear from Table 1 that its performance is not as good as the B3LYP/TZVP/A2 method. However BLYP gives better results than CASSCF and PT2D approaches. Curiously, same results are obtained if the DZVP/A1 basis set is used, as we can see for BLYP/DZVP/A1 results in Table 1.

From the results discussed above, it is obvious that the B3LYP/TZVP/A2 gives good estimations for the vertical singlet–triplet excitation energies in small *trans*-acetylenes. However, if one tries to relate the B3LYP/TZVP/A2 results with those obtained with BLYP/TZVP/A2, from the four values tabulated in Table 1 it is found a linear relationship with a slope of 0.9111, a y -intercept of 0.3646, and a correlation coefficient of 0.9997. Such a relationship is maintained when the whole *trans*-acetylene family is considered. This result is important since the B3LYP method is more expensive than the BLYP, thus for a large system we can use just the BLYP method and the linear relationship to predict a better singlet–triplet excitation energy.

As it has been pointed out, the TDDFT with the B3LYP exchange–correlation functional is not appropriate for linear polyene chains since it predicts narrow vertical singlet–triplet excitation energies when the length of the chain is increased [29]. We can see such a behavior even for small polyene chains in Table 1.

3.2. HOMO–LUMO gap

Before to relate the HOMO and LUMO energy difference with the vertical singlet–triplet excitation energy, we want to explore the behavior of the HOMO and LUMO energies in the *trans*-acetylene family considered in this work. In Fig. 1, we are plotting the B3LYP HOMO and LUMO energies as a function of the number of carbons in the linear polyene set. From this figure, it is clear that the HOMO energy goes up while the LUMO energy goes down to reach a limit value, independently of the basis set used. This observation is in agreement with previous results [30]. Of course, these orbital energy values depend strongly in the basis set but the qualitative behavior is preserved for all of them. The same trend of Fig. 1 was obtained with the BLYP exchange–correlation functional. However, it was found that the B3LYP HOMO energy is deeper than the corresponding BLYP and contrary to this,

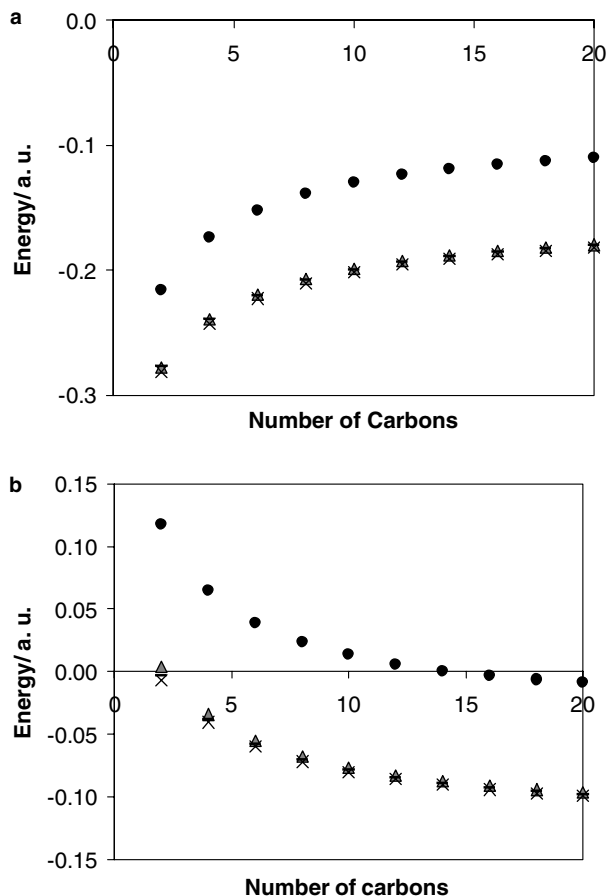


Fig. 1. (a) HOMO and (b) LUMO energies behavior as a function of the number of carbon atoms in the *trans*-polyacetylene obtained with the B3LYP method. ●, STO-3G; ▲, 6-311G**; ○, DZVP/A1; ×, TZVP/A2.

the BLYP LUMO energy is deeper than that obtained with the B3LYP method. This behavior is in agreement with the differences between orbital energies obtained with a non-local or a local potential [31,32]. From this figure it is clear that the minimal basis set gives higher orbital energies than those obtained with others basis sets for about 0.1 a.u. or more.

The increase of the HOMO energy and the decrease of the LUMO energy give, as a consequence, a narrow gap when the number of atoms of carbon is augmented; as it can be seen in Fig. 2. It can be observed that the basis set dependence is important for the gap value. From this figure it is clear that if the basis set size is smaller the gap will be bigger, but the qualitative behavior is preserved. Furthermore, the good results obtained with the minimal basis set imply that the error cancellations, to compute the gap, are important.

Recently the HOMO–LUMO gap has been related with the lowest singlet–singlet transition [33]. However, it has been shown that in halocarbenes the spin-potential can be correlated with the lowest singlet–triplet excitation energy [34]. The relationship between the vertical singlet–triplet excitation energy with the HOMO–LUMO gap obtained with the B3LYP/TZVP/A2 method, is depicted

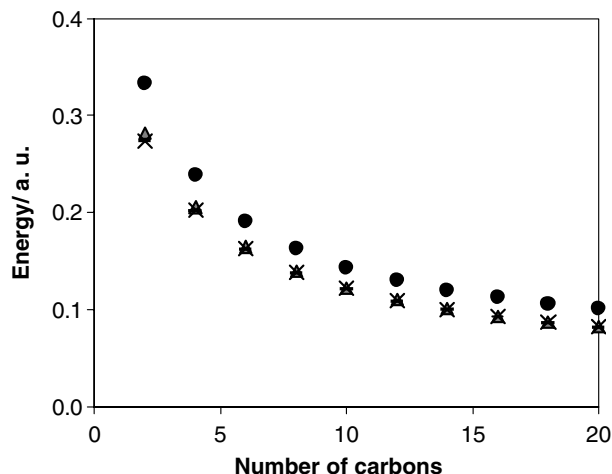


Fig. 2. HOMO-LUMO gap behavior as a function of the number of carbon atoms in the *trans*-polyacetylene obtained with the B3LYP method. ●, STO-3G; ▲, 6-311G**; ■, DZVP/A1; ×, TZVP/A2.

in Fig. 3. From this figure, it is evident that there is a perfect linear relationship between the gap and the vertical singlet-triplet excitation energy. In Table 2, we are reporting the linear parameters obtained with the exchange-correlation functionals and the basis sets functions considered in this work. From Table 2, it is clear that even using the minimal basis set such a linear relationship is preserved. Additionally, we can see that always the gap overestimates the vertical singlet-triplet excitation energy.

3.3. Rotation in the *trans*-butadiene

In the previous section, we discussed the correlation between singlet-triplet excitation energy and the HOMO-LUMO gap for a set of molecules where the geometry was optimized. In this section, a different situation is considered; the rotation around the single bond in the *trans*-butadiene. As in the all *trans*-polyacetylene molecules for the butadiene we also found a linear relationship between

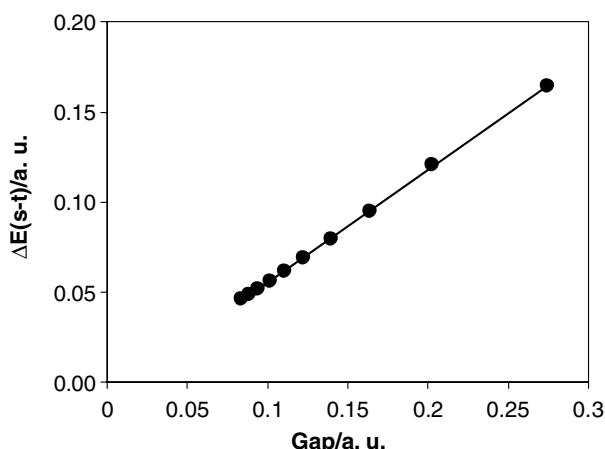


Fig. 3. Relationship between singlet-triplet excitation energy and the HOMO-LUMO gap obtained with the B3LYP/TZVP/A2 method.

Table 2
Parameters of the linear fitting for the singlet-triplet excitation as a function of HOMO-LUMO gap for 10 *trans*-polyacetylene molecules

	Slope	y-Intercept	R^2
<i>BLYP</i>			
STO-3G	0.7466	0.0004	0.9994
6-311G**	0.7953	0.0017	0.9998
DZVP/A1	0.7930	0.0019	0.9998
TZVP/A2	0.8032	0.0015	0.9999
<i>B3LYP</i>			
STO-3G	0.5632	0.0002	0.9990
6-311G**	0.6414	0.0079	0.9655
DZVP/A1	0.6198	0.0069	0.9998
TZVP/A2	0.6305	0.0077	0.9998

the singlet-triplet excitation energy and the HOMO-LUMO gap. The linear parameters of such linear relations are reported in Table 3. It is important to remark that the gap obtained with B3LYP always underestimates the singlet-triplet excitation energy. This is not true for the exchange-correlation functional BLYP with the basis sets TZVP/A2 and DZVP/A1, where correlation coefficient of the linear fitting is worse.

3.4. Diatomic molecules

Now, we will consider the dissociation of two diatomic molecules, which is a different situation to those discussed in previous sections. It has been reported that the B3LYP/aug-cc-pVTZ method gives the same results that the CCSD/aug-cc-pVTZ for the description of the ground state and the lowest triplet state dissociations of the H_2 molecule [35]. Thus, it is interesting to explore if a linear relationship between the singlet-triplet excitation energy and the gap is preserved in this case. In Fig. 4, we are presenting such a relationship. From this figure, it is clear that even in this situation a linear correlation is obtained. It is important to mention that in this example, and in the next, the plot was obtained by using an unrestricted approach since it is necessary for a large separation between the atoms. Because in the unrestricted approach the multiplicity cannot be well defined, we found that if the spin contamination is present then the linear relationship cannot be obtained.

Table 3
Parameters of the linear fitting for the singlet-triplet excitation as a function of HOMO-LUMO gap in the rotation of the *trans*-butadiene

	Slope	y-Intercept	R^2
<i>BLYP</i>			
STO-3G	1.0801	-0.0487	0.9996
6-311G**	1.1008	-0.0398	0.9984
DZVP/A1	0.8569	-0.0041	0.9791
TZVP/A2	0.8759	-0.0062	0.9803
<i>B3LYP</i>			
STO-3G	1.0796	-0.1195	0.9998
6-311G**	1.1069	-0.1045	0.9985
DZVP/A1	1.0967	-0.1011	0.9981
TZVP/A2	1.1076	-0.1021	0.9976

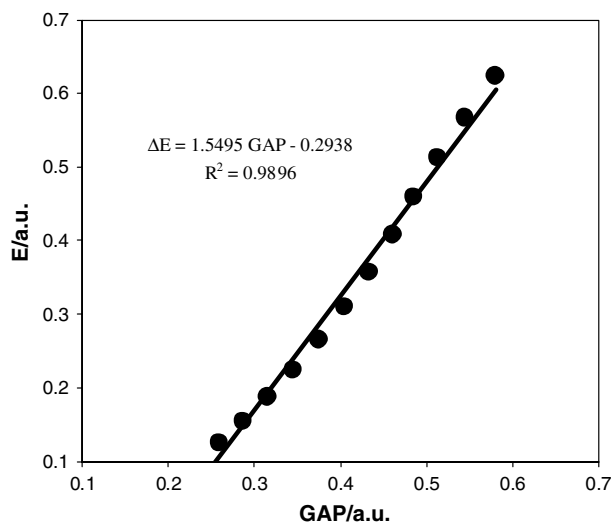


Fig. 4. Relationship between vertical singlet–triplet excitation energy and the HOMO–LUMO gap along of the dissociation of the H_2 molecule. Bond length distances used: 0.3, 0.4, ..., 1.4 Å such that there is not spin contamination.

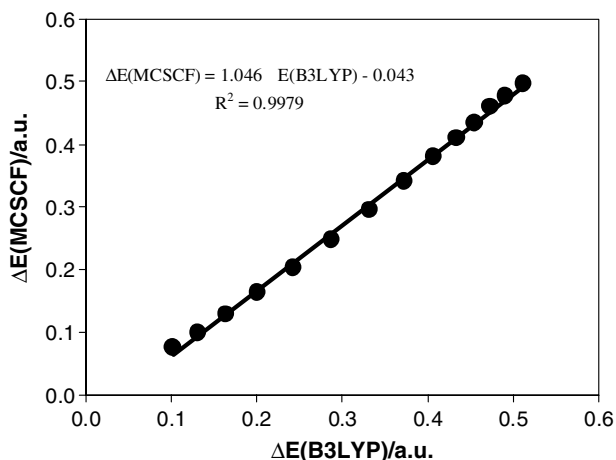


Fig. 5. Comparison of the vertical singlet–triplet excitation estimated with MCSCF, by using 10 active orbitals and eight electrons, and B3LYP methods. In both methods the aug-cc-pVTZ basis set was used.

Another example considered in this work was the FH molecule dissociation. For this system, we evaluated the singlet–triplet excitation energies with B3LYP/aug-cc-pVTZ and they were compared with the excitation energies obtained from MCSCF/aug-cc-pVTZ. The relationship between both methods is depicted in Fig. 5. It is well known that the MCSCF calculations are more expensive than those obtained with the KS method; from Fig. 5, we can see that MCSCF singlet–triplet excitation energies are related in a linear way with those predicted by the B3LYP method. Finally, the B3LYP singlet–triplet excitation energies were correlated with the HOMO–LUMO gap obtained from the ground state with a slope of 0.6696, a y -intercept of 0.1484, and a correlation coefficient of 0.9954.

4. Conclusions

In this work, we have shown that there is a linear relationship between the vertical singlet–triplet excitation energy and the gap obtained with the Kohn–Sham HOMO and LUMO energies, such a relationship is valid even when the exchange–correlation potential does not show the correct asymptotic behavior. As it is known, the Kohn–Sham approach is valid for states with non-holes in the electronic configuration, it looks like that such information is contained in the virtual orbitals since the triplet excited state is favored with respect to the singlet excited state.

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