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On the TD-DFT Accuracy in Determining Single and Double Bonds in Excited-State Structures of Organic Molecules

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We present an analysis on the behavior of the TD-DFT approach in the determination of excited-state structures with particular attention to single and double bonds. The analysis is based on a direct comparison with the highly correlated CASPT2 *ab initio* approach. Six DFT exchange–correlation functionals differing in the Hartree–Fock exchange percentage and the type of correlation functional are considered and applied to the study of seven prototype organic molecules characterized by two families of excitations (acrolein, acetone, diazomethane, and propanoic acid anion for $n-\pi^*$ and *cis*-1,3-butadiene, *trans*-1,3-butadiene, and pyrrole for $\pi-\pi^*$), and three protonated Schiff bases, used as model chromophores for 11-*cis* retinal. Our analysis allows pinpointing specific correlations between accuracy of the various functionals and category of excitation and/or type of chemical bond involved in the corresponding geometry relaxation. We confirm the role of the long-range correction of the potential to obtain a balanced description of excitation energies and excited-state structures, but we also point out that, for a small system, B3LYP and PBE0 also give results close to CASPT2.

1. Introduction

There is a broad interest in the properties of electronic excited states ranging from spectroscopy to photochemistry and biology.^{1,2} For example, the study of fluorescent molecules is crucial for different fields of science and technology encompassing a wide range of industrial applications, such as the development of photovoltaic cells, organic light emitting diodes (OLED), new textiles and plastics, and diagnostic probes in biology and medicine.³ For these applications, fluorescent dyes have to satisfy a number of constraints, such as minimal overlap between absorption and emission bands, large quantum yields, and photochemical stability. Therefore, the understanding and prediction of both the optical and the spectroscopic properties of these chromophores in different environments are major issues.

Nowadays, *ab initio* methods allow for accurately determining a large set of properties for molecular systems in their ground state. On the contrary, calculations of excited-state properties, including emission phenomena such as fluorescence and phosphorescence, are still a challenge, because they require the non-trivial task of an accurate determination of excited-state structures.⁴ On the one hand, fast and cheap purposely tailored semiempirical approaches lack consistency when applied to families of molecules not included in the original training sets. On the other hand, more reliable theoretical tools, such as EOM-CC,^{5,6} MR-CI,^{7,8} CAS-PT2,^{9–11} SAC-CI,^{12,13} are too expensive to afford the study of the large systems of chemical and industrial interest. At the same time, it is well established that the Kohn–Sham approach to density functional theory

(DFT) can provide an accurate description of a large number of physicochemical properties for the ground electronic state.¹⁴ Furthermore, the current accuracy/cost ratio is significantly lower than that of more sophisticated post-Hartree–Fock approaches. In a similar manner, the linear response (LR) approach applied to DFT, also known as time-dependent density functional theory (TD-DFT),¹⁵ could be a viable alternative for the evaluation of excited-state geometries and properties.

In the TD-DFT formulation, based on the extension to the action functional of Hohenberg and Kohn theorems, as in random phase approximation¹⁶ and Tamm–Damcoff¹⁷ approximation, a pseudoeigenvalues equation, where the Lagrange multiplier matrix (Ω) contains excitation energies, can be written down. Consequently, first-order molecular properties can be calculated by analytical derivatives of Ω ,^{18,19} by using a Z-vector approach,²⁰ and this introduces the calculation of third-order derivatives of XC functional used.

The TD-DFT approach presents the typical problems of ground-state DFT methods: the exact XC functional form is unknown, the approximated functionals introduce self-interaction (SI) errors, the asymptotic behavior of XC potential could be incorrect, and the use of a single determinant makes DFT inadequate for cases presenting a near degeneracy of several configurations. Besides, additional drawbacks originating in the LR formulation exist.²¹ Actually, almost all implementations of TD-DFT are based on the adiabatic approximation, for which the action functional could be written by using the XC energy functional used in Kohn–Sham time-independent equation. In other words, there are no memory effects, the only time dependence is indirectly taken into account by the density, and an instantaneous reaction of XC potential to the density variations is assumed. From a more applicative point of view, the use of TD-DFT approach presents some difficulties in describing charge transfer and Rydberg excitations. This

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originates in the form of the operators in the LR-TD-DFT equations and the subsequent incapability to follow the reorganization of charge between two separated regions of space or between orbitals of different spatial extent.^{21,22} Despite these formal limits, there are extended studies that show the very good performances of TD-DFT in reproducing excitation energies and absorption spectra.^{23–26} However, to the best of our knowledge, systematic investigations of the excited-state structures and fluorescent properties have yet to be carried out. In fact, some works, devoted to the implementation of TD-DFT analytical derivatives, have partially (limited number of molecules and functional) analyzed this aspect (see for instance ref 19).

The aim of this Article is to contribute to fill this gap by unravelling specific behaviors of TD-DFT in comparison with the highly correlated CASPT2 method. To this end, we have considered different exchange-correlation (XC) functionals, whose choice reflects the aim of analyzing both the influence of Hartree–Fock exchange (HF-X) percentage once the correlation functional was fixed (B3LYP, BH&HLYP, and CAM-B3LYP), and the influence of the description of correlation at almost the same HF-X (B3LYP, B3P86, and PBE0). BMK functional is also included to have an intermediate HF-X percentage and to test also a functional originally developed for kinetics and chemical reaction description.

This Article is organized as follows: in section 2, we report the computational details together with a brief summary of the methods used (TD-DFT and the various functionals, CASPT2). In section 3, we compare TD-DFT vertical excitation energies and excited-state optimized structures to CASPT2. Finally, in section IV, we report some conclusions and future directions.

2. Computational Details

All DFT and TD-DFT calculations have been carried out with the G09 program,²⁷ using six different exchange-correlation functionals characterized by a different HF-X contribution. The set includes five global hybrids (GH), B3LYP²⁸ (20% of HF-X), B3P86^{28,29} (20% of HF-X), PBE0³⁰ (25% of HF-X), BMK³¹ (42% of HF-X), BH&HLYP³² (50% of HF-X), and one range-separated hybrid (RSH), CAM-B3LYP.³³ In this last functional, the HF exchange percentage smoothly varies between the two asymptotic values of 19% (short-range) and 65% (long-range). The relative performances of GH and RSH for absorption spectra have been evaluated previously.^{23,26,34}

Linear response TD-DFT calculations were carried out to obtain vertical excitation energies, and the recent development of analytical derivatives¹⁹ was used for the exploration of excited-state potential energy surface. Generally, a medium size basis set (valence double- or triple- ζ basis) already gives converged results for valence transitions when both polarization and diffuse functions are added. In particular, Pople's 6-311+G(2d,p) provides converged transition energies of low-lying states for the majority of investigated dyes, while the compact 6-31+G(d) basis represents a valuable compromise between accuracy and computational speed.^{23,35} It has been shown that larger basis sets, including very diffuse functions, are mandatory when higher energy states (e.g., Rydberg) are sought.³⁶ These highly excited cases are not treated in this work; therefore, all the calculations (geometry optimization, absorption, and dipole moments) have been carried out with the 6-31+G(d) basis set. However, basis set effects have been tested by using seven small and medium-sized basis sets during TD-DFT optimizations, including Pople's 6-31G(d), 6-311G(d) and Dunning's cc-pVDZ, cc-pVTZ, *aug*-cc-pVDZ, and *aug*-cc-pVTZ basis sets³⁷ for all systems with all functionals used in this Article. The obtained results well underline that

the convergence is already reached with the selected basis set, 6-31+G(d), and, therefore, they are reported and discussed in the Supporting Information.³⁸

We appraise the qualities of the selected XC functionals by comparing TD-DFT results to CASPT2/6-31G(d) reference values for which the active space was unambiguously selected, to include the valence molecular orbitals, together with lone pair orbitals where appropriate, as reported in ref 39, and CASPT2/cc-pVDZ as reported in ref 40. The CASPT2 calculations we have used are carried out without any diffuse function, and thus are probably insufficient to accurately describe excited states that are spatially extended and have partial Rydberg character. In the present study, however, the focus interest is in the low-lying valence excited states with a compact electron density. In these cases, we are confident that the selected basis is sufficient to have a correct picture as also shown in the study of Schreiber et al.⁴¹

3. Results and Discussion

The core of molecules considered for the present study is constituted by the set of small organic chromophores originally selected by the reference CASPT2 study of Page and Olivucci³⁹ (see Figure 1).

Their excitations can be considered as prototypes of $n-\pi^*$ or $\pi-\pi^*$ transitions. As representative examples of $n-\pi^*$ systems, we studied acrolein (ACR), acetone (ACT), propenoic acid anion (PAA), and diazomethane (DZM), whereas *cis*-buta-1,3-diene (CBD), *trans*-buta-1,3-diene (TrBD), and pyrrole (PYR) constitute the $\pi-\pi^*$ set.

ACR is an example of a conjugated hydrocarbon where the first excited state corresponds to a $n-\pi^*$ transition, and it can be compared to ACT and PAA to get more insights on the impact of the conjugation on $n-\pi^*$ excited-state structures. DZM is a model structure for studying $n-\pi^*$ excitation in diazo-compound. CBD and TrBD are representative systems of the class of conjugated hydrocarbons, and they are used to study $\pi-\pi^*$ excitations. Finally, PYR is a cyclic nitrogen-bearing compound, allowing one to compare the C–N bond behavior in $\pi-\pi^*$ excitations.

As a further analysis, the original set of molecules has been supplemented with three chromophores belonging to the class of protonated Schiff bases (PSB) that present $\pi-\pi^*$ excitations (from now on they will be labeled as MDB, model B, MDC, model C, and MDD, model D; see Figure 1). Recently, these chromophores have been used as model systems in an investigation of the structure relaxation in the excited state of 11-*cis* retinal by means of CASSCF, CASPT2, CC, and QMC methods.⁴⁰ Note that the description of the excited states of medium and large PSB or related cyanine-like molecules remains challenging for TD-DFT that tends to overestimate the transition energies.^{42,43} It appears that RSH functional cannot cure the problem,⁴⁴ although the incorrect TD-DFT predictions are probably not related to the multideterminantal nature of these compounds.⁴⁵

3.1. Ground-State Structures: DFT versus CASPT2. Some of the considered functionals (e.g., B3LYP, B3P86, PBE0, BMK) have been accurately tested on a large number of molecular properties, including ground-state structures of organic molecules. In particular, errors of about 0.01 Å are expected for bond lengths with the considered GHs.^{28–32} No general and extensive tests on geometries have been carried out (there are only on particular type of systems or selected properties), to the best of our knowledge, for the selected RSH. Therefore, before moving to the analysis of excited-state properties and

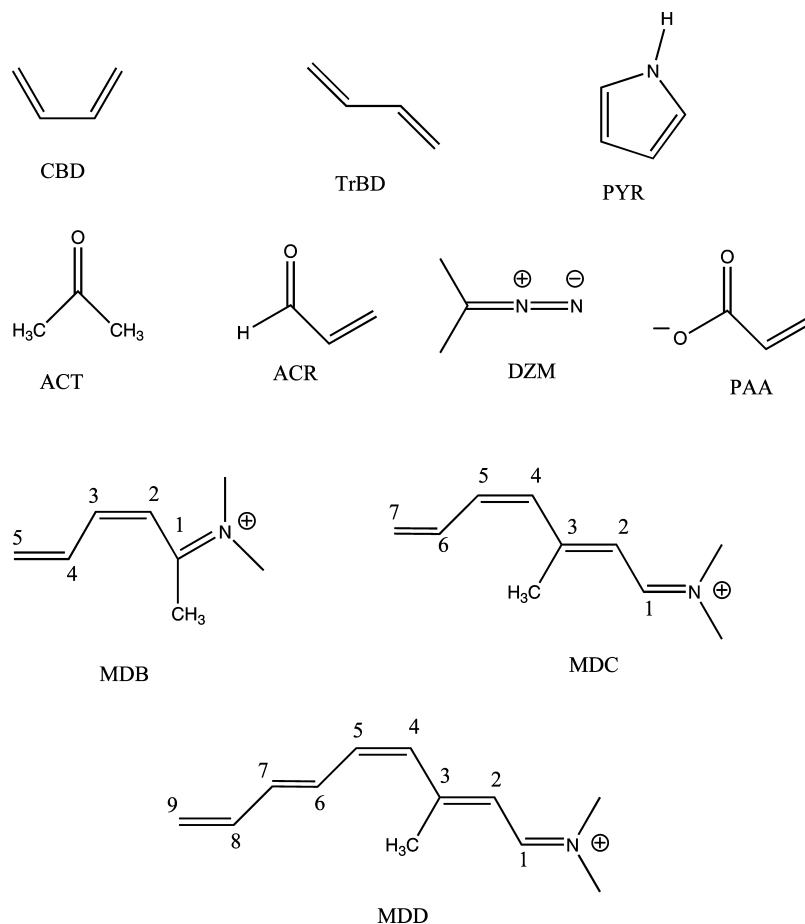


Figure 1. Molecular structures of systems considered in this study. From the top: *cis*-buta-1,3-diene (CBD), *trans*-buta-1,3-diene (TrBD), pyrrole (PYR), acrolein (ACR), acetone (ACT), diazomethane (DZM), propenoic acid anion (PAA), and the three protonated Schiff bases (MDB, MDC, and MDD).

structures, it is interesting to briefly investigate ground-state optimized structures. Table 1 reports the variations of structural parameters for each molecule with respect to CASPT2 values. In this preliminary analysis on GS structures, only the set of molecules proposed by Page and Olivucci³⁹ will be considered.

As shown by the data reported in the table, in most cases DFT overestimates ground-state single bond lengths and underestimates double bond lengths with respect to CASPT2, and this holds for all tested molecular systems, with the exception of *trans*-buta-1,3-diene that shows an opposite behavior. Percentage errors are around 1–2% for the underestimation of double bonds and around 1% for the overestimation of single ones. In more details, C–C single bonds are accurately estimated by PBE0 and BH&HLYP functionals, BMK yielding (>1%) too long bonds (deviations between 0.013 and 0.024 Å). For the other functionals, values are always smaller than 0.017 Å. The sensitivity of the C=C double bonds to the selected functional is larger, with the best agreement reached by B3LYP calculations (between 0.001 and 0.008 Å, corresponding to 0.1–0.3% deviations) and the worst one obtained with BH&HLYP (from 0.012 and 0.021 Å, 0.9–1.5%). This tendency to larger variations is observed also for other double bonds; for example, C=O double bonds present a behavior similar to C=C, the optimal description being obtained with B3LYP (0.006–0.008 Å, ca. 0.5%), whereas BMK and BH&HLYP errors are close to 2%. The CN bond is described with deviations close to 1%, the best performances being again reached with B3LYP (0.002 Å for PYR and 0.007 Å for DZM) and the worst results still coming from BH&HLYP (0.010 Å for PYR and 0.017 Å for

DZM). The DFT-CASPT2 differences for the NN bond of DZM range between 0.7% (BMK) and 2.5% (BH&HLYP).

Angles are very well estimated by all functionals with deviations with respect to CASPT2 values systematically smaller than 1% (0.1–0.8°).

From this first analysis, we can conclude that there is a general behavior of DFT functionals to overestimate single bond lengths and underestimate their double counterparts, which means that DFT provides a slightly too localized picture. Let us highlight that this statement holds only for these small molecules. Indeed, in large conjugated systems, such as polyene oligomers, it is well-known that GHs like B3LYP tend to yield (much) too small bond length alternations, and that RSHs or GHs including a large share of HF-X are necessary to restore a more balanced description.⁴⁶

In summary, for the systems under scrutiny, the deviations are very small in the GS case, with errors smaller than 0.03 Å for bonds and 1° for valence angles. Best (worst) accuracies, in average, are given by B3LYP (BH&HLYP). CAM-B3LYP also shows good performances, in many cases close to B3LYP ones.

3.2. Vertical Excitation Energies: TD-DFT versus CASPT2.

As mentioned in the Introduction, a large number of tests on TD-DFT performances in vertical excitation energies is available in literature. In particular, our recent extensive benchmark on valence excitations shows that GH containing 20–25% of HF-X gives the best agreements with respect to post-HF results, for relatively small molecules.²³ Indeed, the MAEs for considered functionals range between 0.22 eV (B3LYP, PBE0) and 0.45

TABLE 1: Computed Bond Length (Å) and Angle (deg) Differences for DFT/6-31+G(d) Ground-State Structures with Respect to CASPT2/6-31G(d) (6-31+G(d) for PAA)^a

	B3LYP	B3P86	PBE0	BMK	BH&HLYP	CAM-B3LYP	CASPT2
<i>cis</i> -Buta-1,3-diene							
C–C	0.005	–0.001	0.000	0.015	0.000	0.005	1.468
C=C	–0.008	–0.011	–0.011	–0.008	–0.021	–0.016	1.351
C=C–C	0.6	0.4	0.4	–0.1	0.3	0.2	126.7
<i>trans</i> -Buta-1,3-diene							
C–C	–0.004	–0.007	–0.008	–0.004	–0.017	–0.012	1.454
C=C	0.004	–0.001	0.000	0.014	0.002	0.006	1.348
C=C–C	0.7	0.6	0.6	0.2	0.5	0.5	123.6
Pyrrole							
C–N	0.002	–0.004	–0.006	–0.006	–0.010	–0.004	1.375
C=C	0.001	–0.002	–0.003	0.005	–0.012	–0.006	1.380
C–C	0.007	0.002	0.002	0.013	0.000	0.003	1.420
C–N–C	–0.132	–0.026	0.024	0.262	–0.189	–0.222	110.0
C=C–N	0.1	0.1	0.1	0.3	0.3	0.3	107.5
C–C=C	–0.1	–0.1	–0.2	–0.4	–0.2	–0.1	107.5
Acrolein							
C=O	–0.008	–0.012	–0.018	–0.026	–0.023	–0.014	1.226
C–C	0.006	0.001	0.006	0.017	0.000	0.010	1.469
C=C	–0.004	–0.007	–0.011	–0.011	–0.016	–0.011	1.345
O=C–C	0.6	0.7	0.7	0.4	0.5	0.5	123.6
C–C=C	–0.1	–0.4	0.2	–0.5	–0.2	–0.3	121.1
Acetone							
C=O	–0.007	–0.010	–0.012	–0.015	–0.021	–0.012	1.226
C–C	0.008	0.001	0.000	0.016	–0.003	0.001	1.511
C–C=O	–0.1	0.0	0.0	0.0	–0.1	–0.1	121.7
Diazomethane							
N=N	–0.012	–0.015	–0.017	–0.008	–0.029	–0.019	1.158
C=N	–0.007	–0.011	–0.012	–0.014	–0.017	–0.011	1.302
Propenoic Acid Anion							
C–O <i>trans</i>	–0.007	–0.011	–0.013	–0.018	–0.024	–0.014	1.272
C–O <i>cis</i>	–0.006	–0.010	–0.011	–0.016	–0.021	–0.012	1.266
C–C	0.012	0.005	0.006	0.024	0.002	0.007	1.526
C=C	–0.004	–0.007	–0.007	–0.003	–0.016	–0.010	1.343
O=C–C	0.2	0.1	0.0	–0.1	0.0	0.1	116.8
C–C=C	0.6	0.1	0.1	0.0	0.2	0.2	124.0
O=C–O	0.0	0.1	0.2	0.4	0.2	0.0	129.0

^a CASPT2 reference values taken from ref 39 are reported in the last column.

eV (BH&HLYP), CAM-B3LYP and BMK showing an intermediate behavior (0.35 eV). Of course, these are mean values, and the actual performance of a functional significantly changes with the considered chromophore.²³ As for the GS geometries, it is therefore interesting to shortly comment on the vertical absorption energies.

In Table 2, we report the vertical excitation energies for all selected molecules, computed at the corresponding optimized geometries.

There is a general agreement between TD-DFT and CASPT2 results, almost all the functionals showing a MAE ≤ 0.3 eV, a deviation not too far from that obtained on a much larger set.²³ Here, however, the lowest difference is obtained by B3P86 and BMK functionals (MAE of 0.21 and 0.22, respectively). In more details, the differences are of the order of 0.2–0.4 eV for CAM-B3LYP and 0.1–0.3 eV BMK functionals in all molecular systems studied, and in the 0.2–0.6 eV range for the other four functionals. In general, TD-DFT underestimates $n\rightarrow\pi^*$ excitations and overestimates the $\pi\rightarrow\pi^*$ ones. The most valuable performances are obtained by BH&HLYP (BMK) for $\pi\rightarrow\pi^*$ excitations and B3P86 for $n\rightarrow\pi^*$ excitations.

We further note that in the case of our calculation on PSBs, B3LYP is the functional that better performs with respect to CASPT2 data of Valsson and Filippi. In this last case, however,

CASPT2 vertical excitations have been calculated using B3LYP/cc-pVDZ structures.⁴⁰

3.3. Excited-State Structures and Properties. The most relevant geometrical parameters of the optimized geometries for each of the selected excited states are reported in Tables 3 and 4. Nomenclature of bonds is referred to ground-state structure. For each molecule, we have optimized the lowest singlet excited state with the exception of PYR, for which the first low-lying 1B_2 state has been selected, for the sake of consistency with the reference CASPT2 calculation.³⁹

Starting with $\pi\rightarrow\pi^*$ systems, we note that the CC single bonds in CBD and TrBD are overestimated with respect to the reference CASPT2 values, and this holds for all functionals but BH&HLYP and CAM-B3LYP, which underestimate the bond lengths. PBE0 provides the best agreement, with differences less than 0.002 Å (<0.2%). In general, differences for all functionals are less than 0.012 Å.

In the case of PSBs, two types of CC single bonds have to be defined. The first one forms the skeleton of π conjugation, and it is therefore directly involved in the $\pi\rightarrow\pi^*$ excitation, whereas the second one connects the methyl group. The two CC single bonds present different behavior: the length of the first is overestimated by low percentage HF-X functional and underestimated by BH&HLYP and CAM-B3LYP, while the

TABLE 2: Calculated UV Vertical Excitation Energies (eV), Oscillator Strength (in Parentheses), and Symmetry (sym) of Singlet Excited States^a

system	sym	B3LYP	B3P86	PBE0	BMK	BH&HLYP	CAM-B3LYP	CASPT2	MV	RSD
<i>cis</i> -buta-1,3-diene	B ₂	5.00 (0.31)	5.10 (0.32)	5.10 (0.31)	5.30 (0.31)	5.30 (0.32)	5.20 (0.31)	5.60 (0.22)	5.17	0.02
<i>trans</i> -buta-1,3-diene	B _u	5.60 (0.65)	5.70 (0.67)	5.70 (0.67)	5.90 (0.71)	5.90 (0.74)	5.90 (0.70)	6.20 (0.69)	5.78	0.02
pyrrole	B ₂	6.00 (0.18)	6.30 (0.19)	6.20 (0.19)	6.50 (0.29)	6.30 (0.19)	6.20 (0.19)	6.30 (n.a.)	6.25	0.02
acrolein	A''	3.60 (0.00)	3.60 (0.00)	3.70 (0.00)	3.70 (0.00)	4.10 (0.00)	3.80 (0.00)	3.60 (0.00)	3.75	0.05
acetone	A ₂	4.40 (0.00)	4.40 (0.00)	4.50 (0.00)	4.40 (0.00)	4.70 (0.00)	4.50 (0.00)	4.20 (0.00)	4.48	0.02
diazomethane	A ₂	2.90 (0.00)	3.00 (0.00)	3.00 (0.00)	2.80 (0.00)	3.00 (0.00)	2.90 (0.00)	2.70 (0.00)	2.93	0.03
propenoic acid anion	A''	3.60 (0.00)	3.70 (0.00)	3.80 (0.00)	4.30 (0.00)	4.80 (0.00)	4.30 (0.00)	n.a.	4.08	0.10
model B	A'	4.21 (0.64)	4.25 (0.64)	4.29 (0.65)	4.36 (0.67)	4.52 (0.74)	4.31 (0.70)	4.18 (n.a.)	4.32	0.02
model C	A'	3.47 (1.01)	3.51 (1.01)	3.54 (1.04)	3.71 (1.15)	3.58 (1.07)	3.60 (1.09)	3.35 (n.a.)	3.57	0.02
model D	A'	3.00 (1.35)	3.04 (1.36)	3.06 (1.38)	3.15 (1.43)	3.16 (1.49)	3.12 (1.44)	2.87 (n.a.)	3.09	0.02
MAE		0.32	0.26	0.27	0.20	0.32	0.25			

^a CASPT2 values are taken from ref 38 for TrBD, PYR, and ACT, from ref 52 for CBD, from refs 53 and 54 for ACR, from ref 55 for DZM, and from ref 40 for PSBs. See text for details. PAA CASPT2 data are not available (n.a.). Mean values (MV) and relative standard deviations (RSD) are also reported.

TABLE 3: Computed Bond Length (Å) and Angle (deg) Differences for TD-DFT/6-31+G(d) Excited-State Structures with Respect to CASPT2/6-31G(d) (6-31+G(d) for PAA)^a

	B3LYP	B3P86	PBE0	BMK	BH&HLYP	CAM-B3LYP	CASPT2
<i>cis</i> -Buta-1,3-diene							
C–C	0.008	0.003	0.002	0.007	–0.008	–0.003	1.398
C=C	–0.001	–0.003	–0.004	0.005	–0.010	–0.005	1.421
C=Ĉ–C	–0.2	–0.6	–0.5	–0.6	–0.5	–0.5	122.0
<i>trans</i> -Buta-1,3-diene							
C–C	0.005	0.002	0.000	0.006	–0.012	–0.006	1.399
C=C	0.003	0.001	0.000	0.010	–0.005	–0.001	1.421
C=Ĉ–C	0.4	0.4	0.3	0.1	0.3	0.2	124.1
Pyrrole							
C–N	–0.022	–0.019	–0.029	–0.014	–0.033	–0.025	1.416
C=C	–0.011	–0.012	–0.015	0.000	–0.019	–0.013	1.461
C–C	–0.001	–0.004	–0.005	0.001	–0.012	–0.008	1.370
C–N̂–C	–1.4	–1.3	–1.3	–1.5	–5.8	–1.4	107.3
C=Ĉ–N	0.4	0.1	0.3	0.1	0.4	0.4	108.1
C–Ĉ=C	–0.2	–0.2	–0.3	–0.3	–0.2	–0.2	108.2
Acrolein							
C=O	–0.052	–0.059	–0.061	–0.061	–0.065	–0.056	1.277
C–C	0.008	0.004	0.008	0.036	0.028	0.027	1.429
C=C	–0.005	–0.008	–0.013	–0.022	–0.040	–0.032	1.350
O=Ĉ–C	5.3	6.0	5.5	2.5	1.8	2.6	125.4
C–Ĉ=C	0.5	0.4	0.6	0.5	1.0	0.8	122.5
Acetone							
C=O	–0.037	–0.043	–0.048	–0.064	–0.071	–0.053	1.368
C–C	0.008	0.001	0.002	0.027	0.010	0.010	1.489
C–Ĉ=O	0.8	0.8	1.0	1.5	1.6	1.1	117.0
Diazomethane							
N=N	–0.010	–0.013	–0.014	0.012	–0.012	–0.011	1.215
C=N	–0.022	–0.025	–0.030	–0.042	–0.053	–0.036	1.327
Propenoic Acid Anion							
C–O <i>trans</i>	0.021	0.014	0.014	0.016	0.015	0.016	1.272
C–O <i>cis</i>	–0.099	–0.104	–0.106	–0.106	–0.111	–0.100	1.394
C–C	0.023	0.018	0.016	0.017	0.000	0.006	1.401
C=C	0.006	0.004	0.001	0.004	–0.018	–0.009	1.409
O–Ĉ–C	8.9	9.1	9.0	8.8	9.0	8.0	117.3
C–Ĉ=C	–1.6	–1.9	–1.8	–1.6	–0.8	–1.9	126.7
O–Ĉ–O	–4.4	–4.7	–4.7	–4.6	–4.4	–4.3	111.8

^a CASPT2 reference values taken from ref 39 are reported in the last column.

TABLE 4: Computed Bond Length (Å) and Angle (deg) Differences for TD-DFT/6-31+G(d) Excited-State Structures of *cis*-Retinal Model with Respect to CASPT2/cc-pVDZ^a

	B3LYP	B3P86	PBE0	BMK	BH&HLYP	CAM-B3LYP	CASPT2
Model B Cs							
N=C	-0.021	-0.026	-0.027	-0.025	-0.031	-0.024	1.367
C1-C2	0.037	0.029	0.022	0.017	-0.011	-0.001	1.447
C2=C3	-0.056	-0.057	-0.050	-0.026	-0.028	-0.027	1.432
C3-C4	0.030	0.024	0.016	0.012	-0.012	-0.003	1.430
C4=C5	-0.012	-0.015	-0.015	-0.006	-0.016	-0.015	1.396
C-methyl	-0.009	-0.016	-0.016	0.001	-0.012	-0.011	1.499
N-C1-CH ₃	0.7	0.7	0.6	0.3	0.1	0.2	117.6
C3-C4-C5	2.4	2.3	2.1	1.2	1.4	1.4	121.1
Model C Cs							
N=C	-0.016	-0.021	-0.019	-0.019	-0.025	-0.019	1.352
C1-C2	0.003	-0.003	-0.018	-0.003	-0.021	-0.018	1.422
C2=C3	-0.036	-0.037	-0.013	-0.012	-0.019	-0.013	1.419
C3-C4	0.041	0.031	-0.013	0.008	-0.021	-0.013	1.455
C4=C5	-0.033	-0.035	-0.011	-0.008	-0.013	-0.011	1.408
C6-C7	0.016	0.011	-0.006	0.008	-0.012	-0.006	1.432
C8=C9	-0.01	-0.01	-0.02	-0.01	-0.02	-0.02	1.382
C-methyl	-0.01	-0.01	-0.01	0.00	-0.01	-0.01	1.506
N-C1-C2	0.4	0.5	1.0	0.6	1.2	1.0	121.9
C5-C6-C7	2.1	2.0	1.1	1.0	1.2	1.1	120.0
Model D Cs							
N=C	-0.015	-0.020	-0.022	-0.018	-0.024	-0.018	1.352
C1-C2	0.001	-0.004	-0.006	-0.003	-0.021	-0.017	1.413
C2=C3	-0.027	-0.030	-0.026	-0.008	-0.016	-0.010	1.414
C3-C4	0.029	0.020	0.013	0.003	-0.023	-0.018	1.454
C4=C5	-0.041	-0.042	-0.036	-0.013	-0.016	-0.012	1.403
C5-C6	0.032	0.024	0.017	0.008	-0.015	-0.010	1.431
C6=C7	-0.026	-0.028	-0.024	-0.009	-0.017	-0.013	1.397
C7-C8	0.011	0.006	0.004	0.009	-0.008	-0.002	1.428
C8=C9	-0.008	-0.012	-0.012	-0.008	-0.021	-0.018	1.375
C-methyl	-0.005	-0.013	-0.013	0.003	-0.011	-0.008	1.507
N-C1-C2	0.3	0.3	0.4	0.5	0.9	0.9	122.5
C7-C8-C9	2.0	1.8	1.6	1.0	1.1	1.0	121.8

^a CASPT2 reference values taken from ref 40 are reported in the last column.

second one is underestimated. It is worth noting the different behavior of the CC single bond connected to the C=NH₂ group: in MDB as in the other previous systems, deviations from CASPT2 are positive for functionals with low HF-X percentage, but in MDC and MDD, such deviations are negative. This can be related to the position of the bond along the chain and the sigma-inductive effect of the methyl group, which is described in opposite manner by BH&HLYP and CAM-B3LYP. In this case, therefore, the oscillating behavior of low percentage HF-X functional (particularly B3LYP) could be linked to the description of excitation closer to an alternation of bonds after excitation where BH&HLYP and CAM-B3LYP describe a picture of this phenomenon closer to CASPT2 view, with a skeleton relaxation but of lower intensity. However, for all the systems, the differences with respect to CASPT2 are less than 0.04 Å for single bonds.

As in the ground state, CC double bonds are generally underestimated with deviations of ca. 0.001–0.005 Å for both isomers of butadiene and ca. 0.01–0.02 Å for PYR. The only exceptions are the BMK and B3LYP functionals that overestimate the bond distance of TrBD. One can obtain smaller discrepancies by selecting B3LYP (0.001 and 0.003 Å for CBD and TrBD, respectively) or BMK for PYR.

Results for PSB systems are in line with this trend: in general, CC double bonds are underestimated, with deviations from CASPT2 around or lower than 0.04 Å, if we exclude the case of the C₁₃=C₁₄ bond in MDB where 20% of HF-X gives values around 0.05 Å. In all cases, increasing the HF-X percentage

gives values closer to CASPT2; however, the performances are not improved by changing the correlation description. The best agreement is obtained using BMK functional (differences around 0.006–0.026 Å).

The CN bond length of PYR is underestimated with deviations presenting the same sign, but slightly larger amplitude than for the ground state. Once again, the best agreement is obtained with BMK (0.014 Å). In the case of PBS systems, however, values closer to CASPT2 are obtained at the B3LYP level for which errors less than 0.02 Å are found.

All functionals underestimate the C=C–C angle in CBD and PYR by values ranging between 0.2–0.6° and 0.2–0.3°, for CBD and PYR, respectively. Conversely, in the case of TrBD, the angle is overestimated by 0.1–0.4°. The overestimation is shown also in the case of the three PSB systems but with larger values, in function of the position of the bond along the chain.

Concerning the n-π* systems, as for the previous case, TD-DFT CC single bonds are systematically too long with respect to CASPT2, and two different trends that depend on the HF-X contribution can be outlined. Indeed, for ACR and ACT systems, increasing the HF-X contribution induces larger differences (between 0.001 and 0.036 Å) with respect to CASPT2, whereas the opposite behavior is found for PAA, for which the closest agreement is obtained with BH&HLYP. The length of the CC double bond tends to be underestimated for all systems with the exception of PAA with the B3LYP, B3P86, PBE0, and BMK functionals, for which the overestimation is very small (values are very close to CASPT2). The C=O distance is underestimated

TABLE 5: Mean Absolute Differences (MAD) with Respect to CASPT2 Values and Corresponding Relative Standard Deviation (RSD) of Excited-State Bond Lengths (Å), Averaged on Systems Studied

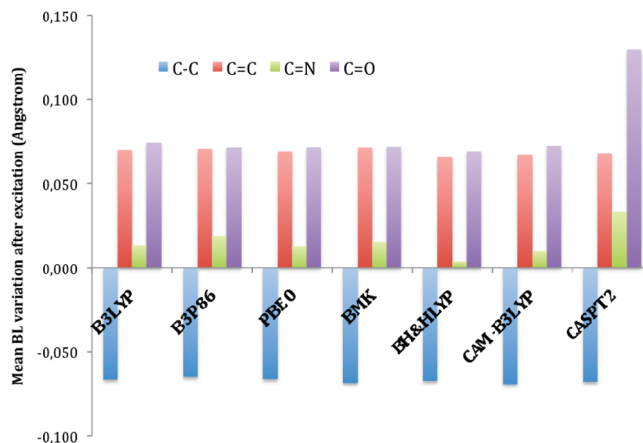
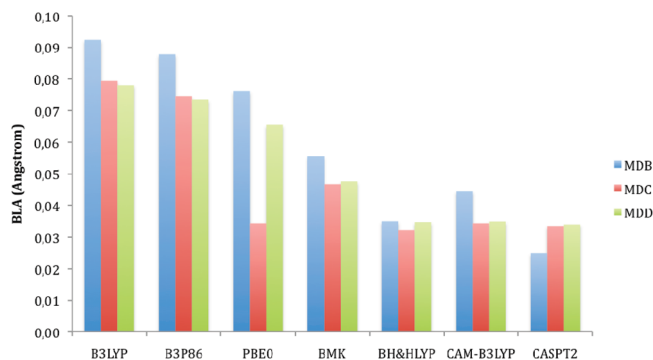
	B3LYP	B3P86	PBE0	BMK	BH&HLYP	CAM-B3LYP
MAD						
C–C	0.015	0.013	0.010	0.009	0.014	0.010
C=C	0.020	0.021	0.017	0.010	0.018	0.014
C=O	0.063	0.069	0.072	0.077	0.082	0.070
C=N	0.032	0.034	0.033	0.032	0.038	0.031
RSD						
C–C	0.84	0.77	0.61	0.97	0.47	0.68
C=C	0.83	0.78	0.78	0.68	0.43	0.55
C=O	0.42	0.38	0.35	0.27	0.25	0.31
C=N	0.15	0.13	0.18	0.41	0.31	0.27

by about 0.06 Å for both ACR and ACT. This behavior is also found for the CO *cis* bond in PAA (0.1 Å underestimation) that presents an enhanced double bond character as compared to the ground state, especially in comparison with the trans analogue. In fact, this bond is shorter than the “trans” CO bond at the ground state and longer at the excited state. This interpretation in terms of changes in the double bond character is also supported by the comparison of the angles C–C=O and C–C–O *cis* that have similar behavior (see below). N=N and C=N bond lengths are both underestimated by all the six functionals, with differences larger than 0.010 Å for the former and between 0.02 and 0.05 Å for the latter, the most accurate estimate being obtained with B3LYP. The C=C=C angle is overestimated in ACR (ca. 0.4°) and underestimated in PAA (ca. 2°), whereas the C=C=O angle is overestimated for the three molecules (ca. 2–5°, 0.8–1°, and 9° for ACR, ACT, and PAA, respectively), including the PAA if we assume that the bond C–O *cis* presents the double bond character. Finally, The O–C–O angle in PAA is understated by about 4°.

Table 5 collects the mean absolute differences (MADs) and relative standard deviations (RSD) of excited-state structural parameters, varying either the system or the functional studied. The first analysis provides insights regarding the general tendency of TD-DFT in reproducing CASPT2 data, whereas the second type of analysis indicates which type of functional shows a more reproducible behavior in estimating the bond type regardless of the selected systems.

From the RSD values reported in the table, we can argue that for CC single and double bonds there is a great dispersion of data in changing system, with the values between 0.97 and 0.47 for single bonds and between 0.43 and 0.83 for double bonds. In contrast, lower data dispersion and absolute differences are found for the C=O (in the range 0.25–0.42 for all functionals) and C=N bond lengths (0.13–0.27), which, therefore, represent a more reproducible geometrical parameter. However, it is worth noting that C=O bonds are presents only for $n-\pi^*$ systems.

In analyzing MAD values, we can quantify the effects of changing HF-X percentage or correlation functional. CC single and double bonds are, in the average, better described increasing HF-X percentage, and also passing from LYP to P86 and PBE correlation description. Smaller MAD values are obtained with CAM-B3LYP and BMK, which, however, gives higher RSD. For C=N bonds, the impacts of both HF-X percentage and correlation are negligible, as the MAD values are very similar for all functionals except for BH&HLYP, which undergoes a larger discrepancy. In the case of C=O, the best agreement is obtained with B3LYP, which, however, yields larger dispersion

**Figure 2.** Computed TD-DFT and CASPT2 absolute bond length variations upon excitations.**Figure 3.** Bond length alternation (BLA) of excited-state structures of PBS systems.

of data. Also, in this case, a good compromise between precision and accuracy is reached with the CAM-B3LYP functional.

Finally, we can conclude that all functionals give, on average, reproducible results for excited-state geometries in comparison to CASPT2, with CAM-B3LYP showing the best performances.

More insights about the description of the entire excitation process by the different functionals could be obtained by comparing the mean bond length variations (BLV) upon excitation for four selected bonds, reported in Figure 2.

As it clearly appears, CC single and double bond variations are well reproduced by all the functionals, the PBE0 approach providing the smallest deviations (<0.005 Å) for both bonds. In contrast, the changes for the C=O bonds are significantly underestimated by all functionals, with errors about 0.06 Å. Here, B3LYP gives slightly smaller errors than PBE0. Finally, CN bond variations are also systematically underestimated at the TD-DFT level, but this effect remains trifling.

To conclude the analysis on excited-state geometries, we report a further comparison between DFT and CASPT2, but this time focused on the description of conjugation in extended $\pi-\pi^*$ systems here represented by the PBSs. Such an analysis is performed in terms of the bond length alternation (BLA) defined as the difference of the average of single and double carbon–carbon bonds along the $\pi-\pi^*$ chain. The results obtained with the different functionals and the reference CASPT2 description are reported in Figure 3.

As it is shown in Figure 3, the increase of HF-X percentage gives a description of the physics of the system closer to the CASPT2, with the long-range corrected scheme giving the best agreement for the longer systems. This is indeed an interesting result, as it shows that CAM-B3LYP is the most “robust”

TABLE 6: Dipole Moment Variations (Debye) between Excited and Ground States^a

system	B3LYP	B3P86	PBE0	BMK	BH&HLYP	CAM-B3LYP	MV	SD
<i>cis</i> -buta-1,3-diene	1.03	0.91	0.96	0.78	0.93	0.98	0.93	0.08
pyrrole	-1.47	-1.14	-1.39	-0.90	-1.37	-1.31	-1.26	0.19
acrolein	-2.40	-2.41	-2.35	-2.35	-2.37	-2.45	-2.39	0.04
acetone	-1.07	-1.08	-1.13	-1.11	-1.32	-1.13	-1.14	0.08
diazomethane	1.41	1.39	1.45	1.47	1.62	1.59	1.49	0.09

^a In both cases, relaxed geometries have been used. Mean values (MV) and standard deviations (SD) are also reported.

TABLE 7: Emission Energies (eV) at Optimized Structures of Excited States Studied^a

system	B3LYP	B3P86	PBE0	BMK	BH&HLYP	CAM-B3LYP	MV	RSD
<i>cis</i> -buta-1,3-diene	4.13	4.20	4.21	4.25	4.20	4.19	4.20	0.01
<i>trans</i> -buta-1,3-diene	4.93	5.02	5.03	5.09	5.06	5.04	5.03	0.01
pyrrole	5.54	5.68	5.69	6.16	5.69	5.64	5.73	0.04
acrolein	2.84	2.83	3.66	3.12	3.51	3.25	3.20	0.10
acetone	3.65	3.69	3.74	3.75	4.11	3.81	3.79	0.05
diazomethane	2.52	2.57	2.56	2.23	2.42	2.46	2.46	0.05
propenoic acid anion	1.49	1.46	1.59	1.98	2.49	2.09	1.85	0.20
MDB	3.91	3.97	4.02	4.08	4.20	4.08	4.04	0.02
MDC	3.27	3.32	3.37	3.54	3.43	3.43	3.39	0.03
MDD	2.79	2.84	2.90	3.08	2.98	2.99	2.93	0.03

^a Mean values (MV) and relative standard deviations (RSD) are also reported.

functional (among the ones investigated here) in consistently describing the changes in the conjugation with the spatial extent⁴⁶ and is compatible with the CASPT2 picture of relaxation pathways.⁴⁰

Finally, in Tables 6 and 7 we report a comparison of dipole moment variations, that is, the difference between excited- and ground-state dipole moments, and emission energies as obtained with the different functionals. As CASPT2 data are not available for these quantities, the comparison is limited to TD-DFT data only.

As it can be seen from Table 6, all functionals describe dipole moment variations in a qualitatively good agreement with what is expected from the nature of the excitation. In fact, with all the functionals we obtain negative variations (i.e., decrease of the dipole) for $n-\pi^*$ systems (ACR and ACT) and positive variations (increase of the dipole) for $\pi-\pi^*$ (CBD). Of course, due to symmetry reasons, TrBD has null dipole in both electronic states. We note that even if pyrrole is a $\pi-\pi^*$ system, it is also an example of so-called five-membered six π -electron aromatic ring molecules in which the heteroatom (here nitrogen) donates two π electrons and each of the four carbon atoms supplies one π -electron. In this case, the excitation leads to a decrease of the dipole instead of an increase as in standard $\pi-\pi^*$ systems. For a parallel reason, also $n-\pi^*$ diazomethane presents a specific behavior with a positive instead of a negative variation as for standard $n-\pi^*$ systems.

Going into more details, some differences appear among the different functionals, with BMK and B3LYP giving the smallest and highest variations, respectively (only for ACT and DZM, CAM-B3LYP gives larger variations than B3LYP). It is worth noting that a general decrease of the module of dipole moment variation with increasing the percentage of HF-X is found even if the trend is not completely monotonic going from B3LYP to BH&HLYP.

Emission energies, reported in Table 7, show a large dispersion with functionals for $n-\pi^*$ systems (especially ACR and PAA), while for $\pi-\pi^*$ systems the differences are quite small. As for dipole moment variations, no clear proportionality or dependence with HF-X percentage can be found. It is interesting to note that dispersion on emission when compared to excitation (last columns in Tables 2 and 7) is almost

unchanged, except in the case of ACR and PAA, where RSD values are double.

From the above analysis, one clear trend common to all molecular systems, types of excitation, and atoms involved emerges: TD-DFT has a tendency to underestimate the length of double bonds as compared to CASPT2 and therefore to exaggerate the double bond character of the relaxed excited state. Clearly, the extent of this trend depends on the character of excitation, with the CO bonds directly involved in the $n-\pi^*$ transition being largely affected. Indeed, TD-DFT gives a more localized description of this transition than do post-HF approaches.

4. Conclusions

We have presented a study on the performances of several TD-DFT functionals in describing excited-state geometries and properties for $\pi-\pi^*$ and $n-\pi^*$ valence excitations. Here, we have selected small organic systems so to have a direct comparison with CASPT2 data available in the literature. Our study shows that all functionals generally give a qualitatively good description of excitation energies and excited-state structures and properties. For these small molecular systems, it is a general behavior of DFT functionals to overestimate single bond lengths and underestimate the double ones, which means that DFT gives a more localized picture, with respect to CASPT2, which is known to provide accurate results.⁴⁷ For this kind of system, where the electron density reorganization remains relatively limited, the best performances are obtained by using low percentage HF-X hybrids functionals, particularly for carbon heteroatom double bonds. Higher percentage HF-X functionals and CAM-B3LYP work better in the case of a stronger modification of the electron density after excitation in $n-\pi^*$ excitations and in extended $\pi-\pi^*$ systems. However, the amount of the change of electron density remains too small during vertical process of small molecules to outperform B3LYP and PBE0 that provide absorption and emission spectra with similar accuracies. Obviously, for transitions with large charge delocalization, as those involved in $\pi-\pi^*$ or $n-\pi^*$ excitations in large conjugated systems or push-pull chromophores, as well as for Rydberg excitations,^{26,36,48-50} one expects that the inclusion of corrections to the long-range correlation and

exchange potential may become mandatory,⁵¹ as we find for the three PSB model systems, in particular to reproduce bond length alternation, as yet pointed out for the analogous ground-state case.⁴⁶ It is our intention to extend our studies to these larger systems, including also different types of excitations and solvent effects.

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Supporting Information Available: Basis set dependence of TD-DFT excited-state structures.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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