

Electronic Transition Energies: A Study of the Performance of a Large Range of Single Reference Density Functional and Wave Function Methods on Valence and Rydberg States Compared to Experiment

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Received September 28, 2009

Abstract: This work reports a comparison among wave function and DFT single reference methods for vertical electronic transition energy calculations toward singlet states, valence and Rydberg in nature. A series of 11 small organic molecules are used as test cases, where accurate experimental data in gas phase are available. We compared CIS, RPA, CIS(D), EOM-CCSD, and 28 multipurpose density functionals of the type LSDA, GGA, M-GGA, H-GGA, HM-GGA and with separated short and long-range exchange. The list of functionals is obviously not complete, but it spans more than 20 years of DFT development and includes functionals which are commonly used in the computation of a variety of molecular properties. Large differences in the results were found between the various functionals. The aim of this work is therefore to shed some light on the performance of the plethora of functionals available and compare them with some traditional wave function based methods on a molecular property of large interest as the transition energy.

1. Introduction

Vertical electronic transition energy calculations are presently routine in physical and theoretical chemistry research because they are a powerful tool for interpreting and often assisting predictions of experimental spectra. Theoretical approaches to treat excited states can be divided into single and multireference methods. The latter ones provide a balanced description of both ground and excited states and they are necessary to describe for instance two-electron excitations or conical intersections. However, multireference methods are computationally expensive and they can be ambiguous to apply, thus requiring considerable expertise in order to obtain meaningful results.

Single reference methods are, on the other hand, straightforward and the quality of the results is easier to evaluate. These methods are also completely defined given the level

of theory and basis set, thus they are accessible even to nonspecialists. However, they can provide an unbalanced description of the ground state compared to the excited states, and they can usually be employed only to describe one-electron transitions. Fortunately, many excitation processes of chemical interest belong to this category, so that single reference methods can be successfully used to obtain quantitative results.

The simplest excited state method is the configuration interaction singles (CIS),¹ also known as Tamm–Dancoff approximation (TDA), where the excited state is described as a linear combination of singly excited determinants from the reference Hartree–Fock (HF) determinant. This method does not include any electronic correlation, since single excitations do not mix with the HF reference. A proposed improvement over CIS is to consider perturbative double excitations corrections to the transition energies, that gives rise to the CIS(D) method.² A different approach is to include selected doubly excited determinants to CIS, obtaining the

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random phase approximation (RPA) method, also known as time-dependent HF (TDHF).³

The extension of density functional theory (DFT) to electronic excitation through the time-dependent formalism (TDDFT), within the adiabatic approximation,^{4–6} represented a fundamental step considering the huge success of DFT in describing ground state phenomena. The advantage of TDDFT over CIS and RPA is the inclusion of correlation effects through the exchange-correlation potential for both the ground and the excited states, without adding significant computational effort. Since the exact density functional is not known, many approximated functionals have been proposed, and new ones continue to be developed. However, this point also represents the greatest weakness of DFT today, as it is not at all easy to decide which functional is better for a particular system in a particular process. And this is especially true for transition energy calculations.

Correlation can also be included in wave function methods, for instance through coupled cluster (CC) theory.⁷ CC is exact when all of the possible excitations are included, but in practice the expansion is truncated at a given order. The most widely used truncation order implies singles and doubles excitations (CCSD). Because of the nonlinearity of the exponential wave operator, higher order excitations are included at this level of truncation, so that CCSD is a dramatic improvement over configuration interaction singles and doubles (CISD).⁷ The success and limitation of CCSD is also related to its computational cost, as it scales iteratively as $O(N^6)$, where N is the number of basis functions, so this method is only feasible for small and medium sized molecules. CC theory was extended to excited states calculation through the equation of motion (EOM) formalism,^{8,9} or alternatively through the linear response (LR) formalism,^{10,11} that are equivalent for transition energies. EOM-CC scales as the ground state at a certain level of truncation, thus the same systems which are accessible at CCSD level can be in general also treated at EOM-CCSD level for the excited states. Although the excitation expansion for the excited states is linear, contrary to the ground state, the inclusion of double excitations introduces enough flexibility in the wave function to allow for an accurate description of many one-electron transitions. The computational effort is much larger than in DFT, but since in CC theory the exact solution is known (it is obtained by including all the possible excitation operators) there is a systematic way to improve truncated CC wave functions, whereas this is not possible with the present formulation of DFT.

Recent studies^{12–15} review and compare the performances of the plethora of DFT functionals on a variety of phenomena and molecular systems. This work fits into this group, presenting a comparison of computed and experimental transition energies for some small representative organic molecules. Only single reference methods are taken into account because their results are unambiguous and therefore they represent useful computational tools even for nontheoretically trained investigators. The range of functionals examined is wide, starting from local spin density approximation (LSDA), to include generalized gradient approximation (GGA), GGA with kinetic energy density or

meta-GGA (M-GGA), hybrid GGA (H-GGA), and hybrid-meta-GGA (HM-GGA) as well as functionals that separate short and long-range exchange contribution (with and without the correct long-range limit). This allows one to draw some conclusions about the progress of DFT development, at least for this property. Even if the number we considered is large, this is nevertheless far from complete. In fact, it would be a nearly impossible task considering the number of existing functionals and the rate of publication of new ones.¹² We point out that we choose *multipurpose* functionals, that is functionals which are not specifically designed for excited state calculations, but are generally used for the calculation of a variety of properties. This work, in connection with others, might thus help the interested investigator to choose a functional which behaves comparably well for ground and excited states and can be used, for instance, for the study of photochemical processes and reactions. Additionally, we also examined the most common single reference wave function methods, CIS, RPA, CIS(D), and EOM-CCSD, for which a hierarchy of accuracy can be more easily defined.

This work follows a previous one¹⁶ where some of us studied the effect of the basis set on electronic transition energies, comparing only RPA, EOM-CCSD, and TDDFT with the B3P86 hybrid functional. The present study focuses on the comparison of different methods, using the 6-311(3+, 3+)G** basis set, that was demonstrated¹⁶ to be sufficiently accurate for this molecular property. The set of molecules has also been extended with respect to ref 16 to include trans-1,3-butadiene,⁵⁴ acetaldehyde,⁵⁵ and a series of azabenzenes.⁵⁶ The latter group of molecules includes excitation toward valence states ($n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$), whereas the rest mainly involves Rydberg states. In total, we considered 69 states. Among these, 30 are valence in nature and 39 are Rydberg.

We emphasize that this work aims to give a qualitative picture of the behavior of the examined methods. This is because the number and nature of the excitations considered is not enough for a statistically meaningful sampling. Alternatively, the rather accurate experimental data and the small number of systems allow a detailed analysis of the results for each molecule. Therefore, the format for the presentation of the results was chosen accordingly.

This work is organized as follows. Section 2 contains a description of the computational methods we considered and the details of the calculations performed. Section 3 collects the results of our calculations and presents a discussion on the performance of the various methods. Section 4 contains a summary of the results and concluding remarks.

2. Computational Details

The geometries of the systems under investigation were optimized for the ground states at the MP2/6-311+G** level of theory. These geometries were used for all the methods in the electronic transition calculations. They are reported in Tables 1–11 in the Supporting Information. This material is available free of charge via the Internet at pubs.acs.org. The basis set used for the latter calculations was 6-311(3+, 3+)G**, previously demonstrated to be adequate for this kind of property.¹⁶ We performed vertical excitation calculations

Table 1. List of Functionals Used in This Work

	year	type	% HF		year	type	% HF
LSDA ^{17,21}	1951	LSDA		B3VP86 ^{18,20,21,23}	1993	H-GGA	20
BLYP ^{18,19}	1988	GGA		PBE1PBE ^{27,28,43,44}	1997	H-GGA	25
OLYP ^{22,19}	2001	GGA		B1B95 ²⁵	1996	HM-GGA	25
BP86 ^{18,23}	1988	GGA		THCTH ³¹	2002	HM-GGA	15
BVP86 ^{18,21,23}	1988	GGA		TPSSh ^{33,46}	2003	HM-GGA	10
PBEPBE ^{27,28}	1997	GGA		M05 ³⁴	2005	HM-GGA	28
HCTH ^{24,29,30}	2001	GGA		BH&H, ^{17,21,19a}	1993	H-GGA	50
THCTH ³¹	2002	M-GGA		BH&HLYP, ^{17,21,18,19a}	1993	H-GGA	50
BB95 ^{18,25}	1996	M-GGA		BMK ³⁶	2004	HM-GGA	42
VSXC ²⁶	1998	M-GGA		M05-2X ³⁵	2006	HM-GGA	56
TPSSTPSS ³³	2003	M-GGA		HSE1PBE ³⁷	2003	H-GGA	25 - 0 ^a
O3LYP ^{22,19,32}	2001	H-GGA	11.61	CAM-B3LYP ³⁸	2004	H-GGA	19 - 65 ^b
B3LYP ^{18-20,45}	1994	H-GGA	20	LC-BLYP ^{18,19,39,40}	2001	H-GGA	LC ^c
B3P86 ^{18,20,23}	1993	H-GGA	20	LC- ω PBE ³⁹⁻⁴²	2006	H-GGA	LC ^c

^a Note that these are not the same as the half-and-half functionals proposed by Becke⁴⁷ ^b Short-range-long-range. ^c The percentage of HF exchange increases as described in refs 39–42.

from the ground state geometry toward singlet excited states. We limited the analysis to singlet states because the experimental data are more reliable.

As mentioned in the introduction, we examined four well-established wave function based methods, CIS, RPA, CIS(D), and EOM-CCSD. These methods are referred in the following as ab initio. One could argue that also pure functionals are ab initio, as they do not contain empirical parameters, but we prefer to put those functionals in the general DFT category, for the sake of simplicity.

The functionals^{17–46} we considered are listed in Table 1. The table indicates the type of functional: LSDA, GGA, M-GGA, H-GGA, and HM-GGA. The year of publication is also reported and, for the hybrid functionals, the percentage of HF exchange. We note that the order of the functionals in Table 1 follows the one of the figures in the results section. We collected the pure functional together, in the order LSDA, GGA, and M-GGA. The hybrid functionals were also collected together, and they were divided into three subgroups: (i) the ones with small HF exchange amount (from O3LYP, 11.61%, to M05, 28%), (ii) the ones with large HF exchange amount (from BMK, 42%, to M05-2X, 56%), (iii) the ones with separated short and long-range exchange (from HSE1PBE to LC- ω PBE). Groups (i) and (ii) were also ordered as H-GGA, HM-GGA. This choice is useful to rationalize the results for the various functionals. The functionals in group (iii) separate close and long-range exchange interaction in a very different way. CAM-B3LYP is hybrid in both short and long-range and it was designed to improve the B3LYP description for long-range phenomena, like polarizability of long chains or charge transfer excitations.⁴⁸ HSE1PBE is hybrid in the short-range and pure in the long-range, and it was designed to study solids, where the exchange interaction decays faster than that of HF. HSE1PBE is also supposed to behave like PBE1PBE at short-range, and thus also for the small molecules we considered. Both CAM-B3LYP and HSE1PBE maintain the same ratio of HF versus DFT exchange at all distances within the long and short ranges, respectively. However, for LC-BLYP and LC- ω PBE this ratio varies so that at long distance they present 100% (exact) HF exchange.^{39–42} The latter two functionals are thus effectively hybrid. We also note that PBE1PBE is often referred in literature as PBE0.

Most of the functionals we tested do not exhibit the correct asymptotic behavior and this may degrade the quality of the description for diffuse states, like Rydberg. The failure occurs due to the poor description of the virtual space. In fact, there is a significant deterioration above the ionization threshold, $-\epsilon(\text{HOMO})$. Although methods exist to add in a correction,^{49,50} it is observed that a sufficiently diffused basis set and the addition of exact exchange help to alleviate this problem.¹⁶ Moreover, these long-range corrections introduce new issues.^{50,51} However, we include two functionals with the correct asymptotic behavior, LC-BLYP and LC- ω PBE, in order to test the effectiveness of such corrections.

All of the calculations were performed with a development version of the Gaussian suite of programs.⁵²

3. Results

The test molecules are as follows: ethylene (D_{2h}), isobutene (C_{2v}), trans-1,3-butadiene (C_{2h}), formaldehyde (C_{2v}), acetaldehyde (C_s), acetone (C_{2v}), pyridine (C_{2v}), pyrazine (D_{2h}), pyrimidine (C_{2v}), pyridazine (C_{2v}), and symmetric tetrazine (D_{2h}). The first three molecules are alkenes, the second group of three molecules are carbonyl compounds and the rest are azabenzenes with a different number of nitrogen atoms.

These molecules were chosen because they have been intensively studied experimentally in gas phase. They also have molecular symmetry, which aids in matching the calculated and measured data. Only well established experimental data were taken into account, in order to ensure a correct matching with the calculated quantities. Experimental vertical transition energies were almost always compared with the calculated data, but in some cases only the adiabatic ones were measured and those are reported in the tables in the Supporting Information. For alkenes and carbonyls, only one or two states for each molecule are valence states ($n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$), whereas the others are Rydberg states. For the azabenzenes, all states are valence in nature. The assignment of the valence states is rather unambiguous, as it was checked by looking at the orbitals mainly involved in the transition (for low lying states, only few orbitals are involved, thus it is easier to consider the orbitals rather than the electron density differences, since there are many states and many methods). The Rydberg states are more difficult

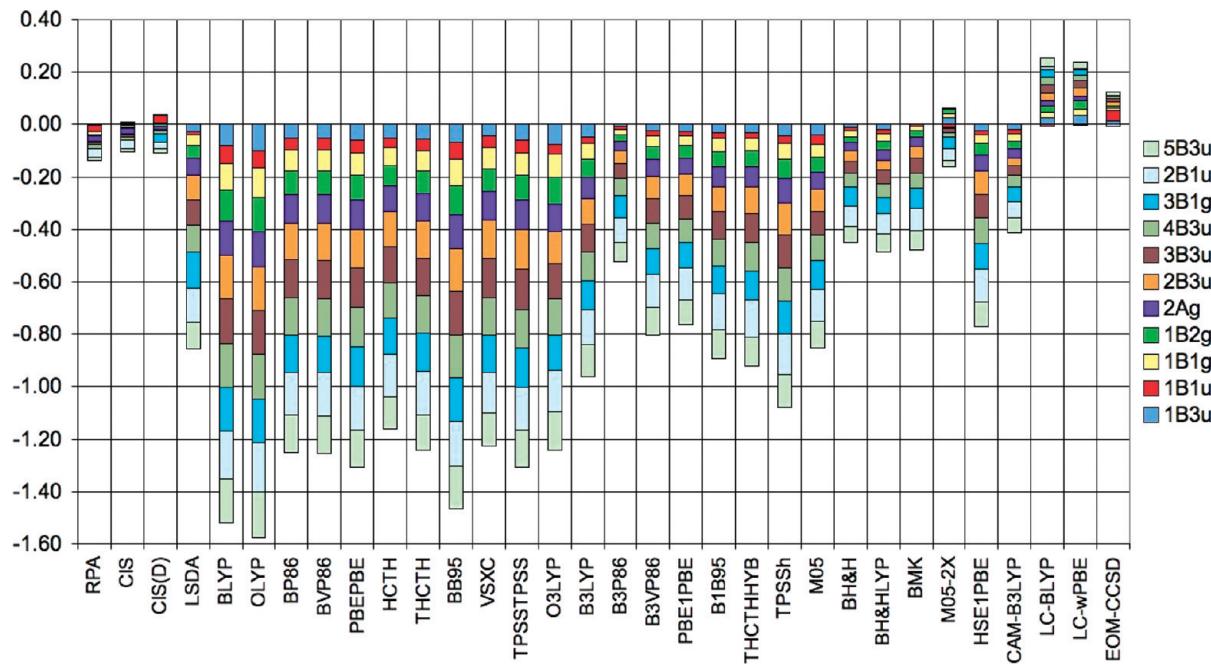


Figure 1. Errors (eV) for ethylene. The $1B_{1u}$ transition is $\pi \rightarrow \pi^*$, the rest are Rydberg.

to assign. We put those states in energy order within each irreducible representation for each method and each molecule, and matched them against the experimental data, sorted in the same manner.^{16,54,55} We made an attempt to use the oscillator strengths (f) to refine the matching, but the values of f are very similar between different states for any particular method, thus the reordering of the states according to f would be as arbitrary as sorting them in energy order.

A clarification about the azabenzenes set is also important. Vibronic effects might be not negligible for some transitions in this set, especially for the $n \rightarrow \pi^*$, which are in principle not allowed by symmetry. For these states, the experimental assignment of the transition energies might also have a larger uncertainty, as these bands have small intensities and may be broad. Our results do not include any vibrational correction, as this represents a large computational effort beyond the scope of this paper. The analysis of vibrational contributions for selected methods will be the subject of a following work.

The results are presented as error bars, where the errors for the various transitions stack one on top of the other in order to give an idea of the cumulative error for a certain method. The error for each transition is defined as follows:

$$\text{Error} = \frac{\Delta E^{\text{calc}} - \Delta E^{\text{exp}}}{n} \quad (1)$$

where n is the number of excitations considered. Thus, a positive error means that the experimental value is overestimated, and vice versa. Moreover by scaling the errors by the number of transitions all the molecules are more directly comparable. We chose this graphical representation of the errors because its visual impact makes the evaluation of the accuracy of a method straightforward. Nevertheless, the numerical values of all the experimental and calculated data and the statistical analysis can be found in Tables 12–25 in the Supporting Information. These tables also report the

nature and the symmetry of the transitions. The performances of the methods are mainly discussed in terms of the cumulative errors, and not focusing on single transitions, because of the large amount of data we considered. Moreover, the performance of a method is judged in comparison to the other methods, in order to follow qualitative trends among the various test molecules. Therefore, a method can be considered to provide a good performance with respect to all the others, but still have a large absolute error for a particular transition.

The computational methods showed similar trends among the molecules within a particular set. In this respect, it is useful to group molecules with similar characteristics.

3.1. Alkenes. The ethylene molecule is one of the simplest systems to study, and many experimental and theoretical results are available, see ref 16 and references therein. We compared the measured and calculated data for eleven transitions. Among them, the $1B_{1u}$ transition is $\pi \rightarrow \pi^*$ in nature, the rest are Rydberg. The errors are reported in Figure 1. All of the ab initio methods, RPA, CIS, CIS(D), and EOM-CCSD, appear to perform quite accurately on this system. The total error is rather similar among those methods, but the first three often underestimate the experiments, whereas EOM-CCSD overestimates them. The same good performance is not shared by DFT functionals. The only ones that get close to the ab initio methods accuracy are M05-2X, LC-BLYP, and LC- ω PBE. The pure functionals (GGA and M-GGA) perform poorly. Hybrid GGA functionals tend to improve the results, but they are still far from experiment. A good performance is also obtained with B3P86, BH&H, BH&HLYP, and CAM-B3LYP. Note that a previous report with PBE1PBE⁵³ suggested that this functional performed very well compared to experiments; although, the excited state symmetries were misassigned. HM-GGA functionals are divided. Most of them perform as poorly as H-GGA, from B1B95 to M05, whereas BMK performs as BH&H and

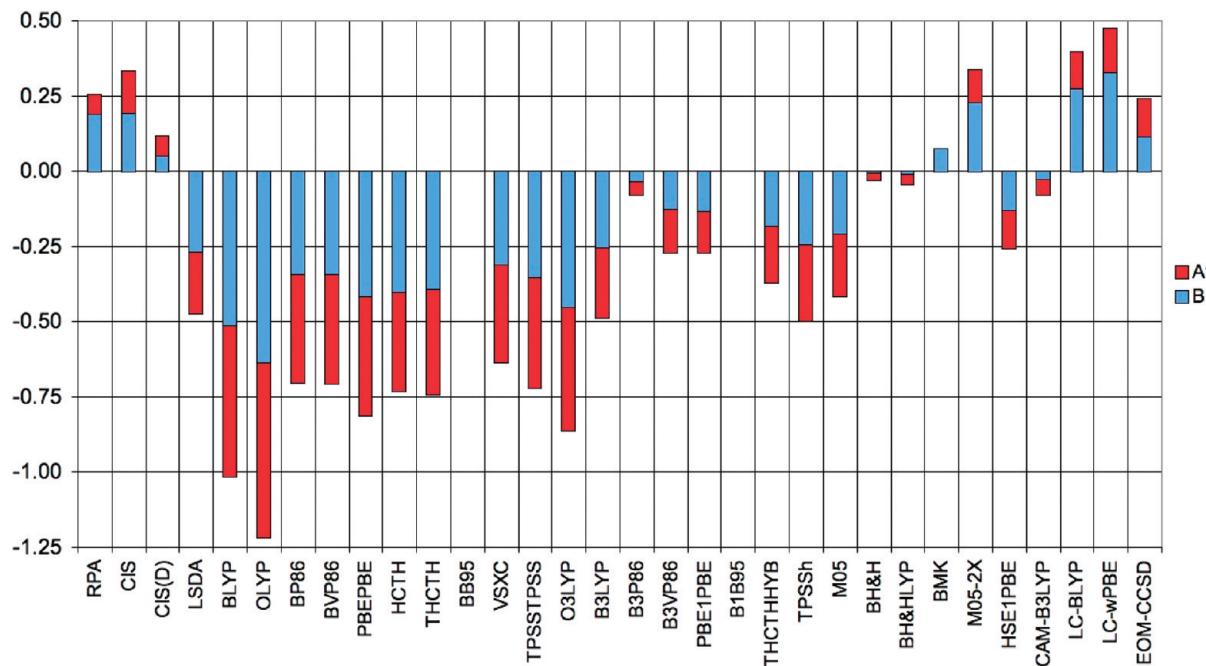


Figure 2. Errors (eV) for isobutene. The SCF of BB95 and B1B95 did not converge. The transitions are Rydberg.

BH&HLYP. The overall performance of the DFT functionals is somehow disappointing for this molecule, considering its limited size and the availability of both experimental and high level computational data. With the only exception of B3P86, larger amount of HF exchange leads to better results.

Experimental data for the first transitions of A_1 and B_1 symmetry are available for isobutene. These states, both Rydberg, were compared with the computed data, see ref 16 and references therein. The error are plotted in Figure 2. For this molecule, we only have a limited set of experimental data, thus exhaustive conclusions cannot be drawn. However, the ab initio methods perform reasonably well with this molecule, with a small overestimation of the experimental results for both transitions. RPA and EOM-CCSD show a similar overall error but differently distributed among the two transitions. CIS performs slightly worse, whereas CIS(D) is even better than EOM-CCSD, probably due to a fortunate cancellation of errors. The functionals usually underestimate the measured transition energies, except for M05-2X, BMK, LC-BLYP, and LC- ω PBE, that contain a large percentage of HF exchange and thus they tend to overestimate the transition energies as the HF methods do. However, some hybrid functionals perform quite well for this system. B3P86, BMK, BH&H, BH&HLYP, and CAM-B3LYP provide considerably smaller errors than the ab initio methods. Among them, B3P86 is the only one with a small contribution of HF exchange. BMK gives the exact excitation energy for the A_1 transition, which is most likely a fortunate combination of error cancellation. Remarkably, the two functionals with the correct long-range limit, LC-BLYP and LC- ω PBE, show larger errors than most of the other hybrid functionals.

Seven experimental transition energies are used as reference to study the accuracy of computed data for the trans-1,3-butadiene.⁵⁴ We did not consider the 2^1A_g state as its assignment is controversial.⁵⁴ The $1B_u$ transition is $\pi \rightarrow \pi^*$

in nature, the rest are Rydberg. The errors are plotted in Figure 3. EOM-CCSD provides this time the best agreement with the experiments. Its largest error is on the first transition, of symmetry B_u , whereas all the others are very small. CIS, RPA, and CIS(D) underestimate the experimental values except for the $1B_u$ transition. However, almost all DFT functionals show very large errors, generally underestimations of the experimental values. The only one that compares well with the ab initio methods is M05-2X. The general trend is that the quality of the results deteriorates for higher excited states. B3P86, BH&H, and BH&HLYP, together with the long-range corrected LC-BLYP and LC- ω PBE are the H-GGA functionals that give a good performance. CAM-B3LYP significantly improves the B3LYP performance but its own total error is comparable to B3P86.

For this set, all of the ab initio methods perform well, with similar accuracy. Alternatively, pure functionals show large underestimation of the experimental results. LSDA is definitely better than GGA and M-GGA functionals. Hybrid functionals benefit from the HF good performance on this group of systems, so that larger percentage of HF exchange corresponds to smaller errors. M05-2X, the functional with the largest amount of HF exchange among the functionals we considered (56%), is the best DFT method for ethene and butadiene, whereas BH&H and BH&HLYP are the best ones for isobutene. LC-BLYP and LC- ω PBE perform as well as M05-2X for ethene, as all the other functionals with large amount of HF exchange for butadiene and worse than most hybrid functionals for isobutene. We also note the good performance of B3P86, even with a modest 20% of HF exchange.

3.2. Carbonyls. Formaldehyde is another small molecule intensively studied experimentally and theoretically, see ref 16, and references therein. The comparison against the experiments is done for eleven electronic transitions

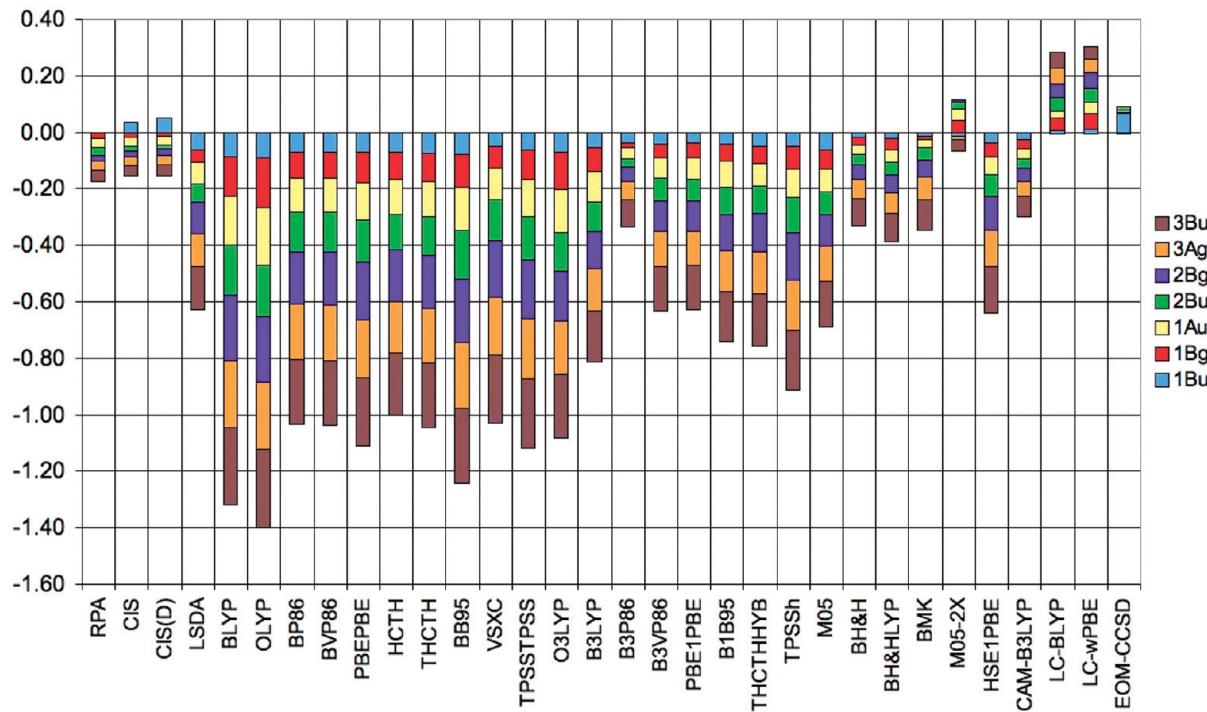


Figure 3. Errors (eV) for trans-1,3-butadiene. The $1B_u$ transition is $\pi \rightarrow \pi^*$, the rest are Rydberg.

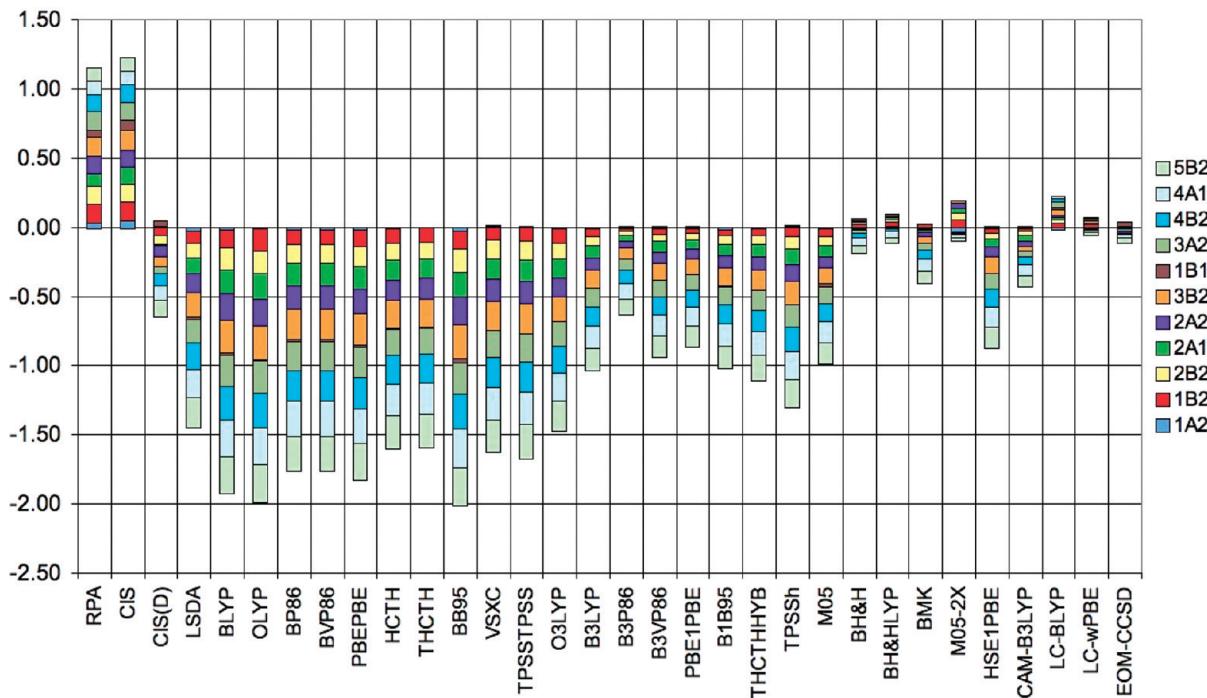


Figure 4. Errors (eV) for formaldehyde. The $1A_2$ transition is $n \rightarrow \pi^*$, the $1B_1$ is $\pi \rightarrow \pi^*$, all the rest are Rydberg.

and the results are plotted in Figure 4. This test differs from the previous ones as this molecule has a carbonyl group, so that the experimental data set includes an $n \rightarrow \pi^*$ transition (corresponding to the lowest, A_2 , excitation). Moreover, the double bond is more polarized than the alkene C=C bond. The $1B_1$ is also valence in nature ($\pi \rightarrow \pi^*$). Both of the valence excitations are well reproduced by most methods. Starting from the ab initio methods, Figure 4 shows very large overestimation of the measured data for RPA and CIS. CIS(D) on the other hand underestimates the experiment, at the same time halving

the total error with respect to the previous two methods. However, only EOM-CCSD provides a very accurate description for all the transitions. As far as DFT is concerned, all of the GGA and M-GGA functionals largely underestimate the transition energies. These errors are even larger than the RPA and the CIS ones. The hybrid functionals perform better than the pure functionals, with the exception of O3LYP. LC- ω PBE is even better than EOM-CCSD. BH&H and BH&HLYP are also quite close to EOM-CCSD. Also BMK, M05-2X, CAM-B3LYP and LC-BLYP perform well. The functionals with large HF

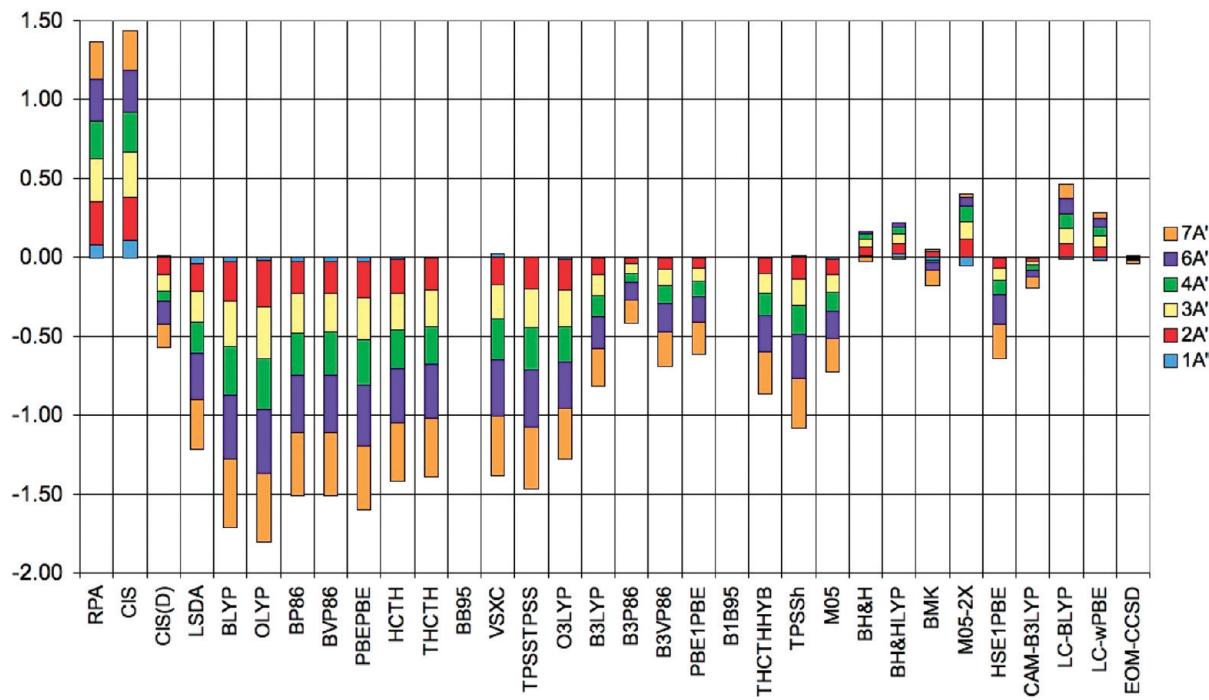


Figure 5. Errors (eV) for acetaldehyde. The SCF of BB95 and B1B95 did not converge. The $1A''$ transition is $n \rightarrow \pi^*$, all the rest are Rydberg.

exchange contribution give a reasonable description of the transitions, close to the EOM-CCSD one.

For acetaldehyde six experimentally determined transition energies⁵⁵ are used to test the various computational methods. The errors are reported in Figure 5. The first transition, which is the only $n \rightarrow \pi^*$ (A''), is well reproduced by all the methods. The assignment of the nature of this transition was done by considering the differences of the excited and ground states CIS densities. CIS and RPA calculations give a poor description of the transitions. However, most of the GGA and M-GGA functionals show larger but opposite errors. CIS(D) improves the CIS performance, but the experiments are underestimated and the errors are still quite large. However, EOM-CCSD gives basically the correct description for all the transitions. Pure GGA and M-GGA classes yield poor results, often worse than RPA and CIS. All of the transition energies are underestimated. O3LYP is the only H-GGA functional with a total error comparable to the pure functionals. Alternatively, B3P86 performs again reasonably well, with total error smaller than CIS(D). M05-2X performance is better than the M05 one. However, M05-2X total error is larger than the H-GGA B3P86. BMK, BH&H, and BH&HLYP results are quite good, as well as the CAM-B3LYP ones. LC-BLYP and LC- ω PBE also perform well, although with larger errors than the functionals with large amount of HF exchange, except M05-2X. Also, LC-BLYP performs worse than B3P86. Among the functionals the best performance is provided by BH&H.

Acetone is another widely studied small molecule, and we can compare the computational methods with experiments on eight electronic transitions, see ref 16 and references therein. The errors are reported in Figure 6. The first excited state is $n \rightarrow \pi^*$ (A_2) and it is well reproduced by all the methods. This case is quite similar to the previous one so it

is not surprising that RPA and CIS largely overestimate all the transitions. CIS(D) does a better job reducing by more than half the total error, but most of the transitions energies are now underestimated. EOM-CCSD gives the best description of this system. The functionals performances are similar to the previous cases, too. Pure functionals errors are quite large, comparable to CIS and RPA. LSDA is the best functional among them. The excitation energies are underestimated. Hybrid functionals perform better, with the constant exception of O3LYP. Among the functionals with smaller percentage of HF exchange B3P86 (H-GGA) and B1B95 (HM-GGA) present the smallest total error, even better than the functionals with the correct asymptotic behavior. CAM-B3LYP provides the best performance among the functionals for this molecule, with BMK and B1B95 also very close.

For the carbonyl compounds, the first consideration is that all the methods, ab initio and DFT, are able to qualitatively reproduce the increase of the $n \rightarrow \pi^*$ transition energy with the number of methyl groups, that is observed experimentally. Approximate ab initio methods like CIS and RPA provide large errors in this case, overestimating the experimental data. CIS(D) improves the description, but there is huge shift with respect to CIS, so that most of the transitions are underestimated, and the total error is still large. However, EOM-CCSD shows very good agreement with experiments for all the transitions. Pure functionals errors are again very large, in many cases larger than the CIS and the RPA ones. Also for this set, LSDA is better than all the other pure functionals. Hybrid functionals are again in between CIS and the pure functionals. Large amount of HF exchange favors better error compensation, as the errors of CIS and pure functionals are comparable but opposite in sign. It is also interesting how functionals with large HF contribution tend

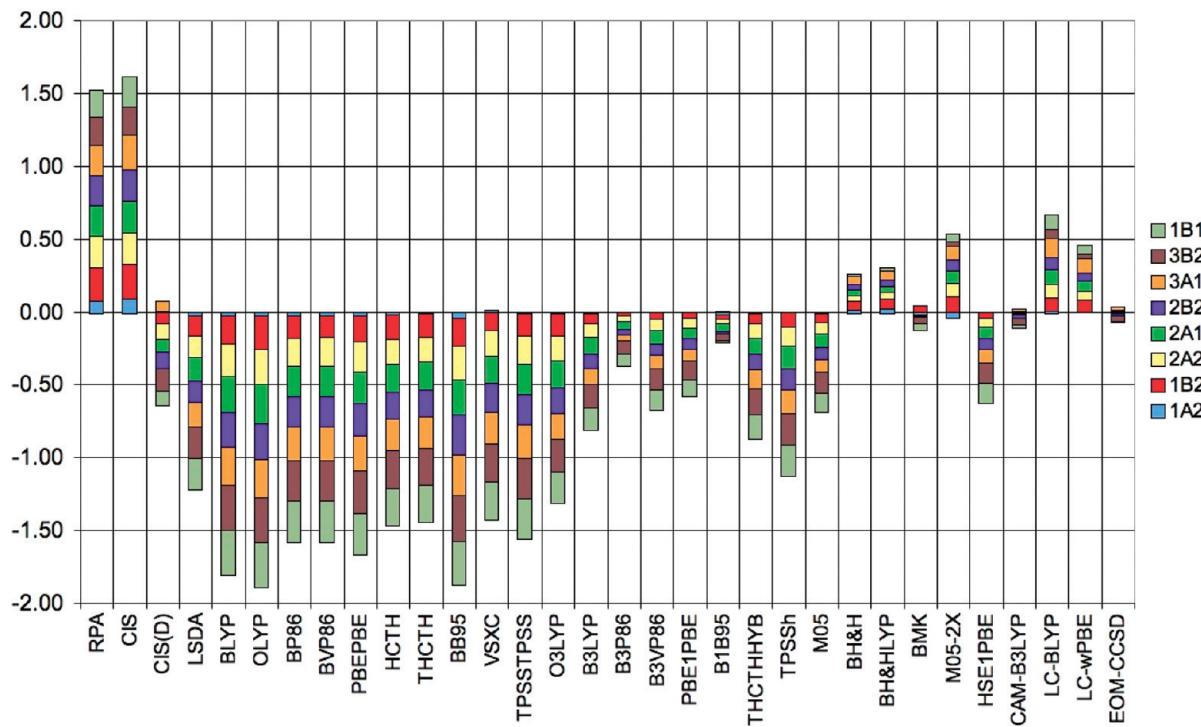


Figure 6. Errors (eV) for acetone. The $1A_2$ transition is $n \rightarrow \pi^*$, all the rest are Rydberg.

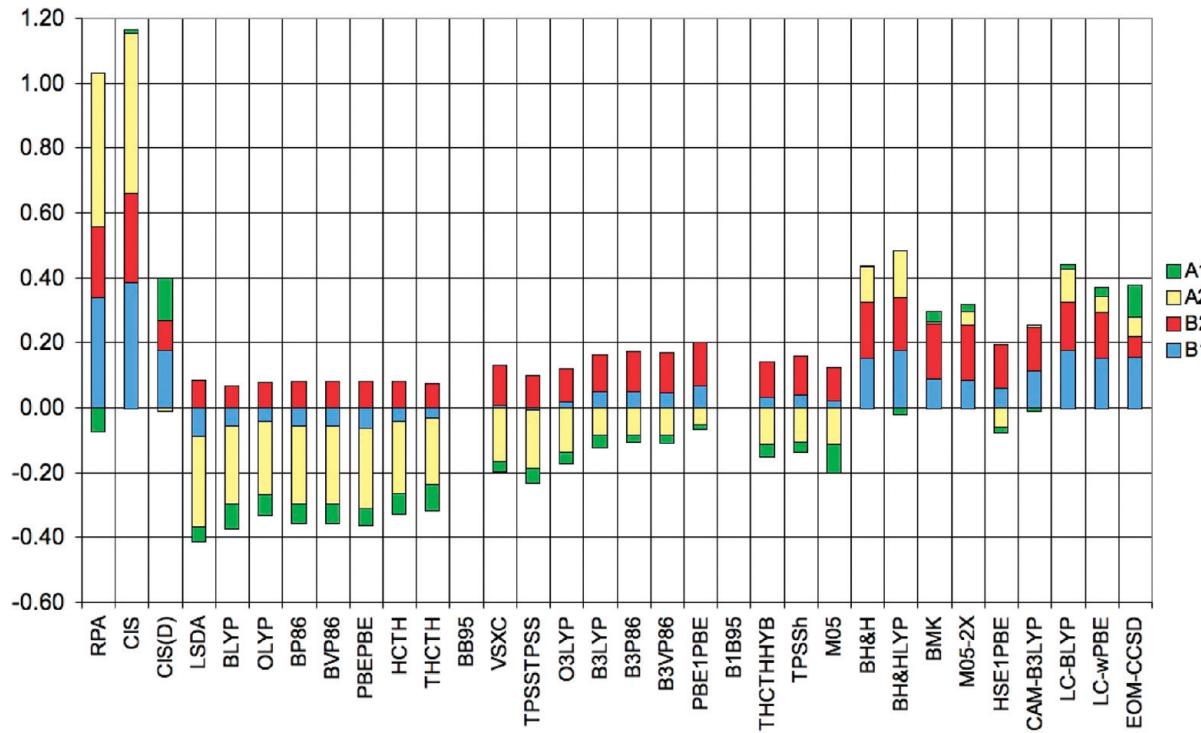


Figure 7. Errors (eV) for pyridine. The SCF of BB95 and B1B95 did not converge.

to overestimate some of the transitions energies just as the ab initio methods do. We note again the good performance of B3P86 among the H-GGA functionals with small amount of HF exchange and of B1B95 for acetone. The functionals with the correct asymptotic behavior, LC-BLYP and LC- ω PBE, do not seem to perform particularly better than noncorrected functionals with a large amount of HF exchange and, for acetaldehyde and acetone, the errors are comparable to or worse than B3P86.

3.3. Azabenzenes. Pyridine is the first azabenzene we considered. It has one nitrogen atom, and experimental data for four valence transitions are available, two of $n \rightarrow \pi^*$ type (B_1 and A_2) and two of $\pi \rightarrow \pi^*$ (B_2 and A_1).^{56–59} The errors are reported in Figure 7. For this system, all of the ab initio methods present quite large errors. Almost all of the transitions are overestimated, except for the A_1 with RPA and A_2 for CIS(D). This molecule clearly shows how double excitation operators are not enough to obtain a good

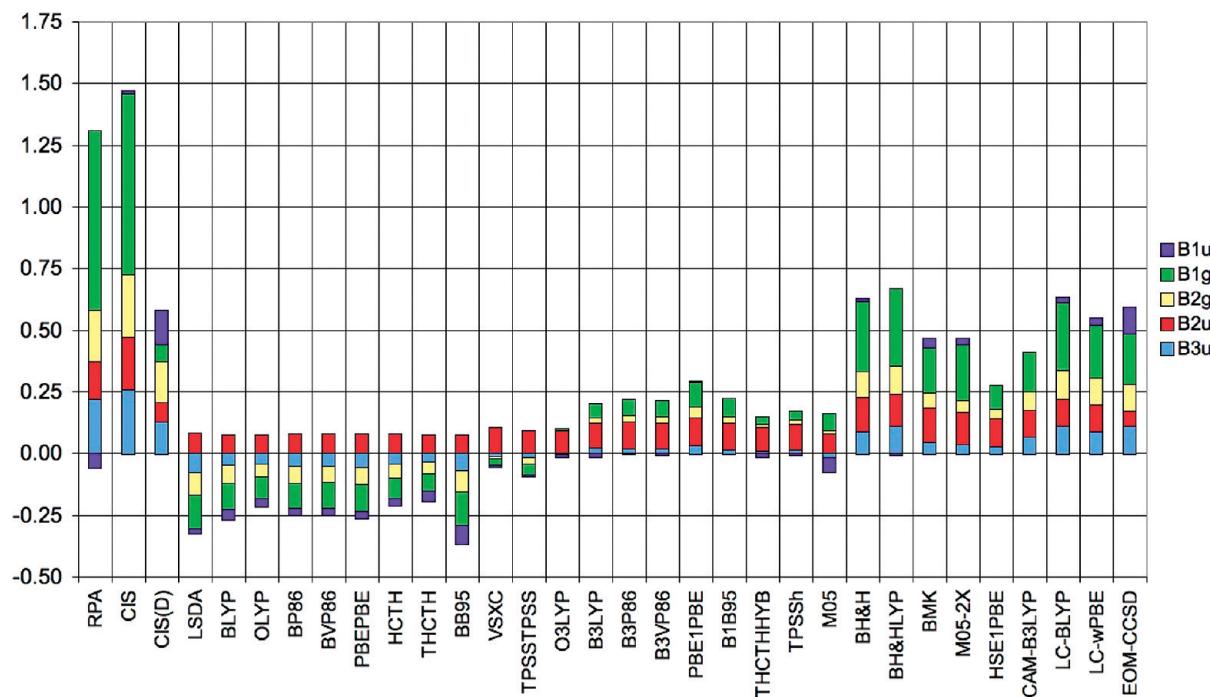


Figure 8. Errors (eV) for pyrazine.

agreement with experiment. In fact, the improvement brought by CIS(D) over CIS is quite small. The case of EOM-CCSD is even more evident, whose performance is, this time, quite worse than the previous cases. Pure functionals underestimate all the excitations but the B_2 ($\pi \rightarrow \pi^*$). They also provide a significantly better description of this system than CIS, RPA, and CIS(D). M-GGA functionals perform slightly better than GGA. Hybrid functionals provide again smaller errors than pure functionals, but this time functionals with a small amount of HF exchange perform quite well, and often better than the ones with large amounts. From Figure 7, we can see for example the large error bars of BH&H and BH&HLYP, and of LC-BLYP and LC- ω PBE, which performed among the best in the previous sections. For this molecule, the best agreement with experiments is achieved with CAM-B3LYP.

For pyrazine (1,4-diazine), five excitations are compared with experiments,^{56,57,60} that include both $n \rightarrow \pi^*$ (B_{3u} , B_{2g} , and B_{1g}) and $\pi \rightarrow \pi^*$ (B_{2u} and B_{1u}). The errors are represented in Figure 8. For this system, most of the considerations reported for pyridine are valid and often enhanced. Ab initio calculated transition energies are quite far from the experimental data. Again, double excitations are not enough to get an accurate description of these transitions, as shown by the poor performances of CIS(D) and EOM-CCSD. However, pure functionals perform drastically better than the ab initio methods. They underestimate all the transition energies but the B_{2u} ($\pi \rightarrow \pi^*$). The behavior of the hybrid functionals is similar to what we found for pyridine. In this case, the dependence on the HF exchange amount is even more evident since the difference between ab initio methods and pure functionals is larger. Indeed, the larger the amount of HF exchange, the larger the error. Thus the best results are obtained with O3LYP, THCTHHYB, and TPSSh. Slightly worse results are obtained with B3LYP, B3P86, B3VP86, B1B95, and M05. Larger errors are shown

by M05-2X, BMK, BH&H, BH&HLYP, CAM-B3LYP, LC-BLYP, and LC- ω PBE. For the latter functionals, the deviations from the experiment are larger than for many of the pure functionals. Interesting in this respect is also the comparison between BB95 and B1B95 and between M05 and M05-2X. The former two show a *decrease* of the total error by a factor of 2, passing from a pure functional to a hybrid one with 25% of HF exchange. The latter two show an *increase* of the error by a factor of 2, passing from 28% to 56% of HF exchange.

For pyrimidine (1,3-diazine), six experimental transition energies are available for comparison, again including $n \rightarrow \pi^*$ (two B_1 and two A_2) and $\pi \rightarrow \pi^*$ (B_2 and A_1) transitions.^{56,57,60} The error bars are reported in Figure 9, and we can see trends that resemble the previous case (see Figure 8). CIS and RPA errors are larger than for pyrazine. CIS(D) and EOM-CCSD are relatively better. In this case, double excitations seem to play a more important role, but the lack of higher order excitations is still evident. Hybrid functionals perform better than the pure ones as long as the HF exchange amount is not larger than 28% (M05). The number of overestimated transition energies also raises with the percentage of HF exchange. B3LYP, B3P86, B3VP86, THCTHHYB, TPSSh, and M05 show the best performances for this molecule.

Pyridazine (1,2-diazine) is the third diazabenzenes. Five transition energies are experimentally available, $n \rightarrow \pi^*$ (two B_1 and A_2) and $\pi \rightarrow \pi^*$ (B_2 and A_1) transitions, and they were used to compare the computed data.^{56,61} The total error bars are plotted in Figure 10. The errors for the ab initio methods are still quite large, and most of the transition energies are overestimated. CIS and RPA are the least accurate. CIS(D) and EOM-CCSD improve the agreement with the experiments, but they are far from the expected accuracy. However, for the B_2 transition ($\pi \rightarrow \pi^*$), CIS(D) shows a larger error than CIS. The DFT functionals show

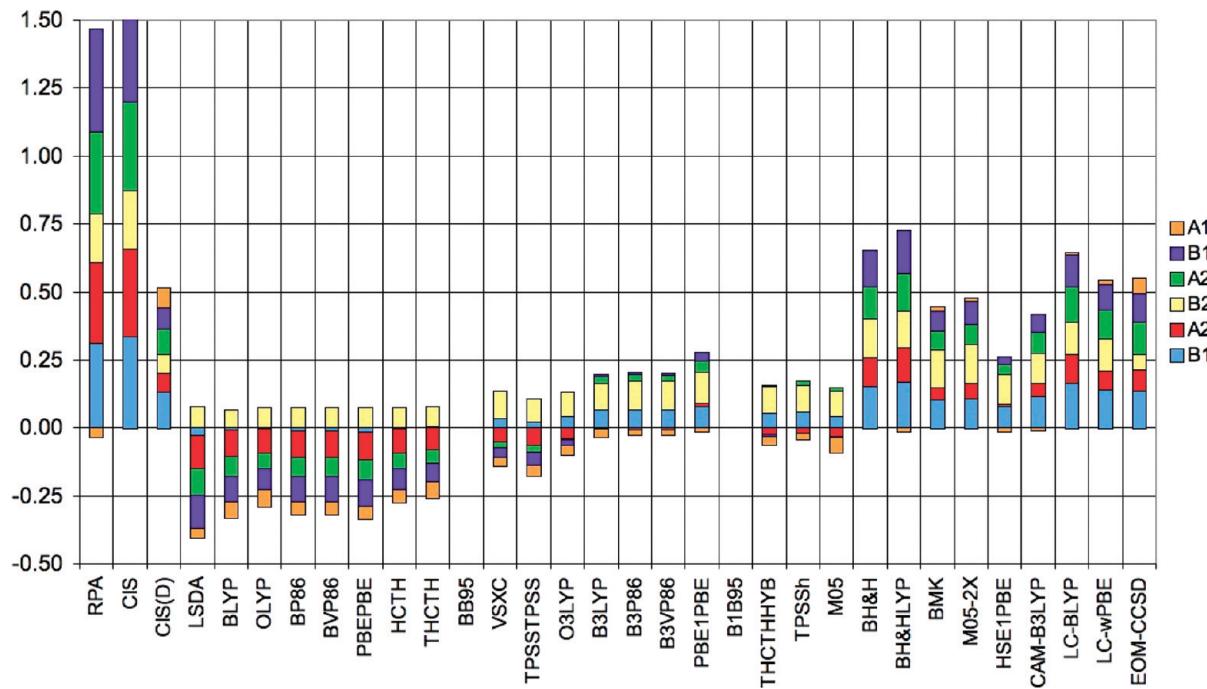


Figure 9. Errors (eV) for pyrimidine. The SCF of BB95 and B1B95 did not converge.

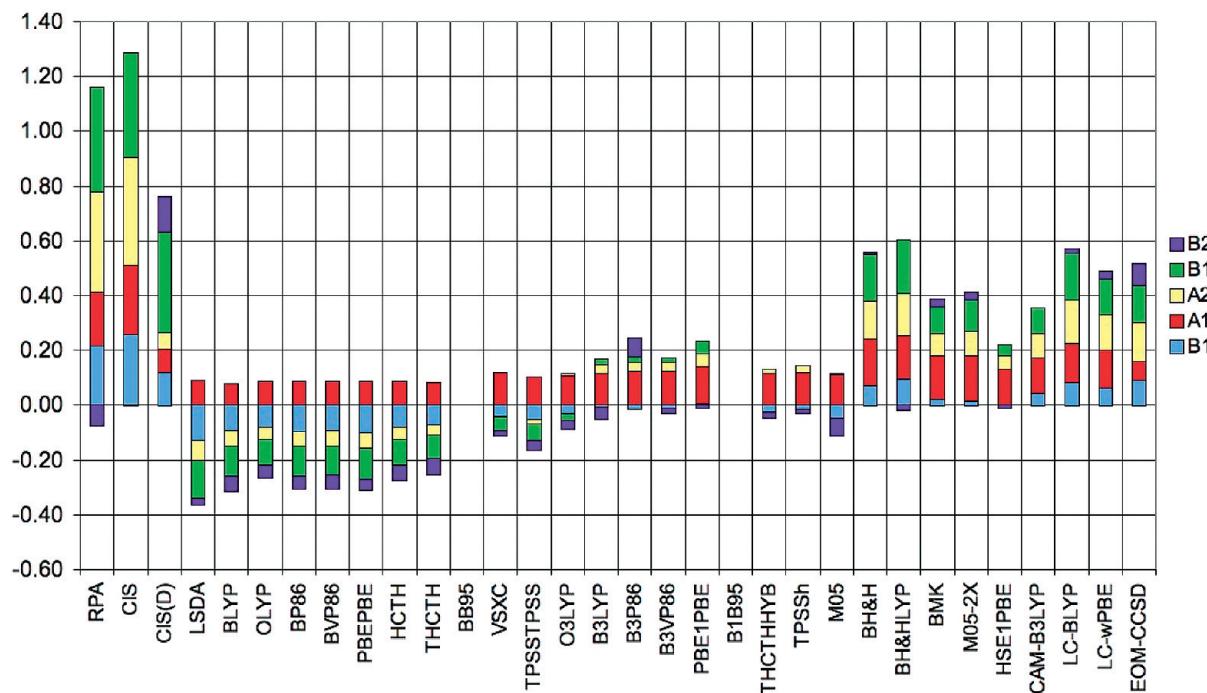


Figure 10. Errors (eV) for pyridazine. The SCF of BB95 and B1B95 did not converge.

trends similar to the previous three molecules. Pure functionals underestimate most of the transition energies, except for the $A_1(\pi \rightarrow \pi^*)$. Hybrid functionals perform generally better than pure functionals. B3VP86, THCTHHYB, and TPSSh show the best agreement with the experiments, and B3LYP, B3P86, PBE1PBE, M05, and HSE1PBE errors are not much larger.

Symmetric tetrazine contains four nitrogen centers. Four transition energies, all $n \rightarrow \pi^*$,^{56,60,62–66} are compared with computed data. The errors are reported in Figure 11. RPA and CIS errors are very large. CIS(D) drastically improves the description. This is the same range of error

provided by EOM-CCSD. GGA and M-GGA functionals total errors are smaller than CIS(D) and EOM-CCSD. Almost all of the hybrid functionals provide superior accuracy than the pure functionals. The best among them, B3LYP, B3P86, B3VP86, PBE1PBE, HSE1PBE, THCTHHYB, and TPSSh have a small percentage of HF exchange. M05-2X, BMK, BH&H, BH&HLYP, CAM-B3LYP, LC-BLYP, and LC- ω PBE show larger errors and they overestimate all of the transitions. Also, this case shows how the azabenzenes are a difficult test set for HF based methods (where among them we can include hybrid functionals with large part of HF exchange and exact long-

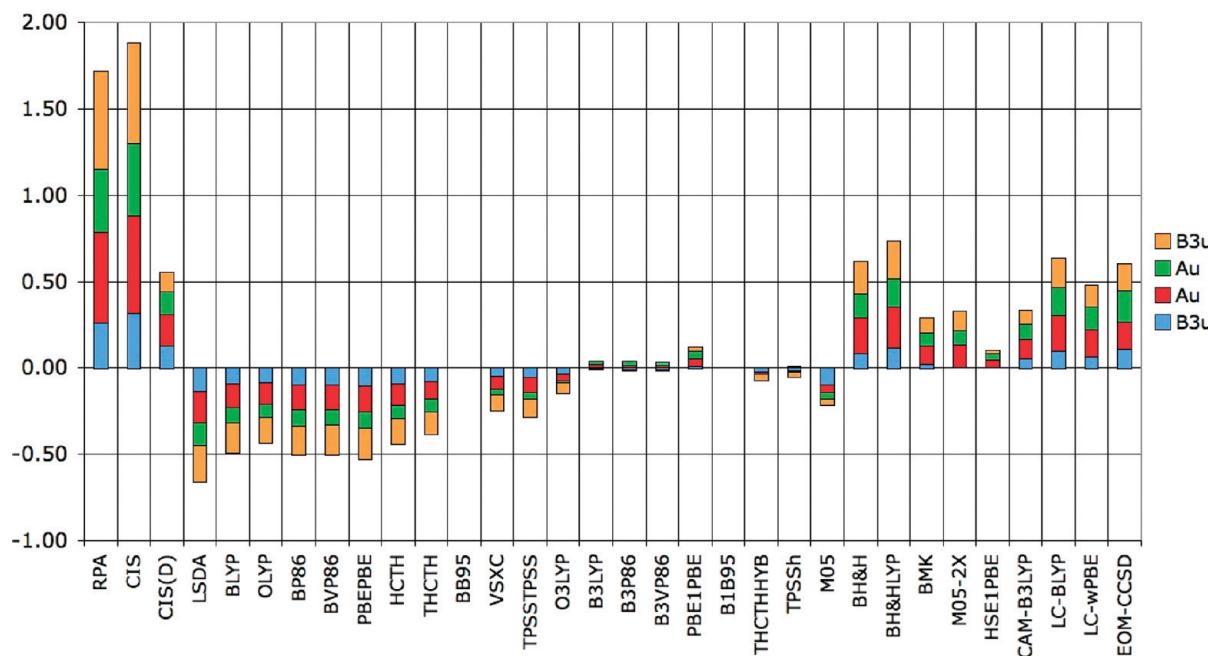


Figure 11. Errors (eV) for S-tetrazine. The SCF of BB95 and B1B95 did not converge.

range functionals). Double excited determinants play a very important role, as evident by comparing CIS and RPA with CIS(D) and EOM-CCSD, but higher excitation are necessary to obtain a better agreement with experiments.

The azabenzenes add another piece of information to the puzzle. In this case, ab initio methods show quite large errors. CIS and RPA are particularly unsatisfactory, with large overestimation of almost all the excitation energies and total errors larger than the pure functionals. CIS(D) improves the results, but in many cases such improvement is small. Surprisingly, EOM-CCSD provides a considerably worse performance for this class of systems than for the previous two. The large basis set employed here allows us to exclude this as a possible cause of the disagreement with the experiments. Del Bene et al.⁵⁶ showed that higher order excitations are necessary to obtain an accurate description of the excitation energies in this type of systems. Nevertheless, the EOM-CCSD errors are not dramatic, if compared to the functional ones for alkenes and carbonyls. Pure functionals perform better than CIS and RPA, and sometimes even better than CIS(D) and EOM-CCSD, underestimating most of the measured data. For this set, there are a few cases where GGA and M-GGA functionals perform better than LSDA. Hybrid functionals in many cases show smaller errors than pure functionals and ab initio methods. However, this time the performance among the hybrid ones is inverted with respect to the previous two sets of molecules. In fact, the functionals with a small contribution of HF exchange often largely outperform the ones with a large contribution. The latter show very large errors when the total error of the ab initio methods is much larger than the one of the pure functionals. LC-BLYP and LC- ω PBE behave like the functionals with fixed ratio of DFT and HF exchange and large percentage of the latter. We also note that in this case the functionals with small percentage of HF exchange are closer to the experiments than EOM-CCSD.

3.4. Discussion. Now that we have condensed the results we obtained into three sets of molecules, we can draw some general conclusions. We do not discuss any statistical analysis because the number and nature of the transitions considered is not a significant statistical sample, as mentioned in the Introduction. In fact, our test set includes only three alkenes and three carbonyl compounds, with mostly Rydberg states, and five azabenzenes with all valence states. The reduction of all of the collected results into few numbers for each method would be misleading, as these numbers would change dramatically by changing the size of the test set. For example, for a method like EOM-CCSD, which does not perform very well with the azabenzenes, but is extremely accurate for the other molecules, the statistical error would be large because the azabenzenes group would be overrepresented. However, for the interested reader, we report a comprehensive statistical analysis in Tables 23–25 in the Supporting Information. The tables report the analysis for all the molecules together, for the first and for all the states. Also, we report the analysis after separation of the azabenzenes group from the other two, again for the first and for all the states. In the following, however, only trends and qualitative behaviors are discussed.

CIS and RPA often provided large errors, except in the alkene set. They almost constantly overestimated the experimental data and there was not a significative difference between their results. Adding perturbative doubles corrections to CIS, CIS(D), led to an improvement of the results, but this was often not impressive, considering the computational cost added to the calculation and comparing with many functional performances. EOM-CCSD did a very good job for alkenes and especially for the aldehydes and acetone, but it was not able to accurately describe the azabenzenes. However, it was shown⁵⁶ that by increasing the excitation manifold, it is possible to obtain a better agreement with the experimental results. This is a very important feature of the coupled cluster theory, even for excited states, that it is

always possible to systematically improve the description of the electronic structure of a molecule. However, this leads to a rapidly increasing computational effort that may become unbearable even for small systems.

Unfortunately, the opposite is true for many of the DFT functionals available nowadays, i.e., the improvements do not become overwhelming from the computational point of view, but they are also not systematic, at least for the excitation energies. Pure functionals showed performances very often worse than CIS, and it is in a way surprising how LSDA errors were in many cases smaller than gradient corrected functionals. Almost all of the experimental data were underestimated.

The behavior of hybrid functionals with a fixed amount of HF exchange mostly relied on the cancellation of errors between the HF and the pure DFT part. In fact, the examples in this work seem to show how the relative accuracy between the CIS and the pure functionals favored the hybrid functionals with more or less HF exchange contribution, depending on the cases. In particular, when CIS accuracy was good, as in the alkene set, hybrid functionals with large part of HF exchange performed better. Also, when both CIS and pure functionals errors were large but comparable and opposite in sign, the errors of functionals with large HF exchange were small, as for the case of the carbonyl compounds. On the other hand, when the CIS errors were much larger than the pure functionals ones, as for the azabenzenes, the trend reversed and the functionals with small percentage of HF exchange clearly outperformed the ones with a large contribution. The sign of the error is also significant for the hybrid functionals along the various sets of molecules. The errors went from negative to mixed to positive, going from the alkenes to the carbonyl systems to the azabenzenes, following the relative magnitude of the ab initio vs the pure functionals errors. This behavior is even more evident when we compare M05 and M05–2X, that mainly differ in the amount of HF exchange, 28% and 56%, respectively. Indeed, we found an almost complete change in the sign of the errors for isobutene, acetaldehyde, and acetone.

The functionals with the correct asymptotic behavior, LC-BLYP and LC- ω PBE, which have a variable amount of HF exchange depending on the distance from the nuclei, showed a consistent overestimation of the transition energies, with a few exceptions as in the formaldehyde, where the overall error was already small. This is a good feature, as it already provides some information on the sign of the expected error. However, the general performance of such functionals is very similar to that of functionals with large (and fixed) amount of HF exchange, thus we can group all those functionals in the same category. We also point out that such correction for the asymptotic behavior cannot be directly applied to functionals which are already hybrid.

A functional that showed a consistently reasonable behavior throughout all of the test cases that we examined was B3P86, that has 20% HF exchange. This functional often performed as well as functionals with large amount of HF exchange, even for cases where the latter were favored, and it obviously performed much better than them for the

azabenzenes. The popular B3LYP provided larger errors than B3P86, which is not surprising if we consider that pure BLYP errors were larger than the BP86 ones. The hybrid functional with the worst performance was O3LYP, which often provided errors of the same order of the pure functionals. BB95 and B1B95 also deserve a separated comment, as they showed numerical instabilities that prevented the convergence of the SCF in six cases out of eleven.

At this point, a comparison with the work in ref 15 may be useful, as it is on the same molecular property and our results may seem to lead to different conclusions. The largest difference is in the definition of the test set: Our set includes 30 valence states and 39 diffuse Rydberg states of small molecules in gas phase, whereas most of the test set in ref 15 is based on experimental data on the first excited state of large chromophores in solution, with a large oscillator strength. Additionally, we used a very large basis set because, as reported in ref 16, the lack of diffuse functions may lead to large errors, not only for EOM-CCSD but also for TDDFT, especially for higher and diffuse states. For low lying states, like the valence states, basis set issues are generally less dramatic. Therefore, the average error of 0.14–0.18 eV reported in the conclusions of ref 15 for PBE1PBE and LC- ω PBE(20), although it still seems optimistic since such an accuracy is not even claimed for an ab initio method like EOM-CCSD,^{56,67} may only apply to the lowest bright state of large chromophores. In fact, the statistical analysis on the first excited state for our test set, reported in the Supporting Information, is in agreement with this result, although our test set is extremely limited. However, note the better performance of B3P86 in this comparison.

Clearly many factors influence the relative accuracy of the various functionals, but this work shows that one of the most important seems to be the error compensation present in the hybrid functionals. For instance, as far as the electronic excitations are concerned, the kinetic energy density contribution does not significantly improve the results of both GGA and H-GGA types of functionals; whereas, it increases the computational effort. Also, the separation of long and short-range exchange seems to be less important than the percentage of HF exchange, as shown by CAM-B3LYP, LC-BLYP, and LC- ω PBE. The case of HSE1PBE is slightly different, as for small molecules like the ones we considered this functional behaves like PBE1PBE.

4. Conclusions

Before summarizing the results reported in this work, we note that this work is not meant to be definitive, since new functionals appear almost monthly and many were left out from our representative set, and since other molecular systems with different characteristics may be studied. Nevertheless, it can bring some light to investigators who are struggling to decide which method is better for their electronic excitation studies, especially among the plethora of DFT functionals available in the computational packages. We show how CIS, RPA and pure functionals are not, in general, a good choice. Hybrid functionals with a fixed amount of HF exchange are often in between those methods, but their better performance seems to be mainly related to

error compensation and, thus, it cannot be systematic. Asymptotically correct functionals seem to show a more consistent overestimation of the experimental data, thus providing a reference for the estimation of the error, although their overall performance is very similar to functionals with large and fixed amount of HF exchange. Remarkably, the best average performance is obtained with a hybrid functional with a small amounts of HF exchange, B3P86, that appeared in 1993 and was not specifically designed for excited state properties. CIS(D) also does not seem a good choice, as its performance is often worse than many hybrid functionals. EOM-CCSD results are very good for alkenes and carbonyls but less for the azabenzenes, where higher order excitations in the cluster expansion seem to be necessary. However, highly correlated wave function-based methods like EOM-CCSD are, at least so far, always more reliable than any DFT functional, because they represent a secure way to approach the experiment and they should be used when possible. However, even if successful approximations to such methods have been proposed and used in many circumstances, DFT still represents the best compromise between accuracy and computational effort. However, large differences in the results are found between the various functionals, thus the choice of the functional can largely affect the accuracy of a calculation. Therefore, we hope that this work can be helpful when it comes to making a decision about which method to use to compute electronic transition energies.

Acknowledgment. M.C. thanks Giovanni Scalmani for useful discussions about the differences among the DFT functionals. The authors also thank Fernando Clemente for reading the manuscript and providing interesting comments.

Supporting Information Available: Tables 1–25, reports the geometry of all the molecules, the calculated and experimental transition energies with their characterization and complete statistical analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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CT9005129