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Extensive TD-DFT Benchmark: Singlet-Excited States of Organic Molecules

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Abstract: Extensive Time-Dependent Density Functional Theory (TD-DFT) calculations have been carried out in order to obtain a statistically meaningful analysis of the merits of a large number of functionals. To reach this goal, a very extended set of molecules (~500 compounds, >700 excited states) covering a broad range of (bio)organic molecules and dyes have been investigated. Likewise, 29 functionals including LDA, GGA, *meta*-GGA, global hybrids, and long-range-corrected hybrids have been considered. Comparisons with both theoretical references and experimental measurements have been carried out. On average, the functionals providing the best match with reference data are, one the one hand, global hybrids containing between 22% and 25% of exact exchange (X3LYP, B98, PBE0, and mPW1PW91) and, on the other hand, a long-range-corrected hybrid with a less-rapidly increasing HF ratio, namely LC-ωPBE(20). Pure functionals tend to be less consistent, whereas functionals incorporating a larger fraction of exact exchange tend to underestimate significantly the transition energies. For most treated cases, the M05 and CAM-B3LYP schemes deliver fairly small deviations but do not outperform standard hybrids such as X3LYP or PBE0, at least within the vertical approximation. With the optimal functionals, one obtains mean absolute deviations smaller than 0.25 eV, though the errors significantly depend on the subset of molecules or states considered. As an illustration, PBE0 and LC-ωPBE(20) provide a mean absolute error of only 0.14 eV for the 228 states related to neutral organic dyes but are completely off target for cyanine-like derivatives. On the basis of comparisons with theoretical estimates, it also turned out that CC2 and TD-DFT errors are of the same order of magnitude, once the above-mentioned hybrids are selected.

1. Introduction

Developing methodological approaches able to accurately deliver the transition energies corresponding to electronically excited-states remains a major challenge for theoretical chemists. Historically, the first computational schemes developed relied on semiempirical theories.[1] The most successful model, namely ZINDO,[2] was purposed-designed to allow quick estimates of the main features of UV/visible spectra and remains popular today. However, the quantitative aspect of the obtained results (absorption wavelengths and transition probabilities) was found to be highly system-dependent, a problematic feature.[3−5] More recently, calculations carried out for organic dyes have indicated that PM5[6] could be a promising approach,[7] but such a claim remains to be tested on a broader set of transitions and molecules. At the other extreme of the theoretical palette, one finds highly correlated ab initio approaches such as SAC-CI, EOM-CC, MR-CI, or CAS-PT2 that allow very accurate

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estimates but are limited to rather small systems due to their extreme computational cost. Two of the most extensive investigations performed with such high-accuracy approaches (CC3 and CCSDR) have been published very recently by Thiel and its co-workers.[8,9] Although these contributions certainly represent a very large computational effort, they have been "limited" to molecules of about 15 atoms (naphthalene was the largest compound treated with CC3) and relied on a diffuse-free polarized triple-ζ basis set. While it is true that CAS-PT2 and CC2, the two "lighter" wave function approaches, could possibly be applied to molecules containing about 40 atoms,[10−18] the current implementations of these *ab intio* theories often do not permit a systematic inclusion of medium effects. This is a problematic drawback, as it is well-known that excited-state properties tend to be more solvent-sensitive than their ground-state counterparts.[19] Clearly, the difficulties to apply the highly correlated approaches to a broad set of molecules in a real-life environment have yet not been completely solved. In terms of computational cost, one finds an intermediate between semiempirical theories and wave function approaches, namely time-dependent density functional theory (TD-DFT).[20−23] TD-DFT is the most widely applied ab initio tool for modeling the electronic spectra of organic and inorganic molecules[24,25] and can be extended to incorporate environmental effects either through a modeling of the bulk environment[19,26−29] or through a variety of QM/MM approaches.[30−35] Despite its successes and versatility, TD-DFT is limited and suffers an important drawback: the quality of the obtained results is profoundly functional-dependent. Indeed, the appropriate selection of the exchange-correlation form is often crucial to grasp chemically sound conclusions. For most excited-states, hybrid functionals that incorporate a fraction of exact exchange (EE) tend to provide more accurate estimates than pure functionals. Anyway, transition wavelengths to excited-states presenting a doubly excited character or a significant charge-transfer nature are traditionally poorly estimated, as are the electronic spectrum of molecules having a strong multideterminantal nature. For sure these deficiencies are related to the approximate nature of today's implementation, as illustrated by the recently developed long-range-corrected hybrids (LCH),[36−44] that appear to correctly appraise the charge-transfer properties. Contrary to the global hybrids (GH), LCH presents an EE percentage depending on the interelectronic distance, allowing a physically correct asymptotic behavior when the two electrons are far apart.

It is quite astonishing that only a limited number of contributions collated the *pros* and *cons* of functionals in the TD-DFT framework, for a significant set of molecules. In Table 1, we summarize the selected methodologies and training sets for twelve investigations tackling this question. One can certainly find many other TD-DFT studies using GH or LCH but often specific to a specific class of molecules.[5,45−53] As can be seen, not only the training set but also the details of the methodologies selected for benchmarking (including the size of the basis set and the possible modeling of solvent effects) differ significantly from one work to the other. We believe it is especially striking

that most studies include only a very small number of functionals (typically three) and that only four works used more than 100 excitations to obtain statistically meaningful conclusions. Considering the different training sets and procedures, it is to be expected that the conclusions of these investigations are not perfectly uniform. While the obtained mean absolute deviation (MAE) for the "best" functional is typically close to 0.25 eV, the actual findings are in fact partly antagonistic, making it difficult to appreciate the "general" functional performance in the TD-DFT framework:

1. Tozer and co-workers concluded that CAM-B3LYP[40] leads to much smaller deviations than B3LYP[54] for a variety of transitions of medium-size chromogens.[55] The average B3LYP error being completely unacceptable (>1.0 eV) for both Rydberg and charge-transfer states.[55,56] For valence transitions, all tested functionals (PBE, B3LYP, and CAM-B3LYP) provided similar MAE (0.27, 0.26, and 0.27 eV, respectively).[55]

2. Rohrdanz and Herbert found that an accurate description of both the ground-state and excited-state properties of large molecules was uneasy with common LCH functionals[57] and subsequently design a LCH functional working for both ground- and excited-states.[58] This new LCH functional provided a MAE of about 0.3 eV.[58]

3. For the λ_{max} related to $\pi \rightarrow \pi^{\star}$ transitions in 100 organic dyes, we found, within the vertical approximation, that PBE0 outperforms LCH and provides a MAE close to 0.15 eV,[59] the errors being of the same order of magnitude for $n \rightarrow \pi^{\star}$ transitions.[60,61] For the same set of $\pi \rightarrow \pi^{\star}$ transitions, CAM-B3LYP provided significantly larger deviations (0.26 eV).[59]

4. Thiel's group used BP86, B3LYP, and BHHLYP and they obtained MAE of 0.52 eV, 0.27, and 0.50 eV, respectively, for more than 100 transitions in small molecules,[62] using their own "best theoretical estimates"[8] as reference values.

5. Dierksen and Grimme concluded from an extensive vibronic investigation of (mainly) hydrocarbons that the optimal global hybrid should contain between 30% and 40% of EE.[63] Comparing their vertical (0−0) TD-DFT data to their solvent-corrected experimental references, we calculated MAE of 0.43 (0.57) eV, 0.21 (0.34) eV, and 0.31 (0.18) eV for BP86, B3LYP, and BHHLYP, respectively.

6. Very recently,[64] Goerigk et al. used the CAS-PT2 result of ref 8 to benchmark double-hybrid functionals[65] and found a MAE of 0.22 eV for B2PLYP and B2GPPLYP, significantly smaller than with B3LYP (0.30 eV) and confirmed this finding on a set of five large chromophores.

Consequently, given an arbitrary molecule, it remains difficult to know without testing what is (are) "reasonably" the most adequate functional(s) to evaluate the electronic spectra. Should one choose a GH or a LCH? Would the error be much larger with a GGA than with a GH? What is the "expected" accuracy with today's computational procedure? Are *ab intio* functionals outperforming (or not) parametrized functionals? Should the chosen functional vary for molecules of different size? Of course, all these questions have been tackled in part in the above-mentioned works, but with no generic answer embraced by a large community. Here, we

Table 1. Training Set and Method Used in Recent Benchmark TD-DFT Calculations[n]

citation		training set				method			comparison
group(s)	ref.	molecules	states	functionals	basis set	solvent	transitions	geometry	
Boeij	14	19 molecules	25 mixed	SVWN, SVWN-VK	ET-pVQZ	none	vertical	BP/TZ2P	mixed[a]
Fabian	3	76 sulfur-bearing dyes	163 mixed	B3LYP	6-31+G(d)	none	vertical	B3LYP/6-31+G(d)	experiment
Fabian	12	21 sulfur-free dyes	54 mixed	B3LYP, B3LYP(TB)	6-31+G(d)	none	vertical	B3LYP/6-31+G(d)	experiment
Grimme	13	14 molecules	22 mixed	B3LYP	TZVP	none	vertical	B3LYP/TZVP	mixed
Grimme	63	40 large molecules[c]	42 $\pi - \pi^\star$[b]	BP86, B3LYP, BHHLYP	TZVP	none[d]	0−0	DFT/TZVP	experiment
Grimme	64	28/5 small/large molecules	142/5 mixed	6/17 functionals[e]	TZVP	none/PCM	vertical/0−0	MP2/DFT	theory[f]/experiment
Herbert	57	9 molecules	29 mixed	LC-PBE, LC-BLYP, LC-PBE0	aug-cc-PVDZ	none	vertical	B3LYP/6-31G(d)	experiment
Matsumura	7	50 organic dyes	50 $\pi - \pi^\star$	B3LYP	6-31G(d), cc-pVDZ	none	vertical	B3LYP	experiment
Tozer	55	18 model molecules	59 mixed	PBE, B3LYP, CAM-B3LYP	cc-pVTZ[g]	none	vertical	Mixed[h]	mixed[i]
Thiel	62	28 small molecules	102 mixed	BP86, B3LYP, BHHLYP, MR-DFT	TZVP	none	vertical	MP2/6-31G(d)	theory[j]
Us	60	34 small dyes	34 $n - \pi^\star$	12 pure and hybrid functionals[k]	Large w. diffuse[l]	PCM	vertical	PCM-DFT	experiment
Us	59	115 organic dyes	118 $\pi - \pi^\star$	6 pure and hybrid functionals[m]	6-311+G(2d,p)	PCM	vertical	PCM-PBE0/6-311G(d,p)	experiment

[a] CAS-PT2, gas-phase measurements, or solvent measurements empirically corrected for solvatochromism. [b] Mainly $\pi - \pi^\star$ transitions corresponding to singlet and doublet excited-states but a few other states. [c] Mainly aromatic and aliphatic hydrocarbons or oligomeric structures with a few heteroatoms. [d] No solvent model in the theory, but the experimental values have been shifted by a constant 0.15 eV (for all solvents) to include solvatochromism. [e] BP86, B3LYP, B2LYP, B2GPLYP, B2PLYP, B2GPPLYP, and B2GPPLYP for the small molecules with PBE, OPBE, BLYP, mPWLYP, TPSS, VSXC, O3LYP, B98, PBE0, BMK, and BHHLYP for the large ones. [f] CAS-PT2 from ref 9, using the same basis set and geometry. [g] d-aug-cc-pVTZ for Rydberg states. [h] Experimental, B3LYP/TZVP, CAM-B3LYP/6-31G(d), or MP2/6-31G(d) geometries, depending on the molecule. [i] CAS-PT2, CC2, or gas-phase experiment, depending on the molecule. [j] Best estimates (generally CC3 or CAS-PT2) from their own ref 8, using the same basis set and geometry. [k] HF, BLYP, PBE, TPSS, B3LYP, PBE0, BMK, LC-BLYP, LC-PBE, LC-TPSS, LC-ωPBE, and CAM-B3LYP. [l] 6-311++G(3d,3p) for nitroso dyes and 6-311++G(2df,p) for thiocarbonyl chromophores. [m] HF, PBE, PBE0, LC-PBE, LC-ωPBE, and CAM-B3LYP. [n] For each contribution, we list the nature of the selected excited-stated, molecules, and functionals as well as a summary of the methodological scheme. In this table, i) "basis set" refers to the basis set used for TD-DFT calculations; ii) "solvent" indicates the consideration or/not of environmental effects; iii) "transitions" indicates if full vibronic calculations have been computed or if vertical values have been used; iv) "geometry" gives the method used to obtain the molecular ground-state structures; and v) "comparison" indicates the origin of the values used as reference data during the statistical analysis.

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have performed benchmarks that are more complete than any previously published data, both from the point of view of the number of molecules considered and of the set of pure and hybrid functionals incorporated.

2. Methodology

2.1. Strategy. As can be seen in Table 1, two philosophies can be used to benchmark TD-DFT functionals: versus experiment (VE) or versus theory (VT). Both approaches have advantages and disadvantages. Trying to closely match experiment (VE) is generally desired in most practical applications and allows to include in the training set a wide range of molecules and compounds. On the other hand, one would normally need to compute the full vibronic spectra (and not "simply" vertical transitions) and to perfectly model the experimental setup (pressure, temperature, full environmental effects, ...), both tasks being impossible for a large set of solvated molecules. Additionally, it is not always straightforward to pinpoint the theoretical transition actually corresponding to the experimental measures, especially for highly excited states. Comparisons with accurate wave function estimates (VT) allows straightforward and physically meaningful comparisons (same conditions, same transitions) but is obviously limited by the availability of theoretical data, i.e. only small molecules can be included. In many cases, CC2 results have been used as reference values for medium size molecules, a strategy that we think unsatisfying. Indeed, we computed a MAE of 0.27 eV (0.30 eV) between the CC2/TZVP and the CAS-PT2/TZVP ("best estimates") values for the 103 singlet-excited excited-states of ref 8.[66] Even for low-lying excited-states, CC2 is often off the theoretical limit by 0.1 eV,[8] a value equal to one-half or one-third of the typical TD-DFT error.

In the following, we will use both philosophies so to be as general as possible. In what concerns the versus theory scheme, we have selected Thiel's set (VT set in the following) and mimic exactly the computational procedure (basis set and geometry). For the VE set, we have used a computational strategy that is at the limit of today's possibilities for such a set of molecules, trying to circumvent the possible limitations of our computational procedure. For the sake of consistency, we have chosen to use a uniform methodology (basis set, solvent effects, ...) for all VE molecules.

2.2. General Computational Procedure. All calculations have been performed with the Gaussian suite of programs, using both the commercial and development versions[67,68] with a tight self-consistent field convergence threshold (10^{-8} to 10^{-10} au). For the VE set, we have followed a well-established three-step approach:[25] i) the ground-state geometry of each compound has been optimized until the residual mean force is smaller than 1.0×10^{-5} au (so-called *tight* threshold in Gaussian); ii) the vibrational spectrum is analytically determined to confirm that the structure is a true minimum; and iii) the vertical transition energies to the valence excited states are computed with TD-DFT. For the VT set, the geometries have been taken from ref 8 and step iii) directly performed.

As the majority of experimental data are obtained in condensed phase, we have included bulk solvent effects in our VE model (all VT calculations are in gas-phase). This was performed at each stage, including geometry optimizations and Hessian calculations, using the well-known Polarizable Continuum Model (PCM),[19] that is able to obtain a valid approximation of solvent effects as long as no specific interactions link the solute and the solvent molecules. Typically solvent−solute hydrogen bonds tend to influence more significantly the $n \rightarrow \pi^\star$ transitions than their $\pi \rightarrow \pi^\star$ counterparts, and we have tried to select aprotic solvent for the former, at least when different experimental values are available. The list of solvent selected is given in the Supporting Information. The default PCM Gaussian parameters have generally been used, though for a few calculations if was necessary to change the atomic raddi (UAKS instead of UA0) or to switch off the presence of smoothing sphere (NoAddSph) to converge the force minimizations. For the records, note that some default PCM parameters might differ between the two versions of the program used. All TD-DFT calculations have been performed within the nonequilibrium approximation, valid for absorption spectra.[19]

2.3. Functionals and Basis Sets. As we want to assess the *pros* and *cons* of a series of DFT approaches, a very extended set of functionals has been used. Apart from the Time-Dependent Hartree−Fock approach (TD-HF, refereed to as HF in the following), the selected functionals can be classified in five major categories: LDA, GGA, *meta*-GGA, GH, and LCH. In the first category, that is expected to be the less efficient we have selected only one functional, SVWN5.[69,70] We have chosen four GGAs, namely BP86,[71,72] BLYP,[71,73] OLYP[73,74] and PBE,[75] whereas we have picked up three popular *meta*-GGA: VSXC,[76] τ-HCTH[77] and TPSS.[78] Twelve global hybrids have been used: TPSSh (10%),[79] O3LYP (11.61%),[80] τ-HTCHh (15%),[77] B3LYP (20%),[54,81] X3LYP (21%),[82] B98 (21.98%),[83] mPW1PW91 (25%),[84] PBE0 (25%),[85,86] M05 (28%),[87] BMK (42%),[88] BHHLYP (50%),[89] and M05−2X (56%).[90] The LCH constitute the last category and use a growing fraction of EE when the interelectronic distance increases. This is formally performed by partitioning the two-electron operator as[36,40,91]

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \, \mathrm{erf}(\omega r_{12})]}{r_{12}} + \frac{\alpha + \beta \, \mathrm{erf}(\omega r_{12})}{r_{12}}$$

(1)

The first term of the rhs of this equation describes the so-called short-range effect and is modeled through DFT exchange, whereas the second term corresponds to the long-range contribution calculated with the HF exchange formula. In eq 1 ω is the range separation parameter, while α and $\alpha + \beta$ define the EE percentage at $r_{12} = 0$ and $r_{12} = \infty$, respectively. The LC model uses $\alpha = 0.00$, $\beta = 1.00$, and $\omega = 0.33$ au^{-1} in eq 1[37,38] and has been applied to both GGA and *meta*-GGA to give LC-BLYP, LC-OLYP, LC-PBE, LC-τ-HCTH, and LC-TPSS. The approach designed by Vydrov and Scuseria,[42,43] namely LC-ωPBE, with $\omega = 0.40$ au^{-1} and $\alpha = 0$, $\beta = 1$, has been used as well. Note that in LC-ωPBE, the short-range exchange functional can be rigorously derived[41,92] by integration of the model

exchange hole.[42,43] We have also used a variation of the LC-ωPBE functional using $\omega = 0.20$ au^{-1} (all other parameters are the same as the original model), here denoted LC-ωPBE(20). Indeed, such smaller ω has been recently found promising for TD-DFT calculations on large molecules.[57,58] Note that the functional designed in ref 58 differs from LC-ωPBE(20) by the use of 20% of short-range exchange. Additionally, the well-known CAM-B3LYP model ($\alpha = 0.19$, $\beta = 0.46$ and $\omega = 0.33$ au^{-1}) has been included in our set.[40] As the sum of α and β is not strictly equal to 1.00 in CAM-B3LYP, the exact asymptote of the exchange potential is lost, whereas a larger percentage of HF exchange is included at short-range. Eventually, we note that all LCH functionals selected in this work use full-range semilocal correlation.

In the VE set, steps i) and ii) of section 2.2 have been performed a split-valence triple-ζ 6-311G(d,p) basis set that delivers fully converged geometrical parameters for most molecules.[93] As our main focus is the TD-DFT part, all optimizations have been achieved with the PBE0 functional, that is suitable for most organic molecules, so to avoid that the quality of the geometry interferes with the evaluation of the performances of the functional for transition energies. In particular, it has been shown that several LCH lead to relatively poor geometries, so that performing geometry optimization and transition energy calculations with the same LCH may yield unsatisfactory results.[57,61] It has been tested that choosing another GH such as B3LYP indeed delivers very similar structural parameters for most molecular families in the VE set. The electronic excitations (step iii) were evaluated with the 6-311+G(2d,p) basis set, as such a basis set often bestows converged transitions wavelengths for medium and large chromophores,[25] as long as no Rydberg state is considered. The second d polarization function has been shown compulsory for indigoids,[94] coumarins,[95] and diarylethenes:[5] this second function is therefore necessary to get closer to converged results. The accuracy of 6-311+G(2d,p) for low-lying excited-states of medium and large molecules can be illustrated by numerous examples: 1) for the λ_{max} of two typical diarylethenes, the differences between the 6-311+G(2d,p) and 6-311++Gp(2df,2pd) results are limited to +0.007 and −0.004 eV;[5] 2) the differences are also negligible (±0.007 eV at most) when adding additional diffuse or polarization functions on the selenoindigo,[96] thioindigo,[45] and indigo[94] structures; 3) for four diphenylamine dyes one notes no variation when using 6-311++G(3d,3p) instead of 6-311+G(2d,p);[97] 4) the first $n \rightarrow \pi^{\star}$ transition of thioacetone computed with 6-311+G(2d,p) is within 0.005 eV of the 6-311++G(3df,3pd) results, for a constant geometry;[48] 5) among the two strong transitions of five 1,4-naphthoquinones, the largest discrepancy noted between 6-311++G(3df,3pd) and 6-311+G(2d,p) is 0.012 eV;[98] 6) the largest deviation between the results calculated with these two basis sets is limited to 0.011 eV both neutral and anionic dinitrophenylhydrazones;[99] 7) the three major transitions of a large tetrakis hydrocarbon undergo no change when shifting from 6 to 311+G(2d,p) to 6-311++G(3df,3pd).[100] Of course, for the small molecule subset and, more specifically, the tiny systems listed in Table

XXVII of the Supporting Information, the errors induced by the 6-311+G(2d,p) choice are certainly non-negligible, and we are far from convergence. In the VT set, we have used the TZVP basis set during the TD-DFT step to be consistent with ref 62. Note that the basis set effects can be large for some cases of the VT set, as discussed previously.[8] In other words, basis sets including diffuse functions would certainly modify the TD-DFT estimates of the VT set, but we have conserved this basis set for the sake of consistency (see below).

2.4. Building the VE Training Set. As we have discussed in the Introduction, building a meaningful training set of molecules is certainly important. In this first work, we focus on the singlet-excited states of (bio)organic molecules that are the focus of most TD-DFT investigations. We have tried to obtain a set of molecules as large as possible and as inclusive as possible. Indeed, our VE training set includes all molecules of refs 1, 7, 10, 12, 59, 60, and 61 as well as the majority of the compounds of refs 55 and 63. We want to highlight that absolutely no structure was simplified with respect to the actual experimental structure, e.g. no *t*-Bu side chain was replaced by a methyl group or a simple hydrogen atom, as common in many theoretical works. Additionally, no system was discarded because of the probable inefficiency of TD-DFT to model them correctly. For instance, we have included many cyanine dyes that, due to their multideterminantal nature,[101] are not satisfactorily modeled even with the most refined functionals.[65,102] The VE set (see the Supporting Information) contains 483 molecules, for a total of 614 excited-states. We have divided our full set of molecules in various subgroups for neutral dyes, charged dyes, hydrocarbons, biomolecules, oligomers, ... In what concerns the dyes, azobenzene, anthraquinone, and triphenylmethane derivatives are strongly represented as they constitute the three most important classes of "absorption" dyes.[103,104] The design of subgroups has been achieved not only to ease the reader's work but also to be able to test the consistency of the TD-DFT estimates within specific structural families. For the record, we note that consistently with ref 8, the VT set contains 28 molecules and 103 excited-states.

2.5. Reference Values. In the VT set, we have selected the reference values which are either the "best theoretical" estimates or the CAS-PT2/TZVP values,[8,62] the latter ensuring perfectly meaningful comparisons from the basis set point of view.[105] In the VE set, choosing appropriate references is more difficult. In most cases, the experimental works only report the longest wavelength of maximal absorption (λ_{max}) with possibly the related molar absorption coefficient. For most dyes or large conjugated molecules, this corresponds to the first low-lying transition with a large oscillator strength, and the comparison between theory and experiment is straightforward. In other cases (typically small chromogens or unconjugated molecules), comparisons could be more difficult, and we used the relative oscillator strength and symmetry of the excited-states to pinpoint the correct transition. For sure, a few specific assignments could be discussed although, on the one hand, their statistical weight is indeed limited, and, on the other hand, a reasonable

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chemical assignment (as the one used here) is often performed in practice, the explicit experimental information for the nature of the excited-state being frequently missing. When the vibronic structure is clearly defined experimentally, as for most hydrocarbons, we have listed in the Supporting Information tables both the transition with the largest molar absorption coefficient (selected in most comparisons for the sake of consistency with other experimental data) and the likely 0−0 peak. Our experience is that both GH and LCH generally provide theoretical spectra that are more easily comparable to experiment, as only a few transitions do present large oscillator strength. With pure functionals, the interpretation tends to be less immediate. Finally, when several experimental values in the same conditions are available, the average value was used for comparisons.

2.6. Limitations. For the VE comparisons, several limitations can be pointed out. The first is certainly the lack of vibronic couplings,[63,106] in our model, meaning that we incorrectly compare purely vertical transitions to experimental transitions. Unfortunately, computations of the Franck−Condon factors require the determination of the Hessian of the relevant excited-state, a task that is very far from today's possibilities with a large basis set, for a large number of functionals and molecules in a solvated environment. The differences between vertical and 0−0 transitions could be sizable:[13,63] in a recent work Grimme and co-workers obtained variations in the 0.24 eV−0.41 eV range for five large chromophores.[64] This clearly indicates that computation of the 0−0 spectra for all molecules would certainly lead to different conclusions regarding the merits of each functionals. On the bright side, using vertical transitions has a practical advantage: such calculations are much faster and are used in the large majority of TD-DFT works. The second possible origin of theory/experiment deviation is the modeling of solvent effect that is limited to a bulk linear-response approach. It is obvious that protic solvents might interact specifically with many chromogens, tuning the computed spectra,[26,107,108] while for molecules undergoing a large change of dipole moment between the ground- and excited-state, like coumarins, a state-specific PCM modeling would be more suited.[109] On the contrary, we believe that the selected basis sets are large enough to induce a negligible error, whereas the choice of PBE0 for optimizing the ground-state geometries should not cause a significant bias but for long oligomeric chains.[102,110,111]

All these limitations do not exist for the VT set, where only the reliability of the theoretical reference could be criticized. While CAS-PT2, CC3, MR-CI, MRMP, ... values used to determine the "best estimates" in ref 8 are certainly not perfect, they are probably close enough to the theoretical limit, so that we assume in the following that the main error originates from the selected functionals, not from the theoretical reference. Of course, when comparing with these "best estimates" (obtained with different basis sets), the lack of diffuse functions in TD-DFT/TZVP might also induce an error. Using CAS-PT2/TZVP results for reference allows to lift this problem, although the errors associated with CAS benchmarks still remains non-negligible for a few specific states.[112]
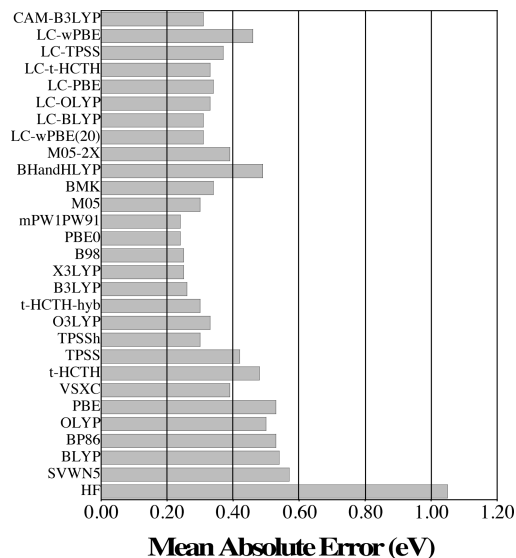

Figure 1. Mean Absolute Error for the full VT set (eV). The "best estimates" of ref 8 are used as references.

3. Results

For such extensive benchmark calculations, it is useless to analyze the computed spectra molecule-per-molecule, as one can always find a case for which a specific functional does provide the most accurate results. Only statistical analysis, allowing to unravel general trends does matter. The transition energies obtained for each molecules/functionals as well statistical results are catalogued in the Supporting Information.

3.1. Analysis of the VT Set. Let us start our comparisons with the VT set. The computed MSE, MAE, and the R^2 obtained through linear fitting for BP86, B3LYP, and BHHLYP are within 0.01 eV of the one reported by Silva-Junior and co-workers[62] for the same methods, confirming that the computational details (DFT integration grid, exact implementation of each functional, ...), that may differ from code to code, have a totally negligible impact. From the Supporting Information, it is clear that benchmarking the TD-DFT/TZVP values wrt the "best estimates" or wrt the CAS-PT2/TZVP references yield similar average deviations and error patterns. Therefore, in the following, we discuss the comparison with the former set of references, except when noted. The amplitude of the MAE for the 29 functionals are depicted in Figure 1. It turns out that HF provides very large errors (|MSE|, MAE, and RMS > 1.00 eV) and overestimates the transition energies in nearly 90% of the cases. It is worth pointing out that the HF errors are even larger for $n \rightarrow \pi^\star$ states with a MAE (RMS) of 1.36 eV (1.47 eV). The especially small HF R^2 (0.73) also indicates inconsistent predictions, and one can definitively rule out the uncorrelated approximation. In fact, using any DFT scheme does reduce the errors by a factor ranging from two to four. As expected, the pure functionals tend to provide too small transition energies, with MSE > 0.2 eV, although two of the *meta*-GGA (VSXC and TPSS) yield significantly more accurate spectral data than SVWN5, BLYP, BP86, OLYP, and PBE, in agreement with the ladder of functionals proposed by Perdew.[22] For instance, VSXC delivers a MAE of 0.39 eV

and a RMS of 0.47 eV, both 0.15 eV smaller than their BP86 counterpart: if only pure functionals are available, using the most refined one is indeed useful. All pure functionals are characterized by R^2 of 0.91 or 0.92, indicating that the chemical ordering is only reasonably restored by these approximations. Global hybrids are more accurate than the GGA and *meta*-GGA, and adding more and more EE tends to shift the transition energies to larger values. Consequently, the MSE evolves quite smoothly with the EE percentage (at the notable exception of M05), remaining slightly positive, as in pure functionals, for TPSSh and becoming largely negative for BHHLYP, that overestimates the transition energies by an average 0.42 eV (0.38 eV when CAS-PT2 values are selected as reference). Pinpointing the four GH presenting the MSE the closest to zero (X3LYP, B98, mPW1PW91, and PBE0) allows to state that functionals containing between 22% and 25% of EE are on the spot. As the exact same four GH provide the smallest MAE (see Figure 1), the smallest RMS and the largest R^2, and as these findings hold for both sets of reference values ("best estimates" and CAS-PT2/TZVP), these methods can be considered as best choice, at least for small molecules. The MAE of all LCH with an $\omega = 0.33$ au is close to 0.3 eV, due to an overestimation of the transition energies. We note that LC-ωPBE, characterized by a larger range-separation parameter, has a larger MAE (0.46 eV), while LC-ωPBE(20) relying on a less rapidly increasing fraction of EE presents a small and positive MSE. While CAM-B3LYP allows more accurate results than LC-BLYP, it remains slightly less efficient than B3LYP. This contradicts the results of Peach and co-workers.[55] A possible explanation of this discrepancy is the small size of the VT molecules: charge-transfer states are not significantly represented, which penalizes the CAM model.

For a more thorough discussion of the accuracy within each chemical family of the VT set, we refer the reader to ref 62 in which BP86, B3LYP, and BHHLYP performances are discussed in detail. The conclusions can be extended to other pure functionals and global hybrids. Nevertheless, as LCH have not been used before for the same set of molecules, it is probably worth discussing further this category of functionals. For the acene series, the B_u states are accurately estimated by LCH, including the correct evolution with oligomer length. For instance, the vertical transition energy to the first B_u state decreases by 1.52 eV (1.77 eV with CAS-PT2) from butadiene to octatetraene, a value nicely reproduced by CAM-B3LYP (1.65 eV). This conclusion is in agreement with the investigation of Peach et al.,[55] though they selected different ground-state geometries and reference values. On the contrary, for the A_g states, that are already poorly described by GH, the LCH are of no help and yield very large errors, e.g. LC-TPSS is 1.97 eV off for hexatriene. Therefore, it appears that all monodeterminantal DFT approaches fail to recover the correct ordering of the A_g and B_u states, at least for medium-sized polyacetylene oligomers.[62,64] For unsaturated cyclic hydrocarbons, LCH tend to outperform the commonly used GH. This is especially striking for norbornadiene for which CAM-B3LYP provides A_2/B_2 states at 5.13/6.03 eV in good agreement with

the reference data (5.34/6.11 eV), whereas PBE0 strongly undervalues these energies (4.91/5.67 eV). For benzene and naphthalene, we found that CAM-B3LYP transitions energies are larger than their B3LYP counterpart for the low-lying states, exactly as in ref 55. This difference between LCH and GH pertains for higher transitions, leading to large deviations for the higher-excited states that are strongly overestimated with all LCH [but LC-ωPBE(20)] but reasonably reproduced with GH like B3LYP or PBE0. This latter finding follows our previous work on Rydberg states.[113] For the heterocyclic structures, the LCH do not cure the most significant GH deficiencies. For instance the first B_{2u} states of pyrazine is located at 5.44 eV with PBE0 and 5.40 eV with LC-PBE but at 4.64 eV with the best wave function scheme (4.85 eV with CAS-PT2). Likewise, the first $\pi \rightarrow \pi^{\star}$ state of *s*-triazine should be close to 5.79 eV but is overvalued by all hybrids (PBE0: 6.24 eV and LC-PBE: 6.21 eV). In addition, we note that the $n \rightarrow \pi^{\star}$ states are extremely sensitive to the EE percentage. Indeed, for the 20 $n \rightarrow \pi^{\star}$ transitions of the heterocycle subset, the MSE (MAE) is 0.66 eV (0.66 eV) with BLYP, 0.13 eV (0.16 eV) with B3LYP, −0.56 eV (0.56 eV) with BHHLYP, −0.09 eV (0.15 eV) with LC-BLYP, and −0.18 eV (0.21 eV) with CAM-B3LYP. For these 20 states, PBE0 and mPW1PW91 give the smallest MAE (0.13 eV), while, on the contrary, LC-ωPBE(20) that was efficient on average is not appropriate (MAE of 0.36 eV). For aldehydes and ketones, LC-GGA, LC-*meta*GGA, and CAM-B3LYP give accurate estimates of the transition energies. The MAE of CAM-B3LYP for this subset is limited to 0.15 eV with only one of the high-energy states of benzoquinone being poorly evaluated. For the amides, the $n \rightarrow \pi^{\star}$ are correctly evaluated by all LCH, but the $\pi \rightarrow \pi^{\star}$ transition energies are significantly overestimated. Eventually, for the four nucleobases, the largest systems of the VT set, we found that the MAE of LCH are significantly larger than these of 25%-GH (LC-OLYP: 0.31 eV, CAM-B3LYP: 0.25 eV versus PBE0: 0.09 eV), the LCH's errors being largest for $n \rightarrow \pi^{\star}$ transitions. For the low-lying states of uracil, a more complete investigation of the merits of different (PCM-)TD-DFT approaches has recently been published by Improta and Barone.[114] Overall, it is worth pointing out that, for the small molecules of the VT set, LCH tend to behave like GH containing a sizable fraction of EE. This is quite obvious by comparing the CAM-B3LYP and BMK columns in the Supporting Information. The similarity is large enough so that the mean absolute difference between the two sets of data is limited to 0.11 eV, whereas the R^2 relating the results of the two functionals attains 0.99.

Previous works on the same set of molecules also used different approaches.[62,64] The DFT MR/CI scheme of ref 62 is more accurate than the four best GH listed above (X3LYP, B98, PBE0, and mPW1PW91), though the differences remains trifling, the multireference MAE being 0.22 eV (instead of 0.24 eV) and the related R^2 reaching 0.96 (instead of 0.95). Determining if these improvements justify the computational effort related to the DFT MR/CI approach probably depends of the nature of the case under scrutiny. CC2 yields larger MAE (0.30 eV) but better correlation ($R^2 = 0.97$)[8] than the 22−25% functionals, clearly hinting that

Extensive TD-DFT Benchmark

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CC2 cannot be viewed as "systematically more accurate" than TD-DFT, nor can it be used to benchmark DFT functionals without adequate testing. Of course, CC2 values are expected to be more basis set dependent than the TD-DFT ones, and our conclusion holds only for medium-size basis sets. However, using the CAS-PT2/TZVP as reference, we obtain a MAE of 0.27 eV for CC2/TZVP and 0.26 eV for PBE0/TZVP, meaning that their performances are extremely similar. At the very least, these results indicate that, although CC2 remains a method of choice to tackle specific problems, its blind and straightforward application does not always guarantee outperforming TD-DFT. Starting with the B2LYP and B2PLYP of ref 64 we have performed a statistical analysis for the same set of reference, that is the "best estimates" not the CAS-PT2 values. We obtain rather poor results with B2LYP (MSE=0.45 eV, MAE=0.52 eV, rms=0.62 eV and R^2=0.90) but very accurate ones for B2PLYP (MSE=0.01 eV, MAE=0.18 eV, rms=0.25 eV and R^2=0.97). These findings are in perfect agreement with the conclusions of Grimme and co-workers:[64] it indeed appears that B2PLYP surpasses significantly all other hybrids (including the DFT MR/CI scheme) as well as CC2. This indicates that such double-hybrid functional might allow the taking of the inner track for accurate spectroscopic estimates.

3.2. The Complete VE Set. A statistical analysis performed for the 29 functionals applied on the 614 excited-states of the VE set can be found in Table 2. We remind that the molecules of this set tend to be (much) larger than in the VT set. The mean signed error (MSE) indicates that pure functionals tend to underestimate the transition energies by approximatively 0.3 eV, though, as in the VT set, the errors are significantly smaller with two of the three *meta*-GGA: VSXC (0.15 eV) and TPSS (0.20 eV). Including a small fraction of exact exchange is sufficient to be much closer to the spot, as illustrated by TPSSh (MSE = 0.05 eV). In fact, the MSE varies quite steadily with the amount of EE included in the GH, being close to zero for about 21% of EE, slightly negative with 25%, and strongly negative for BMK, BHHLYP, and M05-2X. All GH containing between 15% and 27% of EE deliver |MSE| below the 0.10 eV mark and could therefore be considered as satisfactory for this criterion, especially B3LYP and X3LYP. For most LCH, the MSE are similar to those of pure functionals, though with the opposed sign: standard LCH tend to overestimate the transition energies. The error is only acceptable for LC-ωPBE(20) that uses significantly less EE, confirming the conclusions of the Herbert's group.[57,58] On the other hand, we found that CAM-B3LYP, that is characterized by a smaller fraction of EE at a large interelectronic distance (65%), appears more accurate than Hirao's LC-GGA methods, though it still yields a sizable MSE (−0.25 eV). Let us now turn toward the MAE and RMS errors. If HF is clearly an extremely poor approximation for transition energies (MAE of 0.85 eV), the errors remain large for all pure functionals, ranging from 0.32 eV (VSXC) to 0.41 eV (SVWN5). Not surprisingly, they are significantly reduced by adding EE, the minimal MAE for GH being obtained for functionals containing between 22% and 25% of EE (X3LYP, B98, PBE0 and mPW1PW91). The exact same four ap-

Table 2. Statistical Analysis for the Full VE Set (614 Excited-States)[a]

functional	before fitting			after linear regression		
	MSE	MAE	RMS	R^2	MAE	RMS
HF	−0.82	0.85	0.96	0.88	0.37	0.48
SVWN5	0.32	0.41	0.48	0.94	0.28	0.35
BLYP	0.32	0.40	0.47	0.94	0.28	0.35
BP86	0.29	0.38	0.46	0.94	0.28	0.34
OLYP	0.29	0.38	0.45	0.94	0.28	0.35
PBE	0.29	0.39	0.46	0.94	0.28	0.34
VSXC	0.15	0.32	0.39	0.94	0.27	0.34
τ-HCTH	0.27	0.37	0.44	0.94	0.28	0.34
TPSS	0.20	0.34	0.41	0.94	0.27	0.34
TPSSh	0.05	0.26	0.32	0.95	0.24	0.30
O3LYP	0.11	0.26	0.32	0.95	0.24	0.30
τ-HCTH-hyb	0.06	0.24	0.31	0.96	0.23	0.29
B3LYP	0.01	0.23	0.29	0.96	0.22	0.28
X3LYP	−0.01	0.22	0.28	0.96	0.22	0.28
B98	−0.04	0.22	0.29	0.96	0.22	0.28
PBE0	−0.08	0.22	0.29	0.96	0.21	0.27
mPW1PW91	−0.08	0.22	0.29	0.96	0.21	0.27
M05	−0.02	0.25	0.31	0.95	0.25	0.30
BMK	−0.26	0.32	0.39	0.96	0.22	0.27
BHHLYP	−0.36	0.40	0.47	0.95	0.23	0.29
M05−2X	−0.29	0.38	0.45	0.95	0.25	0.32
LC-ωPBE(20)	−0.08	0.22	0.27	0.96	0.20	0.26
LC-BLYP	−0.31	0.35	0.41	0.96	0.22	0.27
LC-OLYP	−0.34	0.37	0.43	0.96	0.21	0.27
LC-PBE	−0.34	0.38	0.44	0.96	0.21	0.26
LC-τ-HCTH	−0.32	0.36	0.42	0.96	0.22	0.28
LC-TPSS	−0.38	0.40	0.46	0.96	0.21	0.26
LC-ωPBE	−0.46	0.48	0.54	0.96	0.23	0.29
CAM-B3LYP	−0.25	0.30	0.36	0.96	0.21	0.26
MLR, eq 2				0.98	0.16	0.20
MLR-P, eq 3				0.97	0.20	0.25
MLR-B, eq 4				0.97	0.20	0.26

[a] MSE stands for the mean signed error (experiment-theory), MAE stands for the mean absolute error, and RMS is the residual mean-squared error. At the bottom of the table, the results obtained through MLR are detailed (see the text for more details). All values are in eV.

proaches have been found most efficient for the VT set. This percentage can therefore be viewed as optimal for computing transition energies of organic derivatives. This is good news: the same amount of EE yields accurate ground-state geometries and spectroscopic properties for the same kind of compounds. LC-ωPBE(20) delivers the same MAE as the best GH, in agreement with refs 57 and 58, whereas CAM-B3LYP remains acceptable (MAE of 0.30 eV). On the contrary, all other LCH yield too large MAE and RMS and could probably be discarded. These trends can be further rationalized by considering the selected error profiles depicted in Figure 2. One clearly notes that the error profile of BP86 is quite loose and moved to the right (too small transition energies). VSXC improves the pattern, confirming that it is one of the most satisfactory pure functional. TPSSh and PBE0 profiles are centered close to zero and are much more tight, the most probable PBE0 error being close to zero. The LC-ωPBE(20) profile is even tighter explaining the small rms, while the CAM-B3LYP sketch remains tight but is clearly unbalanced to the left (too large transition energies).

In Table 2, one notes that the R^2 obtained through linear regression are quite large as could be expected for a broad set of transitions ranging experimentally from 1.56 to 10.27 eV! Obviously, pure functionals are systematically character-
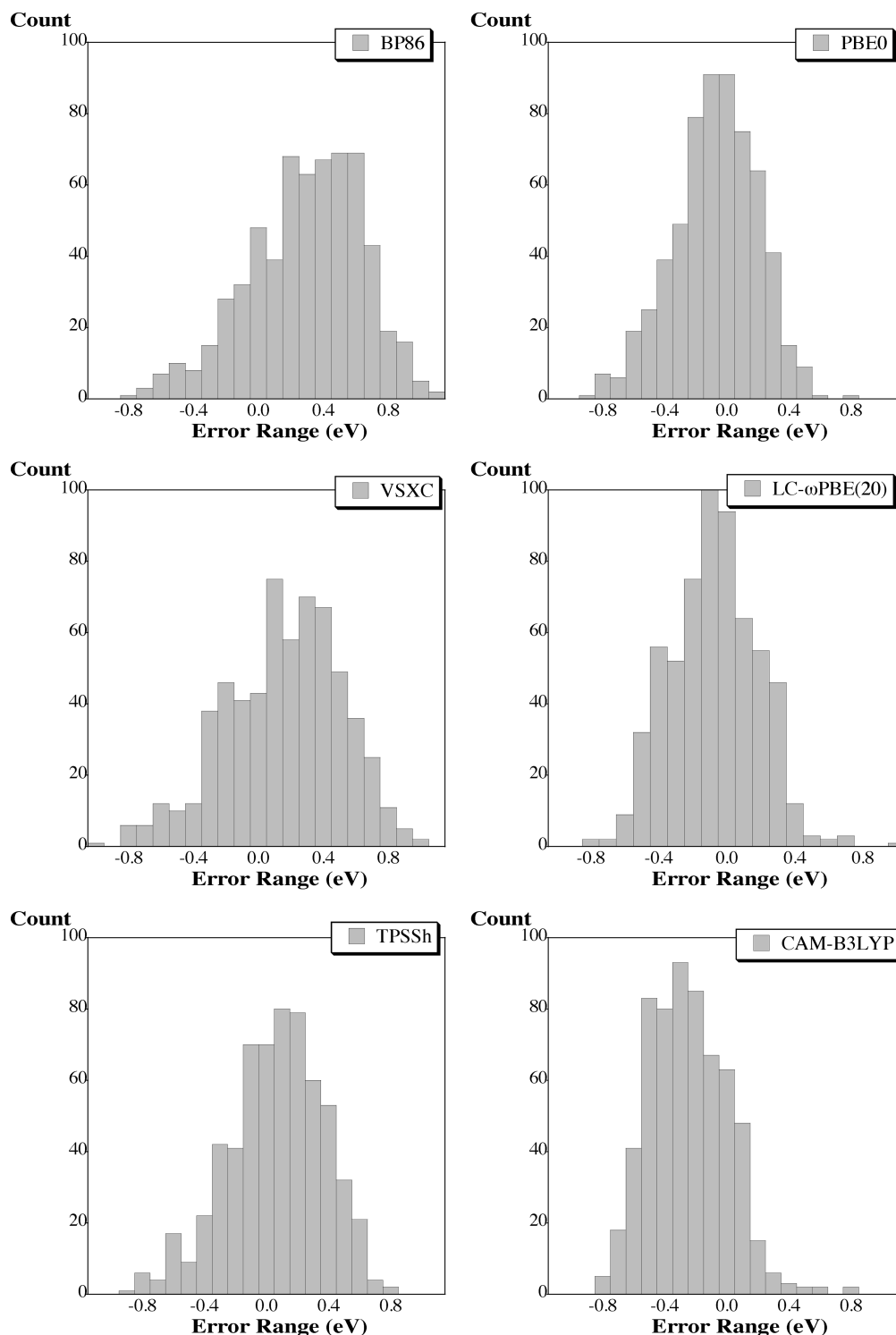
Figure 2. Histogram of the errors (eV) computed on the VE set for six representative functionals.

ized by smaller R^2. Subsequently, linearly correcting the raw GGA estimates decreases the MAE but not to a level competitive with the one obtained with the best unfitted hybrids: when hybrids are at hand, they have to be preferred. All GH and LCH grant a R^2 of 0.95 or 0.96 and a MAE equal or smaller than 0.25 eV when a simple linear correction is applied. Actually, after fitting, all commonly used hybrids deliver similar results, the most accurate results being achieved, on the one hand, with LC-ωPBE(20) for LCH and, on the other hand, with PBE0 and mPWPW91 for the GH. Let us point out that performing such simple linear regression

has an insignificant effect for these "best" functionals, the MAE and rms decreasing by only 0.01 or 0.02 eV. In an attempt to improve the predictive accuracy of TD-DFT, we have associated the results of several functionals through multiple linear regression (MLR).[115−117] Indeed, combining the results obtained through several functionals has been found extremely efficient for anthraquinone derivatives.[25,118,119] In addition, the present set is large enough so to allow meaningful statistical analysis. By removing step-by-step the less significant functionals, we obtained a MLR equation relying on seven functionals

$$E^{\text{MLR}} = -0.17 - 1.49E^{\text{PBE}} + 1.55E^{\tau-\text{HCTH}} + 1.62E^{\text{mPW1PW91}}$$
$$- 1.18E^{\text{M05}} - 0.56E^{\text{BMK}} + 1.99E^{\text{LC}-\text{PBE}} - 0.99E^{\text{LC}-\tau-\text{HCTH}}$$
$$(2)$$

that outperforms any of the simple linear regression by providing a R^2 of 0.98, a MAE of 0.16 eV, and a rms of 0.20 eV. For the record, we note that the P-value in the ANOVA table indicates that there is a statistically significant relationship between theory and experiment at the 99% confidence level, while all seven functional coefficients are also significant at the 99% confidence level. Of course using eq 2 requires to roughly multiply the computational effort by a factor of 7 for a gain of only ∼20% of MAE and ∼23% of rms, compared to the best SLR. Such performance is unlikely to be perceived as efficient for practical applications: there often exists more powerful approaches for such computational cost. For this reason, we have built two other MLR combining one global hybrid and one long-range-corrected hybrid of the Perdew and Becke's families

$$E^{\text{MLR}-\text{P}} = -0.10 + 0.44E^{\text{PBE0}} + 0.53E^{\text{LC}-\text{PBE}} \quad (3)$$

$$E^{\text{MLR}-\text{B}} = -0.13 + 0.24E^{\text{B3LYP}} + 0.74E^{\text{CAM}-\text{B3LYP}}$$
$$(4)$$

For both equations, the sum of the coefficients is close to one, confirming that the raw evolution (slope) provided by TD-DFT is reasonable. These equations improve the R^2 to 0.97 (compares to 0.96 for SLR) but only slightly tune the computed MAE and rms (see Table 2). Indeed, eq 3 provides a MAE and RMS of 0.20 and 0.25 eV, respectively, only 0.02 eV smaller than the one of the raw LC-ωPBE(20) values. Subsequently, using one of the above equations for correcting the transition energies computed on a new molecular structure is unnecessary, though statistical procedures can be very useful if one investigates a single family of compounds.

As an intermediate conclusion of the statistical analysis of the VT and VE sets, we can already state that the "expected TD-DFT" error for an unknown singlet excited-state should be close to 0.22 eV, in quite good agreement with the previous works mentioned in the Introduction. Such accuracy could be obtained by using, either a GH containing between 22% and 25% of EE (X3LYP, B98, PBE0, mPW1PW91) or with a LCH with a relatively small damping parameter ($\omega \simeq 20$), such as LC-ωPBE(20). More specifically, we have to point out that X3LYP yields the smallest MSE, MAE, and rms of all GH for the VE set. Performing a linear correction on the raw computed values levels out the results obtained with all hybrids but does not top the "best" hybrids mentioned above.

3.3. Analysis of VE Subsets. Statistical analysis for various VE subsets can be found in the Supporting Information. As $\pi \rightarrow \pi^\star$ transitions constitute the major portion of the excited-states in the full VE set, it is not surprising that the errors found for these 510 states are very similar to these of Table 2. For the 79 $n \rightarrow \pi^\star$ transitions considered, one finds the smallest deviations for functionals containing between 20% and 25% of exact exchange (B3LYP, X3LYP, B98, PBE0, mPW1PW91) that yield nearly zero MSE as

well as MAE and rms close to 0.15 eV. LCH also deliver small MAE, though slightly larger MSE and RMS than GH. The smaller errors for $n \rightarrow \pi^\star$ than for $\pi \rightarrow \pi^\star$ transition energies is probably related to the more local character of the former in our set. The correlation coefficient being also large for all these schemes, these findings support the conclusions of our previous work:[60] $n \rightarrow \pi^\star$ states could be accurately described by both GH and LCH.

For the subset of charged molecules, significantly larger errors appear, e.g. MAE of 0.34 eV with PBE0 and 0.37 eV with LC-ωPBE(20), due to the large overestimation of the transition energies with otherwise-successful 20–25% GH. Consequently, the inaccuracies are minimal with pure functionals or hybrids containing a very small fraction of EE. This phenomenon is explained by the dominance of cyanine structures in the subset of charged molecules: cyanine, triphenylmethane, and acridine derivatives represent more than half of the transitions investigated. These compounds present a strong multideterminantal nature, at least for systems with more than two or three double bonds,[101] and all DFT functionals are inadequate.[65,102] Therefore, the large MAE listed in the Supporting Information are related to the nature of the molecule, rather than to the presence of a charge. Indeed, by removing the cyanine-like structures from the set, one obtains a MAE of 0.26 eV and a RMS of 0.33 eV for PBE0, similar to the one listed in Table 2. This is also illustrated by anionic hydrazones, for which GH obviously work more accurately than pure functionals. For neutral molecules (502 states), the conclusion follows the one obtained for the full VE set, with minimal discrepancies and maximal correlation coefficients for X3LYP, B98, PBE0, and mPW1PW91 for GH and LC-ωPBE(20) for LCH. This latter functionals delivers a MAE as small as 0.18 eV, illustrating, on the one hand, its efficiency for monodeterminantal structures and, on the other hand, the possibility of going significantly below a ∼0.3 eV average error with TD-DFT, even when absolutely no statistical treatment of the results is performed.

For the 178 states belonging to the family of $\pi \rightarrow \pi^\star$ chromophores, the errors are completely similar to these obtained in our previous work relying on a less extensive set of chromogens,[59] with a MAE of 0.46 eV for PBE (0.45 eV in ref 59), 0.14 eV for PBE0 (0.14 eV in ref 59), and 0.25 eV for CAM-B3LYP (0.26 eV in ref 59). From the tables in the Supporting Information, it is striking that, within our functional list, PBE0, mPW1PW91, and LC-ωPBE(20) deliver the smallest MSE, MAE, and rms; the latter functional additionally providing the largest R^2. For $n \rightarrow \pi^\star$ chromophores (nitrosos, thiocarbonyls, and azobenzenes), the errors are small with all functionals, especially with LC-BLYP, LC-OLYP, and CAM-B3LYP (MAE of 0.07 eV) that also lead to excellent corrections (R^2 of 0.99). The best GH presenting between 20% and 25% of EE are also on the spot (MSE smaller than 0.03 eV and MAE between 0.10 and 0.13 eV), though the correlation with experiment is slightly less impressive (R^2 of 0.99). On the contrary, we have to point out the comparatively large errors of M05 and M05-2X. If one searches for the smallest errors for the neutral dye set (228 states, both types of transitions being incorporated), one
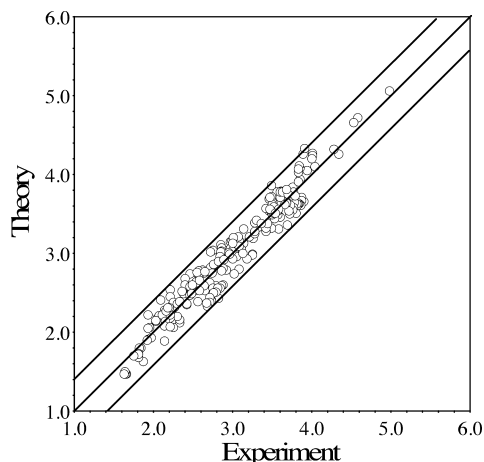
Figure 3. Comparison between the LC-ωPBE(20) and experimental transition energies (eV) for neutral dyes. The central lines indicate a perfect theory/experiment match, whereas the side lines are borders for ± 0.4 eV deviations.

finds MAE of 0.14 eV for PBE0, mPW1PW91, and LC-ωPBE(20). Figure 3 compares the LC-ωPBE(20) and experimental transition energies for these 228 states, and the nice match is obvious: only one case presents a deviation larger than 0.4 eV. For the record, B3LYP (CAM-B3LYP) gives MAE of 0.16 eV (0.21 eV) for the same set of derivatives. In that sense, PBE0 remains perfectly adequate for investigating neutral dyes, clearly supporting the conclusions of our previous investigations on specific families of organic dyes or photochroms.[5,61,95,108,120−126] For sure, there is a partial error compensation between the lack of vibronic contribution in our model and the form of the functional (see the next section), but our calculations confirm the practical ability of the PCM-TD-PBE0 scheme, even when no fitting procedure is activated. For charged dyes, the same conclusion as above pertains: the errors are large due to the multideterminantal nature of both the ground- and excited-states in many cyanine compounds. Clearly TD-DFT can only be used for such systems to obtain qualitative knowledge or to compare systems with the same delocalization length. In that case, fitting the results might allow much more accurate estimates. For instance for arylcarbonium (**AC-a** in the Supporting Information), the B3LYP (CAM-B3LYP) MAE is 0.29 eV (0.54 eV) prior to linear correction but only 0.10 eV (0.04 eV) afterward, although these systems are characterized by two strong absorptions with different physical nature. Note that the impressive performance of CAM-B3LYP after fitting is related to the better consistency of LCH (compared to GH) when only one family of molecules is considered. This effect has already been pointed our previously.[59,102]

For hydrocabons (the set contains both aromatic and aliphatic conjugated compounds), the two 25%-GH and especially LC-ωPBE(20) remain the most efficient (MAE of 0.18 eV and R^2 of 0.96 for the latter), but with errors significantly larger than for neutral dyes. Another striking evolution wrt neutral dyes is that functionals containing a large fraction of EE (BMK, BHHLYP, CAM-B3LYP, ...) are fairly accurate for this subset with relatively small MAE, e.g. 0.23 eV for BMK and 0.22 eV for CAM-B3LYP. This

is in good agreement with the work of Dierksen and Grimme,[63] that concluded that a EE percentage between 30%−40% should be optimal (on average) for spectral calculations on similar compounds. For the 126 excited-states measured on small structures (five or six member rings as well as molecules with less than 14 atoms), the MSE are very close to zero with VSXC, τ-HCTH-hyb, and LC-ωPBE(20). All GH containing between 10 and 25% of EE and LC-ωPBE(20) yielding MAE smaller than 0.30 eV, but not below 0.26 eV, whereas the difference between GH and LCH is more limited for small molecules than for dyes or hydrocarbons. In fact, the vertical TD-DFT approach appears significantly less potent for predicting the λ_{max} of these small structures than for other sets, partly explaining the nonidentical conclusions obtained by different groups previously (see the Introduction). In any case, for small molecules, LC-ωPBE(20), clearly emerges as the most accurate approach with the smallest deviations and the largest correlation coefficient. The biomolecules treated here (33 states) are characterized by a small chromophoric unit, though they can be large molecules. Consequently, they behave analogously to the small structures with minimal theory/experiment deviations for hybrids presenting a small fraction of EE.

In Figure 4, we report, for five functionals of the Becke's family (BLYP, B3LYP, BHHLYP, LC-BLYP, and CAM-B3LYP), the evolution of the MSE, MAE, and RMS for small, medium, and large chromogens. In the Supporting Information, these subsets respectively correspond to the 33 states computed on small molecules (**SC**, less than 14 atoms), 51 states calculated for medium chemicals (**MC**, between 14 and 29 atoms), and 32 states obtained for large compounds (**LC**, more than 30 atoms). Due to the difficulty to build generic and consistent sets for molecules of various sizes, the analysis of Figure 4 allows only qualitative conclusions. Nevertheless, it is clear that, for a given functional, the MSE tend to become more negative (or less positive) as the size of the molecules increases, e.g. for B3LYP the MSE equals 0.09 eV, −0.01, and −0.07 eV for small, medium, and large chromophores, respectively. In other words, as the size of the molecule increases, functionals with a larger EE fraction tend to produce larger errors, which is consistent with our above analysis for the different subsets. Indeed, the MAE and rms of B3LYP, LC-BLYP, and CAM-B3LYP are similar for **SC** but decrease for the former when going to **MC** and **LC**, whereas the average errors of the two LCH tend to increase for larger compounds. Therefore, the excited-states of very extended molecules are not necessarily better described by long-range-approaches, at least in the vertical approximation (see the next section). For these three subsets, B3LYP clearly outperforms the other functionals, as it (almost) systematically yields the smallest deviations. However, it is striking that no functional has a flat error profile for different size of molecules, as one would fancy.

3.4. Importance of Vibronic Effects. As we pointed out in the methodological section, the main weakness of our approach is the lack of vibronic modeling in the VE set: vertical transitions do not physically correspond to λ_{max}. Despite the practical computational advantage of vertical calculations, it is worth estimating the impact of this

Extensive TD-DFT Benchmark

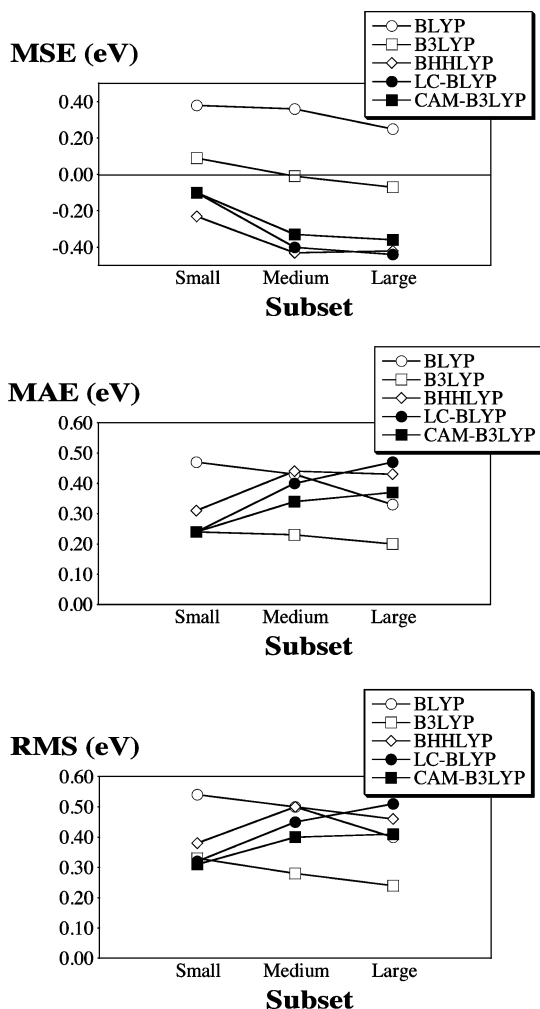*J. Chem. Theory Comput., Vol. 5, No. 9, 2009* **2431**

Figure 4. Evolution of the MSE (top panel), MAE (central panel), and RMS (bottom panel) calculated for the transition energies of small (**SC**), medium (**MC**), and large (**LC**) chromogens.

approximation. A first procedure to tackle this problem is to compare the errors obtained for the VT set (no vibronic effects, purely vertical reference values) and for similar molecules (i.e., small structures) of the VE set (vibronic effects neglected). Such an inspection not only highlights similarities, as the most accurate functionals in terms of MAE and rms are the same in both sets, but also sheds light on the discrepancies, the zero of the MSE being obtained for an EE percentage of ~23% in the VT set but ~14% in the VE subset. Nevertheless, both sets appear to present alike error pattern wrt the chosen functional. Such comparisons are however limited because the transitions considered are different: in the VE case, only bright low-lying states are included.

An alternative scheme is to define a subset of VE molecules with clearly measured 0−0 transition (see tables in the Supporting Information). This leads to 75 states measured for hydrocarbons and oligomers as well as medium and large chromogens (**FS**, **HC**, **OL**, **MC**, and **LC**), that is molecular structures alike the one of ref 63.[127] For this subset, when performing a statistical analysis using the experimental λ_{max} as reference, one obtains MSE and MAE similar to those obtained for the full set of neutral molecules (see Table 3).

Table 3. Analysis of the Importance of Vibronic Effects for Eight Selected Functionals[a]

	vertical vs λ_{max}		vertical vs 0−0		corrected vertical vs 0−0	
functional	MSE	MAE	MSE	MAE	MSE	MAE
BLYP	0.44	0.48	0.35	0.40	0.57	0.58
VSXC	0.29	0.39	0.20	0.33	0.42	0.47
B3LYP	0.13	0.28	0.04	0.24	0.32	0.37
PBE0	0.03	0.24	−0.06	0.22	0.24	0.32
BHHLYP	−0.23	0.30	−0.32	0.34	0.05	0.26
LC-ωPBE(20)	−0.05	0.20	−0.14	0.20	0.16	0.24
LC-TPSS	−0.36	0.36	−0.45	0.45	−0.09	0.18
CAM-B3LYP	−0.19	0.26	−0.28	0.30	0.04	0.21

[a] All values are in eV and are calculated on the 75 states for which experimental 0-0 transitions could be defined. See the text of section 3.4 for more details.

The two most accurate functionals remain PBE0 and LC-ωPBE(20) with MAE of 0.24 and 0.20 eV, respectively. For the same set of excited-states, one can use the measured 0−0 transitions as references for benchmarking functionals. These 0−0 peaks either correspond to the λ_{max} or appear at smaller transition energies than the maximal absorption, the average experimental difference between these two peaks attaining 0.09 eV for the present set. Therefore functionals incorporating less EE, that statistically reduce the gap between ground and excited-states, tend to produce smaller deviations when the 0−0 absorption is used as reference. This is illustrated by the difference between the "vertical vs λ_{max}" and the "vertical vs 0−0" columns of Table 3. Indeed, the MAE of VSXC is reduced from 0.39 to 0.33 eV, whereas the MSE of PBE0 changes from positive (0.03 eV) to negative (−0.06 eV). Nevertheless, the minimal deviations for the selected functionals are once more reached with PBE0 and LC-ωPBE(20). Of course, if a proper Franck−Condon calculation was performed, the calculated transition energies would be smaller than our vertical values. To estimate this effect, we have analyzed the theoretical data reported in ref 63, and we have found that the TD-DFT vertical transition energies of closed-shell molecules are larger than their computed 0−0 counterpart by an average of 0.22 eV for BLYP, 0.28 eV for B3LYP, and 0.37 eV for BHHLYP.[128] There is therefore a smooth relationship between this difference and the EE fraction: ~+0.03 eV per 10% of EE. This allowed us to very roughly estimate the average difference for the other functionals.[129] By shifting our vertical transition energies by this average values, we obtain a qualitative information about the impact of the vertical model ("corrected vertical vs 0−0" columns in Table 3). We are well aware that this represents a extremely crude approximation, as we incorrectly apply a constant shift to all molecules (they are significantly different in practice), but general trends may still emerge. The smallest MAE are now obtained with global hybrids including a large fraction of EE and LCH that become closer to the spot. On the contrary, B3LYP and PBE0 present much larger MSE and MAE, BHHLYP outperforming them significantly. For the record, we note that LC-ωPBE(20) apparently remains satisfactory with a MSE of 0.16 eV and a MAE of 0.24 eV. Of course, as LCH tend to deliver poorer geometries than global hybrids, their use for vibronic calculation certainly remains an open question.

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4. Conclusions

Benchmark calculations aiming at identifying the most efficient functionals for TD-DFT calculations have been performed. Large panels of pure functionals, global hybrids, and long-range-corrected hybrids have been tested for more than 700 excited-states. Assessments have been performed using both highly correlated wave function results and experimental wavelengths as references. It appears that the most accurate estimates are obtained, by using a GH containing between 22% and 25% of EE (X3LYP, B98, PBE0, mPW1PW91) or a LCH with a small damping parameter (LC-ωPBE(20), with $\omega = 0.20$). The four GH provide a mean absolute error smaller than 0.25 eV for both types of benchmarks, although the training set includes compounds known to be difficultly described by TD-DFT. GH containing less (more) exact exchange tend to underestimate (overestimate) the transition energies, LCH with large damping parameter suffering the same problem as global hybrids with 40−50% of exact exchange. For almost all cases, the errors obtained by LDA and GGA are about 50% larger than with the 25%-GH. *Meta*-GGA, especially VSXC and TPSS, yield transition energies in better agreement with reference data than other pure functionals, though they cannot outperform the hybrids. CAM-B3LYP appears to be one of the most satisfying LCH, although the deviations with respect to experiment are larger than with B3LYP for most compounds. The accuracy significantly depends on the set of molecules considered, the errors being very large for cyanine-like derivatives but smaller than average for neutral molecules, dyes, and $n \rightarrow \pi^\star$ excited-states. Indeed, for neutral molecules, the best choice, namely the LC-ωPBE(20) LCH, provides a MAE as small as 0.18 eV, whereas the errors are even smaller for organic dyes: 0.14 eV with PBE0, mPW1PW91, and LC-ωPBE(20). It also turned out that functionals are sensitive to the size of the chromogens investigated (Figure 4), whereas a crude estimation of vibronic effects revealed that hybrids including a large fraction of EE (e.g., BHHLYP) may be more accurate in the framework of Franck−Condon applications than for vertical estimates.

Supporting Information Available: Statistical analysis for various sets of molecules, representation of all investigated chemicals, full tables with all transition energies, bibliographic information for the experimental references. This material is available free of charge via the Internet at http://pubs.acs.org.

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(129) For VSXC, the same as for BLYP: 0.22 eV; for PBE0 and LC-ωPBE(20) that behave similarly: 0.30 eV; for LC-TPSS: 0.36 eV; and for CAM-B3LYP: 0.32 eV. These latter values have been estimated from the amount of exact exchange at intermediate interelectronic distance. For BLYP, B3LYP, and BHHLYP, we stick to Dierksen and Grimme's differences.