

TD-DFT Benchmarks: A Review

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Time-Dependent Density Functional Theory (TD-DFT) has become the most widely-used theoretical approach to simulate the optical properties of both organic and inorganic molecules. In this contribution, we review TD-DFT benchmarks that have been performed during the last decade. The aim is often to pinpoint the most accurate or adequate exchange-correlation functional(s). We present both the different strategies used to assess the functionals and the main results

obtained in terms of accuracy. In particular, we discuss both vertical and adiabatic benchmarks and comparisons with both experimental and theoretical reference transition energies. More specific benchmarks (oscillator strengths, excited-state geometries, dipole moments, vibronic shapes, etc.) are summarized as well. © 2013 Wiley Periodicals, Inc.

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Introduction

The extension of Density functional theory (DFT) to the time-dependent domain, namely time-dependent density functional theory (TD-DFT) has been originally proposed by Runge and Gross 30 years ago.^[1] Ten years later, Casida developed an effective linear-response (LR) formalism for TD-DFT (so-called random-phase approximation or Casida's equations)^[2] allowing to rapidly and efficiently determine the solution of the TD-DFT equations for molecules.^[3] Thanks to these pioneering works, TD-DFT has become an extremely popular approach for modeling the energies, structures, and properties of electronically excited states (ES). Indeed, in 2011, more than 1000 papers devoted to TD-DFT have been published, surpassing by one order of magnitude the output measured one decade before. The applications of TD-DFT encompasses not only the simulation of vertical transition energies, but also the determination of ES structures and emission wavelengths, the computation of vibrationally resolved optical spectra, the estimation of atomic point charges and dipole moments, as well as the simulation of photochemical reactions. These remarkable successes, for a relatively young theory, are related to the valuable accuracy/effort ratio of TD-DFT and to the constant methodological developments in the field that aims to push the TD-DFT towards new frontiers. Like its parent DFT approach, TD-DFT is formally an exact theory, but the actual implementations require the selection of an exchange correlation functional (XCF) which concentrates the approximations of the model. In practice, one can state that LR-TD-DFT inherited from all DFT problems but also presents a few specific drawbacks. In addition, we underline that large efforts have been made to model environmental effects during TD-DFT simulations, notably within the well-known polarizable continuum model (PCM),^[4] and the EFP^[5–7] methods. One can distinguish several implicit approaches, namely, the classical LR,^[8,9] the corrected linear-response (cLR),^[10] the VEM^[11] and the state-specific (SS) approximations.^[12] The three latter, more accurate and physically meaningful, approaches take into account the variations of the polarization of the solvent follow-

ing the electronic density rearrangements of the solute. For each model, one generally distinguishes the equilibrium limit (that corresponds to slow phenomena in which the environment does fully adapt to the considered ES) and the nonequilibrium limit (corresponding to fast phenomena, e.g., absorption and fluorescence, during which only the electrons of the environment reorganize).

In this contribution, our goal is certainly not to describe the TD-DFT methodology—the interested reader could find excellent reviews, perspective articles, books, and special issues elsewhere^[13–36]—nor to list all recent TD-DFT applications but rather to focus on extensive XCF benchmarks performed within the TD-DFT framework. Indeed, since the emergence of hybrid XCF,^[37,38] that contains a fraction of exact exchange (EXX) of Hartree-Fock (HF) form, a large number of new XCF have been proposed^[37–52] in addition to the pure (that is EXX-free) LDA,^[53,54] GGA,^[55–63] and *meta*-GGA^[44,64–68] functionals. In the ES modeling vein of research, one should certainly mention the developments of the so-called range-separated hybrids (RSHs)^[69–79] that include an increasing fraction of EXX when the interelectronic distance increases. This allows to significantly improve the description of charge-transfer (CT) ES that otherwise suffers from the local nature of XCF. More recently, double-hybrid functionals,^[80–83] that explicitly depend on the virtual orbitals, have been extended to TD-DFT by Grimme,^[80,84] who proposed to use a CIS(D) like perturbative correction for the TD-DFT energies, which significantly improved the description of states presenting a double-excited

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nature.^[85,86] Of course, the vast majority of these XCF has been designed (and often parametrized) to reproduce ground state (GS) rather than ES properties. This can be ascribed, on the one hand, to scientific common sense (all ES calculations imply a GS step, so optimizing a functional for ES at the cost of inaccurate GS properties is not very appealing) and, on the other hand, to the difficulty to obtain experimental or theoretical ES reference values that are accurate enough to allow XCF optimization. This is due to the rapidity of the ES phenomena that makes experimental determination a challenge, for example, it is difficult to measure bond lengths and valence angles in the ES. As most compounds exhibiting interesting ES features are large conjugated molecules, the experimental works are often performed in condensed phase, making the simulation of environment a further problem for computational chemists. Therefore, contrary to GS properties, for which many standard benchmark sets have been designed (e.g., G3 for thermochemistry,^[87,88] S22 and S66 for weak-interactions,^[89–92] ISO34 and ISO22 for isomerization energies,^[93] or sets for proton transfer,^[94,95] and GMTKN30 that gathers the majority of set developed for GS properties^[96,97]), a rather diverse palette of properties, training sets and calculation strategies have been proposed to evaluate the pros and cons of XCF within the TD-DFT framework. As we will see in the following, this sometimes leads to nonuniform conclusions. It is also important to underline that the performances of the reported XCF mentioned below correspond to their current implementation in the vast majority of actual TD-DFT codes. There are several methodological aspects related to the transfer of GS XCF to ES applications, a task far from being trivial and implying additional approximations (see the above-mentioned reviews), so that more complete or mathematically refined implementations of XCF to TD-DFT might lead to different conclusions.^[98,99]

In the following, we first present benchmarks performed for transition energies (both vertical and adiabatic phenomena) that are the most intensively studied properties. In that framework, the most significant studies are briefly summarized in

Table 1. In that Table, like in the following of this review, we have mainly selected benchmarks that considered at least three XCF and a diverse set of compounds. Indeed, though one could find a number of studies that considered only one functional applied on a large set of molecules,^[121–132] or tested a large number of XCF but on a rather specific family of compounds,^[97,133–148] these works are often rather specific and the obtained conclusions are sometimes difficult to generalize. We nevertheless briefly summarized a number of them in this review. We also discuss benchmarks that have been performed on other ES properties, that is, geometries, vibrational frequencies, dipole moments, oscillator strengths, vibronic couplings, etc. Eventually, we provide a few generic conclusions summarizing the works reported herein. We have chosen to classify benchmarks into several categories. Some works cannot enter univocally in one predefined box, and some choices have been to be performed, for example, we have decided to present cyanine (CT) benchmarks in the “theory” (“experiment”) sections, that are the most representative, though there exist several cyanine (CT) benchmarks using experimental (theoretical) references.

Vertical Transition Energies

Vertical transition energies are the difference between ES and GS energies computed on a given geometry. One generally tackles the vertical absorption, computed as:

$$E^{\text{vert-abso}} = E^{\text{ES}}(R^{\text{GS}}) - E^{\text{GS}}(R^{\text{GS}}), \quad (1)$$

where R^{GS} is the selected GS geometry. As determining $E^{\text{vert-abso}}$ with TD-DFT is rather fast and does not require higher-order derivatives, the majority of benchmarks has been performed with this convenient, though limited (see below), approach. One can further split the proposed benchmarks into two subgroups, depending on the selected reference data. The first subgroup uses references obtained through highly accurate wavefunction approaches. This strategy presents at least three

Table 1. General presentation of recent TD-DFT benchmarks of transition energies.

| Ref. | Benchmark | States | Functionals | Basis set | Geometry | Solvent |
|-------|---|--------------------|--|---------------------------------------|-----------------------|----------------------------|
| [100] | E^{0-0} vs 0-0 | 34 | 6: LDA BLYP BP86 PBE B3LYP PBE0 | aug-TZVPP | DFT/aug-TZVPP | None |
| [101] | E^{0-0} vs 0-0 | 43 | 3: BP86 B3LYP BHHLYP | TZVP | DFT/TZVP | Empirical ^[a] |
| [102] | E^{vert} vs λ_{max} | 34 | 12: pure and hybrid XCF | 6-311+G(2df,p) | DFT | LR-PCM(neq) |
| [103] | E^{vert} vs E^{vert} | 213 ^[b] | 4: BP86 B3LYP BHHLYP MR-DFT | TZVP | MP2/6-31G(d) | None |
| [104] | E^{vert} vs λ_{max} | 118 | 5: PBE, PBE0, LC-PBE, LC- ω PBE and CAM-B3LYP | 6-311+G(2d,p) | PBE0/6-311G(d,p) | LR-PCM(neq) |
| [105] | E^{vert} vs Mixed | 59 | 3: PBE B3LYP CAM-B3LYP | <i>d</i> -aug-cc-pVTZ/cc-pVTZ | Mixed | None |
| [106] | E^{vert} vs Exp | 96 | 6: LSDA PBE TPSS TPSSH B3LYP PBE0 | 6-311++G(3df,3pd) | DFT/6-311++G(3df,3pd) | None |
| [107] | E^{vert} vs E^{vert} | 102 | 29: pure and hybrid XCF | TZVP | MP2/6-31G(d) | None |
| [107] | E^{vert} vs λ_{max} | 510 | 29: pure and hybrid XCF | 6-311+G(2d,p) | PBE0/6-311G(d,p) | LR-PCM(neq) |
| [108] | E^{vert} vs E^{vert} | 107 ^[c] | 5: LRC- ω PBEh (3 types), ω B97, ω B97X | aug-cc-pVTZ | DFT | None |
| [86] | E^{0-0} vs AFCP ^[d] | 12 | 7: BLYP B3LYP PBE38 BMK CAM-B3LYP B2GPPLYP | def2-TZVPP | PBE/TZVP | LR-PCM(neq) ^[e] |
| [109] | E^{vert} vs E^{vert} ^[f] | 63 | 34: pure and hybrid XCF | TZVP | MP2/6-31G(d) | None |
| [110] | E^{vert} vs Exp | 69 | 26: Pure, global and RSHs | 6-311(3+,3+)-G(d,p) | MP2/6-311+G(d,p) | None |
| [111] | E^{0-0} vs Exp | 17 | 4: B3LYP CAM-B3LYP <i>m</i> CAM-B3LYP LC-BLYP | 6-311+G(d,p) | DFT/6-311+G(d,p) | None |
| [112] | E^{0-0} vs 0-0 | 109 | 6: LSDA PBE BP86 TPSS B3LYP PBE0 | def2-TZVP | B3LYP/def2-TZVP | None ^[g] |
| [113] | E^{vert} vs Mixed ^[h] | 83 | 8: Global and RSHs | Large | DFT and MP2 | None |
| [114] | E^{vert} vs Exp | 41 ^[i] | 11: RSHs | cc-pV[D/T]Z and 6-311G(d,p) | Mixed | None |
| [115] | E^{vert} vs AS ^[j] | 17 | 56: Pure, global and RSHs | <i>d</i> -aug-cc-pVQZ-DK | N/A | None |
| [116] | E^{vert} vs AS ^[k] | 18 | 31: Hybrid XCF | exc-ETDZ | N/A | None |
| [117] | E^{0-0} vs AFCP | 40 | 6: B3LYP PBE0 M06 M06-2X CAM-B3LYP LC-PBE | 6-31+G(d) | DFT/6-31+G(d) | cLR-PCM(neq) |
| [118] | E^{vert} vs Exp | 101 ^[l] | 24: Pure and hybrid XCF | 6-311++G(3df,3pd) | DFT/6-311++G(3df,3pd) | None |
| [119] | E^{vert} vs E^{vert} | 90 ^[m] | 3: PBE B3LYP CAM-B3LYP | <i>d</i> -aug-cc-pVTZ/ aug-cc-pVTZ | MP2/6-31G(d) | None |
| [120] | E^{vert} vs Exp | 69 | 30: Pure, global and RSHs | 6-311(2+,2+)-G(d,p) | MP2/6-311+G(d,p) | None |

Adapted and extended from Ref. [107]. For each contribution, we indicate the nature of the benchmark performed (vertical, or adiabatic, number of ES considered) as well as methodological details (basis set used during the TD step, geometry optimization scheme and use of solvation model).

[a] 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. [b] 142 singlet and 71 triplet ESs. [c] Training set (84) is a subset of Thiel's set; test set (23) is a subset of Tozer's set. [d] The authors transformed the experimental AFCP point into vertical corrections thanks to successive theoretical corrections, see text. [e] Computed with the $E^{\text{vert-abso}}$ PBE0/6-31G(d)//PBE/TZVP. [f] Triplet ES. [g] Comparisons with gas-phase experiments. [h] Using Tozer's 58-state set that contains both experimental and theoretical reference, as well as a subset of Thiel's set. [i] Majority of intermolecular and intramolecular CT states in this set. [j] Multiplicity-changing valence and Rydberg excitation energies of atoms. [k] Atomic spectra for Li to Ne atoms. [l] 63 singlet and 38 triplet states. [m] 45 singlet and 45 triplet states.

benefits: (i) it guarantees the consistency of the protocol (same basis set, geometry and purely vertical transitions); (ii) in principle, it allows to consider any families of molecules including transient species; (iii) it is easy to investigate high-lying ES, for example, Rydberg states, or dark states. However, there is a clear drawback: one needs to have reliable references, which implies the selection of refined and complex methodologies, and consequently, to only work on relatively compact molecules, though some calculations on larger molecules have been reported recently.^[149–151] In practice, authors have turned toward highly correlated wavefunction approaches to compute their reference values. These methods include EOM-CC, MR-CI, CAS-PT2 but also DMC approaches. Nevertheless, despite their quality, these models provide data that are not ‘error-free,’ as the results often depend on the details of the selected protocol (e.g., for CAS-PT2, application of an IEPA shift or not as well as size of the active space). The second approach relies on experimental values. As there is an almost infinite set of measurements of optical spectra, this strategy advantageously allows to consider a wide variety of bright states in extended molecules. However, two problems are encountered: (i) the vast majority of measurements has been performed in condensed phase (and

hence one benchmarks both the quality of the solvent modeling and the XCF accuracy); and more importantly, (ii) at least for ‘real-life’ systems, there is no reliable vertical experimental data available, so that one often compares theoretical $E^{\text{vert-abso}}$ to experimental λ_{max} or to 0-0 energies, and this cannot be viewed as a well-grounded theoretical approach (see adiabatic section below for discussion of the differences between vertical and 0-0 energies). Despite, this fact that will certainly rebuff ‘purists,’ such benchmarks are not useless: most published applications of TD-DFT are performed by comparing experimental λ_{max} measured in solution to $E^{\text{vert-abso}}$.

Comparisons with Theoretical Values

Thiel's set

Amongst all TD benchmark sets, the 28-molecules (see Fig. 1) list defined by Thiel et al. in 2008^[103,152–155] is certainly one of the most popular. Indeed, they investigated all molecules at CAS-PT2, EOM-CC2, EOM-CCSD, and EOM-CC3 levels and considered a large number of ES for each molecules. For most cases, they provided theoretical best estimates (TBE) leading to

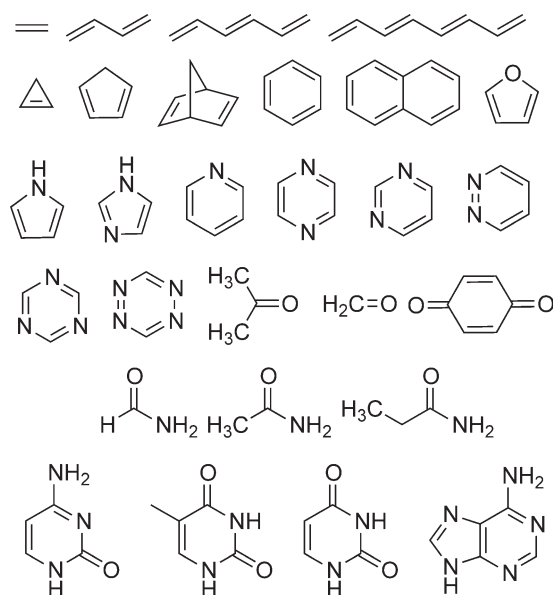


Figure 1. Thiel's 28-molecule set.

104 and 63 highly accurate references for both singlet-singlet and singlet-triplet transition energies. Though all data have been consistently obtained with the diffuse-less TZVP basis set, recent investigations hint that the selection of a much larger basis set, such as *aug-cc-pVTZ*, would have a limited impact on the statistical deviations obtained for the different XCF.^[109,155] Thiel's set of molecules was intensively used to benchmark XCF during the last few years.^[79,85,98,103,107,108,113,156–160] Table 2 lists the mean signed and mean absolute errors (MSE and MAE) obtained with more than 40 TD approaches for singlet-singlet transitions. One notes a clear evolution along the EXX ratio: pure density functionals undershoot transition energies, whereas global hybrids (GHs) including a large (> 50%) share of EXX as well as RSHs relying on an attenuation parameter exceeding 0.3 a.u. suffer from the opposite error. This behavior is not specific to Thiel's set but is rather general. Indeed, for most cases, XCF including larger amounts of EXX provide a more localized description of the ES, and subsequently larger transition energies. Overall, the smallest deviations (0.22 eV) are reached with the two most refined schemes, namely, Grimme's B2PLYP,^[84] a double-hybrid that includes a CIS(D)-like^[161] corrections for the ES part,^[85] and the DFT multireference approach proposed by Silva-Junior et al.^[103] GHs including 20–30% of EXX (e.g., B3LYP,^[37,39] B98,^[41] PBE0,^[42,43] or M06)^[52] yield slightly larger average deviations (ca. 0.25 eV). One particular aspect of Thiel's own studies is that it pointed out that the CC2 approach, sometimes used as a reference for TD-DFT benchmarks of large molecules, was quite far from the TBE, with errors of the same order of magnitudes as the best XCF.^[152] However, the CC2 and TBE vertical energies are nearly parallel so that a very large linear correlation coefficients between CC2 and TBE results was found.

Thiel's set has also been used to benchmark DFT-based methods beyond the conventional LR-TD-DFT scheme. Indeed, a strategy to improve the description of the ES is to rely on dressed TD-DFT that allows a more suitable description of states presenting a significant double-excitation character, as

originally shown by Burke and coworkers for butadiene and hexatriene,^[162] confirmed for longer polyenes by Mazur and Włodarczyk,^[163] and recently, extended to a larger set of molecules by Rubio's and Casida's groups.^[98] A localized HF Kohn-Sham approach has also been tested on Thiel's set and showed successful results.^[158] On the contrary, the DFT-tight binding approach (DFT-TB) unsurprisingly gave larger

Table 2. MSE and MAE obtained with respect to Thiel's TZVP TBE values (103 singlet ES).

| Functional | MSE | MAE | References |
|---|-------|------|------------|
| SVWN5 (X = 0) | −0.48 | 0.57 | [107] |
| BLYP (X = 0) | −0.47 | 0.54 | [107] |
| OLYP (X = 0) | −0.42 | 0.50 | [107] |
| BP86 (X = 0) | −0.44 | 0.52 | [103] |
| PBE (X = 0) | −0.45 | 0.53 | [107] |
| V5XC (X = 0) | −0.22 | 0.39 | [107] |
| τ-HCTH (X = 0) | −0.40 | 0.48 | [107] |
| TPSS (X = 0) | −0.29 | 0.42 | [107] |
| M06-L (X = 0) | −0.14 | 0.35 | [156] |
| M11-L (X = 0) | −0.15 | 0.32 | [79] |
| TPSSH (X = 10) | −0.11 | 0.30 | [107] |
| O3LYP (X = 11.61) | −0.18 | 0.33 | [107] |
| τ-HCTH-hyb (X = 15) | −0.14 | 0.30 | [107] |
| B3LYP (X = 20) | −0.07 | 0.27 | [103] |
| X3LYP (X = 21.8) | −0.05 | 0.25 | [107] |
| B98 (X = 21.98) | −0.02 | 0.25 | [107] |
| PBE0 (X = 25) | 0.05 | 0.24 | [107] |
| mPW1PW91 (X = 25) | 0.02 | 0.24 | [107] |
| M06 (X = 27) | −0.12 | 0.28 | [156] |
| M05 (X = 28) | −0.10 | 0.30 | [107] |
| BMK (X = 42) | 0.25 | 0.34 | [107] |
| BHHLYP (X = 50) | 0.43 | 0.50 | [103] |
| M08-HX (X = 52.23) | 0.23 | 0.34 | [160] |
| B2PLYP ^[a] (X = 53) | 0.45 | 0.53 | [85] |
| M06-2X (X = 54) | 0.23 | 0.34 | [156] |
| M08-SO (X = 56.79) | 0.12 | 0.32 | [160] |
| M05-2X (X = 56) | 0.28 | 0.39 | [107] |
| B2GPLYP ^[a] (X = 65) | 0.63 | 0.70 | [85] |
| M06-HF (X = 100) | 0.32 | 0.55 | [156] |
| HSE (X = 25–00; ω = 0.11) | −0.01 | 0.23 | [79] |
| LC-ωPBE(20) (X = 0–100; ω = 0.20) | −0.08 | 0.31 | [107] |
| LRC-ωPBEh ^[b] (X = 20–100; ω = 0.20) | 0.43 | 0.50 | [113] |
| ωB97X-D (X = 22.20–100; ω = 0.20) | 0.21 | 0.30 | [157] |
| M11 (X = 42.8–100; ω = 0.25) | 0.22 | 0.35 | [79] |
| ωB97X (X = 15.77–100; ω = 0.30) | 0.35 | 0.40 | [157] |
| LC-BLYP (X = 0–100; ω = 0.33) | 0.23 | 0.31 | [107] |
| LC-OLYP (X = 0–100; ω = 0.33) | 0.26 | 0.33 | [107] |
| LC-PBE (X = 0–100; ω = 0.33) | 0.26 | 0.34 | [107] |
| LC-τ-HCTH (X = 0–100; ω = 0.33) | 0.23 | 0.33 | [107] |
| LC-TPSS (X = 0–100; ω = 0.33) | 0.33 | 0.37 | [107] |
| CAM-B3LYP (X = 19–65; ω = 0.33) | 0.22 | 0.31 | [107] |
| LC-ωPBE (X = 0–100; ω = 0.40) | 0.41 | 0.46 | [107] |
| ωB97 (X = 0–100; ω = 0.40) | 0.43 | 0.47 | [157] |
| B2PLYP ^[a] (X = 53; C = 27) | −0.04 | 0.22 | [85] |
| B2GPLYP ^[a] (X = 65; C = 36) | 0.11 | 0.22 | [85] |
| DFT/MRCI | −0.13 | 0.22 | [103] |
| LDAX ^[c] | −0.67 | 0.70 | [158] |
| LHFx ^[c] | −0.11 | 0.33 | [158] |
| DFT-TB ^[d] | −0.42 | 0.49 | [159] |

X indicates the EXX percentage (or its range for RSH), ω is the attenuation parameter in RSH, C is the mixing coefficient for the PT2 part in double hybrids. All data in eV.

[a] Using CAS-PT2 values rather than TBE as reference. [b] Subset of 23 states. [c] Using a localized potential, 101 states, CAS-PT2 reference values. [d] DFT-tight binding approach, 104 states.

deviations, with a MAE of 0.49 eV.^[159] In 2012, Ziegler and co-workers used a subset of 20 ES extracted from Thiel's set to evaluate the relative performance of their self-consistent constricted variational density functional theory approach, (SCF-CV(∞)-DFT, to TD-DFT (and Δ SCF-DFT).^[99] With these models, they compared the results obtained with 3 XCF, LDA, B3LYP, and B3LYP. The CV(∞) [SCF-CV(∞)] MAE computed with these three functionals are respectively 0.27 [0.76], 0.22 [0.47], and 0.29 [0.25] eV and can be compared to their LR-TD-DFT counterparts of 0.52, 0.36, and 0.51 eV, respectively, clearly demonstrating the interest of the constricted variational formalism.^[99]

For the 63 triplets of Thiel's TBE set, the transition energies are almost systematically underrated by TD-DFT irrespective of the selected functional,^[79,103,109,156,157] the absolute errors tending to be larger than for singlets. Overall, M05-2X,^[164] M06-2X,^[52] BMK,^[45] M11-L,^[79] and the DFT/MR-CI schemes have the edge for triplets with MAE smaller than 0.30 eV.^[79,109] In addition, no clear-cut dependence between the MSE and the EXX amount could be found.^[31,79,109] This clearly contrasts with singlet-singlet transitions (see above) and several contributions have been devoted to understand the origins of this difference.^[119,165,166] In particular, Peach and Tozer showed that the erratic triplet behavior was related to GS triplet instabilities,^[166] and that applying the Tamm-Dancoff approximation (TDA) of TD-DFT significantly improves the problematic cases (see also next paragraph).^[119] The same conclusions were simultaneously and independently reached by Brédas and coworkers,^[166] who investigated five polyacenes with several RSHs. It is also noticeable that for these single-triplet transitions, the DFT-TB scheme was very effective with a MAE as small as 0.07 eV for the 63 states of Thiel's set,^[159] which impressively outperforms all 'ab initio' TD-DFT or TDA results published to date.

Tozer's sets

Another popular testing set was designed by Tozer and co-workers using the molecules represented in Figure 2.^[105] This

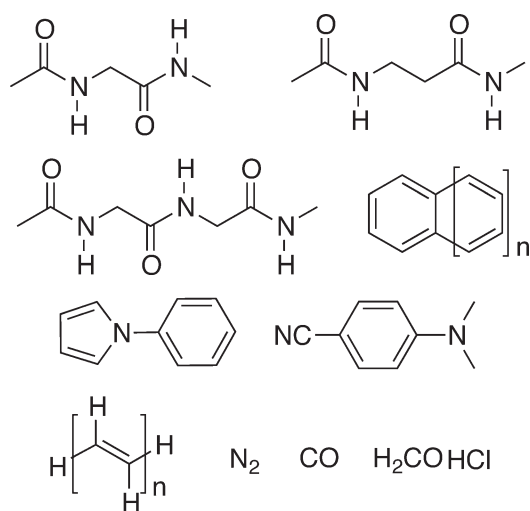


Figure 2. Tozer's set. n goes from 1 to 5 in the polyacene series and from 2 to 5 in the polyene series.

is an extension of a much smaller set of molecules (CO, N_2 , C_2H_4 , formaldehyde, dipeptides, and DMABN) by the same authors.^[167] For the three peptides, that display several intramolecular CT states, CAS-PT2 reference have been used; for the five oligoacenes, the two first ES are considered and CC2 references have been selected, whereas experimental gas-phase results are used for all other molecules. Strictly speaking, this original Tozer's set is therefore a blend between theoretical and experimental references, and we have chosen to locate it in the theoretical Section of this review as the second version proposed by Tozer used wavefunction references.^[119] Tozer and coworkers tested three functionals, PBE,^[58] B3LYP, and CAM-B3LYP^[72] and split the total 59 singlet states into three chemically intuitive categories: local, Rydberg, and CT ES.^[105] For the former, all three functionals are satisfying with MAE of 0.33, 0.22, and 0.27 eV for the GGA, the GH and the RSH, respectively.^[105] For Rydberg states, the errors are significantly larger, and CAM-B3LYP is clearly more accurate, the respective MAE being: 1.84, 1.11, and 0.50 eV. The same holds for CT states with average absolute deviations of 1.37, 0.86, and 0.31 eV, for PBE, B3LYP, and CAM-B3LYP, respectively. This seminal work is a clear-cut proof that both Rydberg and CT states can be correctly restored using RSH. In the line of earlier works,^[168] a criterion based on orbital overlap was proposed (so-called Λ diagnostic) to quantify the CT nature of any transition, and hence, indicate when using RSH becomes mandatory.^[105,135] Since that time, another similar criterion, the density-based t diagnostic, was designed by Le Bahers et al.^[169,170] In 2012, Peach and Tozer proposed a variation of their own set to investigate the triplet instability problem.^[119] They benchmarked PBE, B3LYP, and CAM-B3LYP using EOM-CCSD/*aug-cc-pVTZ* reference values. For singlet states, the TD-DFT PBE, B3LYP, and CAM-B3LYP MAE are 1.19, 0.72, and 0.33 eV, respectively and are only slightly different from their TDA counterpart of 1.11, 0.65, and 0.30 eV, respectively. For the new set of 45 triplet states, the obtained MAE are 1.12 (1.07) eV, 0.72 (0.63) eV, and 0.41 (0.27) eV, using TD-DFT (TDA) in combination with PBE, B3LYP, and CAM-B3LYP.^[119] This demonstrate the interest of combining the TDA model to a RSH XCF for investigating singlet-triplet transitions.

One other extensive use of Tozer's sets was proposed by Head-Gordon and coworkers,^[113] who benchmarked their own ω B97 series^[77,78] and compared the results to Truhlar's M06 hybrids,^[52] B3LYP, and HF. Their work is based on Tozer's sets^[105,119] but some cases have been removed, so that comparing results of different groups is not completely straightforward. The obtained MAE are 0.97, 0.60, 0.26, 0.25, 0.35, 0.44, 0.84, 0.30, and 0.66 eV for HF, B3LYP, ω B97, ω B97X, ω B97-D, LRC- ω PBEh,^[171] M06, M06-2X, and M06-HF,^[172] respectively. The main differences in terms of XCF performances are related to the description of the Rydberg states.^[113] Interestingly, Rohrdanz, Martins, and Herbert also used a subset of Tozer's molecules (23 states of the two dipeptides, the tripeptide, *N*-phenylpyrrole and 4-*N,N*-dimethylamino-benzonitrile) to test their own LRC- ω PBEh XCFs.^[108] They obtained MAE of 0.77 eV for ω B97, 0.48 eV for ω B97X, and 0.25 eV for LRC- ω PBEh, illustrating the performance of the latter for that subset.^[108]

Nguyen and coworkers also investigated a subset of 14 ES extracted from Tozer's set,^[114] and obtained MAE of 0.27 ± 0.02 eV for several variations of the CAM-B3LYP RSH, 0.28 eV with LRC- ω PBEh, and 0.49 eV with ω B97X. Overall, the different benchmarks performed with Tozer's sets, indicates that RSH including very large share of EXX (through large ω values or high long-range EXX limit) tend to provide too large transition energies.

Cyanines

Comparisons with highly accurate theoretical estimates have also helped solving a long-standing TD-DFT problem: the simulation of the optical spectra of cyanine dyes.^[84,107,130,160,173–178] Indeed, as originally shown by Schreiber et al.^[173] for increasingly long streptocyanine dyes, $[R_2N-(CH-CH)_n-CH-NR_2]^+$, TD-B3LYP could not reproduce the experimental absorption wavelengths, nor their evolution with chain length. This was latter confirmed by Champagne and coworkers with B3LYP and PBE0,^[174] as well as by Fabian.^[130] One of us also shown that RSH did not help improving the results,^[107,175] and though the error decreases with double-hybrids,^[84] the MAE remain very large. This apparent qualitative failure of TD-DFT was surprising since early CAS-PT2 calculations not only provided much more accurate absolute values and trends but also indicated that no significant multireference character was at play.^[173] In short, vertical TD-DFT apparently provides very incoherent estimates, typically, 0.5–1.0 eV above the experimental values for long cyanines, irrespective of the computational protocol (XCF, basis set and inclusion or not of environmental effects) and several loopholes were subsequently proposed to simulate cyanine's optical signatures with TD-based approaches.^[176,177] However, Filippi and coworkers very recently performed QMC calculations that provide extremely accurate results, very close to the exact response.^[178] Selecting these highly reliable theoretical values as references, it was found that most hybrid functionals provide transition energies with an error smaller than 0.30 eV.^[160] This error bar is comparable to that of the most modern wavefunction approaches (exCC3 and CAS-PT2 with IEPA shift).^[160,178] In short, in cyanines the measured λ_{\max} apparently correspond to processes significantly deviating from verticality.^[160,178]

Other works

There exists a significant number of works comparing TD-DFT and wavefunction transition energies,^[84,97,136,143,160,178–197] the latter being often obtained with the CC2 or CCSD methods. Most of these investigations are focused on a rather small panel of compounds and we briefly summarize selected examples in this Section. Several investigations presented here have been made on CT derivatives and they complement the dedicated Section below.

In 2007, Grimme and Neese used several procedures to assess their double hybrid functional,^[84] and they notably compared 16 states of 4 molecules (BH, CH₂, N₂, and H₂O) to full-CI reference. In the TDA approximation, the reported MAE are 0.35, 0.39, and 0.59 eV, for B2LYP, B2PLYP, and B3LYP,

respectively.^[84] For 29 states in furan and pyrrole,^[183] the typical deviations with respect to extrapolated CC results were reported to be about 0.5 eV for B97-1^[198] and PBE0 hybrids but significantly larger with the pure HCTH.^[199] These errors were found to decrease when corrections for the asymptotic behavior of the XCF were included.^[183] Zwijnenburg et al. compared CAS-PT2, B3LYP, and BB1K^[200] descriptions of the ES of (SiO₂)₄ clusters and found that the latter functional better reproduced CAS-PT2 values.^[184] For DNA bases and base pairs, Shukla and Leszczynski, compared CC2/def2-TZVP excitation energies to TD-DFT values in both gas and solvent phases.^[188] ω B97X-D emerged as the XCF able to reproduce, in a balanced way, both local and interbase CT ES. For a series of oligothiophenes, Wong et al. compared the TD-DFT results obtained with LC-BLYP,^[70] BHHLYP^[38] and B3LYP to CC2 reference values for both absorption and emission.^[185] The most consistent results were obtained with a modified version of LC-BLYP, whereas B3LYP showed severe problems, attributed to the CT nature of transitions. The same authors studied a series of coumarins used in dye sensitized solar cells (DSSC).^[201] Once again, LC-BLYP^[201] clearly outperformed B3LYP on the basis of CC2 results.^[182] Pastore et al. studied 5 triphenylamine dyes used in DSSC, and found a remarkable agreement between high-level *ab initio* results and the values provided by both MPW1K^[200] and CAM-B3LYP (but not B3LYP).^[136] Cornil and coworkers investigated the interface between TTF and TNCQ considering several layers of the donor/acceptor sandwich.^[197] They tested BHHLYP, LC- ω PBE, and ω B97X, and the latter was found to be the most effective in reproducing CAS-MRCI data.^[197] Again, these findings are related to the CT nature of the investigated transitions (see below). The descriptions of 10 green fluorescent protein (GFP) chromogens with six functionals (PBE, BLYP, B3LYP, PBE0, CAM-B3LYP, and CAM-B3LYP1) was assessed in light of reliable CC2 results.^[191] The smallest MAE (0.15 eV) have been reached with the two GHs (B3LYP and PBE0), the standard CAM-B3LYP being also very satisfying (0.19 eV), whereas the deviations with the three other XCF were at least 0.30 eV. For 16 benzoic acids, Guo et al. compared 6-31+G(d) vertical transition energies computed with 15 XCF to EOM-CCSD references.^[192] The five smallest MAE were obtained with LC- ω PBE (0.49 eV),^[73,74] B2PLYPD (0.59 eV),^[80,84] BMK (0.74 eV), M06-2X (0.75 eV), and ω B97X-D (0.76 eV). Barboza et al. compared the EOM-CCSD and TD-DFT energies for the five lowest ES of fluorene.^[143] To this end, they used a large panel of atomic basis sets and five XCF: B3LYP, B3LYP-CS00,^[202] PBE0, LB94,^[203] and CAM-B3LYP, this latter functional providing the best accuracy. Bernard, Shao, and Krylov benchmarked their own spin-flip (SF) TD-DFT approach for 41 ES (atoms, carbene-like diradicals, substituted benzene radicals, and other small systems), using SF-EOM-CCSD values as reference.^[196] This constitutes the largest SF benchmark to date with 18 XCF, though Li and Liu also proposed a SF benchmark of small systems considering 5 XCF.^[204] The authors of Ref. [196] observed that the best overall performances was obtained for the PBE family (PBE, PBE0, PBE50, and ω PBEh XCF), the smallest MAE being as tiny as 0.09 eV with PBE50.

COMPARISONS WITH EXPERIMENTAL VALUES

Atomic spectra

Atomic spectra obviously allow straightforward theory/experiment comparisons that are not sensitive to geometrical changes. Tao and coworkers, studied 22 ESs of 11 elements with six functionals (LSDA, PBE, TPSS, TPSSH, B3LYP, and PBE0) and the 6-311++G(3df,3pd) basis set.^[106] The MAE are rather insensitive of the selected XCF and in the 0.47–0.51 eV range.^[106] Very recently, Mohajeri and Alipour investigated 18 states in second-row atoms with 31 XCF and a series of basis sets, including exc-ETDZ.^[116] As in Ref. [106], the errors are rather independent of the selected XCF, and the four smallest MAE are obtained with BMK and M06-2X, ω B97, and ω B97X.^[116] However, the MAE reported in Ref. [116] (ca. 0.10 eV) are much smaller than in Ref. [106] (ca. 0.50 eV). This can be explained by the different atomic basis sets, considered states but also by the selected experimental values, for example, the chosen measured reference for the 3S Be ES is 6.46 eV (6.78 eV) in the former (latter) contribution. This is just one illustration of the difficulty to have unambiguous experimental reference values, even for an apparently “basic” case.

In 2011, Yang, Peverati, Truhlar, and Valero investigated the performances of several DFT-based approaches (Δ SCF, conventional and SF TD-DFT) for simulating excitations presenting a multiplicity-change in (neutral or ionic) atoms.^[115] Besides assessing the importance of basis set and relativistic effects, they benchmarked a huge number of XCF. They demonstrate that the smallest deviations were obtained with the Δ SCF approach combined to the OLYP,^[59] O3LYP^[205] and M08-HX^[206] XCF. These schemes provide an accuracy completely comparable to the one obtained with CCSD(T). Conventional TD-DFT was found to be significantly less efficient than Δ SCF, especially for Rydberg ES.^[115]

Small molecules

There is also a large number of TD-DFT works performed by comparing $E^{\text{vert-abs0}}$ to experimental excitation energies of small molecules, for which accurate gas-phase experimental values are at hand. We will first summarize the results of three recent large benchmarks of this category^[110,118,120] and next move to more specific contributions.

Caricato and coworkers build a benchmark set composed of 30 valence and 39 Rydberg experimental ES energies of 11 small molecules (ethylene, isobutene, *trans*-1,3-butadiene, formaldehyde, acetaldehyde, acetone, pyridine, pyrazine, pyrimidine, pyridazine, and tetrazine).^[110] This is an extension of a previous set (ethene, isobutene formaldehyde, and acetone) designed by Wiberg, Trucks, and coworkers.^[207] As can be noticed, most of these compounds are included in Thiel's set, and the work of Caricato therefore considers similar ES but using experimental data as reference. Caricato et al. evaluated the performance 26 XCF as well as the CIS, CIS(D), and EOM-CCSD approaches.^[110] They found that the five XCF providing the smallest MAE are CAM-B3LYP (0.33 eV), M05-2X (0.36 eV), BMK (0.36 eV), LC- ω PBE (0.36 eV), and B3P86 (0.38 eV).^[110] For comparison, EOM-CCSD

yields a MAE of 0.27 eV, whereas CIS(D)'s MAE is 0.49 eV. Interestingly, they also investigated the MAE obtained for the first ES of each molecule, and the error patterns are significantly different. For that subset, the MAE can be as small as 0.12 eV (B3P86), most “traditional” hybrids (e.g., B3LYP, PBE0, M05, TPSSH,^[65] etc.) and CAM-B3LYP being within 0.25 eV of experiment, contrary to EOM-CCSD (0.35 eV).^[110] Using the same set of molecules and applying 30 additional XCF, Isegawa et al. confirmed this finding.^[120] Indeed, 21 out of the 30 tested XCF provided MAE smaller than EOM-CCSD for the 30 valence excitations. As expected the situation is reversed for the 39 Rydberg ES: in that case (and for the full 69 ES set) EOM-CCSD outclasses TD-DFT. A graphical representation obtained for the full set of XCF, reproduced from Ref. [120], can be found in Figure 3. The two best performing XCF for the full set are M06-2X and ω B97X-D with MAE of 0.30 eV. For GHs, the most successful functionals are characterized by an EXX percentage in between 41% and 54%.^[120]

One of the largest recent investigation comparing experimental results to vertical estimations for small molecules is due to Gordon's group.^[118] They assessed 24 functionals for 101 ES (63 singlets and 38 triplets) of various nature measured on 15 small molecules. The CAM-B3LYP and M06-2X XCF are recommended for Rydberg ESs with MAE of 0.22 eV and 0.17 eV, respectively, confirming investigations made by Tozer.^[105] For valence states, Gordon and coworkers showed that B3LYP (MAE = 0.26 eV), X3LYP (MAE = 0.26 eV),^[48] PBE0 (MAE = 0.30 eV), and M06 (MAE = 0.25 eV), four GHs, offer the best performances. For singlet states, the PBE0 and M06-2X provided the smallest errors with deviations of 0.25 eV and 0.22 eV, respectively, were as for triplet states, M06-2X was the most accurate (MAE of 0.24 eV), which is also in the line of what was found on Thiel's set.^[156] Gordon and coworkers also found large errors in the triplet description with CAM-B3LYP (1.10 eV average deviation),^[118] and this could be related to the above-mentioned instability problem. In Ref. [118], the best performing, pure, GGA-GH, and mGGA-GH are M06-L (MAE of 0.39 eV), PBE0 (MAE of 0.28 eV), and M06-2X (MAE of 0.22 eV), respectively, and these findings are very consistent with the results obtained with Thiel's theoretical reference on similar molecules and states.

Let us now turn toward more specific works.^[52,171,172,192,208–214] Probably, one of the first TD-DFT benchmark published is due to Adamo, Scuseria, and Barone.^[179] For CO, formaldehyde, acetone, ethylene, benzene, pyridine, and naphthalene, they investigated the performances of PBE, B3LYP, and PBE0 and compared their results to HCTH values,^[215,216] experiment as well as CAS-PT2.^[179] Adamo et al. reported very good performances of PBE0 with typical deviations of about 0.2 eV.^[179] Casida and Salahub investigated the ES energies of N₂, CO, formaldehyde, and ethylene and compared several XCF (LDA, LB94 and AC-LDA) with both experiment and previous TD-DFT works. The asymptotically corrected (AC) XCF gave the most satisfying results.^[208] Matsuzawa et al. modeled the low-lying ES of formaldehyde, benzene, ethylene, and methane with SVWN and B3LYP and several atomic basis sets, and found that the latter XCF provided estimates closer from measurements.^[209] Della Salla and Göring assessed the relative

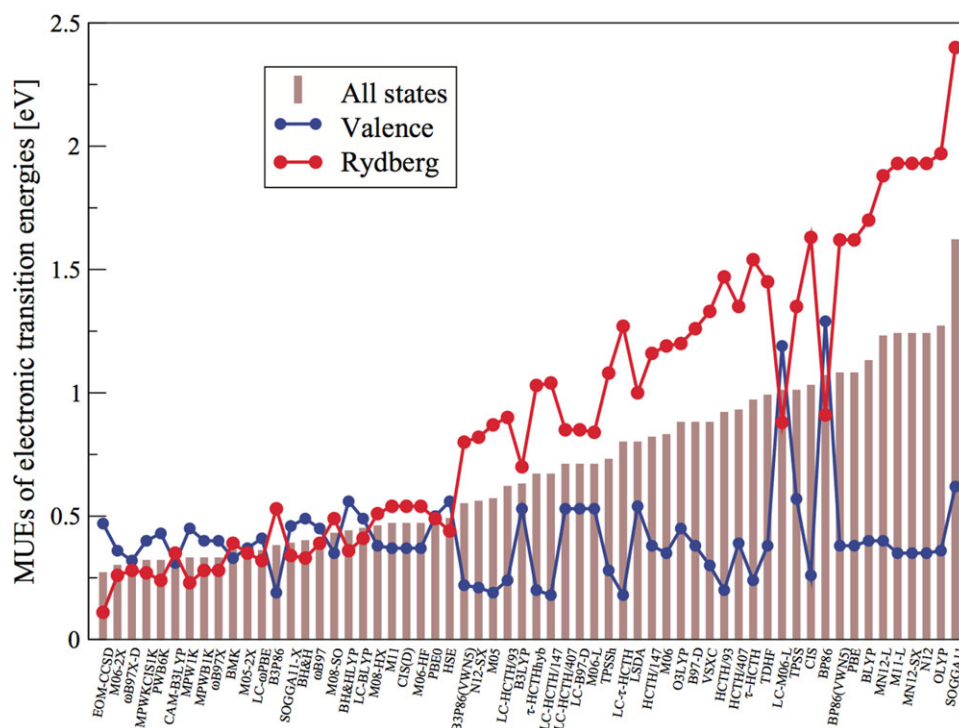


Figure 3. Results obtained on Caricato's set using 56 XCF. Reproduced with permission from Ref. [120], © 2012 American Institute of Physics.

performances of the LHFx, BP86, SOAP,^[217] BPgracLB,^[218] HCTH XCF for 15 ES of N₂, 11 ES in ethylene and 30 ES in benzene.^[219] For these three molecules, BPgracLB provided MAE smaller than 0.25 eV. Tawada et al. investigated the low-lying ES of CO, N₂, ethylene, formaldehyde, and benzene with several XCF (BOP, AC-BOP, PBEOP, BLYP, B3LYP, LC-BOP, LC-PBEOP, and LC-BLYP)^[70] as well as with SAC-CI.^[220] By comparing with experiment, they concluded to the superiority of LC approaches, notably for Rydberg states (typical errors smaller than 0.5 eV).^[220] For 5 ES of RuO₄ and 5 ES of OsO₄, LB94 provides an average deviation of 0.24 eV, whereas revPBE^[221] and SOAP were less accurate.^[210] Imamura and Nakai investigated 6 ES of CO, with several XCF (SVWN5, BLYP, PBE, HCTH, VSXC, B3LYP, PBE0, LB94, BmLbLYP) and PBE0 provided the smallest MAE of 0.39 eV.^[211] The same authors also assessed the same XCF for $1s \rightarrow \pi^*$ core excitations, and the most accurate description was given by BmLbLYP (1.40 eV) and LB94 (2.84 eV).^[211] In another contribution, the $1s \rightarrow \pi^*$ core excitations of five molecules (CO, N₂, ethylene, acetylene, and formaldehyde) have been computed with BLYP, B3LYP, BHHLYP and a newly designed XCF, CV-B3LYP, that yields optimal responses for these core excitations.^[212] Indeed, with the cc-pCVTZ basis set, the obtained MAE are 2.8 eV, 0.3 eV, and 12.0 eV with BHHLYP, CV-B3LYP, and B3LYP, respectively.^[212] Zhao and Truhlar compared the experimental excitation energies of N₂, CO, formaldehyde, and tetracene to TD-DFT simulations relying on GHs (TPSSH, B3LYP, B98, PBE0, M05-2X, and M06-HF).^[172] They extended their investigation to a larger set of XCF in a latter work.^[52] For non-CT transitions (both valence and Rydberg ES, so-called VRES41 set) the smallest deviations are obtained with BMK (0.33 eV), M05-2X (0.34 eV), and M06-2X (0.35 eV).^[52,172]

For valence transitions, the smallest deviations are obtained with GHs having between 10 and 30% of EXX.^[52,172] Ciofini and Adamo benchmarked the PBE0 XCF for the Rydberg states of five molecules (CO, formaldehyde, ethylene, benzene, and pyridine) considering 33 different atomic basis sets.^[214] Once a sufficiently large basis set is used, most ES could be reproduced within a ca. 0.25 eV error, as long as the energy of the considered state remained below a $\epsilon_{\text{HOMO}} + 1$ eV threshold.^[214] Grimme and Neese investigated 20 singlet-triplet excitation energies of small molecules (CO, N₂, formaldehyde, ethylene, butadiene, benzene, and pyridine) and found that B2PLYP outperformed B3LYP (MAE of 0.18 and 0.25 eV, respectively), within the TDA approximation (see Thiel's and Tozer's sets for discussion of TDA/TD-DFT differences for triplets).^[84] In the same time, for small radicals, both XCF provided similar deviations.^[84] In 2008, Rohrdanz and Herbert evaluated ES of CO, formaldehyde, and ethanal for their own LRC-PBE and LRC-PBE0, and determined the optimal ω parameter for these RSH.^[171] Tao and coworkers compared TD-DFT/6-311++G(3df,2pd) vertical energies to experimental data for 8- to 10 low-lying valence and Rydberg ES of CO, N₂, H₂O, formaldehyde, acetone, benzene, and pyridine.^[106] For this 64 ES panel, they obtained average errors decreasing in the PBE, LDA, TPSS, TPSSH, B3LYP, and PBE0 order, well illustrating that hybrids are more accurate. The latter functionals provided relative deviations of 4.4% (ca. 0.30 eV). For their benzoic acid set, Guo et al. compared experimental λ_{max} to PCM-TD-DFT simulations.^[192] The best performances have been obtained with M06-2X (MAE=0.29 eV), ω B97X-D (MAE=0.27 eV), and CAM-B3LYP (MAE=0.24 eV). Dupont et al. investigated the $\sigma \rightarrow \sigma^*$ transitions in five three-electron two-center anions using 35

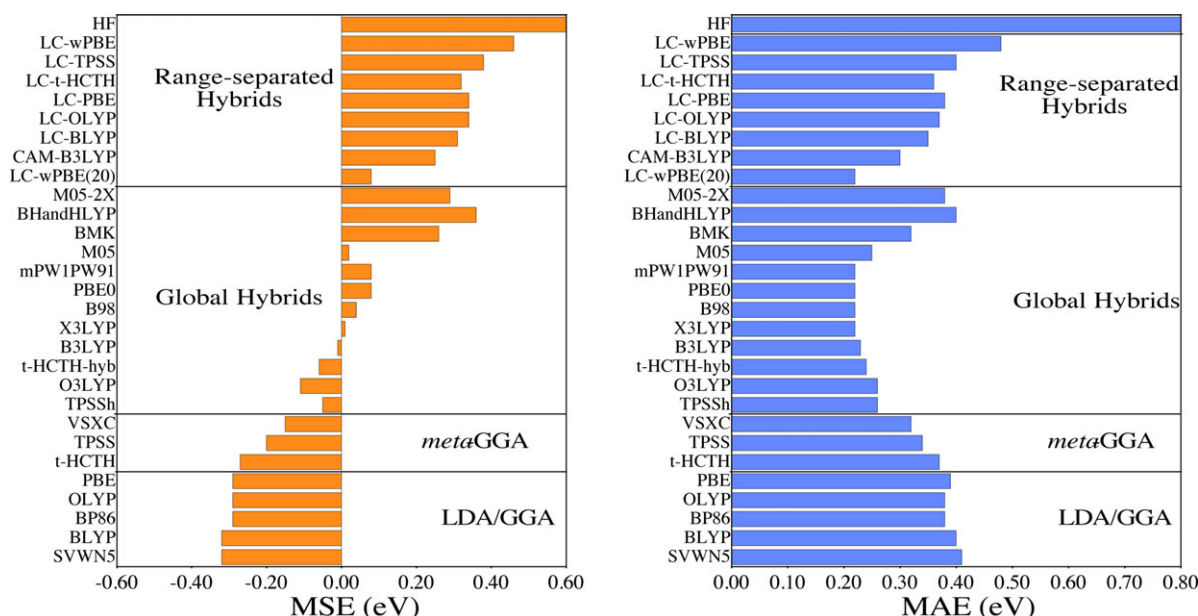


Figure 4. MSE and MAE obtained by comparing 614 experimental λ_{\max} to vertical transition energies. Results adapted from Ref. [107].

XCF and concluded that RSH are in general significantly superior to GHs for these challenging odd-electron systems. This success of RSH could be traced back to a balanced description of both ground (geometry) and ES (λ_{\max}) signatures.^[222] In that specific case, the studied species are unstable, so that adiabatic simulations could not be performed.

“Real-Life” molecules

For molecules of practical interest for technological and industrial applications, most works resort to a comparison between experimental λ_{\max} and $E^{\text{vert-abso}}$. As illustrated in the cyanine Section above, this approximation can be problematic and is certainly not completely satisfying from a theoretical viewpoint, but still represents about 90% of published applications of TD-DFT recently. In that framework, the most extensive comparison was proposed by one of us in 2009 and includes 614 ES and 29 XCF.^[107] The set includes molecules of various sizes and natures, but is clearly focused on low-lying ES of conjugated molecules, notably organic dyes. It is partially based on previous more specific benchmark sets of industrially relevant chromophores^[102,104,132,223–230] and was also used to assess the performances of XCF of the M06,^[156] M08,^[160] and ω B97^[157] families latter. The MSE and MAE obtained in Ref. [107] are depicted in Figure 4. The MSE shows the same trend as in Table 2: pure functionals underestimate the measured λ_{\max} whereas RSH including large amount of EXX, for example, LC- ω PBE, lead to the opposite errors. The smallest MAE are obtained with GHs presenting 15–28% of EXX (0.25 eV or smaller) which is in the line of the conclusions obtained for valence ES in small molecules. Amongst the pure XCF, VSXC,^[64] and M06-L^[66] provided the smallest deviations, whereas the most efficient RSH are CAM-B3LYP, ω B97X-D, and LC- ω PBE(20) with average deviations of about 0.30 eV for the two former and 0.22 eV for the latter.^[107,156,157] In Ref. [107], several sub-

sets have been proposed. The main conclusions could be summarized: (i) the $n \rightarrow \pi^*$ transitions are rather insensitive to the selected XCF and tend to be more accurately described than their $\pi \rightarrow \pi^*$ counterparts, (ii) cyanine-like transitions cannot be adequately modeled in the λ_{\max} with $E^{\text{vert-abso}}$ framework (see cyanine Section above); (iii) for a given XCF, the average deviations obtained for small, medium and large compounds are not equivalent, so that the estimation of the error made on large π -conjugated systems on the basis of simulations performed on model compounds could be difficult.

Other more specific $E^{\text{vert-abso}}$ versus λ_{\max} benchmarks have also been published, and we summarize the most significant results below.

For “real-life” dyes, the first comparisons of two functionals (B3LYP and BPW91) we are aware of was proposed by Guillaumont and Nakamura for 21 ES measured on anthraquinone, indigo, triphenylamine, etc.^[122] They found that the B3LYP MAE (0.21 eV) was significantly smaller than its BPW91 counterpart (0.37 eV). More recently, Matsuura et al. used a more extended set of dyes of the same families and compared TD-B3LYP results to AM1, PM3, and PM5 estimates.^[128] During the last decade, Fabian, proposed a series of pioneering assessments of TD-DFT for the reproduction of the λ_{\max} of several series of dyes,^[122,125,130,231–233] including sulfur bearing dyes in 2001 (163 ES in 76 compounds),^[124] sulfur-free dyes in 2002 (54 ES in 21 compounds),^[125] near-IR absorbers in 2009 (134 ES in 130 compounds).^[130] Fabian typically applied a TD-B3LYP/6-31+G(d) vertical approach and compared the results to experiment, as well as semiempirical results (e.g., PPP and ZINDO). The obtained conclusions, limited to the most popular hybrid, are in the line of the results obtained latter in Ref. [107]. Indeed, Fabian reported failures for cyanine derivatives but acceptable errors for most low-lying ES as well as smaller deviations for $n \rightarrow \pi^*$ than $\pi \rightarrow \pi^*$ transitions. For instance, in 2010, he reported a B3LYP MAE of 0.18 eV for the 102 (non-cyanine)

ES of near-IR dyes,^[130] whereas he mentioned as early as 2001, the striking difference between the MAE obtained for $n \rightarrow \pi^*$ (0.09 eV) and $\pi \rightarrow \pi^*$ (0.24 eV) transitions.^[124]

Ten years ago, Parac and Grimme compared the performances of TD-B3LYP, CC2, and MR-MP2, for reproducing 22 vertical energies of 14 molecules.^[127] The reported MAE for the three methods are 0.26, 0.33, and 0.14 eV, respectively, which was an early demonstration that CC2 and TD-DFT accuracies are equivalent (see discussion for Thiel's set above).^[127] Nguyen and coworkers compared 86 B3LYP triplet-triplet ($T_1 - T_n$) transitions of aromatic derivatives to experimental values, and they reported a very small MAE (0.11 eV) for this set of transitions.^[234] One other early TD-DFT benchmark performed for "real-life" molecules was proposed by van Faasen and Boeij in 2004.^[235] They selected 17 systems, including rather large porphyrin, indigo, decapentacene and compared the performance of SVWN and SVWN-VK approaches using the ET-pVQZ atomic basis set and correcting experimental values for solvatochromism (for the smallest molecules in their set, wavefunction references have been used as well). They found that the VK approach improved the LDA description in all but one (indigo) cases.^[235] In 2004, Dierksen and Grimme also investigated a wide panel of larger organic molecules with three XCF,^[101] but their work is clearly focused on adiabatic rather than vertical energies, and will be therefore discussed latter in this review. In 2008, Rohrdanz and Herbert evaluated their LRC-BLYP, LRC-PBE, and LR-PBE0 RSH on six aromatic chromophores (anthracene, indole, pyridazine, benzocyclobutenedione, benzaldehyde, and pyrrole).^[171] Van Voorhis and coworkers used 16 large dyes and 8 XCF (PBE, B3LYP, PBE0, LR- ω PBE0, PBE4, BHHLYP, M06-2X, and M06-HF) and compared TD-DFT to Δ SCF results.^[236] The smallest TD-DFT MAE (0.27 eV) were obtained with B3LYP, PBE0, and LR- ω PBE0, and the Δ SCF procedure provided similar errors.^[236] In 2011, Goergik and Grimme investigated the ordering of the L_a and L_b states in polycyclic aromatic hydrocarbons using both CC2 and TD-DFT (10 functionals including global, range-separated and double hybrids),^[97] which completes previous studies using RSH^[237] and standard XCF.^[238] The two double-hybrids, namely B2PLYP and B2GPPLYP, allowed to restore the correct state order in most cases and to reach accurate transition energies.^[97] Refaely-Abramson and coworkers compared B3LYP and (optimized) BNL values for the lowest-lying ES of 10 conjugated compounds relevant for organic photovoltaic (thiophene, C₆₀, porphyrin, phthalocyanine, etc.) applications.^[140] Both schemes provided accurate estimates with MAE of 0.19 eV (B3LYP) and 0.16 eV (optimally tuned BNL, OT-BNL).^[140] In a subsequent work by the same group, Kronik and coworkers evaluated the performances of their method (OT-BNL) in light of experiment and showed that OT-BNL outperformed most XCF (PBE, HSE, B3LYP, M06, M06-HF, LC- ω PBE, ω B97X) in reproducing both the fundamental and the optical gaps.^[239] Last year, Syzgantseva et al. benchmarked for 17 epicocconone analogues and found that the PCM-CAM-B3LYP approach was the most efficient, amongst the tested XCF (B3LYP, PBE0, LC-PBE with several ω values and CAM-B3LYP) in order to reproduce the measured λ_{max} .^[147]

Charge-transfer

Charge-transfer ES, in which the electron jumps between two distant positions as a result of photon absorption, are extremely important in key applications such as DSSC and organic electronics. Mainly from comparisons with experiment, it rapidly appeared that these ES cannot be described correctly with "conventional" XCF,^[121,124,168,240–244] that tend to yield too low transition energies and to generate spurious ES, that is, nonphysical low-energy CT ES. It is now well admitted that RSH are an adequate option to describe CT phenomena, thanks to their large amount of EXX at long-range that allows an accurate description of the electron-hole interactions (see also Tozer's sets above). In regards of its importance, we have devoted this Section to works mainly focused on intra and/or intermolecular CT transitions.

In 2002, Cai et al. used both experimental and CAS-PT2 ES values obtained on a porphyrin dimer to exemplify one of the first failure of TD-DFT (SVWN, BP86, HCTH/AC and B3LYP) for extended π -systems.^[240] In the same time, Jamorski studied seven push-pull aromatic derivatives, with LDA and B3LYP, and found that it was difficult to have an accurate balance between the valence (local) and CT ES in these relatively small systems.^[126] In 2003, Liao et al. proposed a series of weakly bound intermolecular complexes between two electron acceptors, tetracyanoethylene (TCE) and chloranil (CA), and five electron-rich aromatic cycles.^[243] They assessed the performances of 11 XCF, including the B1LYP,^[40] B3LYP, mPW1PW91,^[245] BHH, and BHHLYP GHs. They found that the latter that includes 50% of EXX was the only one to furnish reasonable excitation energies.^[243] The same year, Dreuw and coworkers investigated increasingly distant ethylene-tetrafluoroethylene complexes and also found extremely large discrepancies with GHs. They also reported that the asymptotic behavior was directly related to EXX ratio in the tested functionals (SVWN, LB94, B3LYP, BHHLYP).^[241] Dreuw and Liao's complexes rapidly became prototypes for assessing the performances of XCF for intramolecular CT states. In 2004, Dreuw and Head-Gordon provided with their investigation of the zincbacteriochlorin-bacteriochlorin dyad and of the bacteriochlorophyll-spheroidene complex, two additional striking examples of the failures of GHs.^[244] Indeed, the SVWN5, BLYP, and B3LYP XCF miserably failed to produce realistic trends, with errors exceeding 1 eV.

The early demonstration of the performances of RSH has been made using several of these model systems or closely related systems.^[172,220,246–251] Indeed, RSH were purpose-designed to solve the CT catastrophe. The first RSH TD-DFT implementation is due to Tawada et al. who demonstrated that LC-BOP, LC-PBEOP, and LC-BLYP, could reproduce the correct asymptotic behavior for the ethylene-tetrafluoroethylene complex.^[220] Rudberg performed a similar investigation with CAM-B3LYP.^[246] Zhao and Truhlar, showed that the M06-HF XCF, which is not a RSH but includes 100% of EXX, was able to provide very accurate (less than 0.10 eV error) CT energies for both the ethylene-tetrafluoroethylene and NH₃-F₂ complexes.^[172] Such success could not be reached with functionals of the ω B97 series,^[113] nor M06-2X,^[156] though both are more satisfying than B3LYP. In 2006, Cai and coworkers used their

own porphyrin dimer to demonstrate the performances of CAM-B3LYP,^[248] whereas Kobayashi and Amos performed the same work for Dreuw's zincbacteriochlorin-bacteriochlorin dyad.^[249] Lange et al. showed that LRC-PBE could cure the underestimation of CT energies of PBE0 in stacked adenine dimers.^[250]

In 2007, Magyar and Tretiak investigated the relationship between spurious CT states and EXX ratio for 4 large systems having intra or intermolecular CT states.^[252] They found that applying XCF having EXX of 50% or more allowed to strongly decrease the number of parasite states. The same year, Lange and Herbert showed that the introduction of point charges representing the environment allows to reduce the CT contaminations, even with GHs having lower EXX ratio.^[253]

Recently, most CT investigations focussed on pinpointing an adequate hybrid (typically a RSH).^[136,140,114,182,184,197,201,239,254–258] Nguyen and coworkers investigated 19 ES in donor-acceptor complexes between TCE and aromatic compounds with a large panel of RSH and the cc-pVDZ approach.^[114] Besides demonstrating that basis set effects are small, the authors found that the two most effective methods were ω B97X and LC-PBE that provided MAE below the 0.2 eV threshold, whereas all other RSH (CA-PBE, CA0-PBE, HSE, CAM-B3LYP, CA0-B3LYP, LC- ω PBE, and ω B97) gave significantly larger deviations.^[114] The same authors also investigated four coumarin dyes and two stilbene derivatives, showing significant intramolecular CT character, and found that none of the tested RSH was simultaneously accurate for both families of molecules.^[114] Dev et al. benchmarked 6 XCF (PBE, M06-L, B3LYP, M06, CAM-B3LYP, and ω B97) for 16 push-pull dyes used in DSSC, including extended coumarin and triphenylamine derivatives.^[254] They used rather compact atomic basis set, 6-31G(d) and 6-311G(d,p) and accounted for solvent effects through the LR-CPCM model. They compared their results to experimental λ_{\max} and found that CAM-B3LYP was the most accurate (MAE of 0.23 eV with the larger basis set), but that for some molecules, like squaraine, PBE, and M06-L provided values closer from experiment. They interpreted their results using Tozer's Λ .^[254] For push-pull porphyrins used in DSSC, Lee and coworkers benchmarked five functionals (B3LYP, LC- ω PBE, LC-BLYP, CAM-B3LYP and ω B97X-D) and found that the latter (with the default ω value) provided the best match with experiment.^[255] For a strong push-pull chromophore, Gonzalez and coworkers investigated both the linear optical spectra and its resonance Raman counterpart with B3LYP, CAM-B3LYP and M06-2X.^[256] For the former property, the two latter XCF provide satisfying results, whereas resonance Raman spectra is better described with CAM-B3LYP.

Adiabatic Benchmarks

The adiabatic energies, and more precisely the 0-0 energies, can be directly compared to both gas-phase and condensed-phase experimental measurements. The 0-0 energies correspond to the difference of total energies of the ES and GS at their respective minima, corrected for vibrational effects. In the former, the 0-0 band is accurately measured,^[100,112,132] but, as all gas phase measurements, it implies a limitation on the size of molecules that can be treated. In the latter, it is usual to

select the crossing point between fluorescence and absorption curves (AFCP) to determine the 0-0 energies,^[85,86,117,259] which allows to consider large (but only emitting) chromophores. Computations of 0-0 energies, start by the determination of the adiabatic contribution which corresponds to the difference between the ES and GS energies taken at their respective minima, that is,

$$E^{\text{adia}} = E^{\text{ES}}(R^{\text{ES}}) - E^{\text{GS}}(R^{\text{GS}}) \quad (2)$$

which significantly differs from $E^{\text{vert-abso}}$. Indeed, for gas-phase molecules, an extensive B3LYP/def2-TZVP study on more than 100 cases, demonstrated that the ES reorganization energy, $E^{\text{adia}} - E^{\text{vert-abso}}$, attains an average amplitude of -0.33 eV, but with a wide range of variation (ca. from 0 to 2 eV).^[112] For 12 larger molecules, Goerigk and Grimme obtained a mean -0.19 eV correction (PBE/TZVP),^[86] which is also the line of Uppsten and Durbeej's investigation of two biologically relevant chromophores, namely the photoactive yellow protein (PYP) and GFP chromogens. Considering both dyes in gas-phase, to allow comparisons with wavefunction schemes,^[260] and using seven functionals, namely BP86, BLYP, τ -HTCT, B3LYP, PBE0, M06-HF, and CAM-B3LYP, they determined TD-DFT/6-31++G(d,p) reorganization energies of -0.13 ± 0.03 eV (PYP) and -0.08 ± 0.01 eV (GFP).^[260] For 40 solvated fluorophores, simulated with the cLR-PCM model in its equilibrium limit, we obtain an average reorganization energy of -0.24 eV,^[117] and it undergoes a slight increase with the amount of EXX included in the functional: -0.21 eV (B3LYP), -0.21 eV (PBE0), -0.20 eV (M06), -0.25 eV (M06-2X), -0.25 eV (CAM-B3LYP), and -0.33 eV (LC-PBE). In summary, these benchmarks clearly illustrate the large differences between the adiabatic and vertical energies.

To reach the 0-0 energies, it is also required to compute the difference between zero-point vibrational energies (ZPVE) of the ES and GS states,

$$\Delta E^{\text{ZPVE}} = E^{\text{ZPVE}}(R^{\text{ES}}) - E^{\text{ZPVE}}(R^{\text{GS}}) \quad (3)$$

Though TD-DFT Hessian calculations have been very recently described,^[261,262] this task is traditionally accomplished numerically, which requires the computation of $6N+1$ TD-DFT analytic gradients^[100,263] for a N -atom molecule belonging to the C_1 point group. This step rapidly becomes prohibitive, and molecules composed of 100 atoms or more constitute a significant computational challenge, even when a double- ζ basis set is used. By combining the two previous equations, one gets a well-grounded estimate of the 0-0 energies:

$$E^{0-0} = E^{\text{adia}} + \Delta E^{\text{ZPVE}} \quad (4)$$

Given the computational cost of the ΔE^{ZPVE} term, several investigations have been devoted to estimate its magnitude and its methodological (functional and basis set) sensitivity.^[117,260,264,265] For the $n \rightarrow \pi^*$ transition in formaldehyde, the gas-phase PBE0 ΔE^{ZPVE} correction was found to be -0.09 eV, insensitive to the basis set size (going from 6-31G to *aug-cc-pVTZ*) but affected by the environment (ca. $\Delta E^{\text{ZPVE}} = -0.04$ eV in ethanol).^[264] For the $\pi - \pi^*$ band in unsubstituted indole,

7-OH-coumarin and 4-NMe₂-benzofurazan, the ZPVE term is also rather insensitive to both the basis set and the XCF (B3LYP, B3P86, PBE0, BMK, BHHLYP, CAM-B3LYP were tested). Indeed, ΔE^{ZPVE} lies in the -0.15 ± 0.01 eV, -0.14 ± 0.02 eV, and -0.07 ± 0.01 eV domain for these three dyes, respectively.^[265] Uppsten and Durbeej found that the difference between E^{0-0} and E^{adia} ranges from -0.09 to -0.14 eV and from -0.07 to -0.17 eV, for PYP and GFP chromogens, respectively.^[260] The variations can mostly be ascribed to the selected functional, the basis set effects remaining small. For biphenyl, 7-methoxy-coumarin and the BODIPY core, the basis set effects have been rated as negligible, for example, the difference between the PBE0/6-31G(d) and PBE0/*aug-cc-pVTZ* ΔE^{ZPVE} is only 0.01 eV for the former and even smaller for the two other molecules.^[117] For 40 molecules, using six hybrid functionals (B3LYP, PBE0, M06, M06-2X, CAM-B3LYP, and LC-PBE), it was found that the typical functional effect is limited (ca. ± 0.03 eV).^[117] In the same vein, Furche and coworkers,^[112] compared B3LYP and PBE0 ΔE^{ZPVE} and also noticed trifling differences. Overall, ΔE^{ZPVE} is a small but non-negligible correction with an amplitude that significantly depends on the selected molecule, and to a smaller extend on the selected functional. For most medium and large organic molecules, one can roughly estimate ΔE^{ZPVE} to be of about -0.08 ± 0.04 eV. This value is consistent with both the PBE/TZVP data provided by Goerigk and Grimme who reported ΔE^{ZPVE} ranging from -0.04 eV to -0.12 eV for their twelve dye panel,^[86] the set of Send et al. for which the average B3LYP/TZVP ΔE^{ZPVE} is -0.09 eV,^[112] and our 40-fluorophore set (average -0.08 eV).^[117] Recently, Hättig and coworkers demonstrated that B3LYP also provides accurate ΔE^{ZPVE} corrections, thanks to comparison with several wavefunction approaches.^[132]

The theory-experiment deviations obtained with the most significant adiabatic benchmarks to date can be found in Table 3. For gas-phase molecules, the most extensive adiabatic TD-DFT study is due to Furche and coworkers,^[112,266] that have collated a 109-cases database (86 singlet, 12 triplet, and 11 unrestricted transitions) of accurate experimental adiabatic energies of gas phase molecules, most compounds being rather compact but a few exceptions are noticeable (e.g., porphyrin). This set completes a former test of similar molecules made by the same authors.^[100] These authors evaluated the performances of six pure and hybrid functionals, namely LSDA, PBE, BP86, TPSS, B3LYP, and PBE0, but to lighten the computational burden determined the ZPVE correcting term with the B3LYP functional and use it for all other corrections. They latter extended their set to the TPSSh GH.^[266] Amongst all tested XCF, the B3LYP and PBE0 were the most accurate, with MAE below the 0.25 eV limit, whereas errors are much more sizable with pure XCF that tends to significantly undershoot the experimental data. The use of a current-dependent formalism for TPSS and TPSSh (cTPSS and cTPSSh) lead to larger deviations with respect to experiment than in the standard formalism.^[266] Hättig and coworkers recently proposed a 66-cases set containing highly accurate gas phase references of larger molecules,^[132] and they compared the performances of B3LYP to four wavefunction schemes: ADC(2), CC2, SCS-CC2, and SOS-CC2. The mean absolute error

Table 3. MSE and MAE obtained during benchmarks of the 0-0 bands.

| Functional | MSE | MAE | References |
|--------------|-------|------|------------|
| LSDA | -0.18 | 0.25 | [100] |
| | -0.31 | 0.39 | [112] |
| BP86 | -0.22 | 0.31 | [100] |
| | -0.56 | 0.57 | [101] |
| | -0.32 | 0.39 | [112] |
| BLYP | -0.27 | 0.32 | [100] |
| | -0.49 | 0.51 | [86] |
| PBE | -0.24 | 0.30 | [100] |
| | -0.33 | 0.40 | [112] |
| TPSS | -0.20 | 0.32 | [112] |
| cTPSS | -0.26 | 0.34 | [266] |
| TPSSh | -0.08 | 0.26 | [266] |
| cTPSSh | -0.13 | 0.27 | [266] |
| B3LYP | -0.13 | 0.28 | [100] |
| | -0.12 | 0.30 | [267] |
| | -0.33 | 0.34 | [101] |
| | -0.22 | 0.31 | [86] |
| | -0.08 | 0.21 | [100] |
| | -0.14 | 0.27 | [117] |
| | 0.00 | 0.19 | [132] |
| PBE0 | -0.14 | 0.30 | [100] |
| | 0.01 | 0.25 | [112] |
| | -0.03 | 0.22 | [117] |
| M06 | 0.05 | 0.23 | [117] |
| BMK | 0.07 | 0.19 | [86] |
| M06-2X | 0.25 | 0.26 | [117] |
| BHHLYP | -0.01 | 0.18 | [101] |
| CAM-B3LYP | 0.11 | 0.18 | [86] |
| | 0.24 | 0.25 | [117] |
| LC-PBE | 0.56 | 0.57 | [117] |
| ω B97 | -0.05 | 0.25 | [267] |
| B2PLYP | -0.11 | 0.20 | [86] |
| B2GPPLYP | -0.01 | 0.16 | [86] |

See text and Table 1 for more details. All data in eV.

of B3LYP (0.19 eV) was found to be significantly larger than for other approaches, for example, the MAE of SCS-CC2 is limited to 0.06 eV.^[132] This outcome in the line of a former investigation by the same group,^[129] where larger deviations (MAE of 0.29 eV with B3LYP and 0.14 eV with SCS-CC2) have been reported for a set of smaller molecules. Liu et al. used a set of 29 adiabatic energies computed for small compounds, as in Furche original work,^[100] and compared the TDA and TD-DFT version of the B3LYP and ω B97 XCF.^[267] They found that TDA and TDDFT provided very similar energies, the RSH MAE being slightly smaller (0.25 eV) than its B3LYP counterpart.

Grimme and coworkers performed a series of benchmark calculations^[85,86,101] with a focus on “real-life” molecules. In their seminal 2004 paper, they tested three functionals (BP86, B3LYP, and BHHLYP) on 30 singlet-singlet transitions in (mostly aromatic) dyes as well as 13 doublet-doublet transitions in radical compounds. Though some structures were symmetric, computing the ZPVE corrections for all systems in 2004 certainly represented a very demanding task. Solvent effects where empirically accounted by applying a +0.15 eV correcting term to the experimental 0-0 energies (irrespective of the solvent). On average, they found that a 30–40% EXX share would be optimal.^[101] In their more recent investigations,^[84–86] Grimme and coworkers have chosen to first transform the

measured AFCP in “experimental” vertical values by applying successive theoretical corrections. This allows to use faster vertical calculations to estimate adiabatic energies, and they applied such procedure for 12 molecules in 2010.^[86] Indeed, Goerigk and Grimme first determined the difference between LR-PCM and gas-phase PBE0 $E^{\text{vert-abs0}}$ to remove solvent effects. Next, they computed the ΔE^{ZPVE} as well as the difference between the adiabatic and vertical absorption energies, at the PBE/TZVP level to reach “experimental” vertical energies. With this model, they could obtain deviations smaller than 0.2 eV for a recent GH (BMK), a RSH (CAM-B3LYP), as well as their double hybrid (B2GPPLYP) (see Table 3). Interestingly, the CC2 and SCS-CC2 schemes did not significantly outperform CAM-B3LYP in these cases,^[86] contrasting with Hättig results.^[132]

Nguyen, Day, and Pachter compared TD-DFT/6-311+G(d,p) and experimental adiabatic energies, for the first ES of seven small molecules (CO, HCN, CH₂O, CH₂S, CCl₂, C₂H₂, and *trans*-(CHO)₂) and obtained MAE of 0.28, 0.18, 0.24, and 0.27 eV with B3LYP, LC-BLYP, CAM-B3LYP, and *m*CAM-B3LYP, respectively.^[111] They also compared the adiabatic results for seven substituted coumarins and two stilbene derivatives having a CT nature, and the average absolute deviations for the former set are 0.21, 0.26, 0.18, and 0.07 eV in the coumarin series.^[111]

In our latest work dealing with 40 medium and large fluorophores in solution, we did not consider any simplification (the ZPVE has been systematically computed) and used the cLR-PCM solvation model.^[117] A difficulty when modeling solvent effects is that the absorption and fluorescence curves (and hence their crossing point) corresponds to a nonequilibrium phenomena, whereas the 0-0 energies are formally an equilibrium response. To resolve this difficulty, an extra correction has been applied, that is, E^{0-0} is computed as

$$E^{0-0} = E^{0-0}(\text{cLR, eq}) + \frac{1}{2} [\Delta E^{\text{vert-a}} + \Delta E^{\text{vert-f}}] \quad (5)$$

$$\Delta E^{\text{vert-a}} = \Delta E^{\text{vert-a}}(\text{cLR, neq}) - \Delta E^{\text{vert-a}}(\text{cLR, eq}) \quad (6)$$

$$\Delta E^{\text{vert-f}} = \Delta E^{\text{vert-a}}(\text{cLR, neq}) - \Delta E^{\text{vert-f}}(\text{cLR, eq}) \quad (7)$$

We redirect the interested reader to Ref. [117] for more details and appropriate justification of the one half factor in Eq. (5). With this protocol, five out of the tested six functionals provided MAE close to 0.25 eV, with significant overestimation of the transition energies by CAM-B3LYP and M06-2X (see Table 3). However, these two functionals provide more consistent (in terms of correlation with experimental) values, which can be partly explained by the lack of very large discrepancies that are present with GHs like B3LYP or PBE0 (see geometry section below). The difference between the results obtained in the benchmarks of Refs. [86] and [117] that considered similar molecules, is partly related to the different protocols, for example, the use of a constant GGA geometry in the former and the selection of a geometry optimization scheme consistent with the transition energies model in the latter.

Therefore, as in the case of vertical calculations, the typical TD-DFT errors are close to 0.2–0.3 eV and it appears that functionals with large percentage of EXX (both global and range-separated) tend to avoid the largest deviations.

Other Properties

As noted above, though there exists benchmarks performed for other properties than transition energies, they are often more limited due to the difficulty to obtain reliable experimental or theoretical references. Also, they are more focused on a specific subset of molecules, making general conclusions probably out of reach at this stage. We nevertheless summarize the most meaningful investigations in the following.

Geometries

The first benchmark of geometrical structures was performed by Furche and Ahlrichs,^[100] who compared 58 ES structural parameters (40 bond lengths, 15 valence angles, and 3 dihedral angles) of small molecules to experimental values. As in their adiabatic study (see above), they considered six XCF, including two GHs. For their set the MAE are 0.017 Å (2.2°), 0.018 Å (1.9°), 0.015 Å (2.2°), 0.014 Å (2.1°), 0.013 Å (2.1°), 0.015 Å (2.3°), for distance (valence angles) using LDA, BLYP, BP86, PBE, B3LYP, and PBE0, respectively. Therefore, for small molecules, the typical errors are rather insensitive to the selected XCF and comparable to the typical DFT discrepancies reported for GS geometries. Using a very similar set of compact compounds, Liu and coworkers compared TDA and TDDFT results of two functionals to experimental data.^[267] With LR-TD-DFT, they obtained MAE of 0.014 Å (2.3°) and 0.074 Å (2.2°) for B3LYP and ω B97, respectively. The B3LYP values compare favorably with both CC2 and SOS-CIS(D₀) estimates, which gave MAE of 0.029 Å (1.3°) and 0.032 Å (1.2°), respectively,^[267] for exactly the same set of molecules. For similar small molecules, Hättig and coworkers reported average deviations of 0.026 Å with SOS-CC2,^[129] that is in the same range as TD-DFT. The second rather complete investigation is due to Guido et al. who benchmarked the results obtained with six functionals (B3LYP, B3P86, PBE0, BMK, BH&HLYP, and CAM-B3LYP) using CAS-PT2 ES geometries.^[268] Their panel of molecules encompasses three subsets, namely $n \rightarrow \pi^*$ ES (acrolein, acetone, diazomethane and propanoic acid anion), localized $\pi \rightarrow \pi^*$ transitions (*cis*-1,3-butadiene, *trans*-1,3-butadiene, and pyrrole) and cyanine-like transitions in protonated Schiff’s bases (containing 5, 7 and 9 carbon atoms in their conjugated skeleton). Table 4 reports the MAE obtained when considering all investigated systems. It turns out that the TD-DFT/CAS-PT2 discrepancy is rather sensitive to the nature of the considered bond but not to the selected functional, with quite sizable (negligible) errors for the (carbon-carbon) carbonyl bond lengths. However, for

Table 4. Mean Absolute Deviations for ES geometrical parameters of 10 molecules, using CAS-PT2 values as reference.

| Parameter | B3LYP | B3P86 | PBE0 | BMK | BH&HLYP | CAM-B3LYP |
|-----------|-------|-------|-------|-------|---------|-----------|
| C—C | 0.015 | 0.013 | 0.010 | 0.009 | 0.014 | 0.010 |
| C=C | 0.020 | 0.021 | 0.017 | 0.010 | 0.018 | 0.014 |
| C=O | 0.063 | 0.069 | 0.072 | 0.077 | 0.082 | 0.070 |
| C=N | 0.032 | 0.034 | 0.033 | 0.032 | 0.038 | 0.031 |

All values are in Å. Adapted with permission from Ref. [268]. © 2010 American Chemical Society.

the ES bond length alternation in Schiff's bases, BHLYP and CAM-B3LYP provided results in good agreement with the wavefunction reference values, while B3LYP and PBE0 were significantly off.^[268]

For ES intramolecular proton transfer potential energy surfaces, Aquino, Lischka, and Hattig compared TD-DFT (PBE and B3LYP) and RI-CC2 methods for 5 model molecules,^[269] and found that B3LYP provided results in good agreement with the wavefunction reference.

A specific ES geometrical effect that has attracted attention from the TD-DFT community is the modeling of twisted intramolecular CT (TICT) structures, that have often been used to explain dual-fluorescence of emitting molecules containing a flexible donor moiety. The seminal example, namely 4-dimethylamino-benzonitrile, was investigated by Tozer and coworkers in 2009.^[270] Comparing PBE, B3LYP, and CAM-B3LYP to CC2 potential energy surfaces corresponding to the rotation of the terminal dimethylamino group, they brought evidence that the pure functional as well as the GH qualitatively failed to provide a physically sound description of the ES structure. Indeed, both XCF incorrectly predict that the perpendicular orientation that corresponds to a very low overlap between the occupied and virtual orbitals involved in the CT state, is more stable than the corresponding planar structure at the ES. This error is cured using the CAM-B3LYP functional (as well as other RSH) that restores the correct potential energy surface.^[270] Since 2009, very similar trends have been reported for larger molecules, such as Nile Red,^[271] Pigment Yellow 101^[272] boron push-pull containing molecules,^[273] as well as several fluorescein derivatives.^[274] Therefore, there is a consensus in the TD-DFT community that for the geometries of ES corresponding to strong CT transitions, selecting RSH is the safest choice. However, in some extreme cases, like CT states between in perylene-bisimide aggregate, the evolution of the ES energies upon geometrical modification could not be reproduced with global (B3LYP, BHHLYP) nor range-separated (CAM-B3LYP) hybrids.^[275]

Oscillator strengths

The oscillator strengths, f , indicate the probability of a given transition from the GS to the ES and are therefore related to the observed intensities. Several benchmarks have also been performed to determine the most adequate XCF for computing accurate f . The overlapping of several excitation bands combined to line shape broadening often prevents using experimental references to benchmark TD-DFT results. Therefore, most groups used theoretical results, or a blend of theory and experiment to assess XCF.

Tawada et al. determined the oscillator strengths computed on small molecules (N_2 , CO, formaldehyde, ethylene, and benzene) using pure, global, and RSH.^[220] They found that the three tested RSH (LC-BOP, LC-BLYP, and LC-PBEOP) were the most successful in reproducing both SAC-CI and experimental trends. In another early investigation, Miura, Aoki, and Champagne investigated the TD-DFT oscillator strengths com-

puted for benzene, phenol, aniline, and fluorobenzene, and compared the results to both experimental and CC results.^[276] They assessed seven functionals (SVWN, BLYP, PBE, TPSS, B3LYP, PBE0, and BHandHLYP) and concluded that XCF containing larger share of EEX yield larger and more realistic f , and the authors advocated the use of BHHLYP. In 2008, Timzaghaziz et al. compared the computed oscillator strengths to experimental data for a series of derivatives of the GFP chromogens.^[277] They used three pure XCF (PBE, BLYP, TPSS) as well as three hybrids (B3LYP, PBE0, and TPSSH) and applied large basis sets and the PCM environmental model. They found that: (i) TD-DFT overestimated the f ; (ii) TD-DFT f were better fitting experiment than their CIS counterpart; (iii) the f obtained with pure density functionals displayed the largest correlation coefficients with measurements. For their 109-cases set, Silva-Junior et al. reported MAE of 0.128 (0.075), 0.103 (0.055), and 0.096 (0.044) for the f determined with BP86, B3LYP, and BHHLYP using CAS-PT2 (CC2) values as references.^[103] In addition to the confirmation of the results obtained by Miura, this indicates that the CC2 and CAS-PT2 f amplitudes differ quite significantly. In 2012, Bartlett's group simulated the ES of the DNA bases with several EOM-CC approximations as well as with B3LYP,^[150] and found that for most states, B3LYP' f are smaller than their CC counterparts. To our knowledge, Caricato et al. performed the most extensive and significant benchmark of oscillator strengths to date.^[278] Indeed, they considered an extended panel of XCF (28) and used the f of a set of 11 small organic molecules (30 valence states and 39 Rydberg states) that were simulated with a robust wavefunction reference, namely EOM-CCSD. Geometries of the set of molecules have been optimized with MP2/6-311G(d,p) while f were evaluated with 6-311(3+,3+)G(d,p) atomic basis set. For alkene, carbonyl, and azabenzene subgroups BHHLYP, CAM-B3LYP, and LC- ω PBE provided the most accurate results (see Fig. 5). On average, the best TD-DFT performance was reached by CAM-B3LYP closely followed by LC- ω PBE.^[278]

Dipole moments

With TD-DFT, dipole moments can only be obtained when one determines the generalized density of the ES, which requires an additional effort compared to vertical transitions. In their seminal work of Furche and Ahlrichs investigated 10 ES dipole moments of seven diatomic or tetra-atomic molecules for which experimental values are available.^[100] For this set, the three investigated GGA (BLYP, BP86, and PBE), provided a mean absolute deviation of 0.11–0.12 D with respect to measurements, whereas the two hybrids (B3LYP and PBE0) yielded poorer estimates with a MAE of ca. 0.17 D.^[100] For molecules of larger size, the quality of the TD-DFT prediction for ES dipoles can, in practice, only be assessed on the basis of wavefunction approaches. A notable investigation is due to King, who compared EOM-CCSD to TD-DFT (HCTH and B97-1 with and without asymptotic corrections) dipoles for 29 ES of furan and pyrrole.^[183] B97-1 provided more accurate ES dipoles with deviations of about 0.5 D (1.1 D) for furan (pyrrole). Similar

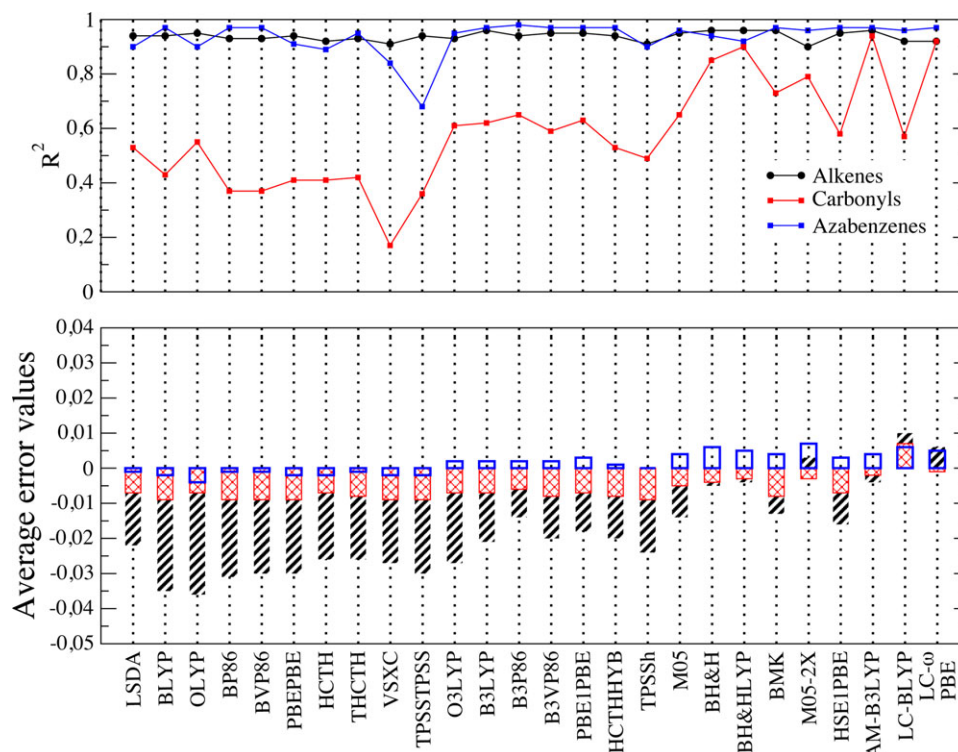


Figure 5. Oscillator strength benchmark.^[278] The top panel show the R^2 value obtained for the three subsets of molecules after the fit of the DFT oscillator strengths against EOM-CCSD values. The bottom panel shows the average error values of oscillator strengths computed with DFT XCF against EOM-CCSD reference value.

comparisons were also performed by Thiel and coworkers using their own benchmark set.^[103] They reported TD-DFT/CAS-PT2 mean absolute deviations of 0.75, 0.59, and 0.61 D with BP86, B3LYP, and B3LYP, respectively with discrepancies exceeding 1 D in 23%, 12%, and 13% of the treated cases, for these three XCF. For the lowest ES of *N*-Phenylpiperidone-malondinitrile, Rothlisberger and coworkers reported a dipole of 19.0 D with PBE0, which perfectly matches both CC2 (19.1 D) and experiment (18.8 D), PBE being less satisfying (16.6 D).^[187] In short, the hybrids outperform the tested GGA contrary to the small molecule cases, and TD-DFT had a tendency to overestimate the ES dipole moments. Interestingly, Ref. [103] reports similar error patterns for both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. More specific studies of ES dipole moments are also available in the literature, and we point out, on the one hand, the work of Guido et al. who reported, using five molecules and six functionals, that the difference between GS and ES dipole moments tends to decrease when using XCF with larger EXX,^[268] and, on the other hand, the investigation of twelve oligothiophene derivatives performed by Wong et al.,^[185] who consistently found that the GS-ES dipole differences are significantly larger with B3LYP than with RSHs.

Vibrational frequencies and vibronic shapes

To the best of our knowledge, the two only benchmark of ES frequencies are due, on the one hand, to Furche and Ahlrichs,^[100] who computed 80 harmonic vibrational frequencies for 27 small molecules (the largest system being benzene and

pyridine) and, on the other hand, to Liu and Liang who used a similar set containing 84 harmonic vibrational frequencies of 24 small molecules (the largest system being benzene and propenal).^[262] Both works compared their TD results to experiment. The MAE that can be computed from their data are 63, 54, 49, 50, 61, and 70 cm^{-1} for LDA, BLYP, BP86, PBE, B3LYP, and PBE0 respectively,^[100] and 57, 42, and 66 cm^{-1} for LDA, BLYP, and B3LYP, respectively.^[261] Liu and Liang also demonstrated that TDA and TDDFT frequencies are highly similar and both are much more accurate than the corresponding CIS data. The fact that GHs are less accurate than GGA is probably related to the limited size of the systems investigated.

There exist several specific (one molecule with several functionals or vice-versa) benchmark studies performed for vibronic shapes.^[12,141,259,279–291] For their 43 molecule set, Dierksen and Grimme found that no universal amount of EXX seems to exist that gives a uniformly good description for all systems and states. Nevertheless an inclusion of about 30–40% of EXX in the functional is found empirically to yield in most cases simulated spectra that compare very well with experiment. For both aza-BODIPY and anthraquinone dyes, similar conclusions have been obtained,^[141,259] that is, functionals including a large share of EXX (BMK and ω B97X-D, respectively), provide very realistic band shapes, though standard hybrids, for example, B3LYP or PBE0, are reasonably satisfying. For the challenging dithiophene case, Stendardo et al. found that the vibrational structure was accurately reproduced by PBE0 and CAM-B3LYP, whereas other tested functionals (BLYP, B3LYP, and B3LYP) provided less impressive match with

experiment.^[290] On the contrary for the small and rigid phenylacetylene, B3LYP is more accurate than both LC-BLYP and CAM-B3LYP (for vibronic couplings).^[289] Obviously, additional investigations using modern functionals to simulate vibronic shapes of a large set of compounds would be welcome to reach general conclusions.

Electron circular dichroism and optical rotations

The electronic circular dichroism (ECD) of 10 molecules (nine organic and one metal complex) have been simulated by Diedrich and Grimme in 2003.^[292] They applied BP86, B3LYP, B3LYP XCF and compared the results to HF, CC2, multireference wavefunction approaches and measurements. None of the tested functional was fully satisfying for all molecules but B3LYP was the most accurate. The ECD spectra of 10 metal complexes have been computed by Rudolph and Autschbach using six pure and hybrid functionals (PBE, BP86, B3LYP, PBE0, CAM-B3LYP, and LC-PBE0).^[293] They concluded that B3LYP and PBE0 provide ECD spectra in good agreement with experiment, whereas pure XCF yield poor results. The two RSH did not give improvements over the spectra calculated with GHs.^[293] Goerigk and Grimme^[294] compared B3LYP, B2LYP, and B2PLYP simulations to experimental spectra for six typical organic molecules and concluded that the latter scheme was the most successful.

Autschbach and coworkers proposed a benchmark set constituted of 45 molecules (including three metal complexes) for which experimental molar optical rotations (OR) are available.^[295] They evaluated the performances of several atomic basis sets and five XCF, namely B3LYP, PBE0, B3LYP, CAM-B3LYP, and LC-PBE0. They found that B3LYP and PBE0 behave similarly and that large share of EXX (B3LYP) or the use of RSH (CAM-B3LYP and LC-PBE0) did not provide systematic improvements of the results. For 13 small organic molecules, Crawford and Stephens obtained a MAE of 25.3 (B3LYP) and 27.4 (CCSD) $\text{deg dm}^{-1} (\text{g/mL})^{-1}$,^[296] but the better performance of TD-DFT can be partly ascribed to error-compensations. For the same set, Bates and Furche found a MAE of 27.6 (TPSS) and 26.0 (TPSSH) $\text{deg dm}^{-1} (\text{g/mL})^{-1}$ and these errors can be slightly decreased when a magnetic XC kernel was included.^[266] For helicenes derivatives, this kernel outperform traditional procedures.^[295] Later the same authors, using a subset of molecules, compared the TD-DFT results obtained with four RSH (LC-PBE, LC-BLYP, LC-PBE0 and CAM-B3LYP) to CC data and found that tuning the ω parameter (that guides the EXX mixing in RSH) could improve the results for the most difficult cases without degrading significantly the quality of the optical rotation computed for small systems.^[297] Overall for ECD and OR, “traditional” GHs seem to provide the best choice.

Hyperpolarizabilities and two-photon absorption

Nonlinear optic (NLO) properties correspond to high-order derivatives of the energy with respect to the electro(magnetic) field amplitude. If several static properties, for example, first and second hyperpolarizabilities can be computed from finite-field or sum-over-state approaches that do not require a TD

approach, dynamic simulations are generally performed with TD-DFT. Since the works of Champagne, Kirtman, Baerends, and coworkers, it is well-known that NLO properties of extended π -conjugated chains are not correctly evaluated with both pure and GHs due to a strong overpolarization under external electric fields.^[298,299] RSH presenting a correct asymptotic behavior cure most of the difficulties,^[70,175,246,300–302] and this of course holds for TD-DFT simulations of NLO properties: RSH are mandatory to obtain qualitatively meaningful results on extended systems. For small molecules, typical hybrids like B3LYP, might provide accurate results and often outperform pure functionals.^[303]

Two-photon absorption (TPA) cross sections is also a NLO property,^[304] that was first computed with TD-DFT by Masunov who considered the B3LYP XCF and fifteen compounds.^[305] To the best of our knowledge, the most extensive benchmark of TPA was performed by Friese, Hattig, and Ruud,^[306] that compared CC2 and TD-DFT simulations (BP86, B3LYP, and CAM-B3LYP) for about 10 representative molecules developing interesting experimental responses, for example, push-pull stilbenes. With CAM-B3LYP, the authors could not detect any significant qualitative deviations with respect to CC2 whereas BP86 and B3LYP provided poorer results. This is in the line of an earlier benchmark of TPA cross-section of Rudberg et al.^[246] This success of the RSH was probably partially related to the selection of molecules presenting a strong CT character in the panel. In another investigation,^[307] it was shown that CAM-B3LYP TPA of H_2O , HF, C_2H_4 , and octatetraene differ by only about 15% from CC3 results, though for the latter molecule, states with a double-excitation character were unsurprisingly incorrectly modeled with TD-CAM-B3LYP.

Conclusions

In this paper, we have reviewed contributions devoted to the assessment of the performances of exchange-correlation functionals within the TD-DFT framework. Due to the inherent difficulty to obtain experimental ES references that are both accurate and easy to model, a wide panel of computational strategies and training sets have been tested, and unsurprisingly, some of the obtained conclusions are not uniform. There is obviously room for improvements in both the XCF-design and protocol sides. However, thanks to the huge amount of TD-DFT benchmarks that have been proposed, a series of general conclusions already emerged. Let us summarize some key findings:

1. As a rule of thumb, increasing the amount of EXX included in the XCF tends to increase the predicted transition energies.
2. For the majority of properties, states and molecules, pure density functionals that do not incorporate EXX, provide poorer estimates than hybrid functionals. In some cases, such as the energy and geometry of CT ES, pure XCF yield dramatic qualitative failures. The only compounds for which EXX-free XCF can be really satisfying are very compact molecules.
3. If, despite their inherent limits, one wishes to apply pure functionals, *meta*-GGA are probably the best choice, especially VSXC and M06-L outperform typical GGA and LDA.

4. In the common but crude vertical approximation, “traditional” GHs (e.g., B3LYP, PBE0, or M06) are rather satisfying and tend to provide deviations of about 0.25 eV for valence ES, but the errors can become much larger for states with a strong CT character as well as Rydberg states. For these states, RSHs or GHs including ca. 50% of EXX are more effective. In these two categories, it appears that, on the one hand, CAM-B3LYP and ω B97X-D and, on the other hand, M06-2X, stands as the best possible choices. Double hybrids, and in particular B2GPLYP bring significant improvements for ES having a doubly excited nature.

5. Both $n \rightarrow \pi^*$ and cyanine transitions are less sensitive to the selected XCF than valence $\pi \rightarrow \pi^*$ and Rydberg transitions. While $n \rightarrow \pi^*$ ES are often accurately described within the vertical approximation, comparisons between vertical TD estimates and measured λ_{max} is bound to fail for cyanine-like ES.

6. Adiabatic transition energies, ES geometries (and consequently vibronic shapes) tend to be more accurately computed with GHs incorporating a large share of EXX (e.g., BMK, B3LYP and M06-2X) or RSH (e.g., CAM-B3LYP and ω B97X-D), especially when spatially delocalized ES are considered. For systems where a twisted/planar intramolecular CT equilibrium is possible, using these functionals becomes mandatory to obtain qualitatively correct trends.

7. The ΔE^{ZPVE} correction term is (almost) insensitive to the selected basis set and can be evaluated with a rather compact model. A typical order of magnitude for ΔE^{ZPVE} is -0.08 eV. This vibrational term is dependent on the functional but the variations typically remain limited. On the contrary, it is significantly system and state dependent.

8. For ECD spectra, RSH do not provide more accurate results than GHs, but the reverse is true for both the TPA cross-section of large conjugated systems and the nonlinear optics properties for which the use of RSH is mandatory.

9. For both ES dipole moments and oscillator strengths, it is yet unclear if RSH significantly improve the description of GHs, but once again, the use of pure functionals should be discouraged.

We underline that these general conclusions apply only to the most common LR formalism of TD-DFT for singlet-singlet electronic transitions. Recently, more refined procedures (e.g., dressed, SF, and CV schemes) have started to be benchmarked as well. For some of the most problematic cases (e.g., transitions with a double excitation character, radicals, etc), these advanced formalisms undoubtedly boost the accuracy of TD-DFT, but it is still too early to draw generic conclusions regarding the relative XCF performances in these advanced methodologies. Likewise, for a given compound or state, several of these generic LR-TD-DFT findings can be made wrong. In our view, they nevertheless provide valuable guidelines on how to treat the “default” cases or unknown families of molecules or ESs.

Acronyms

The reader might find a definition of all acronyms in Table 5.

Table 5. Acronyms used in this review.

| Acronym | Definition |
|------------------------|---|
| AC | Asymptotically corrected |
| ADC(2) | Second-order algebraic diagram construction |
| AFCP | Absorption fluorescence crossing point |
| AM1 | Austin model 1 |
| BODIPY | Boron-dipyrromethene |
| cLR | corrected linear-response |
| CA | Chloranil |
| CAS-PT2 | Complete active space with second-order perturbation theory |
| CCSD | Coupled-cluster singles and doubles |
| CCSD(T) | CCSD with perturbative triple correction |
| CI | Configuration interaction |
| CIS | Configuration interaction singles |
| CIS(D) | CIS with perturbative double corrections |
| CT | Charge-transfer |
| CV | Constricted variational |
| DMABN | 4-(dimethylamino)benzonitrile |
| DMC | Diffusion Monte-Carlo |
| DNA | Deoxyribonucleic acid |
| DSSC | Dye-sensitized solar cell |
| DFT | Density functional theory |
| DFT-TB | Density functional theory – tight binding |
| ECD | Electronic circular dichroism |
| EFP | Effective fragment potential |
| EOM-CC | Equation of motion – coupled cluster |
| ES | Excited state |
| EXX | Exact exchange |
| f | Oscillator strength |
| HF | Hartree-Fock |
| GFP | Green fluorescent protein |
| GGA | Generalized gradient approximation |
| GH | Global hybrid |
| GS | Ground state |
| IEPA | Independent electron pair approximation |
| IR | Infrared |
| λ_{max} | Longest wavelength of maximal absorption |
| LDA | Local density approximation |
| LR | Linear-response |
| MAE | Mean absolute error |
| MP2 | second-order Moller-Plesset |
| MR-CI | Multireference CI |
| MR-MP2 | Multireference MP2 |
| MSE | Mean signed error |
| NLO | Nonlinear optics |
| PCM | Polarizable continuum model |
| PM3 | Parameterized model 3 |
| PM5 | Parameterized model 5 |
| OR | Optical rotation |
| OT | Optimally tuned |
| PYP | Photoactive yellow protein |
| QMC | Quantum Monte-Carlo |
| RSH | Range-separated hybrid (XCF) |
| SAC-CI | Symmetry adapted cluster – configuration interaction |
| SCF | Self-consistent field |
| SCS-CC2 | Spin-component scaling CC2 |
| SF | Spin-flip |
| SOS-CC2 | Spin-opposite scaling CC2 |
| SS | State-specific |
| TBE | Theoretical best estimate(s) |
| TCE | Tetracyanoethylene |
| TDA | Tamm-Dancoff approximation |
| TD-DFT | Time-dependent density functional theory |
| TICT | Twisted intramolecular charge-transfer |
| TNCQ | Tetracyanoquinodimethane |
| TPA | Two-photon absorption |
| TTF | Tetrathiafulvalene |
| VEM | Vertical excitation model |
| VK | Vignale-Kohn |
| XCF | Exchange correlation functional |
| ZPVE | Zero-point vibrational energy |

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