

Cross-Comparisons between Experiment, TD-DFT, CC, and ADC for Transition Energies

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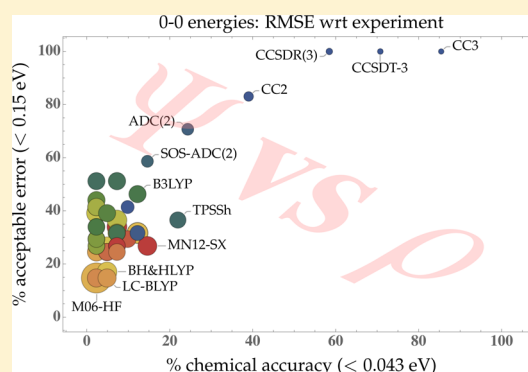
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Supporting Information

ABSTRACT: Considering 41 electronic transitions in small- and medium-sized organic molecules, we benchmark the performances of 36 hybrid functionals within time-dependent density-functional theory (TD-DFT) and nine wave function theory (WFT) methods [CCSDT, CC3, CCSDT-3, CCSDR(3), CCSD, CC2, ADC(3), ADC(2), and SOS-ADC(2)]. Compared to highly accurate experimental 0–0 energies, it turns out that all coupled cluster (CC) approaches that include contributions from the triples [i.e., CCSDT, CC3, CCSDT-3 and CCSDR(3)] deliver a root-mean-square error (RMSE) smaller than or equal to 0.05 eV. The remaining WFT methods [i.e., CCSD, CC2, ADC(3), ADC(2), and SOS-ADC(2)] yield larger deviations with RMSE lying between 0.11 and 0.27 eV. Irrespective of the exchange–correlation functional, TD-DFT yields larger deviations (RMSE \geq 0.30 eV). For vertical transitions without clear experimental equivalents (such as vertical absorption and fluorescence), a comparison between TD-DFT and CC3 provides a globally unchanged ranking of the various functionals. However, the errors on emission energies tend to be larger than on absorption energies, hinting that studying the latter property is not sufficient to gain a complete view of TD-DFT's performances. Finally, by cross-comparisons between TD-DFT and WFT, we observe that the WFT method selected as reference significantly impacts the conclusions regarding the overall accuracy of a given exchange–correlation functional. For example, for vertical absorption energies, the “best” functional is TPSSh (RMSE = 0.29 eV) based on CC3 reference energies, while LC- ω PBE (RMSE = 0.12 eV) is superior to the other functionals when one considers ADC(3) as the reference method.



1. INTRODUCTION

Because excited-state (ES) properties are of prime importance in many fields, intense theoretical efforts have been made during the past decades to develop density-based and wave-function-based methods able to deliver accurate descriptions of these properties.^{1–5} While we now have an extensive panel of methods to compute vertical transition energies between the ground state (GS) and a given ES, predicting their accuracy remains challenging. This is certainly why benchmarks of ES methods have been very popular in the community;^{6–24} see, e.g., a 2013 review related to time-dependent density-functional theory (TD-DFT),²⁵ or a recent overview on the calculations of 0–0 energies.²⁶ However, performing benchmarks requires a suitable and reliable reference, which is challenging for ES properties. Two strategies are commonly employed to select this reference: using either (i) state-of-the-art wave function theory (WFT) methods or (ii) highly accurate experimental data. Obviously, both strategies have their pros and cons.

While the first choice suffers from the limited availability of high-level theoretical values, it allows one to make comparisons on a perfectly equal footing (same basis set, same geometry, and so on). More importantly, one has access to properties that have no experimental counterparts, such as vertical absorption and fluorescence transition energies (see Figure 1). The most famous set of ES based on high-level WFT methods is undoubtedly the valence ES database designed by Thiel and co-workers that encompasses a large number of vertical absorption energies determined at the third-order coupled cluster (CC3) level.^{6,27,28} Recently, some of us have also contributed to the field by providing full configuration interaction (FCI) estimates for 110 low-lying ES in compact molecules,²⁹ therefore giving access to some “ultimate theoretical references” for further benchmarks. Clearly, this strategy suffers from limitations when one considers larger compounds which are more representative of the structures of

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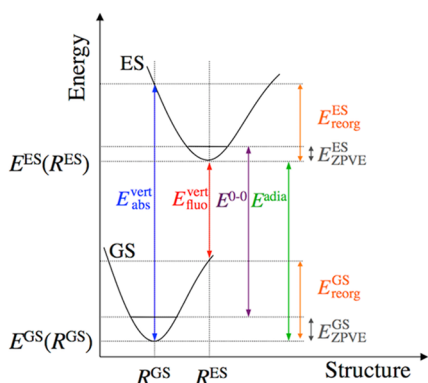


Figure 1. Transition energies benchmarked here. $E_{\text{abs}}^{\text{vert}}$ (blue) and $E_{\text{fluo}}^{\text{vert}}$ (red) are the (vertical) absorption and fluorescence energies, $E_{\text{reorg}}^{\text{GS}}$ and $E_{\text{reorg}}^{\text{ES}}$ (orange) are the (geometrical) reorganization energies, and E^{adia} and E^{0-0} are the adiabatic (green) and 0–0 (purple) energies, respectively. Only E^{0-0} can be “straightforwardly” measured experimentally.

experimental interest, as CC3 and FCI become prohibitively expensive for systems containing more than (roughly) 20 and 10 atoms, respectively. In such a case, it is common practice to consider computationally cheaper WFT methods, such as second-order coupled cluster (CC2),^{21,30–35} coupled cluster singles and doubles (CCSD),^{36,37} or symmetry-adapted-cluster configuration interaction (SAC-CI),^{38–40} to wisely select a suitable exchange–correlation functional (XCF) for subsequent TD-DFT calculations. However, it remains often unclear how the choice of a more questionable reference influences the conclusions regarding the relative and overall accuracies of a given XCF. Here, we propose to provide a response to this question. It should also be pointed out that most theory-vs-theory benchmarks have focused on vertical absorption energies and that much less is known about emission energies.^{38,40,41}

The second strategy, which consists of comparing to experimental data, is advantageous as one has access to a huge number of measurements for compounds of various natures and sizes. However, in sharp contrast to GS properties (thermochemistry, geometrical parameters, and so on) for which theory–experiment comparisons are often direct and straightforward, connections between theoretical and experimental data for ES are more challenging. Indeed, the “simplest” property that can be accurately measured experimentally and is theoretically well defined is the 0–0 energy (Figure 1). However, computing this quantity requires both the GS and ES zero-point vibrational energy (ZPVE) corrections which are generally very expensive from a computational point of view. Additionally, if large compounds are considered, one must take into account solvent effects,^{8,11} which inherently introduce an additional, hardly quantifiable bias. Many benchmarks comparing theoretical and experimental 0–0 energies are available,²⁶ and it has been shown that only CC approaches including contribution from the triples allow one to reach chemical accuracy (i.e., an error smaller than 1 kcal/mol or 0.043 eV),^{42–44} lower order methods delivering significantly larger deviations.^{8,10,13,45}

In the present work, we consider a set of 41 transitions for which both experimental E^{0-0} values and high-quality theoretical CC3 geometries are available.^{41,43,44,46} We perform cross-benchmarks using various levels of theory: TD-DFT with 36 hybrid XCF, several CC methods,⁴⁷ and algebraic

diagrammatic construction (ADC) variants.⁴⁸ We compare each method to experiment as well as between them. First, we clearly evidence that the CC approaches including iterative triples (CCSDT,⁴⁹ CC3,^{50,51} and CCSDT-3⁵²) provide very reliable estimates of the experimental 0–0 energies. Second, using CC3 absorption and emission energies ($E_{\text{abs}}^{\text{vert}}$ and $E_{\text{fluo}}^{\text{vert}}$ in Figure 1) as reference, we assess the accuracy of the XCF within TD-DFT. Third, we show how the reference choice may change the outcome regarding both the absolute and relative performances of the XCF.

2. COMPUTATIONAL DETAILS

Throughout this study, we rely on CC3/def2-TZVPP GS and ES geometries extracted from refs 41, 43, 44, and 46. This choice is justified by the facts that (i) these structures are the most accurate geometries available to date and (ii) CC3 bond distances and valence angles have been shown to be in excellent agreement with their CASPT2 counterparts.⁴⁶ These geometries are available in the Supporting Information (SI). The (vast majority of the) ZPVE required for the computation of the 0–0 energies were obtained at the B3LYP/6-31+G(d) level of theory. Considering a higher level of theory (as, for example, CCSD) to compute this costly quantity is unnecessary (at least for the present set).⁴⁴ This observation is consistent with many literature precedents showing the rather small impact of the level of theory on the magnitude of ΔE^{ZPVE} .^{13,53–55} The ΔE^{ZPVE} values are listed in the SI. To compute transition energies, we systematically select the aug-cc-pVTZ basis set, which is generally sufficiently complete to provide excitation energies close to basis-set convergence for low-lying transitions. We refer the interested reader to ref 44 for an exhaustive basis-set investigation at the CC3 level. For the TD-DFT, we have performed aug-cc-pVQZ calculations with two XCF as well (see Tables S-66 and S-67 of the SI). The variations in TD-DFT transition energies going from aug-cc-pVTZ to aug-cc-pVQZ are as small as 0.005 eV for $E_{\text{abs}}^{\text{vert}}$ and 0.003 eV for $E_{\text{fluo}}^{\text{vert}}$ (for both functionals).

Note that transition energies are identical in the equation-of-motion (EOM) and linear response (LR) CC formalisms. Consequently, for the sake of brevity, we do not specify the EOM and LR terms. The CC calculations have been performed with Dalton⁵⁶ [CC3,^{50,51} CCSDR(3),⁵⁷ CCSD,⁵⁸ and CC2^{59,60}] and Cfour [CCSDT-3⁵² and CCSDT,⁴⁹]⁶¹ whereas the ADC calculations [ADC(3),¹⁵ ADC(2),⁶² and SOS-ADC(2)⁶³] have been performed with Q-Chem.⁶⁴ We applied default convergence thresholds and algorithms. Throughout this study, all electrons are correlated; i.e., the frozen-core (FC) approximation was not applied. We note that while the FC approximation has a trifling impact on both $E_{\text{abs}}^{\text{vert}}$ and $E_{\text{fluo}}^{\text{vert}}$, it has a more substantial effect on E^{adia} and hence E^{0-0} .⁴⁴ We stress that the use of the “full” option with a basis set that do not include core polarization functions is unusual and should be avoided in general. However, as we show below, very similar results are obtained with aug-cc-pCVTZ for both CCSD and ADC(2) methods. All TD-DFT transition energies were computed with Gaussian09/16⁶⁵ using the *ultrafine* quadrature grid. The set of XCF considered in the present work can be found in the SI, and we use standard acronyms below. Total and transition energies are also provided in the SI. In the following, we only discuss statistical quantities.

Table 1. Statistical Analysis of the Errors (eV) with Respect to Experimental 0–0 Energies for 41 Transitions^a

E^{adia}	MSE	MAE	RMSE	STD	MaxA	%CA	%AE
CCSDT ^b	−0.002	0.033	0.044	0.044	0.108	72.4	100.0
CC3	−0.011	0.025	0.036	0.034	0.107	85.4	100.0
CCSDT-3	0.020	0.034	0.040	0.035	0.082	70.7	100.0
CCSDR(3)	0.029	0.042	0.052	0.043	0.109	58.5	100.0
CCSD	0.177	0.177	0.204	0.097	0.429	9.8	41.5
CC2	0.045	0.083	0.112	0.102	0.270	39.0	82.9
ADC(3)	−0.125	0.228	0.271	0.234	0.488	12.2	31.7
ADC(2)	−0.027	0.133	0.171	0.163	0.364	24.4	70.7
SOS-ADC(2)	−0.060	0.141	0.173	0.158	0.397	14.6	58.5
TPSSH	−0.119	0.237	0.318	0.290	0.774	22.0	36.6
B3LYP	−0.192	0.265	0.355	0.292	0.828	12.2	46.3
CAM-B3LYP	−0.100	0.274	0.338	0.317	0.709	9.8	29.3

^aThese results systematically use CC3 geometries and B3LYP ΔE^{ZPVE} so that they only differ by the method used to determine E^{adia} . MSE, MAE, RMSE, STD, and MaxA are the mean signed error, mean absolute error, root-mean-square error, standard deviation, and maximal absolute error, respectively. %CA and %AE are the percentages of cases reaching “chemical accuracy” (absolute error < 0.043 eV) and “acceptable error” (absolute error < 0.150 eV), respectively. ^bResults obtained for a subset of 29 compounds.

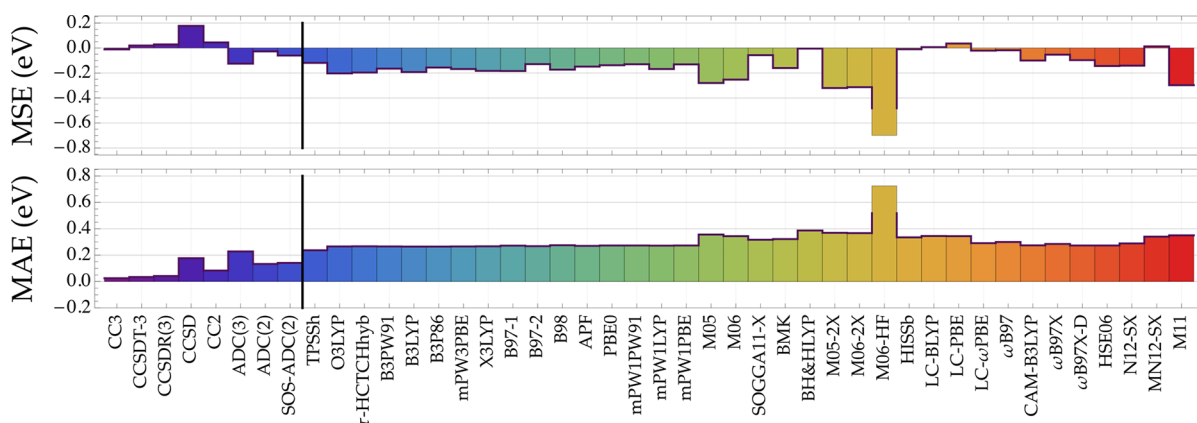


Figure 2. MSE and MAE (eV) with respect to experimental 0–0 energies for various methods.

3. RESULTS AND DISCUSSION

3.1. Comparisons with Experiment. As stated in the Introduction, experimental E^{0-0} values have the indisputable advantage of allowing physically well grounded comparisons. In such a case, the deviation is almost exclusively due to the theoretical approach, the experimental data being typically accurate to 1 cm^{-1} (0.0001 eV). Although the errors originating from the structure (CC3) and the ZPVE term (B3LYP) cannot be considered as negligible, it is reasonable to assume that the main error stems from the adiabatic energy. In Table 1, we provide a statistical analysis of all WFT methods considered here. Consistently with our previous work,⁴⁴ CC3 is very accurate with a MAE of 0.025 eV and an error smaller than 1 kcal/mol (%CA in Table 1) in 85% of the cases. Though CCSDT calculations were achievable for a subset of compounds only, the results clearly hint that CCSDT has no clear-cut advantage compared to CC3, a typical outcome for transitions presenting a dominant single excitation character.^{29,66} CCSDT-3 also yields very satisfying results with a slight drop in accuracy compared to CC3, a conclusion consistent with an analysis performed for small compounds.⁶⁷ Applying a perturbative correction for the triples slightly deteriorates the quality of the 0–0 energies, though 58% of the transition energies are still chemically accurate with CCSDR(3). Impressively, all of the CC approaches including contributions from the triples provide consistently, for each

transition, an error smaller than 0.15 eV (%AE in Table 1), a typical error bar considered as “acceptable” in most ES calculations. It is reassuring to note that these conclusions are perfectly consistent with the ones drawn while comparing $E_{\text{abs}}^{\text{vert}}$ obtained with the same set of WFT methods to FCI estimates.²⁹ Indeed, the previously reported RMSE are 0.05, 0.05, 0.04, and 0.03 eV for CCSDR(3), CCSDT-3, CC3, and CCSDT, respectively, all values being similar to the ones listed in Table 1. None of the WFT methods lacking contributions from the triples is able to deliver chemical accuracy in the majority of the cases. As expected,^{6,16,29,41,67–70} CCSD significantly overshoots experiment, while CC2 is closer, on average, to the reference values but with a RMSE still larger than 0.1 eV. Both approaches have relatively similar reliabilities, as evidenced by their similar STD values. The fact that CC2 delivers more accurate transition energies than CCSD is consistent with Thiel’s results,^{6,27} though it should be noted that the reverse conclusion can be obtained when one considers different sets of molecules or states: for tiny molecules CCSD is more accurate,²⁹ whereas CC2 provides larger deviations for Rydberg states.⁶⁷ For the ADC approaches, the errors tend to be larger, with a rate of chemical accuracy attaining 12%, 24%, and 15% for ADC(3), ADC(2), and SOS-ADC(2), respectively. We note that ADC(3) provides, on average, E^{0-0} significantly smaller than the experimental values (MSE of −0.13 eV). This observation

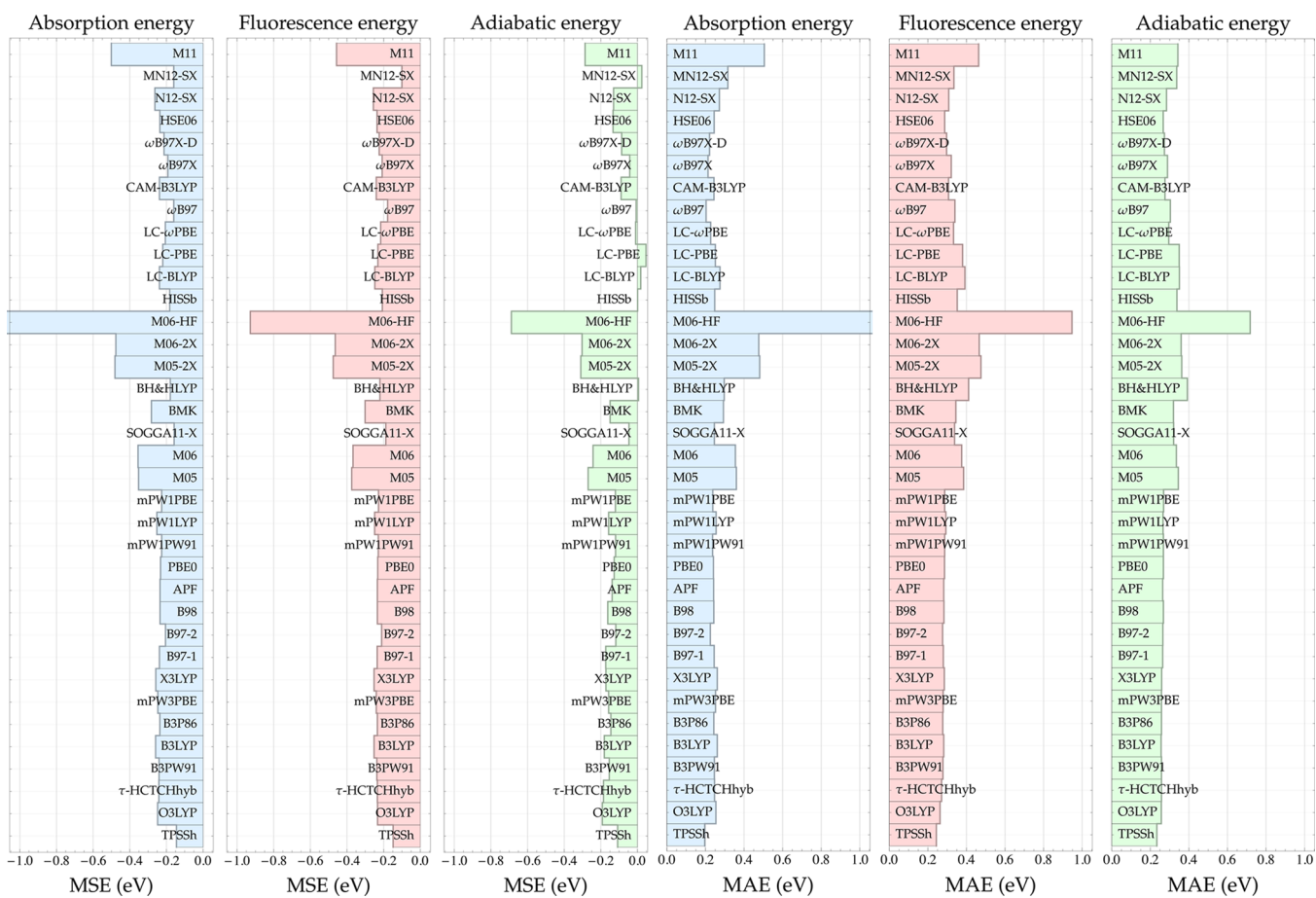


Figure 3. MSE and MAE (eV) with respect to CC3 for TD-DFT transition energies obtained with various XCF: $E_{\text{abs}}^{\text{vert}}$ (blue), $E_{\text{fluo}}^{\text{vert}}$ (red), and $E_{\text{adia}}^{\text{dia}}$ (green).

is, again, consistent with two earlier investigations focusing on absorption energies that respectively returned MSE of -0.15 eV (as compared to FCI)²⁹ and -0.20 eV (as compared to CC3).¹⁵ Finally, given the data of Table 1, one could think that CC3 has a home-field advantage as CC3 geometries are employed in all calculations. However, CCSD//CCSD and CC2//CC2 yield MAE of 0.164 and 0.084 eV, and RMSE of 0.187 and 0.111 eV (respectively), deviations that are on par with the ones determined on the CC3 structures.

In Table S-63 of the SI, we present the statistical results obtained with CCSD and ADC(2) using the aug-cc-pCVTZ basis set. As can be seen, the changes are overall rather small, e.g., the MAE of CCSD is 0.177/0.164 eV without/with core polarization, whereas the STD of ADC(2) are 0.163/0.159 eV. The most significant change is the decrease of the MaxA of CCSD to 0.295 eV, as the description of the exotic isocyanogen is improved significantly with core polarization functions.

We now turn toward TD-DFT. The results obtained with three selected XCF (TPSSh,⁷¹ B3LYP,^{72–75} and CAM-B3LYP⁷⁶) are given in Table 1, whereas the MSE and MAE associated with the entire set of XCF are depicted in Figure 2. (The complete numerical data are available in Table S-4 of the SI.) For the present set of molecules, the general trend of TD-DFT is to underestimate the 0–0 energies with negative MSE for most functionals (except for a few range-separated hybrids). This trend is particularly pronounced for M06-HF,⁷⁷ an expected behavior for an XCF containing 100% of

exact exchange that would generally not be considered to compute transition energies in small organic molecules. The MAE varies from 0.24 eV (TPSSh) to 0.73 eV (M06-HF), most XCF providing a MAE of ca. 0.25–0.35 eV, a typical error for TD-DFT calculations relying on hybrid XCF.²⁵ Acceptable errors (<0.15 eV) are attained for 51% of the transitions with O3LYP⁷⁸ and τ -HCTChyb⁷⁹ but only for 15% of the transitions with M06-HF, LC-BLYP,^{80–84} and LC-PBE.^{83–85} As one can see in Figure 2, in terms of MAE, none of the XCF considered here outperforms WFT methods. In terms of STD, the values are in the 0.28–0.81 eV range, mPW3PBE being the most “reliable” XCF. It is noteworthy that the XCF ranking might change significantly for larger compounds,^{8,25} but it is outside the scope of the present study.

3.2. Comparisons with CC3. As evidenced in the previous section, the overall accuracy of CC3 is excellent, with a MAE (with respect to experiment) smaller by 1 order of magnitude compared to TD-DFT. Therefore, it is reasonable to benchmark TD-DFT against CC3 for three key properties that cannot be obtained experimentally (except for diatomics), namely, $E_{\text{abs}}^{\text{vert}}$, $E_{\text{fluo}}^{\text{vert}}$, and $E_{\text{adia}}^{\text{dia}}$. Note that, in the following, we do compare adiabatic energies rather than 0–0 energies as the latter have the unpleasing feature of being ZPVE-dependent. The respective statistical data are available in Tables S-5, S-6, and S-7 of the SI. A graphical representation of MSE and MAE is provided in Figure 3, whereas the corresponding graphs associated with STD can be found in Figure S-1 of the SI.

Looking at Figure 3, one notices clear similarities between the error patterns associated with each property (see also Figure 2). Indeed, TPSSh remains the most accurate XCF with the smallest MAE (and RMSE) for all properties. For a given XCF, the MAEs are usually comparable for the three sets of transition energies. Nevertheless, for most XCFs, the errors tend to be slightly larger for emission than for absorption. For instance, B3LYP (BH&HLYP⁸⁶) RMSE is 0.37 (0.43) eV for $E_{\text{abs}}^{\text{vert}}$, but 0.42 (0.59) eV for $E_{\text{fluo}}^{\text{vert}}$. These values can be compared to the ones obtained for Thiel's set²⁷ using the so-called "TBE-2" reference: 0.33 and 0.60 eV for B3LYP and BH&HLYP, respectively. The statistical data reported in the SI show that the rate of acceptable errors is typically 40–60% for $E_{\text{abs}}^{\text{vert}}$ but drops to 30–50% for E^{adia} . Likewise, the STD tend to be smaller for vertical absorption energies than for the two other properties (Figure S-1). More specifically, one can notice some contrasted behaviors for specific XCF. For example, HISSb⁸⁷ provides a significant underestimation of $E_{\text{abs}}^{\text{vert}}$ and $E_{\text{fluo}}^{\text{vert}}$ (respective MSE of -0.182 and -0.207 eV), but is right on the money for E^{adia} (MSE of 0.001 eV). Conversely, the MAE associated with M11⁸⁸ is significantly smaller for E^{adia} (0.343 eV) than for $E_{\text{abs}}^{\text{vert}}$ (0.505 eV).

In short, the XCF ranking in terms of MAE (or RMSE) is globally preserved when comparing to experimental E^{0-0} or to CC3 $E_{\text{abs}}^{\text{vert}}$, $E_{\text{fluo}}^{\text{vert}}$, and E^{adia} values, although the absolute error magnitude is generally smaller for $E_{\text{abs}}^{\text{vert}}$ than for $E_{\text{fluo}}^{\text{vert}}$.

3.3. Influence of the Reference. What happens if one cannot afford CC3 calculations and when only "cheaper" references are available? Because the absolute errors with respect to experimental 0–0 energies are larger with TD-DFT than with WFT approaches (vide supra), choosing a cheaper WFT method as reference to benchmark TD-DFT seems like a reasonable idea. To assess this alternative strategy, we have computed the MSE, MAE, STD, and MaxA associated with the same set of XCF as in the previous section using various WFT methods as reference. For the sake of brevity, a list of MAE associated with $E_{\text{abs}}^{\text{vert}}$ is gathered in Table 2, whereas Figures 4, 5, and 6 report temperature maps associated with respectively the MSE, MAE, and STD, of $E_{\text{abs}}^{\text{vert}}$, $E_{\text{fluo}}^{\text{vert}}$, and E^{adia} . The complete set of numerical data can be found in Tables S-8–S-15 of the SI.

As expected from the observations made in section 3.1, the MSE, MAE, and STD patterns obtained with CC3, CCSDT-3, or CCSDR(3) reference values are extremely similar. Hence, one can safely use these methods to provide reference energies for TD-DFT benchmarks. Going to lighter WFT models, the conclusions regarding the most adequate XCF and their statistical performances can vary substantially. Due to its negative MSE with respect to experiment (see Figure 2), this effect is particularly noticeable for ADC(3), as illustrated by the temperature maps reported in Figures 4–6 (which we recall are based on the statistics of 40 transitions). Significant variations of MSE and STD are also observed with both ADC(2) and CC2.

We consider three examples: the first one illustrating the change in quantitative error estimates for a given XCF, and the two latter showing how the choice of a suitable XCF can be affected by the reference. The MAE obtained with B3LYP for $E_{\text{fluo}}^{\text{vert}}$ is 0.28 eV using CC3 as reference but 0.12 and 0.39 eV using ADC(3) and CC2 reference, respectively. Given that the error of TD-DFT is typically below half an electronvolt, these are rather large variations. Besides, if one is looking for the XCF providing the largest percentage of acceptable errors for

Table 2. MAE with Respect to Various Reference WFT Methods for TD-DFT Vertical Absorption Energies Obtained with Various XCF

	CC3	CCSD	CC2	ADC(3)	ADC(2)
TPSSh	0.196	0.233	0.268	0.177	0.268
O3LYP	0.254	0.317	0.371	0.151	0.302
τ -HCTCHhyb	0.247	0.310	0.364	0.146	0.297
B3PW91	0.246	0.308	0.362	0.129	0.292
B3LYP	0.261	0.328	0.382	0.140	0.303
B3P86	0.243	0.305	0.359	0.129	0.291
mPW3PBE	0.252	0.316	0.370	0.129	0.296
X3LYP	0.261	0.327	0.381	0.138	0.304
B97-1	0.245	0.307	0.361	0.135	0.295
B97-2	0.225	0.277	0.327	0.136	0.287
B98	0.243	0.304	0.358	0.135	0.296
APF	0.242	0.304	0.358	0.123	0.291
PBE0	0.241	0.301	0.355	0.120	0.292
mPW1PW91	0.237	0.295	0.349	0.124	0.290
mPW1LYP	0.255	0.321	0.375	0.140	0.304
mPW1PBE	0.238	0.295	0.349	0.123	0.290
M05	0.360	0.421	0.475	0.205	0.405
M06	0.355	0.424	0.478	0.193	0.394
SOGGA11-X	0.246	0.263	0.300	0.160	0.307
BMK	0.293	0.352	0.405	0.148	0.326
BH&HLYP	0.297	0.298	0.347	0.216	0.360
M05-2X	0.481	0.550	0.604	0.288	0.510
M06-2X	0.476	0.545	0.599	0.277	0.505
M06-HF	1.160	1.229	1.283	0.962	1.189
HISSb	0.248	0.273	0.315	0.147	0.309
LC-BLYP	0.275	0.311	0.385	0.128	0.317
LC-PBE	0.251	0.294	0.363	0.106	0.294
LC- ω PBE	0.227	0.277	0.342	0.089	0.266
ω B97	0.203	0.234	0.301	0.115	0.266
CAM-B3LYP	0.244	0.307	0.366	0.113	0.289
ω B97X	0.213	0.262	0.328	0.105	0.271
ω B97X-D	0.221	0.282	0.338	0.103	0.274
HSE06	0.245	0.305	0.359	0.124	0.294
N12-SX	0.272	0.332	0.386	0.145	0.313
MN12-SX	0.316	0.331	0.368	0.271	0.413
M11	0.505	0.570	0.624	0.315	0.530

E^{adia} , one would go for τ -HCTCHhyb (49%), ω B97X (55%),⁸⁹ O3LYP (46%), ω B97X-D (71%),⁹⁰ and ω B97X-D (37%) using CC3, CCSD, CC2, ADC(3), and ADC(2) reference values, respectively. There is obviously a quite large theoretical contrast between O3LYP, a global hybrid containing only a small amount of exact exchange, and ω B97X, a range-separated hybrid with a quite large attenuation parameter. Finally, if one is interested in the reliability of CAM-B3LYP for $E_{\text{fluo}}^{\text{vert}}$, one would get a STD of 0.16 eV as compared to ADC(3) but a much larger deviation, 0.38 eV, when using CCSDT-3 references.

Finally, to determine which computationally efficient WFT method is able to better reproduce the CC3 trends, we have calculated the linear determination coefficient (R^2) between the MAE obtained for 35 XCFs (M06-HF excluded) with CC3 and other WFT approaches (see Figure S-2 of the SI). In the case of $E_{\text{abs}}^{\text{vert}}$, we get R^2 values of 0.96, 0.93, 0.79, and 0.97 for CCSD, CC2, ADC(3), and ADC(2), respectively. For $E_{\text{fluo}}^{\text{vert}}$, the corresponding R^2 are 0.81, 0.89, 0.71, and 0.90, respectively. This means that the correct XCF ranking is globally restored by ADC(2) for both properties. However, ADC(2) over-

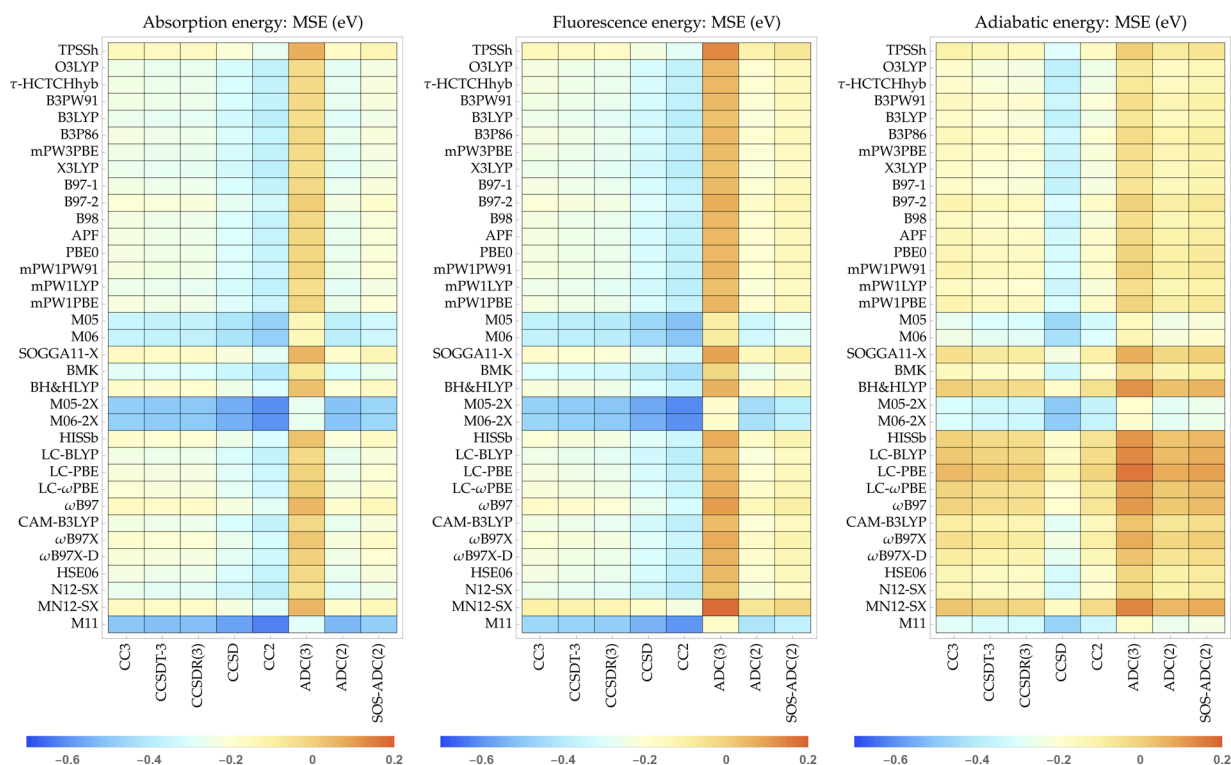


Figure 4. Temperature maps of the MSE with respect to various reference WFT methods for TD-DFT transition energies obtained with various XCF: $E_{\text{abs}}^{\text{vert}}$ (left), $E_{\text{fluo}}^{\text{vert}}$ (center), and E^{adia} (right). All values are in electronvolts. M06-HF, a clear outlier, was excluded from the set.

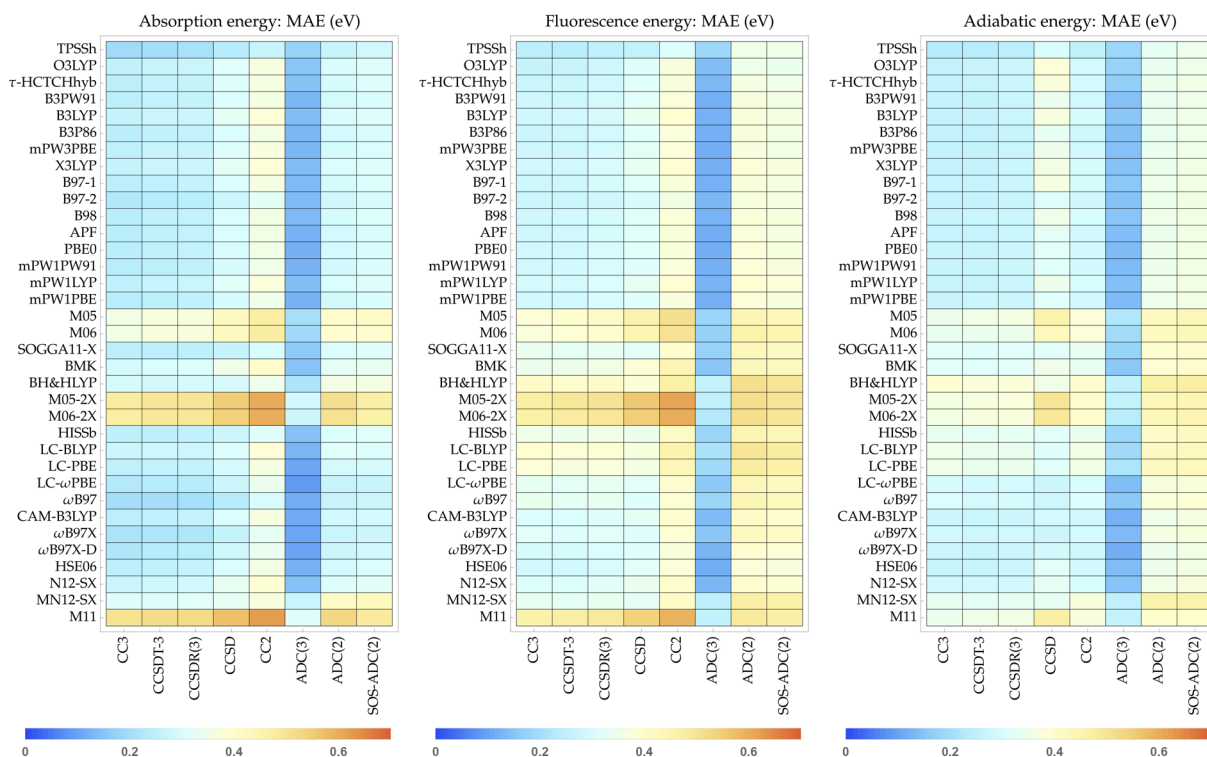


Figure 5. Temperature maps of the MAE with respect to various reference WFT methods for TD-DFT transition energies. See caption of Figure 4 for more details.

estimates the average (over the 35 XCFs) MAE by 0.05 eV ($E_{\text{abs}}^{\text{vert}}$) and 0.09 eV ($E_{\text{fluo}}^{\text{vert}}$) as compared to CC3. As an alternative strategy to select a computationally efficient approach, we show, in Figure S-4 of the SI, MAE temperature plots considering as references CCSD, CC2, and ADC(2)

values shifted by their MSE with respect to the CC3 reference. As one can show, the improvement is large for CCSD, significant for CC2, and smaller for ADC(2), which logically follows their STD listed in Table 1. Therefore, if the systematic error of CCSD for a specific property can be estimated in some

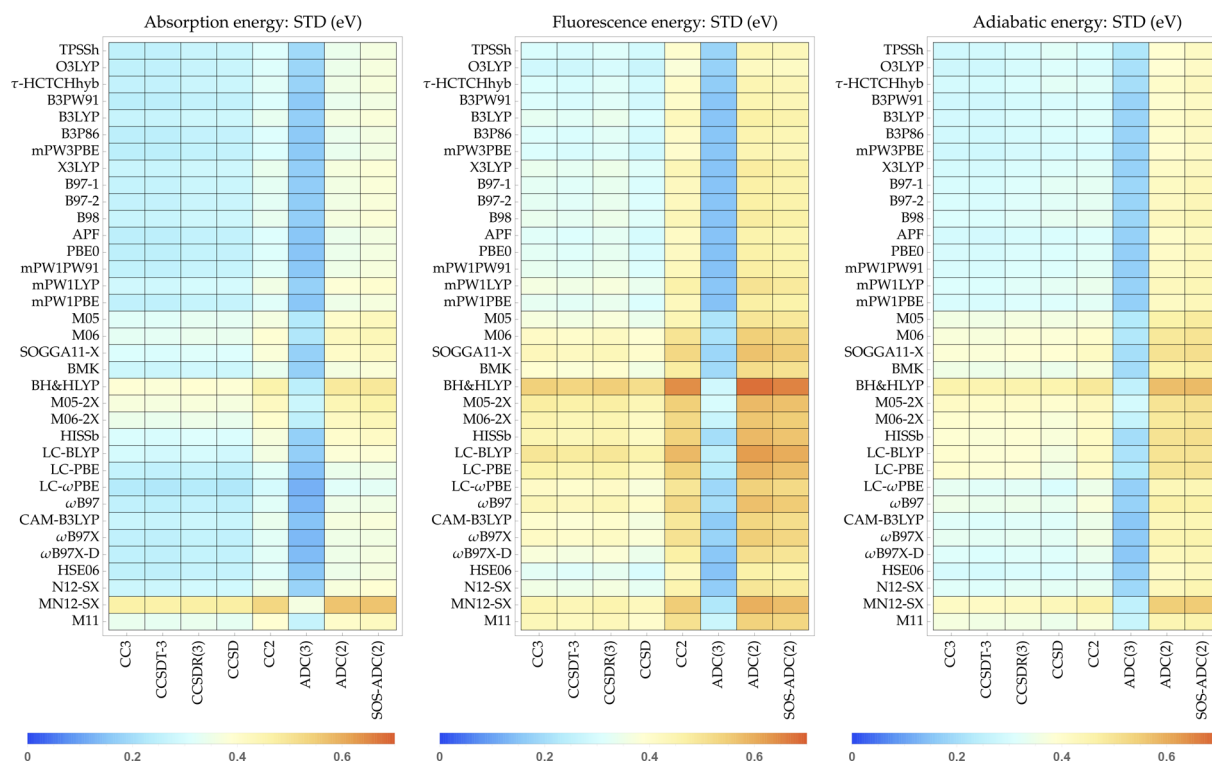


Figure 6. Temperature maps of the STD with respect to various reference WFT methods for TD-DFT transition energies. See caption of Figure 4 for more details.

ways, rigidly shifting the reference values can potentially be a valuable approach.

4. CONCLUSIONS AND OUTLOOK

We have performed cross-comparisons between experiment, TD-DFT, and WFT methods for a set of 41 electronic transitions in organic molecules for which both experimental 0–0 energies and high-level theoretical CC3 geometries are available in the literature. Given that we have considered only relatively compact compounds and low-lying excited states, our goal was not to determine the most accurate XCF—a task tackled many times before—but rather to check the consistency between conclusions drawn with different benchmark strategies.

First, we have performed comparisons with experimental 0–0 energies. In this case, the main source of errors stems from the approximated nature of the theoretical method. All four CC approaches tested in the present study and including iterative or perturbative triples [CCSDT, CC3, CCSDT-3, and CCSDR(3)] deliver accurate results, reaching chemical accuracy in the majority of the cases with, for example, 85% success rate for CC3. In contrast, CCSD overestimates the transition energies (MSE of 0.18 eV), whereas ADC(3) suffers from the opposite problem (MSE of -0.13 eV). The lighter (second-order) variants [CC2, ADC(2), and SOS-ADC(2)] are, on average, more accurate than these two approaches, but still deliver absolute 0–0 energies with errors of ca. 0.1–0.2 eV. Irrespective of the XCF, the MAE associated with TD-DFT exceed their wave function counterparts. For the present set of 0–0 energies, the most accurate XCF turns out to be TPSSh, with a MAE of 0.24 eV and a rate of chemical accuracy of 22%.

Second, we have compared TD-DFT and CC3 results for properties that have no direct experimental equivalents,

namely, $E_{\text{abs}}^{\text{vert}}$, $E_{\text{fluor}}^{\text{vert}}$ and E^{adia} . The error patterns obtained for these three properties are globally similar to the ones obtained for the 0–0 energies. Moreover, the most accurate XCF remains TPSSh, although it should be noted that the absolute errors (MAE and RMSE) obtained for fluorescence and adiabatic energies are generally larger than for absorption energies. Clearly, emission properties are more difficult to describe with TD-DFT than their absorption counterparts.

Third, we have evaluated the impact of choosing a computationally lighter reference method than CC3 to benchmark TD-DFT. We have shown that picking as reference a method such as ADC(3) or CC2—choices that can certainly be viewed as reasonable—can significantly impact (i) the quantitative conclusion (the MAE obtained for a specific XCF can vary by ca. 0.1–0.3 eV, the typical error range of TD-DFT) and (ii) the qualitative ranking (i.e., the designation of the “most accurate” XCF for a specific property).

In short, this contribution comes as a warning: it can be quite dangerous to benchmark TD-DFT using computationally lighter wave function approaches. At this stage of our investigations, we claim that only CC methods including contributions for the triples are accurate enough to offer a safe reference to benchmark TD-DFT. When unavailable, two procedures can be envisaged. First, if the systematic error of CCSD can be estimated, one can correct CCSD transition energies by this error to select a suitable XCF. Second, if the first option is not manageable, ADC(2) seems to offer a reasonable compromise in terms of performance ranking, though the MAE may significantly differ from the one obtained with respect to a state-of-the-art reference such as CC3.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.9b00446.

Experimental references; geometries; ZPVE corrections; additional statistical analyses; total and transition energies (PDF)

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Notes

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