TD-DFT Performance for the Visible Absorption Spectra of Organic Dyes: Conventional versus Long-Range Hybrids

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Abstract: The $\pi \rightarrow \pi^*$ transitions of more than 100 organic dyes from the major classes of chromophores (quinones, diazo, ...) have been investigated using a Time-Dependent Density Functional Theory (TD-DFT) procedure relying on large atomic basis sets and the systematic modeling of solvent effects. These calculations have been performed with pure (PBE) as well as conventional (PBE0) and long-range (LR) corrected hybrid functionals (LC-PBE, LC-ωPBE, and CAM-B3LYP). The computed wavelengths are systematically guided by the percentage of exact exchange included at intermediate interelectronic distance, i.e., the $\lambda_{\text{max}}$ value always follows the PBE $>$ PBE0 $>$ CAM-B3LYP $>$ LC-PBE $>$ LC-ωPBE $>$ HF sequence. The functional giving the best estimates of the experimental transition energies may vary, but PBE0 and CAM-B3LYP tend to outperform all other approaches. The latter functional is shown to be especially adequate to treat molecules with delocalized excited states. The mean absolute error provided by PBE0 is 22 nm (0.14 eV) with no deviation exceeding 100 nm (0.50 eV): PBE0 is able to deliver reasonable estimates of the color of most organic dyes of practical or industrial interest. By using a calibration curve, we found that the LR functionals systematically allow an even more consistent description of the low-lying excited-state energies than the conventional hybrids. Indeed, linearly corrected LR approaches yield an average error of 10 nm for each dye family. Therefore, when such statistical treatments can be designed for given sets of dyes, a simple and rapid theoretical procedure allows both a chemically sound and a numerically accurate description of the absorption wavelengths.

I. Introduction

Though dyes could be classified with respect to the chemical process generating the color (absorption/fluorescence/phosphorescence) or to the nature of the implied excited states ($\pi \rightarrow \pi^*/\pi \rightarrow \pi^*$), one generally groups them according to the nature of their chromophoric unit (Figure 1). The two major families of organic dyes with industrial applications are 9,10-anthraquinones (AQ) and azobenzenes (AB), that represents about 30% and 60% of today’s world dye production, respectively. The longest wavelength of maximal absorption ($\lambda_{\text{max}}$) of AQ covers all the visible region of the electromagnetic spectrum, depending on the nature...
and position of the auxochromic group(s) substituting positions 1-to-8. AB are extremely versatile, with applications going from core of media storages to central building blocks in molecular motors. Of course, several other chromophores related to more specific applications can be pinpointed: (1) naphthoquinones (NQ), implied in several medicinal processes; (2) coumarins (CO), the most efficient fluorescent brighteners; (3) diphenylamine derivatives (DPA), the typical hair dyes with important biological properties; (4) diarylethenes (DA), the prototype molecular switch; and (5) indigoids derivatives (IG, Figure 2) which give loads of structures with several substitution patterns of the outer phenyl rings, of the heteroatoms, as well as different types of linkage between the two parts of the molecule. Developing molecular modelization approaches allowing an accurate prediction of the color of dyes is still a major challenge, because, on the one hand, the average human eye is able to tell apart shades differing by 1 nm only, and, on the other hand, actual stains are medium-sized molecules, possess a dozen π-electrons, and are very sensitive to the environments. Therefore, large-scale highly correlated ab initio approaches such as EOM-CC, MR-CI, or CAS-PT2 remain out of today’s computational reach. Consequently, one could be inclined to select customized semiempirical approaches such as ZINDO, but the consistency of such schemes is often disappointing. Currently, the most widely applied ab initio tool for modeling electronic spectra of structures is the time-dependent density functional theory (TD-DFT). TD-DFT calculations can incorporate environmental effects and quickly give UV/vis spectra for most organic and inorganic dyes. Still, meaningful results can only be attained with a selection of adequate exchange-correlation functionals. It is recognized that conclusions obtained with hybrid functionals tend to be in better agreement with experimental trends than the values computed with pure functionals. Hybrids, originally proposed in the 1990s, include a fraction (α) of exact exchange that is computed with the Hartree–Fock (HF) exchange formula. Despite their countless successes, hybrids also encounter problems that seem (mostly) independent of the functional selected. Typical troublesome properties include van der Waals forces, bond length alternation (BLA) in semiconducting polymers, nonlinear optics (NLO) properties of long π-conjugated chains, and charge-transfer electronic transitions. In these four cases, no single α value provides a small (or consistent) error for increasingly large/spaced compounds. In fact, these DFT limitations have a common origin: the so-called shortsightedness of DFT functionals. In other words, the density is not influenced by a change in the nearby electronic distribution. To circumvent these shortcomings, several strategies have been designed and applied to the problems listed above: the correction(s) of the self-interaction error, the inclusion of the current-density in the formalism, the addition of empirical dispersion terms, and the use of optimized effective potential for exact exchange as well as the explicit consideration of long-range effects (LR). This latter scheme leads to the range-separated hybrids that use a growing fraction of exact exchange when the interelectronic

Figure 1. Sketch of the chromophores investigated in this study.

Figure 2. Studied indigoids derivatives.
distance increases (see section II). In contrast, the hybrids in which the amount of HF exchange is constant all over the space will be referred to as global hybrids in the following (conventional or full-range exchange hybrids have also been used in the literature). It has been demonstrated that range-separated hybrids are very efficient for calculating BLA\cite {ab2} or NLC\cite {61,67,68,82,83,87} properties in conjugated polymers also been used in the literature). It has been demonstrated that range-separated hybrids are very efficient for calculating BLA\cite {ab2} or NLC\cite {61,67,68,82,83,87} properties in conjugated polymers as well as for determining properties of weakly bond complexes\cite {64,70,85} or charge-transfer states in large molecular systems.\cite {64,68,74,77,78,81} Nevertheless, there have been only a few works establishing the abilities of TD-LR-DFT to reproduce experimental UV/vis spectra for a statistically meaningful set of compounds: (1) comparisons of global and range-separated functional performances for the vertical transitions of C==O, N$_2$, C$_5$H$_5$N, H$_2$O, C$_6$H$_6$, and H$_2$C==O demonstrated that, while Rydberg’s states are much better described with the latter, differences remain small for valence excited states;\cite {64,73,85} (2) the emission properties of low-lying excited states of small molecules have also been investigated, and similar conclusions have been drawn;\cite {14} (3) we have studied the localized $n$ $\rightarrow$ $\pi^*$ transitions in nitroso and thiocarbonyl dyes, and it turned out that all hybrid functionals lead to a quite similar accuracy;\cite {88} (4) the $\lambda_{max}$ of four CO dyes are more accurate with global TD-DFT than with (unmodified) TD-LR-DFT;\cite {84} (5) for the $\pi$ $\rightarrow$ $\pi^*$ transitions of 15 AQ, it has been found that range-separated hybrids are further away from experimental values than their global counterparts but offer a much smaller statistical dispersion of the results, allowing more valid chemical insights;\cite {82} and (6) on the contrary, TD-LR-DFT brings no significant correction for cyanine derivatives, as these dyes present a strong multideterminantal nature.\cite {82}

In this paper, we perform a critical assessment of the efficiency and consistency of range-separated hybrids for computing the main $\pi$ $\rightarrow$ $\pi^*$ transition of industrial organic dyes. The generic chromophores we have considered are depicted in Figure 1. It is worth pointing out previous TD-DFT investigations for these compounds. For AQ, the performance of global hybrids has been assessed in refs 19, 22, 46, and 89–93, while our previous work used TD-LR-DFT.\cite {82} Numerous computations of the UV/Visible spectra of AB based on TD-DFT have been published,\cite {46,94–98} but to our best knowledge none used range-separated hybrids. NQ, DPA, and IG have recently been tackled by two of us in refs 99, 100, 101, and 102–105, respectively. For CO, one finds several investigations performed with global hybrids,\cite {106–113} but only one used range-separated functionals and was limited to four molecules.\cite {84} The transition spectra of the photocromic DA switches have also been thoroughly investigated, though only with global hybrids.\cite {15,18,114–123} In fact, the molecules in Figures 1 and 2 include most of the families selected by Guillaumont and Nakamura\cite {46} (we excluded cyanine-like dyes that present a multideterminantal nature) but with (much) more structures in each subset. This paper is organized as follows. In section II, we briefly summarize our computational approach. In section IIIA, the spectra of the various families computed with several pure, global, and range-separated hybrids are compared to experimental data. In section IIIB, we examine the possibilities of statistical treatment of the theoretical $\lambda_{max}$, before concluding in section IV.

II. Methodology

In range-separated functionals, the Coulomb operator is partitioned as\cite {59,60,63,65}

$$
1 = \frac{1 - \left[\alpha + \beta \text{erf}(\omega r_12)\right]}{r_12} + \frac{\alpha + \beta \text{erf}(\omega r_12)}{r_12}
$$

(1)

where $\omega$ is the range separation parameter, while $\alpha$ and $\alpha + \beta$ define the exact exchange percentage at $r_12 = 0$ and $r_12 = \infty$, respectively. In eq 1, $0 \leq \alpha + \beta \leq 1$, $0 \leq \alpha \leq 1$, and $0 \leq \beta \leq 1$, are three conditions to be satisfied. Equation 1 leads to the partitioning of the total exchange energy into short-range and long-range contributions:

$$
E_x = E_x^s + E_x^l
$$

(2)

In this paper, three range-separated functionals have been used: (1) the LC (LC: long-range correction) scheme of Hira\cite {61} applied to the PBE functional,\cite {124} (2) the LC-oPBE functional by Vydrov and Scuseria,\cite {77} and (3) Handy’s CAM-B3LYP (CAM-B3LYP: Coulomb-attenuating method applied to B3LYP).\cite {65} Both LC models use $\alpha = 0$ and $\beta = 1$ in eq 1, i.e. short-range semi-local DFT exchange is combined with long-range HF exchange integrals. Since $\alpha + \beta = 1$, the exchange potential in LC functionals has the exact asymptotic behavior. Note that in LC-oPBE, the short-range exchange functional can be rigorously derived\cite {62,125} by integration of the model exchange hole.\cite {77,78} In CAM-B3LYP, $\alpha = 0.19$ and $\beta = 0.46$ are plugged in, and the exact asymptote of the exchange potential is lost, while a larger percentage of HF exchange is included at short range. The range separation parameter, $\omega$ in LC-PBE and CAM-B3LYP, is set to the standard 0.33 bohr$^{-1}$ value, whereas for LC-oPBE, we use the optimized 0.40 bohr$^{-1}$ value from refs 77 and 78. Recently, such 0.40 bohr$^{-1}$ value has been advocated by Fromager and co-workers,\cite {86} whereas Hira et al. proposed a reoptimized value of 0.47 bohr$^{-1}$ for reaction barriers.\cite {126} As our goal is to assess the merits of range-separated and global hybrids for visible spectra simulations, we have also performed time-dependent calculations with a pure functional (PBE),\cite {124} a global hybrid (PBE0, that contains 25% of exact exchange),\cite {33,34} and the HF approach (in this paper HF results are obtained through the TD-HF approach). Readers interested in the results of other global hybrids, such as the archetype B3LYP, are referred to 89 for AQ, 109 for CO, and 105 for IG. The evolution with $r_12$ of the exact exchange percentage used in the six considered models is sketched in Figure 3. All calculations have been performed with the Gaussian03 suite of programs,\cite {127} except for the LR-DFT calculations that were carried out with a development version of Gaussian,\cite {128} using their standard TD-DFT procedure (ref 129). For each system, the ground-state structure has been determined by a standard force-minimization procedure (ref 129). For each system, the ground-state structure has been determined by a standard force-minimization procedure (ref 129).
Figure 3. Evolution of the percentage of exact exchange included as the function of the interelectronic distance for the six models considered.

is known for providing converged ground-state structural parameters for the largest majority of the compounds. In previous investigations, we have demonstrated that PBE0/6-311G(d,p) geometries are perfectly adequate for most classes of organic dyes investigated here, and we refer the interested readers to these publications for discussion of the basis set effects. TD-DFT is then used to compute the three-to-eight first low-lying excited states of each dye. The resulting electronic excitations have a strong $\pi \rightarrow \pi^*$ character associated with a large oscillator force. We have systematically selected the 6-311+G(2d,p) basis set for these TD-DFT calculations, as it yields perfectly converged $\lambda_{\text{max}}$ for IG, DPA, NQ, and DA dyes. For AQ, a smaller basis set would even be enough to attain the saturation of transition energies. Therefore, we refer the interested readers to these publications for a discussion of the basis set effects. TD-DFT is then used to compute the three-to-eight first low-lying excited states of each dye. The resulting electronic excitations have a strong $\pi \rightarrow \pi^*$ character associated with a large oscillator force.

In many cases, several experimental values are available, and the values reported in Tables 1–5 correspond to the average measure. The selection of the theoretical wavelength is often straightforward: it is the first transition with a significant oscillator force. In fact, to perfectly simulate experimental results, the main missing components are the vibronic couplings. Indeed, in some cases, the inclusion of Franck-Condon factors could be essential to get the best theory/experiment match. However, a systematic computation of such vibronic effects is not practically feasible for our very extended set.

III. Results

A. Comparisons with Experiments. The $\lambda_{\text{max}}$ computed for 24 typical AQ dyes are reported in Table 1. For all compounds, the absorption wavelengths systematically obey: PBE > PBE0 > CAM-B3LYP > LC-PBE > LC-\omega PBE > HF. This means that the larger the exact exchange ratio at intermediate $f_{12}$ (see Figure 3), the smaller the calculated $\lambda_{\text{max}}$. For nitroso and thiocarbonyl compounds, such a systematic relationship could not be unravelled, probably due to the more localized nature of the transition in these $n \rightarrow \pi^*$ chromophores: the mixing percentage at smaller distances had a larger influence. Consistently with our previous studies, PBE0 yields $\lambda_{\text{max}}$ in very good agreement with experimental trends for the short-wavelength dyes, but the discrepancies significantly increase for the compounds with the smallest transition energies. Indeed, in the lower part of Table 1, it is PBE that yields the best estimates. For the 24 AQ, we obtain mean signed errors (MSE, experiment-theory) of 127, 71, 12, 67, 85, and 53 nm for HF, PBE, PBE0, LC-PBE, LC-\omega PBE, and CAM-B3LYP, respectively. The corresponding mean absolute errors (MAE) amount to 127, 74, 19, 67, 85, and 53 nm, indicating that LR-DFT and HF systematically underestimate the $\lambda_{\text{max}}$. Consistently with the findings of ref 82, PBE0 is clearly closer to experiment, with a MAE less than half of the second competitor, namely CAM-B3LYP. However, the ordering of the compounds is also crucial for an efficient molecular design. Range-separated functionals provide the valid 1.4-OH > 1-NH$_2$ classification whereas PBE0 does not, but the reverse situation also appears (1,2-OH versus 1,8-OH), and cases can also be noted in Table 1 for which all approaches fail (2-OH versus 1,2-OH).

The situation differs in Table 2 where the spectra of AB derivatives are listed. Model and real-life AB have been considered, though we have not included OH substituents in the panel as such hydroxy-AB tend to undergo tautomerism that might impede straightforward theory/experiment comparisons. On the contrary, several push–pull molecules (4-NO$_2$, 4′-NH$_2$, and alike) having a strong charge-transfer character are tackled in Table 2. As for AQ, the methodological ordering of $\lambda_{\text{max}}$ follows the amount of exact exchange at medium interelectronic distance. Nevertheless, CAM-B3LYP has now a slight edge over PBE0, and the accuracy difference between the $\lambda_{\text{max}}$ obtained with global and range-separated approaches becomes less striking than for the AQ listed in Table 1. Indeed, we obtain MAE (MSE) of 64 (64) nm, 90 (90) nm, 25 (20) nm, 33 (33) nm, 46 (46) nm, and 20 (15) nm for HF, PBE, PBE0, LC-PBE, LC-\omega PBE, and CAM-B3LYP, respectively. In fact CAM-B3LYP is particularly efficient for structures presenting a small $\lambda_{\text{max}}$ and the theory/experiment discrepancy tends to increase when going down the column. Note that for both AB having a $\lambda_{\text{max}}$ > 500 nm, PBE0 is closer to the experimental reference than the three range-separated functionals: the description of charge-transfer dyes is not
systematically improved by inclusion of LR terms. Finally, the molecular ordering is generally correct although one noteworthy mismatch could be detected (6'-OBu,2,6-NH₂, 3,3'-azopdipyridine versus 4,4'-NH₂): all approaches, but LC-αPBE, disagree with experiments.

Table 3 summarizes our results for a 12 NQ set containing several 2,3-substituted structures that are known to be particularly problematic for global hybrids.¹⁰⁰ For these dyes, CAM-B3LYP outperforms PBE0, but the reverse is true for NQ with auxochroms at positions 5 and 8. One can also note
systematic inversions (2,3-Cl versus 2-OH), but none of the proposed approach allows a \( \lambda_{\text{max}} \) classification clearly more appealing. Indeed, depending on the compounds, smaller (2,6-OH versus 5-OMe) or larger (2-NHMe,3-Cl versus 2-OMe,5,8-OH) proportion of exact exchange might help.

Going from left to right in Table 3, we obtain MAE of 119, 99, 22, 42, 64, and 28 nm (the MSE are 119, −99, −11, 42, 64, and 26 nm). These values are in the line of the results obtained for AQ, although differences between PBE0 and CAM-B3LYP are strongly reduced for NQ.

The spectral data obtained for 10 neutral and charged CO are given in Table 3. The evaluation of the visible spectra
of amino-CO is very challenging as both state-specific solvation and vibronic coupling could play a significant role.\textsuperscript{122,113} Therefore, only hydroxy-CO are included in our set. As for the other dyes, HF (PBE) provides the smallest (largest) $\lambda_{\text{max}}$ and hybrids stand in between, with wavelengths almost proportional to the exact exchange percentage at intermediate $r_1$. For CO, PBE, and PBE0 yield about the same accuracy but with opposite signed errors. Indeed the $\lambda_{\text{max}}$ character, global hybrids like PBE0 provide very accurate estimates for 4-Me,7-OH CO, all hybrids reproduce quite accurately the effect of protonation with predicted bathochromic shifts of 25 nm for 2,4-$\text{NO}_2$-DPA but 50 nm instead of 71 nm for 2,4-$\text{NO}_2$-DPA. However, this problem cannot be corrected by LR-DFT nor PBE nor HF. For the DA of Table 4, that are characterized by a very delocalized first excited state,\textsuperscript{123} we have the reverse situation with a large error with PBE0 (MAE=64 nm), whereas LR-DFT are closer to the experimental data, especially CAM-B3LYP that provides a MAE of 8 nm and a maximal discrepancy limited to 20 nm.

Table 5 lists the results for more than 30 dyes of the IG family. For thioindigo (X=X$\equiv$S) derivatives, the PBE0 functional has been found astonishingly efficient\textsuperscript{104} but is less accurate for indigo (X=X$\equiv$NH) dyes for which B3LYP was more adequate.\textsuperscript{105} In the indirubin isoindigo series (IG-e-IG-i), no global hybrid functional gives the correct ordering of the compounds.\textsuperscript{105} In the IG-a series, modifying only the X and X’ atoms leads to the following $\lambda_{\text{max}}$ ordering (in the nonpolar aprotic solvents used here): NMe,NMe > NH,- NH > NH,S > Se,Se > S,S > O,O. This order is not reproduced by HF (that predicts no difference between thio and selenoindigo), nor PBE (that incorrectly foresees a bigger

<table>
<thead>
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<th>Table 5. Indigoids (IG) Main Visible Transition, Obtained with a IEF-PCM-TD-X/6-311+G(2d,p)//IEF-PCM-PBE0/6-311G(d,p) Scheme$^a$</th>
<th>structure</th>
<th>subst</th>
<th>solvent</th>
<th>HF</th>
<th>PBE</th>
<th>PBE0</th>
<th>LC-PBE</th>
<th>LC-$\beta$PBE</th>
<th>CAM-B3LYP</th>
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<td>574</td>
<td>528</td>
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<td>539</td>
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<td>494</td>
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<td>544</td>
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<td>458</td>
<td>185–187,198</td>
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<td>427</td>
<td>392</td>
<td>434</td>
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<tr>
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<tr>
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<td>536</td>
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<td>448</td>
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<td>IG-h, X'=S none</td>
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<tr>
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<td>391</td>
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<td>519</td>
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<td>258</td>
<td>271</td>
<td>317</td>
<td>199</td>
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$^a$ More details can be found in refs 102–105.
molecules, respectively. The increased performance here overestimates the experimental functional. It is clear that HF (PBE) considerably undershoots comparison is plotted in Figure 4 for the LC-oPBE, respectively. This confirms the superiority of PBE0 for absolute wavelength estimations although LR-DFT appears to be authorized to give more consistent of PBE0 for absolute wavelength estimations although LR-DFT. Overall, the MAE are 170, 96, 19, 23, 71, 78, 0.14 eV and the RMS is 0.17 eV. As we have considered a very extended and diverse set of dyes, this value can be regarded as a new ‘expected accuracy’ for organic dye design with TD-DFT. It is worth comparing this

\[ \lambda_{\text{max}} = \text{for sulfur than amine-based compounds} \] nor PBE0 (that reverses the order of X=Z=Se and X=NH, X=H), but is correctly predicted by the three range-separated functionals, a significant chemical success. Of course, for these six structures, the PBE0 wavelengths are always much closer to experiment than LR-DFT. However, relative changes are also better reproduced by LR-DFT. For instance, the wavelength difference between the selenoindigo and oxy-indigo is 3.0 times larger than the \( \Delta \lambda_{\text{max}} \) separating indigo and its N–Me form (149/50 nm). This ratio is exaggerated by PBE0 (4.6) but reasonably reproduced by LC-PBE (2.5), LC-oPBE (2.4), and CAM-B3LYP (2.8). Concerning the substitution of the outer-phenyl rings, all hybrid schemes provide the correct ordering for thioindigo and indigo but for some cases in which the experimental data are extremely close (within 1 or 2 nm). In the Wille and Lütcke “linkage” series, all IG-e - IG-i, HF, PBE, PBE0, and CAM-B3LYP invert IG-i and IG-f, whereas LC-PBE and LC-oPBE predict almost equal absorption wavelengths for these two dyes, that is certainly a major improvement. A couple of thioindigo structures for which PBE0 produces the largest errors (5-OEt,5′-NO2 and 5-OEt,6′-NO2) are overcorrected by LR-DFT, and even CAM-B3LYP undershoots their \( \lambda_{\text{max}} \) by about 50 nm, confirming that the description of charge-transfer excited states is not systematically improved by range-separated functionals. Overall, the MAE are 170, 96, 19, 70, 99, and 58 nm for HF, PBE, PBE0, LC-PBE, LC-oPBE, and CAM-B3LYP, respectively. This confirms the superiority of PBE0 for absolute wavelength estimations although LR-DFT appears to be authorized to give more consistent chemical conclusions.

**B. Statistical Treatment and Corrections.** Statistical analysis for the three main families (AQ, AB, and IG) and the complete set of dyes are given in Table 6. A graphical comparison is plotted in Figure 4 for the LC-oPBE functional. It is clear that HF (PBE) considerably undershoots (overestimates) the experimental \( \lambda_{\text{max}} \) by 116 and 87 nm on average. Hybrids perform significantly better for all dye subsets (but CO). While CAM-B3LYP yields the smallest MSE and MAE for AB and DA, PBE0 appears more efficient for the other five families. On average, for the full set (118 transitions), we obtain a MAE of 22 nm only with PBE0, whereas CAM-B3LYP produces almost twice this error. Nevertheless, the PBE0 maximal deviations remain unacceptably large: \(-74\) and \(+90\) nm. In the eV scale, the PBE0 MAE attains 0.14 eV and the RMS is 0.17 eV. As we have considered a very extended and diverse set of dyes, this value can be regarded as a new ‘expected accuracy’ for organic dye design with TD-DFT. It is worth comparing this performance with the 0.19 eV (37 nm) MAE obtained with B3LYP/6-31G by Guillaumont and Nakamura for a smaller set of dyes. The two other extended studies are due to Fabian who reported B3LYP/6-31+G(d) MAE of 0.29 and 0.24 eV for \( \pi \rightarrow \pi^* \) transitions in sulfur-free and sulfur-bearing molecules, respectively.\textsuperscript{17,135} The increased performance here reported mainly originates in the use of (much) more extended basis sets and the explicit consideration of solvent effects, that are essential for a realistic simulation of the experimental setups.

**Table 6. Statistical Analysis for the AQ, AB, and IG Series***

<table>
<thead>
<tr>
<th>family</th>
<th>method</th>
<th>MSE</th>
<th>MAE</th>
<th>RMS</th>
<th>( R^2 )</th>
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<tr>
<td>AQ</td>
<td>HF</td>
<td>127</td>
<td>127</td>
<td>132</td>
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<td>PBE</td>
<td>-71</td>
<td>74</td>
<td>80</td>
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<td>19</td>
<td>27</td>
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<td>LC-PBE</td>
<td>67</td>
<td>67</td>
<td>71</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>LC-oPBE</td>
<td>85</td>
<td>85</td>
<td>89</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>CAM-B3LYP</td>
<td>53</td>
<td>33</td>
<td>58</td>
<td>0.98</td>
</tr>
<tr>
<td>AB</td>
<td>HF</td>
<td>64</td>
<td>64</td>
<td>75</td>
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<td>103</td>
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<td>27</td>
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<td>LC-PBE</td>
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<td>LC-oPBE</td>
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<td>46</td>
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<td>CAM-B3LYP</td>
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<tr>
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<td>HF</td>
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<td>170</td>
<td>174</td>
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<tr>
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<td>PBE</td>
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<td>96</td>
<td>116</td>
<td>0.71</td>
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<tr>
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<td>6</td>
<td>19</td>
<td>23</td>
<td>0.93</td>
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<tr>
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<td>LC-PBE</td>
<td>70</td>
<td>70</td>
<td>72</td>
<td>0.97</td>
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<td>LC-oPBE</td>
<td>99</td>
<td>99</td>
<td>101</td>
<td>0.97</td>
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<td></td>
<td>CAM-B3LYP</td>
<td>58</td>
<td>58</td>
<td>60</td>
<td>0.98</td>
</tr>
<tr>
<td>All</td>
<td>HF</td>
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<td>116</td>
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<tr>
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<td>58</td>
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<td>71</td>
<td>71</td>
<td>78</td>
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<tr>
<td></td>
<td>CAM-B3LYP</td>
<td>37</td>
<td>38</td>
<td>46</td>
<td>0.93</td>
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</table>

* All include the complete data from Tables 1–5. All values (but \( R^2 \)) are given in nm.

**Figure 4.** Comparison between the LC-oPBE and measured \( \lambda_{\text{max}} \) (nm) for the full set of transitions. The central line indicates a perfect theory/experiment match.

To check the consistency between experimental and theoretical data, we have performed simple linear regressions on the different dye sets. Results are summarized in Table 6. HF and PBE obviously provide much smaller correlation coefficients than the hybrid approaches. Therefore, one can definitely discard HF and PBE for dye design: they provide not only the poorest absorption wavelength estimates but also the less consistent auxochromatic displacements. Applying a linear correction to the PBE0 data is just useless, as the MAE
and RMS are almost unmodified. On the contrary, the \( R^2 \) obtained with the range-separated functionals is at least 0.93, confirming the interest of such approaches for classifying molecules according to their transition energies. Therefore, a linear correction improves the results of the three TD-LR-DFT schemes, especially for the two LC functionals. For instance, using

\[
\lambda_{\text{best}} = -38.63 + 1.295 \times \lambda^{\text{LC-\ensuremath{o}}\text{PBE}} \tag{3}
\]

provides a MAE limited to 18 nm and a rms of 23 nm, that are at least three times smaller than the uncorrected LC-\( \text{o} \)PBE data. Additionally, this MAE represents a 20% improvement over the (raw or fitted) PBE0 error. The impact of eq 3 is illustrated in Figure 5, and it is striking that the maximal deviations are now limited to +57 and −41 nm, both being smaller than the prior-to-fitting MAE. From Table 6, it is also striking that considering a single dye family and performing a calibration is extremely efficient as a better correlation coefficient and smaller average errors are systematically attained with range-separated functionals. Therefore, if one is able to establish a calibration curve for a given family of dye, the use of TD-LR-DFT should lead to the sufficient accuracy for the design of a new dye structure.

**IV. Conclusions**

Using TD-DFT, we have assessed the efficiency of several functionals for reproducing the experimental UV/vis \( \pi \rightarrow \pi^* \) absorption wavelength of a set of 100+ organic dyes belonging to the classes of major industrial interest: azobenzenes, anthraquinones, indigos, diarylethenes, ... It was found that the computed \( \lambda_{\text{max}} \) systematically obey a PBE > PBE0 > CAM-B3LYP > LC-PBE > LC-\( \text{o} \)PBE > HF order. This result can be rationalized by the total amount of exact exchange in each functional. Overall, PBE0 provides the smallest error with an average absolute deviation limited to 0.14 eV/22 nm. We state that this value should be regarded as a reference expected PCM-TD-PBE0 accuracy for low-lying excited states of conjugated organic compounds. The second best approach, CAM-B3LYP, suffers larger deviations (0.26 eV/38 nm) but appears particularly well suited for studying dyes with a very delocalized excited state. On the contrary, HF and PBE give very poor estimates with average errors of 0.97 eV/116 nm and 0.45 eV/87 nm, respectively. If range-separated hybrids cannot beat PBE0 in terms of absolute \( \lambda_{\text{max}} \), they provide more consistent evaluations of the auxochromic shifts. Indeed, linear fittings demonstrate that LR-functionals systematically give large \( R^2 \). Consequently, using a calibration equation such as eq 3 can considerably improve the accuracy of the LR computations. This is especially true when the statistical treatment is performed for a given dye family, for which average errors close to 10 nm are indeed obtained, allowing an efficient dye molecular design as it combines nearly quantitative wavelength estimates to chemically sound classifications. For the complete set of dyes, using scaled LR-DFT improves the PBE0 MAE by about 20%.

Of course, only low-lying \( \pi^* \) excited states of conjugated organic molecules have been considered in the present investigation. Care should be taken before applying eq 3 to other types of excitations or structures. However, for Rydberg states in small molecules it is clear that range-separated hybrids are adequate, whereas these functionals are as accurate as global hybrids for \( n \rightarrow \pi^* \) transitions. Therefore, this contribution paves the way toward accurate, yet affordable, estimations of the excited-state energies of medium and large molecules. We are currently investigating inorganic structures to test the transferability of this approach.

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**References**

TD-DFT Performance for the Spectra of Organic Dyes


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CT700187Z