

ASSESSMENT OF THE ACCURACY OF TD-DFT ABSORPTION SPECTRA: SUBSTITUTED BENZENES

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Professor Rudolf Zahradník is one of the greatest scientists of chemical physics in the most extended sense. He has led efficiently Czech science in the most difficult decades and is at the origin of its expansion after the 'political independence'. One of us (J. M. André) has benefited personally from Professor Zahradník's highly stimulating and inspiring lectures and seminars, from his support on many occasions and from Rudolf's friendship in several international Academies. It is an honour to dedicate, with respect, admiration and pleasure, this paper to Professor Rudolf Zahradník for his 80th birthday.

Using the parameter-free PBE0 hybrid functional in conjunction with the conducting PCM model, we compute the UV/VIS spectra of a series of solvated phenol and nitrobenzene chromogens. For the first series, the average deviation with respect to experiment is large (about 0.5 eV) but the auxochromic shifts are very accurately and consistently predicted. Therefore, after a statistical treatment, the TD-DFT values are within 0.02 eV of the experimental data. For nitrobenzenes, the average discrepancy is smaller than for phenols, though the impact of individual substitution is much less consistent with experimental trends. We also confirm that push-pull compounds with donor and acceptor groups in meta positions are especially problematic for TD-DFT calculations relying on conventional hybrids, and we unravel the origin of this specific difficulty.

Keywords: Electronic absorption spectroscopy; UV spectroscopy; Nitrobenzene; Phenol; TD-DFT calculations; PBE0 hybrid functional.

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Time-dependent density functional theory (TD-DFT) originally designed by Runge and Gross^{1,2}, has become one of the most widely-used tool for theoretical evaluations of the excited state energies and geometries of small and medium organic and inorganic systems, as well as to study vibronic coupling. This success is due to the TD-DFT's efficiency to quickly produce a valid description of the electronic transition phenomena in molecules. Electron-correlated wavefunction approaches such as EOM-CC, SAC-CI, MR-CI and CAS-PT2 are generally more consistent and accurate than TD-DFT, but their computational cost remains too high to allow large-scale applications on compounds of practical interest. Today's computer technology also practically limits the range of such wavefunction approaches to gas-phase properties. On the contrary, semi-empirical schemes are lightning-fast and yield valuable chemical insights, but lack of consistency. Indeed, it is hard to foresee their successes and failures without a systematic calibration on target chemical families. This contrasts with TD-DFT, for which the major limitations are well-established: it significantly undershoots the transition energies of charge-transfer compounds^{3,4} and is inappropriate for studying multi-determinantal cases. In short, TD-DFT emerges as an interesting quality/effort compromise for simulating absorption and fluorescence spectra of organic and inorganic molecules solvated in nonpolar or polar media^{5,6}. In this respect, we have already demonstrated, in a series of recent investigations, that TD-DFT, combined with a sufficiently extended basis set and an environmental surrounding model, delivers highly accurate data for most organic dyes of industrial interest. That is, even without any statistical correction, the mean absolute deviation (MAE, with respect to experiment) of the longest wavelength of maximum absorption (λ_{\max}) typically lies between 0.05 eV and 0.15 eV⁷⁻¹⁴. In addition, we refer the reader to ref.¹⁵ for an overview of the expected TD-DFT accuracy for organic dyes, and a discussion of the relative efficiency of standard and long-range corrected hybrids.

Organic dyes are frequently made up of aromatic systems combining substituted rings conjugated with carbonyl group(s) and/or azo bridging unit(s)¹⁶. The azo and quinoid structures together represent more than 80% of the annual world production of (metal-free) chromogens. In ref.¹⁷, we have assessed the efficiency of TD-DFT for computing the spectra of conjugated carbonyl compounds. It turned out that our approach, that we have also used in the present work, provides accurate estimations of the experimental values, with a MAE limited to 0.13 eV. More impressively, TD-DFT results were found to be of the same quality as the completely empirical purpose-tailored Woodward-Fieser rules¹⁸⁻²⁰. In the present contribution,

we focus on substituted benzenes, as they are essential structural building blocks for most dyes. More specifically, we evaluate the absorption spectra of phenols and nitrobenzenes. The latter series present the typical (and problematic) charge-transfer nature, though quite similar mono-, di- and trinitrodiphenylamine dyes were correctly described by the same TD-DFT scheme¹².

COMPUTATIONAL DETAILS

We have chosen the Gaussian03²¹ package of programs to perform complete geometry optimisations, vibrational analysis, as well as excited state calculations for a series of 32 phenols and for a series of 63 nitrobenzenes.

The ground-state geometry of each molecule was fully optimised, using the PBE0²² hybrid functional and the split-valence triple- ζ polarised 6-311G(d,p) basis set that is known to lead to converged (DFT) geometrical parameters for most organic compounds²³⁻²⁵. The vibrational spectrum was computed, following each optimisation, and it was systematically checked that all vibrational frequencies were real.

The TD-DFT methodology was then used to compute the vertical transition energies to the low-lying excited states of the benzene derivatives. More specifically, the PBE0/6-311+G(2d,p) level was selected as this combination has been shown to be one of the best approaches for computing UV/VIS spectra of dyes. We refer the interested reader to several papers, refs¹¹⁻¹⁴, for various successful applications of this approach. Here, the electronic excitations present a typical $\pi \rightarrow \pi^*$ character often associated with a large oscillator force, and the choice of the λ_{\max} becomes almost always straightforward. The experimental data listed in Tables I and II were obtained from several sources²⁶⁻³⁰.

At all stages, the bulk solvent effects were evaluated by means of the conducting polarisable continuum model (C-PCM)³¹. The C-PCM model has been favoured because it often allows faster convergence of the calculation than other PCM schemes, without significant modifications of the final results. In continuum models, one divides the model into a solute part, the studied molecule, lying inside a cavity surrounded by the solvent part: cyclohexane or ethanol, for the phenol or nitrobenzene derivatives, respectively. C-PCM returns valid solvent effects when no specific interactions link the solute and the solvent molecules. To build the cavity, we selected the so-called UAKS (united atom topological model for Kohn-Sham model) radii peculiarly optimised for DFT calculations²¹.

RESULTS

Phenol Derivatives

In Table I, we have listed experimental and theoretical λ_{\max} for over 30 phenol derivatives in cyclohexane. The corresponding graphical comparison is provided in Fig. 1. We notice that PBE0 systematically underestimates the experimental wavelengths. Indeed, the mean signed error (MSE, experiment–theory) is equal to the MAE, and for the total set of molecules it attains 25.5 nm, that is 0.461 eV on the energetic scale. Such an average error is much larger than the value deduced for conjugated carbonyls and typical

TABLE I

Comparison between UV/VIS experimental and theoretical λ_{\max} (nm) for phenol derivatives in cyclohexane. All calculations were performed using the C-PCM-TD-PBE0/6-311G+(2d,p)//C-PCM-TD-PBE0/6-311G(d,p) approach. $\Delta\lambda_{\max}$ (nm) is the difference between experimental and theoretical values

Substituent(s)	λ_{\max}			Substituent(s)	λ_{\max}		
	Exp.	PBE0	$\Delta\lambda_{\max}$		Exp.	PBE0	$\Delta\lambda_{\max}$
None	269	242	27	4-NH ₂	304	285	19
2-OMe	273.5	246	27.5	2-C ₂ H ₅	270	242	28
3-OMe	271.5	246	25.5	4-C ₂ H ₅	276	250	26
4-OMe	288	268	20	2-CHMe ₂	270	244	26
2-Me	270	243	27	4-CHMe ₂	275	249	26
3-Me	266	244	22	2-CMe ₃	274	243	31
4-Me	277	251	26	4-CMe ₃	275	248	27
3,5-(OMe) ₂	266	222	44	2-F	266	239	27
3,4-(OMe) ₂	286	264	22	3-F	266.5	239	27.5
2,6-(OMe) ₂	269	244	25	4-F	278.5	253	25.5
2-OMe-4-Me	280	253	27	2-Cl	278	248	30
2-OH	274	247	27	3-Cl	272	246	26
3-OH	273.5	245	28.5	4-Cl	279	255	24
4-OH	292	268	24	2-Br	272	249	23
2-NH ₂	288	263	25	3-Br	272	247	25
3-NH ₂	284	257	27	4-Br	279.5	257	22.5

TABLE II
Comparison between UV/VIS experimental and theoretical λ_{\max} (nm) for nitrobenzene derivatives in ethanol. See Table I for more details

Substituent(s)	λ_{\max}			Substituent(s)	λ_{\max}		
	Exp.	PBE0	$\Delta\lambda_{\max}$		Exp.	PBE0	$\Delta\lambda_{\max}$
None	297	293	4	3-OH-4-NMe ₂	399	402	-3
2-OH	347	356	-9	3-OH-4-NH ₂	390	374	16
3-OH	331	356	-25	3-NH ₂ -4-OH	370	376	-6
4-OH	315	309	6	3-NHMe-4-OH	408	406	2
2-OMe	323	314	9	3-NMe ₂ -4-OH	356	368	-12
3-OMe	324	357	-33	3-NH ₂ -4-OMe	370	418	-48
4-OMe	306	314	-8	3,4-(OH) ₂	349	356	-7
2-NH ₂	406	386	20	3-OH-4-OMe	342	351	-9
3-NH ₂	374	427	-53	3-OMe-4-OH	342	350	-8
4-NH ₂	376	346	30	3,4-(OMe) ₂	337	355	-18
2-NHMe	429	403	26	2,5-(NH ₂) ₂	473.5	486	-12.5
3-NHMe	393	470	-77	2-NH ₂ -5-NHMe	497	527	-30
4-NHMe	388	360	28	2-NH ₂ -5-NMe ₂	493.5	523	-29.5
2-NMe ₂	415	429	-14	2-NHMe-5-NH ₂	498.5	499	-0.5
3-NMe ₂	404	493	-89	2,5-(NHMe) ₂	519.5	540	-20.5
4-NMe ₂	394	371	23	2-NHMe-5-NMe ₂	506.5	535	-28.5
2,3-(NH ₂) ₂	389	365	24	2-NMe ₂ -5-NH ₂	441	525	-84
2-OH-3-NH ₂	394	342	52	2-NMe ₂ -5-NHMe	448	537	-89
2-OH-3-NHMe	403	353	50	2,5-(NMe ₂) ₂	445	560	-116
2-OH-3-NMe ₂	408	369	39	2-OH-5-NH ₂	446	491	-45
2-OMe-3-NH ₂	376	343	33	2-OH-5-NHMe	477	522	-45
2-OMe-3-NMe ₂	388	365	23	2-OH-5-NMe ₂	475	555	-80
2-NH ₂ -3-OH	394	369	25	2-OMe-5-NH ₂	388	444	-56
2-NHMe-3-OH	410	381	29	2-NH ₂ -5-OH	454	436	18
2-NMe ₂ -3-OH	407	405	2	2-NHMe-5-OH	476	457	19
2-NH ₂ -3-OMe	395	376	19	2-NMe ₂ -5-OH	444	486	-42
2,3-(OH) ₂	368	337	31	2-NH ₂ -5-OMe	443	450	-7
2-OMe-3-OH	328	325	3	2-NHMe-5-OMe	466	466	0
2,3-(OMe) ₂	326	327	-1	2,5-(OH) ₂	407	421	-14
3,4-(NH ₂) ₂	408	402	6	2-OH-5-OMe	393	416	-23
3-OH-4-NH ₂	394	374	20	2-OMe-5-OH	368	372	-4
3-OH-4-NHMe	412	397	15				

organic dyes (see previous section), and cannot be significantly decreased by using a more refined EOM-CC approach³⁰. Nevertheless, the auxochromic band shifts are very well reproduced by the TD-PBE0 calculations. For instance, the introduction of an amino group at ortho, meta and para positions of the phenolic function, yields experimental shifts of 20, 15, and 35 nm, respectively; while PBE0 predicts variations of 21, 15, and 43 nm, respectively. Generally, the introduction of electroactive groups leads to bathochromic displacement of the main absorption band of phenol. There are only four measured hypsochromic cases in Table I, and our model accurately foresees three of them (3,5-dimethoxyphenol, *o*- and *m*-fluorophenol). For the fourth “hypso-molecule”, that is *m*-methylphenol, the theoretical and experimental shifts have opposite signs but their magnitude is negligible in both cases (measured: -3 nm, TD-PBE0: +2 nm). In short, though the TD-DFT deviations are beyond the expected values, the consistency of the approach is excellent: all theoretical values present a similar error with respect to reference data. Therefore, performing a simple

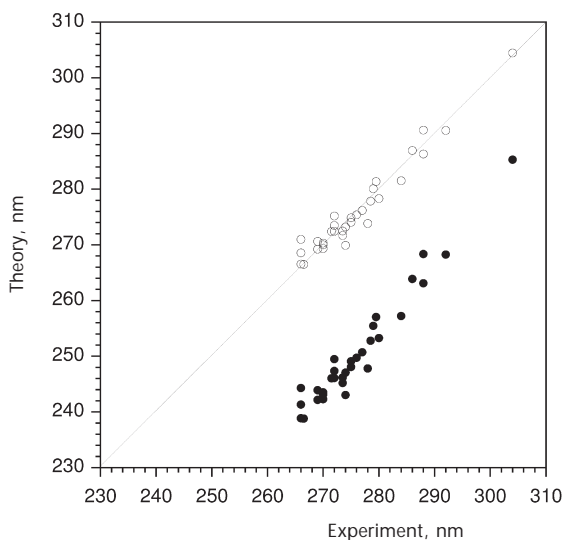


FIG. 1

Comparison between the theoretical [C-PCM-TD-PBE0/6-311+G(2d,p)//C-PCM-PBE0/6-311G(d,p)] and experimental λ_{\max} for phenol derivatives in cyclohexane. The central line indicates a perfect theoretical/experimental match. The full circles correspond to raw theoretical estimations, whereas the open circles are for SLR-estimated values

linear regression (SLR) on the whole set of phenol derivatives appears to be an appropriate approach to improve the predictive ability of our model. Such a procedure leads to the following equations:

$$\lambda_{\max}^{\text{SLR}} = 71.520 + 0.816 \lambda_{\max}^{\text{TD-DFT}} \quad (1)$$

$$E_{\max}^{\text{SLR}} = 1.105 + 0.684 E_{\max}^{\text{TD-DFT}} \quad (2)$$

on the wavelength (nm) and energetic (eV) scales, respectively. Equations (1) and (2) allow to overcome the initial systematic λ_{\max} underestimation by the TD-DFT calculations, and it should be highlighted that the correlation coefficient between the experimental and theoretical values exceeds 97% for both equations. The MAE, after the statistical corrections, are only 1.4 nm or 0.023 eV, approximatively twenty times smaller than for the raw data. Obviously, SLR brings a significant improvement of the theoretical λ_{\max} of absorption, as seen in Fig. 1. We have to stress that such a MAE is small enough to allow the design of new substituted phenols. Indeed, the recognised threshold for efficient "colour" model is 10 nm/0.05 eV on the λ_{\max} .

Nitrobenzene Derivatives

In Table II and Fig. 2, we have compared the experimental results with TD-PBE0 estimations for over 60 substituted nitrobenzenes. For the complete set, the *ab initio* procedure provides a MSE of -9.1 nm, a small underestimation of the experimental λ_{\max} , which corresponds to a 0.037 eV error for the E_{\max} . The energetic MAE is smaller than for phenol derivatives: 0.20 eV (27.3 nm), so that we can state that the accuracy of TD-DFT is not systematically worse for charge-transfer molecules though, as seen below, the theoretical values are much less consistent. Studying the substitution of nitrobenzene by a single donor group unravels an extra effect: the absorption wavelength of the ortho and para structures are reasonably well modelled, while the errors are much larger for electro-active groups in meta position. For instance, for (dimethylamino)nitrobenzenes, the theory/experiment discrepancy is less than 25 nm for both the ortho and para cases, but -89 nm for the meta structure. Therefore, the overall agreement between measured and calculated auxochromic shifts is much less satisfactory than for phenols. Therefore, contrary to the results of the previous section, the SLR corrections,

$$\lambda_{\max}^{\text{SLR}} = 133.675 + 0.652 \lambda_{\max}^{\text{TD-DFT}} \quad (3)$$

$$E_{\max}^{\text{SLR}} = 0.8864 + 0.727 E_{\max}^{\text{TD-DFT}} \quad (4)$$

do not significantly improve the λ_{\max} estimations. After fitting, the MAE are indeed mostly unchanged: 23.1 nm with Eq. (3) and 0.18 eV with Eq. (4). In addition, the poor correlation coefficient (88% for both equations) indicates an unsatisfactory relationship between the experimental and predicted absorption wavelengths for nitrobenzenes.

Two major reasons can explain these divergences between the phenol and the nitrobenzene results. On the one hand, the PCM models are less appropriate for ethanol than for cyclohexane as only continuum effects are accounted for. Indeed, in an alcoholic environment, there are probably strong hydrogen bonds between the oxygen atoms of the nitro group and the (acidic) hydrogen of ethanol. Such specific interactions are unfortu-

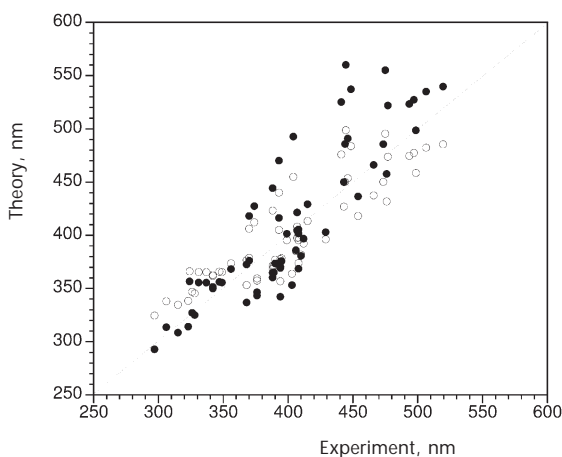


FIG. 2

Comparison between the theoretical [C-PCM-TD-PBE0/6-311+G(2d,p)//C-PCM-PBE0/6-311G(d,p)] and experimental λ_{\max} for nitrobenzene derivatives in ethanol. The central line indicates a perfect theoretical/experimental match. The full circles correspond to raw theoretical estimations whereas the open circles correspond to Eq. (3)

nately not taken into account by PCM models. Second, most of the transitions listed in Table II present a significant charge-transfer character. This is clearly illustrated by Fig. 3 where a sketch of the frontier orbitals implied in the λ_{\max} shows that for both 3-(dimethylamino)nitrobenzene and 4-(dimethylamino)nitrobenzene, a large density displacement from the amino to the nitro group takes place upon electronic excitation. For the para structure, there is already a significant electronic density on the carbon atom bonded to the nitro group, which is obviously not the case for the meta structure. Consequently, the density displacement induced by the photon absorption is larger for the meta compound. This is confirmed by the π orbital of the nitrogen atom of the dimethylamino group, that undergoes a very strong (moderate) occupation variation for the meta (para) dye. Figure 3 directly explains the larger underestimation of the λ_{\max} for the *m* relative positions: the charge-transfer character is enhanced for this isomer, though the transition probability is smaller than for the ortho and para compounds.

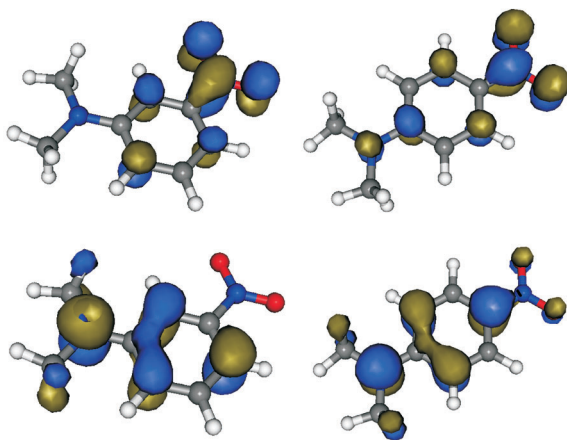


FIG. 3

Sketch of the HOMO (bottom) and LUMO (top) of 3-(dimethylamino)nitrobenzene (left) and 4-(dimethylamino)nitrobenzene (right)

CONCLUSIONS

We have assessed the accuracy of TD-DFT transition energies for two series of substituted benzene derivatives, i.e., phenols and nitrobenzenes. For phenols, the deviations between the TD-DFT λ_{\max} and the experimental values are large, but the auxochromic effects are almost perfectly predicted. Subsequently, a simple linear correction of the TD-DFT values allows an astonishing accuracy of 0.02 eV. For nitrobenzenes, while the average discrepancy (prior to statistical correction) is smaller than for the phenols, the auxochromic displacements are inconsistently foreseen. The main origin of this failure is related to the different error occurring, on the one hand, for ortho and para structures, and, on the other hand, for meta dyes. The latter display a much enhanced charge-transfer character, explaining in turns the larger underestimation of the λ_{\max} for benzene with donor and acceptor group in meta position.

We are currently investigating the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of cyclic and non-cyclic azo derivatives.

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