Verdict: Time-Dependent Density Functional Theory "Not Guilty" of Large Errors for Cyanines

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ABSTRACT: We assess the accuracy of eight Minnesota density functionals (M05 through M08-SO) and two others (PBE and PBE0) for the prediction of electronic excitation energies of a family of four cyanine dyes. We find that time-dependent density functional theory (TDDFT) with the five most recent of these functionals (from M06-HF through M08-SO) is able to predict excitation energies for cyanine dyes within 0.10−0.36 eV accuracy with respect to the most accurate available Quantum Monte Carlo calculations, providing a comparable accuracy to the latest generation of CASPT2 calculations, which have errors of 0.16−0.34 eV. Therefore previous conclusions that TDDFT cannot treat cyanine dyes reasonably accurately must be revised.

1. INTRODUCTION

Cyanines are an important class of dyes, especially in biological and industrial chemistry. The present paper is concerned with the applicability of time-dependent density functional theory (TDDFT) to predict their excitation spectra.

Time-dependent density functional theory has become the method of choice for calculating the energies of electronically excited states of complex systems in both chemistry and physics.[1−3] A number of validation studies have been carried out to determine the limits of its reliability for various types of excitations.[4]

A recent study in this journal tested the M06 family of density functionals for 190 valence excited states, 20 Rydberg states, and 16 charge-transfer states and compared the accuracy to that of several other density functionals.[5] Although many of the excitation types were treated with reasonable success, this study concluded, in agreement with earlier work,[4,6,7] that all functionals showed "dreadful" performances for cyanine dyes, as judged by comparison to experimental excitation energies[8] measured in aqueous solution. Cyanines are charged dyes with two nitrogen atoms and highly delocalized electronic excitations. The poor performance of TDDFT for the cyanines was attributed to "the strong multideterminantal nature of the states of these dyes," i.e., to what is generally called[9] multireference character. This conclusion was especially reinforced by the good agreement with experiment of the calculations[10] carried out by the complete-active-space perturbation theory of order 2 (CASPT2) method,[11] which is designed to be appropriate for systems with multireference character and is generally quite accurate. The poor performance of TDDFT for this class of dyes was dispiriting.

Recently this problem has been re-examined by Send et al.,[13] who drew some very interesting conclusions: First, they concluded that the CASPT2 calculations of ref 10 "do not offer a reliable benchmark for cyanine dyes" because the active space is inadequate and the zero-order Hamiltonian is not optimal. With regard to the latter, ref 10 was carried out with version 5 of the MOLCAS program before the development of the ionization potential electron affinity (IPEA) shift procedure[14] for the zero-order Hamiltonian of CASPT2 calculations. The IPEA shift, which has been the default in the MOLCAS program[15] since version 6.4, increases the excitation energies (and makes them more accurate) by about 0.2 eV.[13] Second, Send et al.[13] concluded that comparison to experiment is not a reliable way to estimate the vertical excitation energies because of the likelihood of nonvertical transitions. Third, Send et al.[13] concluded that the most reliable estimate of the vertical excitation energy should be based on their wave function calculations by an extrapolated approximate coupled cluster singles, doubles, and triples (exCC3) model[16] and by diffusion Monte Carlo[17] (DMC). These are gas-phase results, and adopting either of them as the new benchmark reduces the error attributed to TDDFT.

Nevertheless, Send et al. say that "the TDDFT excitations computed with the hybrid generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA PBE0) are about 0.3−0.5 eV above the exCC3 results. The use of the nonhybrid GGA PBE or the long-range corrected CAM-B3LYP does not lead to a significantly closer agreement with the wave function methods. The same holds for the larger number of GGA

functionals including the Minnesota functionals tested by Jacquemin et al. (Here they cite present refs 4 and 5.) These findings indicate that a closer agreement [of TDDFT] with wave function methods can only be obtained by going beyond the GGA and hybrid-GGA functionals." There are two things wrong with the quoted statement. First, the Minnesota functionals under consideration are neither GGAs nor hybrid GGAs; they include one meta-GGA and several hybrid meta-GGAs. (Meta-GGA denotes adding to a GGA a dependence on either the kinetic energy density or the Laplacian of the density). Second, quantitative comparison of the exCC3 or DMC calculations to the TDDFT ones of ref 5 is impossible based on the available data, because ref 13 presents gas-phase results and all calculations for cyanines in refs 4 and 5 are for liquid-phase solutions.

Conclusions drawn about excitation energies of cationic species in liquid-phase solutions are subject to large uncertainties associated with solvation effects. In the present article, motivated by the stimulating results of Send et al.,[13] we present gas-phase TDDFT calculations by PBE and PBE0 as well as by all eight Minnesota functionals, in particular the meta-GGA M06-L[18] and seven hybrid meta-GGAs (M05,[19] M05-2X,[20] M06-HF,[21] M06,[22] M06-2X,[22] M08-HX,[23] and M08-SO)[23] and compare them to the best estimates available (which are the DMC results) to better understand if cyanine dyes should still be considered a lost case for TDDFT. We note that Send et al. did not test the Minnesota functionals, and in that respect, the present work is complementary to that study.

The importance of cyanines in applications is reflected in the wealth of studies reported mostly in the past decade, besides those already cited, that employed TDDFT,[24−32] density functional vertical self-consistent reaction field (VSCRF) calculations,[33] the solvaton-CS intermediate neglect of differential overlap (INDO) model,[34−36] or INDO/singles-configuration interaction (INDO/CIS)[37] to predict excitation energies and CASSCF to study the excited-state dynamics.[38,39] Unlike the present study, which deals with the simplest cyanines with unsubstituted conjugated hydrocarbon chains known as polymethine chains and amino groups at the edges, all of those studies but one[39] considered more complex cyanines, e.g., with condensed rings either containing the nitrogen atom and/or polymethine carbon atoms or acting as substituents. The present contribution is not concerned with cyanine applications per se, but rather with sorting out the important question of whether the cyanine functionality reveals a serious deficiency of TDDFT.

2. CALCULATIONS AND COMPARISON DATA

We consider here the family composed of the four unsubstituted cationic open-chain cyanine molecules depicted in Scheme 1 (CNx, x = 5, 7, 9, 11; with x indicating the number of backbone atoms). These molecules were all studied in ref 13,

Scheme 1
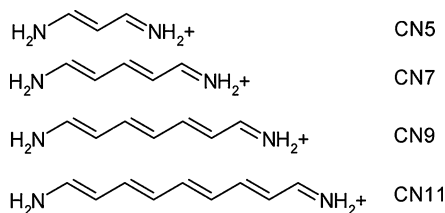
while CN5 and CN7 were already considered by us in ref 5, including solvent effects via a polarizable continuum model. The structure of CN5 is illustrated in Figure 1.
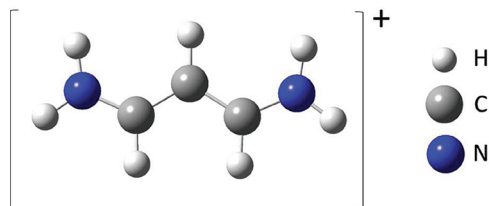

Figure 1. Structure of CN5.

Table 1 shows the key results from ref 13 to which we will compare. The methods employed, in addition to DMC, exCC3, and CASPT2, are coupled cluster theory with single and double excitations[40] (CCSD), the second-order approximate coupled-clusters doubles (CC2) model,[41] complete-active-space self-consistent field[42] (CASSCF), and TDDFT using four density functionals: PBE[43] (which is a GGA), PBE0[44,45] (a hybrid GGA), and CAM-B3LYP[46] (a range-separated hybrid GGA). Two geometries are considered in ref 13: one obtained by Møller−Plesset perturbation theory of order 2[48] (MP2) and one obtained by PBE0. The use of MP2 vs PBE0 geometries in ref 13 gave very similar excitation energies, with differences of 0.03 eV or less.[13]

The present calculations employed the PBE0 cc-pVQZ geometries for all TDDFT calculations in analogy with computational protocol followed in ref 13. Excitation energy calculations presented here employ the large aug-cc-pVTZ[49] basis set, but similar results (within ∼0.1 eV) were obtained with three smaller basis sets for selected test cases. For PBE and PBE0 very similar transition energies were obtained in ref 13 using the ANO-L-VTZP basis set on PBE0 structures.

3. RESULTS AND DISCUSSION

All the transitions studied here are dominated (coefficient ∼0.7) by the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) amplitude. Figure 2 shows the HOMO and LUMO in each case; these orbitals are delocalized over the molecule as expected.

Density functionals under consideration here are listed in the first 10 lines of Table 2 in the chronological order of their development. All the data computed using both the eight functionals of the Minnesota family and the PBE and PBE0 ones for comparison are reported in Table 2. The third to last columns of Table 2 present the mean unsigned errors (MUEs) for this data set of four cyanine excitation energies (CYA4), and the last two columns of Table 2 provide the MUEs of two previously[5] considered databases (VES190 and RES20) computed using the same functionals. (Note that the M08-HX and M08-SO results for these databases are new in the present paper). VES190 contains 190 valence excited-state energies, and RES20 contains 20 Rydberg excitation energies; these databases are included to judge the overall functional performances for the estimation of both valence and Rydberg excitations of simple molecular systems.[5]

The errors given in Table 2 are measured with respect to DMC calculations, taken from ref 13 and considered here as the most accurate values available in the literature for cyanines. It is worth recalling that other accurate post-HF methods, such as the exCC3 method, differ from DMC results, with the

Table 1. Vertical Excitation Energies (ΔE in eV) and Associated Absolute Errors (in eV) with Respect to DMC Results Computed for Cyanine Molecules from Ref 13

	CN5		CN7		CN9		CN11	
	ΔE	lerrl	ΔE	lerrl	ΔE	lerrl	ΔE	lerrl
Best Estimate								
DMC[a]	5.03	–	3.83	–	3.09	–	2.62	–
Single Reference Methods[b]								
exCC3[a]	4.84	0.19	3.65	0.18	2.96	0.13	2.53	0.09
CCSD[a]	4.98	0.05	3.81	0.02	3.11	0.02	– (–)	–
CC2[a]	4.97	0.06	3.79	0.04	3.10	0.01	2.64	0.02
Multireference Methods[c]								
CASPT2, IPEA shift[a]	4.69	0.34	3.53	0.30	2.81	0.28	2.46	0.16
CASPT2, no shift[a]	4.46	0.57	3.30	0.53	2.59	0.50	2.10	0.52
CASSCF[a]	5.32	0.29	3.92	0.09	3.14	0.05	2.39	0.23
TDDFT								
PBE[d]	5.22	0.19	4.11	0.28	3.44	0.35	2.98	0.36
PBE0[d]	5.33	0.30	4.18	0.35	3.50	0.41	3.03	0.41
CAM-B3LYP[d]	5.26	0.23	4.12	0.29	3.44	0.35	2.97	0.35
TDDFT (TDA)								
PBE0[d]	5.84	0.81	4.71	0.88	4.02	0.93	3.54	0.92

[a]MP2/cc-pVQZ geometry. [b]Using the ANO-L-VTZP basis. [c]Using the ANO-L-VXZP (X = Q for CN5,CN7 and CN9; X = T for CN11) basis and the optimal active space as reported in ref 13. [d]PBE0/cc-pVQZ geometry.

	HOMO	LUMO
CN5		
CN7		
CN9		
CN11		
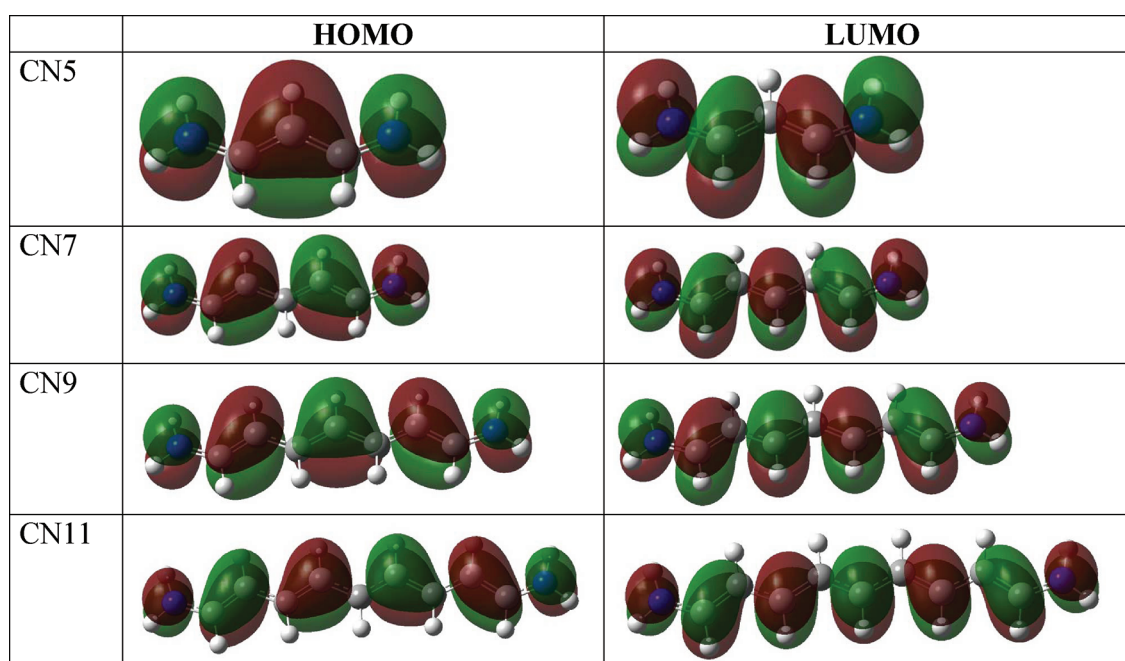
Figure 2. HOMO and LUMO for each of the cyanines in the CY4 database.

differences ranging from 0.19 (CN5) to 0.09 eV (CN11). Even larger differences are found between DMC and CASPT2 (with IPEA shift) results, ranging from 0.34 (CN5) to 0.16 eV (CN11). We note in this regard that we did not optimize geometries with CASPT2.

In general, both CASPT2 (with the IPEA shift) and exCC3 errors decrease as a function of the cyanine length. This finding is consistent with a larger importance of static correlation effects for smaller dyes, as already noticed in ref 13. The excitation energies computed using all post-HF methods are also systematically below the DMC values. On the other hand, TDDFT errors increase as a function of the cyanine length for all functionals, and vertical excitation energies are always overestimated. This is evident in a plot of excitation wavelength

against chain length in Figure 3. As a consequence, errors of exCC3 or CASPT2 relative to the DMC reference should be added to the TDDFT one if one would like to compute the TDDFT accuracy with respect to exCC3 or CASPT2 methods, respectively. The rather large differences between DMC and CASPT2 computed values further underlie the necessity and difficulty of defining trustable benchmarks values for transitions energies. We note though that the DMC results should be especially reliable for the smallest cyanine, and the conclusions we will draw by considering the smallest cyanine should be given extra weight.

Keeping the DMC results as reference, the errors for the Minnesota family of functionals range from 0.10 (CN5 at M06-HF level) to 0.49 eV (CN11 at the M06-L level), while in the

Table 2. Computed Vertical Excitation Energy (ΔE, in eV) and associated absolute deviations with respect to DMC calculations (|err|, in eV) for the cyanine family of molecules together with the Mean Unsigned Errors (MUE, in eV) on the VES190 and RES20 databases computed at the same level of theory

	CN5		CN7		CN9		CN11		CYA4	VES190	RES20
	ΔE	|err|	ΔE	|err|	ΔE	|err|	ΔE	|err|	MUE	MUE	MUE
PBE	5.23	0.20	4.12	0.29	3.45	0.36	3.00	0.38	0.31	0.46	1.95
PBE0	5.34	0.31	4.19	0.36	3.50	0.41	3.04	0.42	0.38	0.19	0.86
M05	5.30	0.27	4.15	0.32	3.47	0.38	3.00	0.38	0.34	0.25	1.16
M05-2X	5.33	0.30	4.17	0.34	3.47	0.38	3.00	0.38	0.35	0.41	0.31
M06-L	5.40	0.37	4.25	0.42	3.56	0.47	3.11	0.49	0.44	0.33	1.62
M06-HF	5.13	0.10	3.98	0.15	3.30	0.21	2.83	0.21	0.17	0.67	0.39
M06	5.23	0.20	4.10	0.27	3.43	0.34	2.98	0.36	0.29	0.25	1.67
M06-2X	5.23	0.20	4.09	0.26	3.41	0.32	2.95	0.33	0.28	0.36	0.35
M08-HX	5.23	0.20	4.09	0.26	3.41	0.32	2.95	0.33	0.28	0.33	0.59
M08-SO	5.16	0.13	4.04	0.21	3.37	0.28	2.91	0.29	0.23	0.37	0.69
exCC3[a]	4.84	0.19	3.65	0.18	2.96	0.13	2.53	0.09	0.15	-.-	-.-
CASPT2[b]	4.69	0.34	3.53	0.30	2.81	0.28	2.46	0.16	0.27	-.-	-.-
DMC[a]	5.03	0.00[c]	3.83	0.00[c]	3.09	0.00[c]	2.62	0.00[c]	0.00	-.-	-.-

[a]From ref 13. [b]CASPT2 results with IPEA shift, from ref 13. [c]By definition.
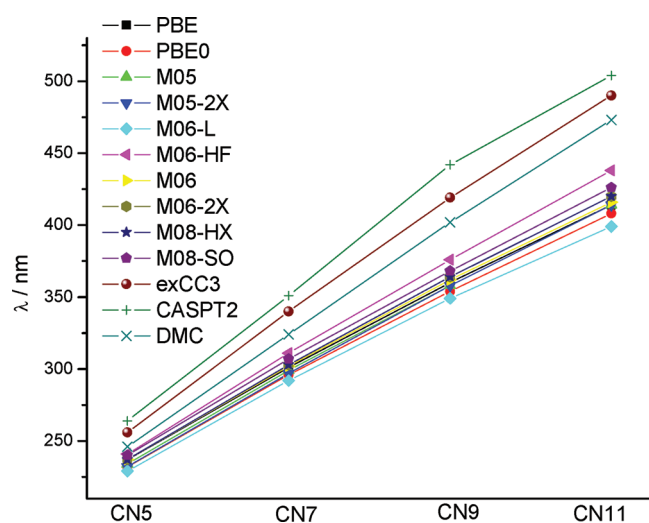

Figure 3. Absorption wavelength in nanometers as a function of chain length.

case of PBE and PBE0, the errors are computed to be between 0.20 (CN5 with the PBE functional) and 0.42 eV (CN11 with the PBE0 functional). However, if we consider only the five most recent Minnesota functionals in the table, the errors range from 0.10 to only 0.36 eV (CN11 with M06).

Comparison with ref 13 data in Table 1 shows that all functionals considered outperform CASPT2 without the IPEA shift for whatever the length of the cyanine molecule is considered. Comparing with the CASPT2 calculations carried out with the IPEA shift for the smallest cyanine (CN5), seven of the eight Minnesota as well as the PBE and PBE0 density functionals perform better than CASPT2 (with errors of 0.20 eV or less for the five most recent functionals), and for both CN5 and CN7, all 10 calculations with the 5 most recent functionals have smaller errors than CASPT2 with the IPEA shift. But for longer cyanine molecules only M06-HF and M08-SO show consistently smaller errors up to CN9. It is also striking to notice is that up to CN11, the errors computed using M05-2X, M06-HF, M06-2X, M08-HX, and M08-SO are *all* below their corresponding MUE for the VES190 set.

The M06 functional, which was the best Minnesota functional in the broad tests for valence excitation states in ref 5, has an error for CN5 that is even smaller than the previous MUE for VES190, and the computed errors increase only up to 0.36 eV in the case of CN11. The M06-HF, M06-2X, M08-HX, and M08-SO functionals all show excellent performances, the best being the M06-HF functional with errors always below than 0.21 eV. Nonetheless, its performance on the VES190 set, with an MUE of 0.67 eV, is not as good as those of other Minnesota family functionals. Overall, the M08-SO functional with errors on cyanines ranging from 0.21 to 0.29 eV, but an MUE on VES190 of only 0.37 eV, seems to offer a better compromise. By looking at all three of the MUE columns in Table 2, we can form a better judgment on the overall balance of the various functionals. We believe that the Minnesota functionals do well for a combination of reasons. Four of the Minnesota functionals with high Hartree−Fock exchange (M06-HF, 100%; M06-SO, 56.79%; M06-2X, 54%; M08-HX, 52.23%) do well in part because high Hartree−Fock exchange eliminates a significant portion of the self-interaction error, which is important because of the partial charge-transfer character of the excitations. However, this is not the entire reason because M06 (27% Hartree−Fock exchange) does better than M05-2X (56%). An important feature of all the Minnesota functionals is the inclusion of kinetic energy density, which allows the density functional to distinguish the regions dominated by the density of a single electron or by electrons in a single orbital from regions with significant contributions from more than one orbital; this kind of discrimination is particularly important for excited states and in the outlying regions of low density. Send et al.[13] analyzed their CASPT2 calculations and found up to 16% double excitation character; TDDFT does not include double excitation character, at least in the (currently conventional) adiabatic approximation used here. The TD-B2PLYP calculations of Grimme and Neese[6] include both high Hartree−Fock exchange and a beyond-TDDFT perturbation correction for double excitations, but their calculated excitation energy for CM11 (∼2.8 eV, computed from their Figure 5) is only slightly more accurate than M06-HF (see Table 2), perhaps suffering in part, as they concluded, because of the deficiencies of their underlying functional.

Coming back to the main points raised in the introduction, we can conclude that:

- Seven of the Minnesota functionals do better than PBE0 for cyanines, although PBE0 had an MUE of 0.19 eV for VES190.
- Several of the density functionals do quite well for cyanines as compared to CASPT2, even with the IPEA correction applied to CASPT2.
- M08-SO has deviations always below 0.41 eV, even with respect to exCC3 values, and always below 0.29 eV with respect to DMC values.

On these bases, we conclude that TDDFT was falsely accused (by several groups, including us) of unusually large errors for cyanines, and cyanines may be removed from the especially troublesome for TDDFT column.

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Notes
The authors declare no competing financial interest.

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