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Artem E. Masunov
University of Central Florida
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Theoretical Spectroscopy of Carbocyanine Dyes Made Accurate by Frozen Density Correction to Excitation Energies Obtained by TD-DFT

ARTËM E. MASUNOV[1,2,3]

[1]*NanoScience Technology Center, University of Central Florida, Orlando, FL 32826*
[2]*Department of Chemistry, University of Central Florida, Orlando, FL 32826*
[3]*Department of Physics, University of Central Florida, Orlando, FL 32826*

ABSTRACT: We present long-awaited answer to the puzzling question of why the TD-DFT fails to predict the excitation energies in polymethine dyes accurately. The density functional theory methods were suspected to be inaccurate due to self interaction error inherent in exchange-correlation potentials. Here we decisively show that it is the linear response approximation that is responsible for these inaccuracies. Next, we use frozen density to evaluate the excitation energy beyond the linear response and increase the accuracy of the predictions. This recipe uniformly improves the accuracy of the first absorption maxima prediction in cyanine homologous series to within 25 nm. © 2010 Wiley Periodicals, Inc. Int J Quantum Chem 110: 3095–3100, 2010

Key words: time-dependent density functional theory; conjugated dyes; absorption wavelength; delta-SCF

Theoretical description of the light absorption by conjugated molecules became an important component in photochemical and photophysical studies of these molecules, essential for both experimental design and interpretation. Many properties of the molecules in their electronic ground states are reproduced in the mean field approximation, also known as Hartree-Fock (HF) theory. In this approximation, each electron is described by an orbital shaped in the mean field created by the density distribution of all other electrons. Electron repulsion is then composed of two terms: classical Coulomb energy and exchange energy E_{HFX}, resulting from quantum nature of electrons. Electron correlation effects are missing from this picture. However, they are

present in the ground and excited states to a different degree, making mean field approximation inaccurate for spectroscopic purposes. Traditionally, post-HF ab initio wavefunction theory (WFT) is used to describe electronic excited states and transition probabilities between them. Although WFT tools are capable to provide quantitative predictions of nearly experimental quality, they are often computationally prohibitive and rarely can be used as a black box. For this reason WFT methods are traditionally combined with semiempirical Hamiltonians (PPP, AM1, PM3, CS-INDO, ZINDO, etc.) to guide the experimental work [1–3]. As a result of semiempirical parameterization, the accuracy varies from one class of the chromophores to another, and only quantitative picture is obtained.

An alternative approach [4] is based on the linear response approximation within density functional theory (DFT), widely known as time-dependent DFT (TD-DFT) [5]. Instead of increasing complexity of the molecular wavefunction, the electron correlation in DFT is introduced in terms of exchange-correlation functional E_{XC}, replacing exact exchange E_{HFX} in HF theory without increase in computational expense. Some empirical parameter fitting is typically involved in the design of the exchange-correlation functional in this formalism, it is largely system-independent. Although exact exchange is nonlocal and orbital-dependent, in DFT the functional E_{XC} is expressed in terms of the total electron density and its gradients (respectively local and semilocal approximation). Unlike exact exchange, E_{XC} includes repulsion of electron from its own density and does not vanish for one-electron systems. This property is known as self-interaction error, and it has both negative and positive effects. As negative result, in DFT bonds are too weak, while electrons are over-delocalized and do not interact with Coulomb asymptotic $\sim 1/r$ at large separations. On a positive site, self interaction is mimicking nonlocal part of electron correlation and should be retained to some degree when improvements to E_{XC} are made. As the result of electron overdelocalization in DFT, even hybrid functionals fail to describe symmetry breaking in the geometry of the ground state of longer polymethines [6]. However, for the chain lengths considered here, experimental evidence suggests no symmetry breaking.

Practically useful step in balancing self-interaction error was made by Becke [7], who suggested to include a fraction of HF exchange energy in E_{XC} functional:

$$E_{XC} = aE_{HFX} + (1 - a)E_{DFX} + E_C \qquad (1)$$

where $a = 0.2$ is empirical parameter, E_{DFX} and E_C are exchange and correlation functionals including local and semilocal terms. The original (B3LYP) [7] as well as more recent hybrid functionals often achieve chemical accuracy in properties predictions [8–10]. Moderate computational costs brings hopes for TD-DFT to be a good candidate for universal black-box approach of spectroscopic accuracy. However, extensive testing revealed various drawbacks in the commonly used TD-DFT implementations, and necessitated further improvements (see recent review [5] for more details).

One improvement important for spectroscopic predictions involves the construction of range-separated hybrid functionals [11, 12], where fraction of HF exchange $a(r_{12})$ depends on the electron–electron distance according to the standard error function [13], linear combination of Gaussian functions or Yukawa potential [14]. In this study we use long-range corrected LC-BLYP [where $a(0) = 0$ and $a(\infty) = 1$ in Eq. (1)] [15], with correct asymptotic for interelecton separation. We also employ coulomb-attenuated functional CAM-B3LYP [where $a(0) = 0.19$ and $a(\infty) = 0.65$ in Eq. (1)], introduced as a compromise in accuracy between ground and excited state properties [13]. The range separated functionals were shown to improve the excitation energies and transition dipole moments for the Rydberg and some of the Charge-Transfer excited states [16], while no change in accuracy was reported for the valence states on average [17].

Another direction of improvement involves the second and higher order corrections to the excitation energies, obtained in linear-response TD-DFT [18]. Perturbative corrections to the oscillator strengths are also possible [19]. On the other hand, the exchange-correlation functional may have strong dependence on frequency [20], and perturbation treatment is not expected to be accurate in these cases. As we will show below, the inaccuracy of the linear response approximation can be corrected without resorting to perturbation treatment.

In this contribution, we focus on the predictions of the vertical transition energy for the excited state of HOMO-LUMO nature. This
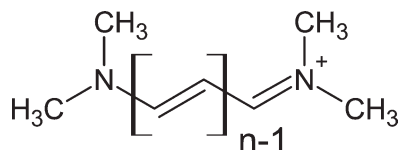
SCHEME 1. Homologous series of carbocyanines ($n = 1–7$) considered in this work.

approximately corresponds to the wavelength maximum λ_{max} on the linear absorption spectrum. Carbocyanines [Scheme 1] present the infamous example of well-documented failure of adiabatic TD-DFT [21, 22]. While conventional TD-DFT correctly predicts λ_{max} increase with the increase in conjugation length, this increase is underestimated for carbocyanines by more than 100 nm. We will analyze the electronic structure of these two excited states, test long-range corrected exchange-correlation functional and note that it improves the situation only partially. Finally, we apply static DFT to evaluate the energy of excited state based on relaxed electron density of the excited state and find that it leads to the excellent agreement with experiment.

All results reported here are obtained with the standard release of Gaussian 2009, Rev. A2 [23]. Molden program is used for all visualizations [24]. Geometry was optimized at B3LYP/TZVP theory level, the same basis set was used to calculate the excitation energies. For a fair comparison with the experiment the polarizable continuum model was used in combination with TD-DFT for the cationic cyanines (experimentally investigated in dichloroethane) [25]. The corresponding wavelengths are reported in the Table I. The relaxed density of the excited state as well as the ground state was obtained to plot the difference density (Fig. 1) and as well as to evaluate the energy.

As one can see from Table I, the popular global hybrid B3LYP performs well for the short chain homologs. However, the deviation from the ex-

perimental wavelength gradually increase as the conjugation chain becomes longer and reach 50 nm for the homolog with four double bonds. For the homologs with the longest chains B3LYP underestimates the absorption wavelength by nearly 130 nm, in agreement with previous studies. Disastrous performance of TD-DFT for the lowest excited state in polymethines was reported repeatedly (see the recent study [22] and references therein). Neither taking solvent into account with Polarizable Continuum Model, nor use of long-range corrected hybrid functionals instead of the global hybrids were reported [10] and in [26] to bring significant improvements. Double-hybrid functionals, developed recently, also fail for cyanines [27] to the best of our knowledge the reason for the large errors was not yet identified.

One of the known problems in linear response TD-DFT is that it produces purely single excitations. Although in the second order TD-DFT double excitations do appear, they do not mix with the single ones [28]. This neglect of the double excited determinants in TD-DFT description of the excited states becomes critical for certain systems. For instance, WFT methods indicate [29], that the lowest A_g state in polyenes acquire larger fraction of this double excitation character with the growth of the conjugated chain. In contrast to polyenes, the lowest excited state in cyanines has been shown by CAS-PT2 method to be almost pure H->L excitation [30] with no appreciable multiconfiguration character.

To identify the reason why TD-DFT fails, we evaluated the total density of the molecule **C2** in the ground and first excited states and plotted their difference on Figure 1(a). Similar difference densities were obtained for other homologs (not shown). In all cases the difference density had maxima (accumulation) at the centers of the even atoms of the conjugated chain, and minima (depletion) at the centers of the odd atoms. The

TABLE I _____

Absorption wavelengths (nm) obtained with TZVP basis set and compared to experimental values, collected in dichloromethane for C1–C7 [25].

Molecule	C1	C2	C3	C4	C5	C6	C7
TD-B3LYP	223	293	381	467	552	628	712
TD-CAM-B3LYP	215	289	380	471	563	649	743
TD-LC-BLYP	209	286	382	482	587	690	811
B3LYP energy/TD-LC-BLYP density	245	334	442	547	651	744	843
Experiment	224	313	416	519	625	735	848
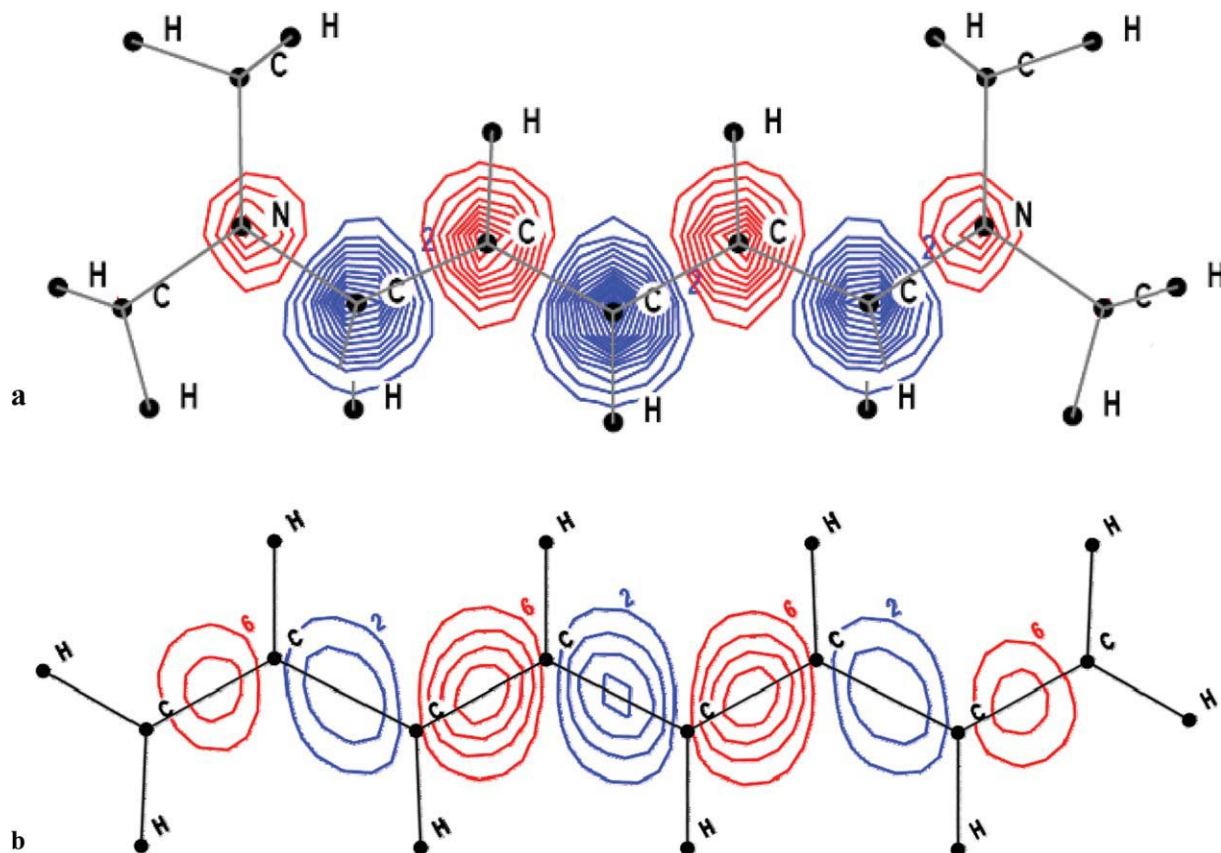
FIGURE 1. Contour values of the difference in total density between the lowest excited state and the ground state for (a) **C2** molecule and (b) octatetraene obtained at TD-DFT/B3LYP/TZVP level of theory and dissected at 1 Å above the molecular plane (each contour value is 0.002e/Å). For carbocyanine the maxima (electron accumulation upon the excitation, blue contours) are centered at the even atoms of the conjugated chain, and the minima (electron depletion, red contours) are localized around the odd atoms of the chain (both C and N). For the polyene the maxima and minima are centered in the midpoints of the single and double bonds, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

main feature in electron density redistribution was the charge transfer from the odd atoms. of the conjugated chain (both N and C atoms), to the even atoms of the chain. For comparison, the difference density in polyene, shown on Figure 1(b), has maxima and minima at the midpoints of the single and double bonds, with the absolute values lower by factor of ~3. Thus, the lowest singlet excitation in carbocyanines has a peculiar charge transfer character, where the charge is transferred by a short distance of one covalent bond instead of between donor and acceptor chemical groups.

It is firmly established that excitations with large charge transfer character are not described well by TD-DFT in combination with global hybrid exchange-correlation functionals, and long-range corrected functionals improve the descrip-

tion [16]. Indeed, one can see from the Table I that for the largest molecule **C7**, LC-BLYP lowers the deviation from the experiment to 38 nm compared to B3LYP with the deviation of 136 nm. CAM-B3LYP produced an intermediate result of 105 nm. This result is in apparent disagreement with the previous study [10], reported range-separates hybrids to yield no improvement. This disagreement can be explained by the difference between the damping parameter for LC-BLYP used here (0.47) and the damping parameter used in (0.33) [10].

To make further improvements in the predicted absorption wavelengths, one has to consider approximations underlying TD-DFT formalism. In essence, the use of the linear response approximation in TD-DFT signifies that excitation

energy is evaluated in the potential generated by the ground state density [31]. This may be a good approximation when excitation does not change the density drastically, but is it not a good approximation for carbocyanines. One can expect, that methods that avoid making such approximation would be more successful. Indeed, the extensions of the static DFT to description of the excited states (known as ΔSCF or eDFT) were found to work better in problematic case of polymethine dyes [32]. Unfortunately, the self-consistent search for a single KS determinant with a Fermi hole is often complicated by convergence problems. However, if the exact electron density of an excited state is known, the common exchange-correlation functionals developed for the ground states recover the excited state energy rather accurately [33].

Here we propose to use the frozen densities of the excited states that are obtained within the TD-DFT approach to evaluate the excitation energies beyond the linear response approximation. We will use the fact that canonical natural orbitals, which diagonalize the total electron density of the excited state, often have occupations close to 2 and 0, except for one pair with occupations close to 1. This allows us to approximate the electron density of the excited state by a single KS determinant with two open shells (coupled either high or low spin). The application of the sum rule then allows one to extract the energy of the singlet state from the energies of the low and high-spin determinants:

$$E_S = 2E_{M=0} - E_T$$

The application of the scheme described above resulted in much improved wavelengths, presented in the last line of the Table I. As B3LYP functional gives a better description of the ground state, it was used to evaluate the energy on LC-BLYP orbitals. The use of B3LYP orbitals produced very similar results (not shown). The frozen density approximation predicts the larger homologs quantitatively, and the error for the entire series is less than 25 nm.

Thus, excited state density of the specific state obtained with TD-DFT, allows us to evaluate the excited state energy directly by evoking frozen density approximation. These energies were found to be more accurate than the ones predicted by TD-DFT for at least one type of the polymethine dyes. On the other hand, the conver-gence problems of ΔSCF are avoided. Clearly, the new method provides improved determination of excitation energies, which goes beyond the linear response approximation. It is in need of further numerical testing, which is currently in progress. So far the results are encouraging, and will be published elsewhere.

References

1. Matsuura, A.; Sato, H.; Sotoyama, W.; Takahashi, A.; Sakurai, M. J Mol Struct (Theochem) 2008, 860, 119.
2. Baraldi, I.; Momicchioli, F.; Ponterini, G.; Vanossi, D. In Advances in Quantum Chemistry; Academic Press: San Diego, 2000; Vol 36, p 121.
3. Jacquemin, D.; Beljonne, D.; Champagne, B.; Geskin, V.; Bredas, J. L.; Andre, J. M. J Chem Phys 2001, 115, 6766.
4. Casida, M. E. In Recent Advances in Density Functional Methods; Chong, D. A., Ed.; World Scientific: Singapore, 1995, p 155.
5. Casida, M. E. J Mol Struct (Theochem) 2009, 914, 3.
6. Iordanov, T. D.; Davis, J. L.; Masunov, A. E.; Levenson, A.; Przhonska, O. V.; Kachkovski, A. D. Int J Quantum Chem 2009, 109, 3592.
7. Becke, A. D. J Chem Phys 1993, 98, 5648.
8. Sousa, S. F.; Fernandes, P. A.; Ramos, M. J. J Phys Chem A 2007, 111, 10439.
9. Zhao, Y.; Truhlar, D. G. J Chem Theory Comput 2008, 4, 1849.
10. Jacquemin, D.; Wathelet, V.; Perpete, E. A.; Adamo, C. J Chem Theory Comput 2009, 5, 2420.
11. Henderson, T. M.; Janesko, B. G.; Scuseria, G. E. J Phys Chem A 2008, 112, 12530.
12. Chai, J. D.; Head-Gordon, M. J Chem Phys 2008, 128, 15.
13. Yanai, T.; Tew, D. P.; Handy, N. C. Chem Phys Lett 2004, 393, 51.
14. Akinaga, Y.; Ten-No, S. Int J Quantum Chem 2009, 109, 1905.
15. Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. J Chem Phys 2001, 115, 3540.
16. Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. J Chem Phys 2004, 120, 8425.
17. Jacquemin, D.; Perpete, E. A.; Scuseria, G. E.; Ciofini, I.; Adamo, C. J Chem Theory Comput 2008, 4, 123.
18. Ziegler, T.; Seth, M.; Krykunov, M.; Autschbach, J.; Wang, F. J Mol Struct (Theochem) 2009, 914, 106.

19. Appel, H.; Gross, E. K. U.; Burke, K. Phys Rev Lett 2003, 90, 4.

20. Maitra, N. T.; Zhang, F.; Cave, R. J.; Burke, K. J Chem Phys 2004, 120, 5932.

21. Jacquemin, D.; Perpete, E. A.; Ciofini, I.; Adamo, C. Acc Chem Res 2009, 42, 326.

22. Fabian, J. Dyes Pigment 2010, 84, 36.

23. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R. E.; Stratmann, O.; Yazyev, A. J.; Austin, R.; Cammi, C.; Pomelli, J. W.; Ochterski, R.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian: Wallingford, CT, 2009.

24. Schaftenaar, G.; Noordik, J. H. J Comput Aided Mol Des 2000, 14, 123.

25. Malhotra, S. S.; Whiting, M. C. J Chem Soc 1960, 6, 3812.

26. Jacquemin, D.; Perpete, E. A.; Scalmani, G.; Frisch, M. J.; Kobayashi, R.; Adamo, C. J Chem Phys 2007, 126, 144105.

27. Grimme, S.; Neese, F. J Chem Phys 2007, 127, 154116.

28. Mikhailov, I. A.; Tafur, S.; Masunov, A. E. Phys Rev A 2008, 77, 012510.

29. Marian, C. M.; Gilka, N. J Chem Theory Comput 2008, 4, 1501.

30. Schreiber, M.; Buß, V.; Fülscher, M. P. Phys Chem Chem Phys 2001, 3, 3906.

31. Hu, C. P.; Sugino, O. J Chem Phys 2007, 126.

32. Toutchkine, A.; Han, W. G.; Ullmann, M.; Liu, T. Q.; Bashford, D.; Noodleman, L.; Hahn, K. M. J Phys Chem A 2007, 111, 10849.

33. Cheng, C. L.; Wu, Q.; Van Voorhis, T. J Chem Phys 2008, 129, 9.