Prediction of charge-transfer excitations in coumarin-based dyes using a range-separated functional tuned from first principles

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We study the description of charge-transfer excitations in a series of Coumarin-based donor-bridge-acceptor dyes. We show that excellent predictive power for the excitation energies and oscillator strengths in these systems is obtained by using a range-separated hybrid functional within the generalized Kohn-Sham approach to time-dependent density functional theory. Key to this success is a step for tuning the range separation parameter from first principles. We explore different methods for this tuning step, that are variants of a recently suggested approach for charge transfer excitations [T. Stein, L. Kronik, and R. Baer, J. Am. Chem. Soc. 131, 2818 (2009)]. We assess the quality of prediction by comparing to excitation energies previously published for the same systems using the approximate coupled-cluster singles and doubles (CC2) method.

Charge transfer excitations in organic systems have attracted much attention as the basis of novel photovoltaic devices.¹² In particular, novel organic dyes¹⁶ have been suggested as a practical means for improving the efficiency of dye-sensitized solar cells, in which charge carriers, photo-generated at the dye, are separated into a typically electron conducting nano-crystalline semiconductor and a typically hole conducting electrolyte.⁷,⁸

Computational studies can be of much value for rationally designing novel charge transfer dyes and for understanding the chemical and physical basis of their properties. Time-dependent density functional theory (TDDFT)⁹ would appear to be the natural first principles theoretical framework for such studies: It is an exact theory in principle¹⁰ and its standard approximate forms have already been proven to yield useful accuracy for the description of excited states in general and optical spectra in particular in broad classes of relatively large systems.¹¹,¹²

Most TDDFT studies of optical absorption spectra are performed by solving a linear-response form of the time-dependent Kohn-Sham equations, using either a (semi-)local or a hybrid exchange-correlation functional, within the adiabatic approximation (i.e., without explicit time-dependence in the functional).¹³,¹⁴ Unfortunately, this procedure fails for charge transfer excitations.¹⁵-¹⁷ Specifically, for long-range transfer excitations, where an electron is excited from a donor D to an acceptor A situated at a large distance R, Mulliken’s rule¹⁸ states that the excitation energy $h\nu_{CT}$ is given by the energy difference of the D…A and the D*…A' ground states, with an additional $1/R$ Coulomb attraction energy:

$$h\nu_{CT} = IP(D) - EA(A) - \frac{1}{R},$$

(1)

where $IP(D)$ and $EA(A)$ are the ionization potential (IP) of the donor and the electron affinity (EA) of the acceptor, respectively.

However, (semi-)local and standard hybrid functionals fail miserably in predicting this limit: The D…A to D+…A' energy difference predicted by them is significantly too low and the $1/R$ distance dependence is either entirely missing (in semi-local functionals) or only partially accounted for (in hybrid functionals). The first problem is a manifestation of a missing (in semi-local functionals) or inadequate (in hybrid functionals) derivative discontinuity¹⁹ and the second is due to spurious self-repulsion of an electron.¹⁶

Much recent work¹⁰-¹³ has been devoted to TDDFT calculations that alleviate these difficulties by using a range separated hybrid (RSH) functional²³,³⁴,³⁹ within the generalized time-dependent Kohn-Sham equation.³⁹,⁴¹ In this approach, the exchange energy functional is split into long- and short-range contributions, e.g., via $r^{-1} = r^{-1} \text{erf} \gamma r + r^{-1} \text{erfc} \gamma r$. The short-range exchange is then evaluated using a local potential, whereas the long-range part is evaluated using a Fock-like operator. In this way, the proper balance between short-range exchange and correlation (essential to many popularly used functionals) can be retained without sacrificing the correct long-range behavior of the potential.

If one postulates a system-independent value of $\gamma$, then a semi empirical approach, in which $\gamma$ is optimized using a molecular training set (see, e.g., ref. ²⁶), may be pursued. However, setting $\gamma$ to a fixed value is an approximation, as $\gamma$ is itself a functional of the electron density.³⁷,⁴⁰ Depending on the exact choice of functional, $\gamma$ may depend strongly on the system under study.²⁰,²¹,²⁴ Moreover, the value of $\gamma$ that is optimal for ground state properties may not necessarily be the one optimal for excited state properties.⁴⁰,⁴² Alternatively, it is possible to tune $\gamma$ from first principles by demanding that it satisfy some additional physical criterion that is relevant for the system and property under study (an issue elaborated below). This method has proven to be highly effective in various ground state studies.⁴³-⁴⁵ Recently, we have shown that such tuning also allows for an excellent description of charge transfer excitations in molecular complexes based on an aromatic donor and a tetracyanoethylene (TCNE)

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acceptor.\textsuperscript{20} This success comes about because the use of an RSH functional automatically eliminates the long-range self-repulsion and therefore obtaining the asymptotic $1/R$ attraction energy. Tuning $\gamma$ can then be viewed as a practical means of addressing the derivative discontinuity problem. Thus, $\gamma$ tuning provides for a TDDFT method of predicting charge transfer states and their properties that is self-contained and requires neither empirical calibration nor input from high-level wave function methods.

In our previous study,\textsuperscript{20} the donor and acceptor units were well-separated. However, many practical charge transfer systems are of the donor-bridge-acceptor type, where there is some degree of arbitrariness in the distinction between the different sub-units. It is one of the purposes of this article to examine whether our suggested approach is equally successful in this more general scenario and to explore other procedures for tuning $\gamma$ in a self-contained first principles approach.

We focus this study on the coumarin-based dyes suggested by Hara et al.\textsuperscript{3,5} for three reasons. First, these dyes were designed and synthesized specifically for enhancing charge transfer excitations in the context of dye sensitized solar cells. Second, Kurasihige et al. have studied theoretically the properties of $s_0 \rightarrow s_1$ charge-transfer excitations in these dyes.\textsuperscript{46} As expected in light of the above discussion, they found that TDDFT methods relying on the B3LYP functional yield excitation energies much lower, sometimes by as much as 0.5 eV, when compared to approximate coupled-cluster singles-doubles (CC2)\textsuperscript{47} calculations. Third, Wong and Cordaro\textsuperscript{51} subsequently employed the RSH functional developed by Hirao et al.\textsuperscript{23,35} to study the same set of dyes. They found that a single range-separation parameter $\gamma$, determined via a best fit to the CC2 results, enabled description of the entire series of dyes. As is again to be expected from the above discussion, the optimal value for $\gamma$ determined by Wong and Cordaro was 0.17$a_0^{-1}$, a value significantly smaller value than that typically used for ground state properties ($\sim$0.3-0.5 $a_0^{-1}$ 22,35,43,48,50). Taken together, these studies and provide useful reference data and establish the importance of developing a first principles $\gamma$ tuning step, which is the main purpose of the present paper.

All calculations presented in this work were performed with the BNL RSH functional,\textsuperscript{53} as implemented in version 3.2 of QCHEM.\textsuperscript{51} The 6-31+G(p,d) basis set recommended in ref. 21 was used throughout.

We start by examining the "parent" coumarin-based dye, C343. Figure 1 shows the dependence of the charge-transfer excitation energy on the range-separation parameter $\gamma$. The excitation energy increases significantly with increasing $\gamma$ in the range [0.1,0.6] $a_0^{-1}$, at a rate of almost 0.1 eV per 0.1 $a_0^{-1}$ change in $\gamma$. Taking the optimal ground-state $\gamma$ value\textsuperscript{51} of 0.5 $a_0^{-1}$ leads to an overestimation of the excitation energy (relative to the CC2 calculation) of 0.35 eV. This overestimate is of the same order of magnitude as the typical B3LYP underestimate, clearly indicating that a preliminary step of tuning $\gamma$ is indeed essential.

![Figure 1: excitation energies of the C343 dye as a function of the range parameter $\gamma$ using BNL/6-31+G(d,p).](image)

The $\gamma$ tuning approach suggested in our previous work\textsuperscript{20} was based on the fact that that in exact Kohn-Sham, the energy of the HOMO orbital is equal to the negative of the IP.\textsuperscript{52,53} Thus, a simple first principles criterion for $\gamma$ could have been

$$-\varepsilon_{\text{HOMO}} = E_{\text{ip}} - N; \gamma - E_{\text{ip}} - N; \gamma,$$  \hspace{1cm} (2)

where $\varepsilon_{\text{HOMO}}$ is the HOMO energy per a specific choice of $\gamma$ and the right hand side of the equation is the energy difference between the ground state energies of the N and the N-1 electron system, per the same $\gamma$. In long-range charge-transfer systems, however, this criterion is insufficent because, as Mulliken’s rule (Eq. (1)) shows, we really need to consider two ground states – that of the neutral donor and that of the negatively ionized acceptor. Because there is only one parameter but two conditions, we minimize the overall discrepancy using the following function:\textsuperscript{20}

$$J_{\gamma} = \sum_{i=D,A} |\varepsilon_{\gamma} - E_{\text{ip}} - N_i; \gamma|,$$  \hspace{1cm} (3)

where $\varepsilon_{\gamma} - E_{\text{ip}} - N_i; \gamma$, $i = D,A^-.$

In the application of this method to the present problem, it is not obvious how to define which part of the donor-bridge-acceptor molecule is the acceptor and which is the donor. Here, we chose to identify the pertinent moieties chemically, "disconnect" them from the molecule (adding hydrogen atoms where necessary), and employ the above criterion.

An alternative approach is to set $\gamma$ by minimizing the function:
\[ J_2 \gamma = \left| \varepsilon_{HOMO}^N + \text{IP}^N N \right| + \left| \varepsilon_{LUMO}^N + 1 + \text{IP}^N N + 1 \right|, \]  
(4)

where \( \text{IP}^N N = E_p^N N - 1; \gamma = -E_p^N N; \gamma \) and the quantities refer to the system as a whole. Effectively, this second approach equates the IP of Mulliken’s limit with the HOMO of the neutral molecule and the EA of Mulliken’s limit with the HOMO of the negatively charged molecule, under the assumption that the donor and acceptor moieties dominate, respectively, the IP and EA. We note that one can instead demand a similar condition involving the LUMO and the EA of the neutral molecule:

\[ J_3 \gamma = \left| \varepsilon_{HOMO}^N + \text{IP}^N N \right| + \left| \varepsilon_{LUMO}^N + 1 + \text{IP}^N N + 1 \right|, \]  
(5)

even though there is no formal equivalent to Eq. (4) involving the LUMO. Surprisingly, results obtained with Eq. (5) were essentially identical to those obtained with Eq. (4), indicating a negligible derivative discontinuity contribution, a point that will be considered in more detail elsewhere. In light of this equivalence, here we only present results obtained with Eq. (4).

Table 1: Excitation energies (eV) and oscillator strengths of coumarin-based dye systems considered in this paper.

<table>
<thead>
<tr>
<th>System</th>
<th>LC21 Exc</th>
<th>BNL*/J1 f</th>
<th>BNL*/J2 f</th>
<th>CC246 f</th>
</tr>
</thead>
<tbody>
<tr>
<td>C343</td>
<td>3.4</td>
<td>0.6</td>
<td>3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>NKX 2388 s-trans</td>
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<td>0.9</td>
<td>3.1</td>
<td>1.0</td>
</tr>
<tr>
<td>NKX 2388 s-cis</td>
<td>2.9</td>
<td>0.8</td>
<td>2.9</td>
<td>0.9</td>
</tr>
<tr>
<td>NKX 2311 s-trans</td>
<td>2.9</td>
<td>1.3</td>
<td>2.9</td>
<td>1.6</td>
</tr>
<tr>
<td>NKX 2311 s-cis</td>
<td>2.7</td>
<td>1.1</td>
<td>2.7</td>
<td>1.3</td>
</tr>
<tr>
<td>NKX 2586 s-trans</td>
<td>2.8</td>
<td>1.8</td>
<td>2.8</td>
<td>2.1</td>
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<tr>
<td>NKX 2586 s-cis</td>
<td>2.7</td>
<td>1.5</td>
<td>2.6</td>
<td>1.7</td>
</tr>
<tr>
<td>NKX 2677</td>
<td>2.7</td>
<td>1.8</td>
<td>2.7</td>
<td>2.0</td>
</tr>
</tbody>
</table>

We tested both tuning schemes on the same set of coumarin-based dye systems computed in ref. 21. In the absence of gas phase experimental data, we compared the results of the two methods to the gas phase CC2 calculations. We show the results in Table 1 and graphically display their deviations in Figure 2. The deviation of the RSH-TDDFT excitation energies from those obtained by CC2 is given in the top panel of Figure 2. Clearly, the deviation is small. For the results previously obtained21 from a BLYP-based RSH functional by fitting the CC2 results, the average deviation is zero by construction. Importantly, the mean absolute deviation (MAD) is a small 0.03 eV, showing that for this family a single value of \( \gamma \), if chosen properly, is sufficient for a proper description throughout. Results obtained with the first tuning approach, which we denote as BNL*/J1, possess a mean deviation of 0.02 eV and an MAD of 0.05 eV, i.e., the BNL*/J1 results are also very close to the CC2 ones. This is an important result because it shows that the accuracy obtained from first principles without consideration of the CC2 data is essentially the same as that obtained by explicit fitting to these data. Results obtained with the second tuning approach, which we denote as BNL*/J2, possess a somewhat larger mean deviation and MAD, of ~0.1 eV. This is still an entirely acceptable difference. One should also bear in mind that the CC2 method is not free from approximations and that its deviations from more accurate methods, e.g., complete active-space second-order perturbation theory (CASPT2) can easily be of similar magnitude.  

Figure 2: Deviation from CC2 results46 for \( s_0 \rightarrow s_1 \) transitions, in the coumarin-based dye systems, of TDDFT calculations performed with the LC-BLYP functional21 and the BNL246 functional. The range separation parameter \( \gamma \) was obtained from fitting the CC2 data in the former functional and from first-principles tuning in the latter functional. Top panel shows deviation in excitation energies; and bottom panel shows relative deviation of oscillator strengths.

A significant practical advantage of the coumarin-based dyes studied here is that they exhibit strong oscillator strengths. In the middle panel of Figure 2, we show the relative deviation of the computed TDDFT oscillator strengths from those given by CC2. Again, BNL*/J1 has a lower deviation, with mean deviation and MAD of about 5%, whereas BNL*/J2 typically exhibits deviations that are twice as large. Interestingly, the results of both BNL* approaches are in better agreement with the CC2 data than those obtained by explicit fitting. Although BNL*/J1 is more accurate than BNL*/J2, both methods have acceptable accuracy and are of predictive value.
In Figure 3 we show the range-separation parameter, γ, determined by BNL*/J1 or J2 methods. In BNL*/J1, γ is consistently within the interval [0.23,0.26] a₀⁻¹ whereas in BNL*/J2 γ is noticeably smaller and is in the interval [0.17,0.21] a₀⁻¹. In light of Figure 1, these facts immediately explain why excitation energies predicted with BNL*/J1 are smaller by ~0.1 eV. Not only are the values of γ different, but the trends are not always the same either. For example, γ in BNL*/J1 is similar throughout, whereas in BNL*/J2 γ for C343 is markedly larger. It is reasonable that C343 would stand out. This "parent" dye differs from all others in both the type of donor and acceptor groups and in the bridge length. Hence, we would expect that this is where the difference in the two methods would be most pronounced. That our method yields quantitatively useful results even for this more difficult case is a clear indication of its generality.

In conclusion, we have shown that charge transfer excitation energies and oscillator strengths of donor-bridge-acceptor systems can be performed reliably using TDDFT with a range-separated hybrid functional. The success of the approach relies on a first principles procedure for tuning the range-parameter.

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