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

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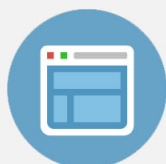
Prediction of charge-transfer excitations in coumarin-based dyes using a range-separated functional tuned from first principles

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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, which are variants of a recently suggested approach for charge-transfer excitations [T. Stein *et al.*, 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. © *2009 American Institute of Physics*. [doi:10.1063/1.3269029]

I. INTRODUCTION

Charge-transfer excitations in organic systems have attracted much attention as the basis of novel photovoltaic devices.[1,2] In particular, novel organic dyes[3–6] have been suggested as a practical means for improving the efficiency of dye-sensitized solar cells, in which charge carriers photogenerated at the dye are separated into a typically electron conducting nanocrystalline 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) (Ref. 9) would appear to be the natural first principles theoretical framework for such studies. It is an exact theory in principle[10] and its standard approximate forms have already been proven to yield usefully accurate descriptions of excited states and optical spectra in broad classes of relatively large systems.[11–14]

Most TDDFT studies of optical absorption spectra are performed by solving a linear-response form of the time-dependent Kohn–Sham equations within the adiabatic approximation (i.e., without explicit time-dependence in the functional).[15,16] Unfortunately, when employed with either a (semi)local or a standard hybrid exchange-correlation functional, this procedure fails for charge-transfer excitations.[17–19] 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 rule[20] states that the excitation energy $h\nu_{CT}$ is given by the energy difference of the $D\cdots A$ and the $D^+\cdots A^-$ ground states, with an additional $1/R$ Coulomb attraction energy

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

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 in predicting this limit. The $D\cdots A$ to $D^+\cdots A^-$ energy difference, as predicted from their eigenvalues spectra, is by them is significantly too low and the $1/R$ distance dependence is either entirely missing (in semilocal functionals) or only partially accounted for (in standard hybrid functionals). The first problem is a manifestation of a missing (in semilocal functionals) or inadequate (in standard hybrid functionals) derivative discontinuity[17,21] and the second is due to spurious electron self repulsion.[18]

Much recent work[11,21–35] has been devoted to TDDFT calculations that alleviate these difficulties by using a range separated hybrid (RSH) functional[25,36–41] within the generalized time-dependent Kohn–Sham equation.[41–43] In this approach, suggested by Savin and co-workers,[44–46] the exchange energy functional is split into long- and short-range contributions, e.g., via $r^{-1} = r^{-1} \operatorname{erf}(\gamma r) + r^{-1} \operatorname{erfc}(\gamma r)$. 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.[47]

If one postulates a system-independent value of γ, then a semiempirical approach, in which γ is optimized using a molecular training set (see, e.g., Ref. 28), may be pursued. However, setting γ to a fixed value is an approximation, as γ is itself a functional of the electron density.[39,42,48] Depending on the exact choice of functional, γ may depend strongly on the system under study.[22,23,26] Moreover, the value of γ that is optimal for ground state properties may not necessarily be

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the one optimal for excited state properties.[28,42] Alternatively, it is possible to tune γ 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.[42,49,50] 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 acceptor.[22] This success comes about because the use of an RSH functional automatically eliminates the long-range self-repulsion and therefore obtains the asymptotic $1/R$ attraction energy. Tuning γ can then be viewed as a practical means of addressing the derivative discontinuity problem. Thus, γ 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,[22] 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 subunits. Here, we examine whether our suggested approach is equally successful in this more general scenario and explore other procedures for tuning γ in a physically motivated, self-contained first principles approach. We focus this study on the coumarin-based dyes suggested by Hara *et al.*[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, Kurashige *et al.*[51] have studied theoretically the properties of $s_0 \rightarrow s_1$ charge-transfer excitations in these dyes. As expected in light of the above discussion, they found that TDDFT methods relying on the B3LYP functional [using the 6-31+G(d,p) basis set] yield excitation energies that are much lower, sometimes by as much as 0.5 eV, then those obtained using approximate coupled-cluster singles-doubles (CC2) (Ref. [52]) calculations [with the SV(P) basis set]. Third, Wong and Cordaro[23] subsequently employed the LC-BLYP RSH functional developed by Hirao *et al.*[25,37] [again with the 6-31+G(d,p) basis set] to study the same set of dyes. They found that a single range-separation parameter γ, 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 γ determined by Wong and Cordaro was $0.17a_0^{-1}$, a value significantly smaller value than that typically used for ground state properties [$\sim 0.3 – 0.5a_0^{-1}$ (Refs. [24], [37], [49], [53], and [54])]. Taken together, these studies provide useful reference data and establish the importance of developing a *nonempirical* γ-tuning step, which is the main purpose of the present paper.

II. COMPUTATIONAL DETAILS

All TDDFT calculations presented in this work were performed with the Baer, Neuhauser, and Livshits (BNL) RSH functional,[49] as implemented in version 3.2 of Q-CHEM.[55] We studied the same set of molecules given in Fig. 1 of Ref. [23].

All ground state structures were optimized within a B3LYP calculation. We used the 6-31+G(p,d) basis set throughout for consistency with the above mentioned LC-BLYP (Ref. [16]) and B3LYP (Ref. [51]) TDDFT calculations of the same molecules.[23] We have additionally verified that this is a sufficiently large basis set by computing the excitation energies for the C343 "parent dye" molecule with basis sets as large as 6-311++G(2d,2p). The maximal difference found was 0.025 eV, which is not significant for the purposes of our discussion below.

We now provide some details of the BNL functional form. A complete account, including details of the derivation, can be found in Refs. [39] and [49]. The basic idea behind the BNL functional is to consider an interelectron potential of the type

$$u_\gamma(r) = \frac{\mathrm{erf}(\gamma r)}{r}. \tag{2}$$

For $\gamma \rightarrow \infty$, this potential reduces to the usual Coulomb one, whereas for $\gamma = 0$ it reduces to the case of noninteracting electrons. Using adiabatic connection theorem considerations, it is then possible to show[49] that the exchange-correlation energy can be written as

$$E_{\mathrm{XC}}[n] = K_X^\gamma[n] + E_{\mathrm{XC}}^\gamma[n], \tag{3}$$

where the first term is the explicit exchange with respect to the interaction $u_\gamma(r)$

$$K_X^\gamma = -\frac{1}{4} \int \int P[n](\mathbf{r},\mathbf{r}') u_\gamma(|\mathbf{r}-\mathbf{r}'|) d^3 r d^3 r', \tag{4}$$

where $P[n](\mathbf{r},\mathbf{r})$ is the density matrix of noninteracting particles. The second term is given by

$$E_{\mathrm{XC}}^\gamma[n] = \langle \psi_{\mathrm{gs}} | \hat{Y}_\gamma | \psi_{\mathrm{gs}} \rangle - \frac{1}{2} \int \int n(\mathbf{r}) n(\mathbf{r}') y_\gamma(|\mathbf{r}-\mathbf{r}'|) d^3 r d^3 r', \tag{5}$$

$y_\gamma(r) = \mathrm{erfc}(\gamma r)/r$, $Y_\gamma = \frac{1}{2}\Sigma_{i \neq j} y_\gamma(|\mathbf{r}_i - \mathbf{r}_j|)$, and ψ_{gs} is the exact ground state wave function of the system.

In practice E_{XC}^γ is approximated via a semilocal energy functional. The K_X^γ term guarantees the correct asymptotic behavior of the functional, whereas the semilocal form allows for an adequate treatment of dynamic correlation. Specifically, in the BNL the exchange is given by Savin's expression for exchange energy per particle of the complementary error function potential.[56] The correlation is given by the standard LYP expression from which 10% of the exchange expression is subtracted—a procedure found empirically to yield the best agreement with the standard G2 benchmark set.[49]

III. RESULTS AND DISUCSSION

We start our analysis by examining the "parent" coumarin-based dye, C343. Figure 1 shows the dependence of the charge-transfer excitation energy on the range-separation parameter γ. The excitation energy increases significantly with increasing γ in the range $[0.1, 0.6]a_0^{-1}$, at a rate of almost 0.1 eV per $0.1a_0^{-1}$ change in γ. Taking the
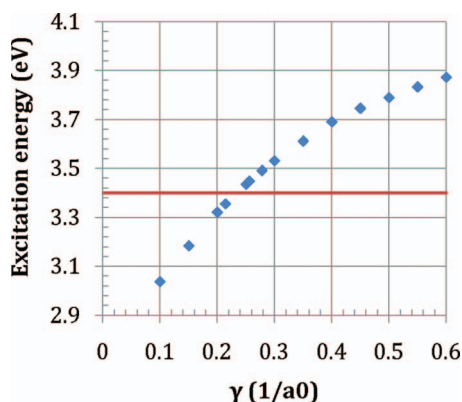
FIG. 1. Excitation energy of the C343 dye as a function of the range parameter γ using BNL[49]/6-31+G(d,p). The CC2 result (Ref. [51]) is given as a horizontal line for comparison.

optimal ground-state γ value[49] of $0.5a_0^{-1}$ leads to an overestimation of the excitation energy (relative to the CC2 calculation, which is 3.4 eV) 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 γ is indeed essential.

The γ tuning approach suggested in our previous work[22] was based on the fact that that in exact Kohn–Sham theory, the energy of the HOMO orbital is equal to the negative of the IP.[57,58] Thus, a simple criterion for γ could have been

$$-\varepsilon_{\mathrm{HOMO}}^{\gamma} = E_{\mathrm{gs}}(N-1;\gamma) - E_{\mathrm{gs}}(N;\gamma), \qquad (6)$$

where $\varepsilon_{\mathrm{HOMO}}^{\gamma}$ is the HOMO energy per a specific choice of γ 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 γ. In long-range charge-transfer systems this criterion is insufficient 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:[22]

$$J_1(\gamma) = \sum_{i=D,A^-} \left| \varepsilon_{\mathrm{HOMO}}^{\gamma,i} + \mathrm{IP}_i^{\gamma}(N_i) \right|, \qquad (7)$$

where $\mathrm{IP}_i^{\gamma}(N_i) = E_{\mathrm{gs}}^i(N_i-1;\gamma) - E_{\mathrm{gs}}^i(N_i;\gamma)$, $i=D,A^-$.

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.[59]

An alternative approach is to set γ by minimizing the function

$$J_2(\gamma) = \left| \varepsilon_{\mathrm{HOMO}}^{\gamma}(N) + \mathrm{IP}^{\gamma}(N) \right| + \left| \varepsilon_{\mathrm{HOMO}}^{\gamma}(N+1) \right.$$
$$\left. + \mathrm{IP}^{\gamma}(N+1) \right|, \qquad (8)$$

where $\mathrm{IP}^{\gamma}(N) = E_{\mathrm{gs}}(N-1;\gamma) - E_{\mathrm{gs}}(N;\gamma)$ 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 which, barring relaxation effect, is the same as the IP of the negatively charged molecule) 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 of the neutral molecule and the EA

$$J_3(\gamma) = \left| \varepsilon_{\mathrm{HOMO}}^{\gamma}(N) + \mathrm{IP}^{\gamma}(N) \right| + \left| \varepsilon_{\mathrm{LUMO}}^{\gamma}(N) + \mathrm{IP}^{\gamma}(N+1) \right|, \qquad (9)$$

even though there is no formal equivalent to Eq. (8) involving the LUMO. Surprisingly, results obtained with Eq. (9) were essentially identical to those obtained with Eq. (8), indicating a negligible[22] discontinuity contribution, a point that will be considered in more detail elsewhere. In light of this equivalence, below we only present results obtained with Eq. (8).

We tested both tuning schemes on the same set of coumarin-based dye systems computed in Ref. [23]. 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 I and graphically display their deviations in Fig. 2. We show the deviations of the RSH-TDDFT excitation energies from those obtained by CC2 in the top panel of Fig. 2. Clearly, the deviations are small. For the results previously obtained[23] from a BLYP-based RSH functional by fitting the CC2 results, the average deviation is

TABLE I. Excitation energies (eV) and oscillator strengths of the coumarin-based dye systems considered in this paper.

System	LC-BLYP[a]		BNL*/J_1		BNL*/J_2		CC2[b]	
	Exc	f	Exc	f	Exc	F	Exc	f
C343	3.4	0.6	3.5	0.7	3.4	0.6	3.4	0.7
NKX 2388 s-trans	3.0	0.9	3.1	1.0	2.9	0.9	3.0	1.1
NKX 2388 s-cis	2.9	0.8	2.9	0.9	2.8	0.9	2.8	1.0
NKX 2311 s-trans	2.9	1.3	2.9	1.6	2.8	1.5	2.9	1.5
NKX 2311 s-cis	2.7	1.1	2.7	1.3	2.6	1.2	2.7	1.3
NKX 2586 s-trans	2.8	1.8	2.8	2.1	2.6	2.0	2.8	2.0
NKX 2586 s-cis	2.7	1.5	2.6	1.7	2.5	1.7	2.7	1.7
NKX 2677	2.7	1.8	2.7	2.0	2.5	1.8	2.7	2.2

[a]Reference [23].
[b]Reference [51].

	C343	NKX 2388 s-trans	NKX 2388 s-cis	NKX 2311 s-trans	NKX 2311 s-cis	NKX 2586 s-trans	NKX 2586 s-cis	NKX 2677	Mean	MAD
■ Fit to CC2	-0.08	0.02	0.05	0.02	0.02	0	0	-0.04	0.00	0.03
■ BNL*1	0.01	0.09	0.11	0.03	0	-0.05	-0.05	-0.02	0.02	0.05
■ BNL*2 or 3	-0.08	-0.06	-0.01	-0.1	-0.11	-0.17	-0.17	-0.23	-0.12	0.12

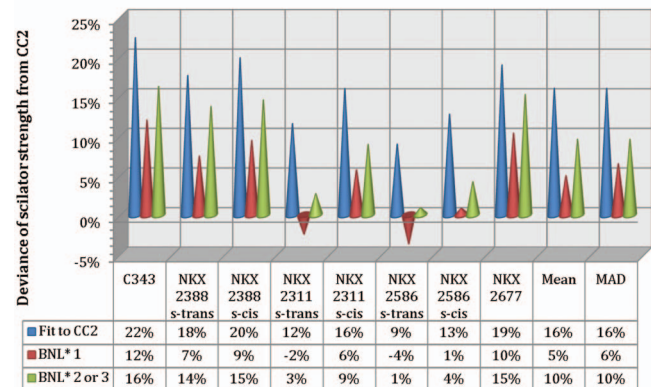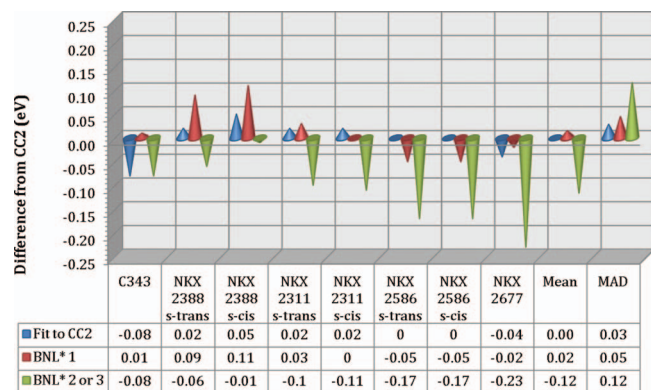|	C343	NKX 2388 s-trans	NKX 2388 s-cis	NKX 2311 s-trans	NKX 2311 s-cis	NKX 2586 s-trans	NKX 2586 s-cis	NKX 2677	Mean	MAD
■ Fit to CC2	22%	18%	20%	12%	16%	9%	13%	19%	16%	16%
■ BNL*1	12%	7%	9%	-2%	6%	-4%	1%	10%	5%	6%
■ BNL*2 or 3	16%	14%	15%	3%	9%	1%	4%	15%	10%	10%

FIG. 2. Deviations of TDDFT from CC2 (Ref. 51) for $s_0 \rightarrow s_1$ transitions, in the coumarin-based dye systems. TDDFT calculations performed with the LC-BLYP functional (Ref. 23) and the BNL (Ref. 49) functional. The range-separation parameter γ was obtained from fitting the CC2 data in the former functional and from nonempirical, physically motivated tuning in the latter functional. Top panel shows deviation in excitation energies. Bottom panel shows deviation of oscillator strengths.

zero by construction. Importantly, the mean absolute deviation (MAD) is a small 0.03 eV, showing that for this family a single value of γ, if chosen properly, is sufficient for a proper description throughout. Results obtained with the first tuning approach, which we denote as $BNL*/J_1$, possess a mean deviation of 0.02 eV and an MAD of 0.05 eV, i.e., the $BNL*/J_1$ results are also very close to the CC2 ones. This is an important result because it shows that the accuracy obtained from physical 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 $BNL*/J_2$, 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.[60]

A significant practical advantage of the coumarin-based dyes studied here is that they exhibit strong oscillator strengths. In the bottom panel of Fig. 2, we show the relative deviation of the computed TDDFT oscillator strengths from those given by CC2. Again, $BNL*/J_1$ has a lower deviation, with mean deviation and MAD of about 5%, whereas $BNL*/J_2$ typically exhibits deviations that are twice as large. Interestingly, the results of both BNL* approaches are
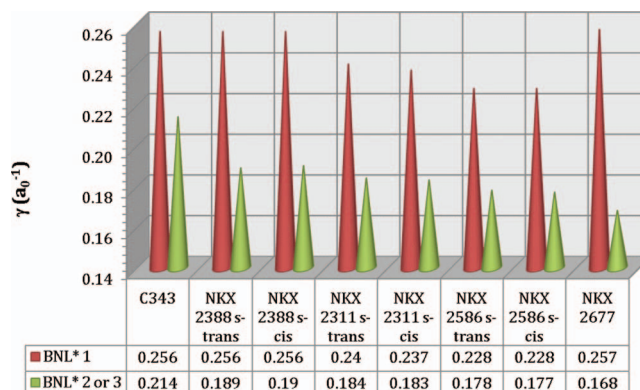

	C343	NKX 2388 s-trans	NKX 2388 s-cis	NKX 2311 s-trans	NKX 2311 s-cis	NKX 2586 s-trans	NKX 2586 s-cis	NKX 2677
■ BNL*1	0.256	0.256	0.256	0.24	0.237	0.228	0.228	0.257
■ BNL*2 or 3	0.214	0.189	0.19	0.184	0.183	0.178	0.177	0.168

FIG. 3. Values of γ obtained from the first principles, physically motivated tuning for each of the coumarin-based systems.

in better agreement with the CC2 data than those obtained by explicit fitting. Although $BNL*/J_1$ is more accurate than $BNL*/J_2$, both methods have acceptable accuracy and are of predictive value.

In Fig. 3 we show the range-separation parameter γ determined by $BNL*/J_1$ or J_2 methods. In $BNL*/J_1$ γ is consistently within the interval $[0.23, 0.26]a_0^{-1}$ whereas in $BNL*/J_2$ γ is noticeably smaller and is in the interval $[0.17, 0.21]a_0^{-1}$. In light of Fig. 1, these facts immediately explain why excitation energies predicted with $BNL*/J_2$ 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 $BNL*/J_1$ is similar throughout, whereas in $BNL*/J_2$ 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. The fact that our method yields quantitatively useful results even for this more difficult case is a clear indication of its generality.

IV. CONCLUSIONS

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 physically motivated, nonempirical procedure for tuning the range-parameter. It therefore emerges as an approach of practical utility for systems too large to be treated with wave function-based approaches such as CC2 or CASPT2.

ACKNOWLEDGMENTS

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