

Charge-Transfer Properties of Dye-Sensitized Solar Cells via Long-Range-Corrected Density Functional Theory

Bryan M. Wong

Materials Chemistry Department, Sandia National Laboratories,
Livermore, CA 94551, U.S.A.

ABSTRACT

The excited-state properties in a series of solar cell dyes are investigated with a long-range-corrected (LC) functional which provides a more accurate description of charge-transfer states. Using time-dependent density functional theory (TDDFT), the LC formalism correctly predicts a large increase in the excited-state electric dipole moment of the dyes with respect to that of the ground state, indicating a sizable charge separation associated with the $S_1 \leftarrow S_0$ excitation. The performance of the LC-TDDFT formalism, illustrated by computing excitation energies, oscillator strengths, and excited-state dipole moments, demonstrates that the LC technique provides a consistent picture of charge-transfer excitations as a function of molecular size. In contrast, the widely-used B3LYP functional severely overestimates excited-state dipole moments and underestimates the experimentally observed excitations, especially for larger dye molecules. The results of the present study emphasize the importance of long-range exchange corrections in TDDFT for investigating the charge-transfer dynamics in solar cell dyes.

INTRODUCTION

Dye-sensitized solar cells (DSCs) have gained immense interest in the last few years due to their potential for converting clean solar energy to electricity at low cost. Originally introduced by Grätzel and co-workers in 1991 [1], several researchers have studied their use in

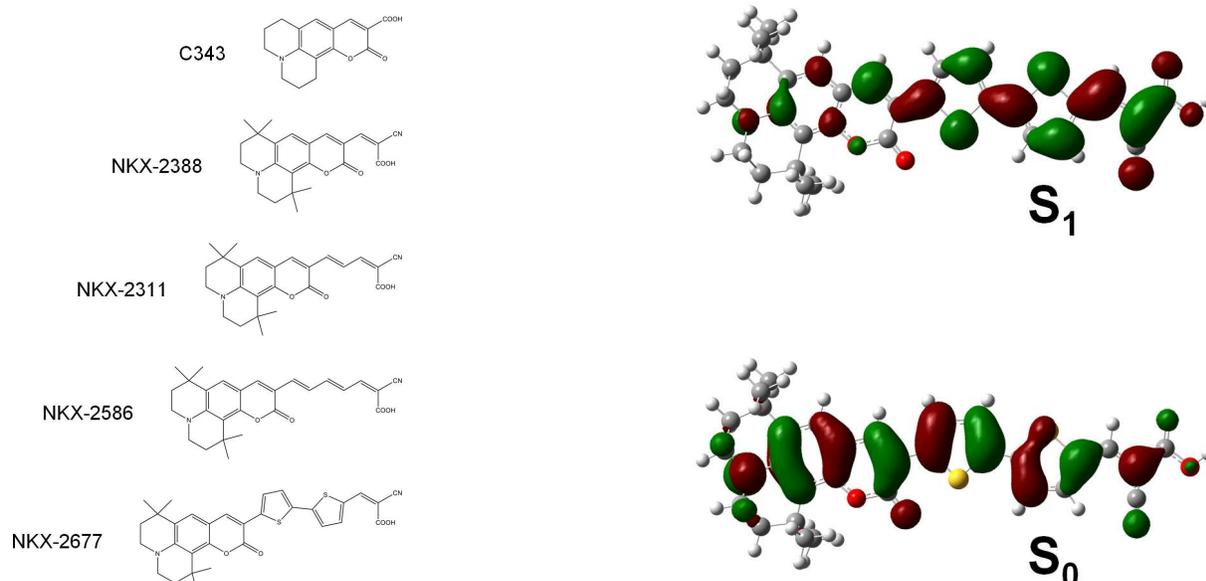


Figure 1. (left) Molecular structures of C343, NKX-2388, NKX-2311, NKX-2586, and NKX-2677. (right) Molecular orbitals for the NKX-2677 S_0 ground state and the S_1 first excited state.

fabricating nanostructured films, improving photovoltaic devices, and to gain a general scientific understanding of charge-transfer between material interfaces. Although the origins of their work had focused on ruthenium dye complexes, current research is now directed towards organic dye sensitizers which are less expensive and easier to synthesize [2]. Recognizing this need for low-cost alternatives to conventional photovoltaics, Hara and co-workers [3-5] recently synthesized a series of coumarin dye molecules comprised of donor, electron-conducting, and anchoring groups for use in solar cell applications. As shown in figure 1, these organic sensitizers consist of an aniline group acting as an electron donor and a cyanoacrylic acid group functioning as an acceptor. These two functional groups are spatially separated from each other by one or more conjugated units which serve as an electron conductor. In particular, the NKX-2xxx series of coumarin derivatives have been reported as promising candidates for DSCs, and the NKX-2677 dye alone has a conversion efficiency of 7.4% which is comparable to ruthenium-based photosensitizers [6].

In order to develop highly efficient sensitizers, the S_1 excited state must possess a significant charge-transfer character which can facilitate electron flow from the light-harvesting functional groups towards the electron acceptor units. Ideally, one would like to use a computational design beforehand to satisfy this requirement and predict the electronic properties which yield an efficient charge separation. An important area where theory should contribute is the prediction of DSC charge-transfer effects arising from different electron donor/acceptor groups in order to ultimately guide the organic synthesis. Unfortunately, despite the growing experimental efforts in DSC synthesis, the quantitative understanding and theoretical prediction of DSC charge-transfer properties is still a major hurdle to overcome in order to achieve a viable technology. While wavefunction-based approaches such as complete active space second-order perturbation theory (CASPT2) can yield accurate predictions, the computational cost of CASPT2 is too high for routine application to molecules larger than about 20 atoms. Consequently, most of the limited studies on DSC dyes have used time-dependent density functional theory (TDDFT) in conjunction with the popular B3LYP hybrid functional to study the optical response of these large molecules [7,8]. However, as shown by Kurashige and co-workers, the application of B3LYP to these large systems leads to a severe underestimation of excitation energies in the charge-transfer states [9].

In this work, the issue of charge-transfer in DSCs is addressed by calculating excited-state energies and properties using the long-range-corrected (LC) TDDFT formalism. Originally proposed by Gill [10] and Savin [11], this range-separation technique partially accounts for long-range charge-separation effects by adding a growing fraction of Hartree Fock (HF) exchange when the interelectronic distance increases (see Theory section). The damping parameter, μ , determines the relative contributions of DFT and HF to the exchange-correlation energy in these functionals. In the present study, the LC-TDDFT technique is used to investigate the excited-state properties of the large DSC dye systems depicted in figure 1. In each case, the LC-TDDFT excitation energies, oscillator strengths, and S_0/S_1 dipole moments are computed as a function of μ and compared against wavefunction-based approximate coupled-cluster singles and doubles (CC2) data. Benchmark calculations for optimizing the range-parameter μ are discussed, and a comparison to predictions by the widely-used B3LYP functional are also examined. Based on overall trends in excitation energies and properties, the LC-TDDFT formalism significantly improves the description of charge-transfer excitations in DSCs and enables a guided approach to maximizing the potential capabilities of future dye sensitizers.

THEORY

In the conventional LC scheme for DFT, the electron repulsion operator $1/r_{12}$ is split into short- and long-range components using the standard error function, erf, as

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}},$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the interelectronic distance between electrons at coordinates r_1 and r_2 , and μ is an adjustable damping parameter having units of inverse length. The first term in the previous equation is a short-range interaction which decays rapidly on a length scale of $\sim 2/\mu$, and the second term is the long-range “background” interaction. For a pure density functional (i.e. BLYP or BOP) which does not already include a fraction of nonlocal HF exchange, the exchange-correlation energy according to the LC scheme is

$$E_{xc} = E_{c,\text{DFT}} + E_{x,\text{DFT}}^{\text{SR}} + E_{x,\text{HF}}^{\text{LR}},$$

where $E_{c,\text{DFT}}$ is the DFT correlational functional, $E_{x,\text{DFT}}^{\text{SR}}$ is the short-range DFT exchange functional, and $E_{x,\text{HF}}^{\text{LR}}$ is the HF contribution to exchange computed with the long-range part of the Coulomb operator. The modified $E_{x,\text{HF}}^{\text{LR}}$ term can be analytically evaluated with Gaussian basis functions, and the short-range $E_{x,\text{DFT}}^{\text{SR}}$ contribution is computed with a modified exchange kernel specific for each generalized gradient approximation.

The key improvement in the LC scheme is the smooth separation of DFT and nonlocal HF exchange interactions through the parameter μ . Specifically, the exchange potentials, $v_{xc}(\mathbf{r})$, of conventional density functionals have the wrong asymptotic behavior, but the LC scheme ensures that $v_{xc}(\mathbf{r})$ smoothly recovers the exact $-1/r$ dependence at large interelectronic distance. For the dye-sensitized solar cells in this work, the performance of a long-range-corrected BLYP functional (LC-BLYP) is investigated. All ground-state geometry optimizations of the coumarin dyes (figure 1) were calculated at the LC-BLYP/6-31G(d,p) level without symmetry constraints, and root-mean-squared forces converged to within 0.00003 atomic units. In the TDDFT calculations, the lowest singlet-singlet vertical excitation was calculated at the optimized ground-state geometries using a larger 6-31+G(d,p) basis set. The vertical excitation energies for all dyes were also calculated as a function of μ ranging from 0 to 0.90 Bohr⁻¹, in increments of 0.05 Bohr⁻¹. All *ab initio* calculations were performed with a locally modified version of GAMESS. Additional details of these *ab initio* calculations are given in reference 12.

DISCUSSION

In each of the ground-state optimizations for the coumarin dyes, the cyanoacrylic acid group becomes coplanar with the polymethine/thiophene chain, indicating a strong conjugation across the valence π orbitals of the C=C double bonds. For the NKX-2388, -2311, and -2586 series of dyes, two different stable isomers are possible. Specifically, the configuration at the single bond between the coumarin moiety and the methine chain can have either an *s-cis* or *s-trans* arrangement. To investigate the acceptable range of the damping parameter μ , the lowest singlet-singlet vertical excitation energy was computed as a function of μ for each of the solar

cell dyes (including both *cis*- and *trans*-isomers for the NKX-2388, -2311, and -2586 coumarins). Using the recent CC2 calculations by Kurashige et al. [9] as reference values, the total root-mean-square error (RMSE) in the excitation energies for all 8 dyes was computed as a function of μ . The full details of the TDDFT and CC2 comparisons can be found in reference 12. A full minimization of the RMSE error yields a range-separation value of $\mu = 0.17 \text{ Bohr}^{-1}$ with an RMS error of 0.04 eV. Surprisingly, this value of μ is considerably smaller than the $\mu = 0.33 \text{ Bohr}^{-1}$ value recommended by Iikura et al. for small molecules [13]. It may be possible that a smaller value of μ is more appropriate for excitations in large molecules since a small μ value enables the short-range Coulomb operator to fully decay to zero on the length scale of the molecule. A more comprehensive investigation of this issue is currently under study in my group.

In all 8 dyes, this $S_1 \leftarrow S_0$ excitation corresponds to a charge-transfer transition from an orbital delocalized on the coumarin moiety to a localized orbital on the cyanoacrylic acid group (cf. figure 1). The ground-to-excited state difference in electric dipole moments, discussed later in this section, is also a direct reflection of electronic charge flow associated with this absorption process. To assess the performance of the LC-BLYP approach, separate geometry optimizations and excitation energies were carried out using the popular B3LYP functional which incorporates a fixed combination of 20% Hartree-Fock, Slater, and Becke's GGA correction in the exchange contribution. All B3LYP ground-state geometry optimizations were computed using the 6-31G(d,p) basis set, and vertical excitation energies were calculated at these optimized geometries using a larger 6-31+G(d,p) basis set. The fully relaxed B3LYP geometries were nearly identical to the LC-BLYP geometries and had slightly longer C=C double bonds by only 0.02 Å.

On a qualitative level, both functionals reproduce the expected trend that the excitation energy decreases as the π -conjugated chain becomes longer. Figure 2 shows in more detail the general trend in the $S_0 \leftarrow S_1$ transition energies between the LC-BLYP, B3LYP, and CC2 results for all 8 solar cell dyes. The diagonal line in figure 2 represents an ideal 100% agreement between the CC2 energies and the corresponding TDDFT results. The most significant feature of figure 2 is the high degree of statistical correlation ($R^2 = 0.98$) exhibited by LC-BLYP, indicative of a simple, systematic error in these excitation energies. In contrast, the same linear fitting procedure for the B3LYP excitation energies yields a poorer correlation with an R^2 value of 0.85.

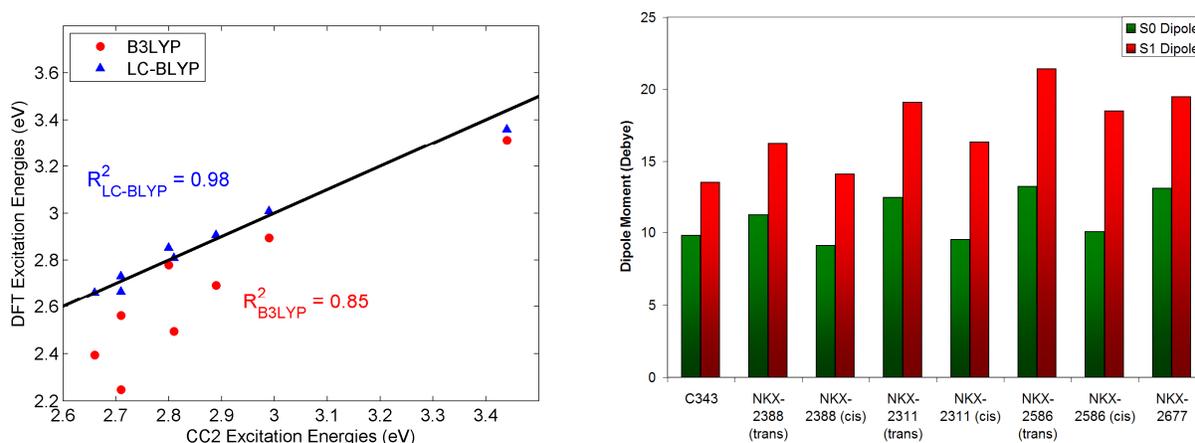


Figure 2. (left) Comparison between TDDFT and CC2 (diagonal line) excitation energies for all 8 coumarin dyes. (right) S_0 ground- and S_1 excited-state dipole moments of coumarin dyes computed at the LC-BLYP/6-31+G(d,p) level of theory.

The B3LYP calculations show good agreement with the CC2 results for the small C343 and NKX-2388 dyes, but the trend in excitation energies is poorly described for the larger coumarin dyes.

To gain further insight into the electronic structure of the excited charge-transfer states, the S_0/S_1 electric dipole moments and oscillator strengths of the $S_1 \leftarrow S_0$ transitions were also computed. In all 8 solar cell dyes, the S_0 molecular orbital is delocalized throughout the entire molecule with maximum density from the nitrogen lone-pair and the π orbitals of the surrounding aryl substituents. The S_1 molecular orbital, on the other hand, is primarily a π^* orbital which is localized on the conjugated chain and cyanoacrylic acid units with density concentrated on the cyano- and carboxylic groups (cf. figure 1). As anticipated from this increased orbital localization, the S_1 electric dipole moment is considerably larger than the S_0 dipole, an electronic signature which reflects a sizable charge transfer in the excited state. Figure 2 compares the S_0 and S_1 dipole moments in all 8 solar cell dyes. The resulting excited-state trends and properties indicate that long-range exchange interactions do indeed play a significant role in these systems, and the LC-TDDFT technique offers an improved treatment over conventional DFT hybrids for capturing the excited-state dynamics in coumarin solar cell dyes.

CONCLUSIONS

In this study, the excited-state energies and properties have been investigated in a series of coumarin dye molecules for use in solar cell applications. For each of the 8 coumarin dyes, excited-state energies and properties were obtained using the TDDFT formalism in conjunction with a functional modified specifically for long-range intramolecular charge-transfer. To investigate the acceptable range of μ , an extensive comparison was made between LC-BLYP excitation energies and previous CC2 calculations. Using this re-optimized value of μ , the long-range-corrected LC-BLYP functional significantly improves the poor description given by

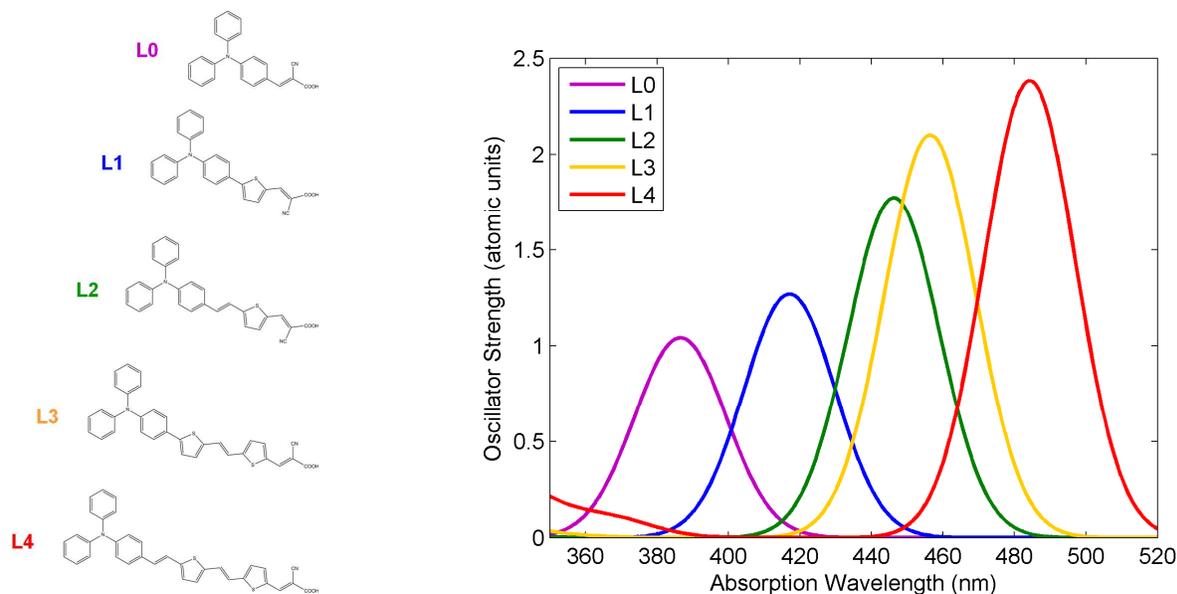


Figure 3. (left) A series of organic chromophores with different conjugated linkers. (right) TDDFT calculations of absorption spectra for the L0-L4 dyes in acetonitrile solution.

B3LYP and correctly reproduces the correct trends among the larger coumarin dyes. In particular, a simple statistical analysis demonstrates that the LC-TDDFT treatment provides a more consistent picture of excitation energies as a function of DSC molecular size.

In closing, the present study provides indications that long-range exchange corrections play a vital role in describing the excited-state dynamics in solar cell dyes. Furthermore, the LC-TDDFT technique offers an improved treatment of excited-state properties and overall trends compared to conventional hybrid functionals like B3LYP. As a result, one can be hopeful that the LC-TDDFT formalism will help provide the insight needed to guide the design of more efficient solar cell dyes. In particular, one promising approach already under study in the Materials Chemistry Department at Sandia National Laboratories is the study of light-harvesting organic systems which can selectively absorb photons with specific wavelengths in the visible region (cf. figure 3). With this in mind, the understanding of critical features such as excitation energies and charge-transfer states using the LC-TDDFT technique will provide a step towards this goal.

ACKNOWLEDGMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

REFERENCES

1. B. O'Regan and M. Grätzel, *Nature* **414**, 338 (1991).
2. L. M. Peter, *Phys. Chem. Chem. Phys.* **9**, 2630 (2007).
3. K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohge, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, and H. Arakawa, *J. Phys. Chem. B* **107**, 597 (2003).
4. K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, and H. Arakawa, *New. J. Chem.* **27**, 783 (2003).
5. K. Hara, Z.-S. Wang, T. Sato, A. Furube, R. Katoh, H. Sugihara, Y. Dan-oh, C. Kasada, and A. Shinpo, *J. Phys. Chem. B* **109**, 15476 (2005).
6. M. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bigonozzi, and M. Grätzel, *J. Am. Chem. Soc.* **123**, 1613 (2001).
7. D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, and L. Sun, *Chem. Commun.* **21**, 2245 (2006).
8. M. Liang, W. Xu, F. Cai, P. Chen, B. Peng, J. Chen, and Z. Li, *J. Phys. Chem. C* **111**, 4465 (2007).
9. Y. Kurashige, T. Nakajima, S. Kurashige, K. Hirao, and Y. Nishikitani, *J. Phys. Chem. A* **111**, 5544 (2007).
10. P. M. W. Gill, *Mol. Phys.* **88**, 1005 (1996).
11. A. Savin, *Recent Developments and Applications of Modern Density Functional Theory*, ed. J. M. Seminario (Elsevier, Amsterdam, 1996), pp. 327-354.
12. B. M. Wong and J. G. Cordero, *J. Chem. Phys.* **129**, 214703 (2008).
13. H. Iikura, T. Tsuneda, T. Yanai, and K. Hirao, *J. Chem. Phys.* **115**, 3540 (2001).