Communication: Orbital instabilities and triplet states from time-dependent density functional theory and long-range corrected functionals

John S. Sears, Thomas Koerzdoerfer, Cai-Rong Zhang, and Jean-Luc Brédas

View Online

Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Communication: Orbital instabilities and triplet states from time-dependent density functional theory and long-range corrected functionals

John S. Sears, Thomas Koerzdoerfer, Cai-Rong Zhang,[a)] and Jean-Luc Brédas[b)]
School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics,
Georgia Institute of Technology, Atlanta, Georgia 30332-0400, USA

Long-range corrected hybrids represent an increasingly popular class of functionals for density functional theory (DFT) that have proven to be very successful for a wide range of chemical applications. In this Communication, we examine the performance of these functionals for time-dependent (TD)DFT descriptions of triplet excited states. Our results reveal that the triplet energies are particularly sensitive to the range-separation parameter; this sensitivity can be traced back to triplet instabilities in the ground state coming from the large effective amounts of Hartree-Fock exchange included in these functionals. As such, the use of *standard* long-range corrected functionals for the description of triplet states at the TDDFT level is not recommended. © *2011 American Institute of Physics*. [doi:10.1063/1.3656734]

I. INTRODUCTION

Density functional theory (DFT) and its time-dependent extension (time-dependent density functional theory; TDDFT) have become the methods of choice for quantum-mechanical applications in many areas of chemistry. Recently, long-range corrected (LRC) hybrid functionals have generated a significant amount of attention in the literature.[1] Indeed, they have been shown to improve upon the standard hybrid functionals for numerous properties of particular interest; examples include: fundamental gaps and ionization potentials (IPs),[2,3] bond-length alternations in π-conjugated materials,[4] molecular polarizabilities and hyperpolarizabilities,[5] or vibrational frequencies and IR/Raman intensities.[6] Primarily, however, it is the outstanding performance of LRC-hybrids for charge-transfer excitations that makes this new class of functionals particularly interesting for TDDFT applications in organic electronics.[7–9]

The central premise underlying all LRC functionals is a separation of the Coulomb operator into short-range (SR) and long-range (LR) components that can be treated separately. For instance, a semilocal exchange-correlation functional can be used for the SR and Hartree-Fock for LR. The most popular approach to the range separation (and the one employed in this work) is to partition the Coulomb operator via the standard error function:

$$\frac{1}{r} = \frac{erf(\omega r)}{r} + \frac{erfc(\omega r)}{r}. \tag{1}$$

The range-separation parameter ω determines the separation/partitioning of the SR and LR components. Initial work in this area assumed a single, system-independent range-separation parameter dependent only upon the underlying exchange-correlation functional.[10] However, recent work has revealed that ω should depend primarily on the electronic structure of the system and only to a much lesser extent on the particulars of the semilocal exchange-correlation functional employed.[11] In this work, as has been done previously by others as well,[2] we will use the "IP-tuning" to determine the optimal range-separation parameter. This is done by minimizing the difference between the highest occupied orbital eigenvalue and the computed ionization potential, i.e.,

$$\Delta_{IP}(\omega) = \left| -\varepsilon_{HOMO}^{\omega} - (E_{gs}(\omega, N) - E_{gs}(\omega, N-1)) \right|. \tag{2}$$

The range-separation parameters determined by minimization of Eq. (2) have been shown to improve the description of properties related to the IP and the fundamental gap for a series of systems.[2,3] The IP-tuning procedure is completely self-consistent and non-empirical as it simply requires that the resultant generalized Kohn-Sham solution obey a property that is identically satisfied for an exact Kohn-Sham (and generalized Kohn-Sham) approach.

While a complete description of the TDDFT machinery has been presented elsewhere,[12–14] it is important to note that linear-response TDDFT comprises a generalization of ground-state DFT whereby the determination of the excitation spectra can be reduced to the solution of an eigenvalue problem. Casida *et al.*[15] have shown that, for the case of a simple two-state model system, the solutions to the TDDFT equations for the singlet (S) and triplet (T) excitation energies υ_S and υ_T simplify to

$$\upsilon_S = \sqrt{\Delta\varepsilon[\Delta\varepsilon + 2(K_{\uparrow,\uparrow} + K_{\uparrow,\downarrow})]}, \tag{3}$$

$$\upsilon_T = \sqrt{\Delta\varepsilon[\Delta\varepsilon + 2(K_{\uparrow,\uparrow} - K_{\uparrow,\downarrow})]}. \tag{4}$$

Here, $\Delta\varepsilon$ denotes the difference in the occupied and virtual orbital energies (this difference is always positive due to the aufbau principle); $K_{\uparrow,\uparrow}$ and $K_{\uparrow,\downarrow}$ represent the same-spin and opposite-spin occupied-virtual coupling matrix

---

a)On leave from Department of Applied Physics, Lanzhou University of Technology, Lanzhou, China.
b)Electronic mail: jean-luc.bredas@chemistry.gatech.edu. Also at Department of Chemistry, King Abdulaziz University, Jeddah, Saudi Arabia.

elements, respectively. Casida *et al.* underline that in the case of a bond-breaking process, the triplet energy (υ_T) approaches zero and eventually becomes imaginary and trace this back to symmetry breaking in the ground-state wavefunction. By analyzing the stability condition for the two-state model system, these authors observe that the ground-state becomes unstable vs. symmetry breaking at the very point where $[\Delta\varepsilon + 2(K_{\uparrow,\uparrow} - K_{\uparrow,\downarrow})]$ becomes negative. Through Eq. (4), it can be seen that this is identically the point where υ_T becomes imaginary; thus, the term giving rise to symmetry breaking in the ground state is also responsible for the imaginary root corresponding to the triplet excitation in the TDDFT equations. Casida *et al.* also show that, at least for the two-state model, the triplet energies taken either from the Tamm-Dancoff approximation[16–18] or as the differences in the self-consistent field (SCF) energies of the singlet and triplet spin states (ΔSCF), are not affected by the symmetry-breaking instability in the ground state. This conclusion will be particularly relevant for understanding the results presented below.

The stability conditions both for HF (Refs. 19 and 20) and DFT (Ref. 21) have been discussed previously, and a description of the classes of instabilities has been formulated by Cizek and Paldus.[20] Here, we highlight a few concepts that are essential to the present work. Solution of the SCF equations (either in HF or DFT) ensures a vanishing first-order variation in the energy functional with respect to orbital rotations. However, convergence of the wavefunction to even a local minimum requires positive definiteness of the molecular orbital Hessian. If the Hessian is not positive definite, i.e., it has at least one negative eigenvalue, then there exists a lower energy SCF solution which may (or may not) break some of the imposed restrictions upon the wavefunction. Central to our work is the existence of instabilities breaking the imposed spin symmetry of the wavefunction. These arise when a spin-contaminated unrestricted Kohn-Sham (UKS) or HF (UHF) solution can be found that is lower in energy than the restricted closed-shell solution (RKS or RHF, respectively); here, we will denote these instabilities as RKS-UKS (or RHF-UHF) instabilities.

RKS-UKS (and RHF-UHF) instabilities are known to occur often for systems far from equilibrium.[15] HF is also known to exhibit RHF-UHF instabilities in many systems even at equilibrium. While the latter are largely corrected at the DFT level, the amount of included exchange in any hybrid-DFT approach can strongly impact the presence of RKS-UKS instabilities.[22] Of relevance to the results presented here is that the large amounts of exchange included in standard LRC functionals can easily introduce RKS-UKS instabilities in the electronic ground state of some molecules. As is demonstrated below, the presence of these instabilities has a significant impact on the description of triplet states with these functionals.

In this Communication, we explore the nature of the orbital instabilities and the TDDFT description of the triplet states in linear acenes for several LRC functionals. The description of the singlet excited states in these systems (especially for the ^1L_a state) has proven challenging for many DFT functionals, and it has been shown recently that the LRC func-
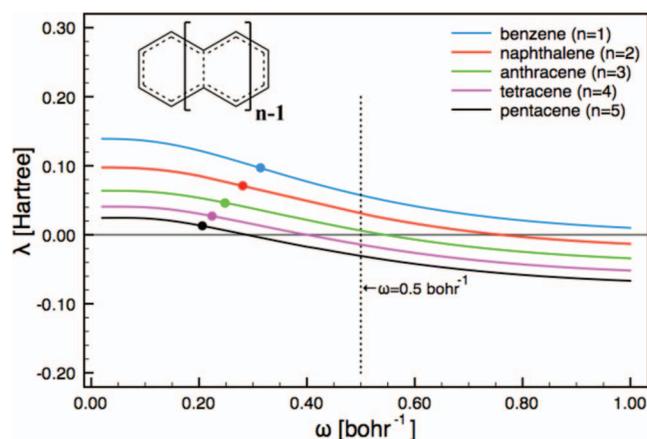

FIG. 1. Lowest RKS-UKS orbital Hessian eigenvalue from the BNL functional as a function of the range-separation parameter for the linear acenes (see chemical structure in inset). The vertical dashed line at $\omega = 0.5$ bohr^{-1} indicates the values obtained with BNL using the default range-separation parameter. The points individually highlighted on each of the curves are those obtained with the IP-optimized ω.

tionals provide for an improved description of these singlet excitations.[23–25] Given the growing popularity of these LRC DFT approaches, our results should provide significant and timely guidance into obtaining reliable triplet energies with these functionals.

II. THEORETICAL METHODS

The geometries of the linear acenes for benzene through pentacene (see inset of Figure 1 for chemical structures) were completely optimized at the frozen-core MP2/cc-pVTZ level using MOLPRO 2010.1.[26] Single-point computations were performed at the DFT/TDDFT level using QChem[27] and the same cc-pVTZ basis set. Several long-range corrected functionals were employed, including LRC-BOP,[28, 29] ωPBE,[30] ωPBEh,[30] ωB97,[31] ωB97X,[31] ωB97X-D,[10] and BNL.[32] In all LRC functionals, both the default ω from the literature as well as the IP-optimized ω obtained from Eq. (2) were employed. In addition, computations were carried out with the widely used standard hybrid functional B3LYP as well as with HF theory. The singlet ground-state wavefunctions were optimized via restricted Kohn-Sham computations and the stability of the RKS wavefunctions was examined through diagonalization of the molecular orbital Hessian. TDDFT computations were performed with each of the functionals for the first excited singlet (S_1) and triplet (T_1) states, both with and without the Tamm-Dancoff approximation.

III. RESULTS AND DISCUSSION

All linear acenes examined in this work exhibit RHF-UHF orbital instabilities in the ground-state wavefunction with RHF-UHF Hessian eigenvalues (λ) ranging from –0.025 hartree in benzene to –0.094 hartree in pentacene. The complete results for each molecule are included in the supplementary material.[33] In all cases, the magnitude of the instability (based on the absolute magnitude of the eigenvalue corresponding to the RHF-UHF instability) increases with the

size of the system. Thus, it should be expected that the existence (or absence) of RKS-UKS instabilities strongly depends on the amount of HF exchange included in the functional. This is highlighted in Fig. 1 where the lowest eigenvalue of the RKS-UKS molecular orbital Hessian (λ) is plotted as a function of the range-separation parameter (ω) for the linear acenes using the LRC BNL functional. Increasing the ω value implies the inclusion of a greater amount of HF exchange; in the limit of $\omega \rightarrow \infty$, the functional includes 100% HF exchange.

The results obtained for the standard BNL functional, which uses a ω of 0.5 bohr^{-1}, are indicated by a vertical line in Fig. 1. With the default range-separation parameter, the closed-shell RKS ground-state wavefunction exhibits an RKS-UKS instability for tetracene and pentacene, with the RKS solution for anthracene very close to the instability point. Interestingly, the IP-optimization of ω largely removes the problems associated with the orbital instabilities in the ground-state wavefunction. The IP-optimized ω-values for each system are given as dots on the curves in Fig. 1. The tuning of the range-separation parameter effectively reduces the amount of HF exchange with increasing system size, and provides for a greater stability of the ground-state wavefunction. It should be pointed out, however, that it is not necessarily the case that the IP-optimized ω always provides for a stable ground-state RKS wavefunction. Indeed, we have found that with the optimized ωPBEh, for which we calculate an optimized range-separation parameter of 0.157 bohr^{-1} in the case of pentacene, there exists an RKS-UKS instability (λ = −0.007 hartree). More importantly, the lack of an orbital instability in the RKS reference *does not preclude deficiencies in the TDDFT description of the triplet state*, as is demonstrated below.

The occurrence of an RKS-UKS instability in the ground-state wavefunction has been shown above, for the specific case of the LRC functionals, to depend heavily on the amount of HF exchange incorporated into the functional. As has been underlined by Casida *et al.*[15] the existence of an RKS-UKS instability in the ground-state wavefunction manifests itself in numerical difficulties in the full TDDFT description of the triplet state. In this instance, the eigenvalue corresponding to the TDDFT excitation from the ground state to the first triplet state becomes imaginary. In fact, this has been observed in the full TDDFT computations for tetracene and pentacene when using the LRC functionals with the default range-separation parameter. While this occurs for the full TDDFT and only for the triplet excitations, the Tamm-Dancoff approximation (TDA) (through the neglect of the off-diagonal blocks) does not suffer from these issues. The effect can be clearly observed in Fig. 2 where we present the TDDFT and TDA-TDDFT results for the S_1 and T_1 states of anthracene with the LRC BNL functional as a function of the range-separation parameter. As can be seen readily from the figure, the TDA introduces a nearly constant offset of ~0.2 eV in the S_1 state. In the limit of no HF exchange (ω = 0), the TDDFT and TDA-TDDFT results for the triplet state are nearly identical. However, unlike the results for the singlet excitations, the TDDFT excitation for the triplet state quickly diverges from the TDA-TDDFT result. This is
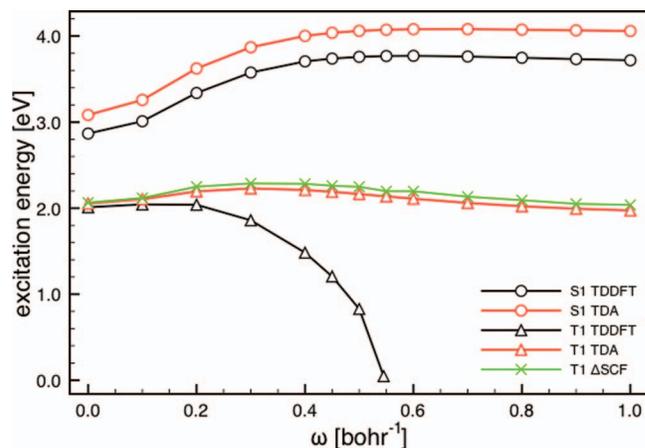

FIG. 2. TDDFT and TDA-TDDFT (and ΔSCF T_1) excitation energies for anthracene in a cc-pVTZ basis using the BNL functional as a function of the range-separation parameter.

because, as ω increases, the ground state moves closer to the instability; for anthracene, the instability occurs at $\omega \sim 0.55$ bohr^{-1} and the TDDFT description of the triplet state passes through zero at this point. As a consequence, the TDDFT and TDA-TDDFT results start diverging long before the actual occurrence of the RKS-UKS instability in the ground-state wavefunction; for the case of anthracene, the difference is already approaching 0.5 eV at $\omega = 0.3$ bohr^{-1}. This divergence of the full TDDFT results will manifest itself in
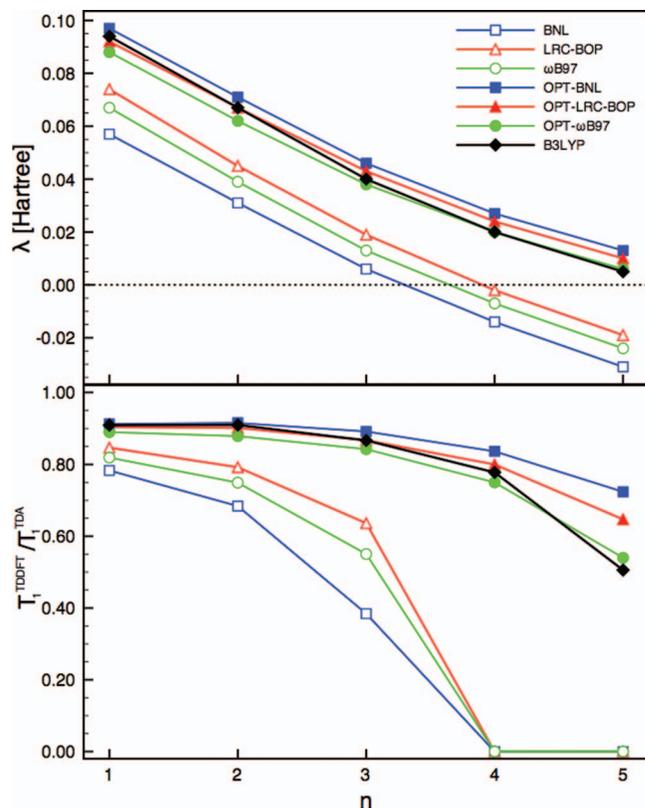

FIG. 3. (Upper panel) Lowest RKS-UKS Hessian eigenvalue (λ) for the linear acenes as a function of the number of fused rings (n). (Lower panel) Ratio of the full TDDFT triplet energy (T_1^{TDDFT}) to the Tamm-Dancoff triplet energy (T_1^{TDA}) for the same functionals.

many applications as a strong sensitivity of the singlet-triplet (S_1-T_1) splitting as a function of the range-separation parameter, *even for cases where the ground-state RKS solution does not exhibit an instability*. This effect has been observed previously by us, for instance, in pentacene where the difference between the TDDFT T_1 energy and the TDA-TDDFT T_1 energy remains ∼0.5 eV even when using optimized range-separation parameters.[34]

While (for simplicity of discussion) the results presented above have been restricted to the LRC BNL functional, it should be pointed out that the conclusions are completely general and hold for the seven LRC functionals we have considered. In other words, the results are independent of the nature of the semilocal exchange-correlation functional employed. To illustrate this point, Fig. 3 displays the lowest RKS-UKS Hessian eigenvalue as well as the ratio of the triplet energies computed from TDDFT and TDA-TDDFT. This ratio should be near 1 but will approach zero as the full TDDFT description of the triplet diverges (we set imaginary excitation energies to zero). While the standard LRC-hybrids all show instability in the ground state for tetracene and pentacene, the IP-optimization stabilizes the ground state. However, even with IP-optimized LRC-hybrids, the onset of the problems related to triplet instability can be clearly seen. Figure 3 also shows that, in contrast to the standard LRC-hybrids, the performance of the IP-optimized hybrids for the TDDFT triplet energies is comparable to that of the widely used regular hybrid B3LYP.

IV. CONCLUSIONS

We have demonstrated that the large effective amounts of exchange included in standard long-range corrected hybrid functionals result in RKS-UKS instabilities for the linear acenes beyond anthracene. More importantly, the presence of these instabilities or nearby instabilities in the ground-state wavefunction leads to a possible divergence of the TDDFT excitations for the lowest triplet states and a strong sensitivity to the exact value of the range-separation parameter. The Tamm-Dancoff approximation is shown to remove this sensitivity completely, as is the ΔSCF approach.

The IP-optimization of the range-separation parameter is observed to prevent the RKS-UKS instability in most instances, thus making the performance of the LRC-hybrids for triplets comparable to standard hybrids such as B3LYP. In general, however, the Tamm-Dancoff approximation and the ΔSCF approach are the only recommended methods for computing triplet energies with long-range corrected hybrid functionals. Based upon the results presented here, triplet energies from LRC-hybrids using a full TDDFT approach should be considered with great care, in particular when employing the standard range-separation parameter for large π-conjugated systems.

ACKNOWLEDGMENTS

[1]R. Baer, E. Livshits, and U. Salzner, *Annual Review of Physical Chemistry* (Annual Reviews, Palo Alto, CA, 2010), Vol. 61, p. 85.

[2]S. Refaely-Abramson, R. Baer, and L. Kronik, Phys. Rev. B **84**, 075144 (2011).

[3]T. Stein, H. Eisenberg, L. Kronik, and R. Baer, Phys. Rev. Lett. **105**, 266802 (2010).

[4]D. Jacquemin, E. A. Perpete, G. Scalmani, M. J. Frisch, R. Kobayashi, and C. Adamo, J. Chem. Phys. **126**, 144105 (2007).

[5]H. Sekino, Y. Maeda, M. Kamiya, and K. Hirao, J. Chem. Phys. **126**, 014107 (2007).

[6]C. A. Jimenez-Hoyos, B. G. Janesko, and G. E. Scuseria, Phys. Chem. Chem. Phys. **10**, 6621 (2008).

[7]D. Jacquemin, E. A. Perpete, I. Ciofini, and C. Adamo, Theor. Chem. Acc. **128**, 127 (2011).

[8]T. Stein, L. Kronik, and R. Baer, J. Am. Chem. Soc. **131**, 2818 (2009).

[9]T. Stein, L. Kronik, and R. Baer, J. Chem. Phys. **131**, 244119 (2009).

[10]J. D. Chai and M. Head-Gordon, J. Chem. Phys. **128**, 084106 (2008).

[11]T. Körzdörfer, C. Sutton, J. S. Sears, and J. L. Bredas (unpublished).

[12]E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

[13]R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. **256**, 454 (1996).

[14]M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).

[15]M. E. Casida, F. Gutierrez, J. Guan, F. X. Gadea, D. Salahub, and J. P. Daudey, J. Chem. Phys. **113**, 7062 (2000).

[16]Y. L. Wang and G. S. Wu, Int. J. Quantum Chem. **108**, 430 (2008).

[17]C. P. Hsu, S. Hirata, and M. Head-Gordon, J. Phys. Chem. A **105**, 451 (2001).

[18]S. Hirata and M. Head-Gordon, Chem. Phys. Lett. **314**, 291 (1999).

[19]W. H. Adams, Phys. Rev. **127**, 1650 (1962).

[20]J. Cizek and J. Paldus, J. Chem. Phys. **47**, 3976 (1967).

[21]R. Bauernschmitt and R. Ahlrichs, J. Chem. Phys. **104**, 9047 (1996).

[22]O. B. Lutnaes, T. Helgaker, and M. Jaszunski, Mol. Phys. **108**, 2579 (2010).

[23]N. Kuritz, T. Stein, R. Baer, and L. Kronik, J. Chem. Theory Comput. **7**, 2408 (2011).

[24]R. M. Richard and J. M. Herbert, J. Chem. Theory Comput. **7**, 1296 (2011).

[25]B. M. Wong and T. H. Hsieh, J. Chem. Theory Comput. **6**, 3704 (2010).

[26]H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz, *et al.*, MOLPRO, version 2010.1, a package of ab initio programs, 2010, see http://www.molpro.net.

[27]Y. Shao, L. F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. DiStasio, Jr., R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. Van Voorhis, S. Hung Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Z. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer III, J. Kong, A. I. Krylov, P. M. W. Gill, and M. Head-Gordon, Phys. Chem. Chem. Phys. **8**, 3172 (2006).

[28]A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[29]T. Tsuneda, T. Suzumura, and K. Hirao, J. Chem. Phys. **110**, 10664 (1999).

[30]O. A. Vydrov and G. E. Scuseria, J. Chem. Phys. **125**, 234109 (2006).

[31]J. D. Chai and M. Head-Gordon, Phys. Chem. Chem. Phys. **10**, 6615 (2008)

[32]E. Livshits and R. Baer, Phys. Chem. Chem. Phys. **9**, 2932 (2007).

[33]See supplementary material at http://dx.doi.org/10.1063/1.3656734 for the complete results.

[34]C. R. Zhang, J. S. Sears, V. Coropceanu, and J. L. Bredas (unpublished).