

## Excitonic effects in a time-dependent density functional theory

Kirill I. Igumenshchev

*Department of Chemistry, University of Rochester, Rochester, New York 14627, USA*

Sergei Tretiak<sup>a)</sup>

*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA;*

*Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA; and*

*Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

Vladimir Y. Chernyak

*Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA*

(Received 1 June 2007; accepted 26 July 2007; published online 18 September 2007)

Excited state properties of one-dimensional molecular materials are dominated by many-body interactions resulting in strongly bound confined excitons. These effects cannot be neglected or treated as a small perturbation and should be appropriately accounted for by electronic structure methodologies. We use adiabatic time-dependent density functional theory to investigate the electronic structure of one-dimensional organic semiconductors, conjugated polymers. Various commonly used functionals are applied to calculate the lowest singlet and triplet state energies and oscillator strengths of the poly(phenylenevinylene) and ladder-type (poly)(*para*-phenylene) oligomers. Local density approximations and gradient-corrected functionals cannot describe bound excitonic states due to lack of an effective attractive Coulomb interaction between photoexcited electrons and holes. In contrast, hybrid density functionals, which include long-range nonlocal and nonadiabatic corrections in a form of a fraction of Hartree-Fock exchange, are able to reproduce the excitonic effects. The resulting finite exciton sizes are strongly dependent on the amount of the orbital exchange included in the functional. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2773727]

### I. INTRODUCTION

Conjugated polymers are organic macromolecules that have a backbone chain with overlapping  $\pi$  orbitals and alternating double/single bonds. These materials possess semiconducting properties since the  $\pi$  orbitals form delocalized valence and conduction wave functions, which support mobile charge carriers.<sup>1</sup> Since the discovery of enhanced conductivity in doped polyacetylene in 1977,<sup>2-4</sup> a new field of research located at the boundary between chemistry and condensed-matter physics has advanced very rapidly. In recent technological application, conjugated polymers with conducting properties revolutionize our approach to optoelectronics.<sup>5-21</sup> These materials possess a number of advantages over traditional semiconductors, and in addition, are considerably cheaper to manufacture. Polymers exhibit the electrical and optical properties of semiconductors and metals while retaining the attractive mechanical properties and processing advantages of polymers. They can emit light, whose color is defined by the chemical structure.<sup>5-7,11,15,16,22,23</sup> The advantages of plastic electronics are multifarious (e.g., electronic newspaper). Display technology based on organic light-emitting diodes has already hit the commercial market. Conjugated polymers can generate electrical current upon absorbing light and therefore can be used in photovoltaic devices.<sup>9,12</sup> Similar to inorganic semi-

conductors their conductivity depends on the doping level that in turn depends on the oxidation state of the polymer, which can be controlled electrochemically. Other numerous applications based on conducting polymers have been suggested: these include electrochemical cells,<sup>22</sup> photodetectors,<sup>13</sup> transistors,<sup>24,25</sup> light-emitting field-effect transistors,<sup>20,21,26</sup> chemical and biosensors,<sup>27,28</sup> organic solar cells,<sup>29</sup> imaging devices,<sup>8,19,30</sup> and solid-state lasers.<sup>10,14,31</sup>

From a fundamental scientific perspective, conjugated polymers are one-dimensional molecular systems with complex electronic structure that is challenging to describe due to electron-electron correlation phenomena and strong electron-photon coupling.<sup>3,32-36</sup> Subsequently, despite mobile  $\pi$ -electron systems that suggest delocalized wave functions,<sup>37-40</sup> the photoinduced dynamics shows signature of various static and dynamic bound/localized states that can be described as quasiparticles, such as excitons, polarons, bipolarons, solitons, breathers, etc.<sup>3,33,35,41-49</sup> Chemical defects, interchain interactions, and conformational disorder that appear due to the soft structure of the material facilitate localization as well.<sup>33,47,50-58</sup> The interplay between localization and delocalization defines the charge<sup>1,49,59-65</sup> and energy transfer<sup>66-71</sup> efficiency and ultimately the material's optoelectrical properties and its suitability for technological applications.<sup>64,72-78</sup> Theoretical description of the electronic structure of conjugated polymers has gradually migrated from effective solid-state band models [e.g., Su-Shrieffer-

<sup>a)</sup>Electronic mail: serg@lanl.gov

Heeger model)<sup>3,79</sup> to the semiempirical quantum-chemical approaches (e.g., Pariser-Par-Pople (PPP) and intermediate neglect of differential overlap (INDO) Hamiltonians)<sup>32,33,47,55,80</sup> and to modern first-principles molecular modeling methods [e.g., density functional theory (DFT) and time-dependent DFT (TD-DFT) techniques].<sup>57,81–91</sup> With improvement in theoretical methodology, more complex electronic phenomena have been addressed, including exciton-phonon interactions,<sup>3,92</sup> properties of triplet and singlet manifolds,<sup>44,47,81,85,87,91</sup> charged states,<sup>59,60,69</sup> vibrational spectral line shapes,<sup>33,55,92</sup> adiabatic and nonadiabatic excited state dynamics and relaxation,<sup>33,54,55,93</sup> and spectral signatures of aggregation,<sup>46,57</sup> etc.

Furthermore, conjugated polymers constitute an excellent testing case for application and development of modern electronic structure methods, since these materials span the range between solid-state and finite molecular systems. *Ab initio* based many-body theory methods for electronic spectra are computationally expensive. For example, Green's functions approach via the solution of the Bethe-Salpeter equation (BSE) adds self-energy corrections (*GW*) to the local density approximation (LDA). This method has demonstrated significant electron-electron interactions and determined the exciton binding energy, which was found to be strongly affected by intermolecular interactions<sup>57,86</sup> compared to the isolated chains.<sup>87</sup> However, this approach was applied only to a narrow range of electronic phenomena in conjugated polymers.<sup>57,86,87</sup> The approach based on time-dependent density functional theory is numerically simpler, and recently became a method of choice for calculations of electronic excitations in finite molecular systems, as well as solids.<sup>94,95</sup> The low computational cost allows treating molecular systems that involve hundreds of atoms. TD-DFT can be viewed as an extension of the density functional theory, where electronic excitations are associated with the poles of the exact charge density response.<sup>95–97</sup> This method accounts for many-body effects via the time-dependent exchange-correlation (xc) potential  $v_{xc}$  and its functional derivatives  $f_{xc}$ .<sup>94–96</sup> Understanding and deriving  $f_{xc}$  are central goals in the improvement of TD-DFT. A frequently employed adiabatic approximation that neglects the memory effects in the density does not always produce accurate results.<sup>88,98</sup> For example, in solids it fails to capture excitonic effects.<sup>97</sup> Recent studies explored a connection of TD-DFT to Görling-Levy perturbation theory,<sup>99,100</sup> the *GW* approximation<sup>97,99</sup> (*GWA*), and the BSE approach.<sup>101–103</sup> The latter, for example, showed that inclusion of a long-range tail ( $\sim 1/q^2$ ) in  $f_{xc}$  is necessary to reproduce the optical spectra in solids. Incorrect long-range functional asymptotics and the missing discontinuity of the approximate xc potentials with respect to the number of particles lead to the inability of TD-DFT, which utilize the popular generalized gradient approximation (GGA) density functionals, to describe electronic excitations with a long-range spatial extent, e.g., charge transfer states.<sup>104–107</sup> Subsequently, hybrid density functionals that account for the orbital exchange in the exchange-correlation functional via Fock-type integrals over the Kohn-Sham (KS) orbitals<sup>108,109</sup> have been so successful for TD-DFT applica-

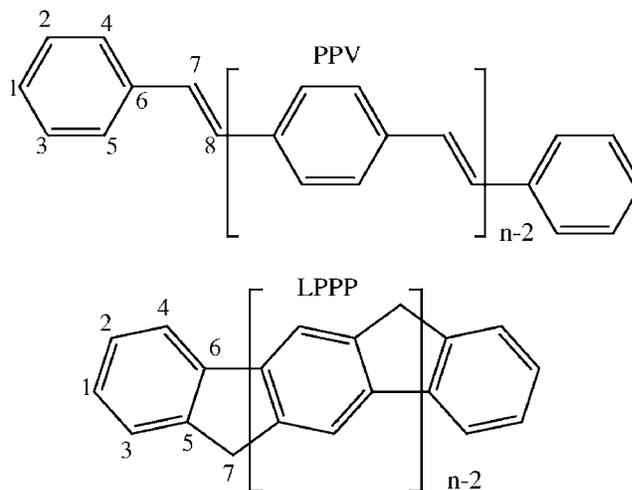


FIG. 1. Structure and atom labeling of poly(*p*-phenylene vinylene) (PPV) and ladder-type poly(*para*-phenylene) (LPPP) polymers.

tions to a broad variety of molecular systems. In particular, several successful attempts have been made to develop new specific functionals that are free of the charge-transfer problems. These include asymptotically corrected functionals based on the Hartree-Fock exchange LC-TD-DFT and CAM-B3LYP,<sup>112–114</sup> and “simple correction schemes.”<sup>115,116</sup> The frequency dependence of the  $f_{xc}$  kernel<sup>117,118</sup> is also necessary for reproducing strongly correlated excited states such as double excitations in finite molecules.<sup>119</sup> The recent non-local density current VK functional<sup>120</sup> has shown high promise by reproducing the size scaling of static polarizabilities in several conjugated chains.<sup>121</sup> However, there is no well defined systematic procedure for incorporating the frequency dependence in the density functional  $f_{xc}$  kernel.

In this article, we explore the applicability of six commonly used density functional models for resonant optical properties of one-dimensional conjugated polymers, ranging from small oligomers in the regime of quantum confinement all the way to the infinite-chain length limit. Previously we have reported failures of the LDA and gradient-corrected models to describe excitonic effects in poly(*p*-phenylene vinylene) (PPV).<sup>88</sup> Here we expand this study and investigate in detail how well various DFT functionals reproduce the lowest singlet  $1^1B_u$  and triplet  $1^3B_u$  spin states in oligomers of various lengths ( $N=2–20$ ) of PPV and ladder-type poly(*para*-phenylene) (LPPP). The results of these studies are expected to be similar for any other one-dimensional polymeric chain featuring delocalized  $\pi$ -electronic system, irrespective of the particular chemical composition. The manuscript is organized as follows. The details of our computational approach are presented in Sec. II. In Sec. III we analyze the results of our numerical simulations. The emerging trends are rationalized in the framework of the simplest tight-binding model for the density functional in Sec. IV. Finally, we summarize our findings in Sec. V.

## II. METHODS

PPV and LPPP structures are shown in Fig. 1. These are probably the most investigated conjugated luminescent poly-

mers that produce red/yellow and blue emissions, respectively. We built PPV and LPPP oligomers of increasing length up to 20 and 19 repeat units, respectively. GAUSSIAN 98 suite<sup>122</sup> has been utilized for geometry optimizations followed by electronic excitation computations using TD-DFT approach with different density functionals. The 6-31G basis set has been used in all our calculations. To be clear on the method performances, all DFT methods have been applied to the same optimized geometry. Namely, molecular geometries have been optimized using the Hartree-Fock (HF) approach, which we previously found<sup>123</sup> to be superior to the DFT approach by reproducing accurately bond-length alternation parameter in similar conjugated systems, when compared to experiment. Next we have calculated up to ten singlet and triplet electronic states for each molecule using the TD-DFT technique.

We employed *six* most popular functionals: pure local spin density approximation (LSDA), gradient-corrected functionals (PBEPBE and BLYP), and hybrid functionals (B3LYP, PBE1PBE, and BHandH that contain 20%, 25%, and 50% of the HF exchange, respectively). Calculations using TD-HF approach coupled with *ab initio* and semiempirical INDO/S Hamiltonians (ZINDO) have been conducted as well, to explore the limiting case with 100% of the HF exchange. The LDA is the oldest density functional model developed for a free-electron gas. It has been a foundation for later development of all exchange-correlation kernels. In spite of its simplicity, the LDA still provides meaningful results for many systems such as metals and solids. Gradient-corrected methods (GGA) notably improve the accuracy by implementing the derivatives of the density. Excellent results have been achieved with these semilocal GGA functionals for electronic structure of many small molecules. Finally, more accurate functionals require further long-range information about the density contained in the Kohn-Sham orbitals. A step toward a general orbital exchange-correlation functional is the exact-exchange which has recently become popular in the solid-state-physics community. In practice, it is often done approximately by replacing the local exact exchange potential by a fraction of nonlocal Hartree-Fock exchange. These hybrid functionals generally avoid many failures of GGA models. For example, they somewhat offset the problem with charge-transfer states in TD-DFT that appear due to an improper asymptotic behavior of the effective potential, and a derivative discontinuity as the number of particles changes through integer values.<sup>124</sup> Finally, the ZINDO approach is based on all-valence semiempirical parametrization, which has been successfully used for calculations of molecular electronic spectra for several decades (e.g., Refs. 32 and 47). It is an aging model limited by parametrization. All these quantum-chemical methods summarized in Table I are standard in various computational packages such as GAUSSIAN, TURBOMOLE, QCHEM, JAGUAR, GAMESS, etc.

TD-DFT calculations provide the excited state energies and the corresponding oscillator strengths. The latter are related to the transition dipole moments, which, in turn, are the expectation values of the dipole operator on the transition densities. The transition density matrix reflects the changes in the electronic density induced by an optical transition

TABLE I. Hamiltonian models and density functionals used for calculations.

	Gradient corrected	LDA	HF exchange
HF	No	0	1
ZINDO	No	0	1
BHandH	No	0.5	0.5
PBE1PBE	Yes	0.75	0.25
B3LYP	Yes	0.8	0.2
BLYP	Yes	1	0
PBEPBE	Yes	1	0
LSDA	No	1	0

from the ground state to an excited state. Here we use contour plots of these quantities<sup>47,125</sup> to analyze spatial delocalization of the underlying photoinduced excitons. The GAUSSIAN code has been locally modified in order to output the transition density matrices.

### III. NUMERICAL RESULTS

We start with analyzing the size-scaling behavior of the excitation energies with the oligomer size. The lowest singlet excited state ( $1^1B_u$  or  $S_1$ ) plays a major role in absorption, photoluminescence, and carrier transport. This excitation is represented by a strongly bound exciton and involves substantial electronic correlation effects. The major contribution to this state comes from the highest occupied-lowest unoccupied molecular orbitals (HOMO-LUMO) gap. The lowest triplet excited state ( $1^3B_u$  or  $T_1$ ) is energetically well below its singlet counterpart by  $\sim 1$  eV due to strong electronic exchange effects dictated by the one-dimensional nature of the material. This nonemissive excitation frequently appears as a result of an electron-hole recombination.<sup>73</sup> The computational results that show the size scaling of these three quantities (energies of  $T_1$ , HOMO-LUMO gap, and  $S_1$ ) for PPV and LPPP oligomers are displayed in Fig. 2. As expected,<sup>47</sup> for all methods the computed frequencies exhibit nearly linear scaling with the inverse chain length and saturate to constants in a long chain limit. Both PPV and LPPP polymers show the same trends. The triplet states show the fastest saturation (top panel). The HOMO-LUMO gap (middle panel) and the corresponding correlated singlet state energy (bottom panel) exhibit very similar size scaling. The observed deviations from the linear scaling can be described by simple fitting expressions.<sup>44</sup>

The saturated values of the computed excitation energies that correspond to the infinite-chain limit together with the corresponding experimental data are shown in Tables II (PPV) and III (LPPP). We note that LSDA and gradient-corrected functionals produce very similar results. Hybrid functionals lead to consistent blueshifts of the singlet transition energy depending on the amount of HF exchange contained in the functional. The latter quantity is a critical variable that affects the singlet-triplet splitting. At the LSDA/GGA limit, the energies of the  $T_1$  and  $S_1$  states virtually coincide. However, at the *ab initio* HF limit the triplet energies become negative, manifesting the triplet instabilities inherent to the TD-HF technique. Overall, the hybrid function-

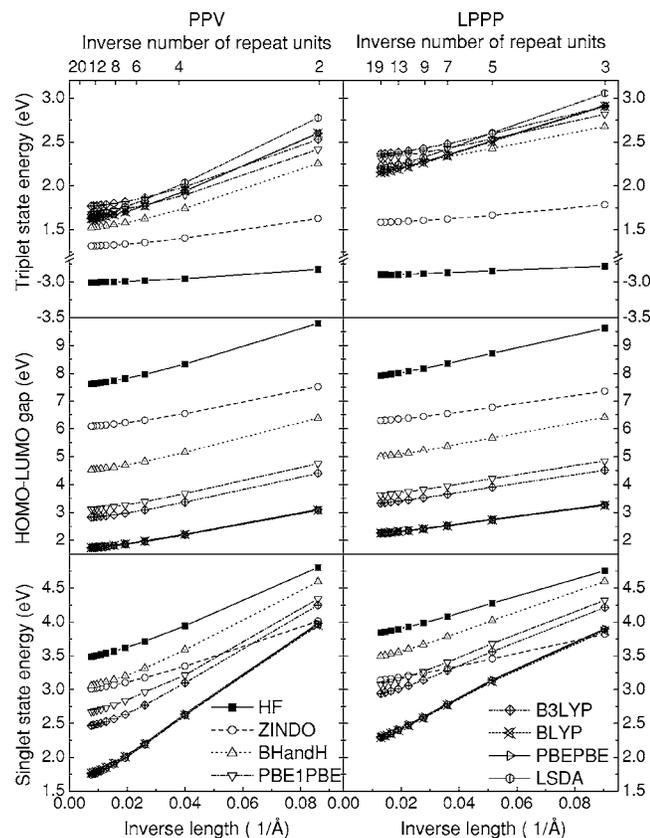


FIG. 2. Calculated energies of triplet  $T_1$  (top) and singlet  $S_1$  (bottom) states, and HOMO-LUMO gaps (middle) as a function of an inverse length for PPV (left) and LPPP (right) oligomers.

als span the midrange and result in the best agreement with experimental data (see Tables II and III), whereas the pure and GGA functionals consistently underestimate the band gaps of both PPV and LPPP.

Figure 3 displays the variation of the oscillator strengths  $f$ , which corresponds to the  $S_1$  state, as a function of the chain length. This quantity determines the probability of an optical transition to the given electronic state. Only the HF and hybrid functionals produce the correct linear scaling of  $f$  with the chain length. Oscillator strengths calculated using the LSDA and gradient-corrected functionals exhibit drastically different scaling properties. Namely,  $f$  initially increases, reaches its maximum at  $\sim 50$  Å, and then starts decreasing. Such behavior of the band-gap oscillator strength is inconsistent with simple physical reasoning and experimental observations.

TABLE II. Comparison of calculated asymptotic singlet ( $S_1$ ) and triplet ( $T_1$ ) state energies, HOMO-LUMO gaps, and experimental data (Ref. 39) in PPV.

Method	Triplet (eV)	Singlet (eV)	LUMO-HOMO (eV)
HF	-3.01	3.42	7.53
ZINDO	1.31	2.96	6.04
BHandH	1.50	2.99	4.44
PBE1PBE	1.67	2.57	3.04
B3LYP	1.75	2.39	2.75
BLYP	1.60	1.63	1.67
PBEPBE	1.60	1.64	1.68
LSDA	1.62	1.61	1.65
Experiment	1.3	2.5	

TABLE III. Comparison of calculated asymptotic singlet ( $S_1$ ) and triplet ( $T_1$ ) state energies, HOMO-LUMO gaps, and experimental data (Ref. 134) in LPPP.

Method	Triplet (eV)	Singlet (eV)	LUMO-HOMO (eV)
HF	-2.91	3.74	7.74
ZINDO	1.57	3.06	6.20
BHandH	2.21	3.37	4.84
PBE1PBE	2.29	2.94	3.48
B3LYP	2.33	2.80	3.19
BLYP	2.07	2.05	2.16
PBEPBE	2.09	2.07	2.13
LSDA	2.10	2.05	2.11
Experiment	2.1	3.7	

To rationalize these trends we further apply the two-dimensional real-space analysis of the calculated transition density matrices, which characterize the electronic transitions between the ground and electronically excited states.<sup>47</sup> Within the TD-HF approach, these quantities are given by  $(\xi_\nu)_{mn} = \langle \nu | c_m^\dagger c_n | g \rangle$ , where  $c_m^\dagger$  ( $c_m$ ) are the creation (annihilation) operators of an electron at the  $m$ th atomic orbital, and  $|g\rangle$  ( $|\nu\rangle$ ) is the ground (excited) state many-electron wave function. The diagonal elements  $(\xi_\nu)_{mm}$  represent the net charge induced in the  $n$ th orbital by an external field. The off-diagonal elements  $(\xi_\nu)_{nm}$  with  $m \neq n$  represent the joint probability amplitude of finding an electron and a hole located at the  $m$ th and  $n$ th orbitals, respectively.<sup>47</sup> Thus, the transition densities allow to interpret the electronic transitions in terms of the optically induced charges and electronic coherences. A very similar, although conceptually more involved, interpretation can be applied to the transition densities obtained via the TD-DFT approaches (in the same way as molecular orbitals of a noninteracting KS system can be used for an orbital analysis of a real interacting system).

Figure 4 displays the contour plots of the transition density matrices that correspond to the  $S_1$  and  $T_1$  states in PPV<sub>20</sub> and are computed using various methods. At the HF limit the electron-hole pair created upon an  $S_1$  optical excitation is delocalized over the entire chain (the diagonal in the plot).

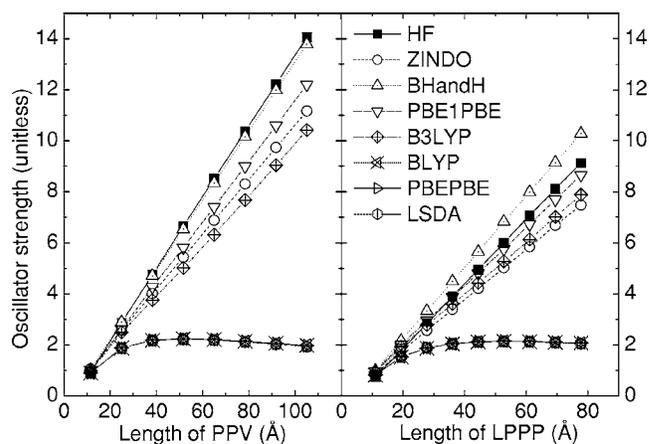


FIG. 3. Calculated size scaling of oscillator strength for  $S_1$  singlet state of PPV (left) and LPPP (right) oligomers.

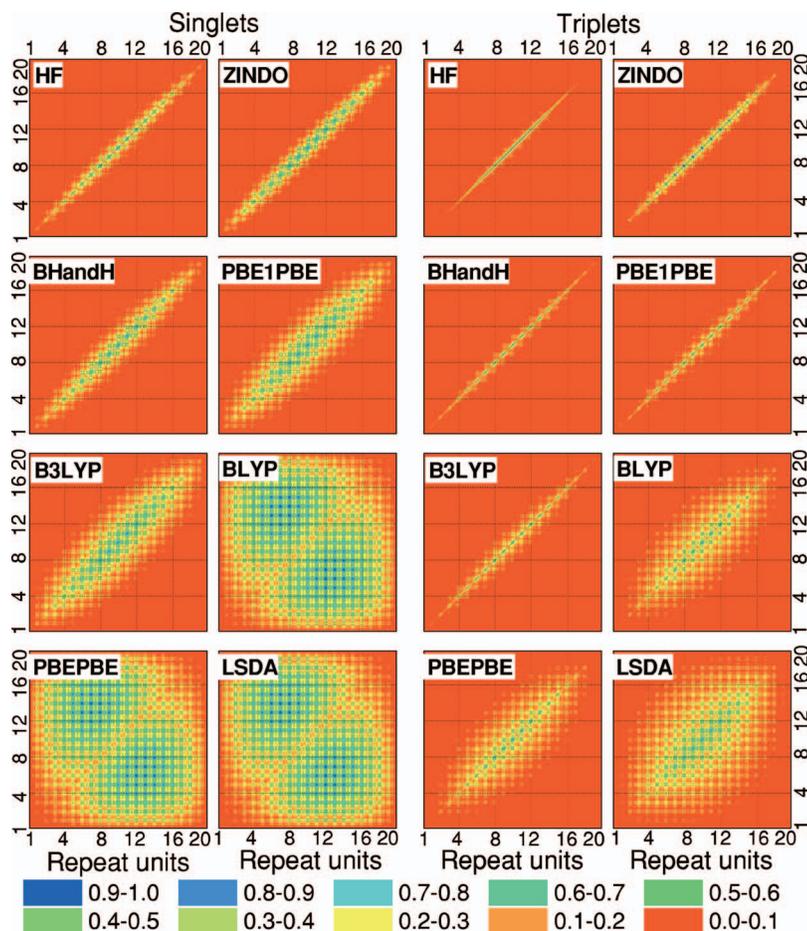


FIG. 4. (Color) Contour plots of transition density matrices from the ground state to the first singlet  $S_1$  (left) and triplet  $T_1$  (right) excited states in  $PPV_{20}$  oligomer calculated with different methods. The axis labels represent the individual repeat units along the oligomer chain according to the labeling in Fig. 1. The color code is given in the bottom. Each plot depicts probabilities of an electron moving from one molecular position (horizontal axis) to another (vertical axis) upon electronic excitation.

The exciton size is about 2 repeat units (largest off-diagonal extent of the nonzero matrix area). This exciton size grows when going to the semiempirical ZINDO approach and hybrid functionals. Finally, a completely delocalized state corresponding to the *unbound* exciton (noninteracting electron-hole pair) emerges at the LSDA and GGA limits. An electron (hole) tends to stay in the first (second) half of the chain or *vice versa*. This indicates an effective *repulsive* Coulomb interaction between an electron and a hole. The diagonal elements are small and, therefore, the oscillator strength of the transition is low. The higher-lying singlet excited states of PPV, analyzed in detail in Ref. 88, have diagonal nodes. This pattern is a consequence of the standing wave formation for excitonic states in finite systems.<sup>36</sup> If the exciton size is finite (hybrid DFT and HF limit), the lowest excitonic state shown in Fig. 4 collects almost the entire oscillator strength from its parent excitonic band. In contrast, in the limit of the delocalized exciton (LSDA and GGA approaches), the band-gap oscillator strength becomes dispersed among a large number of quasidegenerate states that correspond to unbound excitons. This explains the anomalous scaling behavior of the band-gap oscillator strength in Fig. 3.

The transition density delocalization patterns of the triplet state (Fig. 4) follow the trends observed for  $S_1$ . The  $T_1$  is a strongly localized tightly bound exciton, where the distance between an electron and a hole does not exceed 1 repeat unit for all hybrid DFT and HF based methods. However, in the LSDA limit,  $T_1$  corresponds to a delocalized nearly unbound

excitation with a finite size. In contrast to the  $S_1$  state, the GGA functionals noticeably decrease  $T_1$  exciton size, which still remains significant. For such localized excitations, the semilocal nature of the density gradients in GGA makes a difference, compared to the LSDA. Large electron-hole separation in unphysically delocalized  $S_1$  and  $T_1$  states computed using the LSDA and GGA methods constitutes a formal reason why the energies of these state coincide (i.e., the mutual spin direction is irrelevant). In contrast, compared to the  $S_1$  state, the  $T_1$  excitation is more localized with a much larger exciton binding energy for the methodologies that reproduce the excitonic effects. The latter rationalizes a substantial singlet-triplet splitting and is consistent with the experimental data.

Exactly the same trends appear in the calculated excitonic properties of the LPPP shown in Fig. 5. Compared to PPV, the LPPP features more delocalized  $\pi$ -electronic system, and, consequently, slightly larger excitonic sizes, calculated with the hybrid DFT and HF approaches. A spatial distribution of the excitonic wave function can be analyzed by taking vertical slices of the transition density matrices, which are shown in Fig. 6 for several approaches. These plots are related to the probability distributions of an electronic wave function when the hole is fixed in the middle of the molecule. The oscillatory nature of the curves points to the effects of the Peierls distortion, typical for conjugated chains. For example, the peaks in the plots that correspond to the  $S_1$  and  $T_1$  of PPV are related to the double bonds in

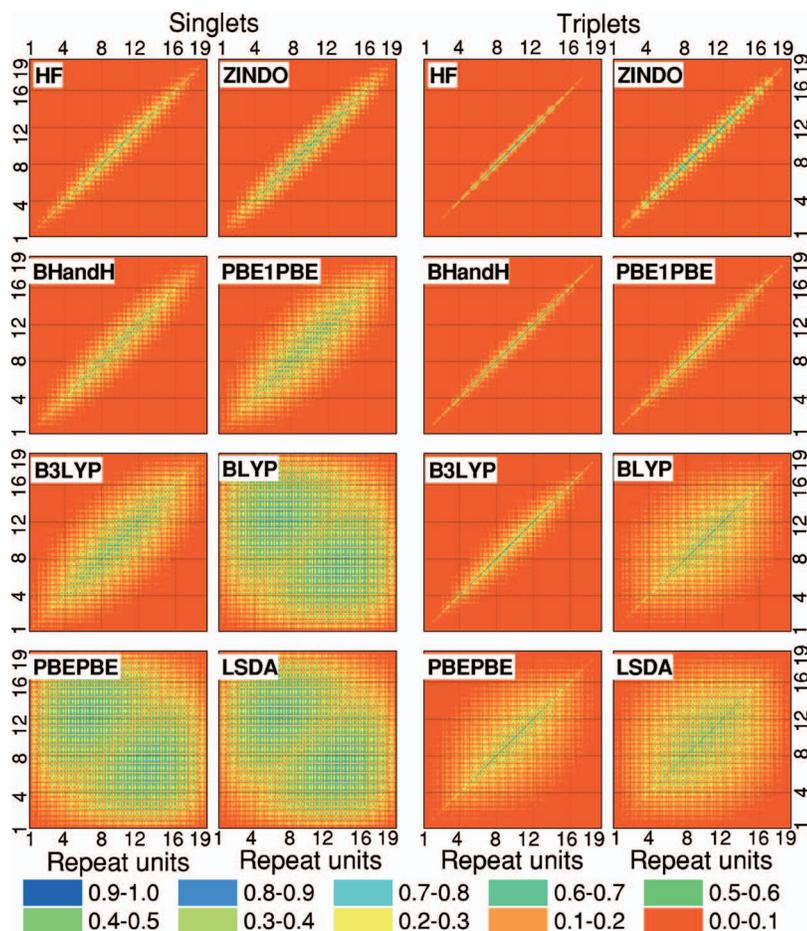


FIG. 5. (Color) Same as Fig. 4 but for LPPP<sub>19</sub> oligomer.

vinylene units. The vanishing amplitudes in the LPPP plots manifest the carbon atoms with the  $sp^3$  hybridization in the fluorene units, which do not participate in the optical excitation. Figure 6 clearly shows that the electron-hole interactions can be interpreted as a competition between the long-range Coulomb attraction induced by the HF exchange (for both singlet and triplet states) and local strong repulsion brought in by the LSDA component (for the singlet states only). The exciton size and, therefore, the effective Coulomb attraction between an electron and a hole naturally depend on the amount of the HF exchange in the functional.

Figure 7 emphasizes this attraction-repulsion interplay by comparing the variations of the  $S_1$  energy (correlated gap) and the uncorrelated HOMO-LUMO gap for small and large chains of PPV and LPPP, as a function of the Hamiltonian model. The correlated gap is smaller than the HOMO-LUMO gap for both molecules in the HF method since the effective electron-hole attraction stabilizes the HOMO-LUMO gap (that corresponds to noninteracting particles). The situation is opposite for small molecules treated using the LSDA or gradient-corrected models, due to electron-hole repulsion. In large chains, when an electron and a hole can be well separated and their localized repulsion is no longer relevant, the band gap asymptotically coincides with the HOMO-LUMO gap (a typical property of TD-DFT in solids<sup>102,103</sup>).

Thus the TD-LSDA and TD-HF roughly represent the two extreme cases of delocalized Wannier-Mott and local-

ized Frenkel excitons, respectively. Previous theoretical and experimental studies have unambiguously shown that conjugated polymers belong to an intermediate class (charge-transfer excitons) that can be efficiently described by hybrid functionals, spanning the whole range between the HF and LSDA extremes. For example, the exciton size in PPV is about 6–7 (B3LYP), 5–6 (PBE1PBE), 3–4 (BHandH) repeat units in TD-DFT approaches, compared to 4–5 repeat units in INDO/S semiempirical model,<sup>32,47</sup> 5–6 (Ref. 126) and 4–5 (Ref. 127) repeat units in correlated GWA and BSE *ab initio* approaches, and 5–7 repeat units in experiment<sup>128–130</sup> (given the uncertainty of conformational disorder and interchain interactions).

#### IV. DISCUSSION

To rationalize our numerical results we consider a model density functional based on the PPP Hamiltonian for an infinite one-dimensional  $\pi$ -conjugated chain, where each carbon atom  $n$  has a single  $\pi$  orbital with the nearest-neighbor hopping  $t_{2n,2n\pm 1} = (1 \pm \zeta/2)t_0$  ( $\zeta$  being Peierls distortion parameter).<sup>47</sup> This simple model captures the principle features of the optical response in conjugated polymers, yet allows for an analytical analysis of the capabilities of different density functional schemes to represent the relative electron-hole motions for the relevant photoexcitations. On the level of adiabatic TD-DFT, the system can be described as a clas-

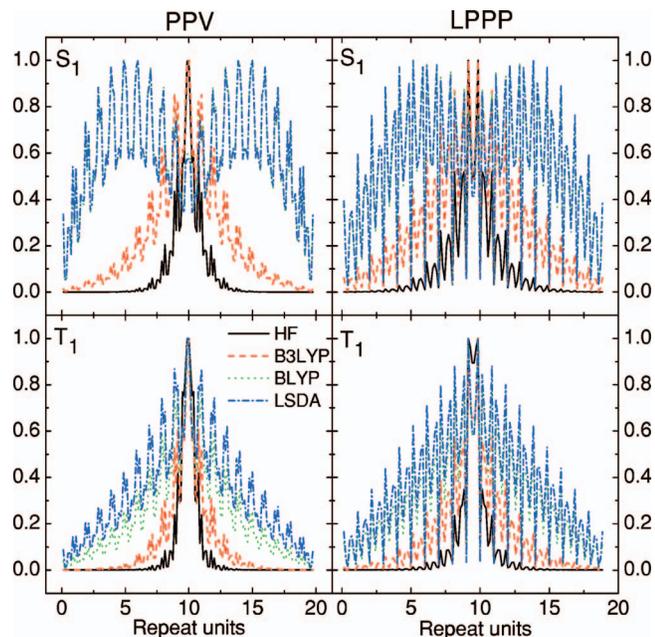


FIG. 6. (Color) Vertical slices of transition density matrices corresponding to  $S_1$  (top) and  $T_1$  (bottom) states in  $PPV_{20}$  (left) and  $LPPP_{19}$  (right) oligomers. These plots show the distribution of an electronic wave function when the hole is fixed in the middle of an oligomer.

sical Hamilton dynamics in the phase space of KS single-electron density matrices  $\rho_{mn}$  with the Poisson bracket<sup>118</sup>

$$\{\rho_{mn}, \rho_{kl}\} = i(\delta_{nk}\rho_{ml} - \delta_{lm}\rho_{kn}), \quad (1)$$

and the KS Hamiltonian

$$H(\rho) = \sum_n \left( t_{n,n+1} \rho_{n+1,n} + \frac{1}{2} \sum_{mn} U_{m-n} \rho_{mm} \rho_{nn} + c_x \frac{1}{2} \sum_{mn} U_{m-n} \rho_{mn} \rho_{nm} + E_{xc}(\rho_{nn}) \right), \quad (2)$$

where the first term represents the electron kinetic energy

and nuclear attractions, the second one stands for the Coulomb interaction, whereas the third and the fourth terms describe the electronic exchange and correlations.  $U_{m-n}$  stands for the Coulomb potential and  $E_{xc}$  is a (semi)local exchange-correlation functional (if the orbital overlap is neglected) that may include electron density gradients. The hybrid mixing parameter  $c_x \leq 1$  (Ref. 131) accounts for the amount of the HF exchange. Due to the symmetry translational breaking (Peierls-type transition), the ground state is represented by the bond-length alternation wave (rather than charge density wave) with  $\bar{\rho}_{nn} = 0.5$  for all  $n$ . This implies that the ground-state Coulomb and exchange-correlation potentials are homogeneous, and the KS orbitals are determined by the hopping term solely. In the momentum representation and the basis set of molecular orbitals (characterized by their momenta  $-\pi \leq s \leq \pi$  with respect to the discrete translation over a unit cell), the linear response is given by the deviations  $\xi_{ss'}$  of the particle-hole components of the KS density matrix from its ground state and is typically represented in the basis of transition densities (electronic eigenmodes).<sup>132</sup> The total momentum of an electron-hole pair is a well defined quantum number in our case of an infinite chain. We also assume that the optical wavelength is small compared to the inverse bond length. Subsequently, the modes with the zero momentum that contribute to the optical response can be described by the functions  $\bar{f}_{\pm}(s)$  ( $\bar{f}_+$  and  $\bar{f}_-$  being particle-hole and hole-particle components, respectively). Since typically  $|f_-| \ll |f_+|$ , we set  $f_-(s) = 0$  for a qualitative analysis, thus omitting the processes that do not conserve the number of electron-hole pairs. This approximation is related to the so-called Tamm-Dancoff approach.<sup>133</sup>

The hybrid density functional case [Eq. (2)] can be considered within the framework of Ref. 132 by weighting the exchange terms with  $c_x$  and using the renormalized potential  $U_{m-n}^r = U_{m-n} + \delta_{mn} f_{xc}(\bar{\rho}_{nn} = 0.5)$  (here  $f_{xc} = v'_{xc} = E''_{xc}$ ) to include

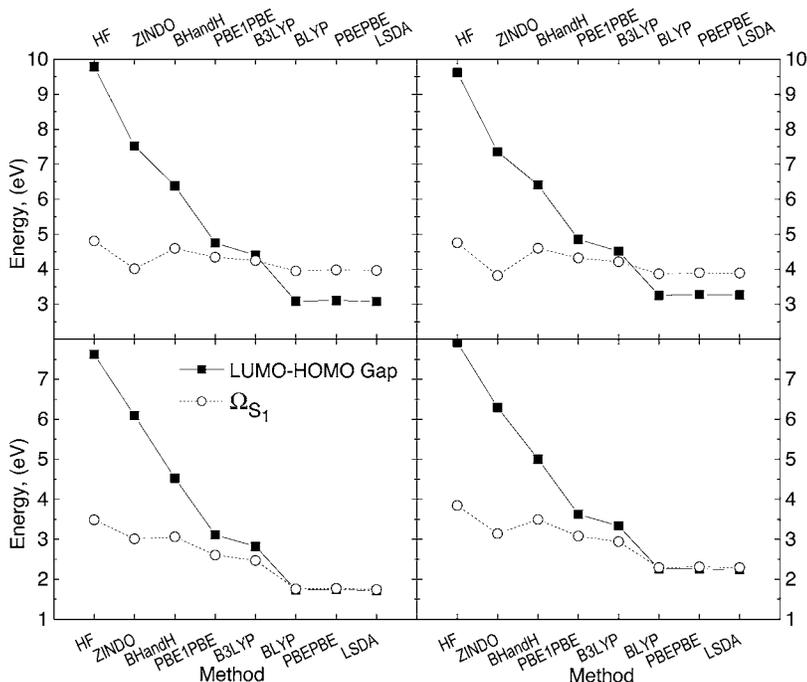


FIG. 7. Variation of HOMO-LUMO gap and  $S_1$  singlet state energy as a function of Hamiltonian model in the short,  $PPV_2/LPPP_3$ , (top-left/top-right panel) and long,  $PPV_{20}/LPPP_{19}$ , (bottom-left/bottom-right panel) oligomers, which mimic confined and infinite-chain limits, respectively.

the effects of electronic exchange and correlations. This allows to recast the TD-HF eigenmode equation [Eq. (D9) in Ref. 132] for TD-DFT case in a form

$$(\epsilon(s) - \Omega)\bar{f}_+(s) + c_x \int \frac{ds'}{2\pi} \bar{V}^{(0)}(s-s')\bar{f}_+(s') + \bar{V}^{(r)} \times (0) \int \frac{ds'}{2\pi} \bar{f}_+(s') = 0, \quad (3)$$

with  $\epsilon(s) = 2t_0(\zeta^2 + 2(1 - \zeta^2)(1 + \cos s))^{1/2}$ ,  $\Omega$  is an excitation frequency, and  $\bar{V}^{(0)}(s-s')$  being an effective Coulomb potential [Eq. (D10) in Ref. 132]. The presence of the HF exchange is accounted for by means of the following two numbers: The coefficient  $c_x$  and the renormalized quantity  $\bar{V}^{(r)} \times (0) > 0$  (instead of  $\bar{V}^{(1)}(0) > 0$  [Eq. (D10) in Ref. 132] used in the pure TD-HF case). Using an effective mass approximation and switching back to the coordinate representation (the latter should be considered as a mathematical trick, since the obtained 1D coordinate is not directly related to the original polymer chain), Eq. (3) can be interpreted as a 1D Schrödinger equation, where the  $c_x \bar{V}^{(0)}$  term represents the long-range binding potential, whereas the  $\bar{V}^{(r)}$  term stands for the local repulsive contact potential. This implies that without the HF hybrid mixing a bound state may not be formed in an infinite system, with the optical gap given by its HOMO-LUMO counterpart. Note that  $\bar{V}^{(1)}(0) > 0$  reflects the repulsive nature of the electron-electron Coulomb interaction, whereas the binding property of  $\bar{V}^{(0)}$  in Eq. (3) is inherited from the attractive nature of the Fock exchange (i.e., the Coulomb attractive electron-hole interaction). Formally the different signs of the Hartree and Fock interactions arise from different types of pairing when the fermion version of the Wick theorem is applied.

## V. CONCLUSION

The most notable result of the presented study is the failure of the common DFT based methods to predict correct exciton binding properties for both triplet and singlet states in conjugated polymers. This is demonstrated by our numerical studies of two common conjugated polymers, PPV and LPPP, and is clearly shown by the two-dimensional analysis of the relevant transition density matrices in Figs. 4 and 5. For the lowest singlet excited state, the LSDA and GGA based methods result in unphysical unbound exciton states due to an effective Coulomb repulsive interaction. The situation is quite similar for the lowest triplet excited state, although this excitation emerges as a weakly bound exciton slightly below the dissociation limit. These results are signified in an incorrect behavior of common spectroscopic observables, such as a lack of singlet-triplet splitting and vanishing oscillator strength (per unit length) of the band-gap exciton, which are inconsistent with the experimental data. Correlated methods such as GWA and BSE (which may be built on the top of LSDA) overcome this problem<sup>97,99,101-103</sup> but can be practically applied only to infinite-dimensional systems when periodic boundary conditions can be imposed. Hybrid functionals circumvent this problem as well by mix-

ing the exact HF exchange, which effectively is an extension to the nonadiabatic TD-DFT. The latter follows from the fact that the Fock exchange terms are adiabatic in terms of the KS density matrix and can be recast as a nonadiabatic functional of the electron density alone. An appropriate amount of the exact HF exchange can be further fine-tuned by fitting to the size scaling of the experimental spectroscopic observables. Moreover, there have been several recent successful attempts to develop new asymptotically corrected hybrid functionals, where the amount of HF exchange varies with the distance, such as LC-TD-DFT (Refs. 110 and 111) and CAM-B3LYP.<sup>112-114</sup> These new developments correct several TD-DFT failures, most notably problems with charge-transfer states, and potentially allow fine-tuning of the presence of excitonic effects. Thus, overall hybrid functionals represent a practical and accurate way to correctly describe excited states at all molecular length scales from small clusters to bulk materials.

## ACKNOWLEDGMENTS

We thank Richard L. Martin and Rudolph J. Magyar for their critical comments. V.Y.C. acknowledges the support through the start-up funds from Wayne State University. The authors acknowledge support of Center for Integrated Nanotechnology (CINT) and Center for Nonlinear Studies (CNLS) at Los Alamos National Laboratory operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under Contract No. DE-AC52-06NA25396.

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