# Excited States of Donor and Acceptor Substituted Conjugated Oligomers: A Perspective from the Exciton Scattering Approach

Hao Li,[†] Chao Wu,[‡] Sergey V. Malinin,[†] Sergei Tretiak,*[,§] and Vladimir Y. Chernyak*[,†]

[†]Department of Chemistry, Wayne State University, 5101 Cass Avenue, Detroit, Michigan 48202, United States, [‡]Department of Chemical and Biomolecular Engineering, University of Notre Dame, 182 Fitzpatrick Hall, Notre Dame, Indiana 46556, United States, and [§]Theoretical Division, Center for Nonlinear Studies, and Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

**ABSTRACT** Quantum-chemical computations allow one to predict a variety of interesting electronic properties of donor and acceptor substituted conjugated molecules. However, the complexity of such systems often limits physical interpretation of the computations and makes them impossible in larger molecules. In this study, the exciton scattering (ES) methodology is extended to analyze the excited-state structure of donor and acceptor substituted conjugated oligomers. The extracted reflection phases, transition charge, and dipole parameters of the modified termini are used to quantify the influence of the substitution on the molecular electronic and optical spectra. In particular, intuitive relationships between the substituent's electron withdrawing or donating ability and the ES parameters are discussed. A good agreement of the absorption spectra between the ES approach and the reference quantum-chemical computations demonstrates that the ES approach is qualified for such conjugated push—pull systems.

**SECTION** Molecular Structure, Quantum Chemistry, General Theory
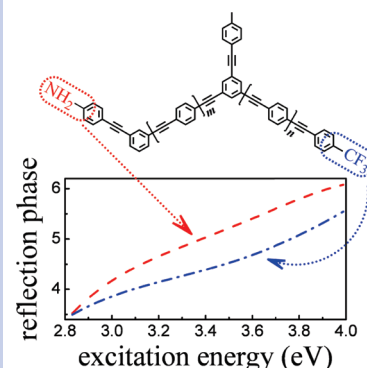
Conjugated polymers have been intensively studied for their interesting photophysical and carrier transport properties, as well as technological advantages over traditional semiconductors.[1−3] Conjugated polymers can be used in organic light-emitting diodes,[4] single-molecule switches,[5] organic solar cells,[6] transistors,[7−9] and imaging devices.[9−11] The prominent electric and optical properties of conjugated molecules are due to their quasi-one-dimensional system of delocalized $\pi$-electrons subject to strong electron—electron correlations and electron—phonon coupling, which gives rise to their complex electronic structure.[1,2,12] Understanding the excited state electronic structure of conjugated molecules and the underlying structure—property relations is, therefore, a nontrivial task important for design of novel organic electronic materials.

We have recently developed the exciton scattering (ES) approach for numerically efficient calculations of optical spectra in large branched conjugated molecules,[12,13] where electronic excitations are represented by excitons. Our approach is based on a simple and physically intuitive picture: electronic excitations are viewed as states of a quantum particle on a graph whose edges and vertices represent the molecular linear segments and vertices (termini, joints, and branching centers), respectively. Therefore, finding transition energies $\omega$ and exciton wave functions boils down to solving a "particle in a box" problem: one needs to solve a set of $\omega$-dependent homogeneous wave equations (ES equations) that describe scattering at the vertices and propagation along the linear segments. In an infinite linear chain, the exciton quasimomentum $k$ is conserved, so that the polymer backbone is characterized by the dispersion relation $\omega(k)$. Molecular vertices locally violate the discrete translational symmetry and cause ES described by $\omega$-dependent unitary and symmetric $n \times n$ scattering matrices, $n$ being the vertex degree. In particular, exciton reflection at a molecular terminus is described by a reflection amplitude $r = e^{i\phi}$ parametrized by a reflection phase $\phi(\omega)$. In addition to $\omega(k)$ and the scattering matrices, the molecular building blocks (repeat units and vertices) are characterized by the $\omega$-dependent transition charge and dipole coefficients that relate transition dipoles and charges of individual repeat units and vertices to local values of the exciton wave function and thus can be used to calculate the total transition dipole. All these ES parameters can be obtained using results of a chosen traditional quantum-chemical technique for excited states (the reference method) in molecules of moderate size, and tabulated for further applications. For large branched conjugated molecules, numerical solution of the ES equations is much more efficient than application of the reference quantum-chemical method. Indeed, such a large molecule typically contains large numbers but only several types of building blocks; using the same ES parameters for the same

building blocks effectively accounts for this symmetry. The ES approach can efficiently calculate transition frequencies and oscillator strength for all possible branched conjugated molecules composed of characterized building blocks as well as the reference quantum chemistry would do if it were not for limitations imposed by computational expense. Ultimately, the quasiparticle description of the ES approach can serve as a foundation for treating effects of disorder and exciton−phonon interactions, which is necessary for efficient modeling of energy transfer in conjugated systems.

Previously we applied the ES methodology to phenylacetylene (PA)[32] oligomers with *ortho-* and *meta-*conjugated double joints using the time-dependent density-functional theory (TDDFT)[14] and the time-dependent Hartree−Fock (TDHF) theory[15−17] as a reference quantum chemistry. The results of the ES approach were quite accurate, even in molecules where segment lengths are similar to the exciton size (1−2 repeat units): ES excitation energies were typically within several milli-electron volts of the values obtained in quantum-chemical computations, whereas oscillator strength deviations did not exceed several percent; the results were more accurate for molecules with longer linear segments.

So far we have focused on the applications of the ES approach to pure hydrocarbon systems, i.e., molecules without extraneous polar moieties that could noticeably perturb the $\pi$-electron density distribution and possibly violate the electron−hole symmetry. Presence of electron-donating and/or -accepting groups in conjugated systems is known to substantially modify their electronic and optical properties, which is important for various potential applications.[18−31] For example, linear conjugated molecules with donor and acceptor end-groups can show an increase of nonlinear optical response by orders of magnitude.[28,29]

In this work, we illustrate the capability of the ES methodology by considering PA oligomers with several common electron donor or acceptor end-groups. Qualitatively, such polar moieties modify the terminal potential experienced by a photoexcited electron or hole. From the ES perspective, since the violation of the electron−hole symmetry is expected to be localized near the modified termini,[33] they can be characterized by the energy-dependent ES parameters—the reflection phase as well as the transition charge and dipole parameters—which uniquely identify each substituent. Consequently, these ES parameters can be used to quantify the effect of substitution on the electronic spectrum of the molecule. Further, they can be added to the library of molecular building blocks, which enables us to apply the ES approach to any system with characterized donor and acceptor moieties.

As examples, we consider the termini of PA oligomers with three polar substituents in *para* position: two acceptor ($-CF_3$ and $-NO_2$) and one donor ($-NH_2$) groups. To obtain the reflection phases of the modified ends from the quantum-chemical calculations, we use linear molecules with only one substitution (see inset in Figure 1). The exciton reflection in such molecules is determined by two reflection phases $\phi_H$ and $\phi_X$ for the terminus without substitution (i.e., hydrogen-terminated) and with the substituent X, respectively. Excitations in the given exciton band satisfy a quantization condition that has exactly the same form as that for a
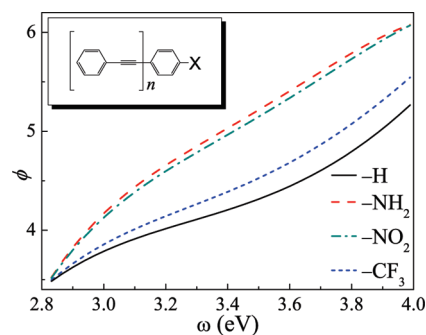


**Figure 1.** The reflection phases $\phi_X$ of the modified molecular termini and the reflection phase $\phi_H$ of the neutral (H-terminated) molecular end. Inset: linear PA oligomers with a substituent X (X = $-NH_2$, $-NO_2$, and $-CF_3$) on one end, which are used to extract and tabulate the reflection phases.

"particle in a box" and can be rewritten as

$$\phi_X = 2\pi n - 2kL - \phi_H \tag{1}$$

where $k$ is the wavenumber, $L$ is the molecular length, and $n$ is an integer. Since we have previously extracted $k(\omega)$ and $\phi_H(\omega)$ (functions of excitation energy that describe the properties of the backbone and the neutral terminus, respectively),[15] $\phi_X(\omega)$ can be readily found from the quantum-chemical transition energies. Once both reflection phases at the termini as well as the wavenumber are known functions of $\omega$, one can solve eq 1 for $\omega$ to calculate the excitation energies in the given exciton band in a linear molecule with an arbitrary length, which is the simplest application of the ES approach.

Our computational strategy to tabulate $\phi_X$ for a modified terminus is as follows: Quantum-chemical computations are performed to obtain excited states in linear molecules with one modified terminus (see inset in Figure 1). We emphasize that any quantitatively accurate approach for computing excited states, such as TDDFT, can be used as a reference quantum-chemical method.[14] Here we rely on the home-made collective electronic oscillator (CEO) technique[36,35] based on the TDHF theory combined with the semiempirical INDO/S (intermediate neglect of differential overlap parametrized for spectroscopy) model Hamiltonian. We start with the ground-state geometry optimization of all compounds done at the Austin model 1 (AM1) level using the Gaussian 03 package.[34] Then the excited states are calculated with the CEO code providing us with the energies, transition dipoles, and transition density matrices for the electronic excitations of each molecule. A detailed review of this approach can be found in ref 35. By checking the structure of the transition density matrices, we single out the lowest-energy exciton band.[15] Eventually, we use eq 1 to calculate the values of the reflection phase at the available excitation energies.

In principle, the electronic spectrum of only one long molecule is sufficient to obtain $\phi_X(\omega)$ of each substituent. We use a training set that consists of several linear molecules with different lengths between 20 and 50 repeat units to get more energy points within the exciton band. This allows us to confirm the main assumption of the ES approach that the scattering phases are local properties of the vertices. For future application of the ES approach, we tabulate the new
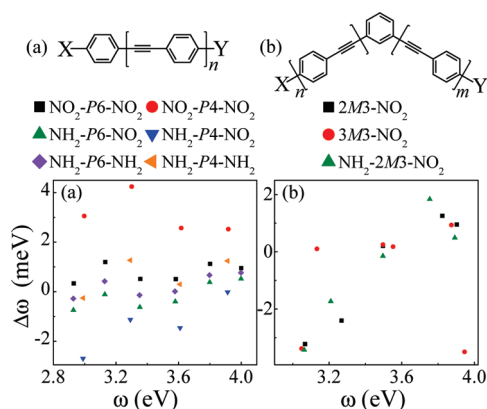
**Figure 2.** Accuracy of the ES method demonstrated as differences between excitation energies obtained by the ES approach and the CEO technique for several selected molecules: (a) linear molecules ([X−]P*n*[−Y]) and (b) molecules with a *meta* junction ([X−]*nMm*-[−Y]), where *m* and *n* denote the lengths of the linear segments, whereas X and Y are possible substitutions.



**Figure 3.** The transition charge $q^{(X)}(\omega)$ (top panel) and dipole $d^{(X)}(\omega)$ (bottom panel) parameters of donor/acceptor modified (−NH$_2$, −NO$_2$, and −CF$_3$) and neutral (−H) termini.

reflection phases using piecewise polynomial fitting. The resulting reflection phases are shown in Figure 1. As expected, the chemical structure of the substituent and its electron withdrawing/donating capacity modify the functional behavior of $\phi_X$, which, in turn, alters the resulting optical spectra.

We observe that substitution decreases the excitation energies for a given oligomer length, which corresponds to the increase of the reflection phase of the terminus. It is known that any substitution with a donor or acceptor end-group extends the conjugation and increases the amplitude of the zwitterionic resonant form responsible for a partial charge transfer along the chain,[37,38] which in turn results in the red (bathochromic) shifts of the optical spectra. These phenomena can be easily quantified within the ES picture, where the excited states are associated with states of a quantum particle (exciton). The dependence of the scattering phase on the excitation energy (or wavenumber) can be understood as a measure of the conjugation length and strength. A higher value of the reflection phase $\phi_X$ corresponds to a longer conjugation, which implies that the exciton experiences a softer potential at the terminus.

Because of the electron−hole symmetry, one cannot deduce from the reflection phase energy dependence whether the substituent is a donor or an acceptor. Instead, the reflection phase is determined by the effective conjugation. The strong $\pi$-acceptor (−NO$_2$) and $\pi$-donor (−NH$_2$) groups similarly affect the conjugation, whereas for the weak $\pi$-acceptor (−CF$_3$) the reflection phase is closer to that of the unmodified end (see Figure 1).

Finally, to verify the quality of the fitting functions representing the reflection phases of the donor and acceptor modified termini, we apply the ES approach to several types of PA molecules. Figure 2 shows the differences between the transition energies predicted by the reference quantum-chemical calculation (the CEO method, where the numerical cost grows as $O(N^3)$ with the number of electrons $N$) and the ES approach (where the numerical cost is negligible). For the linear and *meta* molecules shown in Figure 2, the differences are small (several milli-electron volts, and smaller for longer
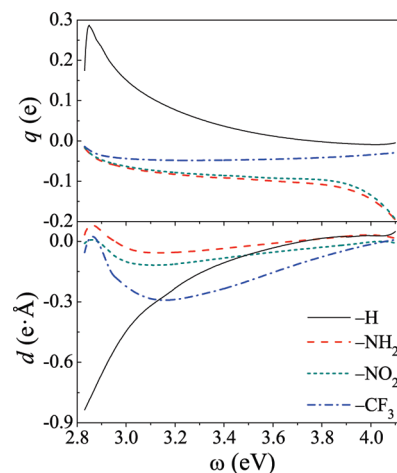
linear segments); for *ortho* molecules, the differences are similarly small. This accuracy is similar to what we previously observed for ES applications to PA molecules without extraneous groups.[15]

Following the methodology developed in ref.[17] ES-dipoles, we can also obtain the energy-dependent parameters necessary to model the transition dipole moments of the substituted oligomers. These charge and dipole parameters relate the transition charge and dipole of the terminus to the local excitation amplitudes. For a given terminus, these parameters are calculated from the CEO transition density matrices between the ground and excited states in five linear molecules with the lengths varying from 15 to 30 repeat units (see inset in Figure 1). In addition to the contributions of the matrix elements corresponding to the terminal atoms, we take into account the deviations of the transition charges and dipoles of the nearby repeat units from their asymptotic standing-wave forms. The transition charge and dipole parameters of the termini are shown in Figure 3. We note that the charge and dipole parameters of −NO$_2$ and −NH$_2$ substituted termini are similar because of their similar influence on $\pi$-conjugation, whereas they are quite different for a weaker acceptor −CF$_3$.

Together with the reflection phases, the transition charge and dipole parameters of the donor and acceptor substituted termini can be used within the ES approach to calculate the absorption spectrum of any PA compound including these modified termini. We show a comparison of the ES and CEO absorption spectra for three molecules in Figure 4. The relative differences of the ES and CEO transition dipoles with respect to that of the brightest state in the given molecule are less than 5%.

In this article, we show that the effects of chemical substitutions with donor and acceptor moieties can be naturally incorporated into the ES framework designed for multiscale modeling of excited state structure and spectroscopy of large conjugated molecular systems.[14] From the perspective of the ES approach, these chemical modifications modify the reflection phases and dipole parameters of molecular termini. Thus, the donor or acceptor ability of a substituent is uniquely
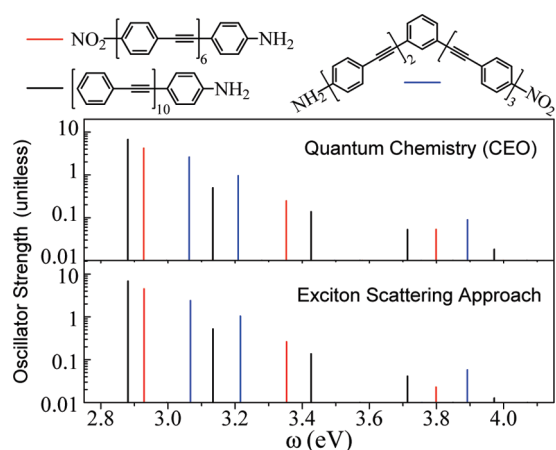
**Figure 4.** Accuracy of the ES method: comparison of optical spectra obtained with the CEO quantum-chemical technique (top panel) and the ES approach (bottom panel) for selected molecules.

imprinted in the functional form of the energy-dependent ES parameters that characterize the particular group. Within the ES approach, these newly characterized termini are merely additional molecular building blocks whose scattering parameters, combined with the previously extracted ones,[14,15,17] can be used to treat an entire variety of molecules with such substitutions.

The accuracy of the ES method for donor and acceptor substituted molecules is similar to what we previously observed for unmodified oligomers, namely, a few milli-electron volts for transition energies and a few percent for transition dipole moments. Thus, the ES approach accurately reproduces the reference quantum chemical calculations at a greatly reduced numerical cost, which marks its usefulness for computing the electronic spectra of giant molecular systems and/or combinatorial "click chemistry" studies to achieve desired photophysical properties of organic conjugated compounds.

## AUTHOR INFORMATION

### Corresponding Author:
*To whom correspondence should be addressed. Electronic address: serg@lanl.gov (S.T.); chernyak@chem.wayne.edu (V.Y.C).

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