P H Y S I C A L   R E V I E W   L E T T E R S

Multiscale Modeling of Electronic Excitations in Branched Conjugated Molecules Using an Exciton Scattering Approach

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The exciton scattering (ES) approach attributes excited electronic states in quasi-1D branched polymer molecules to standing waves of quantum quasiparticles (excitons) scattered at the molecular vertices. We extract their dispersion and frequency-dependent scattering matrices at termini, ortho, and meta joints for π-conjugated phenylacetylene-based molecules from atomistic time-dependent density-functional theory (TD DFT) calculations. This allows electronic spectra for any structure of arbitrary size within the considered molecular family to be obtained with negligible numerical effort. The agreement is within 10–20 meV for all test cases, when comparing the ES results with the reference TD DFT calculations.

Theoretical understanding and simulation of electronic spectra in nanosized molecular systems are important areas of research in physics and chemistry. Commonly used quantum-chemical methodologies, such as time-dependent density-functional theory (TD DFT), are generally able to provide quantitatively correct results [1,2]. However, the substantial numerical cost of such approaches [$\mathcal{O}(N^2) - \mathcal{O}(N^4)$, N being the system size] makes computations for large molecules with thousands of atoms prohibitively expensive. This calls for development of multiscale ladder-type approaches.

Recently we proposed an exciton scattering (ES) approach [3] designed for molecular systems where excited states can be described as strongly bound electron-hole pairs (excitons) [4–6]. This picture holds for low-dimensional (quasi-1D) geometries, where strong Coulomb correlations result in exciton binding energies comparable to the optical gap [4,5]. Conjugated organic macromolecules and molecular wires featuring delocalized π-electron states, which are promising for numerous technological applications, are examples of such systems [7–11]. However, explicit computation of excited states in large conjugated molecules is not feasible with quantum-chemical approaches (e.g., TD DFT) that properly account for electron exchange and correlations. In this Letter we develop an efficient multiscale modeling procedure based on the ES approach and demonstrate its remarkable accuracy in reproducing the electronic spectra of test polymers.

The excitation quasimomentum k in an infinite polymer chain is well defined due to its discrete translational symmetry. The excitations are characterized by the spectrum $\omega(k)$ that relates the excitation frequency ω to the quasimomentum, as well as by their size l_e, i.e., a typical distance between the electron and the hole. At length scales longer than l_e, the conjugated polymer molecules are represented by graphs whose edges correspond to linear chains [8–13], which allows for the development of a

phenomenological theory. The main idea behind the ES approach is the representation of excited states in a branched conjugated molecule by states of quasiparticles (excitons) on the corresponding graph (see Fig. 1) [3,14]. The picture of plane waves scattered at the molecular vertices is asymptotically exact in long linear segments, $l \gg l_e$. The computation of the excited state electronic structure in large molecules is divided into two steps: (i) retrieving the exciton properties in the molecular building blocks and (ii) solving a generalized "particle in a box" problem. Step (i) involves quantum-chemical calculations in simple molecular fragments and requires limited numerical effort. The numerical effort of step (ii) depends on the number of linear segments rather than on the number of single-electron orbitals, which substantially reduces computations in macromolecules.

In a segment α between vertices a and b an exciton wave function is given by a superposition of plane waves:

$$\psi_\alpha(x_\alpha) = a_{\alpha,ab} \exp(ik_{\alpha,ab}x_\alpha) + a_{\alpha,ba} \exp(ik_{\alpha,ba}x_\alpha), \quad (1)$$

where an integer x_α labels repeat units in the segment. The quasimomenta $k_{\alpha,ab}$ and $k_{\alpha,ba}$ are related to the excitation frequency ω through the exciton spectrum: $\omega(k_{\alpha,ab}) = \omega(k_{\alpha,ba}) = \omega$. Time reversal invariance in the absence of magnetic field results in the symmetric spectrum $\omega(-k) = \omega(k)$; hence, $k_{\alpha,ab} = -k_{\alpha,ba}$. Denoting the values of the outgoing and incoming plane waves at a joint a by $\psi_{\alpha a}^{(+)}$ and $\psi_{\alpha a}^{(-)}$, respectively, we have the following relation in the segment of l_α repeat units [15]:

$$\psi_{\alpha b}^{(-)} = \psi_{\alpha a}^{(+)} \exp[ik_{\alpha,ab}(\omega)l_\alpha]. \quad (2)$$

A frequency-dependent $n \times n$ scattering matrix $\Gamma_{a,\alpha\beta}^{(n)}(\omega)$ describes a vertex of degree n:

$$\psi_{\alpha a}^{(+)} = \sum_{\beta \ni a} \Gamma_{a,\alpha\beta}^{(n)}(\omega)\psi_{\beta a}^{(-)}. \quad (3)$$
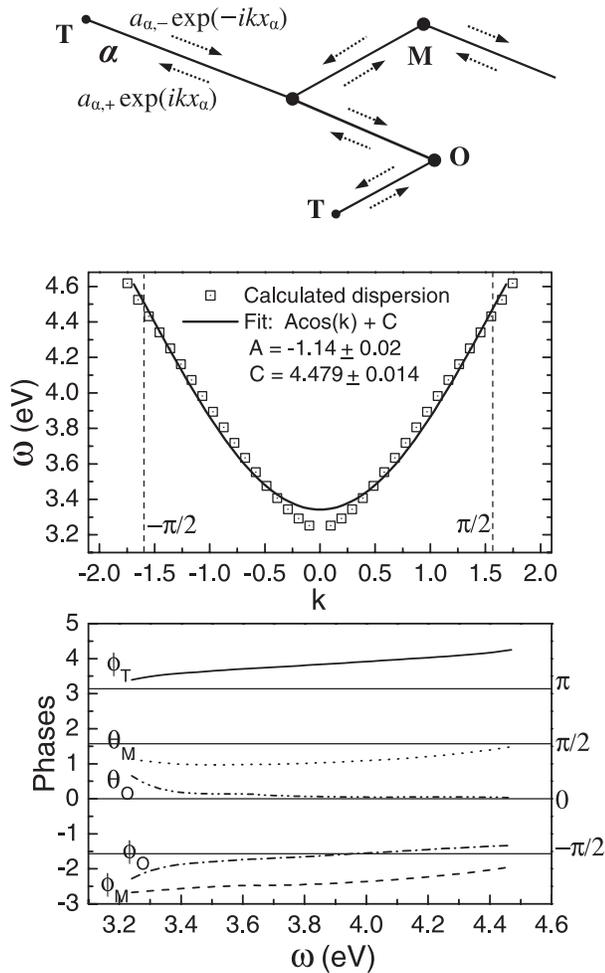
FIG. 1.   Top: within the ES model, the molecule is represented by a graph, and excited states are viewed as quasiparticles described by wave functions. Middle: dispersion of the lowest exciton band in phenylacetylene oligomers derived from the TD DFT calculations. Bottom: phases parametrizing the ES matrices at the chain termini (ϕ_T), ortho (ϕ_O and θ_O), and meta (ϕ_M and θ_M) joints.

FIG. 2.   Top: electronic spectra calculated using the ES model and direct TD DFT computations for selected compounds including linear chains (P); ortho (O) and meta (M) molecules are shown in the insets. Bottom: deviations between the ES and TD DFT results. The agreement improves for larger compounds.

Equations (2) and (3) constitute a frequency-dependent homogeneous system of linear equations with the same number of equations and unknown amplitudes $\psi^{(\pm)}_{\alpha a}$. Given the exciton dispersion $\omega(k)$ and the ES matrices $\Gamma_{a,\alpha\beta}(\omega)$, the values of ω for which the system has nonzero solutions provide the transition frequencies between the ground and excited states, whereas the amplitudes $\psi^{(\pm)}_{\alpha a}$ determine the spatial distribution of the excitations.

While the ES approach can be applied in any low-dimensional system (e.g., conjugated polymers, molecular quantum wires, and carbon nanotubes) featuring tightly bound excitons, we focus on a particular class of molecules that consist of phenylacetylene (PA) linear chains without extraneous vertices (see the insets in Figs. 2 and 3). Conjugated PA oligomers are the building blocks for many macromolecules such as dendrimers [11–13]. We

use model chemistry for excited states based on the TD DFT [16]. The geometry optimization of each structure is followed by the calculation of up to 20 excited states using the Gaussian 03 software [17] with the 6-31G basis set and the hybrid Becke-half-and-half-Lee-Yang-Parr (BHandHLYP) functional containing 50% of orbital exchange. The BHandHLYP model properly describes electronic excitations in π-conjugated polymers as tightly bound excitons [18], which results in correct size-scaling trends of the chain polarizabilities [19]. Exciton wave functions that characterize joint electron-hole motion are probed by the TD DFT transition density matrix [14,18] $\rho^{(\nu)}_{mm'} = \langle\Psi^{(\nu)}|c^\dagger_m c_{m'}|\Psi^{(0)}\rangle$ between the ground state $\Psi^{(0)}$ and the excited state $\Psi^{(\nu)}$ with $c^\dagger_m$ (c_m) being the electron creation (annihilation) operators on the mth atomic orbital.

To study scattering from the molecular ends and the exciton dispersion we consider finite linear oligomers P (see Fig. 2). The scattering at the ends is described by a unitary 1×1 matrix $\Gamma^{(1)}(\omega) = \exp[i\phi_T(\omega)]$, i.e., a unimodular complex number determined by its frequency-dependent phase. Equations (2) and (3) result in the following quantization condition:

$$kl = \pi n - \phi_T. \qquad (4)$$

Here l is the length of the molecule in repeat units, and n is an integer labeling the excited states. In the ES approach, $k(\omega)$ and $\Gamma(\omega)$ are independent of the segment length, being solely determined by the molecular structures of the polymer backbone and scattering centers.

We extract $k(\omega)$ and $\phi_T(\omega)$ from the results for the excited state energies and the corresponding transition density matrices in linear molecules of different lengths (P10–P43, 12 molecules in total). In principle, the exciton spectrum can be found from the data in very long oligomers, where the effect of the terminal scattering is negligible. The latter can be further retrieved using the data from shorter oligomers. However, since the numerical methods are naturally restricted to moderate oligomer lengths, neglecting the scattering phase in Eq. (4) completely (or fixing it, e.g., at the hard-wall value $\phi_T = \pi$ for all energies) would not make a sufficiently accurate approximation for the spectrum. Simultaneous evaluation of two smooth functions $k(\omega)$ and $\phi_T(\omega)$ can be performed based on the available set of energies ω where the functions obey Eq. (4) for different molecular lengths l and numbers of standing wave nodes $(n - 2)$. We use two numerical methods dubbed as two-point and four-point approaches [15], both derived from the Taylor expansion, and apply the piecewise polynomial least squares fit to tabulate the functions $k(\omega)$ and $\phi_T(\omega)$ for their further use (see Fig. 1). We note that $\omega(k)$ can be adequately approximated by a single cosine, which suggests that the strongest effective interaction in the molecule occurs between neighboring repeat units. We find a substantial frequency dependence of the scattering phase in the range $\pi < \phi_T < 2\pi$, which deviates from the hard-wall reflection implying $\phi_T = \pi$. One can refine the accuracy of the derived $k(\omega)$ and $\phi_T(\omega)$ by including TD DFT results from more and longer molecules.

Next we consider molecules with two linear segments linked by a symmetric joint through meta (M) or ortho (O) substitutions (see Fig. 2). The symmetry suggests the following parametrization of the scattering matrices:

$$\Gamma^{(2)}(\omega) = \begin{pmatrix} r & t \\ t & r \end{pmatrix}, \qquad r(\omega) = \sin\theta(\omega)\exp[i\phi(\omega)],$$
$$t(\omega) = i\cos\theta(\omega)\exp[i\phi(\omega)], \qquad (5)$$

where the reflection $r(\omega)$ and transmission $t(\omega)$ amplitudes are expressed in terms of two frequency-dependent phases $\theta(\omega)$ and $\phi(\omega)$. Since in the ES approach only a quantitative difference between the meta and ortho joints appears in the scattering matrices, the following simple analysis is valid for both cases. Molecules with equal arms of length l are symmetric with respect to the joint, and consequently all excitations there are either even or odd. Equations (2) and (3) imply two separate quantization conditions:
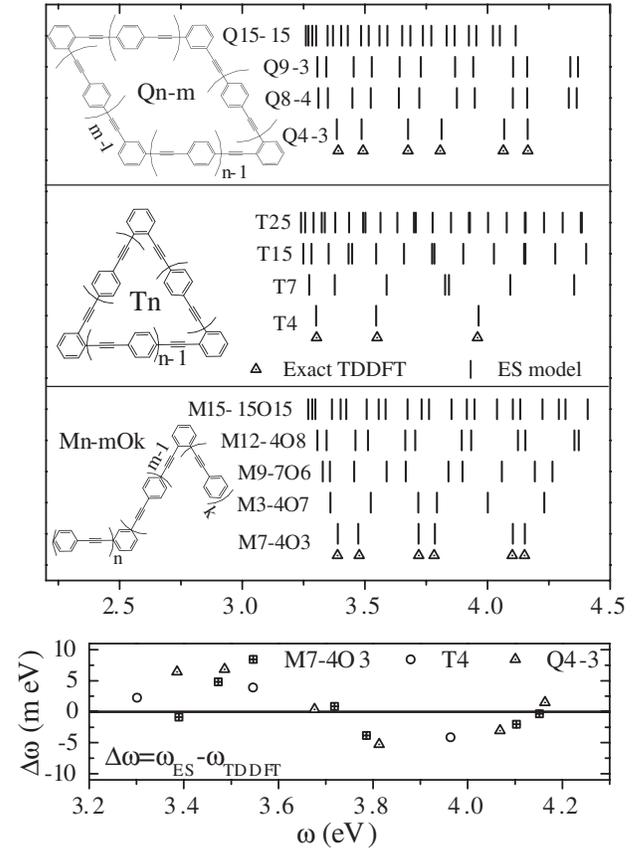
FIG. 3.   Top: electronic spectra calculated using the ES model for selected compounds shown in the insets. TD DFT results are not available for the largest molecules. Bottom: deviations between the ES and TD DFT results.

$$2kl = 2\pi n \pm \theta - (\phi + \phi_T) \mp \pi/2, \qquad (6)$$

where the upper and lower signs correspond to even and odd modes, respectively, and n is an integer which increases by one for every higher mode of the same parity. The combinations $\phi(\omega) \pm \theta(\omega)$ can be found for any excited state of corresponding parity by applying Eqs. (6) with $k(\omega)$ and $\phi_T(\omega)$ already retrieved from linear molecules. Thus, we calculate TD DFT electronic spectra of the meta- and ortho-conjugated molecules $Ml - l$ and $Ol - l$ for $l = 14, 15$; then we use piecewise smooth fitting functions to approximate the combinations $\phi(\omega) \pm \theta(\omega)$ and obtain these phases separately. The results for both M and O joints are shown in Fig. 1. Our calculations confirm the known qualitative properties of the joints [11,13]. Phases ϕ_O and θ_O for the ortho joint are close to those for the ideal transmission ($-\pi/2$ and 0, respectively), whereas meta joint phases ϕ_M and θ_M are near the values of the complete terminal reflection (ϕ_T and $\pi/2$, respectively). This indicates that the ortho joint is almost transparent to excitons and the meta joint acts as a chain terminus.

The components of the ES model ($k(\omega)$, $\phi_T(\omega)$, $\phi(\omega)$, and $\theta(\omega)$) enable efficient computation of electronic spec-

tra in arbitrary PA-based molecular structures with M and O joints in the energy range corresponding to the lowest exciton band 3.2–4.6 eV. The accuracy of the extracted ES data can be verified by comparing the energies predicted by the ES model with those obtained from direct quantum-chemical calculations. Figure 2 shows this comparison for selected P, M, and O molecules. Overall, deviations of the ES theory from the reference TD DFT calculations are within 20 meV even for the smallest test molecules. Naturally, the accuracy of the ES model increases with the increasing linear segment length. The excited state energies seem to be rather insensitive to the non-negligible ratio of the exciton size to the segment length. Figure 2 shows that the electronic spectra of P and O molecules have many similarities because the O joint is nearly transparent to the excitons. In contrast, the spectra of the M molecules exhibit typical features of localized Frenkel excitons such as the Davydov splitting.

Finally, Fig. 3 shows the calculated electronic spectra of more complex compounds with M and O joints. In this case the direct TD DFT results are available for the smallest molecules only, and the ES model shows excellent agreement within 10 meV. Notably, the average accuracy of even high-quality quantum-chemical calculations of molecular excited states such as TD DFT is about 0.1–0.3 eV compared to the experimental data [1,2]. Where available, the results of numerically expensive atomistic calculations are nearly exactly reproduced by the ES model with negligible computational expense.

In summary, the ES approach has been used to study electronic spectra of conjugated phenylacetylene polymers. We extracted the parameters of the ES model from the TD DFT results in simple PA molecules, although virtually any quantum-chemical approach capable of describing correlated molecular excited states would be suitable as well. The ES approach, combined with a particular quantum-chemical method, is designed to predict the electronic spectra in large molecules. Once the components of the ES model including the exciton dispersion spectra and scattering matrices are tabulated, the electronic spectra of arbitrary structures can be easily obtained. In this Letter we have considered molecular ends, as well as ortho and meta joints. Application of the ES approach to the joints of higher order is left for future studies.

Comparisons with time-consuming full TD DFT calculations showed deviations not exceeding $\sim$10–20 meV. This demonstrates the great potential of the ES approach for computational design of molecular structures with desirable electronic and optical properties.

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