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Exciton scattering approach for optical spectra calculations in branched conjugated macromolecules

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ABSTRACT

The exciton scattering (ES) technique is a multiscale approach based on the concept of a particle in a box and developed for efficient calculations of excited-state electronic structure and optical spectra in low-dimensional conjugated macromolecules. Within the ES method, electronic excitations in molecular structure are attributed to standing waves representing quantum quasi-particles (excitons), which reside on the graph whose edges and nodes stand for the molecular linear segments and vertices, respectively. Exciton propagation on the linear segments is characterized by the exciton dispersion, whereas exciton scattering at the branching centers is determined by the energy-dependent scattering matrices. Using these ES energetic parameters, the excitation energies are then found by solving a set of generalized "particle in a box" problems on the graph that represents the molecule. Similarly, unique energy-dependent ES dipolar parameters permit calculations of the corresponding oscillator strengths, thus, completing optical spectra modeling. Both the energetic and dipolar parameters can be extracted from quantum-chemical computations in small molecular fragments and tabulated in the ES library for further applications. Subsequently, spectroscopic modeling for any macrostructure within a considered molecular family could be performed with negligible numerical effort. We demonstrate the ES method application to molecular families of branched conjugated phenylacetylenes and ladder poly-*para*-phenylenes, as well as structures with electron donor and acceptor chemical substituents. Time-dependent density functional theory (TD-DFT) is used as a reference model for electronic structure. The ES calculations accurately reproduce the optical spectra compared to the reference quantum chemistry results, and make possible to predict spectra of complex macromolecules, where conventional electronic structure calculations are unfeasible.

1. Introduction: the ES concept

Organic conjugated materials have attracted considerable attention for their technological advantages, interesting photophysical and photochemical properties, low cost, light weight, flexibility, and convenience of solution-based processing techniques [1–8]. The remarkable electronic and optical properties of conjugated molecules are attributed to delocalized $\pi-$electron systems that reside on the quasi-one-dimensional molecular backbones, which can be constructed and tuned synthetically [9–13]. Therefore, synthetic design of conjugated molecular structures targeting specific optoelectronic properties, requires theoretical understanding and numerical modeling of their electronic excitations. However, the excited state electronic structure of conjugated molecules is complex due to their low dimensionality, strong electronic correlations and significant electron–phonon coupling [14–17]. Only a few quantum-chemical methodologies that are capable of adequate accounting for electron exchange and correlations, can be applied to serve the above purpose [18–20]. Alas, even numerically efficient methods that satisfy the above requirements (such as time-dependent density functional theory, TD-DFT [21]), are prohibitively expensive for the excited states computations of large systems, due to the unfavorable scaling of the numerical cost $[\mathcal{O}(N^2) - \mathcal{O}(N^5), N$ with being the number of electron orbitals] [22–24]. On the other hand, even large conjugated structures consist of

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a limited number of elementary molecular blocks [2,11]. This opens an opportunity to apply a multiscale concept for efficient description of electronic excitations in a macromolecule by first characterizing the excited states of each building block followed by expressing the electronic properties of the entire structure in terms of the building block data. The exciton scattering (ES) approach [16,25] accomplishes this goal by introducing a rigorous algorithm based on quasi-particle description of electronic excitations.

Indeed, previous studies in the 1990s interpreted excited electronic states in quasi-one-dimensional organic semiconductors as bound electron–hole pairs (excitons) with an emphasis on the relative motion of electrons and holes [26,27]. Consequently, a simple and intuitive picture of optical responses emerged from a real-space analysis of the single-electron transition density matrices defined as

$$(\xi_\nu)_{nm} = \langle \nu | c_n^\dagger c_m | g \rangle. \quad (1)$$

Here, $|g\rangle$ ($|\nu\rangle$) denotes the ground (excited) state many-electron wavefunction, $c_n^\dagger$ (c_m) is the Fermi creation (annihilation) operator of the nth (mth) atomic orbital. Subsequent investigations on electron energy loss spectroscopy (EELS) in linear conjugated oligomers [28,29] revealed an importance of the “center-of-mass” exciton motion related to the diagonal direction in the transition density matrix (Eq. (1)), in contrast to the off-diagonal pattern characterizing the exciton type.

The concept of the ES method first formulated in Ref. [16] attributes a branched conjugated macromolecule (e.g., Fig. 1a) to a graph (Fig. 1b), whose edges and nodes represent the linear segments (composed of the repeat units) and molecular vertices (Fig. 1c), respectively. Exciton motions on such graph form plane waves that scatter at branching centers, joints, and molecular termini. Here both electron and hole move together, and a typical distance between these particles (exciton size) l_e can be quantified as the off-diagonal extent of the transition density matrices (see contour plots in Fig. 1e). In the simplest case of a perfect infinite linear chain, the exciton quasimomentum k is a well-defined quantum number that reflects translational symmetry. Therefore, all electronic excitations can be characterized by the dispersion relation $\omega(k)$, which connects the exciton frequency (energy) ω to its momentum. In finite oligomers, electronic states become discrete, and each state features a characteristic standing wave structure in the diagonal direction of the transition density matrix. For example, the contour plots of the latter in Fig. 1e correspond to the lowest five excitations in a linear molecule P10 (Fig. 1d). This standing wave pattern is observed in all conjugated macrostructures (e.g., Fig. 1a), where the exciton size l_e is small compared to the typical linear segment length L. Therefore, the proposed quasiparticle representation, which is asymptotically exact in the long segment $L \gg l_e$ limit, is expected to be adequate. Exciton scattering at branching centers and molecular termini are further described using frequency-dependent $n \times n$ scattering matrices $\Gamma^{(n)}(\omega)$, n

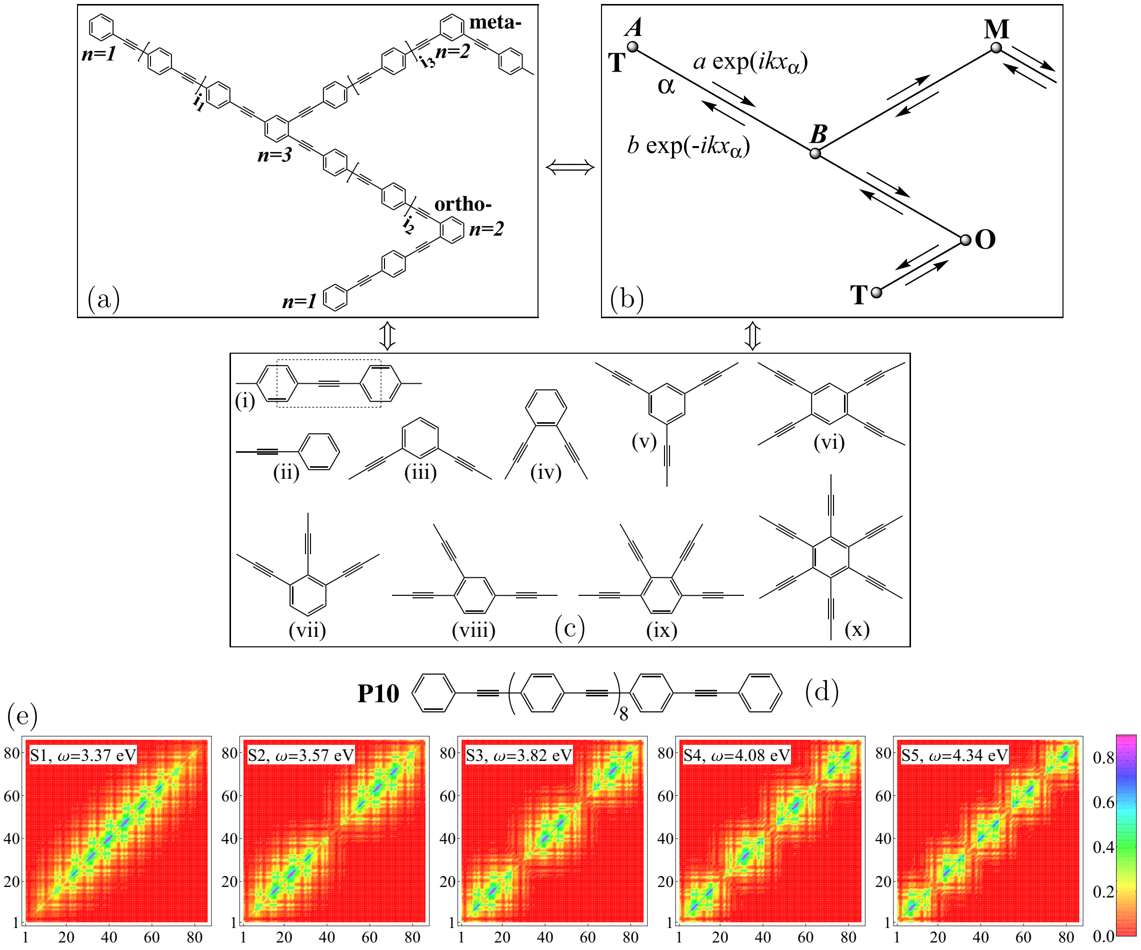

Fig. 1. Illustration of the ES approach. (a) structure of a conjugated molecule; (b) exciton scattering picture on the quasi-1D graph of the molecule; (c) building blocks of phenylacetylene (PA) molecules; (d) linear PA molecule consists of 10 repeat units; (e) exciton-scattering patterns given by the contour plots of transition density matrices from ground state to excited state in the molecule shown in (d).