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How Geometric Distortions Scatter Electronic Excitations in Conjugated Macromolecules

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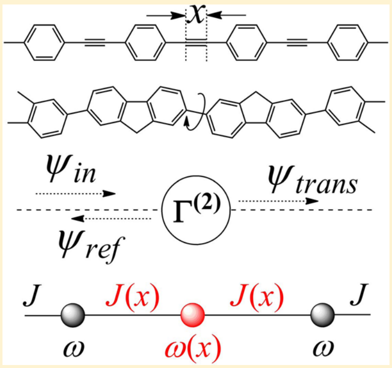

ABSTRACT: Effects of disorder and exciton−phonon interactions are the major factors controlling photoinduced dynamics and energy-transfer processes in conjugated organic semiconductors, thus defining their electronic functionality. All-atom quantum-chemical simulations are potentially capable of describing such phenomena in complex "soft" organic structures, yet they are frequently computationally restrictive. Here we efficiently characterize how electronic excitations in branched conjugated molecules interact with molecular distortions using the exciton scattering (ES) approach as a fundamental principle combined with effective tight-binding models. Molecule geometry deformations are incorporated to the ES view of electronic excitations by identifying the dependence of the Frenkel-type exciton Hamiltonian parameters on the characteristic geometry parameters. We illustrate our methodology using two examples of intermolecular distortions, bond length alternation and single bond rotation, which constitute vibrational degrees of freedom strongly coupled to the electronic system in a variety of conjugated systems. The effect on excited-state electronic structures has been attributed to localized variation of exciton on-site energies and couplings. As a result, modifications of the entire electronic spectra due to geometric distortions can be efficiently and accurately accounted for with negligible numerical cost. The presented approach can be potentially extended to model electronic structures and photoinduced processes in bulk amorphous polymer materials.

SECTION: Spectroscopy, Photochemistry, and Excited States

Conjugated polymers and oligomers have found a variety of optoelectronic applications, spanning organic solar cells,[1−3] light-emitting devices,[4−6] single-molecule switches,[7−9] field-effect transistors,[10−12] and so on. The preeminent electronic and photovoltaic properties of conjugated molecules are attributed to the complex many-body system of delocalized π-electrons, involving strong electron correlations and electron−phonon couplings. Because the processes of light absorption, emission, photoinduced charge, and energy transfer are all determined by excited-state electronic structures, including their coupling to vibrational modes, theoretical understanding and modeling of electronic excitations in real molecular environment turn into an essential and challenging research area in electronically functional materials.[13−16] However, being prohibitively expensive, modern quantum-chemical computations are very limited in the simulation of large conjugated materials.

We have recently developed the exciton scattering (ES) approach[17−26] that efficiently characterizes the electronic excited states in branched conjugated macromolecules using a quasiparticle representation. Within the ES approach, a quasi-1-D molecular structure is considered as a graph that consists of edges and nodes denoting molecular linear segments and vertices, respectively. Electronic excitations in a conjugated molecule are ascribed to quantum quasiparticles (excitons) moving along linear chain and being scattered at molecular vertices. In the case when linear molecular components are long enough compared with the electron−hole separation length scale, that is, $l_e \ll L$ (l_e and L are the exciton size and the linear segment length, respectively), which is usually true for branched conjugated molecules, the exciton wave function of a linear segment can be represented by a standing wave formed by a pair of plane waves propagating in opposite directions. Therefore, the electronic excitations of a particular exciton type can be described by the properties of the molecular building blocks. In particular, the exciton dispersion $\omega(k)$, which relates the exciton energy, ω, to its quasimomentum, k, represents the wave propagation along any linear segments formed by identical repeat units, whereas an $n \times n$ (n being the vertex degree) exciton scattering matrix, $\Gamma(\omega)$, which can be viewed as a microscopic boundary condition, specifies the wave scattering at the molecular vertex by transforming the n incoming wave amplitudes to the outgoing counterparts. Consequently, finding the excitation energies, ω, and the exciton wave functions is equivalent to solving a generalized "particle in a box" problem, which contains a set of ω-dependent linear wave equations (the

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so-called ES equations). Given the exciton dispersion, $\omega(k)$, and scattering matrices, $\Gamma(\omega)$, which can be extracted from commonly used quantum chemical computations in molecular fragments of moderate size,[20,25,26] the ES approach substantially reduces the numerical expense of the excited-state computations to the cubic order in the number of the linear segments, which otherwise scales as $O(N^2)-O(N^5)$ (where N is the number of electron orbitals) in modern quantum chemical methodologies.[27]

Founded on the concept of plane waves and building blocks, the ES approach works amazingly well for static and ideal molecular structures with certain tolerance to slight geometric deformations.[21,22] However, the plane-wave nature of the ES method prevents its direct application to photoinduced dynamics that involves coupling of electronic excitations to static and dynamical disorder. To address the above issue, we have recently reformulated the ES approach to conjugated molecules in terms of effective tight-binding models,[28] where electronic excitations are attributed to excitons residing on the sites of an irregular lattice that represents the repeat units and scattering centers. Such methodology allows the exciton scattering properties associated with molecular building blocks to be characterized by effective tight-binding models so that molecular distortions can be explicitly accounted for by identifying the dependence of the model parameters (on-site energies and hopping constants) on the molecular geometry. The lattice morphology and model parameters for ideal molecular geometry can be acquired from the reference quantum-chemical computation processed by the ES analysis. In particular, the graph structure (its sites and their connectivity) can be determined by analyzing the properties of the scattering centers along with the exciton dispersion, whereas the Hamiltonian parameters (on-site energies and hopping constants) for ideal geometry can be identified by requiring the lattice model to numerically reproduce the exciton dispersion and scattering matrices, previously extracted from the reference quantum chemistry.[28,29]

We extend the capability of the ES methodology to the case of nonideal molecular geometries to incorporate the effect of disorder and exciton−phonon coupling, both determined by the dependence of the excited-state electronic structure on the molecular geometry distortions. The following strategy has been adopted: characterizing the localized change of excitation properties at the deformation with respect to its magnitude, coupled to the excited-state structure of the attached molecular segments. In particular, we first apply the ES analysis to a set of localized distortions of identical type yet different magnitudes, being treated as effective scattering centers. We further identify the dependence of the tight-binding parameters on the distortion magnitude by comparing the exciton scattering, induced by a localized distortion, with the exciton scattering in the lattice model with modified parameters, requiring the two scattering matrices to be as close as possible. The above strategy can be implemented as a practical tool by invoking a natural locality principle: for a local geometry distortion, only the lattice parameters in a small neighborhood of the distortion position should be modified. This results in a description of the vibronic coupling in terms of distortion-induced modification of a limited number of the lattice parameters due to the locality principle.

For practical implementation of the aforementioned scheme, the simplest instance is to consider a geometric distortion, localized within a repeat unit of a linear chain in symmetric fashion with respect to the repeat unit center. Because the above distortion breaks down the translational symmetry of the chain, it is natural, within the ES framework, to treat it as a symmetric scattering center (double joint), which can be described by a 2 × 2 scattering matrix $\Gamma(k)$. For a molecular vertex possessing high geometric symmetry, the scattering matrix can be parametrized in terms of scattering phases associated with the symmetry, that is, by diagonalizing it in a quasimomentum-independent fashion using the irreducible representations of the vertex's symmetry group, as discussed in detail in our previous work.[24] As a result, a set of quasimomentum-dependent scattering phases $\phi_j(k)$ with $j = 1, \ldots, \deg\,\Gamma$ can be obtained so that $e^{i\phi_j}$ represents the eigenvalues of $\Gamma(k)$. In our case of symmetric double joints, $\phi_0(k)$ and $\phi_1(k)$ have been extracted with respect to even and odd parity, respectively. Note that the exciton dispersion $\omega(k)$ and the scattering matrix of the terminus $e^{i\phi_T}$ can be extracted, in advance, from the quantum-chemical calculations in unperturbed linear molecules.

In what follows, we illustrate how to parametrize the effects of geometrical disorder on electronic excitations in conjugated molecules using examples of bond-length alternation in phenylacetylenes (PA) oligomers and single bond rotation in polyfluorene (PFO)-based molecules. (See Figure 1a,b for the molecular structures.) All reference excited-state computations are performed using TD-DFT methodology with a hybrid range-corrected functional CAM-B3LYP[30,31] and 6-31G basis set. Ground-state molecular geometries of unperturbed structures have been optimized at the same CAM-B3LYP/6-31G level, whereas a geometry perturbation has been introduced manually by adjusting the triple bond length or the dihedral angle in a repeat unit with the optimized structure. Because of the improved description of long-range exchange-correlation potential in CAM-B3LYP model, the functional adequately describes $\pi \rightarrow \pi^*$ excitations in conjugated molecules as tight-bound excitons.[32−34] Excited-state compu-

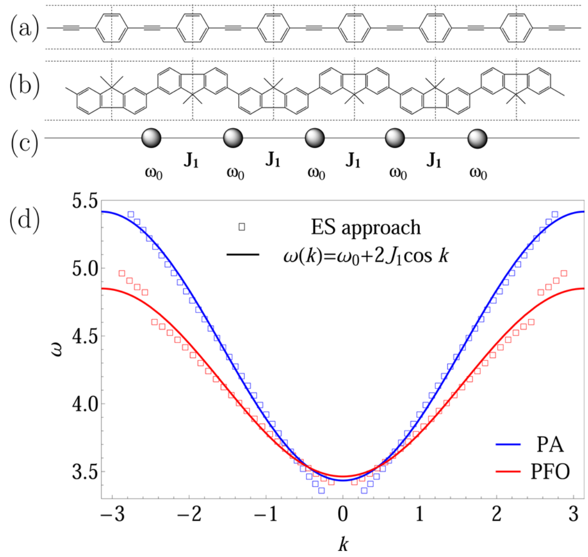

Figure 1. (a) Linear phenylacetylene (PA) molecule, (b) linear poly(9,9-dimethylfluorene) (PFO) molecule, and (c) the relevant nearest-neighbor-hopping lattice model. (d) Exciton dispersions of the lowest exciton band in PA (blue) and PFO (red), obtained from quantum-chemical computations (solid) and from the tight-binding models (squares).

tations for up to 30 vertical excitations have been conducted with Gaussian 09 computational package[35] for selected ideal linear molecules with the length of odd number of repeat units ranging from 5 to 19 and for the molecules with the deformation located in the middle of the chain to maintain the high symmetry of the effective joint.

The dispersion relations for light excitons (fundamental $\pi - \pi^*$ exciton band at low energy) in PA and PFO molecules have been obtained from the reference quantum chemistry of the corresponding unmodified linear molecules and further approximated by the nearest-neighbor-hopping model, as illustrated in Figure 1. Technical details can be found in our previous work.[18,28] Albeit three cosine Fourier modes, characterizing hopping distance up to three repeat units, can describe the exciton dispersions with better quantitative satisfaction, the nearest-neighbor hopping is much stronger than the other two parameters ($|J_1| \gg |J_2|,|J_3|$). Therefore, only the nearest-neighbor hopping is considered in this paper to take advantage of the analytical simplicity of the tight-binding models.

It is worth mentioning that the splitting of the light-exciton band has been observed in PFO backbones (Figure 1d). The reason is that the PFO structure can be viewed as an alternating composition of two similar repeat units of different types (divided in the middle of each phenyl ring) so that the repeat unit defined in Figure 1b consists of the combination of the two similar components, which result in two subexciton bands within the original one. This argument will be addressed elsewhere by considering a small perturbation on the tight-binding picture in a PFO-like molecular family. The band splitting, as an internal fine feature of the unsplitted band, has been ignored to spotlight the geometric distortion effect.

The triple-bond stretching mode in PA molecules has been investigated first because it is one of the most common intramolecular vibrational modes coupled to the electronic system and is easily probed by Raman spectroscopy. For the sake of simplicity, we restrict such a C≡C stretch to one repeat unit of fixed length and secure the middle of the triple bond at the center of the repeat unit, as shown in Figure 2a. The triple bond length modification is ranging from −5 to 5% (with 1% interval) compared with its value in the equilibrium structure without breaking any chemical bond. A modified repeat unit of a certain degree is treated as a molecular vertex of a particular type and is described by a set of scattering phase pairs $\phi_0(k)$ and $\phi_1(k)$ (Figure 2c,d), related to even and odd parity of the scattering, respectively. These scattering phases have been retrieved from the reference quantum chemistry for different deformation values following the technique outlined in ref 24. In a special case of the unmodified repeat unit, the phases are k-independent ($\phi_0 = 0$ and $\phi_1 = \pi$), which ensures a complete wave transmission, that is, vanishing reflection, due to the transparency of repeat unit in the ES picture. As shown in Figure 2c,d, extracted from the parent TDDFT calculations, the scattering phases are evenly distribute on both sides of $\phi_0 = 0/\phi_1 = \pi$ with respect to the stretching orientation as a result of the symmetrical alternation. This reflects similar increase (decrease) of π-conjugation with decreasing (increasing) of bond-length alternation parameter.

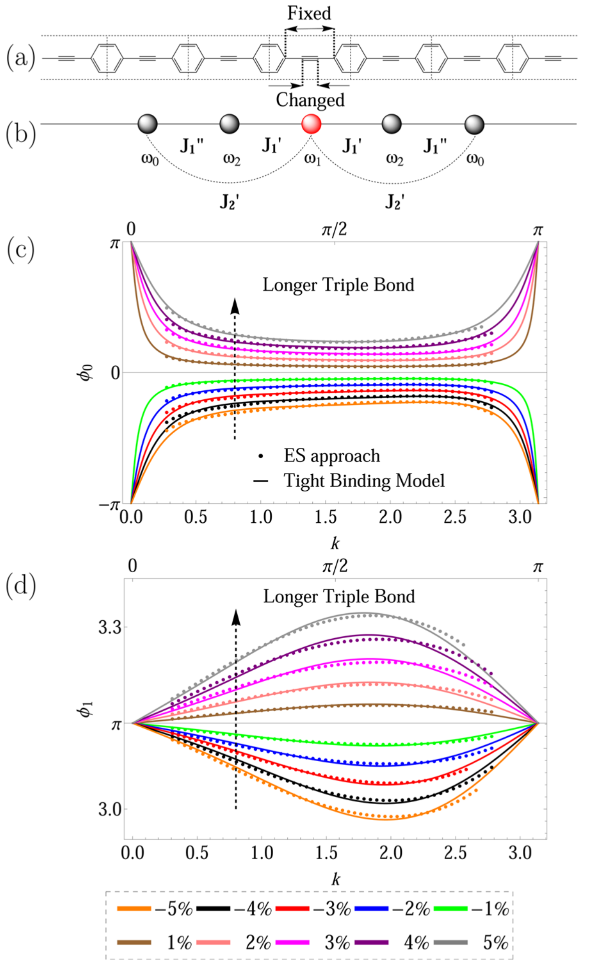

Figure 2. (a) Triple-bond stretching mode in PA molecules and (b) the related tight-binding model. (c) Scattering phases ϕ_0 (k) and (d) ϕ_0 (k) extracted from quantum-chemical computations (dots) and the depicted tight-binding model (curves).

Previously we have characterized how a molecular vertex affects the number of excitonic states in a molecule in terms of the analytical and topological properties of the ES matrix.[28,29,36] In the case of PA bond-length alternation, the topological charge $Q_T = (w(\Gamma) - 1)/2 = 0$ has been found due to $w(\phi_0) = w(\phi_1) = 1$, where the winding number w describes how many times the scattering amplitude $e^{i\phi(k)}$ winds over the unit circle it resides on, while the quasimomentum k goes once over the Brillouin zone. In addition, a bound state localized in the vicinity of the stretched C≡C has been observed in the structures with triple-bond length change >3% or has been expected in sufficiently long molecules with moderately stretched (≲3%) triple bond. The bound state appears either below or above the exciton band in the cases of increased or decreased C≡C bond length, respectively, and possesses identical scattering symmetry of even parity due to the odd number of repeat units in all tested molecules. Consequently, the analytical charge of the joint representing the deformed repeat unit is then found as the sum of the topological charge Q_T and the number of bound states, that is, $Q_A = Q_T + 1 = 1$, for all C≡C stretching of different magnitudes. The above analysis indicates that each considered molecular joint contributes one excitonic state in addition to the number of unmodified repeat units in the molecule. Therefore, a lattice site has been introduced to the tight-binding subgraph that describes the joint. Balancing between simplicity and accuracy, the morphology of the tight-binding model, which describes bond length alternation, is determined within the nearest-neighbor hopping regime and shown in Figure 2b.

The five parameters (ω_1, ω_2, J_1', J_1'', and J_2') of the above tight-binding model are sufficient to accurately replicate the ES model. The presence of the next-nearest-neighbor hopping J_2' allows the scattering phases to be reproduced with better accuracy. The comparison of the scattering phases obtained from the reference quantum chemistry and the lattice model counterparts is shown in Figure 2c,d. Among the five geometry-dependent tight-binding parameters, only ω_1 demonstrates substantial changes, which goes along with the locality principle (Figure 3), whereas the other parameters are less important but result in more accurate tight-binding description. As a matter of fact, in all of our tests, from the simplest tight-binding model with only the on-site energy varied (ω_0 to ω_1) to the most accurate model with many parameters, only the on-site energy of the distorted unit is considerably modified, and an approximately identical linear relation to the bond length alternation amplitude has been obtained in all tested cases. The physical picture behind this observation is that the C≡C bond stretching in PA molecules particularly affects the corresponding on-site energy because the excitonic wave function amplitudes are the largest on the triple-bonded atoms. The triple bond stretching does not violate the planar nature of the PA structure. Therefore, such mild deformations will not break the π-electron conjugation and results in almost trivial variations of the hopping constants (<0.03 eV).

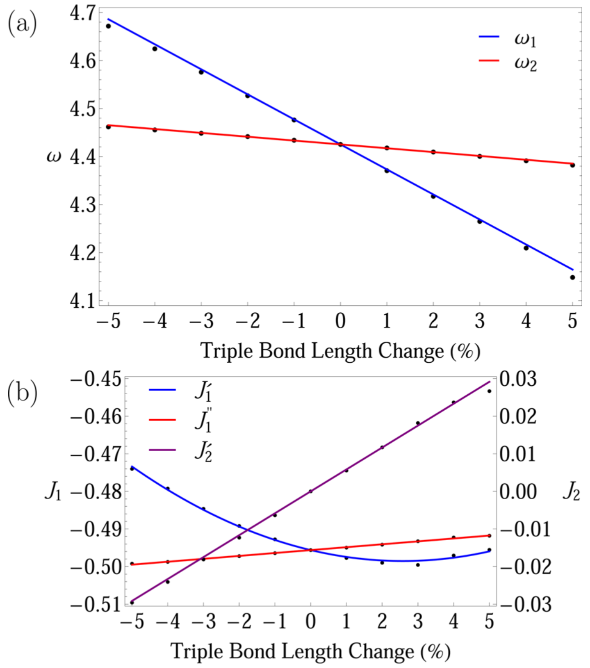

Figure 3. Tight-binding parameters for the model shown in Figure 2b with respect to the percentage change in the triple bond length in PA molecules. (a) On-site energies ω_1 and ω_2. (b) Nearest-neighbor hopping J_1', J_1'' and the next-nearest-neighbor hopping J_2'.

In addition to bond-length alternation, single bond rotation, as another typical conformational deformation, has been studied in poly(9,9-dimethylfluorene) (PFO) molecules (Figure 1b) by altering the torsional angle between the neighboring fluorene groups. PFO polymers usually exhibit torsionally disordered configurations in amorphous glassy phase (α-phase), characterized by large torsional angles between adjacent fluorenes in dilute solutions, whereas planarized conformation (β-phase) is often observed in condensed states.[37−40] Here we have investigated the role of single bond rotation on electronic excitations starting from the β-phase PFOs, which have the higher degree of organization and an extended conjugation. Furthermore, the obtained ES/tight-binding properties related to the conformational disorder have been compared with their counterparts in the α-phase PFO, hence justifying the capability of the ES approach to describe the effect of conformational changes on the excited-state electronic structure. Similar to the procedures, implemented for PA molecules, the single bond rotation in PFOs has been manually applied to the central repeat unit of the chain (Figure 4a) by varying the torsional angle between two adjacent biphenyls from 0 to 90° with 15° increment. By applying the ES analysis, two sets of phases have been obtained with respect to the scattering symmetry, as shown in Figure 4c.

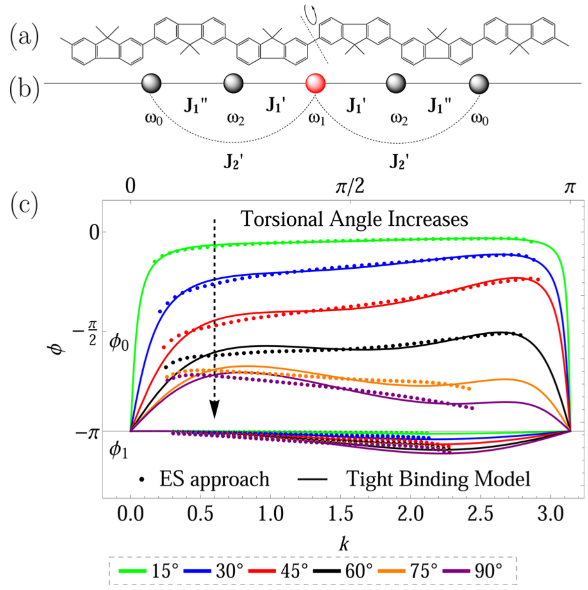

Figure 4. (a) Single bond rotation in β-phase PFOs and (b) the related tight-binding model. (c) Scattering phases ϕ_0 (k) and ϕ_0 (k) extracted from quantum-chemical computations (dots) and the depicted tight-binding model (curves).

According to the TDDFT computation, the PFO repeat unit involving the single bond rotation contributes one excited state within the fundamental $\pi - \pi^*$ exciton band, which indicates the analytical charge $Q_A = 1$. Accordingly, the tight-binding model, that describes the twisted repeat unit, is represented by a single lattice site connecting to the two linear segments. To simulate the scattering phases accurately, we have built the tight-binding subgraph with five parameters (ω_1, ω_2, J_1', J_1'' and J_2') to describe the C − C rotation, as shown in Figure 4b. It is worth mentioning that in both cases of triple bond stretching and single bond rotation, the exciton scattering phase ϕ_1 as a function of the geometrical modification, does not change substantially, $\phi_1(k) \approx \pi$ (Figures 2d and 4c) compared with $\phi_0(k)$. This indicates the applicability of simpler tight-binding models in the case of $\phi_1 = \pi$ because fitting only $\phi_0(k)$ requires fewer lattice parameters to be varied.

By analogy to the bond length alternation in PA molecules, the on-site energy ($\omega_0 \to \omega_1$) undergoes a significant change (4.16 to 4.68 eV) due to the large exciton amplitude on the single-bond carbon atoms, connecting the biphenyl rings. Moreover, the nearest-neighbor-hopping constant J_1' noticeably varies from −0.35 to −0.24 eV compared with the alteration of <0.03 eV in the case of triple bond stretching. Larger torsional angle results in weaker exciton coupling of the adjacent building blocks because the C−C rotation diminishes the overlap of the p orbitals and is more likely to break the π-conjugation compared with the C≡C stretching. The on-site energy ω_1 has been adequately described by a linear function of cos 2θ (θ being the rotation angle), which simply reflects the torsional effect (Figure 5). The results qualitatively agree with the multidimensional exciton model developed in ref 41 based on INDO computations for PA oligomers.

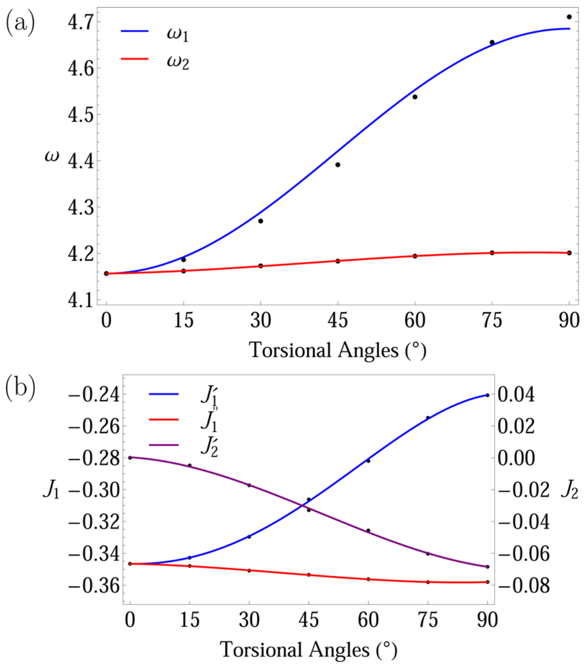

Figure 5. Tight-binding parameters for the model shown in Figure 4b with respect to the torsional angle between adjacent biphenyls in PFO molecules. (a) On-site energies ω_1 and ω_2. (b) The nearest-neighbor hopping J_1', J_1'' and the next-nearest-neighbor hopping J_2'.

Alternatively, the ES analysis has been conducted using the quantum-chemical results of α-phase PFO molecules. The dihedral angle of ~37° between alternatively twisted biphenyl units has been observed in the CAM-B3LYP/6-31G optimized geometries and is confirmed by experimental measurement.[42,43] Within the nearest-neighbor-hopping lattice model, the exciton dispersion in an infinite linear chain is characterized by the on-site energy $\omega_0 = 4.40$ eV and the hopping constant $J_1 = -0.29$ eV. The counterparts in β-phase PFOs are $\omega_0 = 4.17$ eV and $J_1 = -0.35$ eV. According to the retrieved relation between the tight-binding parameters and the single bond rotation angle, for the torsional angle of 37°, one can find the on-site energy ω_1 of 4.35 eV and the nearest-neighbor-hopping constant J_1' of −0.31 eV, which are in excellent agreement with the lattice parameters (increased on-site energy and decreased coupling strength due to the twisted deformation) that we have obtained for the α-phase PFOs. This testifies the robustness of the tight-binding framework in characterizing the conformational effects on electronic excitations. Furthermore, compared with ω_1 and J_1', minor variations in the nearby tight-binding parameters, such as <0.05 eV in ω_2 and 0.01 eV in J_1'', validate that the geometrical effects can be identified within a localized tight-binding subgraph.

Finally, we evaluate the performance of the ES and the tight-binding representations for geometrical disorders by performing calculations for several test molecules with multiple distortions of different magnitudes randomly placed on the chain and compared obtained results to the direct quantum-chemical calculations of electronic spectra. Figure 6c displays such comparisons for two different molecular systems (Figure 6a,b) in terms of quasimomentum k. Overall, a very good agreement in k has been observed from the three methods in the tested medium size molecules. Because the ES approach is asymptotically exact for long molecules of the scale of the exciton size, we reasonably expect better accuracy in larger molecules, where the quantum-chemical computations become increasingly expensive.

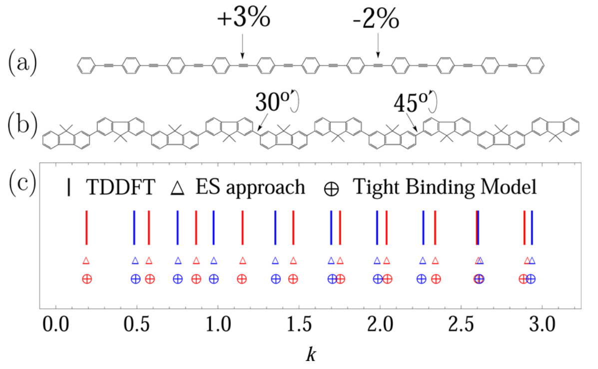

Figure 6. Comparison of quantum-chemical computation, the ES, and the tight-binding approaches in exciton momentum, k, for selected molecules: (a) PA in red and (b) PFO in blue.

In conclusion, we have demonstrated how to describe the effect of structural deformations on electronic excitations in conjugated molecules using effective tight-binding models in the case of triple bond stretching and single bond rotation as representative examples. Viewing a localized geometrical distortion as an effective scattering center for electronic excitations, the related tight-binding structure can be constructed using the ES approach as a necessary bridge, and a small number of lattice parameters describing exciton properties can be obtained as being dependent on the magnitude of the disorder, such as the bond length and the torsional angle. The impact of conformations on excited-state structure has been locally identified within the tight-binding subgraph representing the effective scattering center through the geometry-dependent tight-binding parameters. In other words, electronic excitations in the vicinity of the deformation have been identified by geometry-dependent exciton on-site energies and incorporated into the states of the polymer through the parametrized exciton coupling strengths between the deformation and the chains. The presented approach relies on the excited-state data of the reference quantum chemistry, further processed via the ES approach and tight-binding models, hence gaining a simple and straightforward description of structural distortions on the phenomenological scale instead of the microscopic electronic structures. Following the presented strategy, problems involving coupling between electronic and vibrational motions in conjugated structures can be reformulated and tremendously simplified by utilizing the explicit dependence of the ES lattice parameters on the distortion of molecular structure. Such straightforward relations have important ramifications in the design and synthesis of organic photovoltaics for desirable functionalities and applications. This approach allows for the derivation of the reduced exciton−phonon Hamiltonian, due to the explicit description of electronic excitations. In particular, within a harmonic approximation for vibrational motions, which are linearly coupled to the excitons, the exciton−phonon interactions are adequately described by a set of multidimensional spectral densities. Therefore, well-developed methodologies for Frenkel exciton systems can be readily implemented to characterize a variety of photoinduced processes in conjugated bulk nanostructured materials, which is prohibitive using conventional atomistic simulations.

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Notes

The authors declare no competing financial interest.

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