

Exciton scattering approach for branched conjugated molecules and complexes. III. Applications

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The exciton scattering (ES) approach is an efficient tool to calculate the excited states electronic structure in large branched polymeric molecules. Using the previously extracted parameters, we apply the ES approach to a number of phenylacetylene-based test molecules. Comparison of ES predictions with direct quantum chemistry results for the excitation energies shows an agreement within several meV. The ES framework provides powerful insights into photophysics of macromolecules by revealing the connections between the molecular structure and the properties of the collective electronic states, including spatial localization of excitations controlled by the energy. © 2008 American Institute of Physics. [DOI: 10.1063/1.3005649]

I. INTRODUCTION

While branched conjugated molecules find an increasing number of applications,¹⁻¹² it becomes more and more important to have convenient design tools for characterization of their optical properties. Traditional quantum chemistry approaches to the excited state electronic structure are time consuming and numerically intensive. Therefore, the calculations are often limited to molecules too small to be of experimental and practical interest.

In the preceding parts^{13,14} we have developed the exciton scattering (ES) model^{15,16} for excited state electronic structure in branched conjugated molecules and demonstrated how the parameters the ES model can be extracted from quantum chemistry calculations in molecular fragments of reasonable size. For phenylacetylene oligomers, we have obtained the exciton dispersion $\omega(k)$, the scattering matrix $\Gamma(\omega)$ at molecular ends, and the scattering matrices $\Gamma_{ij}^{(2)}(\omega)$ for two molecular joints that correspond to meta- and orthoconjugations. This allows us to apply the ES model to perform the excited state electronic structure calculations in any branched phenylacetylene-based molecule with the ortho- (*O*) and meta- (*M*) joints. As argued in the first manuscript of the series, the ES model becomes asymptotically exact when the linear segments are long compared to the exciton size. However, a practical question remains of how accurate the ES model is in smaller molecules. In this third part of the series we consider several branched molecules and compare the results of the ES approach to the results of the direct quantum-chemical calculations. We show that the agreement is excellent for molecules with the linear segment length down to three repeat units. Using the ES language, we describe possible localization of excitations in certain molecular segments. Future developments are outlined in the concluding discussion.

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II. APPLICATION OF EXCITON SCATTERING MODEL

The ultimate goal in developing multiscale approaches such as the ES model is to come up with an efficient design tool for optical materials based on branched organic macromolecules and structures. We are now in a position to verify the predictions of the ES model by comparing the excited state energies obtained within the ES approach to supramolecular quantum chemistry computations for several test molecules. Below we apply the ES model to four families of phenylacetylene-based molecules.

As a first example we consider zigzag molecules that contain linkages through both meta- and ortho positions of phenyl rings referred to as meta- and ortho joints, respectively (see Fig. 1). We use the notation $l_1Ol_2Ml_3$ for these isomers showing the order of the linkage between segments with l_1 , l_2 , and l_3 repeat units. The molecules considered below are separated at the metajoint into two parts with equal numbers of repeat units, $l_1+l_2=l_3$. The test molecules are designed to study how a competition of the weak exciton reflection at the ortho joint and the weak exciton transmission through the metajoint affects the overall excited state electronic structure. We designate two different three-segment zigzag forms as *cis* and *trans* according to the positions of the peripheral branches with respect to the central one. The present implementation of the ES model is local and cannot distinguish these two molecular structures. Their electronic spectra from quantum chemistry calculations are also very similar. Only the transition oscillator strengths of the isomers are substantially different, which will be addressed in detail using the ES approach in our future studies.

The other test molecules have cyclic shapes: triangles, parallelograms, and hexagons. We consider only equilateral triangles and hexagons to minimize the distortion of the ortho- and metajoints caused by the constrained geometry. Parallelograms are characterized by two lengths of adjacent segments.

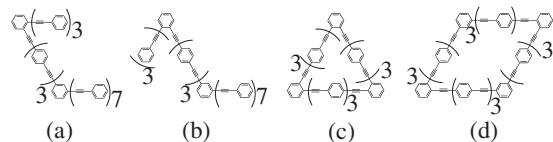


FIG. 1. Examples of molecules studied in this article: (a) *cis*-3O4M7, (b) *trans*-3O4M7, (c) T4, and (d) Q4-4.

A. Accuracy of the ES model predictions

To quantify the accuracy of the ES method we consider the differences between the excited state energies calculated within the ES approach and direct quantum-chemical computations. As in the previous paper of the series, we use the collective electronic oscillator (CEO) code¹⁷⁻²⁰ for excited state calculations to extract the ES ingredients that characterize elementary molecular building blocks. We are not limited by this specific model quantum chemistry, which has been chosen as a matter of convenience. Previously we reported applications of the ES model to similar systems using the time-dependent density functional theory technique¹⁵ as the underlying quantum chemistry method. Although this might seem obvious, we emphasize that when comparing the results of the ES model with the quantum-chemical computations, the building blocks should be characterized by using the same model quantum chemistry.

When we apply the ES approach, we find the excited state energies and spatial localization of the excitations by solving the set of the homogeneous linear ES equations¹⁴ on the graph corresponding to the molecule considered. The wavenumber k and the scattering matrices in the ES equations should be viewed as functions of energy. We use the inverse dispersion $k(\omega)$ and the energy-dependent scattering phases tabulated as piecewise overlapping polynomial functions, which results in the equations for the wave amplitudes with the coefficients that explicitly depend on the energy. Then the excitation energies are found by setting the determinant of the set to zero and solving the resulting polynomial equation numerically. The application of the ES model is similar to solving a generalized “particle in a box” problem.

Figure 2 and Table I show a comparison of the ES model predictions with the direct CEO results obtained for two isomer pairs of zigzag molecules 3O4M7 and 4O5M9. We emphasize that the ES approach in its present implementa-

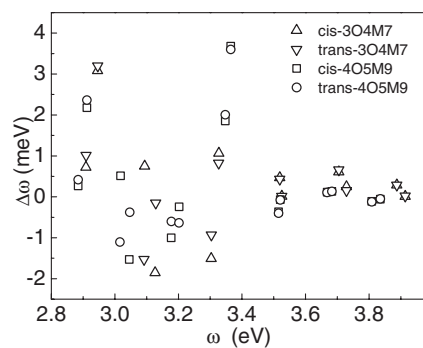


FIG. 2. Energy difference between the CEO and ES results for excitation energies in zigzag test molecules.

TABLE I. Light-exciton spectra: comparison of the quantum chemistry (CEO) and ES results (in eV).

| M7-7 | ES M7-7 | <i>cis</i> -3O4M7 | <i>trans</i> -3O4M7 | ES 3O4M7 |
|----------|----------|-------------------|---------------------|----------|
| 2.901 32 | 2.902 33 | 2.908 91 | 2.909 20 | 2.908 19 |
| 2.935 08 | 2.935 04 | 2.945 89 | 2.946 01 | 2.942 81 |
| 3.090 91 | 3.090 69 | 3.093 88 | 3.091 60 | 3.093 13 |
| 3.126 58 | 3.126 48 | 3.126 76 | 3.128 46 | 3.128 61 |
| 3.307 94 | 3.308 02 | 3.303 32 | 3.303 89 | 3.304 82 |
| 3.328 63 | 3.328 63 | 3.327 16 | 3.326 91 | 3.326 09 |
| 3.524 83 | 3.524 74 | 3.519 21 | 3.519 17 | 3.518 74 |
| 3.526 02 | 3.525 89 | 3.525 50 | 3.525 49 | 3.525 48 |
| 3.713 46 | 3.713 52 | 3.704 93 | 3.704 99 | 3.704 32 |
| 3.734 04 | 3.734 39 | 3.729 05 | 3.728 95 | 3.728 80 |

tion provides identical excited states for both *cis* and *trans* isomers, whereas the CEO method yields energy differences of up to about 2 meV. These differences can be attributed to different nonlocal couplings between the segments of the isomers. In fact, this deviation from the ES prediction lies within the typical range of differences between the ES and CEO energies, which are likely, in part, the result of long-range Coulomb interaction. Nevertheless, the accuracy is amazing considering that the shortest arm, which constitutes the major error source, contains only three or four repeat units. Larger deviations of energies in the region from 3.3 to 3.5 eV can be attributed to strong mixing between the light and heavy excitons induced by the scattering at the nonplanar orthojoints. In this region, the scattering phases of the light exciton at the nonplanar orthojoint appear to be less well defined.¹⁴ Effects of the scattering between different exciton bands will be considered in the future studies.

Unlike the zigzag molecules, the cycle molecules such as triangles, parallelograms, and hexagons have planar geometries. However, these closed molecules have another weak geometry modification localized near the joints: due to repulsion of the side hydrogen atoms, the molecular segments bend outward. Since this modification of the optimized geometry proves to be less important for the electronic structure than the nonplanarity of orthojoints, it does not require additional adjustments in the scattering phases.

For the triangle and parallelogram test molecules, we achieve similar accuracy (see Fig. 3) as for zigzag molecules. The application of the ES approach, however, requires taking into account differences in the optimized molecular geometry. All ortho- and metajoints are planar in the triangle and parallelogram structures, whereas in two-segment orthomolecules with free ends, the arms are twisted out of plane of the phenyl ring joint by a small angle due to steric interactions. We can obtain the scattering phases of the planar orthojoint from the quantum-chemical results in the planar orthomolecules. Since the deviation of the geometry from the torsionally relaxed case is not large, the overall energy dependence of the phases is only slightly changed, and, therefore, only a small number of data points (excitation modes) are sufficient to evaluate the phases corresponding to the modified geometry.

In the hexagon H3 with the sides of three repeat units we observe that the difference of the ES and CEO excitation

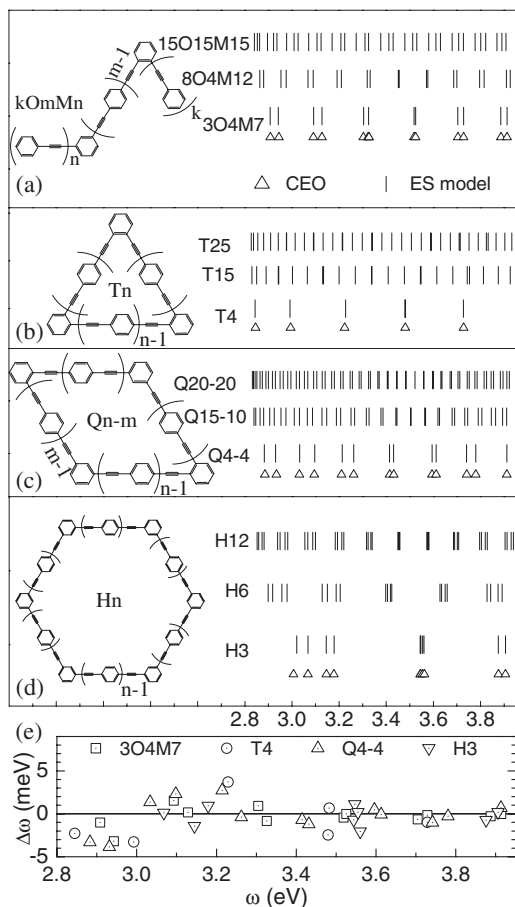


FIG. 3. [(a)–(d)] Electronic spectra (vertical lines) calculated using the ES model for selected compounds shown in the insets. Quantum chemistry results (CEO) are not available for the largest molecules (triangles). (e) Deviations between the ES and CEO results.

energies $\Delta\omega$ does not exceed 3 meV [except for the first excited state with $\Delta\omega=13$ meV, not shown in Fig. 3(e)]. The ES picture predicts that the apparent quadruplets in the spectra of hexagon molecules become degenerate around $\omega=3.5$ eV, where the transmission through the metajoint vanishes.

Since the ES model is based on the asymptotic behavior of the exciton wave functions, another way to determine the adequacy of the model in molecules with short linear segments would be to compare the exciton wave functions obtained from the CEO calculation (as described in Ref. 13) with their asymptotic oscillating shapes, predicted by the ES model. Figure 4 shows that even in the segment with three repeat units the agreement of the wave functions is quite good.

B. New insights provided by the ES approach

The results presented above demonstrate that the ES approach constitutes an accurate and efficient tool for computing the excited electronic states in branched organic structures. In this section we show that it also provides simple yet deep insights into the excited state electronic structure. This turns the ES model into a powerful tool for efficient design of optical and electro-optical materials.

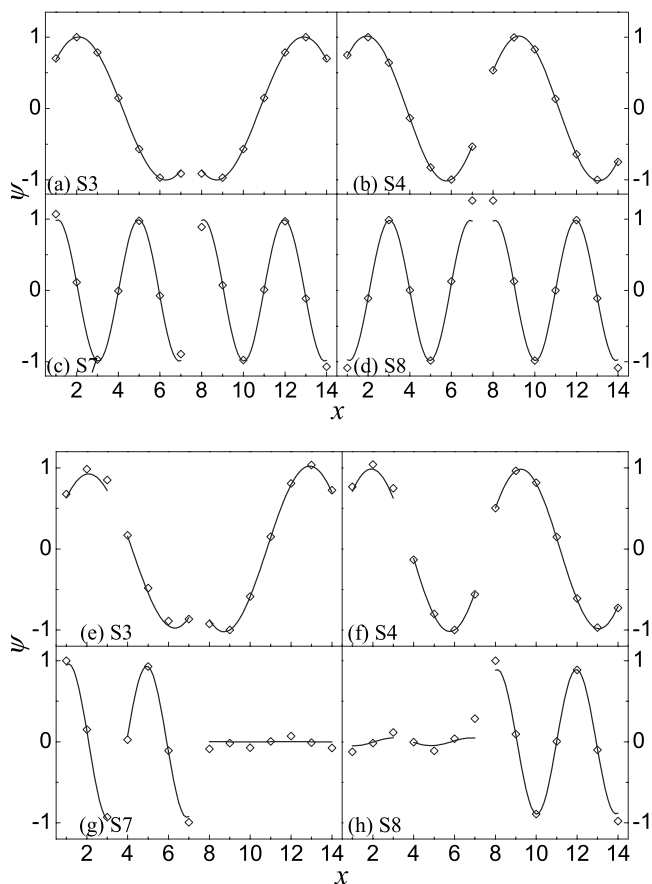


FIG. 4. Normalized exciton wave functions for modes 3, 4, 7, and 8 in *M7-7* [top, (a)–(d)] and *3O4M7* [bottom, (e)–(h)]: a comparison of the asymptotic form with the ES parameters (line) and the quantum chemistry results (diamonds). Note that the exciton wave function is defined only at integer positions of repeat units; the lines are merely guides to the eye.

To illustrate these points we start with the zigzag molecule *3O4M7*. In Table I we show the excitation energies in *M7-7* and *3O4M7* obtained with both the CEO technique and the ES approach. If the transmission through the ortho-joint were ideal, the *3O4M7* would have the same excitations as the *M7-7*, both in terms of the excited state energies and the transition density matrices or the exciton wave functions derived from them. However, the effects of weak scattering at the ortho-joint lead to substantial differences in the excited state structure for different electronic modes (see Fig. 4). This reflects a competition between a weak reflection and a weak transmission at the ortho- and metajoints, respectively. The weak transmission through the metajoint corresponds to weak coupling between the two arms. The mode is fully localized on one arm if the transmission is absent. If these localized modes are identical, the transmission, no matter how weak it is, will lead to a formation of symmetric and antisymmetric modes with some energy difference between them, usually referred to as the Davydov splitting. In the symmetric metamolecules, the modes do appear in pairs, and the Davydov splitting characterizes the strength of the exciton transmission through the metajoint.

The weak reflection at the ortho-joint leads to some small energy shift, which can be regarded as a measure of the exciton reflection, once the ES picture is adopted. In a more

general sense, spatial localization of the excitations can be viewed as a competition of the energy differences between localized excitations (associated with symmetry breaking and, therefore, often referred to as disorder) and coherent coupling between these modes. If the disorder is strong compared to the coupling, the disorder wins the competition, and the excitations stay localized. In the opposite limit, the coherent coupling causes the excitation delocalization. Stated in terms of ES, if the transmission through the metajoint in the *3O4M7* or similar molecules is strong compared to the reflection at the orthojoint, the modes should be very similar to those in the *M7-7* or corresponding similar molecules. In the opposite limit, when the reflection at the orthojoint dominates the transmission through the metajoint, the excitations in the *3O4M7* molecules should be localized at the linear segment. The situation here is very interesting and nontrivial since the scattering amplitudes at both joints are energy dependent. Apparently the differences in the possible mode structures, described above, will drastically affect the optical properties of these organic molecules.

The ES interpretations provide a microscopic insight into the structure of electronic excitations and allow making predictions on the optical properties without performing quantum-chemical computations in large molecules. For example, we can see from the exciton wave functions that the modes S3 and S4 are very similar for both *3O4M7* and *M7-7* (see Fig. 4). This means that although the orthojoint in *3O4M7* causes some energy difference in the two segments separated by the metajoint, the coupling between them is still strong. Stated differently, the Davydov splitting (induced by the coherent coupling) is not influenced much by the presence of the orthojoint (disorder). This is consistent with the ES picture: at the relevant energy $\omega \approx 3.1$ eV, the phase θ_O for the orthojoint is very close to zero, whereas there is a noticeable deviation of θ_M from $\pi/2$ for the metajoint (see Fig. 4 in Ref. 14). Since the reflection probability is given by $\sin^2 \theta$, at this energy the transmission through the metajoint dominates the reflection at the orthojoint, which leads to delocalization of the optical excitations. Note that the structure of these excitation modes could be predicted by just examining the scattering amplitudes at the relevant joints at the corresponding energy values, which is a qualitatively correct, although simplified picture. The exciton wave functions of modes S3 and S4 in *3O4M7* show some deviations from even and odd functions, whereas the symmetry obviously exists in *M7-7*.

For the modes S7 and S8 located close to $\omega = 3.5$ eV, the exciton wave functions are remarkably different (see Fig. 4). Although the energy difference (disorder) caused by the orthojoint is still more or less the same as in the lower modes, the communication between the arms separated by the metajoint is virtually completely blocked: as clearly seen in the exciton wave function plots, the excitons are localized on either of the arms. This phenomenon could be predicted and interpreted without quantum chemistry calculations by examining the scattering amplitudes. Since θ is close to $\pi/2$ for the metajoint at the relevant energy $\omega \approx 3.5$ eV, the exciton transmission through it becomes negligible, and the disorder wins the competition. Using the pre-ES language,

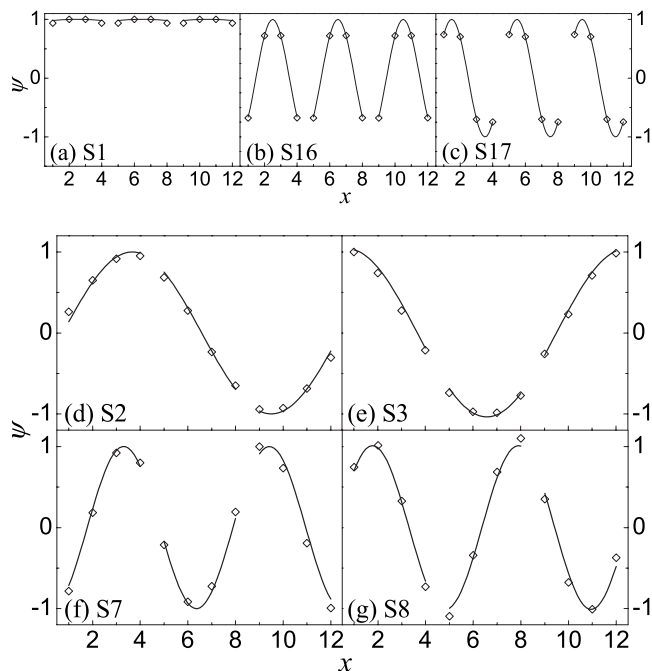


FIG. 5. Normalized exciton wave functions for modes in the triangle molecule T4: singlets [top, (a)–(c)] and two degenerate doublets [bottom, (d)–(g)]. The asymptotic form with the ES parameters (line) is compared with the quantum chemistry results (diamonds).

we can tell that this means that the Coulomb coupling between the excitations at the arms is weaker than the energy difference and is unable to prevail over the localization trend. It is worth noting that modes S7 and S8 constitute the only pair with such a pattern in *3O4M7*. This behavior can be easily rationalized using the ES interpretation by examining the dependence $\theta_M(\omega)$ and $\theta_O(\omega)$: a narrow region around $\omega \approx 3.5$ eV is the only one where the reflection at the orthojoint can dominate the transmission at the metajoint. The Davydov splitting in symmetric *M* molecules disappears at this energy.

To further explore the interpretation and predictive capabilities of the ES approach we consider cyclic phenylacetylene molecules in the form of equilateral triangles. The molecules have the C_{3v} symmetry group which consists of the C_3 rotations combined with three symmetry planes perpendicular to the molecular plane. Due to the C_3 symmetry all modes can be characterized by their angular momenta $m=0, \pm 1$, whereas the mirror symmetry results in the double degeneracy of the $m=\pm 1$ modes, hereafter referred to as the *p*-modes; the $m=0$ modes will be naturally referred to as the *s*-states. The first seven excitations are presented in Fig. 5, which includes the exciton wave functions plotted based on the ES model, as well as the wave functions derived directly from the transition density matrices obtained in CEO quantum chemistry computations. The lowest energy excitation is an *s*-mode. The next two excitations are two pairs of doubly degenerate *p*-modes. Modes S16 and S17 [see Figs. 5(b) and 5(c)] represent two different *s*-states, although their energies differ by less than 1 meV (obtained via the CEO calculation). The profiles of the exciton wave functions show almost ideal transmission through the orthojoints. Therefore, the wave functions resemble those in a circular aggregate.

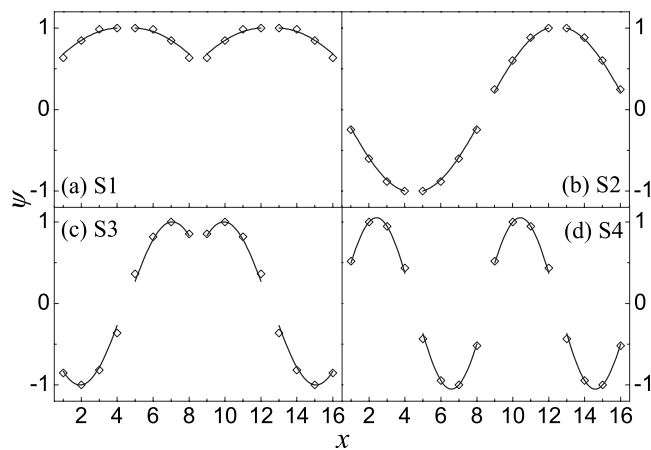


FIG. 6. Normalized exciton wave functions in the parallelogram $Q4-4$: a comparison of the asymptotic form with the ES parameters (line) and the quantum chemistry results (diamonds). The metajoints are between the repeat units 8 and 9, as well as 16 and 1.

In general, a parallelogram molecule Q_{n-m} does not have any additional symmetries that would lead to degeneracies in the spectrum. Two metajoints with weak exciton transmission separate the parallelogram molecule into two equal two-segment parts with almost independent excitons. Since the orthojoints are almost transparent to the excitons, the resulting patterns of the excitation localization (see Fig. 6) are very similar to the ones in the metamolecules with equal arms of length $m+n$.

In the hexagon molecules [see Fig. 3(d)] the spectrum consists of sextuplets formed in the result of Davydov splitting due to weak transmission through the metajoints. Because of the hexagon symmetry C_{6v} , the excitations can be characterized by the angular momenta $m=0, \pm 1, \pm 2, 3$. Each sextuplet has four distinct excitation energies since the states with opposite angular momenta $m=\pm 1$ and $m=\pm 2$ form two degenerate doublets (due to mirror symmetries). The splitting vanishes together with the transmission amplitude near $\omega=3.5$ eV.

Based on our understanding of the triangle and parallelogram structures, we can extend our studies to two-dimensional (2D) graphenelike sheets, which can be considered as potential improvements over carbon nanotubes for future electronic and electro-optical materials.

III. SUMMARY

The series of three manuscripts reports in detail the development of the ES approach for excited state electronic structure of branched conjugated macromolecules and molecular structures. In the first manuscript of the series we introduced the ES approach, where the excited electronic states are described by quasiparticles. The quasiparticle wave functions are represented by plane waves on the linear molecular segments, and are connected at the molecular ends, joints and branching points by means of the ES matrices. The latter can be viewed as generalized boundary conditions. We have also provided microscopic definitions for the ingredients of the ES model in terms of the many-electron wave

functions as well as many-body Green's functions. The ES approach becomes asymptotically exact, when the linear segments in the molecule under study are long compared to the exciton relative size. It was also shown that the knowledge of the exciton spectra $\omega(k)$ and ES matrices $\Gamma_{\alpha\beta}^{(n)}$, which can be obtained from quantum chemistry results for simple and universal molecular fragments, allows an extremely efficient calculation of the excitation energies in all branched molecules that contain the described vertices.

In the second manuscript of the series we have demonstrated how to extract the parameters of the ES model from quantum chemistry computations using the semiempirical CEO method as an example. We have determined the exciton spectra in phenylacetylene linear segments for two types of excitons: the light exciton with the bandwidth of about 1 eV, and the heavy exciton whose band with the width of about 0.1 eV is located inside the light exciton band. We have also determined the ES matrix $\Gamma^{(1)}(\omega)=\exp[i\phi_T(\omega)]$ at the chain termini, as well as the scattering matrices $\Gamma_{\alpha\beta}^{(2)}(\omega)$ at both meta- and orthodouble joints. The scattering at the chain termini is described by one frequency-dependent phase $\phi_T(\omega)$, whereas the scattering matrices for the double joints are parametrized by two pairs of frequency-dependent phases $\theta(\omega)$ and $\phi(\omega)$ which are related to the reflection coefficient and the scattering phase, respectively. Our calculations show that the orthojoint is practically transparent for almost all values of frequencies, whereas the metajoint shows some weak transmission which describes the coherent coupling between the excitations localized on different sides of the metajoint.

In this manuscript we have compared the results of the simple ES calculations with the direct CEO computations for several test molecules. We have demonstrated that an extremely simple ES approach delivers not only qualitatively reasonable results, which were expected by us at the beginning of these studies, but also provides an amazing accuracy, sufficient for all practical purposes, even in the case of short linear segments that contain two to three repeat units. Short linear segments (one to two repeat units) connected to the longer ones can be described more accurately as effective vertices that link longer branches.

Considering the examples of zigzag, triangle, parallelogram, and hexagon molecules, we have demonstrated how to examine, interpret, and predict the influence of the geometrical and topological arrangements and cross-joint interactions by using a simple and transparent ES language. By controlling the energy input into the system, drastically different behavior can be induced, for example, we can turn on and off a molecular circuit and even control the flux by changing the energy that controls scattering properties. The ES approach provides clear visualization and simple yet deep microscopic insights into the structure of electronic excitations in branched molecules. This indicates that the approach can become a powerful tool for efficient design of organic-based optical and electro-optical materials.

IV. DISCUSSION: DIRECTIONS OF FUTURE RESEARCH

In this section we describe some directions of the future research in the ES area, starting with the immediate extensions. First of all, we plan to extract the scattering matrices $\Gamma_{\alpha\beta}^{(n)}(\omega)$ for triple ($n=3$) all-metaconjugated joints, and symmetric quadruple ($n=4$) joints. Due to the high symmetry, the parametrization of these two types of joints is simple. The symmetric triple and quadruple joints are described by two and four frequency-dependent phases, respectively. All these phases can be extracted independently from the modes of the corresponding symmetry, which requires calculations on the same level of complexity as those for the scattering phases of the double joints (reported in the second paper¹⁴ of the series). The tabulated properties of the four types of joints will enable one to apply the ES approach to the excited state electronic structure in a huge variety of branched molecules and molecular structures, including one-dimensional molecular wires based on branched structures as repeat units, as well 2D organic sheets,²¹ where the ES approach seems to be the only feasible option.

In addition to the ES approach for calculation of excited state energies, the first paper¹³ of the series introduces an ES formalism to describe the transition dipoles for the optical transitions. The values of the transition dipoles are crucial for the modeling of all experimental spectroscopies²² and, subsequently, for design of optical and electro-optical materials. We intend to extract the transition dipole ingredients of the ES model in the nearest future. The transition dipoles in quantum chemistry are calculated from the transition density matrix obtained in terms of atomic orbitals. The transition density matrix is linearly related to the asymptotic exciton wave function both far from and close to the vertices because of linearity of the problem. Once the exciton dispersion and the scattering matrices are available, one can calculate the exciton wave function corresponding to the excitation. Subsequently, one can determine the dipole parameters of the ES approach by comparing the dipole contributions of vertices and repeat units with the exciton wave function. Our preliminary results, restricted to linear molecules, indicate that the transition dipoles can be predicted in the ES approach with reasonable accuracy.

We anticipate that analysis of exciton wave functions will also be helpful in retrieving the ES matrices of the higher-degree joints that do not possess such high degree of symmetry as the ones described earlier. In this case the scattering matrices contain more parameters than can be found from the quantum chemistry energies in molecules with different linear segments attached to the joint. Using the information about the wave functions reduces the extraction of the scattering matrix to a linear problem. An efficient and stable algorithm, which allows us to treat the branching centers of any degree, will be described in detail in our future publications.

Another extension of the ES approach concerns scattering between different exciton types coexisting at the same energies. Although we have observed some effects of mixing of light and heavy excitons, we have primarily stud-

ied light excitons which form a much broader energy band. These mixing effects certainly deserve a separate detailed investigation.

An interesting application of the ES approach would be the treatment of charge-transfer processes upon optical excitations, e.g., considering the electronic spectra of donor/acceptor substituted molecules.^{23–25} Our previous studies^{26,27} have demonstrated that the exciton picture is still valid in this situation: the donor/acceptor induced charge-transfer processes lead to a modification of the “bulk” exciton shape near the substitutions, as well as to the formation of localized excitons, accompanied by the electron-hole symmetry breaking. These effects can be readily incorporated to the ES model by modifying the scattering phases for the molecular termini, represented by the donor/acceptors. These scattering phases should show more interesting dependencies on the frequency. In particular, using the standard Kramers–Kronig relations, one can obtain the energies of the bound (localized) excitons from the analytical continuation of the scattering phases extracted from quantum chemistry computations.

So far we have been discussing the vertical (purely electronic) excitations in branched conjugated structures. Realistic modeling of photoinduced dynamics requires that the effects of electron-phonon coupling, as well as energetic and positional disorder are incorporated in the theory.^{28–31} This will constitute the next level of the ES approach. The reason we are so optimistic about such kind of a nontrivial extension of the ES theory is the shape of the exciton dispersion: with good accuracy it can be represented as $\omega(k) = \omega_0 + 2J \cos k$, which resembles a result in a tight-binding lattice model with the nearest neighbor hopping. Note that such a form of the exciton dispersion is a signature of the small exciton size of the order of one to two repeat units. The latter suggests that the joints and molecular termini could be quite likely also described by some effective tight-binding models. In this case the ES ingredients can be expressed through a small number of the tight-binding constants, including the on-site energies ω_0 , the hopping constants J , as well as their counterparts that describe the joints and termini. Therefore, the vibronic coupling, as well as disorder can be incorporated by introducing the dependence of the tight-binding parameters on the vibrational coordinates. The photoinduced dynamics in branched conjugated systems, which includes effects of localization, self-trapping, incoherent energy transfer (exciton relaxation dynamics), etc., can be treated by using standard methods of condensed matter theory, where excitons are viewed as the quasiparticles that represent the primary electronic excitations.

We would like to emphasize that the ES model is a truly multiscale approach to electronic excitations in branched conjugated molecules. Unlike previously proposed techniques (e.g., the Frenkel exciton model^{31–33}), the ES approach does not require rather arbitrary partition of branched molecules into chromophores or any assumptions about their interactions. One can anticipate that the numerical accuracy of the ES approach might decrease when some realistic symmetry-breaking effects, such as molecular defects or inhomogeneity of the environment, are taken into account. Nevertheless, we believe that the ES approach will be useful

for practical applications since, as discussed above, the ingredients of the ES model can be expressed through a small number of parameters of an effective lattice model and still very well describe noninteracting excitations. The ES approach is asymptotically exact in the limit of the vanishing exciton size and works surprisingly well in fragments whose length is comparable to the exciton size. In addition to being an efficient and accurate method to predict the results of the best available quantum chemistry, among the obvious advantages of the ES approach is its capability to provide clear interpretation of the excitation properties based on the molecular symmetry.

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