# Exciton scattering approach for branched conjugated molecules and complexes. II. Extraction of the exciton scattering parameters from quantum-chemical calculations

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We obtain the parameters of the exciton scattering (ES) model from the quantum-chemical calculations of the electronic excitations in simple phenylacetylene-based molecules. We determine the exciton dispersion and the frequency-dependent scattering matrices which describe scattering properties of the molecular ends as well as of meta- and orthoconjugated links. The extracted functions are smooth, which confirms the validity of the ES picture. We find a good agreement between the ES and quantum-chemical results for the excitation energies in simple test molecules. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3005648]

## I. INTRODUCTION

In the previous paper[1] of the series we have developed the formalism of the exciton scattering (ES) approach to the excited state electronic structure in branched conjugated molecules.[2,3] Within the ES approach a branched molecule is described by a graph[4–6] whose edges correspond to the linear segments, whereas the vertices stand for molecular ends and joints between segments. The parameters of the ES model, which characterize molecular building blocks, include an exciton dispersion and energy-dependent scattering matrices for the vertices. Once the parameters are determined, the application of the model involves quite simple calculations that are common in the context of elementary quantum mechanics: a generalized "particle in a box" problem.

We could have extracted the ES parameters from quantum-chemical results directly by invoking their asymptotic definitions. In particular, to obtain the exciton dispersion, one can analyze electronic spectra computed in very long (ideally, infinite) linear chains. Alternatively and more generally, the parameters of the dispersion curve can be found from the exciton wave functions expressed via the transition density matrices. Exciton scattering matrices for each vertex can be independently retrieved from the asymptotics of the scattered waves far from the scattering centers. However, the algorithms for excited state calculations in infinite (i.e., asymptotically large) systems with translational symmetry are generally not available through the quantum chemistry codes. To overcome this difficulty we develop a strategy for extracting all ingredients of the ES model from the quantum chemistry calculations in finite molecular fragments with different lengths of linear segments.

In this manuscript we demonstrate how to extract the exciton spectra $\omega(k)$, the scattering matrices $\Gamma_{ij}^{(1)}(\omega)$ on the molecular ends (vertices of degree one), and $\Gamma_{ij}^{(2)}(\omega)$ for molecular double joints (vertices of degree two). These calculations are performed for phenylacetylene linear segments and benzene rings as joints using a semiempirical time-dependent Hartree–Fock (TDHF) technique[7–10] as a basic model quantum chemistry. There are two types of degree-two joints in these compounds: a metaconjugation which is known to be almost fully reflecting,[10–13] and an orthoconjugation which has recently been shown to cause very weak reflection.[3,14] Our results quantify these qualitative statements. More complicated cases of higher-degree branching will be considered in future studies.

Subsequently, the tabulated ingredients of the ES model allow computation of the excited electronic states in arbitrary phenylacetylene molecules that involve branching of the order not higher than two. In the third manuscript[15] of the series we illustrate such simulations and validate the obtained results versus the direct quantum-chemical calculations.

## II. HOW TO RETRIEVE THE ES MODEL INGREDIENTS FROM THE QUANTUM CHEMISTRY DATA

Before the ES approach can be applied to compute the excitation energies in large molecules, we need to characterize the molecular building blocks. In this section we describe the procedure that allows us to obtain the parameters of the ES theory from quantum-chemical computations in simple molecular fragments.

### A. Quantum-chemical calculations

We demonstrate the application of the ES model using an example of phenylacetylene polymers without extraneous vertices. These molecular structures are building blocks of macromolecules, such as dendrimers, with many potential optical applications.[11,14] To retrieve the ES parameters of linear segments, molecular termini, and double joints, we per-

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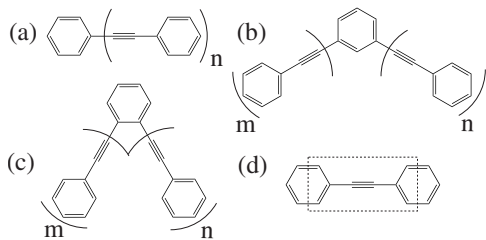b)Electronic mail: chernyak@chem.wayne.edu.

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FIG. 1. Phenylacetylene-based molecules studied: (a) linear chains, (b) meta- and (c) orthosubstituted two-segment molecules denoted by *Pn*, *Mm-n*, and *Om-n*, respectively; (d) definition of one repeat unit.
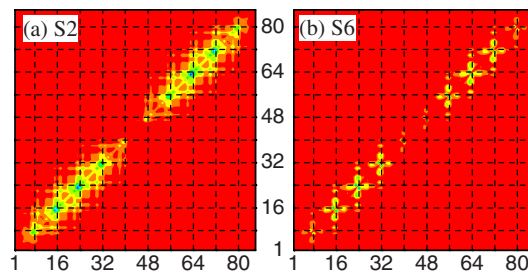


FIG. 2. (Color online) Examples of transition density matrices for the light (a) and heavy (b) excitons in the linear molecule P10 of ten repeat units. Joint electron-hole motion is similar in these modes: both excitations are the second states in the respective excitonic bands, and their standing waves have one node.

form quantum-chemical calculations in several types of phenylacetylene-based molecules: linear, meta-, and orthoconjugated molecules of different lengths (see Fig. 1). The ground state geometries of all molecules are optimized using the semiempirical Austin model 1 Hamiltonian,[16] which adequately reproduces the molecular ground state geometries, particularly in hydrocarbon compounds. GAUSSIAN 03 package[17] is used to perform the ground state optimizations.

The collective electronic oscillator (CEO) code[7–10] is then applied to calculate energies, transition dipoles and transition density matrices of the first 40 excited states in all molecules. This technique combines semiempirical Hamiltonians with a TDHF formalism, and makes computation of an excited state manifold not substantially more numerically demanding than ground state calculations. For CEO calculations we use Zerner's intermediate neglect of differential overlap/spectroscopy model[18–20] specifically parametrized to reproduce spectroscopic observables. Such CEO modeling has been successfully applied in the past to calculate optical properties of a variety of conjugated chromophores such as polymers (also with donors and acceptors), dendrimers, and biological light-harvesting complexes.[7–10] The convergence criterion used in our CEO computations ensured that numerical errors of the CEO implementation are typically less than 0.01 meV for all excited state energies.

We computed excited state properties for molecules of length from 2 to 55 repeat units. By inspecting the corresponding transition density matrices (see Fig. 2), we selected the lowest exciton band for a detailed analysis. This band corresponds to the dipole-allowed delocalized exciton, responsible for optical absorption and emission properties of phenylacetylene molecules,[10] referred to as a light exciton. Inside the light-exciton band with the width of about 1 eV, there is a narrower band whose width is around 0.1 eV. These excitons will be naturally referred to as heavy excitons. The higher energy weakly allowed band of more spatially localized heavy excitons is associated with the triple bond excitation. The analysis presented below can be performed for any exciton band.

To determine the ingredients of the ES model, we further analyze the calculated electronic spectra. Such an approach, referred to as the energy method, is based on the premise that the properties of the molecular building blocks depend on the energy only and are independent of the molecular size. Then, to determine the parameters of the ES model from the

quantum chemistry, in addition to the molecular spectra, we need only limited data from the transition density matrices such as the number of nodes in the standing waves. This technique is best suited for treatment of simple and symmetric scattering centers, such as the ones considered in this work (see Fig. 1). We extract the parameters of the ES model in two steps. First, we consider excited states in the linear molecules of different lengths to extract the exciton dispersion and the scattering amplitude at the ends. We further use these ingredients to retrieve the scattering matrices at the meta- and orthojoints from quantum-chemical calculations in two-segment molecules.

## B. Use of the symmetries

Extraction of the ES model parameters can be substantially simplified by using all available symmetries of the problem. The most universal symmetry is the unitarity of the scattering matrices which reflects the probability conservation (unitarity) in quantum mechanics. Another symmetry involved in our case is the time-reversal symmetry, since there are no external magnetic fields. In particular, the time-reversal symmetry that changes the momentum sign implies the symmetric shape $\omega(-k) = \omega(k)$ of the exciton spectrum. Such implications follow from the linear relation between the multielectron state and the exciton wave function.[1]

For arbitrary $n \times n$ scattering matrices $\Gamma_{ij}^{(n)}(\omega)$, the unitarity and the time-reversal symmetry assume

$$\Gamma^{\dagger}(\omega)\Gamma(\omega) = I, \quad \Gamma^{*}(\omega)\Gamma(\omega) = I, \quad \Gamma^{T}(\omega) = \Gamma(\omega), \quad (1)$$

where $I$ is the unit matrix. Here the third relation (which states that the scattering matrix is symmetric) obviously follows from the first two.

In the case of the molecular end ($n = 1$), the unitarity implies a parametrization $\Gamma^{(1)}(\omega) = \exp(i\phi_T(\omega))$ by a single frequency-dependent phase $\phi_T(\omega)$, hereafter referred to as the scattering phase.

For the double joints (e.g., meta- or orthosubstituted linkages between two linear segments, as shown in Fig. 1), the unitarity means that the $2 \times 2$ matrices belong to the group $U(2)$, and, therefore, can be represented as $\Gamma_{ij}^{(2)}(\omega) = \exp(i\phi(\omega))\bar{\Gamma}_{ij}^{(2)}(\omega)$, where $\bar{\Gamma}_{ij}^{(2)}(\omega)$ belongs to the group $SU(2)$ of unitary $2 \times 2$ matrices with the unit determinant. These matrices are determined by three parameters:

$$\bar{\Gamma}^{(2)}(\omega) = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}, \quad |a|^2 + |b|^2 = 1, \quad b^* = -b, \quad (2)$$

where the third equation follows from the third condition in Eq. (1). Equation (2) suggests the following parametrization of the scattering matrices that describe the properties of any double joint:

$$\Gamma^{(2)}(\omega) = \begin{pmatrix} \sin\theta\exp(i\phi + i\varphi) & i\cos\theta\exp(i\phi) \\ i\cos\theta\exp(i\phi) & \sin\theta\exp(i\phi - i\varphi) \end{pmatrix}. \quad (3)$$

Finally, the mirror symmetry of the meta- or orthojoints entails $\varphi(\omega)=0$, and we arrive at the general parametrization

$$\Gamma^{(2)}(\omega) = \begin{pmatrix} \sin\theta\exp(i\phi) & i\cos\theta\exp(i\phi) \\ i\cos\theta\exp(i\phi) & \sin\theta\exp(i\phi) \end{pmatrix} \quad (4)$$

of the scattering matrices for the symmetric joints of degree two in terms of two frequency-dependent phases. In particular, the reflection $r(\omega)$ and transmission $t(\omega)$ amplitudes are expressed as

$$r(\omega) = \sin\theta(\omega)\exp[i\phi(\omega)],$$
$$t(\omega) = i\cos\theta(\omega)\exp[i\phi(\omega)], \quad (5)$$

which means that $\theta(\omega)$ and $\phi(\omega)$ describe the scattering probabilities and phases, respectively.

## C. Numerical procedure and results

We start our analysis with the simplest case of finite linear ($P$) molecules (Fig. 1). The only scattering processes occur at the ends and are described by a unitary $1 \times 1$ matrix, i.e., a unimodular complex number determined by its phase: $\Gamma^{(1)}(\omega) = \exp[i\phi_T(\omega)]$. The exciton wave function far from the scattering centers is represented by a linear superposition of two-plane waves with opposite wavevectors $k>0$ and $-k$

$$\psi(x) = a\exp(ikx) + b\exp(-ikx). \quad (6)$$

The amplitudes of the plane waves are connected by two linear relations imposed on the molecular ends. The relations are compatible and allow for nonzero solutions if the following quantization condition for the wavevector is satisfied:

$$kl = \pi n - \phi_T. \quad (7)$$

Here $l$ is the molecular length in repeat units and $n$ is an integer that labels the excited states. As found below, we have $\pi < \phi_T < 2\pi$ in the entire light-exciton band with $\phi_T(\omega)$ being a monotonically increasing function of the excitation energy $\omega$ (see Fig. 4). This should be compared to the hard-wall reflection phase $\phi_T = \pi$. Consequently, in Eq. (7) the integer $n \geq 2$ is related to the number of nodes in the exciton wave function given by $n-2$.

Scattering at the molecular end adjacent to the $x=1$ repeat unit results in the following asymptotic form of the exciton wave function:

$$\psi(x) \propto \cos\left[k\left(x - \frac{1}{2}\right) + \frac{\phi_T}{2}\right], \quad (8)$$

where $k = k(\omega)$ and $\phi_T = \phi_T(\omega)$ are determined by the excited state energy $\omega$. Equation (7) determines the excitation ener-

gies $\omega$ in a linear oligomer, if the functions $k(\omega)$ and $\phi_T(\omega)$ are given. The key feature of the ES approach is that these functions are independent of the segment length: $k(\omega)$ depends only on the repeat unit structure, whereas the scattering matrices are also determined by a chemical composition of the scattering center.

We use the numerical data for the excited state energies and the corresponding transition density matrices in linear ($P$) molecules of different lengths. Simultaneous evaluation of two smooth functions $k(\omega)$ and $\phi_T(\omega)$ based on the set of discrete numbers (molecular spectra) is not a trivial task. The values of the functions obey Eq. (7) at given discrete energies $\omega$, with molecular length $l$ and the number of nodes $n-2$ being the additional parameters. The lowest excited state of the molecule corresponds to $n=2$, and for each following excited state, $n$ increases by one, as long as the relative electron-hole motion remains the same, i.e., we stay within the same exciton band, which can be verified by checking the shapes of the transition density matrices (see Fig. 2). The results, however, usually turn out to be so accurate that any excited states, erroneously attributed to the band under consideration, produce noticeable deviations and can be easily singled out.

The relative relevance of the scattering phase is determined by the molecular length, which allows us to separate contributions of two unknown functions. When the excited states in the vicinity of the given energy $\omega$ are considered in the molecules of increasing lengths, the scattering phase $\phi_T(\omega)$ drops out of Eq. (7). This corresponds to the restoration of translational invariance in the limit of infinitely long molecules. Neglecting the scattering phase in Eq. (7) completely (or setting its value, for example, to the hard-wall value $\phi_T = \pi$ for all energies) would not make a sufficiently accurate approximation for the spectrum even if the longest available molecules are used, since the numerical methods are naturally restricted to the moderate oligomer lengths. This approximation can be referred to as a one-point approach, to ensure the consistency with the subsequent description, because only one data point is used to evaluate a single value of the inverse spectral function $k(\omega)$.

We further introduce the two-point approach, which can be exact with respect to the quantum chemistry (i.e., the two-point approach does not create an additional inaccuracy compared to the existing numerical errors) for a certain energy, if two excited states with this energy exist in molecules of different lengths. The approach is also useful for close energies $\omega_1$ and $\omega_2$, if the changes in functions $k(\omega)$ and $\phi_T(\omega)$ between $\omega_1$ and $\omega_2$ are negligible. The values of the functions are easily found from Eq. (7) applied to two molecules:

$$k = \frac{\pi(n_1 - n_2)}{l_1 - l_2}, \quad \phi_T = \frac{\pi(n_2 l_1 - n_1 l_2)}{l_1 - l_2}, \quad (9)$$

where the indices 1 and 2 denote the quantities of the corresponding excited states and molecules. The results exhibit degeneracies at $n_1 = n_2$ and $n_1/l_1 = n_2/l_2$ which are typical and should be avoided in all $n$-point approaches. Apart from these degeneracies, in the practical situations, the two-point approach fails to yield the results of desired accuracy if the
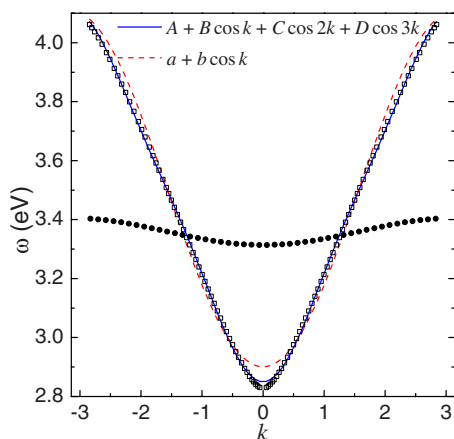
FIG. 3. (Color online) Dispersions of two lowest-energy excitons in phenylacetylene oligomers, the light (squares) and heavy (filled circles) excitons. The light-exciton dispersion is approximated by one cosine (dashed line, the parameters are $a=3.504$, $b=-0.603$) and three cosine harmonics (solid line, the parameters are $A=3.490$, $B=-0.589$, $C=-0.009$, and $D=-0.042$).

energies $\omega_1$ and $\omega_2$ are too separated. However, it may still be useful if the changes in the functions $k(\omega)$ and $\phi_T(\omega)$ between $\omega_1$ and $\omega_2$ are properly evaluated. Obviously, the latter is locally impossible with only two data points used. This can be performed, for instance, by using an extrapolation involving neighboring groups of data points and estimating the derivatives of the functions, which is feasible because of their smoothness. We use the two-point approach for estimates at low energies near the bottom of the exciton band, where the functions $k(\omega)$ and $\phi_T(\omega)$ are not smooth, and straightforward inclusion of further data points compromises the accuracy due to the associated wider range of energies.

It is clear that one can achieve better accuracy of values $k(\omega)$ and $\phi_T(\omega)$ when more data points are present in the vicinity of the energy $\omega$, which requires numerical computations for more and longer molecules.

For most energies we employ the four-point approach. Truncating the Taylor expansion of Eq. (7) applied to four data points with energies $\omega_i$, with $i=1,\ldots,4$, in the vicinity of energy $\omega$, we calculate the values of the functions $k(\omega)$ and $\phi_T(\omega)$ and their derivatives $k'(\omega)$ and $\phi_0'(\omega)$. We disregard groups of points leading to the degenerate cases everywhere. Corrections due to the second derivatives can be easily estimated and serve as another criterion for the appropriate choice of points. Since there is enough data available from molecules with lengths $l>10$, we do not use shorter molecules to avoid their influence on the otherwise relatively smooth behavior of $k(\omega)$. We apply a piecewise polynomial least-square fit to tabulate the functions $k(\omega)$ and $\phi_T(\omega)$ for their further use.

The results obtained from the linear oligomers are presented in Figs. 3–5. The dispersion in Fig. 3 is a smooth function everywhere at $k\neq 0$ but has a possible weak cusp at $k=0$, which may be an effect of the long-ranged Coulomb interaction. We cannot exclude the cusp, since it is obtained by extrapolation in the lowest part of the spectrum, where relative errors might be considerable. We note that, besides the weak cusp, the spectrum $\omega(k)$ can be adequately approximated by a single cosine, while the fit significantly improves

if three first cosine harmonics are included. This suggests that the effective interactions in the molecule are limited to the neighboring repeat units. In fact, the exciton size (a typical electron-hole separation) does not exceed two- to three-repeat units.

The phase $\phi_T(\omega)$ of reflection at the molecular end is shown in Fig. 4. The energy dependence of the phase is quite strong. If the phase $\phi_T$ is plotted as a function of the wavenumber $k$ the dependence turns out to be different from a
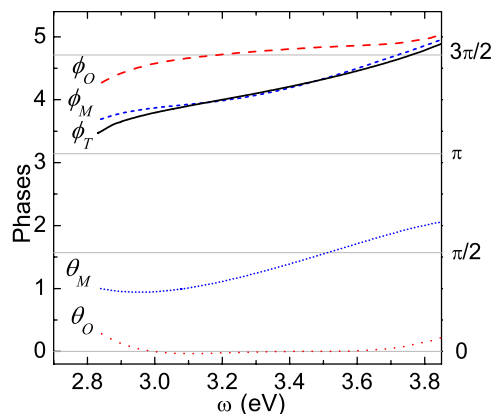


FIG. 4. (Color online) Scattering phases: at the molecular terminals, $\phi_T$ (solid black line); at the orthosubstituted linkages, $\phi_O$ and $\theta_O$ (red dashed and dotted lines); at the metasubstituted linkages, $\phi_O$ and $\theta_O$ (blue dashed and dotted lines).
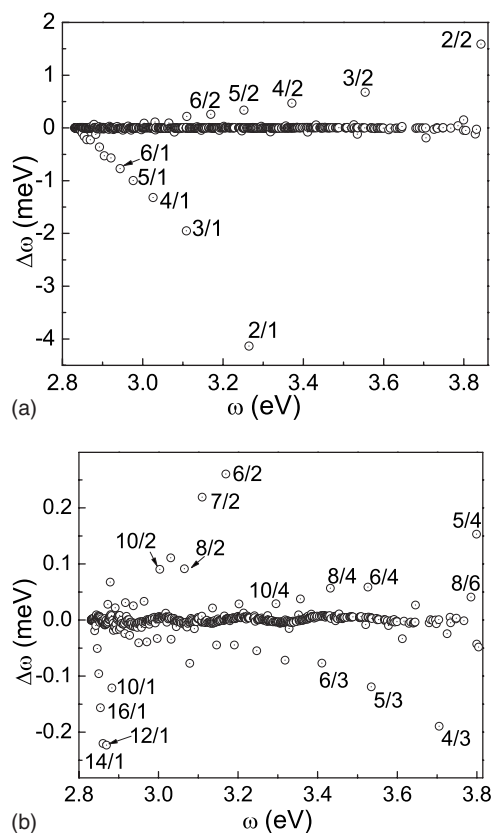


FIG. 5. Deviations between the CEO excitation energies in the linear molecules and the smooth dispersion of the ES model: (a) all states and (b) a zoomed in view (note that the numerical accuracy of the CEO method was estimated as 0.01 meV). The $m$th mode in the molecule $Pn$ is denoted by $n/m$.

linear one, which indicates that the scattering is not of the hard-wall type even if the "wall" is shifted from the chain terminal.

Figure 5 shows deviations from the ES dispersion in linear oligomers. The energy differences presented are obtained by subtracting the smooth fit $\omega(k)$ from the quantum-chemical energies. The deviations approach the numerical CEO accuracy 0.01 meV and vanish for longer molecules, which is the expected asymptotic behavior. However, the deviations are amazingly small even for short oligomers. For two- and three-repeat unit molecules the ES energies are within 1–5 meV from the quantum chemistry results, although these oligomers are certainly not longer than the exciton size.

Next we determine the scattering properties of the degree-two vertices. To that end we consider molecules with two linear segments of equal lengths, so that the test molecules preserve the mirror symmetry of the joint under study. Pure phenylacetylene compounds allow for two types of nontrivial links: the connections through meta-($M$) and ortho-($O$) substitutions (see Fig. 1). Linear molecules can be viewed as a trivial case of para-($P$) substitution.

Scattering processes at the meta- or ortholinks are described by $2 \times 2$ matrices $\Gamma^{(2)}(\omega)$ which can be parametrized by two phases according to Eq. (4). Since within the ES approach only a quantitative difference between the meta- and orthojoints appear in the scattering matrices, we can derive the general relations for both cases simultaneously. In each linear segment, the exciton wave function far from the scattering centers is represented by a linear combination of plane waves running in opposite directions. Their amplitudes are connected by a set of linear equations—the ES equations[1]—which describe free-particle propagation along the linear segments and scattering at the vertices. In a molecule with two segments of $l_1$ and $l_2$ repeat units, nontrivial solutions of the ES equations exist if

$$(\sin \theta e^{i(2kl_1+\phi+\phi_T)} - 1)(\sin \theta e^{i(2kl_2+\phi+\phi_T)} - 1)$$
$$+ \cos^2 \theta e^{2i(kl_1+kl_2+\phi+\phi_T)} = 0, \tag{10}$$

which is as an energy quantization condition provided $k$, $\phi_T$, $\phi$, and $\theta$ are given functions of energy. In the case of equal arms, $l_1=l_2=l$, the molecules have the mirror symmetry with respect to the joint, and, consequently, all excited states must be either even or odd. Equation (10) can then be reduced to two decoupled equations that correspond to two possible values of the excited state parity. Thus, we obtain the relations

$$2kl_1 = \pm \theta - (\phi + \phi_T) \mp \frac{\pi}{2} + 2\pi n, \tag{11}$$

where the upper and lower signs correspond to even and odd modes, respectively, and $n$ is an integer which increases by one for each higher mode of the same parity. The lower bound for $n$ as well as its exact relation to the number of nodes depend on the definitions of the scattering phase ranges. Besides the circular ($2\pi$) invariance, the scattering matrix in Eq. (4) is invariant with respect to the simultaneous shift of $\phi$ and $\theta$ by $\pi$. We fix the definition of $n$ for the lowest modes and hence define the range of $\phi$ and $\theta$.

Since the functions $k(\omega)$ and $\phi_T(\omega)$ have already been tabulated, the combinations $\phi(\omega) \pm \theta(\omega)$ of the phases which characterize the double joints can be found at any excitation energy of the symmetric two-segment molecules using Eq. (10) without introducing further numerical errors. We approximate the combinations $\phi(\omega) \pm \theta(\omega)$ by piecewise smooth fitting functions and thus obtain the phases separately.

An additional complication appears in orthoconjugated phenylacetylene molecules: we have to distinguish two types of the orthojoint. One is found in unconstrained geometries, i.e., molecules without loops, such as in two-segment ortholinked molecules. The arms of these orthomolecules are twisted out of plane of the linking phenyl ring in the opposite directions by $\sim 1.3°$ due to steric interactions, thus making the joint itself nonplanar. The geometry of the nonplanar orthojoint is almost independent of the length of the segments attached to the joint. Therefore, there is a clear geometrical distinction between the nonplanar and planar orthojoints. The latter type occurs, for example, in cycle molecules such as triangles.[15] We also observe that the planar orthojoint corresponds to a local minimum of energy in unconstrained structures and can be found after a symmetry-constrained optimization of geometry. This is a practical way to achieve the same geometry in two-segment ortho-molecules as in planar cycle structures. The scattering properties of the joint are naturally affected by its geometry. The phases describing the scattering of light excitons at the two types of the orthojoint are similar but consistently different. In contrast to the planar orthojoint, the empirical scattering phases of the nonplanar joint appear to be somewhat irregular in the vicinity of the heavy exciton band. This indicates a possible scattering between the light and heavy excitons at the nonplanar orthojoint. While strictly speaking the ES model with the single exciton is not justified in this energy range, approximations of the scattering phases for the nonplanar orthojoint by smooth functions provide an adequate accuracy in practice. When applying the ES model (for example, in Ref. 15), we will use different scattering phases for planar and nonplanar orthojoints.

The scattering phases for meta- and planar orthojoints are shown in Fig. 4. We note that the energy dependencies of the scattering phases obtained on the basis of the CEO method and the time-dependent density functional theory[2] have very similar shapes. The scattering phases for the meta- and orthojoints should be compared to values that correspond to total reflection and ideal transmission, respectively. The transmission coefficient is given by $\cos^2 \theta$ according to Eq. (5). Our results show that the metaconjugation does not present an impenetrable barrier for all energies. However, at a certain energy $\omega \approx 3.5$ eV near the middle of the band $\theta = \pi/2$, and the metajoint completely blocks transmission of light excitons. At the same time we note that the reflection amplitude phase at the metajoint is almost identical to the scattering phase $\phi_T$ at the molecular end for all energies. The phases in the scattering matrix for the orthojoint are close to the ideal transmission values, $\phi = 3\pi/2$ and $\theta = 0$. The energy-dependent corrections are small, but can still be adequately described by smooth functions.
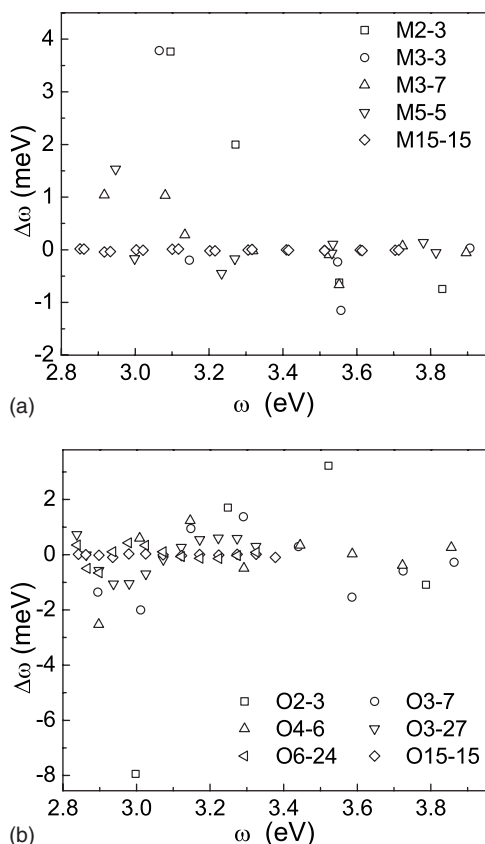
FIG. 6. Difference between the ES and CEO results for excitation energies in selected (a) meta- and (b) orthoconjugated molecules. X$y-z$ stands for an X-conjugated molecule (X=$M$ or $O$) that consists of two segments with $y$ and $z$ repeat units.

The accuracy of the phases that describe the $M$ and $O$ joints can be checked by comparing the energies predicted by the ES model with those from the quantum chemistry in two-segment molecules. To make a more convincing case, for comparison we include the data that have not been used yet in extracting the scattering phases.

We obtain the excitation energies from Eq. (10) after all the necessary parameters have been tabulated as functions of energy. Figure 6 shows a comparison of the energies obtained using the ES approach and the CEO computations for selected $M$ and $O$ molecules. As shown in Fig. 6, for $M$ molecules most energy differences are within 1 meV, and for $O$ molecules this range widens to 2 meV. For short two-segment molecules the deviations are similar to those in short linear molecules.

The results presented above validate the exciton scattering model for linear and single-joint molecules. In the following paper[15] we apply the ES model to more complex molecules and discuss how features of the molecular spectra can be understood within the ES model.

## III. DISCUSSION

The ES approach can be applied to any quasi-one-dimensional molecular system (e.g., conjugated polymers or molecular quantum wires) with tightly bound excitons. In this manuscript we have characterized the building blocks of phenylacetylene polymers without extraneous vertices: we have obtained the exciton dispersion $\omega(k)$, the scattering matrices $\Gamma_{ij}^{(1)}(\omega)$ for the molecular ends, and $\Gamma_{ij}^{(2)}(\omega)$ for the double joints. As expected, the dispersion relation and the scattering matrices are smooth functions of energy. Our results refine earlier reports[3,10–14] concerning the properties of the ortho- and metajoints. We observe that the transmission is energy, dependent for both joints. The metajoint does not completely block excitations except for an isolated energy value, whereas the phases of the reflection amplitudes at the metajoint and the molecular end are close for all energies. We find that, although the orthojoint seems to be transparent to the excitations, its scattering matrix has a small detectable deviation from the ideal transmission case. We check the applicability of the ES model and the quality of the extracted parameters by comparing the excitation energies from the ES and CEO calculations in several simple one- and two-segment molecules. Although in short molecules (as the molecular length becomes comparable to the exciton size) the ES model is expected to fail, we are able to obtain surprisingly small errors of order of 1–5 meV, given the excitation energy on the order of 3–4 eV (see Fig. 3). In longer molecules the deviations of energies are typically well below 1 meV. Finally, we observe the dependence of the scattering properties of the joints on their geometry. This can be important, for example, in the circular and dendritic aggregates,[21–24] where the geometry is constrained. This also demonstrates the capability of the ES approach to deal with the molecular geometry distortion, which is crucial for future applications of the ES approach to treat effects of exciton coupling and molecular disorder.

To find the ES parameters of complex asymmetric scattering centers we may need a more general wave function method. Here we use only the energy method for simpler building blocks which proves to yield generally smaller errors than the wave function method. The results of the wave function method are more sensitive to the deviations from the ES picture due to the finiteness of the exciton size. Such deviations clearly appear in the vicinity of scattering centers. Consequently, the estimates for the wavenumber and the scattering phases depend on the choice of the region where the exciton wave function can be assumed to have its asymptotic form. To emphasize an additional advantage of the energy method we recall that the main goal of the ES theory is calculating optical properties of branched molecules. The energy method is designed to produce more accurate results for the transition frequencies. However, the scattering center should have a sufficiently high symmetry to be treated by the energy method. Direct extraction of the wavenumbers from the transition density matrices can still be used occasionally to support the energy approach in the regions and for molecules where the latter becomes less accurate.

Possible further developments include a study of the scattering involving different exciton types, taking into account the finiteness of the exciton size and long-range interactions. Other exciton types can be treated in the future using the same ES approach. It is noteworthy that quantum-chemical calculations to tabulate the ES parameters of the

building blocks have to be done only once. The parameters then allow instantaneous simulations in arbitrary structures composed of the molecular building blocks at negligible computational cost, i.e., building the correspondent molecular graph (lego-type design) and solving the scattering problem on the graph.

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