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Exciton scattering approach for branched conjugated molecules and complexes. IV. Transition dipoles and optical spectra

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The electronic excitation energies and transition dipole moments are the essential ingredients to compute an optical spectrum of any molecular system. Here we extend the exciton scattering (ES) approach, originally developed for computing excitation energies in branched conjugated molecules, to the calculation of the transition dipole moments. The ES parameters that characterize contributions of molecular building blocks to the total transition dipole can be extracted from the quantum-chemical calculations of the excited states in simple molecular fragments. Using these extracted parameters, one can then effortlessly calculate the oscillator strengths and optical spectra of various large molecular structures. We illustrate application of this extended ES approach using an example of phenylacetylene-based molecules. Absorption spectra predicted by the ES approach show close agreement with the results of the reference quantum-chemical calculations. © *2010 American Institute of Physics*. [doi:10.1063/1.3366521]

I. INTRODUCTION

In the previous articles,[1–3] the exciton scattering (ES) approach has been developed as an efficient and accurate multiscale method to calculate the electronic excitations in branched conjugated molecules.[1–3] Within the ES approach, we attribute the electronic excitations in the quasione-dimensional molecule to the states of a quantum quasiparticle (exciton)[4–12] on the corresponding graph, forming standing waves as a result of quantum scattering on molecular ends and vertices.[13–16] The behavior of the exciton in the molecular building blocks, including the repeat units and scattering centers, is described by the dispersion relation $\omega(k)$ (relating the quasimomentum k to the energy) and the scattering matrices $\Gamma^{(n)}(\omega)$, respectively. These ES parameters can be extracted from the reference quantum-chemical calculations of small fragments representing elementary molecular units or chemical building blocks. Once the parameters are determined, the excitation energies of any large superstructure composed of previously characterized "building blocks" can be calculated by solving a generalized "particle in a box" problem.[15,16] The ES approach is thus somewhat similar to a simple free-electron theory of excitations in conjugated molecules developed, for example, in Refs. 17 and 18.

The energies of electronic excitations constitute an important piece of information for describing optical properties of materials, since they indicate the positions of the absorption peaks. However, the optical properties also depend on the transition dipole moments of excited states. These quantities determine whether respective electronic transitions carry oscillator strengths that define the intensities of the corresponding peaks in the optical spectra.[19] In this work, we demonstrate how to calculate the transition dipole moments within the ES framework.

In the context of the ES approach, the wave function for a stationary state of the "particle in a box" problem, which has a standing-wave form, should be interpreted as a distribution of the excitation amplitudes on the linear segments. The idea behind the calculation of transition dipoles within the ES approach is that the contribution of a building block to the total dipole is proportional to the local excitation amplitude. Specifically, transition charges and dipoles of building blocks can be determined using a small number of energy-dependent parameters. These dipole and charge parameters can also be extracted from the reference quantum-chemical computations in molecules of moderate sizes and tabulated in addition to the scattering parameters for the excitation energies. Consequently, the transition dipole moment magnitudes can be computed efficiently for any molecule that consists of characterized building blocks, similarly to computation of excitation energies within the ES approach. Excitation energies and transition dipole moments allow us to calculate optical spectra. On several examples of phenylacetylene π-conjugated molecular structures,[6,12,20–23] we found that the absorption spectra predicted by our extended ES approach accurately reproduce the results of the respective direct quantum-chemical calculations.

The manuscript is organized as follows: The formalism for the extension of the ES approach to calculation of transition dipole moments is presented in Sec. II. We show that the dipole properties of building blocks are fully characterized by several energy-dependent parameters, and how these dipole ingredients can be retrieved from the quantum-chemical calculations in molecules of moderate size. In Sec. III we illustrate application of this methodology to sev-

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eral building blocks of conjugated phenylacetylenes: repeat units, molecular ends, and double joints. In Sec. IV we use the extracted ES parameters to calculate the transition dipoles in several test molecules and compare the ES results to direct quantum-chemical calculations.

II. TRANSITION DIPOLES WITHIN THE ES APPROACH

A. Generalized ES approach

In this section we review and generalize the ES approach. Within this theory, an excitation in a conjugated molecule is viewed as a quantum particle (exciton) on the corresponding graph. In an infinite linear segment, the common motion of an electron and a hole that form the exciton, is described by a plane wave parameterized by the exciton quasimomentum. The spatial distribution of delocalized electronic excitation in a complex branched conjugated molecule can be characterized by the exciton wave function given by a set of standing waves on molecular linear segments α

$$\psi_\alpha(x_\alpha) = a_\alpha \exp(ikx_\alpha) + b_\alpha \exp(-ikx_\alpha), \tag{1}$$

where the wavenumber k is related to the excitation energy ω through the dispersion relation $\omega(k)$, and the wave function is defined at integer points x_α. Note that the excited state has a standing-wave structure only sufficiently far from the molecular vertices (in comparison with the exciton size), which implies that the ES approach can be justified only if molecular linear segments are long compared to the typical distance between the electron and the hole in the exciton (exciton size).

In the following, to simplify the description, we assume that at a given energy there is only one exciton type. We choose to formulate the ES approach using the standing wave associated with the transition dipole distribution in real space, which has substantial intuitive advantage: As for a quantum particle, for the first excitation in the linear molecule this exciton wave function is symmetric and has no nodes, whereas for the second excitation it is antisymmetric (with one node), etc. This choice implies that the exciton wave function should be defined as a vector that can be represented by a unit vector $\boldsymbol{n}_\alpha$ in the direction of the repeat unit's axis and a projection $\psi_\alpha(x_\alpha)$ on that axis

$$\boldsymbol{\psi}_\alpha(x_\alpha) = \psi_\alpha(x_\alpha)\boldsymbol{n}_\alpha. \tag{2}$$

The first version of the ES approach[1] was formulated in terms of the projections of the wave function ψ. However, this approach, when applied to complex structures with loops, requires inverting signs of some elements of scattering matrices for certain positions of vertices in the graph. The reason for this complication was possible conflicts in structures with loops between orientations which were necessarily included in definitions of scattering matrices based on projections. The representation (2) is especially useful when the repeat units can be viewed as straight but $\boldsymbol{n}_\alpha$ can slowly vary from repeat unit to repeat unit, whereas the local projection $\psi_\alpha(x_\alpha)$ of the wave function is not affected by this weak deformation.

Within the ES approach, the excitation amplitude can be found by solving simple wave equations describing propagation along linear segments and scattering at vertices. These equations, referred to as ES equations, can be formulated in terms of the incoming and outgoing waves $\psi_{\alpha b}^{(\pm)}$ defined as the values of two plane-wave components of the asymptotic standing wave continued to the vertex. In this notation incoming (+) and outgoing (−) waves are specified in the linear segment α at the vertex b. Propagation along the segment α of length l_α between the vertices b and c is expressed by the equation

$$\boldsymbol{\psi}_{\alpha b}^{(-)} = \boldsymbol{n}_{\alpha b}(\boldsymbol{n}_{\alpha c}, \boldsymbol{\psi}_{\alpha c}^{(+)})\exp(ikl_\alpha), \tag{3}$$

where we introduced unit vectors corresponding to the directions of the segment's ends (we define these unit vectors as the unit vectors of the first and last repeat units), and $(\cdot,\cdot)$ stands for the scalar product.

Scattering matrices $\Gamma(\omega)$ quantify scattering at the molecular vertices

$$\boldsymbol{\psi}_{\alpha b}^{(+)} = \boldsymbol{n}_{\alpha b}\sum_{\beta \ni b}\Gamma_{b,\alpha\beta}(\omega)(\boldsymbol{n}_{\beta b}, \boldsymbol{\psi}_{\beta b}^{(-)}). \tag{4}$$

We note that specifying directions on all segments connected to the vertex is necessary to describe the scattering.

If the exciton dispersion $\omega(k)$ and the energy-dependent scattering matrices for all vertices are known, from Eqs. (3) and (4) one can find the excitation energies and the exciton wave function up to a normalization factor. We assume the following normalization condition of the exciton wave function

$$\sum_{\alpha \in \mathcal{M}_1}\sum_{x_\alpha=1}^{l_\alpha}\psi_\alpha(x_\alpha)\psi_\alpha^*(x_\alpha) = 1. \tag{5}$$

The amplitudes of the exciton wave function ψ_α are directly related to the transition density matrices obtained in quantum-chemical calculation,[1] which reflects changes in the single electron density matrix[24] due to optical excitation. The matrix elements of the transition density matrix between the ground state $|g\rangle$ and excited state $|\nu\rangle$ many-electron wave functions are defined as

$$(\xi_\nu)_{nm} = \langle \nu | c_n^\dagger c_m | g\rangle, \tag{6}$$

where $c_n^\dagger$ (c_m) are the Fermi creation (annihilation) operators for the nth (mth) basis set orbital. In the time-dependent density functional theory[25,26] or time-dependent Hartree–Fock[27,28] (HF) approximation the transition density matrices are obtained as eigenvectors diagonalizing an appropriate Liouville operator. These eigenvectors in the orthonormal basis set are normalized with the condition

$$\mathrm{Tr}(\bar{\rho}[\xi_\nu^\dagger, \xi_\nu]) = 1, \tag{7}$$

where $\bar{\rho}$ represents the ground-state single-electron density matrix in the HF approximation[24,29] or Kohn–Sham representation.[30,31] This expression reduces to the usual scalar product in the Tamm–Dancoff approximation.[32] Consequently, the normalization condition of the exciton wave function (5) naturally follows from Eq. (7).

B. Calculation of the transition dipole moments in the ES approach

To extend the ES approach to calculation of the transition dipole moments, we follow the way how they are calculated from the transition density matrix given in the basis of atomic orbitals, where the dipole matrices $\hat{\boldsymbol{\mu}}_{nm} = \langle n|\hat{\boldsymbol{\mu}}(\mathbf{r})|m\rangle$ are local (here $\hat{\boldsymbol{\mu}}(\mathbf{r})$ is the dipole operator).[29,33] After assuming for simplicity the orthogonality of the basis set orbitals, the transition dipole moment for optical excitation to state ν is defined as

$$\boldsymbol{\mu}_\nu = \mathrm{Tr}(\hat{\boldsymbol{\mu}}\xi_\nu). \tag{8}$$

Equation (8) basically involves a sum over all orbitals with the proper account of their overlapping. We separate the molecule into building blocks (repeat units and vertices) that occupy certain regions of space. Since the dipole matrices $\hat{\boldsymbol{\mu}}_{nm}$ are local (i.e., they have dominant block-diagonal structure with each block corresponding to the basis functions on the same atom), we can identify the transition charge and dipole of individual molecular units.[1] The building block's dipole is defined with respect to a point "attached" to the particular building block and chosen in the same way for all building blocks of this type.

For any wavenumber k, there are two linearly independent standing waves. One of them is the exciton wave function. The second standing wave $\tilde{\psi}(x)$, referred to as a dual wave function, can be introduced as a formal derivative of the wave function $\boldsymbol{\psi}(x)$ by considering its argument x as a continuous variable. The following definition of $\tilde{\psi}(x)$ is invariant with respect to the choice of orientations on the linear segments

$$\tilde{\psi}(x) = \frac{1}{k}\mathrm{div}\ \boldsymbol{\psi}(x) \equiv \frac{1}{k}\frac{d(\boldsymbol{\psi}(x),\boldsymbol{n}_x)}{dx}, \tag{9}$$

where $\boldsymbol{n}_x$ is the unit vector in the positive x direction. The normalization of the dual wave function is determined by the normalization of the wave function. The relation (9) and the identification of the wave function with the transition dipole distribution imply the dual wave function is associated with the transition charge distribution.

The exciton wave function and dual exciton wave function are reduced characteristics of the excitation strength that are linearly and locally related to the transition density matrix in an infinite polymer.[1] Therefore, far from vertices, the transition dipoles and charges of repeat units are proportional to the exciton wave function and dual exciton wave function, respectively. If the deviations of the charges and dipoles of repeat units from standing waves are localized near the vertices, and the linear segments are sufficiently long, we can include all such deviations into vertex contributions. Thus, in the molecule with long linear segments it is possible to take into account all contributions to the transition dipole.

The approach described above ensures that the charge and dipole of the building block is independent of its position within the molecule and depends only on the local amplitude of the excitation. For repeat units, the excitation strength is characterized by the exciton wave function and dual exciton wave function. For a vertex of degree n, the excitation strength can generally be determined by any n amplitudes of incoming or outgoing waves in the wave function or dual wave function, since the amplitudes are related to each other with the help of Eqs. (4) and (9). We choose to use the amplitudes of incoming waves in the exciton wave function and dual exciton wave function for the transition dipole and charge, as they have the corresponding symmetries. Symmetries of repeat units and vertices determine how many parameters are necessary to describe their transition dipoles and charges.

Combining all contributions, we find the following general expression for the total transition dipole of the excited state:

$$\boldsymbol{\mu} = \sum_{\alpha\in\mathcal{M}_1}\sum_{x_\alpha=1}^{l_\alpha}\left(q(\omega)\boldsymbol{r}^{(\alpha)}_{x_\alpha}\tilde{\psi}_\alpha(x_\alpha)+d(\omega)\boldsymbol{\psi}_\alpha(x_\alpha)\right) + \sum_{b\in\mathcal{M}_0}\sum_{\alpha\ni b}\left(q_{b\alpha}(\omega)\boldsymbol{r}_b\tilde{\psi}^{(-)}_{\alpha b}+d_{b\alpha}(\omega)\boldsymbol{\psi}^{(-)}_{\alpha b}\right), \tag{10}$$

where we introduced energy-dependent charge coefficients $q(\omega)$ and $q_{b\alpha}(\omega)$ as well as dipole tensor parameters $d(\omega)$ and $d_{b\alpha}(\omega)$ for repeat units and vertices, respectively. $\mathcal{M}_0$ and $\mathcal{M}_1$ represent sets of molecular vertices and linear segments, respectively. The first and last two terms in Eq. (10) stand for contributions of repeat units and vertices, respectively. The dipole tensor parameters represent the most general forms of linear transformations between vector wave functions and vectors of transition dipoles. The positions $\boldsymbol{r}^{(\alpha)}_{x_\alpha}$ and $\boldsymbol{r}_b$ refer to the repeat unit x_α in the segment α and the vertex b, respectively. In the following, the parameters $q(\omega)$, $d(\omega)$, $q_{b\alpha}(\omega)$, and $d_{b\alpha}(\omega)$ will collectively be referred to as dipole ES parameters.

III. EXTRACTION OF THE TRANSITION CHARGE AND DIPOLE PARAMETERS FROM QUANTUM-CHEMICAL CALCULATIONS

Within the ES approach, the transition charge and transition dipole parameters characterizing different building blocks are necessary for the calculation of the total transition dipole moment of the entire structure. In this section, we demonstrate how these dipole parameters can be retrieved from the quantum-chemical computations in conjugated molecules of moderate sizes using an example of phenylacetylene molecules.

A. Quantum-chemical computations

We consider phenylacetylene-based molecules with four types of building blocks (see Fig. 1), including a repeat unit, a molecular terminal, and metaconjugated and orthoconjugated linkages. The transition charge and dipole parameters of these building blocks are retrieved from the quantum-chemical calculations performed in linear molecules as well as meta- and orthoconjugated molecules of different lengths.[2] The ground state geometries are optimized using the semiempirical Austin Model 1 Hamiltonian,[34] which adequately reproduces the molecular ground state geometries, particularly in π-conjugated hydrocarbon compounds.[2]

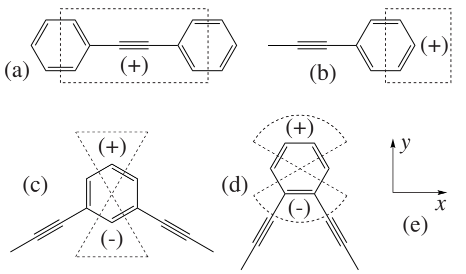

FIG. 1. Building blocks of phenylacetylene-based molecules: (a) repeat unit, (b) molecular terminal, (c) metaconjugated, and (d) orthoconjugated linkages (joints). The atoms in the region marked with "(+)" should be considered as part of the vertex, whereas those in the region marked with "(−)" should be "deducted" from the joint due to the overlap of the attached repeat units. (e) The coordinate system for the transition dipole in the vertices is shown here.

GAUSSIAN 03 package[35] is used for the ground state optimizations.

The collective electronic oscillator[12,36,37] (CEO) representation is used to compute the excited states in all molecules. In this technique the HF ground state density matrix and the INDO/S (intermediate neglect of differential overlap/spectroscopy) semiempirical Hamiltonian are employed in the TDHF equation to compute the excitation energies and other molecular spectroscopic observables. The computation cost per excited state is comparable to that of the ground state.[12] The CEO approach has been successfully applied for computing the optical excitations of large conjugated molecules. The excitation energies, oscillator strengths, the transition density matrices in the molecular orbital space and atomic orbital space are obtained.

B. Transition charge and dipole ES parameters of repeat units

The transition charge $q(\omega)$ and dipole $d(\omega)$ parameters of a repeat unit are retrieved from the quantum chemistry data of linear molecules. Since the ES approach is asymptotically exact for molecules whose length is larger than the exciton size[1] (2–3 repeat units in phenylacetylenes), the molecules selected for the parameter extraction should not be too short. To obtain the parameters at low energy, the molecules should be as long as possible. We computed the first 25–40 excitations in molecules of length between 10 and 59 repeat units. We focus on the lowest excitonic band (2.83–4.1 eV), which appears as a strong peak in the optical absorption spectra (band-gap transition). These delocalized light excitons,[2] which can be distinguished from other exciton types with the help of the transition density matrices, are chosen for the detailed analysis. To determine the dipole parameters with adequate accuracy in the large portion of the band (for the energies higher than 2.9 eV), it is sufficient to perform quantum chemistry calculations in several molecules shorter than 20 repeat units. We use several additional longer molecules to improve accuracy at the lower energies.

In these linear molecules, for each excited state in the band of light excitons corresponding to fundamental optically active excitonic band at the band gap, we calculate the exciton wave function and dual wave function from Eqs. (3)–(5) and (9) with the ES parameters extracted previously.[2] Then we use the approach outlined in Sec. II B to compute the transition charges $Q(x)$ and dipoles $\boldsymbol{\mu}(x)$ of repeat units from the corresponding transition density matrix. The charge parameter $q(\omega)$ can be found from the ratio $Q(x)/\tilde{\psi}(x)$ far from the molecular ends. For light excitons the transition dipoles are directed along the repeat units. Therefore, the dipole tensor of the repeat unit is proportional to the unit matrix. We can use the ratio $\mu(x)/\psi(x)$ of projections far from the molecular ends to determine its only parameter $d(\omega)$ (we use the same notation for the tensor and the value of its identical diagonal components).

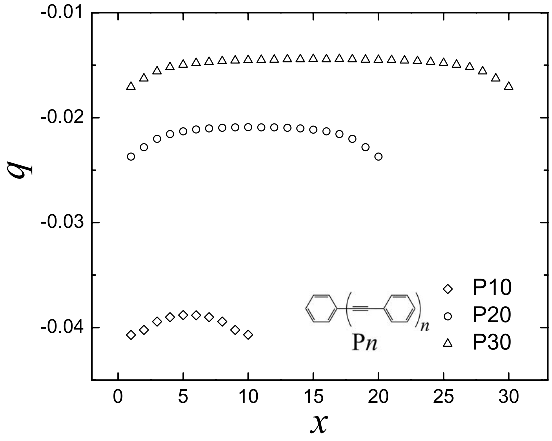

FIG. 2. Ratios $Q(x)/\tilde{\psi}(x)$ of the repeat unit's transition charges and values of the dual exciton wave function for the first mode at all repeat units [see Fig. 1(a)] along linear molecules of different lengths. (The molecular structure is shown in the inset).

At the repeat units close to the scattering centers, the profiles of the transition dipole and charge distributions deviate from the standing waves (see Fig. 2). In general, the deviations of the ratios $Q(x)/\tilde{\psi}(x)$ and $\mu(x)/\psi(x)$ from the constants are localized within several repeat units from the scattering center. To calculate the dipole parameters of the repeat unit, we exclude results from three repeat units adjacent to the scattering center as well as repeat units where the denominator in $Q(x)/\tilde{\psi}(x)$ or $\mu(x)/\psi(x)$ is small and take the average over remaining repeat units. The extracted parameters for the repeat unit shown in Fig. 3 are smooth functions of the energy.

C. Transition charge and dipole ES parameters of scattering centers

Since vertices violate discrete translational symmetry of the polymer, one can expect that transition charges and dipoles of repeat units near vertices deviate from the standing-wave forms of their distributions found far from vertices. Thus, there are two types of contributions to the transition charge and dipole of a vertex: the internal contribution from all the atoms inside the vertex, and the external contribution from the transition charge and dipole deviations on the repeat units close to the vertex. The internal transition charge and dipole can be directly calculated from the transition density matrix. The deviations on the repeat unit x_α of linear segment α can be found as

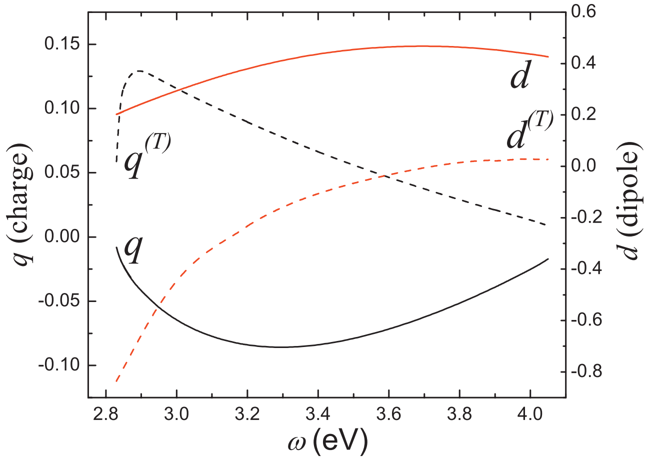

FIG. 3. Dipole parameters q and d of the repeat units (solid lines) and real coefficients $q^{(T)}$ and $d^{(T)}$ (dashed lines) that parameterize the dipole parameters of the molecular ends [see Fig. 1(b)].

$$\Delta Q(x_\alpha) = Q(x_\alpha) - q(\omega)\tilde{\psi}_\alpha(x_\alpha), \tag{11}$$

$$\Delta \boldsymbol{\mu}(x_\alpha) = \boldsymbol{\mu}(x_\alpha) - d(\omega)\boldsymbol{\psi}_\alpha(x_\alpha), \tag{12}$$

where $Q(x_\alpha)$ and $\boldsymbol{\mu}(x_\alpha)$ are the transition charge and dipole of the repeat unit x_α. The ES parameters of repeat unit $q(\omega)$ and $d(\omega)$ have been retrieved in Sec. III B. Since the effect of the scattering center is typically localized within three repeat units, the external contributions can be found as sums over three adjacent repeat units in each branch attached to the vertex. The external contribution to the transition charge of the vertex b is a sum of deviations in all repeat units in attached segments α: $\Delta Q_b = \Sigma_{x_\alpha} \Delta Q(x_\alpha)$. In the external contribution to the transition dipole of a vertex, the transition dipole due to the transition charge corrections within the attached linear segments have to be considered in addition to the deviations of the transition dipoles: $\Delta \boldsymbol{\mu}_b = \Sigma_{\alpha,x_\alpha} \Delta \boldsymbol{\mu}(x_\alpha) + \Sigma_{\alpha,x_\alpha}(\boldsymbol{r}_{x_\alpha}^{(\alpha)} - \boldsymbol{r}_b)\Delta Q(x_\alpha)$.

The transition charge and dipole parameters of molecular ends are also extracted from the quantum chemistry data of linear molecules. The internal transition charge and dipole are attributed to the three carbon atoms and three hydrogen atoms of the terminal as shown in Fig. 1(b). The external contribution is from the three repeat units close to the terminal. In the transition dipole calculation [Eq. (10)], the ES parameters $d_{T\alpha}(\omega)$ and $q_{T\alpha}(\omega)$ of the molecular terminal are defined with respect to the incoming waves of the exciton wave function and dual wave function, respectively. Note that the dipole parameter of the terminal is represented by a diagonal matrix whose diagonal elements are all equal. We use the same notation $d_{T\alpha}$ for both the tensor and its diagonal components. Since the incoming wave are linearly related to the full exciton wave function (which includes both incoming and outgoing waves), the latter can be used instead to define real-valued charge and dipole parameters of the terminal. Comparing its transition dipole and charge with the exciton wave function, we obtain the real-valued parameters $q^{(T)}(\omega)$ and $d^{(T)}(\omega)$ shown in Fig. 3. They can be used to parameterize the complex-valued dipole and charge parameters, $d_{T\alpha}$ and $q_{T\alpha}$ which enter the general expression (10) for the total transition dipole and are defined with respect to incoming waves]

$$d_{T\alpha} = (1 + e^{i\phi_T})d^{(T)}, \tag{13}$$

$$q_{T\alpha} = -i(1 + e^{i\phi_T})q^{(T)}. \tag{14}$$

The extraction of the ES parameters of the double joints (represented by a metaconjugated or orthoconjugated benzene ring) requires the quantum-chemical calculations in the two-arm molecules, hereafter referred to as V-shape molecules. Several symmetric metaconjugated and orthoconjugated molecules of moderate size are used to retrieve the transition charge and dipole parameters for the joints.

In the benzene ring of the linkage, the part of the structure marked with "(−)" in Fig. 1 is counted twice due to the overlap between the joint and the attached repeat units. Therefore, the contributions of the transition charge and dipole from the overlap region should be subtracted from those from the region marked with "(+)" when computing the internal contribution of the transition charge and dipole of the joint. The transition charge and dipole deviations in the three repeat units on each side of the joint are considered as the source of the external contribution to the joint.

For the planar molecules considered, the dipoles lie in the molecular plane and can be described by two components in the coordinate system shown in Fig. 1. In symmetric two-segment molecules, the excitations can be either symmetric or antisymmetric, with the symmetry being defined as the symmetry of the x projection of the transition dipole distribution. The transition charge distribution and the y projection of the transition dipole distribution have the same symmetry that is opposite to the symmetry of the x projection of the transition dipole distribution.

The number of parameters necessary for describing vertices can be generally determined from their symmetry. The transition charge and dipole of a symmetric V joint [V being meta (M) or ortho (O) joint] can be described by one and two real parameters, respectively. As it has been done for the terminals, it is more convenient to deal with real-valued parameters extracted from the transition charge and dipole distributions and afterwards relate them to the parameters that appear in Eq. (10).

Two charge parameters for the segments are equal, and we can use a single real parameter to express the charge through the values of the dual wave function. The real-valued charge parameters of the double joints $q^{(V)}(\omega)$ are obtained by dividing the transition charge by the sum of the values of the dual wave functions on both sides of the joint. Therefore, the transition charge parameters of a double joint, in terms of the incoming waves of the dual wave functions, can be expressed as

$$q_{V\alpha} = (1 + ie^{i(\phi_V + \theta_V)})q^{(V)}, \tag{15}$$

where ϕ_V and θ_V (V stands for M or O) represent the scattering phases at the symmetric joint V which appear in the transformation between the incoming waves and full wave functions.

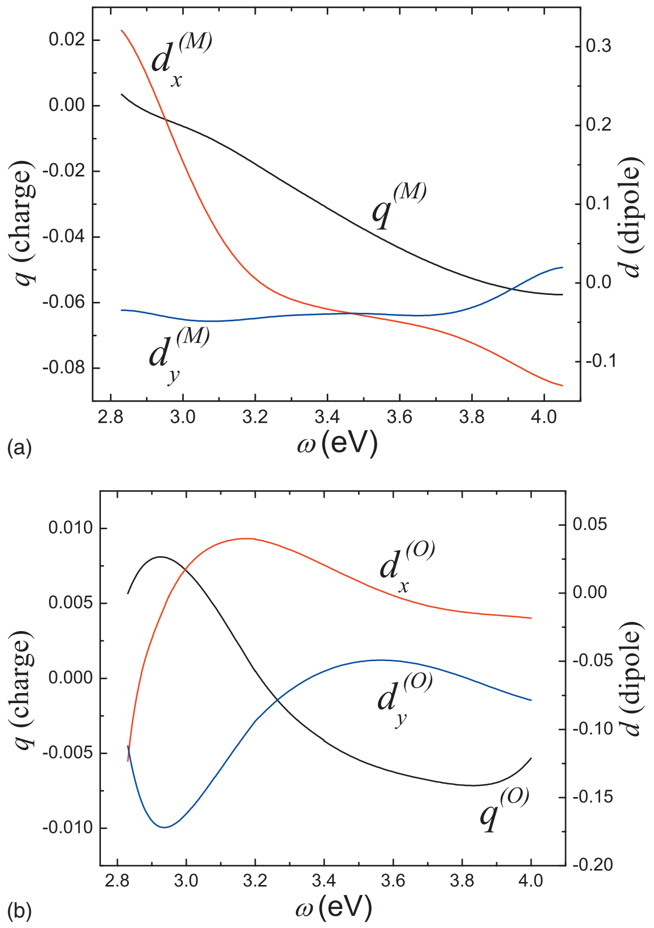

FIG. 4. Real coefficients $q^{(V)}$, $d_x^{(V)}$ and $d_y^{(V)}$ that parameterize the dipole ES parameters of the meta ($V=M$) and ortho ($V=O$) joints.

We observe that the transition dipoles of the double joints are directed along the x and y axes for symmetric and antisymmetric modes, respectively. This indicates that the dipole tensors $d_{V\alpha}$ associated with two segments ($\alpha=1,2$) attached to the double joint are equal, with x and y being their principal axes. Real-valued dipole parameters of symmetric double joints can be defined with respect to linear combinations of the exciton wave functions or dual wave functions with the proper symmetry. In particular, we define $d_x^{(O)}(\omega)$ as a real parameter that relates the sum of projections $(\boldsymbol{\psi}_1,\boldsymbol{n}_1)+(\boldsymbol{\psi}_2,\boldsymbol{n}_2)$ onto the corresponding segments to the x component of the dipole of the orthojoint. Next, $d_x^{(M)}(\omega)$ relates the difference of the dual wave functions $\tilde{\psi}_1-\tilde{\psi}_2$ to the x component of the dipole of the metajoint. The parameters $d_x^{(O)}(\omega)$ and $d_x^{(M)}(\omega)$ are defined differently to avoid numerical errors that would appear because of the weakness of transmission through the metajoint. Finally, we define $d_y^{(V)}(\omega)$ (where $V=M$ or $V=O$) in the same way for both joints as a real parameter that relates the sum of the dual wave functions $\tilde{\psi}_1+\tilde{\psi}_2$ to the y component of the dipole. Thus, for light excitons, the dipole contribution of each symmetric double joint is determined by two real parameters, which are shown in Fig. 4. The complex parameters used in Eq. (10) are expressed through the real parameters as

$$d_{M\alpha,x}=d_x^{(M)}(i+e^{i(\phi_M-\theta_M)})/(\boldsymbol{n}_\alpha,\boldsymbol{n}_x), \tag{16}$$

$$d_{O\alpha,x}=d_x^{(O)}(1+ie^{i(\phi_O-\theta_O)})/(\boldsymbol{n}_\alpha,\boldsymbol{n}_x), \tag{17}$$

$$d_{V\alpha,y}=d_y^{(V)}(i-e^{i(\phi_V+\theta_V)})/(\boldsymbol{n}_\alpha,\boldsymbol{n}_y), \tag{18}$$

where the last equation represents equations for both the meta ($V=M$) and ortho ($M=O$) joints, and $\boldsymbol{n}_\alpha$, $\boldsymbol{n}_x$, and $\boldsymbol{n}_y$ are the unit vectors in directions of attached linear segments α and along x and y axes.

Geometry distortions due to steric interactions appear in planar orthoconjugated molecules. First, for the optimized planar geometry, the angle between the segments attached to the orthojoint is about 65° (different from $\pi/3$). This angle, measured between triple bonds adjacent to the orthojoint, appears to be the property of the joint independent of the overall molecular structure, as we observe almost the same value in several types of molecules with different lengths of linear segments. The external contribution to the dipole parameter of the orthojoint depends on this angle. However, the dipoles of the vertices are usually much smaller than the total dipole of the molecule (our approach is asymptotically exact for long linear segments with many repeat units, whose dipoles are comparable to or larger than dipoles of vertices). More important is the orientation and position of repeat units over the full length of the linear segments. The segments tend to be straight if their ends are not constrained, such as in two-segment orthomolecules or in zigzag molecules considered below. In fact, the direction of the triple bonds changes by less than a half degree between the orthojoint and the end of the long segment attached to the joint, with the most change happening within 2–3 repeat units from the joint. Thus, in the arms with free ends, the angle between symmetric triple bonds starts at 65° for repeat units adjacent to the orthojoint and saturates at 65.73°–65.75°. The situation is different if the arms are constrained as in molecules with loops including triangles and parallelograms. In the equilateral triangle, for example, the segments are bent outwards, and this distortion is not localized near the orthojoints.

IV. ACCURACY OF THE ES MODEL FOR TRANSITION DIPOLE MOMENTS

We recently demonstrated[2,3] how the ES model can be applied to compute excitation energies in branched conjugated molecules. In this section, we use the same types of molecules to test how well the dipole extension of the ES approach works that allows us to predict absorption spectra. Before the transition dipoles are calculated, the excitation energies and exciton wave functions are found by applying the energetic ES approach with the previously extracted dispersion relation and scattering matrices.

First, in order to check the quality of the ES dipole and charge parameters for molecular ends and repeat units, we compare ES estimates calculated from Eq. (10) and quantum-chemical results in linear molecules. The ES approach delivers good accuracy of such calculations as shown in Fig. 5. Although the ES approach is asymptotically exact for long molecules,[1] and the dipole parameters are extracted from the molecules longer than 10 repeat units, for short molecules the relative error of the calculation is acceptable

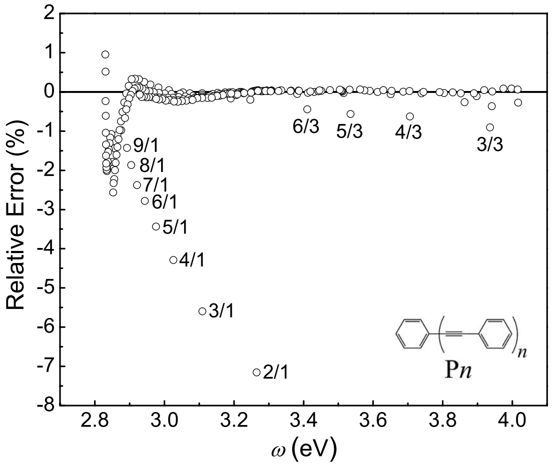

FIG. 5. Relative deviations of the transition dipoles in linear molecules (shown in the inset) calculated using the ES approach compared to CEO computations. The mth mode in the molecule Pn is denoted by n/m.

(<10%). For molecules whose length is larger than the exciton size (>3 repeat units), the relative error is less than 5%.

Next, we verify the accuracy of the transition charge and dipole parameters that describe the metaconjugated and orthoconjugated joints by comparing the transition dipoles calculated within the ES approach and by the quantum-chemical computations in V-shape molecules. For selected molecules, the relative error of the transition dipole shown in Fig. 6 is calculated by comparing the ES result with that of the brightest state from the quantum chemistry data.

In the ES calculation of transition dipoles in molecules with orthojoints, taking into account actual geometry turns out to be important. Although the linear segments connected by the orthojoint can be considered straight, the angle between them is 65.75°. We use this geometry in all molecules with unconstrained orthojoints.

The scattering phases for the meta and orthojoints are close to the values that correspond to total reflection and ideal transmission, respectively.[2] Consequently, the exciton is more confined within the linear segments in a metaconjugated molecule than in an orthoconjugated molecule. Since stronger reflection at vertices typically leads to larger deviations of excitations from the plane-wave forms, the errors of the ES approach can be expected to be larger in short metaconjugated molecules than in orthoconjugated molecules of the same length. For example, we observe that the error of the brightest state (the second mode) for $2M3$ is larger than for $2O3$ (see Fig. 6).

At this point, we can apply the ES approach to the spectroscopic calculation in complex molecules that include the four types of building blocks shown in Fig. 1. As the next example we consider three-segment zigzag molecules including meta and/or orthojoints. The notation $l_1V_1l_2V_2l_3$ for the zigzag molecules shows the order in which the vertices V_1 and V_2 connect linear segments with l_1, l_2, and l_3 repeat units. Three-segment zigzag molecules have two stereoisomers, *cis* and *trans*. Within the ES approach, the excitation energies are determined by how the building blocks are locally connected to each other, which is identical in both isomers. As a result, the ES excitation energies of the two isomers are equal. Figure 7 shows the transition energies and dipoles of isomers of $5O7O3$. Although the excitation distribution in the linear segments of isomers is the same, they have different transition dipoles because of different mutual orientation of the segments. For the molecule *trans*-$5O7O3$, the strongest optical transition is the third excited state, while it is the second excited state in *cis*-$5O7O3$. Compared with

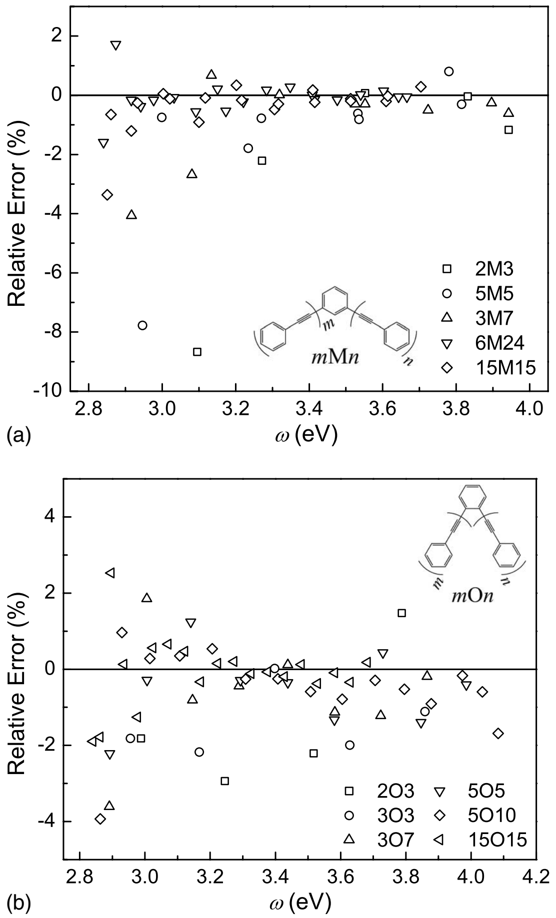

FIG. 6. Deviations between the ES and CEO transition dipoles relative to the transition dipoles of the brightest states in metaconjugated and orthoconjugated molecules (shown in the insets).

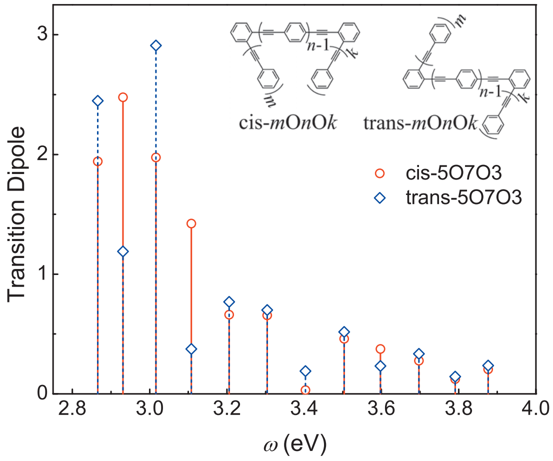

FIG. 7. The transition dipoles of zigzag isomers (shown in the inset) computed by the ES approach. The excitation energies are identical for isomers.

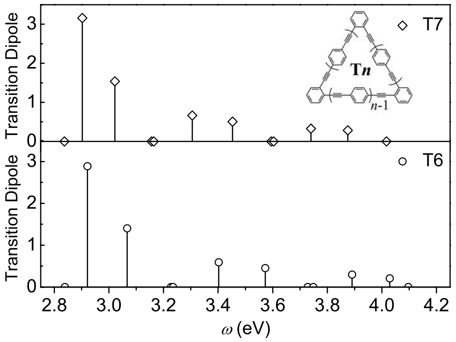

FIG. 8. The transition dipoles of triangle molecules *T*6 and *T*7 (shown in the inset) computed by the ES approach.

the quantum chemistry results, the deviation of the transition dipole calculated by ES approach is less than 6%.

For equilateral triangle molecules, we obtain similar accuracy as for zigzag molecules. Figure 8 shows transition dipoles of the two triangle molecules *T*6 and *T*7 (*Tn* denotes the triangle molecule with the side of n repeat units) computed by using the ES approach. In the actual optimized geometry the segments of the triangle molecules are slightly bent outwards because the angle between them at the ortho-joints is about 65°. The accuracy of the transition dipole calculation is not improved if orientations and positions of repeat units are modified according to the actual geometry. Due to the symmetry, all modes in the triangle molecules can be characterized by their angular momenta $m=0, \pm 1$.[3] For $m=0$ states, the transition dipoles of the three sides are equal because of the rotation symmetry. As a result, in the spectrum of a triangle molecule, all such states are dark (shown with zero dipoles in Fig. 8), and only the doubly degenerate modes with $m=\pm 1$ are visible. The results for triangle molecules illustrate that the ES approach works well for the electronic excitations with energy degeneracy.

V. CONCLUSION

In this manuscript we have generalized the formalism of the ES approach[1–3,15,16] for electronic excitations in branched conjugated molecules and extended it to calculation of oscillator strengths. Together with the original ES approach that we recently developed, this extension allows one to calculate efficiently optical spectra in large conjugated molecules using previously tabulated ES parameters obtained from quantum-chemical calculations of basic molecular building blocks. The ES approach can be applied to conjugated molecules where electronic excitations are tightly bound spatially localized excitons. In the ES model, they are viewed as quasiparticles on the graph that represents the molecule (the molecular vertices and linear segments are represented by the vertices and edges of the graph). Within the ES approach we assume that the properties of the molecular building blocks (repeat units and molecular vertices) depend only on the energy. The excited state energies and distributions of the excitation amplitude are found within the ES approach by solving a generalized "particle in a box" problem on the graph with the given exciton dispersion relation and scattering matrices. In addition, we introduce the transition charge and dipole parameters of the ES approach that characterize how contributions of building blocks to the total transition dipole depend on the local excitation amplitudes.

The ES parameters of the building blocks can be extracted from the results of quantum-chemical computations in relatively small molecular fragments. The ES approach is designed to predict the results of the quantum chemistry that is coupled to the ES model. In this regard, the ES approach complements the established quantum-chemical methods, extending their capability while avoiding the difficulties characteristic of their use in large molecules with complex excitations.

We have shown that the transition dipole extension of the ES approach allows calculation of oscillator strengths with sufficient accuracy. Qualitative features of optical spectra of branched conjugated molecules can also be understood with the help of the ES approach. In particular, the effects of symmetry on the spectra can be easily explained within the ES approach. One can also rationalize how small modifications of the molecular geometry, which do not change excitation energies, affect the intensities of spectral peaks.

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