Exciton scattering approach for branched conjugated molecules and complexes. I. Formalism

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We develop a formalism for the exciton scattering (ES) approach to calculation of the excited state electronic structure of branched conjugated polymers with insignificant numerical expense. The ES approach attributes electronic excitations in quasi-one-dimensional molecules to standing waves formed by the scattering of quantum quasiparticles. We derive the phenomenology from the microscopic description in terms of many-electron excitations. The presented model can be used to compute both excited state frequencies and transition dipoles in large molecules after the ES ingredients are extracted from smaller molecular fragments. © *2008 American Institute of Physics.* [DOI: 10.1063/1.3005647]

I. INTRODUCTION

Conjugated organic molecules and molecular wires constitute a class of systems with complex electronic structure that are promising materials for a number of technological applications.[1–5] The complexity of the electronic structure originates from the delocalized nature of π-electron states, strong Coulomb electron-electron interactions, and low-dimensional (quasi-one-dimensional) geometry.[6–9] The latter effectively enhances the effects of electron-electron correlations. Electronic excitations in such systems can be thought of as bound electron-hole pairs (excitons).[8–16] However, as opposed to the case of conventional semiconductors, the electron-hole pair picture of optical excitations is only qualitative due to strong electron correlations. In particular, the exciton binding energy is comparable to the optical gap.[12,17–21] This implies that the excited states are, strictly speaking, superpositions of excitations that contain different numbers of electron-hole pairs.[22,23] This calls for computational methods that account for electron exchange and correlations,[24,25] such as the time-dependent density functional theory (TDDFT).[26–28]

However, explicit computations of electronic excitations in large conjugated macromolecules and molecular structures are numerically expensive [the effort scales as $\mathcal{O}(N^2)$ $-\mathcal{O}(N^4)$ with the number of orbitals N] and rarely feasible even if efficient TDDFT approaches are implemented.[28,29] On the other hand, the structure of the aforementioned molecules involves linear segments of oligomers connected to each other at branching centers,[5,30–36] which allows one to develop phenomenological theory.[37,38]

Excited states in conjugated molecules are complex many-particle excitations. Nevertheless, their quasimomentum k is well defined in an infinite one-dimensional chain (polymer) due to discrete translational symmetry. The excitations in infinite polymer chains can be characterized by their spectrum $\omega(k)$ which describes the dependence of the excitation frequency ω on its momentum k.[19,39] We will concentrate on the electron-hole nature of the excited states[8,9,11] because following the transitions of single electrons turns out to be sufficient for building a phenomenological model. A low-energy excitation in a semiconducting polymer is characterized by its size l_e which has the meaning of a typical distance between the electron and the hole.[8,16,24,25] Thus, the excited states can be viewed as bound excitons, which justifies that below we will simply refer to them as excitons. Stated differently, using the ideas of condensed matter physics, excitations in polymer chains can be considered as quasiparticles regardless of how complex their internal electronic structure could possibly be.

We consider an excited state in a finite-size linear oligomer, whose length is large compared to the exciton size, $l \gg l_e$, which naturally resembles the problem of a quantum particle in a box. The length scale separation can be taken into account to substantially simplify the calculations and their interpretations in the branched conjugated molecules. The wave function for the common motion of the quasiparticle components is represented by a standing wave[37,38,40,41] that results from interference of the plane waves moving in opposite directions and being scattered at the ends of the linear segment. This results in a discrete spectrum of electronic excitations determined by the quasiparticle spectrum $\omega(k)$ and the boundary scattering conditions. The latter are described by the energy-dependent exciton scattering (ES) amplitudes.

We are now in a position to describe the main idea of the ES approach developed in this paper. Consider a large branched macromolecule or molecular structure of size L that consists of linear polymer segments of typical size l, so that $l_e \lesssim l \lesssim L$, connected to each other via branching centers. An excited state can be viewed as a quasiparticle (exciton) that moves along the linear segments as a plane wave and

gets scattered at the molecular ends and branching points, resulting in a standing wave.[37] Within the ES picture, computation of the transition energies and dipole moments that correspond to excited electronic states is reduced to finding the standing waves formed by a respective quantum particle. This is an extremely simple task even for huge macromolecules[17,42–44] once the exciton spectrum and scattering matrices are known. The latter should be retrieved beforehand from quantum-chemical calculations. Thus, the computation of the excited state electronic structure in large molecules can be divided into two steps: (i) retrieving the quasiparticle properties and (ii) applying the ES theory to large molecules of interest. Step (i) can be accomplished by performing calculations in relatively simple molecular fragments, so that the numerical effort has nothing to do with the supramolecular size L.[38] The numerical effort involved in step (ii) depends on the number of linear segments rather than on the number of single-electron orbitals, and therefore, computations in large structures and macromolecules can be easily performed.

The ES approach to the excited state electronic structure in branched conjugated systems has been briefly described in our earlier papers.[37,38] This manuscript is the first in the series of three papers, devoted to a detailed description of the ES model. It is focused on the development of the ES formalism and is organized as follows. In Sec. II we introduce the ES picture for excited state electronic structure and the ingredients of the ES model and describe how it can be used to compute the relevant information on the excited states. In Sec. III we show how the ES model can be derived in terms of fully microscopic theory. Some details of the alternative microscopic picture within the many-body Green function formalism are presented in the Appendix.

II. EXCITON SCATTERING PICTURE

We start with formulating the ES model for a branched conjugated molecule. A branched conjugated molecule consists of linear segments connected via branching units. Each linear segment contains a certain number of identical repeat units. The branching units can be represented by benzene rings (for example, in phenylacetylene dendrimers), nonphenyl based branching centers (e.g., nitrogen or phosphorus), as well as more complicated objects (e.g., paracyclophen bridges). A branched molecule can be naturally associated with a nonoriented graph $\mathcal{M}$, whose vertices $a \in \mathcal{M}_0$ represent the branching units, whereas the edges $\alpha \in \mathcal{M}_1$ correspond to linear segments.[45–47] We will use the notation $a \in \alpha$ that means the edge α contains the vertex a or, using the molecular language, the linear segment α is connected to the branching unit a. The length l_α of the edge α is the number of repeat units in the corresponding linear segment. We also denote by n_a the number of linear segments connected to the branching unit a, which is also referred to as the degree of the corresponding vertex. Note that a vertex with $n_a = 1$ represents a molecular terminal, and a vertex with $n_a = 2$ is a joint connecting two linear segments. The branching proper occurs if $n_a \geq 3$. A simple oligomer that consists of l repeat units and two end groups is represented by a

graph with two vertices a and b, with $n_a = n_b = 1$, connected by a single edge $\alpha \ni a, b$ of the length $l_\alpha = l$. The repeat unit positions in a linear segment α will be denoted by integers x_α with $x_\alpha = 1, \ldots, l$. We will also denote by $\mathbf{r}_a$ and $\mathbf{r}_{x_\alpha}^{(\alpha)}$ the real-space positions of the branching centers and repeat units, respectively. We naturally assume that their sizes are small compared to the optical wavelength.

The ES model treats electronic excited states (also referred to as excitons) in a branched molecule as quantum quasiparticles on the corresponding graph $\mathcal{M}$. Excitons move freely along the linear segments, while they get scattered at the vertices, including the segment ends (terminals). In this section we formulate the ES model, also providing some physical motivation. The derivation of the ES approach, as well as attributing the ES model ingredients to microscopic many-body quantities will be presented in Sec. III.

Presently it is widely accepted that excited states in conjugated systems can be attributed to excitons that represent bound states of the relative electron-hole motion.[11–16] The ES model focuses on describing the collective electron-hole motion along the branched molecule. Compared to an infinite linear chain, the relative motion of an electron and a hole in a real molecule is weakly perturbed provided the exciton is not too close to the segment ends, joints, and branching centers. This is conceptually similar to how elementary particles are interpreted in the quantum field theory, where an elementary particle in a translationally invariant system is treated as an excited state with a given momentum value. Note that elementary particles can be (and usually are) some complex excitations in a quantum system with a macroscopically large number of degrees of freedom; in particular, sometimes they can be represented as many-particle (dressed) excitations in some systems of strongly interacting reference particles (e.g., electrons coupled to either photons or phonons). Adopting this language, excitons can be considered as complex many-particle dressed excitations in a strongly correlated many-electron system that are only qualitatively interpreted as states that involve an electron and a hole. The ES approach, on the other hand, treats excitons as elementary particles without paying much attention to their complex structure in terms of the correlated electrons.

We describe an excited state (exciton) of energy ω, measured with respect to the ground state and hence identified with the transition frequency, by its wave function given as a set of expressions on all linear segments $\alpha \in \mathcal{M}_1$. On the edge $\alpha \ni a, b$ which connects vertices a and b, the wave function is represented by a linear superposition of wave functions (see Fig. 1):

$$\psi_\alpha(x_\alpha) = \psi_{\alpha,ab}(x_\alpha) + \psi_{\alpha,ba}(x_\alpha),$$

$$\psi_{\alpha,ab}(x) = a_{\alpha,ab} \exp(ik_{\alpha,ab}x), \qquad (1)$$

$$\psi_{\alpha,ba}(x) = a_{\alpha,ba} \exp(ik_{\alpha,ba}x),$$

where $\psi_{\alpha,ab}$ and $\psi_{\alpha,ba}$ describe two plane waves propagating along the linear segment α from a to b and from b to a, respectively. Their quasimomenta (wavevectors) $k_{\alpha,ab}$ and
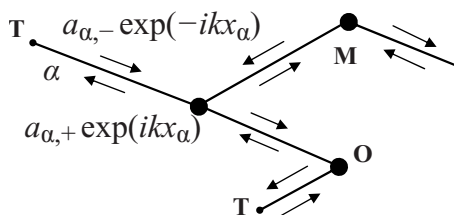
FIG. 1. In the ES model, the molecule is represented by a graph. Excited states are viewed as quasiparticles scattered at the vertices. Scattering centers of order n are characterized by $n \times n$ scattering matrices. Shown are molecular termini (T) ($n=1$), double meta- and orthojoints ($n=2$), and a triple branching center ($n=3$).

$k_{\alpha,ba}$ are related to the frequency ω through the exciton spectrum $\omega(k)$:

$$\omega(k_{\alpha,ab}) = \omega(k_{\alpha,ba}) = \omega. \tag{2}$$

Time reversal invariance in the absence of a magnetic field results in the symmetric spectrum $\omega(-k) = \omega(k)$, which yields the same absolute values of the quasimomenta: $k_{\alpha,ab} = -k_{\alpha,ba}$. We denote the values of the outgoing and incoming plane waves at the vertex a by $\psi_{\alpha a}^{(+)}$ and $\psi_{\alpha a}^{(-)}$, respectively. These can be defined by continuing the asymptotic forms of the plane waves to the scattering center, as shown in Sec. III. Combining the definitions of $\psi_{\alpha a}^{(+)}$ and $\psi_{\alpha a}^{(-)}$ with expressions of the exciton wave functions in Eq. (1), we arrive at the following relation:

$$\psi_{\alpha b}^{(-)} = \psi_{\alpha a}^{(+)} \exp[ik_{\alpha,ab}(\omega)l_\alpha], \tag{3}$$

which does not depend on how the repeat units are numbered on the linear segment $\alpha \ni a, b$. There are two such relations on each segment.

Within the ES model the vertices are described on the level of scattering of incoming plane waves. In a vertex that connects n linear segments, an incoming wave in one of the segments generates n outgoing waves, i.e., $n-1$ transmitted and one backscattered. The amplitudes of the outgoing plane waves are related to the incoming wave amplitudes by means of a frequency-dependent $n \times n$ scattering matrix $\Gamma_{a\alpha\beta}(\omega)$. The off-diagonal and diagonal elements of Γ describe transmission and reflection processes, respectively. Using our notation this can be represented by the following relation:

$$\psi_{\alpha a}^{(+)} = \sum_{\beta \ni a} \Gamma_{a,\alpha\beta}(\omega) \psi_{\beta a}^{(-)}. \tag{4}$$

A vertex connecting n branches is described by n linear equations, which expresses the fact that the amplitude of the outgoing wave is a result of the scattering of all incoming plane waves with the amplitudes weighted by the corresponding elements of the scattering matrix.

The relations on the segments [Eq. (3)] together with the vertex relations [Eq. (4)] will hereafter be referred to as ES equations. The ES equations constitute a frequency-dependent homogeneous system of linear equations for the amplitudes $\psi_{\alpha a}^{(\pm)}$ with the number of equations matching the number of variables.[37,38] In fact, attaching a new segment to the existing vertex adds four new variables and four new equations: two relations in the form of Eq. (3) describe the propagation of the waves along the additional segment,

whereas the other two relations in the form of Eq. (4) express the outgoing waves at the ends of the segment. The values of frequency ω for which the system has a nonzero solution describes the transition frequencies between the ground and excited states, whereas the amplitudes $\psi_{\alpha a}^{(\pm)}$ combined with Eq. (1) and definition of the amplitudes provide the exciton wave function that correspond to the excited state. Given the exciton dispersion $\omega(k)$ and the scattering matrices $\Gamma_{a,\alpha\beta}(\omega)$ as an input, we can obtain the energies of the electronic excited states by solving the system of ES equations given by Eqs. (3) and (4).

Next, we demonstrate how the transition dipoles, which determine the intensities of optical transitions, can be described in the framework of the ES approach. Again, we employ the fact that the molecule consists of only a few types of building blocks, namely, the repeat units (monomers) and specific vertices. The building blocks of the same type are assumed to be geometrically indistinguishable throughout the branched molecule. This allows us to introduce quantitative characteristics of the transition charge distribution that are equivalent for the geometrically equivalent building blocks. These quantities whose microscopic definitions in terms of the charge and dipole moment operators, respectively, are presented in Sec. III include $q(\omega)$ and $\boldsymbol{d}^{(\alpha)}(\omega)$ which describe the repeat units, as well as $q_{a\alpha}(\omega)$ and $\boldsymbol{d}_{a\alpha}(\omega)$ which describe the branching centers. Apart from their trivial orientation dependence, $\boldsymbol{d}^{(\alpha)}(\omega)$ and $\boldsymbol{d}_{a\alpha}(\omega)$ depend only on the energy. They relate charges and dipole moments induced at repeat units and branching centers to the local values of the exciton wave function. Then the transition dipole μ for an excited state described within the ES model by an exciton wave function $\psi_\alpha(x_\alpha)$ with $\alpha \in \mathcal{M}_1$ is given by

$$\mu = \sum_{\alpha \in \mathcal{M}_1} \sum_{x_\alpha=1}^{l_\alpha} (q(\omega) \boldsymbol{r}_{x_\alpha}^{(\alpha)} \widetilde{\psi}_\alpha(x_\alpha) + \boldsymbol{d}^{(\alpha)}(\omega) \psi_\alpha(x_\alpha))$$
$$+ \sum_{a \in \mathcal{M}_0} \sum_{\alpha \ni a} (q_{a\alpha}(\omega) \boldsymbol{r}_a + \boldsymbol{d}_{a\alpha}(\omega)) \psi_{\alpha a}^{(-)}, \tag{5}$$

where $\widetilde{\psi}_\alpha$ is linearly related to the exciton wave function ψ_α according to Eq. (21). The functions $q(\omega)$, $\boldsymbol{d}^{(\alpha)}(\omega)$, $q_{a\alpha}(\omega)$, and $\boldsymbol{d}_{a\alpha}(\omega)$ can be retrieved from the transition dipoles obtained by quantum-chemical calculations in simple molecules of different lengths with different types of branching centers.

The ES equations [Eqs. (3) and (4)] together with Eq. (5) constitute a full set of equations/expressions to determine the optical properties of electronic transitions in a branched conjugated molecule.[37,38]

III. MICROSCOPIC VIEW OF EXCITON SCATTERING

In Sec. II we have formulated the ES picture of electronic excitations in branched organic molecules and presented a method of calculating their relevant optical properties in terms of the parameters of the elementary building blocks such as quasiparticle spectra and scattering matrices. Here we derive the ES model by expressing the relevant properties of its building blocks in terms of the transition density matrices which provide a reduced microscopic de-

scription of many-electron excited states. The ES model constitutes an asymptotically exact picture for optical excitations in the limit when the exciton size l_e is small compared to a typical linear segment length.

An excited many-electron state with the wave function $|\Psi^{(\nu)}\rangle$ can be described by the transition density matrix $\rho^{(\nu)}$ with its elements defined as[16,24,25]

$$\rho_{mm'}^{(\nu)} = \langle \Psi^{(\nu)}|c_m^\dagger c_{m'}|\Psi^{(0)}\rangle. \tag{6}$$

Here $|\Psi^{(0)}\rangle$ is the ground state wave function of the system, and $c_m^\dagger$ (c_m) are electron creation (annihilation) operators on the mth atomic orbital.

We start with considering an infinite linear chain (a polymer). Due to its translational symmetry, the quasimomentum k is a well-defined quantum number, and all excited states can be labeled as $\Psi_\gamma(k)$ by their quasimomenta k and some additional set of quantum numbers, referred to as γ. The numbers γ describe relative electron-hole motion. In an infinite chain, the excited state $\Psi_\gamma(k)$ has the energy $\omega_\gamma(k)$ with respect to the ground state. The corresponding many-electron wave function $\Psi_\gamma(k,\{r_i\})$ is the eigenfunction of lattice translations:

$$\Psi_\gamma(k,\{r_i + la\}) = e^{ikl}\Psi_\gamma(k,\{r_i\}), \tag{7}$$

where r_i denote the electron coordinates, l is an integer, and a is the repeat unit length. This implies that the quasimomentum k is defined as a dimensionless quantity.

The excitonic (bound electron-hole) nature of optical excitations, being expressed in terms of the many-electron system, means that for a given value of k, the lower part of the excitation spectrum $\omega_\gamma(k)$ is discrete. Stated differently, the quantum number γ is discrete and labels exciton bands in the optical region. For a given value of γ, we can interpret $\omega_\gamma(k)$ as the dispersion of the quasiparticle (exciton) γ. Since the symmetries of different excitons are generally different, the corresponding bands may overlap. A real-space examination of the appropriate transition densities allows one to distinguish a specific excitonic band in the molecular spectra.[16,24,25,48] Thus, we can omit the discrete index γ and consider $\omega(k)$ as the spectrum of all possible excitons that belong to the specific band γ. Any many-electron state with a certain quasimomentum in an infinite polymer is an eigenstate of the many-body Hamiltonian. Therefore, quasimomenta k that label different states can assume any value in the interval of length 2π; for a symmetric Brillouin zone it is natural to choose $-\pi < k \le \pi$.

Using a reduced description in terms of the transition density matrix allows us to visualize the symmetry of the many-particle wave function. Due to the equivalence of the repeat units, it is convenient to switch to new notations with the atomic orbitals labeled within the repeat units. In these notations the transition density matrices $\rho_{mm'}^{(\nu)}(x,x')$ between the ground state and the excited state are defined via the creation (annihilation) operators $c_{x,m}^\dagger$ ($c_{x,m}$) on the mth orbital of the xth repeat unit. For instance, for an excited state with the quasimomentum k we have

$$\rho_{mm'}^{(k)}(x,x') = \langle \Psi(k)|c_{x,m}^\dagger c_{x',m'}|\Psi^{(0)}\rangle. \tag{8}$$

In an infinite polymer $-\infty < x, x' < +\infty$, and the ground state wave function $\Psi^{(0)}$ is obviously invariant with respect to the translations by an integer number of repeat units, i.e., its quasimomentum is zero. We employ the definition of the quasimomentum in Eq. (7) to obtain how the transition density matrix is transformed as a result of a shift by l repeat units:

$$\rho_{mm'}^{(k)}(x+l,x'+l) = e^{ikl}\rho_{mm'}^{(k)}(x,x'). \tag{9}$$

This symmetry with respect to the discrete translations enables us to introduce Bloch functions $\xi_{mm'}^{(k)}(l)$ (see Ref. 40):

$$\rho_{mm'}^{(k)}(x,x') = e^{ikx}\xi_{mm'}^{(k)}(x-x'). \tag{10}$$

Identity (10) reflects the separation of the collective electron-hole motion from the internal exciton degrees of freedom. In addition, we note that there is an antilinear correspondence between the transition density matrices and the excited state wave functions, i.e., if $\rho^{(k_i)}$, $i=1,2$, corresponds to $\Psi(k_i)$, for any numbers a_1 and a_2 we have

$$a_1\Psi(k_1) + a_2\Psi(k_2) \leftrightarrow a_1^*\rho^{(k_1)} + a_2^*\rho^{(k_2)}. \tag{11}$$

These features show that the transition density matrix can be naturally interpreted as a wave function, which is factorized into the parts corresponding to the center of mass and relative motions of the electron-hole pair in an infinite polymer. The center-of-mass component is naturally described by an exciton wave function,

$$\psi(k,x) = e^{ikx}. \tag{12}$$

The relative motion component is described by a matrix which depends on the specific solution of the related many-body problem.

Discrete translational symmetry of the ideal infinite polymer is violated in real molecular systems. Molecular ends and branching points give rise to the ES, which is the scope of our interest. Besides, the finite size of the molecules to a large extent determines their observable optical properties. Other symmetry-breaking factors, such as interaction with the environment or imperfection of the molecular geometry, which result in the reduction in the conjugation length, should be a subject of future studies.

We proceed to a microscopic description of the excited states in the linear segments of finite lengths. A segment end can be either a terminus of the molecule or a vertex of degree 2 and higher which connects the segment with other linear segments. Note that a molecular terminal can be represented by a "natural" free end or by a donor/acceptor substitution. We assume that the exciton dispersion $\omega(k)$ of a linear segment is determined by the repeat unit structure only and is unaffected by the presence of the vertices that violate the translational symmetry. This property is a consequence of the exciton size being small compared to the linear segment length. The dispersion $\omega(k)$ is given by an even function due to the time reversal symmetry.

A general form of an excited state with the energy ω is a linear combination of the excitons with different quasimo-

menta k that satisfy the equations $\omega_\gamma(k) = \omega$. In the simplest case when a single exciton band is involved at the energy ω, the corresponding quasimomenta on the segment α between vertices a and b have opposite signs: $k_{\alpha,ba} = -k_{\alpha,ab}$.

Molecular ends and joints can mix excitations with different quasimomenta which exist on the segments at a given energy. The amplitudes in these superpositions of states become linearly dependent, which is formalized by introducing the scattering matrices. Far from the scattering centers, namely, at distances exceeding the exciton size, the excited state has an asymptotic form of a linear combination of the Bloch plane waves allowed at the energy ω:

$$\Psi_\omega = a^*_{\alpha,ab} \Psi(k_{\alpha,ab}) + a^*_{\alpha,ba} \Psi(k_{\alpha,ba}), \tag{13}$$

with the complex conjugated coefficients. Due to relation (11), this form corresponds to the exciton wave function given by the linear superposition of the plane waves in Eq. (1).

We use the conventional formulation of the scattering in terms of the wavepacket dynamics (see, for example, Ref. 49). This separates in time the components of the stationary excitons that have certain quasimomenta. A linear relation between them is equivalent to the relation between the corresponding incoming and outgoing wavepackets. Since excited states in the infinite polymer are characterized by well-defined quasimomenta, a wavepacket far from scattering centers can be decomposed into the plane waves. A scattering matrix establishes a linear relation between the incoming and outgoing waves. Specifically, we formally continue the asymptotic plane waves to the scattering point and relate thus determined values of the incoming and outgoing components of the exciton wave functions. Since a scattering center is located between two repeat units labeled by integer numbers, its position on a given segment can be specified by the corresponding half-integer coordinate. While being one of possible choices, this definition has the advantage that the ideal transmission between two neighboring repeat units (e.g., the transmission between neighboring repeat units that are not separated by a scattering center) is described by the energy-independent unit transmission amplitude. We illustrate this definition by considering an excited state which has the form given by Eq. (13) on a linear segment α of length l_α far from its ends. The asymptotic form of the exciton wave function is specified by Eq. (1). If the repeat units are labeled from a to b by $x_\alpha = 1, \ldots, l_\alpha$ and $k_{ab} = -k_{ba} > 0$, the values $\psi^{(-)}$ and $\psi^{(+)}$ of the incoming and outgoing wave functions, respectively, are defined at the scattering centers a and b as

$$\psi^{(-)}_{\alpha,a} = \psi_{\alpha,ba}(1/2), \quad \psi^{(-)}_{\alpha,b} = \psi_{\alpha,ab}(l_\alpha + 1/2),$$

$$\psi^{(+)}_{\alpha,a} = \psi_{\alpha,ab}(1/2), \quad \psi^{(+)}_{\alpha,b} = \psi_{\alpha,ba}(l_\alpha + 1/2). \tag{14}$$

We note that, since the scattering matrices connect the plane wave asymptotics only, the stationary exciton wave function is generally discontinuous at the scattering centers.

In the ES picture, each scattering center (vertex) is described by a frequency-dependent scattering matrix $\Gamma_{a,\alpha\beta}(\omega)$, according to Eq. (4). If several exciton types are present at the same energy, the objects $\psi^{(\pm)}_{\alpha,a}$ and $\psi^{(\pm)}_{\alpha,b}$ are vectors, and the scattering matrices acquire two additional indices. On

this level of description, there is no essential difference between such multiexciton scattering and the processes that involve only one exciton type.

General properties of the scattering matrices in the ES picture can be easily obtained from the definition of the exciton wave function in terms of many-particle excitations. Quantum-mechanical scattering unitarity on the level of many-body states implies the unitarity of the ES matrix formulated in terms of the reduced exciton wave functions ψ due to relation (11). Besides, the scattering matrices possess the symmetry of the scattering center. For example, in many cases the joint connecting two linear segments is mirror symmetric, which leads to the equality of reflection amplitudes in both directions.

Although we have already introduced the reduced exciton wave functions ψ microscopically, it would be insightful and convenient for future applications to derive an explicit relation between the exciton wave function and the corresponding transition density matrix. For the sake of simplicity we consider the case of the repeat unit being symmetric with respect to the mirror reflection (or inversion) transformation I. The symmetry transformation, applied to a repeat unit, transforms the mth orbital to the orbital denoted by $I(m)$. Starting with a normalized many-electron states $\Psi(k)$ and $\Psi(-k)$, we obtain

$$\xi^{(-k)}_{mm'}(x - x') = -\xi^{(k)}_{I(m)I(m')}(x' - x), \tag{15}$$

where we introduced the minus sign in the right-hand side by choosing the proper phase of the wave function corresponding to $\Psi(-k)$.

Note that Eq. (15) ensures that certain linear combinations of the transition density matrix elements behave as the corresponding exciton wave function. For simplicity, we consider the matrix elements between the atomic orbitals within the same repeat unit. By applying Eqs. (10) and (15) to the excited state Ψ_ω with the energy $\omega = \omega(k)$ described by the exciton wave function

$$\psi(x) = a_k \exp(ikx) + a_{-k} \exp(-ikx), \tag{16}$$

we obtain the following relation for the elements of the corresponding transition density matrix ρ:

$$\rho_{mm'}(x,x) - \rho_{I(m)I(m')}(x,x)$$
$$= (a_k e^{ikx} + a_{-k} e^{-ikx})(\xi^{(k)}_{mm'}(0) - \xi^{(k)}_{I(m)I(m')}(0))$$
$$= (\xi^{(k)}_{mm'}(0) - \xi^{(k)}_{I(m)I(m')}(0))\psi(x), \tag{17}$$

which provides a direct way to extract the exciton wave function from the transition density matrix.

We conclude this section by outlining a microscopic interpretation of the ES theory parameters $q(\omega)$ and $\boldsymbol{d}(\omega)$ which describe the transition dipole properties of the repeat unit. To that end we introduce the operators $\hat{q}(x)$ and $\hat{\boldsymbol{d}}(x)$ of the charge and the dipole moment, respectively, of the repeat unit x. They can be expressed in terms of the electron density operator $\hat{\rho}(\boldsymbol{r})$ as

$$\hat{q}(x) = \int_{V_x} d\mathbf{r}\hat{\rho}(\mathbf{r}), \quad \hat{\mathbf{d}}(x) = \int_{V_x} d\mathbf{r}(\mathbf{r} - \mathbf{r}_x)\hat{\rho}(\mathbf{r}), \quad (18)$$

where the integration is performed over the region V_x occupied by the repeat unit x. The matrix elements of $\hat{q}(x)$ and $\hat{\mathbf{d}}(x)$ between the ground state $\Psi^{(0)}$ and the excited state $\Psi(k)$ with the quasimomentum k can be written as

$$\langle \Psi(k)|\hat{q}(x)|\Psi^{(0)}\rangle = q(k)\exp(ikx),$$
$$\langle \Psi(k)|\hat{\mathbf{d}}(x)|\Psi^{(0)}\rangle = \mathbf{d}(k)\exp(ikx), \quad (19)$$

where we have introduced the functions $q(k)$ and $\mathbf{d}(k)$ of the quasimomentum only. These can be easily expressed in terms of the Bloch functions $\xi_{mm'}^{(k)}(x-x')$ [see Eq. (10)] weighted with the overlap integrals of the atomic orbitals. Only the diagonal matrix elements $\xi_{mm}^{(k)}(0)$ would contribute if the electronic orbitals were well localized on the corresponding atoms. The mirror or inversion symmetry of a repeat unit represented by Eq. (15) implies $q(-k)=-q(k)$ and $\mathbf{d}(-k)=\mathbf{d}(k)$. Taking the exciton wave function in its asymptotic form [Eq. (16)], we obtain the contribution of the repeat unit x to the transition dipole in the form

$$\langle \Psi_\omega|\mathbf{r}_x\hat{q}(x) + \hat{\mathbf{d}}(x)|\Psi^{(0)}\rangle = q(\omega)\mathbf{r}_x\tilde{\psi}(x) + \mathbf{d}(\omega)\psi(x). \quad (20)$$

Here the function $\tilde{\psi}(x)$ is dual to the exciton wave function (16) and given by

$$\tilde{\psi}(x) = a_k \exp(ikx) - a_{-k}\exp(-ikx). \quad (21)$$

Thus we have derived the bulk part of the transition dipole in Eq. (5). Near the branching centers the transition density matrix deviates from the form prescribed by the asymptotic form of the exciton wave function. The contribution of a branching center to the transition dipole can be accounted for by introducing the corresponding charge and dipole moment. Their magnitudes can be represented as linear combinations of the incoming wave values $\psi_{(-)}$ because of the linearity of the problem, which yields the second term in the right-hand side of Eq. (5). Instead of $q(k)$ and $\mathbf{d}(k)$ for $k>0$, we can use the energy-dependent functions:

$$q(\omega) = q[k(\omega)]\left(\frac{dk}{d\omega}\right)^{1/2},$$
$$\mathbf{d}(\omega) = \mathbf{d}[k(\omega)]\left(\frac{dk}{d\omega}\right)^{1/2}. \quad (22)$$

Here additional factors appear as a result of the conversion from the wavevector to the frequency δ-function normalization of the excited states. In addition, the phase of the wave function $\Psi(k)$ is chosen to make $q(\omega)$ and $\mathbf{d}(\omega)$ real.

IV. DISCUSSION

In the present manuscript we have developed a formalism for the ES picture of electronic excitations in branched conjugated molecules. In the ES model, the excitations are viewed as quasiparticles (excitons) on the graph that represents a branched conjugated molecule. The molecular build-
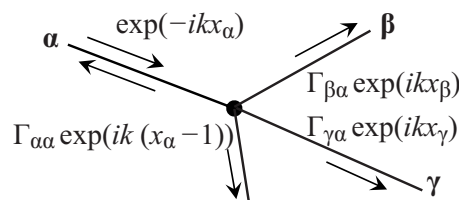

FIG. 2. A scheme of the exciton wave function specified by Eq. (A4).

ing blocks, i.e., linear segments and scattering centers (which include molecular termini as well as branching centers of degree 2 and higher), correspond to edges and vertices of the graph. The behavior of the excitons in the building blocks is characterized by the parameters of the ES approach: the exciton dispersion on the edges and the frequency-dependent matrices that describe the ES at the vertices. The parameters of the building blocks can be determined from the microscopic quantum-chemical computations. In this manuscript we have also presented an ES formalism to describe the electronic transition dipoles. The multiscale ES approach is based on the length scale separation, where the exciton size (a typical distance between the electron and the hole in the bound pair) is small compared to a typical linear segment length in a molecule.

Application of the ES approach to a large branched molecule is as simple as the solution of the generalized "particle in a box" problem on the corresponding graph. The ES approach provides a useful and numerically inexpensive tool to calculate electronic spectra of large molecular structures. The approach is designed to predict the results of quantum chemistry that is coupled to the ES model. In the following manuscript we demonstrate how to obtain the ES parameters in practice (the dispersion and the scattering matrices) from quantum-chemical calculations in simple molecular fragments. In the third paper of the series we apply the ES model to perform calculations for some test molecules and compare the results to those obtained in direct quantum-chemical computations.

The representation of the electronic molecular excitations by quasiparticles opens a path to refining the ES picture, in particular, by taking into account long-range Coulomb interactions and effects of disorder and a realistic environment. The parameters of the ES model can be adjusted to better reproduce experimental observations if the initial approximation for the parameters is based on a quantum-chemical method that adequately describes the nature of excitations.

APPENDIX: MICROSCOPIC FORMALISM IN TERMS OF GREEN FUNCTIONS

In Sec. II we have described the ES picture of electronic excitations in branched organic molecules and formulated a method of calculating optical observables in terms of the relevant properties of the elementary building blocks (i.e., a quasiparticle dispersion, scattering matrices, and transition dipole parameters). In Sec. III the ingredients of the ES model have been interpreted microscopically using the language of many-electron wave functions. In this appendix, for the sake of completeness, we develop a microscopic description of the ES using an alternative language of many-body Green functions.[50] We define the retarded two-point Green functions of the repeat unit's charge and dipole operators as the following spectral decompositions:

$$G^{(0)}(x,x';\omega) = \sum_\gamma \int \frac{dk}{2\pi} \frac{\langle\Psi^{(0)}|\hat{q}(x)|\Psi_\gamma(k)\rangle\langle\Psi_\gamma(k)|\hat{q}(x')|\Psi^{(0)}\rangle + \text{c.c.}}{\omega - \omega_\gamma(k) + i0},$$ (A1)

$$G^{(1)}(x,x';\omega) = \sum_\gamma \int \frac{dk}{2\pi} \frac{\langle\Psi^{(0)}|\hat{\boldsymbol{d}}(x)|\Psi_\gamma(k)\rangle\langle\Psi_\gamma(k)|\hat{\boldsymbol{d}}(x')|\Psi^{(0)}\rangle + \text{c.c.}}{\omega - \omega_\gamma(k) + i0}.$$ (A2)

To simplify notations we omit the matrix structure of dipole-dipole Green functions $G^{(1)}$. Combining Eq. (A1) with Eq. (19) and applying the result to the region of frequencies where only one exciton band exists, we obtain the following microscopic interpretation of ES theory ingredients $q(\omega)$ and $\boldsymbol{d}(\omega)$ in terms of the Green functions:

$$\text{Im } G^{(0)}(x,x';\omega) = 2q^2(\omega)\cos[k(\omega)(x - x')],$$

$$\text{Im } G^{(1)}(x,x';\omega) = 2(\boldsymbol{d}(\omega))^2 \cos[k(\omega)(x - x')].$$ (A3)

Microscopic interpretation of the scattering matrices $\Gamma_{a,\alpha\beta}(\omega)$ as well as the charges $q_{a\alpha}(\omega)$ and the dipoles $\boldsymbol{d}_{a\alpha}(\omega)$ induced on a branching center can be obtained by considering a system that contains semi-infinite linear chains attached to the branching center. We express the Green functions in terms of the exciton spectrum $\omega(k)$, as well as the functions $q(\omega)$ and $\boldsymbol{d}^{(\alpha)}(\omega)$ that determine the charges and dipoles induced at a repeat unit. We count the repeat units x_α on the linear segments starting from the branching center. We also consider the frequencies at which only one exciton type exists. In the full analogy with the infinite polymer, we can introduce a retarded repeat unit charge Green function $G^{(0)}_{\alpha\alpha'}(x_\alpha,x'_{\alpha'};\omega)$ for a semi-infinite branched polymer. A degree-n vertex admits n independent exciton wave functions with the energy $\omega = \omega(k)$. We choose the scattering states so that an incoming wave is present only in the branch (α), which corresponds to the following asymptotic wave function expression in the segment β (also see Fig. 2):

$$\psi^{(\alpha)}_\beta = \delta_{\alpha\beta} \exp(-ikx_\beta) + \Upsilon_{\beta\alpha} \exp(ikx_\beta),$$ (A4)

where the matrix Υ is obtained from the scattering matrix by a phase shift of the diagonal elements according to Eq. (14):

$$\Upsilon_{\alpha\alpha'} = (e^{-ik} - 1)\delta_{\alpha\alpha'}\Gamma_{\alpha\alpha} + \Gamma_{\alpha\alpha'}.$$ (A5)

Using the asymptotic exciton wave functions given by Eq. (A4), we obtain the asymptotic form $\bar{G}^{(0)}$ of the Green function $G^{(0)}$ for $x'_{\alpha'} \gg 1$ and $x_\alpha \gg 1$ in terms of the scattering matrix elements:

$$\text{Im } G^{(0)}_{\alpha\alpha'}(x_\alpha,x'_{\alpha'};\omega)$$
$$\approx \text{Im } \bar{G}^{(0)}_{\alpha\alpha'}(x_\alpha,x'_{\alpha'};\omega)$$
$$= -2\delta_{\alpha\alpha'}q^2(\omega)\cos(k(x_\alpha - x'_\alpha)) + q^2(\omega)$$
$$\times[\Upsilon_{a,\alpha'\alpha}(\omega)\exp(ik(x_\alpha + x'_{\alpha'})) + \text{c.c.}],$$ (A6)

where $k > 0$ is the solution of $\omega_\gamma(k) = \omega$, and the relation of Υ to the scattering matrix Γ is given by Eq. (A5).

To provide microscopic interpretation of the quantities $q_{a\alpha}(\omega)$ and $\boldsymbol{d}_{a\alpha}(\omega)$ which determine the contributions of the vertex to the transition charge and dipole, we introduce the following operators of the full transition charge and dipole, respectively, induced at a branching center:

$$\hat{q}_a = \int_{V_a} d\boldsymbol{r}\hat{\rho}(\boldsymbol{r}), \quad \hat{\boldsymbol{d}}_a = \int_{V_a} d\boldsymbol{r}(\boldsymbol{r} - \boldsymbol{r}_x)\hat{\rho}(\boldsymbol{r}),$$ (A7)

where the integration is performed over the vertex volume. We define the mixed retarded Green functions of the branching center and the repeat units in the linear segments as

$$G_{a\alpha}^{(0)}(x;\omega) = \sum_{\gamma} \int \frac{d\varepsilon}{\pi} \frac{\langle \Psi^{(0)}|\hat{q}_{\alpha}(x_{\alpha})|\Psi_{\gamma}(\varepsilon)\rangle\langle\Psi_{\gamma}(\varepsilon)|\hat{q}_a|\Psi^{(0)}\rangle + \text{c.c.}}{\omega - \varepsilon + i0},$$

$$G_{a\alpha}^{(1)}(x;\omega) = \sum_{\gamma} \int \frac{d\varepsilon}{\pi} \frac{\langle \Psi^{(0)}|\hat{d}_{\alpha}(x_{\alpha})|\Psi_{\gamma}(\varepsilon)\rangle\langle\Psi_{\gamma}(\varepsilon)|\hat{d}_a|\Psi^{(0)}\rangle + \text{c.c.}}{\omega - \varepsilon + i0},$$

(A8)

using spectral decompositions similar to Eq. (A1), in terms of the many-body eigenstates $\Psi_{\gamma}(\omega)$ that are assumed to be normalized to the δ function in the frequency space:

$$\langle\Psi_{\gamma}(\omega)|\Psi_{\gamma'}(\omega')\rangle = 2\pi\delta_{\gamma\gamma'}\delta(\omega-\omega'). \qquad (A9)$$

Note that the degeneracy of the many-body eigenstates $\Psi_{\gamma}(\omega)$ implies that, besides energy, an additional discrete quantum number is included in the notation ω.

In the ES expression for the transition dipole [Eq. (5)] the contributions of the repeat units are computed as if the exciton wave functions are represented by plane waves for all repeat units. However, this is true only for those repeat units whose distance from the branching centers exceeds the exciton size. Yet, Eq. (5) can still be correct if the charges and dipoles induced on the branching centers include not only the obvious direct contributions but also the corrections resulting from the differences between the actual contributions of the repeat units near the branching centers and their approximations with asymptotic exciton wave functions. Since these corrections are essential only for the repeat units located close to the branching centers (at distances of about the exciton size), it is natural to incorporate these corrections into the branching center contributions when building the ES model. This implies the partitions $q_{a\alpha}(\omega)=q_{a\alpha}^{(0)}(\omega)+q_{a\alpha}^{(1)}(\omega)$ and $\boldsymbol{d}_{a\alpha}(\omega)=\boldsymbol{d}_{a\alpha}^{(0)}(\omega)+\boldsymbol{d}_{a\alpha}^{(1)}(\omega)+\boldsymbol{d}_{a\alpha}^{(2)}(\omega)$ into the bare contribution and corrections: $q_{a\alpha}^{(1)}(\omega)$ is the correction to the total charge of the repeat units, $\boldsymbol{d}_{a\alpha}^{(1)}(\omega)$ is the correction to the vertex dipole due to the corrections to the total charges induced on the repeat units, and finally $\boldsymbol{d}_{a\alpha}^{(2)}(\omega)$ is the correction to the vertex dipole due to corrections to dipoles of the repeat units. The bare contributions can be retrieved from the $x_{\alpha}\gg 1$ asymptotic form of the mixed Green functions:

$$\text{Im}\, G_{a\alpha}^{(0)}(x_{\alpha};\omega) \approx 2q_{\alpha}(\omega)q_{a\alpha}^{(0)}(\omega)\cos[k(x_{\alpha}-1/2)]$$
$$- \sum_{\beta \ni a}(q_{\beta}(\omega)q_{a\beta}^{(0)}(\omega)\Gamma_{a,\alpha\beta}(\omega)$$
$$\times \exp[ik(x_{\alpha}-1/2)] + \text{c.c.}),$$

(A10)

$$\text{Im}\, G_{a\alpha}^{(1)}(x_{\alpha};\omega) \approx -2\boldsymbol{d}_{\alpha}(\omega)\boldsymbol{d}_{a\alpha}^{(0)}(\omega)\cos[k(x_{\alpha}-1/2)]$$
$$- \sum_{\beta \ni a}(\boldsymbol{d}_{\beta}(\omega)\boldsymbol{d}_{a\beta}^{(0)}(\omega)\Gamma_{a,\alpha\beta}(\omega)$$
$$\times \exp[ik(x_{\alpha}-1/2)] + \text{c.c.}).$$

The correction terms can be retrieved from the asymptotic $x_{\alpha}\gg 1$ form of the Green functions $G_{\alpha\alpha'}(x_{\alpha},x'_{\alpha'};\omega)$ with $x'_{\alpha'}$ being kept finite:

$$\sum_{\alpha' \ni a} \sum_{x'_{\alpha'}=1}^{\infty} \text{Im}(G_{\alpha\alpha'}^{(0)}(x_{\alpha},x'_{\alpha'};\omega) - \bar{G}_{\alpha\alpha'}^{(0)}(x_{\alpha},x'_{\alpha'};\omega))$$

$$\approx 2q_{\alpha}(\omega)q_{a\alpha}^{(1)}(\omega)\cos[k(x_{\alpha}-1/2)] + \sum_{\beta \ni a}(q_{\alpha}(\omega)q_{a\beta}^{(1)}(\omega)$$

$$\times \Gamma_{a,\alpha\beta}(\omega)\exp[ik(x_{\alpha}-1/2)] + \text{c.c.},$$

$$\sum_{\alpha' \ni a} \sum_{x'_{\alpha'}=1}^{\infty} \boldsymbol{r}_{x'_{\alpha'}}^{(\alpha')} \text{Im}(G_{\alpha\alpha'}^{(0)}(x_{\alpha},x'_{\alpha'};\omega) - \bar{G}_{\alpha\alpha'}^{(0)}(x_{\alpha},x'_{\alpha'};\omega))$$

$$\approx 2q_{\alpha}(\omega)\boldsymbol{d}_{a\alpha}^{(1)}(\omega)\cos[k(x_{\alpha}-1/2)] + \sum_{\beta \ni a}(q_{\alpha}(\omega)\boldsymbol{d}_{a\beta}^{(1)}(\omega)$$

$$\times \Gamma_{a,\alpha\beta}(\omega)\exp[ik(x_{\alpha}-1/2)] + \text{c.c.}, \qquad (A11)$$

$$\sum_{\alpha' \ni a} \sum_{x'_{\alpha'}=1}^{\infty} \text{Im}(G_{\alpha\alpha'}^{(1)}(x_{\alpha},x'_{\alpha'};\omega) - \bar{G}_{\alpha\alpha'}^{(1)}(x_{\alpha},x'_{\alpha'};\omega))$$

$$\approx 2\boldsymbol{d}_{\alpha}(\omega)\boldsymbol{d}_{a\alpha}^{(2)}(\omega)\cos[k(x_{\alpha}-1/2)] + \sum_{\beta \ni a}(\boldsymbol{d}_{\alpha}(\omega)\boldsymbol{d}_{a\beta}^{(2)}(\omega)$$

$$\times \Gamma_{a,\alpha\beta}(\omega)\exp[ik(x_{\alpha}-1/2)] + \text{c.c.}.$$

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