Exciton dynamics in branched conducting polymers: Quantum graphs based approach

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We consider dynamics of excitons in branched conducting polymers. An effective model based on the use of quantum graph concept is applied for computing of exciton migration along the branched polymer chain. Condition for the regime, when the transmission of exciton through the branching point is reflectionless is revealed.

1. INTRODUCTION

Modeling the charge carrier migration in conducting polymers is of practical importance for material and device optimization in organic electronics. Effective functionalization of conducting polymers for different purposes requires understanding of the mechanisms for charge transport and their utilization. So far, considerable progress has been made in the developing of different models for charge carrying quasiparticles in conducting polymers, such as polarons, excitons and solitons \cite{14, 15, 16, 17, 18, 19}. Excitons, which are the bound electron-hole pair states, appear, e.g., in photovoltaic processes in conducting polymers interacting with optical field. Charged solitons in conducting polymers provide another mechanism for charge transport. When charge is trapped in the phonon cloud by forming a bound state, they are called polarons. Each mechanism for charge carrier transport plays important role depending on the type of the functionalization method. Therefore effective utilization of these mechanisms in organic electronics requires developing different effective models for charge carrier dynamics. Among these three mechanisms of charge transport, exciton mechanism is of special importance for practical applications in organic photovoltaics. Tight binding theory of excitons in conducting polymers was proposed in \cite{14}. Different aspects of excitons, including band structure calculations, field induced ionization, continuum approach for exciton transport and optical properties of conducting polymers have been studied in the Refs. \cite{16, 17, 18, 19}. In \cite{20} dynamic model of self-trapped excitons is studied using the Schrödinger equation on polymer lattice by taking into account exciton-phonon interaction. Different aspects of exciton dynamics, such as ultrafast exciton dissociation \cite{21}, excitation dissociation at donor-acceptor polymer heterojunctions \cite{22}, exciton diffusion have been studied by E. Bittner and co-workers.

Most of the conducting polymers synthesized so far have linear (unbranched) structure. However, conducting polymers that have branched architecture attracted much attention recently (see, e.g. Refs. \cite{23, 24, 25, 26}). These are kinds of polymers, in which linear chain splits into the two or more branches starting from some point, which is called branching point, or node, or vertex. The structure of a branching can have different architecture, e.g. can be in the form of star, tree, ring, etc. These latter implies the rule for branching and called branching topology. When the topology of a polymer is very complicated, it is called hyperbranched polymer. Branched polymers differ from their linear counterparts in several important aspects. Such polymer forms a more compact coil than a linear polymer with the same molecular weight. Also, depending on the topology of branching, electronic and elasticity properties can be completely different than those of linear polymers. Despite the considerable progress made in the synthesis and study of branched conducting polymers, the problem of the charge carrier dynamics in such structures is still remaining as less studied topic.

In this paper we consider dynamics of excitons in branched conducting polymers by modeling them in terms of so-called quantum graphs. The latter are the system of quantum wires connected to each other according to some rule, which is called topology of a graph. Linear, i.e., unbranched counterpart of this system have been extensively studied earlier in the literature within the different approaches (see, e.g., Refs. \cite{27, 28, 29}). Here we propose a model, which uses the linear Schrödinger equation on metric graphs. Apart from branched polymers, quantum graphs have been extensively studied earlier in different contexts \cite{21, 22, 23, 24, 25, 26}.

Simplest graph topology is called star graph, which presents simple Y-junction with three branches. Advantage of modeling branched structures by metric graphs is the fact that it allows to describe the structure as one-dimensional, or quasi-one dimensional system. Here we consider star shaped branched polymers where the exciton dynamics is described by the Schrödinger equation on metric star graph. This paper is organized as follows. In the next section we give formulation of the problem together with the description of the model. In section III we apply the model to the exciton dynamics in star-shaped conducting polymers. Section IV extends to the model for other branching topologies, such as loop- and tree-shaped polymers. Finally, section V presents some concluding remarks.
2. STEADY STATE EXCITONS IN A STAR-BRANCHED POLYMER

Excitons in conducting polymers are the main charge carriers in photophysical processes and organic optoelectronic devices. Developing realistic models exciton migration is of crucial importance for engineering novel functional materials and optimization of existing ones. Apart from the exciton transport, description of steady state excitons allows to understand basic factors playing import role in exciton-lattice exciton phonon and other interactions. Different models for exciton dynamics in conjugated polymers have been proposed so far in the literature (see, e.g., Refs. [34]-[38]). For conducting polymers, due to their quasi-one dimensional ad periodic structure, a polymer chain can be considered as a one-dimensional lattice of monomers. Therefore most of the models describing excitons in conducting polymers are the 1D models. This allows, e.g., to use 1D tight-binding approach, to calculate band structure and charge carrier migration. Such approach was proposed first in [8]. Here we consider dynamics of excitons in a branched conducting polymers, i.e. consists of three polymer chains which are connected to each other at single monomer (see, Fig. 1). The model we will use in this paper is close to that proposed by Abe in the Ref. [35] and assumes neglecting by electrons-phonon interactions, considers lattice as rigid and Coulomb interaction between the electron is assumed to be weak compared to that of between the electron and the hole. Also, to avoid appearing of the infinite binding energy, we include a cut-off length into the Coulomb potential [35]. Then the attractive Coulomb potential between the electron and hole can be written as

\[ V(x) = -\frac{1}{|x + \xi|}. \]

Here we consider such polymers in branched conducting polymers. The branching is assumed to be in the form of Y-junction (see, Fig. 1). Such system can be mapped onto the basic star graph presented in Fig. 2.

Assuming that the length of polymer is much longer than its width (which implies that the branches of the polymer are long enough, i.e. contains more enough monomers), the dynamics of electron-hole pair can be described in terms of the stationary Schrödinger equation on metric graph, which is given by (on each branch of the graph presented in Fig. 2) (in the units \( \hbar = e = 1 \))

\[ \left( \frac{p^2}{2\mu} - \frac{1}{|x + \xi_j|} \right) \psi_j(x) = E_b \psi_j(x), \quad (2.1) \]

where \( p = -i \frac{d}{dx}, \) \( E_b \) is the binding energy for electron-hole pair, \( j \) is the number of branch. Coulomb potential describes electron-hole interaction and \( \mu \) is the reduced mass given by

\[ \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}, \]

To solve Eq. (2.1), one needs to impose the boundary conditions at the branching points (vertices) of the graph. Here we impose them as the continuity of the wave function at the branching point:

\[ \psi_1(0) = \psi_2(0) = \psi_3(0) \quad (2.2) \]

and the Kirchhoff rule, which is given by

\[ \sum_{j=1}^{3} \frac{d}{dx} \psi_j(x = 0) = 0. \quad (2.3) \]

As the analytical solution of Eq. (2.1) is not possible, one needs to solve it numerically for the boundary conditions (2.2) and (2.3). To do this, we expand the wave function, \( \psi_j \) in terms of the complete set of eigenvalues of star graph:

\[ \psi_j(x) = \sum c_{n,j} \psi_{j,n}(x), \quad (2.4) \]
where \( \phi_{j,n}(x) \) are the eigenvalues of the unperturbed quantum star graph given by the following Schrödinger equation [54]:

\[
-\frac{1}{2} \frac{d^2}{dx^2} \phi_j = \varepsilon \phi_j
\]

(2.5)

with the boundary conditions

\[
\phi_1(0) = \phi_2(0) = \phi_3(0)
\]

and current conservation

\[
\sum_{j=1}^{3} \frac{d}{dx} \phi_j(x = 0) = 0,
\]

and the Dirichlet BC at the bond ends given by

\[
\phi_1(L_j) = \phi_2(L_j) = \phi_3(L_j) = 0.
\]

Explicitly, the eigenfunctions \( \phi_{j,n} \) can be written as [54]

\[
\phi_{j,n}(x) = \frac{B_n}{\sin (k_n L_j)} \sin (k_n (L_j - x)),
\]

(2.6)

where

\[
B_n = \left[ \sum_j (L_j + \sin (2k_n L_j)) \sin^{-2} (k_n L_j)/2 \right]^{-1/2}.
\]

Eigenvalues, \( \varepsilon \) can be found from the following secular equation:

\[
\sum_{j=1}^{3} \tan^{-1} \sqrt{2\varepsilon L_j} = 0.
\]

Inserting Eq. (2.4) into (2.5) and multiplying both sides to \( \phi_{j,m}^* \) and integrating by taking into account the normalization conditions given by

\[
\int \phi_{j,m}^* \phi_{j,n} dx = \delta_{mn},
\]

the eigenvalues, \( E_n \) can be found by diagonalizing the matrix \( W_{mn} \), which is given as

\[
W_{mn} = (\varepsilon_n \delta_{mn} + V_{mn}),
\]

(2.7)

with \( \delta_{mn} \) being the Konecker symbol and

\[
V_{mn} = -\sum_{j=1}^{3} \int \phi_{j,m}^* \phi_{j,n} dx,\]

In numerical calculations we choose \( \xi_1 = \xi_2 = \xi_3 = 1 \).

3. TRANSPORT OF EXCITONS

Important issue in modeling of exciton dynamics conducting polymers is migration of excitons along the polymer chain. In case of branched conducting polymer dynamics become richer due to the transmission or reflection of exciton at the branching point. Here we consider this problem by modeling exciton dynamics in terms of time-dependent Schrödinger equation on metric graph which is given by (in the system of units \( \mu = \hbar = 1 \))

\[
i\partial_t \psi_j + \partial_x^2 \psi_j + \left( \frac{1}{x + \xi_j} \right) \psi_j = 0, \quad a > 0, x \geq 0
\]

(3.1)

where \( \mu \) is the reduced mass, \( \xi_j \) is the cutoff length and \( j \) is the branch number. The boundary conditions are imposed as

\[
\alpha_1 \psi_1(0, t) = \alpha_2 \psi_2(0, t) = \alpha_3 \psi_3(0, t),
\]

(3.2)

current conservation

\[
\sum_{j=1}^{3} \frac{1}{\alpha_j} \partial_x \psi_j(x = 0, t) = 0,
\]

(3.3)

where \( \alpha_j, j = 1, 2, 3 \) are real constants. Dirichlet boundary conditions are imposed at the end of each branch:

\[
\psi_j(x = L_j, t) = 0, \quad j = 1, 2, 3.
\]

(3.4)

Here we use concept of so-called transparent boundary conditions (TBC) for quantum graphs, which was introduced recently in the Ref. [66]. Unlike the scattering matrix based approach widely used in quantum mechanics, this novel approach allows to introduce reflectionless propagation of the waves in terms of boundary conditions for the wave equation. Although explicit form of these boundary conditions are very complicated and numerical solution of the problem requires using highly accurate and stable discretization scheme, application of the approach to quantum graphs allows considerable simplification. Namely, as it was shown in [66], under certain constraints, transparent boundary conditions become equivalent to usual continuity and Kirchhoff rules given by

![Graph](image-url)
Eqs. (3.2) and (3.3). Therefore method proposed in [66] may become powerful approach for solving the problem of reflectionless wave propagation in branched structures modeled in terms of quantum graphs. Here, referring for the details to [66], we briefly recall the description of the approach. Consider the wave going from the first to second and third branches, i.e., the initial condition is compactly supported in the first branch We separate the whole domain, i.e., the graph into the interior and exterior domains. Then the “interior” problem for the first bond, $b_1$ can be written as

$$i\partial_t \psi_1 + \partial_x^2 \psi_1 + \left(\frac{2\mu}{x+a}\right) \psi_1 = 0, \quad (3.5)$$

$$\psi_1(x,0) = \psi^I(x)$$

$$\partial_x \psi_1(x=0,t) = (T_+ \psi_1)(x=0,t),$$

$$\psi_1(x=L_1,t) = 0.$$

Exterior problems for $b_{2,3}$:

$$i\partial_t \psi_{2,3} + \partial_x^2 \psi_{2,3} + \left(\frac{2\mu}{x+a}\right) \psi_{2,3} = 0, \quad (3.6)$$

$$\psi_{2,3}(x,0) = 0,$$

$$(T_+ \psi_{2,3})(x=0,t) = \partial_x \psi_{2,3}(x=0,t),$$

$$\psi_{2,3}(x=L_{2,3},t) = 0.$$

The second order transparent boundary condition at $x = 0$ with (3.2) is the following [66]:

$$\partial_x \psi_{2,3}(x=0,t) = -e^{i\frac{\pi}{2}} e^{i\frac{2\mu}{x+a}} \partial_t \int_0^t \psi_{2,3}(0,\tau)e^{-i\frac{2\mu}{x+a}\tau} \sqrt{t-\tau} d\tau$$

$$-\frac{\alpha_1}{\alpha_{2,3}} e^{i\frac{\pi}{2}} e^{i\frac{2\mu}{x+a}} \partial_t \int_0^t \psi_1(0,\tau)e^{-i\frac{2\mu}{x+a}\tau} \sqrt{t-\tau} d\tau. \quad (3.7)$$

From (3.3) and (3.7) we have

$$\partial_x \psi_1(x=0,t) = \alpha_1^2 \left(\frac{1}{\alpha_2^3} + \frac{1}{\alpha_3^3}\right) e^{i\frac{\pi}{2}} e^{i\frac{2\mu}{x+a}} \partial_t \int_0^t \psi_1(0,\tau)e^{-i\frac{2\mu}{x+a}\tau} \sqrt{t-\tau} d\tau.$$

It was shown in [66] that the vertex boundary conditions given by Eqs. (3.2) - (3.4) become equivalent to the transparent boundary conditions given by Eq. (3.7), provided parameters $\alpha_j$ fulfill the following sum rule:

$$\frac{1}{\alpha_1^3} = \frac{1}{\alpha_2^3} + \frac{1}{\alpha_3^3} \quad (3.8)$$

The check this, in. Fig. 4 the profile of the exciton’s wave function is plotted at different time moments. Reflectionless transmission of the exciton through the polymer branching point can be seen from this plot.

Fig. 5 presents the reflection coefficient determined as the ratio of the partial norm for the first bond to the total norm

$$R = \frac{N_1}{N_1 + N_2 + N_3}.$$

is plotted as a function of $\alpha_1$ for the fixed values of $\alpha_2$ and $\alpha_3$. As it can be seen from this plot, at the value of $\alpha_1$ that provides fulfilling of the constraint (3.8), the reflection coefficient becomes zero, which confirms once more that the sum rule in Eq. (3.8) makes the vertex boundary conditions in Eqs. (3.2) - (3.4) equivalent to the transparent ones.

4. CONCLUSIONS

We studied steady states and migration of exciton in branched conducting polymers. A model based on the use of quantum graph concept, described by the linear Schrödinger equation on metric graphs is applied. The
main focus is given to calculation of the energy spectra of steady state exciton and to the transport along the polymer chains accompanied the transmission (reflection) of exciton at the branching points. Combining the quantum graphs and transparent boundary conditions concepts, constraints providing the reflectionless transmission of exciton through the branching point is derived in the form of simple sum rule. Numerical computations showing such transmission are provided in addition to the analytical results. The model proposed in this work can be extended to the case of more complicated branching topologies. Also, it can be applied for modeling of exciton migration in polymer based thin film organic solar cells, where polymer chains packed on the cell create complicated branched structures.
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