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Ultrafast exciton migration in an HJ-aggregate: Potential surfaces and quantum dynamics

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ABSTRACT

Quantum dynamical and electronic structure calculations are combined to investigate the mechanism of exciton migration in an oligothiophene HJ aggregate, i.e., a combination of oligomer chains (J-type aggregates) and stacked aggregates of such chains (H-type aggregates). To this end, a Frenkel exciton model is parametrized by a recently introduced procedure [Binder et al., J. Chem. Phys. **141**, 014101 (2014)] which uses oligomer excited-state calculations to perform an exact, point-wise mapping of coupled potential energy surfaces to an effective Frenkel model. Based upon this parametrization, the Multi-Layer Multi-Configuration Time-Dependent Hartree (ML-MCTDH) method is employed to investigate ultrafast dynamics of exciton transfer in a small, asymmetric HJ aggregate model composed of 30 sites and 30 active modes. For a partially delocalized initial condition, it is shown that a torsional defect confines the trapped initial exciton, and planarization induces an ultrafast resonant transition between an HJ-aggregated segment and a covalently bound "dangling chain" end. This model is a minimal realization of experimentally investigated mixed systems exhibiting ultrafast exciton transfer between aggregated, highly planarized chains and neighboring disordered segments.

1. Introduction

The understanding of exciton dynamics in semiconducting polymers is an important aspect in assessing and optimizing the performance of organic photovoltaic materials. Efficient exciton transport to donor/acceptor interfaces, within a typical diffusion length of the order of 10 nm, is a prerequisite for charge separation at donor–acceptor bulk heterojunctions [1–4]. Exciton transport has been found to be significantly enhanced in regioregular phases, e.g., of H-aggregate type [5–7] where stacked oligomers are aligned in a face-to-face fashion. While exciton migration is often treated in a kinetic regime where a hopping-type dynamics is driven by thermal fluctuations, a series of recent experimental observations have highlighted the importance of ultrafast coherent transport [8–10] - even at room temperature, and despite the presence of a high-dimensional phonon environment.

Excitons in conjugated polymer materials have typically been found to be delocalized over 2–10 monomer units, and spatial confinement is taken to occur within "conformational subunits" delimited by conjugation breaks or chemical defects [11–13]. Since the latter define the effective extension of the optically excited chromophore, the expression "spectroscopic units" has been alternatively used [12,13]. However, the details of the dynamics of the initially excited, partially delocalized excitonic species have remained elusive. According to Refs. [14,15], exciton transfer occurs from delocalized, vibrationally relaxed states to local exciton ground states (LEGS) [14,16,17], which in turn undergo rapid, femtosecond scale dynamical localization due to vibrational relaxation of high-frequency modes [15]. In Ref. [18], it was conjectured that torsional conformational change leads to a dynamical expansion of the exciton by several monomer units, thus allowing for efficient downhill excitation energy transfer. Recent results of coherent electronic two-dimensional (2D) spectroscopic studies [19] of a low-temperature self-aggregated poly-phenylene vinylene phase indicate an ultrafast initial exciton relaxation step – essentially corresponding to LEGS formation – followed by exciton migration in the aggregate.

The theoretical investigation of exciton dynamics often relies upon the use of model Hamiltonians – in particular, the Frenkel [5], Holstein [15,16,20], and Merrifield [21,22] Hamiltonians – along with certain assumptions about the nature of the elementary chromophores that are involved in the dynamics. Indeed, monomer-based representations [23,24] as compared with delocalized "spectroscopic unit" representations [25] generally yield different predictions for the dynamics [26]. Furthermore, the role of

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electron–phonon coupling is still controversial, as is the polaronic nature of the photogenerated exciton species [27,28].

Against this background, we seek to obtain an unbiased representation of exciton dynamics, by deriving an exciton Hamiltonian from electronic structure calculations for suitable oligomer species [23,24,29]. The Hamiltonian is set up in a monomer basis, using a mapping approach that we recently introduced in Ref. [30], a variant of which will be applied in the present work.

In the mapping approach [30], an inverse eigenvalue problem is solved to define an effective Frenkel Hamiltonian in a unique fashion, based upon electronic structure calculations for oligomer species that are large enough to exhibit excitonic properties [29]. Specifically, the procedure of Ref. [30] uses information from potential energy surface (PES) points for the electronic ground state and any two of the lowest adiabatic states of the excitonic manifold of interest, in order to map these PES points upon the eigenvalues of an effective Frenkel Hamiltonian and predict the full excitonic manifold at the chosen geometry. Since the procedure works in a point-wise fashion, PES sections with anharmonic dependencies upon a chosen set of coordinates can be explored. A prerequisite of the mapping procedure is the assignment of the relevant states, which can be carried out by a transition density analysis [31,32]. Typically, excitonic manifolds can be clearly distinguished from charge transfer states [24,29,31].

In the present work, the approach of Ref. [30] is generalized to two-dimensional so-called HJ-aggregates [6,7], which combine intra-chain head-to-tail alignment and inter-chain face-to-face alignment. For representative oligothiophene (OT) fragments, we construct PESs for models typically comprising 20–30 sites, as a function of both intra-chain and inter-chain modes. Finally, efficient multiconfigurational wavefunction techniques, in particular the Multi-Layer Multi-Configuration Time-Dependent Hartree (ML-MCTDH) method [33–36] are employed to carry out high-dimensional quantum dynamical calculations.

In our dynamical investigations, we focus upon a minimal model for exciton transfer between planarized, HJ-aggregate type OT segments and covalently connected unaggregated segments. Recent spectroscopic investigations using pump–probe spectroscopy [37] indicate ultrafast energy transfer between planarized and adjacent disordered fragments, such that these two types of chromophores must be directly connected – presumably such that the unaggregated segments form "dangling ends" of stacked arrays. In our minimal model of these coexisting aggregated and unaggregated segments, we investigate under which circumstances ultrafast exciton transfer is likely to occur, as a function of a dynamically relaxing torsional defect. In this context, we will further investigate the role of exciton delocalization in the dynamics, and the polaronic nature of the excitonic quasiparticles.

The remainder of the paper is organized as follows. We first address the site-based Frenkel Hamiltonian that is used in this work (Section 2). In Section 3, we detail the mapping procedure, as a generalization of the procedure introduced in Ref. [30], that leads to a set of high-dimensional coupled PESs. Based on these potential surfaces, Section 4 addresses a quantum dynamical study of exciton transfer in an oligothiophene HJ aggregate. Finally, Section 5 summarizes and concludes.

2. Site-based Frenkel Hamiltonian

To represent a typical HJ-aggregate, we consider a two-dimensional lattice composed of identical monomers labeled with indices (μ, ν) as its vertices, see Fig. 1. In the direction of index μ, M chains are arranged to form a stack. In the direction of index ν, N_μ monomers are covalently joined to form oligomeric chains, where the chain length may depend on the chain index μ. At this point we will limit our model to geometries for which the stacking direction is roughly orthogonal to the direction of the chains, so that monomer (μ, ν) physically neighbors monomers $(\mu - 1, \nu)$ and $(\mu + 1, \nu)$.

2.1. Hamiltonian in site-based monomer representation

The system Hamiltonian includes both vertex contributions $(\widehat{V}^{\text{vertex}})$ and excitonic couplings $(\widehat{V}^{\text{exc}})$,

$$\begin{aligned}\widehat{H} = \widehat{T}(\{x_{\mu,\nu}\}, \{\chi_{\mu;\nu,\nu'}\}, \{\xi_{\mu,\mu';\nu}\}) \\ + \sum_{\mu=1}^{M}\sum_{\nu=1}^{N_\mu}\Big(\widehat{V}^{\text{vertex}}_{\mu,\nu}\Big(\{x_{\mu,\nu}\}, \{\chi_{\mu;\nu-1,\nu}\}, \{\chi_{\mu;\nu,\nu+1}\}, \{\xi_{\mu-1,\mu;\nu}\}, \{\xi_{\mu,\mu+1;\nu}\}\Big) \\ + \widehat{V}^{\text{exc}}_{\mu,\nu}\Big(\{\chi_{\mu;\nu-1,\nu}\}, \{\chi_{\mu;\nu,\nu+1}\}, \{\xi_{\mu-1,\mu;\nu}\}, \{\xi_{\mu,\mu+1;\nu}\}\Big)\Big)\end{aligned} \tag{1}$$

Here, $\{x_{\mu,\nu}\}$ denotes a set of local modes comprising all relevant intra-monomer degrees of freedom of monomer (μ, ν), while $\{\chi_{\mu;\nu-1,\nu}\}$ and $\{\chi_{\mu;\nu,\nu+1}\}$ denote sets of correlated modes comprising all relevant inter-monomer (intra-chain) degrees of freedom which are shared by monomers $\nu - 1$ and ν as well as ν and $\nu + 1$, respectively, within the same chain μ. These modes "link" neighboring monomers and are typically of torsion or bond stretch type. Likewise, the set of correlated modes $\{\xi_{\mu-1,\mu;\nu}\}$ and $\{\xi_{\mu,\mu+1;\nu}\}$ comprises all relevant inter-chain degrees of freedom which are shared between monomers carrying the index $\mu - 1$ and μ as well as μ and $\mu + 1$, respectively, at the same lateral position ν. These modes typically correspond to inter-chain distance, shift and tilt coordinates (which are here defined in keeping with our initial assumption of orthogonal stacking). Fig. 1 illustrates the connectivities within the two-dimensional lattice.

On the r.h.s. of Eq. (1), $\widehat{T}$ denotes the kinetic energy, $\widehat{V}^{\text{vertex}}_{\mu,\nu}$ denotes the vertex potential that carries electronic offsets along with interactions with local modes $(\{x\})$ and nearest-neighbor correlated modes $(\{\chi\}, \{\xi\})$ involving the site (μ, ν). The excitonic coupling Hamiltonian $\widehat{V}^{\text{exc}}_{\mu,\nu}$ describes nearest-neighbor couplings at the monomer-monomer junctions and generally depends on the sets of correlated modes $\{\chi\}$ for intra-chain couplings and $\{\xi\}$ for inter-chain couplings.

As in our previous treatment [30], summations over the full physical range of μ and ν include sets of "virtual" ("dangling") modes $\{\chi_{\mu;0,1}\}$ and $\{\chi_{\mu;N_\mu,N_\mu+1}\}$ at the left and right ends of the single chains as well as $\{\xi_{0,1;\nu}\}$ and $\{\xi_{M,M+1;\nu}\}$ at the bottom and top ends of the stack. These virtual modes are conventionally set to fixed values which reflect the symmetry of the system. By their inclusion, our model is able to counter edge effects in finite-sized systems to a first approximation.

In the present study, we are going to focus on the effect of correlated modes, similarly to our recent investigation [30]. (However, we note that the presence of local modes can have a significant effect on the dynamics, as detailed in [38].).

In this case, the kinetic energy contribution of Eq. (1) reduces to the following form,

$$\begin{aligned}\widehat{T}(\{\chi_{\mu;\nu,\nu+1}\}, \{\xi_{\mu,\mu+1;\nu}\}) = \left(-\frac{\hbar^2}{2m_\chi}\sum_{\mu=1}^{M}\sum_{\nu=1}^{N_\mu-1}\frac{\partial^2}{\partial\chi^2_{\mu;\nu,\nu+1}} - \frac{\hbar^2}{2m_\xi}\sum_{\mu=1}^{M-1}\sum_{\nu=1}^{N_\mu}\frac{\partial^2}{\partial\xi^2_{\mu,\mu+1;\nu}}\right)\hat{\mathbf{1}} \\ \equiv T(\{\chi_{\mu;\nu,\nu+1}\},\ \{\xi_{\mu,\mu+1;\nu}\})\hat{\mathbf{1}}\end{aligned} \tag{2}$$

where a normal-mode type form of $\widehat{T}$ is used for all modes (noting that for torsional modes, m_χ is to be replaced by the moment of inertia). The above form of the kinetic energy can be adapted to more accurate expressions including non-separable terms.