Spectroscopy, Relaxation, and Transport of Molecular Excitons in Noisy and Disordered Environments

by

Chern Chuang

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Abstract

In this thesis contribution we theoretically investigate the spectroscopy, relaxation, and transport properties of Frenkel excitons in molecular aggregates, with extensive comparison to or prediction of experimental observables. Particular emphasis is devoted to the effects of thermal noise, static disorder, and system dimensionality. Our key contributions are summarized as the following. We study the spectroscopic signatures of excitonic molecular aggregates of dimensionality larger than unity as functions of temperature and disorder strength. These findings are applied to the determination of essential system characteristics and quantitatively explain the spectroscopic traits seen in experiments where either the temperature or disorder strength is altered. A classification scheme generalized from Kasha’s seminal work on J- and H-aggregates is proposed that is compatible with experimental observations previously unexplained. We recognize the importance of long-wavelength approximations in understanding the density of states in two-dimensional excitonic aggregates. And for tubular aggregates this leads to a simple expression for the energy gap between the parallel- and the perpendicular-polarized peaks useful in inferring key system parameters. This long-wavelength approach is then extended to the analysis of 2D excitonic molecular aggregates in general. A universal scaling relation concerning the steady-state diffusive transport of excitons in molecular tubes is predicted and analyzed, where the key order parameter is identified as the ratio between the localization length of the exciton wavefunctions and the tube circumference. A unified theoretical framework is proposed to explain the relaxation of hot excitons generated in emissive conjugated polymers across three orders of magnitude in timescale, with quantitative agreements with experiments.

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Chapter 1

Introduction

1.1 Light-Harvesting Processes in Natural and Artificial Systems

Solar energy provides for most of the activities on Earth including ones involved in modern human societies. This statement can be understood in a broad sense that even fossil fuels produced millions of years ago from anaerobic decompositions of biomasses, which owe their very existence to photosynthesis, are a form of solar energy. On the other hand, solar energy sources that are renewable have become increasingly invested in the forefront of energy industry. [8, 9, 10, 11]

Apparently, understanding the machinery of photosynthetic organisms, a role model of harvesting solar energy at highest known efficiencies and robustness, is the cornerstone of such effort. On the other hand, artificial photovoltaic cells designed to convert photon energy into electricity share considerable structural similarity with their natural counterparts, where the energy is converted to chemical forms like hydrocarbons. We shall walk through a typical process of light harvesting that they have in common below.

Firstly, the process starts with photons absorbed at parts of the devices that can be thought of the antennae of the system. This creates excitations of the states of materials composing the antennae. Specifically, certain valence electrons are disturbed
and moved out of their equilibrium positions, while the jolted electrons and the holes left behind interact in fashions that resemble the electron and the proton of a hydrogen atom: an exciton. The suffix "-on" refers to the quantum and particle-like nature of this entity analogous to photons, the quanta of light.

The excitons carry the bulk of the energy inherited from the original photons and find their ways to the next step of the process. Here one is concerned with the transport of excitons. While the excitons themselves are well-defined virtual particles, one has to keep in mind that the nature of excitons being disturbances to the host materials. Consequently, all the relevant degrees of freedom (DOFs) in the material, including inter- and intra-molecular geometry, vibrational modes, and the omnipresent photon vacuum, contribute to both the nature and the transport of excitons.[9, 12]

The transport continues until the putative next and final phase of an exciton's journey that could be one of the following: emissive or non-emissive decay back to ground state, or charge separation. In terms of the light-harvesting efficiency only the last is considered a successful harvest of solar energy given an absorbed photon. Therein the hole and the electron comprising the exciton dissociate from each other, creating an electric current which can be utilized to drive the working mechanisms of the light-harvesting apparatus in question. In the case of a photosynthetic organism a chain of electron transport follows which builds up a proton gradient across the chloroplast membrane, which is later used in driving the ATP synthase. In the case of a photovoltaic cell the current is the direct output of the cell.

In this thesis contribution we are mainly concerned with the former two processes of exciton dynamics: the absorption and the transport of excitons. In particular, our discussion is based on the so-called system-bath model. Herein the DOFs directly involving the excitons (the system) are treated explicitly while the effects of other DOFs on the system (the bath) are accounted for to a lesser degree, where only certain statistical properties of them are involved. In this context we are dealing with a quantized system coupled to its containing environment, this is often referred to as an open quantum system in the literature. We shall go through the key theoretical
concepts surrounding the discussion of the spectroscopy and transport of excitons in this context in the next section, followed by a brief survey of two broad categories of systems that we will base our study upon.

1.1.1 Molecular Excitons in the Condensed Phase

Now that we are narrowing down to the study of molecular excitons. The term molecular excitons traces back to the celebrated study of Davydov[13]. In contrary to excitons in, for example, inorganic semiconductors, the hole and the electron of a molecular excitons are usually restricted to the same molecule, sometimes referred to as a chromophore. However, it is vital to recognize that despite this quality of the molecular excitons, the wavefunction describing the center-of-mass of a molecular exciton can be extended across multiple molecules. This is attributed to the excitonic couplings among the molecules that delocalize the exciton wavefunction.

While the delocalization is a key quantum effect in the picture, molecular excitons, constituting the system aspect of our concern, are not isolated from the rest of the universe. As mentioned, all the relevant DOFs including the detailed geometry of the molecules and the inter- and intra-molecular vibrational modes are collectively referred to as the environment or the bath, relative to the system. They contribute negatively to the delocalization of excitons, i.e. effectively localizing them. It can be said that the competition between the two opposing forces represents the most important and also the most intriguing facet of studying the dynamics of molecular excitons in the condensed phase.

As far as the dynamics of the excitons is concerned, we can distinguish two different types of environmental DOFs basing on the time scale involved: static disorder and dynamical noise. The former is the roughness of the energy landscape that remained still when traversed by the excitons, while the latter is the incessant kicks upon the excitons from the surroundings upon which the temperature of the environment can be defined. These two, while both serving as localizing factors for the exciton wavefunction, contribute very differently towards the exciton dynamics. Their influence, in particular, on the exciton spectra and transport will be discussed intensively in
While the theoretical foundations will be laid down in the next chapter in more detail, it is worthwhile for a glimpse over some features of the above mentioned competitions among the three different factors: excitonic couplings, thermal noises, and static disorder. To name a few, the most salient difference between absorption spectra of excitonic systems with and without couplings is the shift of the main absorption peaks, which in some cases can be differentiated with bare eyes seeing significant color changes. Whereas the noise and disorder enter in more subtle ways as affecting the line shapes of the peaks which can be systematically deconvoluted.

From the aspect of transport, in terms of excitons being carriers of energy from the absorbed photons, we once again see an interesting interplay between the three factors. While it is intuitive that the couplings, serving to delocalize exciton wavefunctions, helps out in transport, the roles the two localizing forces play are more than trivial. On the one hand, increasing magnitude of static disorder monotonically decreases the mobility. On the other hand, the study of transport in noisy environment has been a central focus in condense phase physics since Kramers's prediction of his celebrated turnover problem[14]: The rate of a particle escaping a local minimum increases in the weak noise regime, attains a peak value at a critical noise strength, and decreases in the strong noise regime.

In the remainder of this chapter we provide brief overviews of two families of material systems in which we will explore the spectroscopy and transport of molecular excitons: Pigment-protein complexes in photosynthetic organisms and self-assembled molecular aggregates. We are interested in these photophysical processes, where different combinations of the three key players determine the outcomes of such processes in the relevant parameter regimes.
1.2 Molecular Excitons in Real Systems

1.2.1 Pigment-Protein Complexes in Photosynthetic Systems

Advances in analytical chemistry and X-ray crystallography have rendered atomistic details of light-harvesting protein complexes available. The first one of them is the Fenna-Matthews-Olson (FMO) complex with its detailed structure revealed as early as 1975. And scores of other different complexes with ever increasing spatial resolution follow the track. This allows the photophysics of the complexes to be characterized, through molecular dynamics (MD) simulations and/or quantum chemical calculations, to an unprecedented degree that we have confidence in building theoretical models with minimal numerical cost without losing track of the essential physics and, perhaps more importantly, biology.

These pigment-protein complexes have a few things in common: A set of pigment molecules like bacteriochlorophylls residing in close proximity (typically tens of Angstroms) surrounded by protein residues. As such, the excited state manifold of the pigment molecules can serve as the system and vibrational modes from both the pigments and the proteins coupling to the prescribed molecular excited states can serve as the bath. As far as light-harvesting processes are concerned, we look for signs of how Nature perfects their efficiency and robustness in shaping the properties of both the system and the bath. While this pursuit is by itself scientific interesting, it also has the potential of unraveling certain routes for rationally designing artificial light-harvesters in the energy industry.

In the past decades there has been an intense interest on what role quantum coherence plays in natural photosynthesis since the pivotal work of Fleming et al.. In particular, it was found that there are long-lasting quantum beats of time-resolved spectral signals from the FMO complexes at physiological temperatures. Recently there are also studies disputing that the seen beats are not of biological relevance, [15, 16] We argue that regardless of the final answer to that question, the efforts devoted which paved the road for improved methodologies and deeper insights into understanding exciton dynamics in this context are certainly rewarding, as will be
covered partly in this contribution.

1.2.2 Excitonic Molecular Aggregates

Another enormous class of excitonic molecular systems are the molecular dye aggregates. In a broad sense this includes molecular crystals, thin films of such crystals with varying domain sizes or even amorphous samples of such, conducting polymers, and self-assembled aggregates. In this contribution we restrict ourselves to the last on the list except in Chapter 7, devoted to studying the relaxation of hot excitons in emissive conducting polymers.

In such restricted definition of a molecular aggregate, the constituent molecular dye is often an **amphiphile**, a molecule that is partly hydrophilic (water-loving) and partly hydrophobic (water-fearing), or simply a surfactant. It is known that surfactants are keen to form different structures ranging from micelles to lamella to minimal surfaces of exotic geometries and topologies, depending on the concentration and the competition between the hydrophilic and the hydrophobic forces.

Similar to the pigment-protein complexes, here one can also define the excitonic system being the excited state manifold of the comprising dye molecules and the vibrational modes of both the dyes and the solvent molecules constitute the bath. In contrary to the natural counterpart, the lacking of protein scaffoldings makes the determination of the aggregate structure a extremely delicate exercise: The dominating forces are the van der Waals force and in some cases $\pi-\pi$ stacking or hydrogen bonding, interactions that are on the same energy scale as thermal energy.

As a consequence, in many cases the structural stabilizing forces in self-assembled molecular aggregates win dominance by demanding a semi-crystalline formation, much similar to molecular crystals. However, the key difference herein is that such structures allow much stronger randomness and simultaneously reduced dimensionality. By former we refer to the DOFs that are less dominating in the potential energy landscape, for examples the conformations of the side chains or the exact positions of nearby solvent molecules. By latter we mean the overall geometry is oftentimes described by sheets, tubes, supercoils, helices and such, instead of a 3D crystal.
In the materials presented in this thesis, we shall explore different aspects of the above mentioned qualities of excitonic molecular aggregates. In particular, in the context of ordered aggregate structures with excitonic interactions, we put a strong emphasis on how the features of structural regularities and reduced dimensionality surface in the spectroscopy and transport properties.

1.3 Thesis Contribution

In this section we summarize the papers published and ones yet to be published that are included or not included in this thesis.

The following chapters have been published in peer-reviewed scientific journals, while the rest are in preparation.


The author also contributes to the following publications, not included in the thesis.

- Photochemical Control of Exciton Superradiance in Light Harvesting Nanotubes, *submitted* - fifth author
Chapter 2

Theoretical Background

In this chapter we lay down the theoretical materials that serve as a common basis for the thesis. We will start by defining the Hamiltonian for the system and the essential characteristics of its environment, the bath. We then introduce necessary concepts and useful machineries sequentially following the timeline of a molecular exciton. Starting from spectroscopic considerations where they are created, the excitons proceed to relax with the phonon environment that contains them. Typically one can define a timescale when the initial transient dynamics has decayed and a steady-state can be characterized, typically referred to exciton diffusion. At the end of the dynamics where the host material returns to the ground state, we look at the thermal state of the system from which either fluorescence emission, non-radiative quenching, or charge separation can take place.

2.1 Frenkel Exciton Hamiltonian

While we have been referring to the major quantity of interest of this thesis contribution to molecular excitons, it is necessary to clearly define in a more restrictive way what is really meant by such terms. Firstly we restrict to excitons with vanishing total spin, i.e. singlet excitons. The excitonic couplings among singlet excited states of different molecules are an electric dipolar form, given that the separation between the molecules are larger than their dimension. This is in contrast with triplet excitons,
excluded in this contribution, coupling through exchange interactions, which decays much faster as a function of inter-molecular separation.

As mentioned, an exciton is composed of a hole and an electron much like a hydrogen atom. Thus, the wavefunction of such an entity is a function of both the internal, relative position of the hole and the electron and the center-of-mass coordinate. The delocalization we referred to in the previous chapter corresponds to the extent of the wavefunction in terms of the latter. On the other hand, in the context of molecular excitons, it is useful to adopt the notion of classifying excitons basing on the internal coordinate. If the hole and the electron are tightly bound to the same molecule the exciton is referred to as a Frenkel exciton. Otherwise it is a charge-transfer exciton, referencing the fact that the positive and the negative charges are separate onto different molecules.

With this prior knowledge, we proceed to construct the basis that span the system Hilbert space. For an excitonic molecular aggregate comprising $N$ identical molecules we expect a Hilbert space of the size $2^N$, where each of the molecule can be either in the excited state or the ground state equivalent to a spin-1/2 system. We further constrain ourselves to the one-particle Fock space and write the system Hamiltonian as

$$\hat{H}_s = \sum_{n=1}^{N} |n\rangle \langle n| \epsilon_n + \sum_{n \neq m} |n\rangle \langle m| J_{nm}. \quad (2.1)$$

where the basis ket $|n\rangle$ refers to the state that all molecules being in the ground state except for the $n$th one. $\epsilon_n$ and $J_{nm}$ are the on-site energy of site $n$ and the excitonic coupling between sites $n$ and $m$, respectively. We should note that the restriction onto this $N$ dimensional space prohibits our discussions of photo-physical processes involving multiple excitons. Exciton-exciton annihilations are one such example. Hereon hatted quantities are reserved for operators, boldfaced ones are for vectors, and otherwise are scalars.

Here the system is completely specified by all the $N(N+1)/2$ matrix elements
\( J_{nm} = J_{mn} \) is enforced. Their actual values depend keenly on the geometry of the aggregates, the geometry of the molecules in question, and the nature of the excited states. In real samples of molecular aggregates one expects fluctuations of both the diagonal and the off-diagonal matrix elements. When the exciton dynamics of interest is considerably faster than such fluctuations, the randomness of \( \epsilon_n \) and \( J_{nm} \) is considered constant, referred to earlier as static disorder. In this limit, Schroedinger equation for the system can be directly integrated. The eigenvectors and the corresponding eigenvalues, referred to as the exciton states, obtained from diagonalizing \( H_s \) contain the full information content for predicting the excitonic properties

\[
|k\rangle = \sum_n \phi_n^k |n\rangle, \quad \epsilon_k = \langle k|H_s|k\rangle, \tag{2.2}
\]

where \( \phi_n^k \) is understood as the wavefunction amplitude of exciton state \( k \) at site \( n \).

### 2.2 System-Bath Models

However, the above static model for a molecular aggregate is rarely useful, given the fact that in the lifetime of a singlet molecular exciton, on the order of nanoseconds, many of the relevant vibrational DOFs would have relaxed. It is then necessary to consider the dynamics of these DOFs as the bath with respect to the system. The simplest non-trivial realization of a vibrational bath is one that is described by a collection of quantum harmonic oscillators of various frequencies,

\[
\hat{H}_b = \sum_i \omega_i \hat{b}_i^\dagger \hat{b}_i \tag{2.4}
\]

that are coupled linearly with the system

\[
\hat{H}_{sb} = \sum_{n,m} \sum_i g_{nm,i} (\hat{b}_n^\dagger + \hat{b}_n)|n\rangle \langle m|, \tag{2.5}
\]
where $\omega_i$ is the frequency and $\hat{b}_i^\dagger$ ($\hat{b}_i$) is the creation (annihilation) operator of oscillator $i$. Hereon we take the values of both reduced Planck constant and the Boltzmann constant to be unity, $\hbar = k_B = 1$. We further assume diagonal system-bath couplings, meaning the coupling terms

$$g_{nm,i} = \delta_{nm}g_{nn,i}. \quad (2.6)$$

Under the current approximations, the bath is essentially represented by the coupling terms $g_{nn,i}$. It is customary to replace the summation over the harmonic modes $i$ by integration over a continuous spectral density, $J_n(\omega)$, which is essentially the density of states of the bath weighted by coupling strength. For our purpose the spectral density is typically a simple analytic function specified by two parameters. One example is given by the exponential form

$$J(\omega) = \frac{\pi \lambda}{(n_b - 1)!} \left( \frac{\omega}{\omega_c} \right) e^{-\omega/\omega_c}, \quad (2.7)$$

where $\lambda = \int J(\omega)/(\pi \omega)$ is the reorganization energy, a measure of the overall system-bath coupling strength, and $\omega_c$ is the cut-off frequency, defining the timescale of the bath. $n_b$ specifies the scaling behavior of the system-bath coupling at low frequency: $n_b > 1$, $n_b = 1$, and $n_b < 1$ correspond to a super-Ohmic, an Ohmic, and a sub-Ohmic bath, respectively.

Since we are interested only the system dynamics and that the physical size of the bath is much larger than that of the system, it is customary to consider the influence of bath on the system as if the bath is always in its equilibrium, or the thermal state. This means that whenever the bath DOFs are considered, the state of which is completely defined by a certain temperature $T$. This will appear in our discussions of spectroscopy and relaxation in the next sections.

Equipped with the above specifications of the system-bath model, we are now in a position to look at the spectroscopy, relaxation, and transport of molecular excitons.
2.3 Linear Spectroscopy

The most accessible piece of information regarding spectroscopy is the linear spectra, including the absorption and the fluorescence emission. These two measure processes that connect the \( N \) dimensional single-exciton manifold, spanned by the basis kets \(|n\rangle\)'s, and the global ground state \(|0\rangle\) of the system. As such, the main character in this context is the so-called transition dipole operators

\[
\hat{\mu} = \sum_n \vec{\mu}_n (|0\rangle\langle n| + |n\rangle\langle 0|),
\]  

where \(\vec{\mu}_n\) is the transition dipole moment of molecule \(n\). In terms of the light-matter interaction, the dipole operators are those directly coupled to the electric component of the photon field, \(\hat{\mu} \cdot \vec{E}(t)\).

Following the standard textbook Golden rule expressions for the transitions between the ground and the excited state manifold, the linear spectra can be expressed as averages of the two-point time autocorrelation functions of the dipole operators in the interaction picture,

\[
\hat{\sigma}(t) = \langle \hat{\mu}(t)\hat{\mu}(0) \rangle_B, \quad (2.9)
\]
\[
\sigma(t) = \langle \hat{\sigma}(t) \rangle_S, \quad (2.10)
\]

where in the first line the spectrum operator \(\hat{\sigma}(t)\) is defined by the autocorrelation function with average over bath DOFs taken. While the final observable spectrum is defined as the Fourier transform of the scalar spectral function \(\sigma(t)\) after averaging over the system DOFs in the second line. Both averages deserve attention in our quest of understanding the spectral properties of molecular excitons.

So far we have not specified whether it is the absorption or the emissions spectra that we are looking at. The very distinction between the two stems from the definition of thermal state that the averages are taken. As stated in the previous section, the bracket in Eq. 2.9 is understood as taking average over bath DOFs in the thermal state, specified by the bath temperature. In the case of absorption spectrum, the
overall state of system plus bath is the direct product of the bath thermal state and
the system identity operator:

$$\hat{\rho}_b = \frac{e^{-\hat{H}_b/T}}{\text{Tr } e^{-\hat{H}_b/T}} \otimes \hat{I}_s. \quad (2.11)$$

On the other hand, the prerequisite of linear fluorescence emission for molecular
excitons is that the system is in full equilibrium with the bath while hosting a single
excitation. This requires the overall system plus bath state to be the full thermal
state of the two parts combined:

$$\hat{\rho}_{s+b} = \frac{e^{-(\hat{H}_s+\hat{H}_b+\hat{H}_{sb})/T}}{\text{Tr } e^{-(\hat{H}_s+\hat{H}_b+\hat{H}_{sb})/T}}. \quad (2.12)$$

In the limit of weak system-bath coupling, $\lambda \to 0$, the eigenstates of the system $|k\rangle$'s are a good reference for the thermal state, and the equilibrium populations of
the exciton states are Boltzmann-distributed. However, in intermediate or strong
system-bath coupling regimes this is not true and significant system-bath entangle-
ment follows. While in this contribution we do not explicitly discuss the consequence
of until in Chapters 5 and 6, the readers are referred to the discussion by Ma et al..
[17]

The average over system is understood as the summation over individual terms
in the light-matter interactions $\vec{\mu}_n \cdot \vec{E}$. Typically, the length scale of the molecular
system (nanometers) is much smaller than the wavelength of photons corresponding
to the ground and excited state energy gaps (microns). This means that the electric
component of the photon field can be treated as a uniform one. Be expressing the
dipole operator in the exciton state basis $|k\rangle$, we can then define the oscillator's
strength $f_k$ for each of the exciton state:

$$\vec{\mu}_k = \sum_n \phi_n^k \cdot \vec{\mu}_n, \quad (2.13)$$

$$f_k = |\mu_k|^2. \quad (2.14)$$
In the absence of thermal noise, the absorption spectrum is given by the superposition of $\delta$-peaks located at the eigenvalues $\epsilon_k$ with heights $f_k$, referred to as the stick spectrum. Otherwise Eq. 2.9 needs to be evaluated and line shape functions specific to the form of system-bath interaction arise, whose convolution with the stick spectrum gives the final spectrum,

$$A(\omega) \propto \sum_{k=1}^{N} f_k \delta(\omega - \epsilon_k). \quad (2.15)$$

Lastly, we will be frequently concerned with systems possessing translational symmetries. For such cases there are only a handful of exciton states with non-vanishing oscillator's strength owing to the Bloch theorem. This is sometimes referred to as the bright states in the far-field limit, and the criteria of being bright are called the selection rules. We will be revisiting these points in later chapters.

2.4 Relaxation and Transport

We now move on to the discussion of the actual dynamics of excitons. The selection rules of absorption of a particular molecular excitonic system define a unique initial condition, from which the exciton system relaxes by exchanging energy with the bath and approaches equilibrium. In the process of equilibration transport of exciton probability amplitude is possible. In particular, at the steady-state one typically finds diffusive transport, where the exciton motion is similar to that of a random walker on a lattice grid.

2.4.1 Relaxation in the Weak System-Bath Coupling Regime

The concept of thermal state is briefly reviewed in the previous section. We now investigate the process of relaxation connecting the initial condition of a system-bath state to the thermal equilibrium. While this is in general a formidable task in the realm of open quantum systems, where the focus has been the development of numerous non-perturbative methods since the seventies, in this contribution we will
restrict ourselves to the perturbative, weak coupling regime.

The dynamics of the system DOFs can be summarized by the reduced density matrix by tracing out the bath DOFs from the total density matrix, \( \rho_s(t) = \text{Tr}_b \rho(t) \). In general, given a separable the system-bath initial state, \( i.e. \) a direct product state, the system reduced density matrix evolves according to the Nakajima-Zwanzig equation of motion:

\[
\frac{\partial}{\partial t} \hat{\rho}_s(t) = -i \left[ \hat{H}_s, \hat{\rho}_s \right] + \int_0^t \mathcal{K}(t, t') \hat{\rho}_s(t') dt',
\]

(2.16)

where the first term describes the system Liouvillian dynamics and the memory kernel \( \mathcal{K} \) summarizes all system-bath correlations in the second term. This form of equations are sometimes referred to as quantum master equations.

The decaying time scale of the memory kernel, and consequently the numerical cost of propagating system dynamics, depends on the strength of the system-bath coupling and the timescale of bath DOFs. In the weak coupling regime and with no explicit time dependencies of the Hamiltonians, one can assume the Markovian approximation and the equation of motion reads

\[
\frac{\partial}{\partial t} \hat{\rho}_s(t) \approx -i \left[ \hat{H}_s, \hat{\rho}_s \right] + \mathcal{K}_M \hat{\rho}_s(t),
\]

(2.17)

where the kernel \( \mathcal{K}_M \) is interpreted as a superoperator acting on the reduced density matrix. Notice that the time integral of the second term is dropped and the evolution of the reduced density matrix depends only on its current value. As such, Markovian systems are memoryless accordingly.

As mentioned above, the weak coupling regime is synonymous to identifying the exciton states \( |k\rangle \)'s as a staging point of discussing system dynamics. The Redfield equation, derived from the above mentioned set of assumptions, \([18, 19]\) describing the dynamics of the reduced density matrix elements \( \rho_{kl}^{(s)} = \langle k | \hat{\rho}_s | l \rangle \) can be written as

\[
\frac{\partial}{\partial t} \rho_{kl}^{(s)} = -i \varepsilon_{kl} \rho_{kl}^{(s)} + \mathcal{R}_{kl, k' l'} \rho_{k' l'}^{(s)},
\]

(2.18)

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where $\epsilon_{kl} = \epsilon_k - \epsilon_l$ and $R_{kl,k'l'}$ is the Redfield tensor.

To proceed with the evaluation of the Redfield tensor, it is necessary to address a critical and convenient property of a bath consisting of a collection of quantum harmonic oscillators. Due to the Wick’s theorem[20], all dynamical processes near equilibrium obeying detailed balance of such harmonic DOFs can be summarized by the two-point autocorrelation function of some linear combinations of their creation and annihilation operators in the interaction picture. In our context it is most convenient to define a collective bath coordinate for site $n$: $\hat{B}_n = \sum_i g_{i,nn}(\hat{b}_i + \hat{b}_i^\dagger)$ such that the autocorrelation function reads

$$C_n(t) = \langle \hat{B}_n(t) \hat{B}_n(0) \rangle_b = \frac{1}{\pi} \int_0^\infty J_n(\omega) \left[ \coth \left( \frac{\omega}{2T} \right) \cos(\omega t) - i \sin(\omega t) \right] d\omega$$

Before we arrive at a working expression for the system dynamics in the weak coupling regime, a final digression on the physical interpretation of Eq. 2.18 is due. The diagonal elements of the reduced density matrix in the exciton basis are the populations of the exciton states, while the off-diagonal elements are the coherences between two states. Eq. 2.18 describes kinetic processes between all four combinations of population and coherence: population to population ($\rho_{kl}^{(s)} \rightarrow \rho_{kl}^{(s)}$), population to coherence ($\rho_{kl}^{(s)} \rightarrow \rho_{kl}^{(s)}$), coherence to population ($\rho_{k'l'}^{(s)} \rightarrow \rho_{kl}^{(s)}$), and coherence to coherence ($\rho_{kl}^{(s)} \rightarrow \rho_{kl}^{(s)}$). In solving Eq. 2.18 one readily finds that processes corresponding to finite $|\epsilon_{kl} - \epsilon_{k'l'}|$ involve integrals of rapid oscillations, which vanish on average. By disregarding these contributions we obtain the Markovian-Redfield dynamics in the secular limit, where populations and coherences are decoupled

$$\frac{\partial}{\partial t} \rho_{kk}^{(s)} = \sum_{l \neq k} W_{kl} \rho_{ll}^{(s)} - W_{kk} \rho_{kk}^{(s)},$$

$$\frac{\partial}{\partial t} \rho_{kl}^{(s)} = \left( -i\epsilon_{kl} + \frac{W_{kk} + W_{ll}}{2} \right) \rho_{kl}^{(s)}.$$
where

\[ W_{kl} = \sum_{n=1}^{N} |\psi_n^k \phi_n^l|^2 \frac{J_n(|\epsilon_{kl}|)}{e^{\epsilon_{kl}/T} - 1}, \]  
\[ W_{kk} = \sum_{l \neq k} W_{lk} \]  

are the relaxation rate matrix elements, which are strictly positive.

The implications of Eqs. 2.20 and 2.21 are clear: Given the initial condition, populations and coherences in the exciton basis evolve independently. Eq. 2.20 describes the conservative kinetics among the exciton states obeying detailed balance, that the ratio of the forward and backward rates between two states equals the ratio of their Boltzmann factors, \( W_{kl}/W_{lk} = \exp(\epsilon_{kl}/T) \). And the coherences oscillate at the frequency of the energy difference between the given two states while decay according to the outgoing population rates. This guarantees the reduced density matrix to be always positive semidefinite and the thermal state at \( t \to \infty \) is the Boltzmann distribution with vanishing coherences.

### 2.4.2 Steady-State Diffusive Transport

The relaxation processes of excitonic systems can often be separated into two regimes in time: the transient ballistic dynamics and the steady-state diffusive dynamics. In the former the exciton wavepacket evolves as if it is propagating through free space, while in the latter it moves more like a random walker. The definite character in distinguishing these two types of dynamics is conveniently given by the mean squared displacement (MSD)

\[ M(t) = \sum_n n^2 \cdot \rho^{(s)}_{nn}, \]  

where, for the sake of simplicity, we assume a one-dimensional lattice for the excitonic system that the site label \( n \) coincides with the coordinate of the site, and the reduced density matrix is evaluated in the site basis. The quantity of interest is the time
exponent when the difference of MSD between two times is fitted to a power-law expression

\[ M(t) - M(t') \propto t^\alpha. \]  

(2.25)

For free particle propagation \( \alpha = 2 \), and for a diffusive one \( \alpha = 1 \), while more subtle cases are also possible. For examples one finds a super-diffusive (sub-diffusive) motion for \( \alpha > 1 \) (\( \alpha < 1 \)). In higher dimensions MSD is a tensor by straightforward generalizations of Eq. 2.24. The prefactor in the diffusive case is proportional to the diffusion coefficient.

The transitions from ballistic to diffusive motion for an exciton is, naturally, of considerable interest. In terms of transport a ballistic movement is faster than a diffusive one in the long run, obviously. The time it takes from the initial transient dynamics to evolve into such transition is sometimes called the *dephasing* time, referring to the lack of coherent phase information for the particle wavefunction at different time and space. Thus the transition itself is also indicating the lost of quantum quality to a certain degree.

The cause of dephasing in our single-body context is thermal noise and static disorder. Only in a selective few cases this can be solved analytically\[21, 22\], that in general numerical evaluation of the dynamics is required. While it is in principle straightforward to compute \( \alpha \) directly from propagating the exciton dynamics, the numerical cost can be quite demanding, considering that one needs to avoid boundary effect which necessitates large sample sizes. Alternatively, one can calculate the diffusion coefficient by invoking the Green-Kubo relation

\[ D = \frac{1}{\text{Tr}} \int_0^\infty \langle \hat{j}(t)\hat{j}(0) \rangle_s dt, \]  

(2.26)

where \( \hat{j} = i[\hat{H}_s, \hat{n}] \) is the flux operator in the interaction picture and \( \hat{n} = \sum_n n\langle n|n| \) is the position operator. The advantages of utilizing Eq. 2.26 include not having to wait for the ballistic-diffusive transitions and faster sample size convergence.
2.4.3 Generalized Förster-Type Transfer

There is a particular type of diffusive transport that deserves special attention. There are systems with constituent sites categorized into groups, where the excitonic interactions are strong within the groups and weak among different groups. In photosynthetic organisms the groups within an exciton-harvesting network are individual pigment-protein complexes. And examples of artificial molecular systems include conjugated polymers with strong in-chain and weak cross-chain couplings and molecular crystals/aggregates with strong anisotropy.

Under the prescribed situations one expects the timescales for thermalization within and across the groups to be separated. In other words, the transfer of excitons (energies) from one group, referred to as the donor, to another group, the acceptor, takes place with full thermalization within the donor group with little quantum coherence between the donor and the acceptor. This is called Förster resonance energy transfer (FRET), after the pioneering work of Förster in 1948[23]. The FRET rate from a donor to an acceptor can expressed as

\[ k_{\text{FRET}} = \frac{1}{2\pi} J_{\text{DA}}^2 \int E_D(\omega)A_A(\omega) d\omega, \tag{2.27} \]

where \( J_{\text{DA}} \) is the excitonic coupling between the donor and the acceptor, and \( E_D(\omega) \) and \( A_A(\omega) \) are the donor emission and the acceptor absorption spectra, respectively.

In the case where both the donor and the acceptor are monomeric, the quantities involved in Eq. 2.27 have straightforward interpretations: \( J_{\text{DA}} \) is the scalar excitonic coupling and both \( E_D(\omega) \) and \( A_A(\omega) \) are the far-field spectra. Since the latter are experimentally measurable and the former is inversely proportional to the donor-acceptor separation \( R_{\text{DA}} \) cubed (excitonic couplings are of dipolar form), Eq. 2.27 finds wide use in the context of biophysics where the dynamics of large biomolecules with fluorescent dyes attached can be monitored through the quantum yield of the donor emission[24, 25].

The situation becomes more interesting beyond the monomeric case. Sumi[26] recognizes that when the physical size of the donor/acceptor group is comparable
to separation $R_{DA}$ between them, which applies to the examples mentioned above, two important points need to be addressed. Firstly the dipolar form of the excitonic coupling $J_{DA}$ no longer holds, and finer details of the molecular geometry other than dipolar orientation and the separation $R_{DA}$. As a consequence, the spectra $E_D$ and $A_A$ are also not the experimental measurable far-field ones anymore. This indicates that the selection rules are altered and dark states that do not contribute to energy transfer in the far-field limit now play a role. In essence one needs to consider the near-field effects. The rate of transfer between the donor and the acceptor groups can be written as

$$k_{FRET} = \frac{1}{2\pi} \int \text{Tr} \  \hat{J}^T \hat{E}_D(\omega) \hat{J} \hat{A}_A(\omega) d\omega,$$

(2.28)

where $\hat{J} = \sum_{nm} J_{nm} |n_D\rangle \langle m_A|$ is the excitonic coupling operator and the spectral operators are given by Eq. 2.9, where the thermal states being averaged over with are given by Eqs. 2.12 and 2.11 for $\hat{E}_D$ and $\hat{A}_A$, respectively.

While Eq. 2.28 does come to the rescue of the original FRET rate Eq. 2.27 in terms of the above mentioned two points, there is an additional new piece of physics that we have not covered. Since the thermal state of the donor is one with full system-bath Hamiltonian, the stronger the donor system-bath coupling ($\hat{H}_{sb}^{(D)}$), the larger deviation from the selection rule dictated by the donor system Hamiltonian ($\hat{H}_s^{(D)}$). This is understood as a different mechanism of the breakdown of selection rules, or dark states brightening, than the near-field effect mentioned above. We, again, shall return to this in the later chapters.
Chapter 3

Scaling Relations and Optimization of Excitonic Energy Transfer Rates between One-Dimensional Molecular Aggregates

In this chapter we study the distance, chain length, and temperature dependence of the electronic couplings as well as the excitonic energy transfer rates between one-dimensional (1D) chromophore aggregates. In addition to the well known geometry dependent factor that leads to the deviation from Förster's classic $R_{DA}^{-6}$ scaling on the donor-acceptor separation, non-monotonic dependence on aggregate size and the breakdown of far-field dipole selection rules are also investigated in detail and compared to prior calculations. Our analysis provides a simple, unifying framework to bridge the results of the ground state electronic couplings at low temperatures and those from the classical rate-summation at high temperatures. At low temperatures and in the near-field limit, the exciton transfer integral scales as $R_{DA}^{-1}$, in analogy to that of electric monopoles. For the case of aligned 1D J-aggregates we predict a maximal excitonic energy transfer rate at temperatures on the order of the intra-aggregate coupling strength.
3.1 Introduction

More than half a century after its development, the theory of Förster resonance energy transfer (FRET) has received increased attention in the field of condensed matter sciences owing to technological advances to manipulate molecules on the nano scale and to decipher the molecular details of important biological systems. The FRET theory has found wide applications in the study of conformational dynamics and excitation energy transfer (EET) of polymers, be it biological systems like DNA and proteins or artificial ones with promising physical properties such as conjugated polymers[27]. The popularity and success of the FRET theory can be ascribed to an insightful approximation made by Förster: treating the Coulomb interaction between the donor-acceptor pair only to the second order, which can then be expressed in terms of the respective transition dipole moments. By incorporating the square of the donor (acceptor) transition dipole into the expression of the donor emission (acceptor absorption) spectrum, the FRET rate is conveniently written down as a combination of experimental measurables, in particular the overlap between the donor's emission spectrum and the acceptor's absorption spectrum. Furthermore, it gives rise to the classic $R_{DA}^{-6}$ dependence on the donor-acceptor separation $R_{DA}$ of the EET rate, which is a manifestation of the dipolar interaction as well. As a consequence, variations of the measured FRET rate (in time) imply variations of the chromophoric donor-acceptor separation to the sixth power. See some of the recent reviews for more in depth discussions[27, 25, 28, 29, 30].

However, the validity of Förster's original theory is questionable in numerous circumstances. Sumi[26] was the first to point out that in multichromophoric (MC) systems, where the exciton may be delocalized over several chromophores, considerable contributions to exciton transport arise from optically dark states. While this situation is typical in the light-harvesting apparatus of photosynthetic bacteria and green plants, as well as synthetic molecular systems such as organic photovoltaic systems and the low-dimensional aggregates formed by amphiphilic cyanine dyes[31], the FRET theory can critically underestimate the EET rate[27, 26]. The essential point
is that in many cases the physical dimension of aggregates is comparable to or exceeds the separation $R_{\text{DA}}$. This leads to the failure of the dipole approximation. Recently, we developed numerical and analytical methods to systematically evaluate EET rates in multichromophoric systems. For the current study, we will adopt physical approximations to establish scaling laws and refer readers to a series of papers for details of rate calculations[17].

In a recent work by Emelianova et al., the authors considered the energy diffusion in organic molecular crystals[32]. Due to the reduced energetic disorder in these materials, 2D-delocalized excitons were proposed as primary agents for EET, where the reduced dimensionality results from the high anisotropy in electronic couplings: strong couplings in the $ab$ plane while couplings between layers are considerably weaker. They found a peculiar temperature dependence of the interlayer EET rate, namely for the J-aggregate configuration the rate is peaked at intermediate temperatures as opposed to the monotonic behavior for the H-aggregate case. This can be attributed to the contribution from the optically forbidden states that are close to the bottom of the exciton band, which also leads to the deviation from the $R^{-4}$ scaling of the interlayer coupling obtained with classical theory[33]. The peaking of the EET rate at an optimal temperature originates from the maximal overlap between the thermal population distribution of exciton states and the EET rates among individual donor-acceptor states[34]. This is one of the many aspects of achieving efficient and robust EET through optimal system-bath interactions[34, 35, 36], which are often found in natural light-harvesting systems and have profound implications on improving current solar energy industry.

The present work concerns a similar scheme with a change in dimensionality. We look at the EET between close-lying 1D chromophore aggregates, see the schematics in Fig.3-1[37]. This is in part motivated by the technological advancement of manufacturing devices containing aligned conjugated polymers[38] as well as growing single-crystalline organic thin films[39]. In such cases, the EET in the direction perpendicular to the stronger-coupled dimension becomes a central issue in controlling the anisotropy of the devices. For example, anisotropy of exciton transport
has been observed in phthalocyanine and porphyrin derivatives thin films [40]. Clear indication of faster exciton diffusion within 1D columnar aggregate structures and slower inter-stack exciton transfer was characterized through analyzing the fluorescence anisotropy decay of the systems [41, 42, 43]. On the other hand, there are several previous studies on the photophysics of conjugated oligomers/polymers [44, 45, 24, 46], where non-monotonic dependence on chain length and deviation from the \( R^{-6} \) scaling were observed. It should be noted that analytical results for this system have been obtained in the zero-temperature limit [47, 48], which are valid for conjugated polymers/oligomers since the gaps between exciton levels are much larger than the thermal energy in these systems.

Here we extend the analysis of Emlianova et al. to the EET in these 1D systems and obtain closed expressions for the transfer integrals as functions of the quasi-momenta of the 1D excitons. We first discuss the classical results obtained with the sum-over-rates approach. The corresponding quantum results, which account for the electronic couplings among all states of the donor and the acceptor aggregates, are presented thereafter. The proper recovery of the classical expression is presented and discussed, as well as its use to explain prior observations with emphasis on the scaling relations and temperature dependence of EET rate.

### 3.2 Classical FRET: Sum over Rates

Let us first consider the classical FRET rates between linear aggregates consisting of identical chromophores, whose results shall serve as references in the following sections. Treating all the chromophores as two level systems, the coupling Hamiltonian is written as

\[
H_{DA} = \sum_{m=1}^{N_D} \sum_{n=1}^{N_A} J_{mn} |m\rangle \langle n|,
\]

where for notational simplicity \( m \) (\( n \)) always refers to the site label of the donor (acceptor) aggregate, and \( |x\rangle \ (x = m, n) \) represents the state where the \( x^{th} \) site is in
its excited state and all others being in the ground state. \( N_\text{D} \) and \( N_\text{A} \) are the number of monomers in the donor and the acceptor aggregates, respectively. The couplings \( J_{mn} \) will be approximated by dipole-dipole interaction

\[
J_{mn} = \frac{\vec{\mu}_m \cdot \vec{\mu}_n}{r_{mn}^3} - 3 \frac{(\vec{\mu}_m \cdot \vec{r}_{mn})(\vec{\mu}_n \cdot \vec{r}_{mn})}{r_{mn}^5},
\]

with \( \vec{\mu}_m \) and \( \vec{\mu}_n \) being the transition dipole moments and \( r_{mn} \) the distance between sites \( m \) and \( n \) of the respective aggregates. The magnitudes of the dipole moments are set to unity. The FRET rate between the donor and the acceptor aggregates is written down as a summation over the individual rates of all donor-acceptor pairs, regardless of the intra-aggregate couplings, as follows\cite{27}

\[
k_C = \frac{2\pi}{\hbar} \frac{1}{N_\text{D}} \sum_{m=1}^{N_\text{D}} \sum_{n=1}^{N_\text{A}} J_{mn}^2 S_{mn}.
\]

Here \( S_{mn} \) denotes the overlap integral between the lineshapes of monomer \( m \) and \( n \). The above expression indicates that no coherence exists between any two sites, and at high temperatures the quantum expression discussed in the next section should reduce to this classical one. In addition, treating \( S_{mn} \) as constants, we focus our study essentially on the inter-aggregate couplings \( J_{mn} \). The latter has the unit of energy squared, where we have set \( \mu^2/4\pi\epsilon_0 \) to unity and left only the distance dependence explicit. To get the physical EET rate one has to return to Eq.(3.3) and pick up suitable estimations of the above mentioned parameters as in Ref.[32]. Also, the \( N_\text{D}^{-1} \) factor corresponds to an average over all donor chromophores, accounting for an equal distribution of the initial excitation.

In this study we will consider a convenient setup of system geometries, as shown in Fig.3-1. Two extreme cases are considered, in (a) the two linear chromophoric aggregates are aligned in parallel with all the transition dipole moments pointing along the axis of aggregation, while in (b) the dipoles are perpendicular to the axis.

\footnote{The entity \( S_{mn} \) should not be confused with the overlap integral of the donor emission and the acceptor absorption spectra, which contain the information of oscillator strengths of respective species. It is of the unit of inverse energy. See the discussion in Ref.[27] and Ref.[24].}
in the plane of paper. We refer to the former as a perfect J-aggregate and the latter as a perfect H-aggregate for obvious reasons. For simplicity we set \( N_D = N_A = N \).

Discussions on a more general scheme are presented in the Appendix. In the following \( R \) denotes the separation between the aggregates. In the continuum limit (\( R \gg a \), where \( a \) is the intra-aggregate spacing) and taking \( S_{mn} \) as constants one can write

\[
k_C^{(J)} \propto \frac{1}{N} \int_{0}^{N} dx_1 \int_{0}^{N} dx_2 \left[ \frac{R^2 - 2a^2(x_1 - x_2)^2}{(R^2 + a^2(x_1 - x_2)^2)^{5/2}} \right]^2
\]

\[
= \frac{2}{N} \int_{0}^{N} dx (N - x) \frac{(R^2 - 2a^2x^2)^2}{(R^2 + a^2x^2)^5}
\]

\[
= \frac{27}{64aR^5} \arctan \left( \frac{Na}{R} \right) + \frac{11}{64R^4(N^2a^2 + R^2)} + \frac{1}{32R^2(N^2a^2 + R^2)^2} + \frac{3}{8(N^2a^2 + R^2)}
\]

Figure 3-1: System geometries examined in this study. (a) Energy transfer between two linear aggregates with all the transition dipole moments parallel to the axis of aggregation. This is referred to as a perfect J-aggregate. (b) Parallel linear aggregates with transition dipole moments perpendicular to the direction of aggregation and lying in the plane of super-aggregate structure. This is referred to as a perfect H-aggregate. In both cases \( R \) is the separation between the aggregates, \( a \) is the intra-aggregate spacing between chromophores, and \( N \) is the number of chromophores in each aggregate.

While the above result is complicated, it reduces to simple classical results in the two opposite limits as follow

\[
k_C^{(J)} \propto \begin{cases} \frac{27\pi}{128aR^5}, & R \ll Na \\ \frac{N}{R^6}, & R \gg Na. \end{cases}
\]

Upon inspection of the above results, a few rationalizations are drawn. First of
all, in the far-field limit where the separation is much larger than the length of the aggregates, the well known $R^{-6}$ dependence is recovered, while in the opposite, near-field limit the rate scales as $R^{-5}$, reflecting the one dimensional geometry. Secondly, the factor of $N$ in the far-field result comes from the number of acceptors, whereas there is no $N$ dependence in the near-field limit. This results from the fact that we are essentially looking at the dipolar interaction (squared) between a monomer and a one dimensional chain of dipoles, which is really a result of classical electrostatics.

Similarly one finds the results for perfect H-aggregates as

$$k_{C}^{(H)} \propto \begin{cases} \frac{123\pi}{128a} \frac{1}{R^5}, & R \ll Na \\ \frac{4N}{R^6}, & R \gg Na. \end{cases}$$ (3.6)

These results serve as our guideline for the quantum calculation of the EET rates, which in the high temperature limit should reduce to the former.

### 3.3 Quantum FRET: Sum over Dipoles

The starting point of our investigation of the EET rates between chromophoric aggregates is the multichromophoric FRET rate in the secular approximation,

$$k_Q = \frac{2\pi}{\hbar} \sum_{\mu=1}^{N_D} \sum_{\nu=1}^{N_A} \left| \sum_{m=1}^{N_D} \sum_{n=1}^{N_A} J_{mn} C_{\mu m} C_{\nu n}^{*} \right|^2 S_{\mu \nu} \rho_{\mu} \tag{3.7}$$

$$= \frac{2\pi}{\hbar} \sum_{\mu=1}^{N_D} \sum_{\nu=1}^{N_A} |J_{\mu \nu}|^2 S_{\mu \nu} \rho_{\mu}, \tag{3.8}$$

which is obtained by approximating the donor emission and the acceptor absorption spectra being diagonal in the exciton basis[26]. $C_{\mu m}$ is the wavefunction amplitude of exciton state $\mu$ on site $m$. $J_{\mu \nu}$ and $S_{\mu \nu}$ refer to the electronic coupling and the lineshape overlap matrix elements in the exciton basis, respectively. $\rho_{\mu}$ is the probability density distribution of the donor. We adopt the convention where Roman letters
represent dummy indices in the site basis while Greek letters are reserved for those in the exciton basis.

At high temperatures, the lineshape overlap $S_{\mu\nu}$ can be treated as unity. In other words, the homogeneous linewidth is broader than the exciton bandwidth. Thus, by expanding the absolute square in Eq.(3.7), one can show that the MC-FRET expression reduces to the classical FRET expression as follows.

$$k_Q \approx \sum_{m,m'=1}^{N_D} \sum_{n,n'=1}^{N_A} (\sum_{\mu=1}^{N_D} C_{m\mu}^\mu C_{m'}^{\mu*}) (\sum_{\nu=1}^{N_A} C_{n\nu}^\nu C_{n'}^{\nu*}) J_{mn} J_{m'n'}$$

$$= \sum_{m,m'=1}^{N_D} \sum_{n,n'=1}^{N_A} \rho_{mm'} \delta_{nn'} J_{mn} J_{m'n'}$$

$$= \text{Tr} \rho |J|^2 = k_C. \quad (3.9)$$

We now analyze the actual quantum expression in more detail. For long linear chromophoric chains intended in this study, neglecting disorder, the exciton states are given by the Bloch states $|\mu\rangle = (1/\sqrt{N}) \sum_{m=1}^{N} \exp \left( 2\pi i \mu m / N \right) |m\rangle$. This is true as long as the intra-aggregate Hamiltonians $H_D$ and $H_A$ commute with the translational symmetry of the system. In this basis the coupling matrix is diagonal $J_{\mu\nu} = \delta_{\mu\nu} J_{\mu\nu}$[37], regardless of the type of aggregates (J- or H-). In the following we will focus on the calculation of $J_{\mu\nu}$ for both perfect J- and H-aggregates. In the continuum limit this is equivalent to the evaluation of the integrals

$$J_{\mu\nu}^{(J)} = \frac{2}{N} \int_{0}^{N} dx (N-x) \frac{R^2 - 2a^2x^2}{(R^2 + a^2x^2)^{5/2}} \cos \left( \frac{2\pi \mu x}{N} \right), \quad (3.10)$$

and

$$J_{\mu\nu}^{(H)} = \frac{2}{N} \int_{0}^{N} dx (N-x) \frac{a^2x^2 - 2R^2}{(R^2 + a^2x^2)^{5/2}} \cos \left( \frac{2\pi \mu x}{N} \right). \quad (3.11)$$
3.3.1 $J_{\mu\mu}$ with $\mu = 0$

For the case of $\mu = 0$ the integrals can be carried out straightforwardly.

$$J^{(1)}_{\mu=0} = \frac{2}{Na^2} \left( \frac{1}{R} - \frac{1}{\sqrt{R^2 + N^2a^2}} \right) = \begin{cases} \frac{2}{Na^2 R}, & R \ll Na \\ \frac{N}{R^3}, & R \gg Na, \end{cases} \quad (3.12)$$

which has been obtained previously[47, 48]. Here we will iterate its significance and physical interpretation, in conjunction with our $\mu \neq 0$ results discussed below, for a comprehensive understanding. See Fig.3-2. The $R$ dependence is drawn in part (a), with the near- and the far-field limits indicated in dashed and dotted lines, respectively. While the far-field result $R \gg Na$ indeed corresponds to the classical $R^{-3}$ scaling in Eq.(3.5), the near-field limit is particularly interesting. The $R^{-1}$ scaling can be rationalized as the destructive interference between contributions from adjacent monomers[35, 36], leaving only the couplings between monopoles at the both ends. This is valid in the regime where $Na \gg R > a$, and is shown schematically in Fig.3-3(a). Through the successive cancellation of contributions from adjacent, opposite charges, we are left with the interactions among the ones at the very tails of the chains, which obey the $R^{-1}$ dependence of monopolar field.

Another interesting point worth noting is the $N$ dependence of the above expressions in Eq.(3.12), as shown in Fig.3-2(b). It is evident that in the far-field limit the coupling is simply proportional to $N$. However, the inverse proportionality in the near-field limit can be understood from the argument of the effective monopole interactions made in the previous paragraph, in combination with the fact that the monopole charges scale inversely proportional to the square root of $N$, owing to the amplitude of the wavefunction on each site. The opposite dependence on $N$ in the two limits implies an optimal coherence length which can be obtained from maximizing
Figure 3-2: $R$ and $N$ dependence of $|J_{J=0}^{(j)}|^2$. (a) $R$ dependence, both axes are in log scale. In accordance to the asymptotic limits shown in Eq.(3.12), the quantity scales as $R^{-2}$ and as $R^{-6}$ in the near- and the far-field limits, respectively. (b) $N$ dependence, both axes are in linear scale. The square coupling diminishes at both ends of the $N$ axis and reaches a maximum at $N = N_m$ given $R$.

Figure 3-3: Schematic illustrations of effective interaction between the exciton ground states of different geometries. (a) Effective interactions between linear aggregates. (b) Effective interactions between a single chromophore and a linear aggregate.

Eq.(3.12):

$$N_{\text{max}} = \sqrt{\frac{1 + \sqrt{5}}{2} \frac{R}{a}} \approx 1.27 \frac{R}{a},$$

(3.13)
where one obtains maximal coupling. We acknowledge that this result was adopted
from Eq.(33) of Ref.[23], included here for the completeness of our discussion. This
is also a manifestation of the quantum interference among different donor-acceptor
pairs, since classically one expects a linear dependence on system size regardless of
the ratio between Na and \( R \). This agrees with the results of Brédas et al.[44] who
quantitatively studied the \( R \) and \( N \) dependence of the exciton coupling between
close-lying polyacetylene molecules in a similar scheme, in line with the earlier work
of Spano and coworkers[46].

Rossky et al., using semiempirical Pariser-Parr-Pople Hamiltonian on the level of
single configuration interaction, have calculated the EET rate between tetraphenyl-
porphyrin and oligofluorene[24]. In this case the system resembles a monomer in-
teracting with a linear chain of chromophores. They showed that the \( R \) dependence
of the rate becomes weaker as \( R \) reduces, and reaches \( R^{-2} \) at the nearest distances
allowed by steric hindrance. With minor modification of our result, it can be shown
that the coupling \( J^{(J)}_{\mu=0} \) of the totally symmetric exciton state with the monomer at
distance \( R \) equals

\[
J^{(J)}_{\mu=0} = \begin{cases} \frac{8}{N^{5/2}a^3}, & R \ll Na \\ \frac{\sqrt{N}}{R^3}, & R \gg Na, \end{cases}
\]

which indeed shows no dependence on \( R \) in the near-field limit and an \( R^{-1} \) one in the
small-intermediate \( R \) regime. This can also be understood through a similar argument
of destructive quantum interference, as shown in Fig.3-3(b). Here the monomer feels
an effective, nearly uniform field created by the opposite charges at the ends of the
chain. As such, one obtains the independence on \( R \) when \( R \ll Na \). Similar to
the case of parallel 1D chains as discussed earlier, there is also a non-monotonic \( N \)
dependence, and an optimal chain length is given by

\[ \hat{N}_{max} = \frac{2R}{\sqrt{\alpha a}} \approx 0.89 \frac{R}{a}. \]  

We note that there is a recent experimental study considering an artificial system comprises chromophoric molecules intercalated onto linear DNA scaffold, which is covalently bonded to a porphyrin acceptor anchored on lipid vesicles\[49\]. The authors found enhanced absorption of the whole complex comparing to the direct excitation of the porphyrin due to the antenna effect. Our analysis above can be applied directly to this system, that given the monomer-chain separation one can determine an optimal chain length that maximizes the EET rate.

### 3.3.2 $J_{\mu\mu}$ with $\mu \neq 0$

To obtain closed expressions for $J_{\mu\mu}$ in general, additional assumptions need to be made. Explicitly, we drop the $-x$ in the parentheses and extend the upper limit of integration to infinity in Eqs.\(3.10)\) and \(3.11). In doing so we essentially assume the long chain limit, and the following expressions can be obtained.

\[ J^{(j)}_{\mu\mu} \approx \frac{8\pi^2 \mu^2}{N^2 a^3} K_0(\tilde{\mu}), \]  

and

\[ J^{(H)}_{\mu\mu} \approx -\frac{4\pi^2 \mu^2}{N^2 a^3} [K_0(\tilde{\mu}) + K_2(\tilde{\mu})], \]  

where $K_\alpha$ is the modified Bessel function of the second kind and $\tilde{\mu} = 2\pi |\mu| R / Na$. These are the main results of the current study. Taking the long chain limit of Eq.\(3.12), one obtains vanishing $J^{(j)}_{\mu=0}$, which agrees with the above expression and can be attributed to the fact that $K_0$ diverges logarithmically at the origin. However $K_\alpha(z)$ with $\alpha > 0$ diverges as $z^{-\alpha}$, thus $J^{(H)}_{\mu=0}$ has a finite value. On the other hand, in the $R \gg Na$ limit the above expressions reduce to a delta function at $\mu = 0$, which is the correct far-field selection rule. This correctness arises from the fact that
the seemingly contradicting application of the long chain limit and then the $R \gg Na$ limit does not spoil the $\mu$ dependence qualitatively. Thus, the strength of the selection rule is easily seen as a function of $R$ with Eq.(3.16).

![Figure 3-4: (a) Dependence of the inter-aggregate coupling on the exciton state label $\mu$ (quasi-momentum). Here only the case for J-aggregates $J^{(J)}_{\mu\mu}$ is shown. The results from the exact summation of Eq.(3.8) (blue circles), the numerical integration of Eq.(3.10) (green squares), and the analytical expressions Eq.(3.16) (red line) and (3.18) (cyan dashed line). The maximum happens at $\mu_m \approx 3Na/4\pi R$. We have taken $N = 200$ and $R = 5a$. Only half of the first Brillouin zone is plotted since $J_{\mu\mu}$ is symmetric with respect to $\mu = 0$. (b) The temperature dependence of the overall transfer rates calculated through Boltzmann averaging over all states. Hollow markers refer to those of the perfect J-aggregates, and filled ones the perfect H-aggregates. The rates are normalized to their values at infinite temperature, where all states contribute equally. The temperature is in units of the nearest-neighbor intra-aggregate coupling $J_{n-n}$ over Boltzmann constant $k_B$. Circles, squares, and triangles represent the rates when the inter-aggregate separation $R$ is equal to 1, 1.5, and 2 times of the intra-aggregate spacing $a$, respectively. In this figure the aggregate size $N$ is set to 100.

For a more intuitive physical picture, we make use of the asymptotic form of the Bessel function $K_\alpha(z) \approx \sqrt{\pi/2z} \exp(-z)$ and obtain

$$|J_{\mu\mu}| = \frac{4\pi^2}{\sqrt{a^5 R}} \left( \frac{|\mu|}{N} \right)^{3/2} e^{-2\pi |\mu|R/Na}, \quad (3.18)$$

which indicates a polynomial $\mu$ dependence with exponential cutoff, with the maximal value occurs at $\mu_{\text{max}} = 3Na/4\pi R$. It is worth noting that since we retain only the zeroth order term in the asymptotic expansion, Eq.(3.18) works for both the perfect
J- and H-aggregates. However the $K_2$ term in the H-aggregates case decays much faster than $K_0$. Consequently, the true peak value of $J^{(H)}_{\mu\mu}$ occurs at $\mu \ll N$, i.e. the major contribution to the EET rate comes from the $\mu = 0$ state, which is the highest lying state for H-aggregates.

The feature of a maximal coupling at a finite quasi-momentum $\mu = \mu_{\text{max}}$ is especially prominent when the inter-aggregate separation $R$ is comparable to the intra-aggregate spacing $a$. See Fig.3-4(a) for illustration. Here we present the results from the exact sum of $J^{(J)}_{\mu\mu}$, the numerical integration of Eq.(3.10), and its continuum approximated expressions Eq.(3.16) and (3.18). The approximations invoked in obtaining the closed expressions are validated by the close match of these results. We note that in the limit of $\mu \rightarrow N/2$, the above mentioned results trifurcate due to: the difference between the exact summation and numerical integration, and the error originating from dropping the $-x$ term in Eq.(3.10). This is similar to the 2D case investigated by Emelianova et al.[32], which leads to the possibility of tuning the exciton hopping rate as a function of temperature, given a particular system geometry.

Along the same line, we also present here the temperature dependence of the total transfer rates at several different separations $R$ as shown in Fig.3-4(b). The eigenenergies of the aggregates are obtained by assuming all intra-aggregate interactions to be dipolar. Here we neglect the contribution from the spectral overlap between the donor and the acceptor, and compute the EET rate purely on the basis of Boltzmann averaging over all states. Regardless of $R$, the EET rate between perfect H-aggregates is always a monotonically increasing function of temperature, as the only contributing states are at the top of the exciton band. On the other hand, the perfect J-aggregate case shows more interesting behavior. The rate shows a peak value at around $T_m \approx J_{n-n}/k_B$ for $R > a$ cases. This is attributed to the interplay between the thermal population of the exciton band (see Ref.[50] for detail) and the functional form of $J^{(J)}_{\mu\mu}$. At low temperatures, none of the contributing states is occupied and the EET is suppressed. The rate rises at moderate temperatures and reaches the peak value when there is significant overlap between the Boltzmann
distribution and $J_{\mu\mu}^{(j)}$, and then decays at higher temperatures due to the population spread to higher-lying non-contributing states.

We note that very similar non-monotonic behavior has been observed previously through the model study on the HJ-aggregates by Spano et al.[51]. They found peaked radiative decay rates of stacked conjugated polymer dimers at temperatures where $k_B T \approx J_{\text{inter}}$ ($J_{\text{inter}}$ denotes the inter-polymer excitonic coupling). We remark that not only the EET rates but also other spectroscopic properties of this interesting system setup show rich physics. This has implications on how we can design and control the energy migration pathways in low dimensional systems such as dye aggregates and thin films[34, 35, 40, 41, 42, 43].

Lastly, in the high temperature limit where all states in the exciton band are equally populated, the average EET rate should recover the classical FRET result. This is demonstrated as follows.

$$
\frac{1}{N} \sum_{\mu} |J_{\mu\mu}^{(j)}|^2 \approx 2 \int_0^{\infty} d\mu \left[ \frac{8\pi^2 \mu^2}{N^2 a^3} K_0 \left( \frac{2\pi |\mu| R}{Na} \right) \right]^2 = \frac{27\pi}{128a} \frac{1}{R^5},
$$

which coincides with the result in Eq.(3.5), as predicted by Eq.(3.9). The same argument applies to the perfect H-aggregates case as well.

### 3.4 General Considerations of Parallel Dipole Chains

![Figure 3-5](image_url)

Figure 3-5: Additional system geometries considered in the Appendix. (a) A pair of perfect H-aggregates with their dipole orientations turned perpendicular to the plane of the aggregates. (b) General 1D linear aggregates with slanted dipole orientations, making an angle $\theta$ with the axis of aggregation.
3.4.1 Perfect H-Aggregates: Another Possibility

In the main text we have explained only one of the two possible relative orientations for perfect H-aggregates. Explicitly, the configuration with all dipoles lying within the plane of the pair of the chains was chosen. There is another possibility with all dipoles pointing outward (or inward) of this plane. In other words the second case is obtained by rotating the dipoles ninety degrees with respect to the axes of aggregation, see Fig.3-5(a). The dipolar interaction between such two perfect H-aggregates has a particularly simple form:

\[ J_{mn}^{(H)} \left( \frac{\pi}{2}, \frac{\pi}{2} \right) = \frac{1}{r_{mn}^3}, \]  

(3.20)

where the arguments in the expression \( J^{(H)}(\phi_1, \phi_2) \) represent the azimuthal angles of the two aggregates, so that the case discussed in the main text is denoted as \( J^{(H)}(0, 0) \).

In the Bloch basis the coupling becomes

\[ J_{\mu\nu}^{(H)} \left( \frac{\pi}{2}, \frac{\pi}{2} \right) = \delta_{\mu\nu} \frac{4\pi|\mu|}{N a^2 R} K_1(\tilde{\mu}). \]  

(3.21)

In the high temperature limit, the even averaging over all states of the above result reduces to the classical value of \( 3\pi/8aR^5 \).

We note that the cross term \( J^{(H)}(0, \pi/2) \) vanishes. As a consequence, the electronic coupling between perfect H-aggregates with arbitrary configuration \((\phi_1, \phi_2)\) can be written as

\[ J^{(H)}(\phi_1, \phi_2) = \cos \phi_1 \cos \phi_2 J^{(H)}(0, 0) + \sin \phi_1 \sin \phi_2 J^{(H)} \left( \frac{\pi}{2}, \frac{\pi}{2} \right). \]  

(3.22)

This works in both site and Bloch basis, except that there is an additional diagonal selection rule in the latter.
3.4.2 Slanted Dipoles

Generically speaking, the dipoles constituting realistic aggregates make an angle \( \theta \) with the aggregation axis as shown in Fig.3-5(b). Then both the components of perfect J-aggregates and H-aggregates contribute to the couplings and, consequently, the EET rate. In addition to the above "diagonal terms", the cross term \( J^{(M)} \) between a J- and an H-configuration also becomes non-negligible as \( \theta \) is neither close to zero nor ninety degrees. It takes the following form,

\[
J_{mn}^{(M)} = -3aR(m-n)/r_{mn}^5, 
\]

or in the Bloch basis,

\[
J_{\mu\nu}^{(M)} = -\delta_{\mu\nu} 8\pi^2i/\eta^2a^3 \mu^2K_1(\hat{\mu}), 
\]

which is purely imaginary.

Noting that the above mentioned \( J^{(H)}(\pi/2, \pi/2) \) does not contribute to the mix term, the most general form of the coupling between 1D aggregates can be expressed as

\[
J(\theta, \phi_1, \phi_2) = \cos^2 \theta J^{(J)} + \sin^2 \theta J^{(H)}(\phi_1, \phi_2) + \sin \theta \cos \theta J^{(M)}(\cos \phi_1 + \cos \phi_2) \]

3.5 Conclusion

In summary, we have studied systematically the EET rates between two parallel one dimensional chromophore aggregates. Assuming the electronic couplings between individual pairs of chromophores to be dipolar, we first looked at the results predicted by the classical Förster theory which assumes independent hopping events among donor/acceptor pairs. However, when there is significant intra-aggregate coupling and at lower temperatures, the delocalized nature of Frenkel excitons gives rise to novel phenomena which deviates from the classical result. In this case one inevitably needs to take into account the delocalized quantum nature of excitons. The recovery
of the classical expression from the quantum one in the high temperature limit was verified and discussed. We have derived analytical expressions for the EET rates which we have used to explain the results of several preceding investigations in the literature. The results for perfect J-aggregates, where all dipoles lie in parallel to the axis of aggregation, are particularly pertinent to the photophysics of conjugated polymers. The breakdown of the far-field selection rule when the separation is comparable to or even smaller than the exciton size can be easily seen with the analytical expressions. Moreover, a non-monotonic temperature dependence of EET rates with a maximum at moderate temperature regime is predicted, where the thermal energy is on the order of the intra-aggregate couplings. Accordingly, our results can be applied to the design principle of artificial light-harvesting devices where directional EET is preferred. Depending on situations, the geometric arrangement of molecules or temperature can be tuned to either enhance or suppress the EET along the direction of interest.
Chapter 4

Quantum Diffusion on Molecular Tubes: Universal Scaling of the 1D to 2D Transition

The transport properties of disordered systems are known to depend critically on dimensionality. In this chapter we study the diffusion coefficient of a quantum particle confined to a lattice on the surface of a tube, where it scales between the 1D and 2D limits. It is found that the scaling relation is universal and independent of the disorder and noise parameters, and the essential order parameter is the ratio between the localization length in 2D and the circumference of the tube. Phenomenological and quantitative expressions for transport properties as functions of disorder and noise are obtained and applied to real systems: In the natural chlorosomes found in light-harvesting bacteria the exciton transfer dynamics is predicted to be in the 2D limit, whereas a family of synthetic molecular aggregates is found to be in the homogeneous limit and is independent of dimensionality.

4.1 Introduction

Transport of energy or charge carriers is of fundamental importance in terms of both scientific interest and its technological relevance. The seminal work of Anderson
states that the presence of static disorder leads to a metal-to-insulator transition or even totally prevents transport in lower dimensions[52, 53]. Upon coupling to fluctuating environment, localized quasi-particles can overcome energetic barriers, and the system becomes conductive again[54]. While transport ceases to exist in both the zero coupling limit (Anderson localization) and the strong coupling limit (dynamical localization), the intervention of environmental noise with intermediate strength can maximize the conductivity[55, 56, 57].

Compared to classical hopping kinetics, where the governing rate equations are given in the coordinate basis, the motion of quantum particles on a disordered and noisy lattice is more involved. In fact, in the weak system-environment coupling limit, the dynamics of the particle wavefunction can be cast into rate equations in the eigenbasis. This implies that quantum enhancement of the conductivity can be characterized by the average size of the wavefunctions, the localization length, since this corresponds to the step size of each hopping event[57, 58]. An immediate consequence arises if one considers the different scaling behaviors of the localization length in different dimensions. It is expected that, for example, the quantum enhancement is much stronger in 2D with respect to that in 1D, given the same disorder and noise strength.

In this chapter we investigate the diffusive dynamics of a quantum particle on a tubular lattice in the axial direction, in which the transport properties scale between the 1D and the 2D limits. Recently, the optical and dynamic properties of excitons in natural[59, 60, 61] and synthetic[62, 63, 64, 6, 65, 66] self-assembled tubular molecular aggregates have drawn much attention. The combination of their quasi-one-dimensional (wire-like) structure and the attenuation of exciton localization due to their inherent (locally) 2D nature, makes such tubular aggregates potentially ideal for exciton transport in, for instance, photovoltaic devices[67]. A natural order parameter in this regard is the radius of the tube, where the axial conductivity is found to be an increasing function of the radius until a critical radius is reached and levels off as it approaches the 2D limit. We found that the scaling relation is universal, independent of the parameters chosen. Moreover, the critical radius is shown to be directly propor-
tional to the localization length in the corresponding 2D system. A phenomenological expression is proposed and shown to reproduce the radius dependence quantitatively, which is applied to several real systems in different limiting parameter regimes and predict their respective radius-(in)dependent diffusion constant.

4.2 Calculation of Quantum Diffusion

The Haken-Strobl-Reineker (HSR) model is employed to characterize the system of interest coupled to a classical Markovian noisy environment\cite{68, 21, 22}. The dynamics of the system is described by the stochastic Schrödinger equation

\[ i \frac{d}{dt} \psi(t) = \hat{H}_s \psi(t) + \sum_n F_n(t) \hat{V}_n \psi(t), \]  

where \( \hat{V}_n = |n\rangle \langle n| \), \( F_n(t) \) are Gaussian stochastic processes with zero mean \( \langle F_n(t) \rangle = 0 \) and finite second order autocorrelation \( \langle F_n(t)F_m(s) \rangle = \Gamma \delta_{nm} \delta(t-s) \), with \( \Gamma \) the dephasing rate. The system Hamiltonian \( \hat{H}_s \) is characterized by a nearest-neighbor coupled square-lattice with periodic boundary condition in one direction (circumference) and isotropic coupling constant \( J \). The number of sites \( (R) \) along the tube’s circumference is referred to as the radius of the tube. The energy of site \( n \), \( \epsilon_n \), is taken to be an independent Gaussian random variable with standard deviation \( \sigma \).

The central physical observable in this Letter, the diffusion coefficient \( D \) in the direction along unit vector \( \vec{u} \), is given by the Green-Kubo expression,

\[ D(u) = \frac{1}{Z_s} \int_0^\infty dt \text{Tr} \left[ e^{-\beta \hat{H}_s \hat{j}(u,t)} \hat{j}(u) \right], \]  

where \( Z_s \) is the system partition function. In the context of the HSR model we will take \( \beta = 0 \) (infinite temperature), so \( Z_s = N \), where \( N \) is the size of the system. The time integration can be carried out analytically.

\[ D(u) = \frac{1}{N} \sum_{\mu,\nu=1}^N \frac{\Gamma}{\Gamma^2 + \omega_{\mu\nu}^2} |\hat{j}_{\mu\nu}(u)|^2, \]  

\[ \text{65} \]
where \( j_{\mu\nu}(u) \) is the flux operator in the eigenbasis and \( \omega_{\mu\nu} = \omega_\mu - \omega_\nu \) is the energy difference between states \( \mu \) and \( \nu \). See detailed derivations in the Supplemental Material. It typically takes up to 100 sites in the axial direction to converge the results for the range of disorder strength covered in this Letter. The diffusion coefficient obtained through Eq. (4.3) is quantitatively agreeing with that from propagating Eq. (4.1) as was done in Ref. [57]. For consistency we present exclusively the data obtained with Eq. (4.3) in this Letter. An efficient method of propagating Eq. (4.1) in the weak coupling regime \( (\Gamma/J \ll 1) \) is also presented in the Supplemental Material. The same methodology is applicable to the case where the system is weakly coupled to a real quantum bath in the low temperature regime, as elaborated in later sections.

The present model is exactly solvable in two limiting cases. Firstly, the dynamics of homogeneous system \( (\sigma = 0) \) can be solved analytically and shows transient ballistic behavior before transitions to diffusive motion[21, 57]. The dynamics is independent of dimensionality, and the diffusion coefficient is given by[58]

\[
D_{\text{hom}} = 2J^2/\Gamma, \tag{4.4}
\]

which can be obtained by assuming Bloch wavefunctions \( \phi_m^\mu = \exp(i\mu m)/\sqrt{N} \) in Eq. (4.3). In fact, decoupling of directions is valid as long as the wavefunctions of the system can be factorized: \( \Psi(\vec{n}) = \psi(n_1)\psi(n_2)\cdots\psi(n_M) \). One such example is given by stacks of homogeneous rings with energy bias among different rings[46, 69]. In the opposite extreme where either disorder \( (\sigma/J \gg 1) \) or system-environment coupling \( (\Gamma/J \gg 1) \) is large, all quantum coherence is destroyed. The particle behaves classically and can be described by a hopping rate between connected sites[70, 34, 36]

\[
D_{\text{hop}} = \frac{2J^2\Gamma}{\Gamma^2 + \sigma^2}. \tag{4.5}
\]

Since the hopping events are independent along different directions, independence on dimensionality is also expected. We conclude that prominent radius dependence is expected only if the wavefunctions are non-separable and with finite noise strength.

In the weak damping regime with finite disorder, through a scaling argument, one
can show that the diffusion coefficient can be estimated by

\[ D_{\text{coh}} = \Gamma \xi^2, \quad \text{(4.6)} \]

where \( \xi \) is the localization length. This relation is very useful since it connects the dynamical observable (diffusion coefficient) with a static property of the system and a single parameter characterizing the system-environment coupling[55, 57], as will be exploited in the following section. We provide the detailed derivation of Eqs. (4.3), (4.4), and a heuristic derivation of Eq. (4.6) in the Supplemental Material.

### 4.2.1 Efficient Disorder Sampling in the Redfield Regime: HSR Model

Intuitively, significant \( R \)-dependence exists only in the weak to moderate noise strength regime. In the case where \( \Gamma/J \ll 1 \), the system dynamics can be accurately described by the Redfield equations. Thus, the population dynamics is governed by master equations in the eigenbasis

\[ \dot{\rho}_{\mu \nu} = \sum_\nu W_{\mu \nu} \rho_{\nu \nu}, \quad \text{(4.7)} \]

with the rate matrix element given by

\[
W_{\mu \nu} = \Gamma \sum_n \phi_n^\mu|\phi_n^\nu|^2 \\
W_{\nu \mu} = -\Gamma \sum_n \phi_n^\nu|\phi_n^\mu|^2 = -\sum_{\nu \neq \mu} W_{\mu \nu}. \quad \text{(4.8)}
\]

We use Greek letters for the eigenstates of the system and Roman letters for the local basis throughout. Now, an expression for the time-dependent diffusion coefficient can be obtained straightforwardly by taking the time derivative of the mean squared
displacement,

\[ D(t) = \sum_n n^2 \sum_\mu |\phi_n^\mu|^2 \sum_\nu W_{\mu\nu} \rho_{\nu\nu}(t) \]  \hspace{1cm} (4.10)

\[ = \frac{\Gamma}{2} \sum_{m,n,\mu} \left( m^2 |\phi_m^\mu|^2 |\phi_n^\mu|^2 - n^2 \right) \rho_{nn}(t). \]  \hspace{1cm} (4.11)

Several remarks are due with regard to the derivation of the last expression. Firstly in deriving it we assume that all coherence in the eigenbasis vanishes, which is valid in the steady-state limit (\( \Gamma t > 1 \)) where diffusive dynamics dominates. In practice we propagate the system to, for example, \( t = 10/\Gamma \) from a \( \delta \)-localized initial state before any significant boundary effect arises. Second, by assuming periodic boundary condition, the same set of Redfield rate matrix elements can be used to propagate \( N_t = N \cdot R \) different initial conditions in a matrix multiplication fashion, where \( N_t \) is the total number of sites and \( N (R) \) is the axial (circumferential) dimension of the tube sample. Note that this is extremely economical numerically and is working best for when looking at large, for example, 2D systems. The result agrees quantitatively well with the Green-Kubo expression Eq. 4.3.

### 4.3 Numerical Results

We start by discussing the diffusion constants in 1D and 2D. It has been shown that the localization length scales linearly with the mean free path in 1D and exponentially in 2D[71]. A common and useful measure of the localization length is given by the inverse participation ratio (IPR), defined for each of the eigenstates as \( \text{IPR}_\mu = 1/\sum_m |\phi_m^\mu|^4 \). Due to the high temperature characteristic of the HSR model we average over all eigenstates and fit the IPR of disordered 1D and 2D square lattices according to

\[ \xi^{1D} = \text{IPR}^{1D} \sim a_1 l, \]  \hspace{1cm} (4.12)

\[ (\xi^{2D})^2 = \text{IPR}^{2D} \sim a_2 l \exp(b_2 l), \]  \hspace{1cm} (4.13)
where \( l = \frac{J^2}{2}\) is the mean free path, and length scale is measured in units of the lattice constant. The results are shown in Fig. 4-1(a). These expressions provide a simple way of estimating the diffusion coefficient in the weak damping regime given the disorder strength \( \sigma \), where Eq. (4.6) applies. Note that in 1D the IPR is directly interpreted as the localization length, while in 2D its square root is. This is because it is the diffusion along one particular direction that concerns us.

Thouless and Kirkpatrick proposed an interpolating formula for the general case which was proven to be valid for most of the parameter ranges of interest[54, 57]:

\[
D_{\text{interp}} = \left[ \left( \frac{2J^2}{\Gamma + \sigma/2} \right)^{-1/2} + (\Gamma \xi^2)^{-1/2} \right]^{-2}.
\] (4.14)

In Fig. 4-1(b) this interpolation result is shown as a function of \( \Gamma \) and compared to the numerically exact results obtained from Eq. (4.3), averaging over 100 realizations of disorder. At a given disorder strength \( \sigma \) one expects an optimal dephasing rate maximizing transport[57, 72]. The interpolation formula not only describes the two limits correctly, but also captures the maxima almost quantitatively, showing the transition between the two transport mechanisms. Note that this expression also reproduces the convergence of diffusion constants in different dimensions in the homogeneous limit, i.e., Eq. (4.4).

We next look at the radius dependence of the diffusion constant in a tube. Since the diffusive motion in the large dephasing limit is independent of dimensionality and the \( \Gamma \) dependence is well described by Eq. (4.14), we will focus on the Redfield regime (\( \Gamma/J \ll 1 \)) while the effect of finite \( \Gamma \) is analyzed in the Supplemental Material. This dependence should be bounded from below by the results of 1D diffusion and from above by 2D diffusion, as seen in Fig. 4-1(c). The diffusion constant increases as the tube radius \( R \) increases until the trend is attenuated at the inflection point \( R = R_c \), denoted as the critical radius. This radius dependence is universal across the entirety of the parameter space we scanned, as shown in Fig. 4-2, where the data is rescaled.
Figure 4-1: (a) IPR dependence on the disorder strength in 1D and 2D. The parameters fitted in Eqs. (4.12) and (4.13) are $a_1 = 6.2$ and $(a_2, b_2) = (67, 6.7)$. The numerical data are shown in symbols. We use 4900 sites for 1D system (black circles), and 2D systems with 70×70 (blue circles) and 90×90 (blue asterisks) square lattices. (b) Comparison between the results of Eq. (4.3) and those of Eq. (4.14). The lower (black) circles and solid line refer to 1D systems and the upper (blue) circles and line represent 2D systems. In both cases we set $\sigma/J = 1$. (c) Radius dependence of $D$ with $\sigma/J = 1$ and $\Gamma/J = 10^{-4}$. The solid line is the fitting according to Eq. (4.15), with the corresponding fitted parameters $R_c$ and $D^{2D}$ indicated.

according to the phenomenological expression

$$D(R) = D^{1D} + (D^{2D} - D^{1D}) S \left( \frac{R - 1}{R_c} \right),$$

where $S(0) = 0$, $S(\infty) = 1$, and $dS/dx$ is everywhere positive for $x > 0$. Here we chose $S(x) = 2 \arctan(x)/\pi$. To demonstrate the generality of this observation, we also present the universality found for systems with realistic quantum bath treated under

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1The numerical evaluation of Eq. (4.3) is demanding for 2D lattices. We fix the number of sites in the axial direction to 100, with sites on the circumference up to 50. Both $D^{2D}$ and $R_c$ are fitted according to Eq. (4.15).
Figure 4-2: Relative diffusion coefficient \( \tilde{D} = (D(R) - D^{1D})/(D^{2D} - D^{1D}) \) as a function of rescaled radius \( \tilde{R} = (R - 1)/R_c \). The solid line is the fitting function \( S(x) \) and the dashed line indicates \( \tilde{R} = 1 \). Inset (left) shows data from Eq. (4.3) before rescaling: From top \( (\sigma/J = 2, \text{ blue}) \) to bottom \( (\sigma/J = 5, \text{ red}) \) with 0.5 increment and interpolating color gradient. Inset (right) shows data from the quantum bath calculations with varying temperatures: From top \( (T/J = 7, \text{ red}) \) to bottom \( (T/J = 0.7, \text{ blue}) \) with 0.7 decrement.

The universality can be explained by the following interpretation. One expects a strong radius dependence of the diffusion coefficient only if the particle wavefunction fully delocalizes around the tube. This is no longer valid as the radius becomes larger than its critical value, where the wavefunction occupies only partially the space in the circumferential direction. Essentially, this picture identifies the critical radius with the localization length in the corresponding 2D system, as is illustrated in Fig. 4-3. In determining the radius dependence, one compares two length scales of the system: the circumference of the tube and the inherent localization length along the circumference. This makes our theory predictive on the axial diffusion coefficients of general tubular systems, given the knowledge of the localization length obtained from...
experiments or \textit{ab initio} calculations, as demonstrated in the next section. We note that this picture can also be applied to understanding the optical selection rules for the dichroism spectra of tubular systems[77].

4.3.1 Radius Dependence at Finite $\Gamma$

We focus on the radius dependence of the diffusion coefficient by focusing on the Redfield ($\Gamma/J \ll 1$) regime above, since the dynamics of the quantum particle in question becomes independent of the tube radius when $\Gamma/J$ is large. This is presented in Fig. 4-4, while the universal scaling relation with changing $\Gamma/J$ is shown in Fig. 4-5(a). It can be seen that the general trend of interpolating $D$ between $D^{1D}$ and $D^{2D}$ as a function of $R$ is similar. The fitted critical radius $R_c = R_c(\Gamma)$ is a monotonic decreasing function of $\Gamma$ (Fig. 4-5(b)). We point out that the fitted $R_c$ is noisy at large $\Gamma/J$ since very little $R$ dependence can be recorded in that regime, represented by the red lines in the inset of Fig. 4-5(a).

The dependence of $R_c$ on $\Gamma$ can be understood as follows. In the weak system-environment coupling regime, the static disorder dominates in determining the localization length and thus the critical radius. At higher coupling strength both static disorder and dynamical noise contribute to the localization of the wavefunction. In
accordance to the physical picture discussed earlier, we expect $R_c \approx \xi^{2D}(\sigma, \Gamma)$. The localization length monotonically decreases as $\Gamma$ increases, and eventually the classical hopping mechanism takes over and the dependence on dimensionality is lost. In other words, the 2D enhancement of quantum diffusion is attenuated by the decoherence from strong thermal noise.

Upon closer inspection of Fig. 4-4 one finds the majority of the difference between $D^{1D}$ and $D^{2D}$ is manifested in the difference between $D^{R=3}$ and $D^{1D}$ at intermediate $\Gamma$ values. This is an artifact originating from the geometric model we use: From 1D to $R = 2$ to $R = 3$ the number of coupled nearest-neighbors increases discontinuously from two to three to four, respectively. In contrast, in all cases with $R > 3$ the coupling terms of a given site remains the same (four). Thus, in the strong dephasing regime ($\Gamma/J > 1$) the $R$ dependence of the diffusion constant can be described by a two-step function: $D^{1D} < D^{R=2} < D^{R=3} = D^{2D}$. The asymptotic value of $R_c$ in this limit can be obtained by minimizing the following mean squared error.

$$
\epsilon(R_c) = \left[ \frac{2}{\pi} \arctan \left( \frac{1}{R_c} \right) - \frac{D^{R=2} - D^{1D}}{D^{2D} - D^{1D}} \right]^2 + \sum_{R=3}^{\infty} \left[ \frac{2}{\pi} \arctan \left( \frac{R-1}{R_c} \right) - 1 \right]^2.
$$

Assuming $(D^{R=2} - D^{1D})/(D^{2D} - D^{1D}) = 0.49$, which is obtained by averaging our data in the range of $0.5 < \Gamma/J < 5$ where this phenomenon is most salient, the limiting value of the critical radius is given by $\tilde{R}_c = 0.47$, indicated by the dashed
Figure 4-5: (a) Relative diffusion coefficient as a function of the rescaled radius, with the convention following Fig. 4-2(b). Data are taken from $\Gamma/J = 10^{-4}$ (blue) to $10^1$ (red) with $\sigma/J = 1$. The inset shows the original data before rescaling. (b) $\Gamma$ dependence of $R_c$ fitted from Eq. (10) with $\sigma/J = 1$. The dashed line is the asymptotic value of $R_c$ obtained by minimizing Eq. (4.16). The error bars show the range of standard deviation, obtained by standard bootstrap Monte Carlo sampling within the original raw data set.
Consequently, the critical radius (2D localization length) calculated in the Redfield regime is an upper bound of its actual value. However, since the dependence on dimensionality is suppressed in the large $\Gamma$ regime, the error in estimating $D(R)$ is small.

### 4.4 Estimates for Real Systems

There are numerous examples of exciton transport in tubular aggregates consisting of organic chromophores. Amongst the best known examples found in nature are the chlorosomes in green sulfur bacteria[59], which serve as the antenna of the light-harvesting apparatus. Diffusive transport of excitons in chlorosomes has been identified[78, 4]. The above scaling argument predicts the exciton diffusion on chlorosome tubes to be in the 2D limit, because the critical radius $R_c$ is much smaller than the typical radius found in the organism, see Table 4.1². This implies the chlorosomes fully exploit the enhancement and robustness of quantum transport in 2D compared to 1D, while taking the advantage of broad absorption spectrum induced by strong homogeneous ($\Gamma$) and inhomogeneous ($\sigma$) broadening mechanisms³.

Families of synthetic self-assembled tubular molecular aggregates exist as well, mimicking chlorosomes with axial length up to micron scale[79, 80, 62]. One such aggregate, composed of the dye molecule C8S3, has been recently characterized[6, 81]. Due to the reduced static disorder and strong exciton coupling strength ($J \approx 8\sigma$, see Table 4.1), the system is in the homogeneous limit and the diffusion coefficient becomes independent of dimensionality or radius. This conclusion is supported by the well-defined absorption selection rules arising from the wavefunctions fully delocalized

---

²We use an effective nearest-neighbor coupling which accounts the same bandwidth as a 2D dipolar lattice. The dephasing rate $\Gamma$ is estimated by taking the fast bath limit of a quantum bath such that the bath correlation function becomes a $\delta$-function, e.g. $\Gamma \approx 2\lambda/\beta\omega_c$ for a Drude-Lorentz bath $J(\omega) = 2\lambda\omega_c/\omega_c^2 + \omega^2$.

³We note that the chlorosome tubes lie horizontally on the baseplate above the FMO complexes and the reaction centers. However the 2D enhancement of quantum diffusion applies to the circumferential transport as well. Also, under high photon influx the excitons can migrate axially and reach unoccupied reaction centers.
around the circumferences[79, 6]. The large localization length in such systems can be utilized in transporting the excitons efficiently along the tubes[81, 67].

There are other instances where radius (in)dependence of transport in tubular systems is seen. It has been shown that the exciton mobility in semiconducting single-walled carbon nanotubes increases linearly with radius[82]. This implies that the reduced disorder in clean carbon nanotube samples gives rise to large localization length[83], so the system is in the $R \ll R_e$ limit that shows linear radius dependence. In addition, molecular tubes based on tobacco mosaic virus protein monomers designed to mimic natural light-harvesting arrays were synthesized[84]. It is found that the exciton dynamics can be described appropriately by classical hopping kinetics[85, 7], thus the independence of dimensionality is predicted (see Table 4.1). Lastly, quantum diffusion of excitons in aggregated phycocyanin thin films has been experimentally characterized recently[86], where the delocalization of excitons explains the enhancement of the diffusion length compared to the estimate of classical hopping theory. While this artificial system serves as an example of quantum diffusion in 2D, the naturally occurring form of phycocyanin in most cyanobacteria self-assembles into a finite 1D wire[87]. It is our ongoing effort to analyze this interesting system in this regard.

Both the HSR model and the weak-coupling secular Redfield method applied to isotropic nearest-neighbor coupled square lattices are an over-simplification of the real systems\(^4\). Richer physical content can be expected when considering more realistic aspects. For examples, it has been shown that environmental memory effects can enhance diffusive transport[34, 4]. The anisotropy from nontrivial molecular arrangement could, for example, render a helical character to the exciton wavefunction[88, 77, 89, 90]. Moreover, the statistics of disorder[91] and long-range interactions[92] are both critical in determining the localization length. We expect the $R$-dependence to be more involved in these and other possible generalizations, since the functional

\[ J(\omega) = \frac{2\lambda\omega_\perp}{(\omega_\perp^2 + \omega^2)} \]

\(^4\)We use an effective nearest-neighbor coupling which accounts the same bandwidth as a 2D dipolar lattice. The dephasing rate $\Gamma$ is estimated by taking the fast bath limit of a quantum bath such that the bath correlation function becomes a $\delta$-function, e.g. $\Gamma \approx \frac{2\lambda}{\beta\omega_c}$ for a Drude-Lorentz bath.
Table 4.1: Parameters and axial exciton diffusion estimated for three exemplary real tubular systems at room temperature. \( J, \sigma, \Gamma \) are given in cm\(^{-1}\), diffusion coefficients are in nm\(^2\)/ps, and \( R (R_c) \) is unitless representing the (critical) number of molecules in the circumference. The parameters for \( J, \sigma, \Gamma, \) and \( R \) from top to bottom are deduced from Ref. [4], [5, 6], and [7], respectively. The other quantities are calculated using Eqs. (4.12), (4.13), and (4.14). We take \( R_c = \xi^{2D} \) since the ratio between \( \xi^{2D} \) from Eq. (4.13) and the fitted \( R_c \) from Eq. (4.15) is close to unity in our calculations.

dependence of the localization length on the additional model parameters varies. However, once given these parameters and thus the localization length, the transition from 1D to 2D can be compactly characterized by the ratio between radius and the localization length. Consequently, we believe the universal scaling relation investigated in this Letter can serve as a generic guidance. Finally the theoretical framework developed here also applies to, for example, the in-plane exciton mobility as a function of the thickness of thin films, which is predicted to scale between the 2D and the 3D limits.

4.4.1 Quantum Bath: Temperature Dependence

In order to better describe the real systems listed in Table 4.1, where the room temperature thermal energy is comparable to or smaller than the energy gaps, we employ the secular Redfield method with a real quantum bath characterized by cubic super-Ohmic spectral density to simulate the diffusive dynamics. Under this assumption, we again obtain a master equation in the eigenbasis as in Eq. (4.7), albeit with a different set of scattering rates among the states obeying detailed balance:

\[
\begin{align*}
W_{\mu\nu} = \sum_n|\phi^\mu_n|^2|\phi^\nu_n|^2S_d(\omega_{\mu\nu})\bar{n}(\omega_{\mu\nu}, T) \tag{4.17}
\end{align*}
\]
where $S_d(\omega)$ is the bath spectral density and $\bar{n}(\omega, T) = \left[ \exp(\omega/T) - 1 \right]^{-1}$ is the Bose-Einstein distribution. We choose the temperature range to be in the thermally activated regime that the diffusivity is exponentially proportional to temperature, see Ref.[58] for details and the caption of Fig. 4-6 for the parameters used, which is reasonably attached to the systems in Table 4.1. The numerical procedure is the same as the one described in the first part of the Supplemental Material, that we first propagate the system to steady state from a localized initial state. The diffusion coefficient can then be estimated through Eq. (4.10). Notice that Eq. (4.11) works only for the high T HSR model where forward and backward rates between states are equal in magnitude.

The universality of the radius dependence is demonstrated in Fig. 4-6. Here vary the disorder strength while keeping the temperature constant, similar to that in Fig. 4-2(a), where the effect of varying temperature is shown in Fig. 4-2(b). Obviously, different theoretical models give different estimations to the localization length that might obey different scaling laws. However, given the localization length the system length scale can be renormalized accordingly and one observes the universal radius dependence, as is illustrated in Fig.4-3.

### 4.5 Conclusion

We have developed a theoretical framework and efficient numerical procedure to model exciton dynamics in tubular molecular aggregates in the presence of environmental noise and disorder based on the HSR model and the secular Redfield model. The central observation is that the diffusion coefficient along the axial direction increases as a function of the tube radius. This dependence is found to be universal across the full parameter range of interest, and can be succinctly characterized by the ratio between the tube circumference and the localization length of the corresponding 2D system. For the chlorosome tubes found in green sulfur bacteria, the exciton transport is found to be in the 2D limit. On the other hand, in a synthetic system with self-assembled cyanine dye molecules mimicking chlorosomes, the excitons are in the
homogeneous limit where independence of dimensionality is predicted. Our findings are useful when exploiting the structure-property relation in designing robust and efficient artificial light-harvesting devices.

4.6 Derivations of Equations

4.6.1 Derivation of Eq. 4.3

The flux operator \( \hat{j}(\mathbf{u}, t) \) and its time derivative is given by

\[
\hat{j}(u) = i \sum_{n,m} (\mathbf{u} \cdot \mathbf{r}_{nm}) J_{nm} |m\rangle \langle n|,
\]

(4.18)

\[
\frac{d}{dt} \hat{j}(t) = i \left[ \hat{j}(t), \hat{H}_S \right] - \frac{\Gamma}{2} \sum_n \left[ \hat{V}_n, \left[ \hat{V}_n, \hat{j}(t) \right] \right].
\]

(4.19)

We then write the flux operator in the eigenbasis

\[
\hat{j}_{\mu\nu}(\mathbf{u}) = i \sum_{n,m=1}^{N} (\mathbf{u} \cdot \mathbf{r}_{nm}) \phi_n^{\mu*} \phi_m^{\nu} J_{nm},
\]

(4.20)
where $\omega_{\mu \nu}$ stands for the energy difference between eigenstates $\mu$ and $\nu$, $r_{mn} = r_m - r_n$ is the vector connecting the two sites, and $\phi^\mu_m$ is the wavefunction amplitude of state $\mu$ at site $m$. Starting from Eq. (4.19), one can obtain the formal solution for the flux operator in the Heisenberg picture,

$$\hat{j}(t) = e^{iH_0 t}j(t)e^{-iH_0 t}e^{-it}. \tag{4.21}$$

Substituting the above expression into Eq. 4.2, the Green-Kubo formula, carrying out the integration over time, and inserting two completeness relations in the system eigenbasis, we readily arrive at Eq. 4.3.

### 4.6.2 Derivation of Eq. 4.4 from Eq. 4.3

In the homogeneous limit the wavefunction is given by the Bloch function, $\phi^\mu_m = e^{2\pi i\mu m/N}/\sqrt{N}$. Moreover, the coupling is translationally invariant, so $J_{n,m} = J(|\Delta|)$, where $\Delta = m - n$. Thus,

$$D_{\text{hom}} = -\frac{1}{N^3} \sum_{\mu,\nu} \sum_{n,m,n',m'} J_{n,m}J_{n',m'}(m - n)(m' - n')e^{2\pi i[\mu(m' - n) + \nu(m - n')]}$$

$$= -\frac{1}{N^3} \sum_{\mu,\nu} \sum_{\Delta,\Delta'} \sum_{n,m,n',m'} \delta_{\Delta,\Delta'} \frac{\Gamma\delta_{\mu,\nu}}{\Gamma^2 + \omega_{\mu\nu}^2} e^{2\pi i\Delta' + \nu\Delta} J(|\Delta|) J(|\Delta'|) \Delta' \sum_{n,n'} e^{2\pi i(n' - n)(\mu - \nu)}$$

$$= -\frac{1}{N} \sum_{\Delta,\Delta'} J(|\Delta|) J(|\Delta'|) \Delta' \sum_{\mu,\nu} \frac{\Gamma\delta_{\mu,\nu}}{\Gamma^2 + \omega_{\mu\nu}^2} e^{2\pi i\Delta' + \nu\Delta}$$

$$= -\frac{1}{\Gamma} \sum_{\Delta,\Delta'} J(|\Delta|) J(|\Delta'|) \Delta' \delta_{\Delta,\Delta'}$$

$$= \frac{1}{\Gamma} \sum_{\Delta} J(|\Delta|)^2 \Delta^2. \tag{4.22}$$

Now clearly for nearest-neighbor coupling the above reduces to Eq. 4.4. This result can also be generalized to higher dimensions by simply treating all dummy indices as vectors (in position or momentum space). For long-range coupling an effective coupling $\tilde{J} = \sum_{\Delta} J(|\Delta|) |\Delta|$ can be defined to reproduce the diffusion coefficient of a nearest-neighbor coupled lattice, which, as forecasted, is dimension independent.
4.6.3 Heuristic Derivation of Eq. 4.6

Here we present a heuristic derivation of Eq. 4.6 ($D_{coh} = \Gamma \xi^2$) in the weak coupling (Redfield) regime for 1D systems, where $\xi$ is the localization length of the system at a given disorder strength. This expression was proposed on the ground of scaling arguments and verified numerically previously[57]. We start from two basic notions of quantum dynamics in disordered media in the weak coupling limit: Firstly the dynamics is adequately described by hopping rates among eigenstates, according to Eq. (4.7), where the transfer rate between states is given by Eq. (4.8). Second, a mean position $x_\mu = \langle \mu | x | \mu \rangle$ can be defined for each of the eigenstates. We argue that, again based on scaling and dimensional analysis, the diffusion coefficient is given by the following expression:

$$D_{1D} = \frac{1}{N} \sum_{\mu, \nu} W_{\mu \nu} x_{\mu \nu}^2,$$  \hspace{1cm} (4.23)

where $x_{\mu \nu} = x_\mu - x_\nu$ is the separation of the mean positions, and $W_{\mu \nu}$ is the transfer rate between states $\mu$ and $\nu$. To proceed we also need to specify the form of the wavefunctions. Here we assume a simple exponential decay ansatz:

$$\langle x | \mu \rangle = \frac{1}{\sqrt{\xi}} e^{-|x-x_\mu|/\xi}.$$  \hspace{1cm} (4.24)

With this, the Redfield rates can be obtained as

$$W_{\mu \nu} = \frac{\Gamma}{\xi^2} \left( |x_{\mu \nu}| + \frac{\xi}{2} \right) e^{-2|x_{\mu \nu}|/\xi}.$$  \hspace{1cm} (4.25)

And the average in Eq. (4.23) can be carried out straightforwardly.

$$D_{1D} = \frac{\Gamma}{\xi^2} \int_{-\infty}^{\infty} dx x^2 \left( |x| + \frac{\xi}{2} \right) e^{-2|x|/\xi} = \Gamma \xi^2.$$  \hspace{1cm} (4.26)
Chapter 5

Spectroscopic Classification of Multi-Dimensional Excitonic Molecular Aggregates

In this chapter, we establish a classification scheme for two-dimensional excitonic molecular aggregates using spectral line shape theory. Anisotropy of dipolar couplings among the chromophores combined with higher dimensionality of the aggregate structure introduce nontrivial excitonic band structures leading to dark band edge J-aggregates, bearing spectroscopic signatures distinctively different than those described in the framework of Kasha’s theory. We show that power-law scaling of temperature dependence of absorption peak width and shift can be used as inputs to probe the fine structure of the excitonic density of states. We also demonstrate that in tubular aggregates with rotational/helical symmetry, the energy gap between the parallel-polarized and the perpendicular-polarized peaks is a simple function of the tube geometry. This information considered collectively, we provide a quantitative and systematic protocol for inference of the microscopic packing conditions in two-dimensional excitonic molecular aggregates. We use C8S3 light harvesting nanotubes (LHNS) as our primary example and determine a packing structure and Hamiltonian broadly consistent with measured temperature dependent experimental observables.
5.1 Introduction

Structure-property relationships are the cornerstone of chemical and material science. Since their discovery in the 1930s, molecular aggregates composed of organic dyes have been of scientific interest as a means of manipulating absorption and emission in a macroscopic structure. Investigations of Jelley[93] and Scheibe[94] showed that cyanine dyes display shifted and narrowed absorption peaks above certain dye concentrations. These reversible changes were associated with these dyes assuming a three-dimensional regular aggregate structure. Kasha et al.[95, 96] provided a microscopic interpretation of these color shifting aggregates: Dyes assemble either head-to-tail (J-aggregates) and co-facially (H-aggregates) inducing red or blue-shifts respectively.[97, 98, 99, 12, 100] Later, building on Kasha’s work for 1D aggregates with dipolar interactions Knapp ascribed the observed line width narrowing to delocalization of the center-of-mass exciton wave function.[101, 102, 103, 104] Delocalization leads to decreased disorder experienced by the excitons reducing the line width by a factor of $\sqrt{N}$, where $N$ is the delocalization length.[105, 91]

Excitons residing in aggregates are embedded in a complex environment. Depending on the time-scale of environmental fluctuations relative to the exciton lifetime these dynamics either present as dynamical noise, or static disorder and contribute to the line shape observed in spectroscopic measurements. While Knapp focuses on the influence of static disorder on the absorption line width, intra- or/and inter-molecular vibrational modes contributing to the dynamically noisy environment for the excitons require distinct theoretical treatment. For examples, Spano and coworkers[99] considered intra-molecular vibrational modes strongly coupled to the excitons that lead to phonon progressions in the spectra and associated the relative peak intensities of a progression with the types of (J- or H-) aggregation, which finds use in the structural inference of conjugated polymers.

Dynamic fluctuations can be modulated using temperature. Knoester et al.[76, 106] developed a theoretical framework to quantify the power-law temperature dependence of spectral line width, where the vibrational modes belonging to nearby dyes

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and solvent molecules are collectively represented by a bath spectral density function. They argued that the exponent of the power-law temperature dependence could be partitioned into contributions from the characteristics of both the excitonic system, with a typical 1D tight-binding density of states (DOS), and the bath spectral density. By measuring from cryogenic to room temperatures the spectral line shape can be used to infer the system and bath DOSs in the low-energy region covered by the thermal energy (200 cm\(^{-1}\)). This physical picture is also adopted in the following discussion.

Despite the above-mentioned efforts in quantifying all the relevant degrees of freedom, numerous spectroscopic features observed in molecular aggregate systems remain unaccounted for. There is a large family of molecular aggregates evading even qualitative inference of their microscopic structures. These include cyanine dye aggregates fabricated with the Langmuir-Blodgett technique[107, 108] and a variety of tubular aggregates,[98] which are inherently two-dimensional. For example, there are molecular aggregates reported

- with red shifted peaks whose widths are comparable to their monomeric counterparts,
- with non-monotonic \(T\)-dependent fluorescence lifetime,
- with blue-, red-, or non-shifting peaks as functions of temperature.

All of these features are incompatible or unexplained given the existing framework of 1D J- or H-aggregates. More specifically, they possess spectroscopic characters of both J- and H-aggregates simultaneously. In this manuscript we aim to provide a unified and broadened theoretical framework that accounts for these features as well as an empirical protocol that can be used to maximize the amount of information inferred about the aggregate structure and its environment using temperature dependent absorption and emission spectroscopy. Spectral line shape of molecular aggregates. We
start our theoretical considerations from a Frenkel exciton Hamiltonian

\[
\hat{H}_s = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{n \neq m} J_{n,m} |n\rangle\langle m|,
\]

(5.1)

where \(\epsilon_n\) and \(J_{n,m}\) are the site energy and the excitonic coupling, \(|n\rangle\) represents the state where the designated site is in the excited state while all other sites in the ground state, and bold letters are used to indicate site vectors since we are concerned with generic multi-dimensional lattices. To introduce thermal effects, the environmental degrees of freedom are represented as a collection of harmonic oscillators bilinearly coupled independently to each molecule

\[
\hat{H}_b = \sum_i \omega_i \hat{b}_i^\dagger \hat{b}_i
\]

(5.2)

\[
\hat{H}_{sb} = \sum_n \sum_i g_{n,i} \left( \hat{b}_i^\dagger + \hat{b}_i \right) |n\rangle\langle n|
\]

(5.3)

where \(\hat{b}_i^\dagger\) and \(\hat{b}_i\) creates and annihilates a phonon with frequency \(\omega_i\) and \(g_{n,i}\) is the exciton-phonon coupling strength. Typically we express the set of bath modes by a continuous spectral density profile \(D_b(\omega) = \pi \sum_i g_i^2 \delta(\omega - \omega_i)\).

The focus of our discussion in this contribution is the linear absorption spectrum, which in the time domain can be expressed as \(I(t) = \langle \hat{\mu}(t)\hat{\mu}(0) \rangle\), where \(\hat{\mu}\) is the transition moment operator and the bracket represents thermal average over the system plus bath degrees of freedom. In the Markovian Redfield approximation, the spectral line shape is given as

\[
I(t) \approx \sum_k f_k e^{-i(\epsilon_k + G_k)t},
\]

(5.4)

and

\[
\Re G_k = \sum_{l \neq k} \frac{O_{kl}}{\epsilon_{kl}/T - 1} D_b(|\epsilon_{kl}|),
\]

(5.5)

\[
\Im G_k = \sum \frac{2O_{kl} \mathcal{P}}{\pi} \int_0^\infty \frac{d\epsilon}{\epsilon/T - 1} \frac{\epsilon_{kl}^2}{\epsilon^2 - \epsilon_{kl}^2}.
\]

(5.6)
where $\epsilon_k$ and $f_k$ are the energy and oscillator's strength of exciton state $k$ obtained by diagonalizing the system Hamiltonian in Eq. 5.1, and $O_{kl} = \sum_n |\phi_n^k \phi_n^l|^2$ is the wave function overlap between the states.[18, 17, 109, 110] There is a principal value integration over a Fano-like line shape in Eq. 5.6, while Eq. 5.5 is derived from a similar integral with the line shape replaced by a Dirac delta function of the energy gap $\delta(\epsilon - \epsilon_{kl})$. This implies that the influence of scattering is more nonlocal in terms of the energy gap. More importantly, the contribution to the imaginary part (peak shift) is anti-symmetric with respect to the gap. In this regard, one can rewrite Eqs. 5.5 and 5.6 as

$$W_0 = \Re G_{k=0} = \int \frac{d\epsilon}{e^{|\epsilon - \epsilon_0|/T} - 1} D_s D_b(|\epsilon - \epsilon_0|) + \int_{-\epsilon_0}^{\epsilon_0} d\epsilon D_s D_b(|\epsilon - \epsilon_0|), \quad (5.7)$$

$$S_0 = \Im G_{k=0} = \frac{2}{\pi} P \int d\epsilon \int_0^{\infty} d\epsilon' \text{sgn}(\epsilon - \epsilon_0) \cdot \frac{D_s(\epsilon) D_b(\epsilon')}{e^{\epsilon'/T} - 1} \frac{|\epsilon - \epsilon_0|}{e^{\epsilon'/T} - 1}, \quad (5.8)$$

where we focus on the total scattering amplitude of the bright state with energy $\epsilon_0$ and replace the summation by integration over the system DOS $D_s(\epsilon)$. In Eq. 5.7 the first term is symmetric with respect to $\epsilon_0$ while the second one is $T$-independent existing only for states having lower energy than the bright state, originating from transitions accompanying spontaneous emission of phonons.[76, 106, 80] While the first term vanishes at 0 K, there is a residual homogeneous width that is indistinguishable from inhomogeneous broadening given by the second term.

On the other hand, the anti-symmetry about $\epsilon_0$ in Eq. 5.8 assures that the states higher in energy push the bright state lower in energy with increasing temperature, i.e. a further red shift in J-aggregates. In the contrary, the absorption peaks of H-aggregates shift further toward the blue at higher temperatures. However, for cases where the bright states are located in the middle of the exciton band, the net shift depends on the relative abundance of weighted system DOS (the integrand in Eq. 5.8) higher and lower in energy than the bright states. We shall return to this in the following sections.
5.2 Molecular Packing Condition and Density of States

The classification of 1D aggregates is rather straightforward. Extending the Kasha model mentioned above and considering the constituent molecules as simple dipoles, the angle $\theta$ between the dipoles and the axis of aggregation completely determines the excitonic band structure: J-aggregates with $\theta < \theta_m$ and H-aggregates with $\theta > \theta_m$, where $\theta_m = \arccos(1/\sqrt{3})$.[51, 69] On the other hand, there is a large class of cyanine dye molecules forming ribbons, tubes, or planar 2D aggregates, which can harbor higher complexity, require additional geometric considerations.

We follow the seminal work of Kuhn et al.[111] addressing monolayers of a series of dye compounds, where the planar aggregates are modeled by tiling rectangular bricks with an offset between adjacent chains of molecules. See Fig. 5-1 for example, where we illustrate the model with the cyanine dye 3,3'-bis(2-sulfopropyl)-5,5',6,6'-tetrachloro-1,1'-dioctylenzimidacarbocyanine (abbreviated as C8S3). We define a slip parameter $s$ measuring the extent of mismatch along the molecular long axis between adjacent molecules. As a function of the slip, the excitonic couplings in Eq. 5.1 can be calculated between any pair of molecules in the aggregate, using different levels of approximation to the transition charge density: simple dipole, extended dipole, and transition charges, as shown in Fig. 5-1(b). In panel (c) three different 2D molecular tiling are shown in the upper row while the corresponding DOSs and the locations of the bright state are shown in the lower row.

Among the three examples provided, the latter two are J-aggregates and the first is an H-aggregate basing on their bright state energies. However, unlike the third aggregate, where the bright state is also the ground state, the bright states of the former two are located within the band. We deliberately refer to such aggregates as having dark band edges (DBE), which is not possible for simple 1D aggregates, and the opposite cases as with bright band edges (BBE). This originates from the anisotropic nature of in-plane dipolar coupling, that the sign of the coupling varies sensitively with the dipole orientations, which are thoroughly sampled within a 2D planar configuration. In other words, the bright state wave function harnesses both
positive and negative couplings, and introducing nodal lines (finite quasi-momenta) in the direction where the positive contribution dominates sometimes lower the energy.
5.3 Classification Scheme of Excitonic Molecular Aggregates

Here we go into detail of classifying molecular aggregates basing on their excitonic DOS and the locations of their bright states within. We start by illustrating the criteria with the well-known 1D aggregate models, and the 2D models and other more generic case follow naturally.

5.3.1 1D Aggregates

As a straightforward extension of Kasha’s dimer model[95, 96], a translationally symmetric 1D chain of molecules can be constructed by specifying the angle between the chain axis and the transition dipoles. In Fig. 5-2 we show three criteria concerning the spectroscopic property of an aggregate: the monomer-aggregate peak shift, $T$-dependent peak shift, and the low $T$ peak width. As indicated in the figure, clearly all three observables undergo a phase transition as functions of the dipole angle: When $\theta < \theta_m$ one obtains a J-aggregate with little low $T$ peak width and peak shifting to the red with increasing $T$, and vice versa for $\theta > \theta_m$ that correspond to H-aggregates. All three criteria give the same amount of qualitative information.

5.3.2 2D Aggregates

In striking comparison to the 1D case visited above, for 2D aggregates the story becomes much more involved. According to our discussion of absorption line shape, there are qualitative differences between DBE and BBE J-aggregates. First, in DBE J-aggregates the second contribution to the line width in Eq. 5.7 dominates in the low temperature regime, leading to a $T$-independent width similar to that of a typical H-aggregate. Secondly, while BBE J-aggregates are predicted to experience further red shifts upon increasing the temperature, the same is not necessarily true for DBE J-aggregates. Depending on the relative exciton DOS above versus below the bright state, weighted by the integrand in Eq. 5.8, DBE J-aggregates can be further classi-
Figure 5-2: Phase space diagrams of the C8S3 tiled in 1D fashion. (Top) The traditional definition of J- and H-aggregates basing on the shift relative to the monomer absorption peak. (Center) Calculated peak shift between $T = 5$ K and 300 K according to Eq. 5.8. (Bottom) The residual homogeneous width at 0K given by the second term in Eq. 5.7.

As shown in Fig. 5-3, we summarize the three different criteria for classifying excitonic molecular aggregates in the context of C8S3 rectangular 2D tiling model, given the slip parameter. Starting from the top panel, the distinction between J-(r.h.s. of the dashed line) and H-aggregates (l.h.s.) is solely based on the shift of the absorption peak relative to the monomer spectra. There is a critical slip parameter ($s_c = 3.5$ for C8S3) where the net excitonic shift vanishes, similar to the magic angle $\theta_m$ the 1D model proposed by Kasha. We also note that the shift in question is purely due to the excitonic couplings among the molecules in the aggregate, and the
Figure 5-3: Phase space diagrams of the C8S3 rectangular tiling model. (Top) The traditional definition of J- and H-aggregates basing on the shift relative to the monomer absorption peak. (Center) Calculated peak shift between $T = 5$ K and 300 K according to Eq. 5.8. (Bottom) The residual homogeneous width at 0K given by the second term in Eq. 5.7.

Inductive and dispersive contributions omnipresent in real systems must be carefully accounted for separately.[112]

Next, we show the $T$-dependent spectral shift between 5 K and 300 K calculated with Eq. 5.8. As discussed previously, the net $T$-dependent shift depends on the relative abundance of weighted system DOS. Thus, the quality of being a J- or H-aggregate does not necessitate the sign of the $T$-dependent shift. In our particular case there is a narrow window $3.5 < s < 4.5$ where one finds J-aggregates that undergo blue shifts upon increasing temperature. In principle the $T$-dependent shift can also be non-monotonic, that the accessible weighted system DOS from the two sides could scale differently as a function of temperature. Consequently, the location of the phase-separating dashed line is not definite relative to the one in the top panel, and there could also be multiple such lines. These are not the case in the C8S3 rectangular 2D tiling model, where red-shifting H-aggregates are also not possible.

Finally, the residual homogeneous width at 0K is presented in the bottom panel.
The dash line separates BBE aggregates to the right and DBE aggregates to the left. In contrary to the central panel, the phase-separating line herein must be located in the J-aggregate regime (r.h.s. to the dashed line in the top panel). In other words, we predict sizable contribution to the line width of all H-aggregates of this origin, explaining the lack of motional narrowing seen in experiments.4,11

We emphasize that all the dashed lines in the three panels coincide in the case of Kasha’s 1D model at the magic angle $\theta = \theta_m$. In other words, all 1D J-aggregates are with BBE and experience further red shift upon increasing temperature. Essentially, the additional geometric degrees of freedom in convolution with the anisotropic nature of electronic couplings among molecular Frenkel excitons in 2D aggregates lead to the existence of such multitude of excitonic properties.

Quantitative inference of packing condition. Apart from the classification scheme provided above, quantitative $T$-dependence can be obtained by evaluating Eqs. 5.7 and 5.8 and compared to experiment. Specifically, Knoester et al. put forward an account for the power-law behavior seen in the $T$-dependence of absorption line width in cyanine dye J-aggregates. At low temperatures, one observes

$$W_0 = aT^p + b \quad (5.9)$$
$$p = d_s + d_b + 1 \quad (5.10)$$

where $d_s$ is the power-law exponent of the system DOS near the bright state and similarly $d_b$ is that of the bath spectral density. For example, 1D aggregates ($d_s = -0.5$) immersed in a cubic super-Ohmic bath ($d_b = 3$) we have $p = 3.5$. With similar derivation, one can show that the spectral shift as given in Eq. 5.8 can also be cast into the same form in the low temperature regime. However, as discussed by Renge and Wild,[113] the spectral shift is also significantly affected by the thermal expansion effect of the matrix, where the change in density between 0K and room temperature could be as large as 6 percent. This not only modifies the separations among the packed molecules but also alters the dielectric constant of the matrix, amounting to spectral shift on the order of a few hundreds of wavenumbers. These quantities,
considered collectively altogether, can be used in the inference of molecular packing conditions.

We now proceed to interpret the $T$-dependent absorption line shape of the inner-wall of the C8S3 LHN. Firstly we assume that the bath spectral density of the LHN is the same as its constituent monomers, which is fitted using standard Kubo line shape theory (cite Mukamel) to be a sum of two shifted Drude-Lorentz functions:

$$D_b(\omega) = \sum_{i=1,2} \lambda_i \gamma_i \omega \left( \frac{1}{\gamma_i^2 + (\omega + \omega_{0,i})^2} + \frac{1}{\gamma_i^2 + (\omega - \omega_{0,i})^2} \right)$$

(5.11)

where $\lambda_{1/2} = 450/550$, $\gamma_{1/2} = 100$, and $\omega_{0,1/2} = 50/1200$ are the reorganization energy, cut-off frequencies, and the shifted central frequencies, with all parameters given in wavenumbers. We note that this is an Ohmic bath ($\lim_{\omega \to 0} D_b(\omega) \propto \omega^1$, i.e. $d_b = 1$.

We assume that the thermal expansion of the sugar matrix follows a strict $T^{1.14}$ relation fitted from experiment28 and the dielectric constant scales linearly with the density.29

In our rectangular brick model, the system DOS scaling power $d_s$ is completely determined by the slip parameter $s$. In Fig. 5-4(a) we show the peak width and shift fitted in form of Eq. 5.9 as functions of $s$.

Experimentally we find that the absorption peak width and shift scale as $T^{2.5}$ and $T^{2.0}$, respectively. The closest match to the C8S3 LHN is determined to be in the range of $5.0 < s < 5.3$. We note that it has been established that both of the two walls of the C8S3 LHN contain two molecules per unit cell. The above assignment in the context of the rectangular brick model with a single molecule per unit cell should be considered as a simplified model with the closest possible excitonic spectral properties to the real system. We show the quantitative agreement between the simulated $T$-dependent spectra of the prescribed model and the experimental results in Fig. 5-4(b). The low energy shoulder is assigned to the formation of LHN bundles (cite) while the higher energy peak above $1.7 \cdot 10^4$ cm$^{-1}$ belongs to the outer wall.
5.4 Parallel- and Perpendicular-Polarized Peaks in Tubular Aggregates

For tubular aggregates, another subclass of aggregate geometry commonly seen in self-assembled dye systems, the most distinguishing spectroscopic feature is that they support nontrivial linear and circular dichroism signals. For each optical transition of each molecule in a unit cell, two peaks arise in the absorption spectrum: one polarized along the axial direction (parallel-polarized) and the other in the radial direction (perpendicular-polarized). In this section we demonstrate how both the additional degrees of freedom and constraints can be seamlessly integrated into our analysis above.

It is convenient to characterize the tubular structure by starting with a 2D pla-
nar molecular tiling and then assign a *chiral vector* of suitable tilting angle and radius,\[114, 112\] see Fig. 5-5. Once given the parent 2D lattice and the chiral vector, the exciton Hamiltonian Eq. 5.1 can be readily derived. We adopt periodic boundary condition in the axial direction, which is equivalent to applying full helical-rotational symmetry.\[115\] We refer the readers to Ref. \[114\] for detailed geometric constructions of such aggregate structures. In the homogeneous limit, it suffices to recognize that the exciton states corresponding to the parallel- and the perpendicular-polarized peaks are both nodeless along the axial direction, while the latter has one nodal plane dissecting the circumference and the former has none. This leads us to consider the excitonic interaction between two finite strips of dipoles in parallel and look at its matrix element bracketed by nodeless Bloch states, see Fig. 5-6(a):\[69\]

\[
J(\theta, x) \approx dx \cdot \frac{\rho^2 b}{L} \int_0^L dy_1 \int_0^L dy_2 \left[ \frac{x^2 + (y_1 - y_2)^2}{x^2 + (y_1 - y_2)^2} \right] - 3 \frac{x \sin \theta + (y_1 - y_2) \cos \theta}{[x^2 + (y_1 - y_2)^2]^{5/2}}
\]

\[
= dx \cdot \frac{2\rho^2 b}{L} \left[ \left( \frac{1}{x} - \frac{1}{\sqrt{x^2 + L^2}} \right) \cos^2 \theta - \frac{L^2}{x^2 \sqrt{x^2 + L^2}} \sin^2 \theta \right]
\] (5.13)

In Eq. 5.12 we take the continuum approximation and the plane of excitonic chromophores is represented by the average transition dipole moment density $\rho = \mu/A$, where $\mu$ is the magnitude of transition dipole and $A$ is the unit cell area projected onto the plane. We also assume that the tube radius is much larger than the molecular dimension, which is commonly the case found in real systems,\[98\] such that the curvature effect can be safely discarded. This validation of this assertion is demonstrated in Fig. 5-7, where we compare the DOSs of tubes with their parent 2D planar structure.

By inspecting the form of Eq. 5.13, we notice that the two terms in the bracket originate from the parallel component ($\theta = 0$, 1D J-aggregate) and the perpendicular component ($\theta = \pi/2$, 1D H-aggregate), thus the respective signs. Most importantly, by taking the long chain limit $L \to \infty$, only the latter, negative term survives. This implies that introducing nodal lines (or helices) in the circumferential direction always increase the energies of the exciton states. Consequently, this result predicts that the parallel-polarized peak is always lower in energy than the perpendicular-polarized peak.
Figure 5-5: The available chiral vectors (open circles) with $s = 5$ tube radius $29.5 < R < 34.5$. The blue arrow represents one particular chiral vector. Note that the length of a chiral vector corresponds to the circumference of the corresponding tube.

Figure 5-6: (a) Decomposition of a tubular excitonic aggregate with helical/rotational symmetry into axial strips of interacting dipoles. (b) The energy gap between the parallel- and the perpendicular-polarized absorption peaks as a function of the chiral angle. The chiral vectors are the same with those in Fig. 5-5 indicated with open circles.

This also implies that our classification scheme presented above can be directly applied to tubular aggregates by focusing on the line shape of the parallel-polarized peak, provided that the tube radius is much larger than the dimension of the constituent
dyes.

We can take one step further and calculate the energy gap between the two peaks, resulting in

\[ E_{\perp} - E_{||} \approx \lim_{b \to 0} \lim_{L \to \infty} 2 \int_{b}^{2\pi R} dx \left[ \cos \left( \frac{x}{R} \right) - 1 \right] J(\theta, x) = \frac{4\rho^2}{R} \left[ \text{Si}(\pi) - \frac{2}{\pi} \right] \sin^2 \theta \]

where Si(x) is the sine integral and we take the limit of infinitesimal strip width b in light of the continuum approximation assumed. This result is universal in the sense that it naturally excludes dependence on microscopic packing condition. Specifically in our case this refers to the slip parameter, and the sole dependence on the excitonic properties of the dye molecule is the average transition dipole density. While at the first glance the pure dipolar interaction assumed seems fairly restricted, we again argue that Eq. 5.14 is valid in the limit of large tube radius. We corroborate this assertion by calculating the energy gap for a large family of tubular aggregates with
a variety of parameters, including tube radius, chiral angle, slip parameter, and even with the three different methods of estimating the excitonic coupling demonstrated in Fig. 5-1(b). The result is in excellent agreement with Eq. 5.14 as shown in Fig. 5-6(b).

Essentially, the universality of the energy gap in question concerns only the long wavelength, coarse-grained properties of the excitonic system. It does not inherit information from the detailed packing condition nor the complexity of the short-range interactions on the scale of individual molecules. Eq. 5.14 together with the sum rule of linear dichroism spectrum[114], \( I_\perp/I_\parallel = \tan^2 \theta \), lends us additional leverage in determining the chiral angle and the dielectric constant in the system given the tube radius. For the inner wall of the C8S3 LHN we conclude that \( \theta \approx 50^\circ \) and \( \epsilon_r = 1.9 \), in agreement with previous results of similar systems.[112]

5.5 Conclusion

We present a generalized classification scheme for inferring the structure-property relations in excitonic molecular aggregates that are inherently two-dimensional. The scheme is based on careful analysis of the spectral line shape as a function of temperature, given the relative location of the bright state in the excitonic density of states. Our theory is consistent with established understanding of excitonic molecular aggregates and explains phenomena observed experimentally that are unaccounted for previously. A universal expression for the energy gap between the parallel- and the perpendicular-polarized absorption peaks is established for the first time. We demonstrate the usefulness of the present framework by a stepwise unraveling of microscopic packing conditions and other relevant parameters of a tubular aggregate consisting of C8S3 dye molecules.
Chapter 6

Long-Wavelength Descriptions of the Excitonic Density of States and Their Spectroscopic Signatures

In the last chapter we briefly explored the continuum limit of excitonic dipolar interactions in 2D molecular aggregates. The result is useful in the context of identifying spectroscopic properties that are of long-wavelength characters, coinciding with the applicability of continuum description. In particular, we focused on the energy gap between the perpendicular- and the parallel-polarized peaks of a generic tubular aggregates. As mentioned in the earlier chapters, the quality of the simple dipole description for the excitonic interactions between molecular chromophores decays severely if the separation between the molecules is comparable to their sizes. Within certain critical radius, significant deviations from the simple $R^{-3}$ scaling relation occur. It is then necessary to go to higher orders in the description of the transition density profile. As a consequence, the number of geometric parameters increases dramatically as well. Thus identifying the physical properties similar to the aforementioned energy gap effectively prevents such cumbersome tasks.

In the current chapter we further extend such analysis to the excitonic dispersion relations in general. It is found that one can effectively dismantle the full system Hamiltonian into its short- and long-range components, where each can be character-
ized accurately and analytically. With the dispersion relations and the corresponding excitonic density of states at hand and making use of the classification scheme proposed in the previous chapter, we identify the key spectroscopic signatures that reflect either the short- or the long-range part of the contribution to the excitonic couplings.

6.1 Excitonic Dispersion Relations of 2D Molecular Aggregates

By dispersion relation we naturally assume full translation symmetry of the aggregate structure in question. Consequently, the Hamiltonian is diagonalized by the Bloch functions with the quasi-momenta as a complete set of quantum numbers. As mentioned, here we will attempt to separate the contributions to the excitonic coupling into the short- and the long-range parts. Taking advantage from the fact that the energy band structure is additive, the dispersion relations corresponding to the two parts can be summed up to the final, full result.

For the sake of clarity we shall adopt a rather simplified model for a 2D molecular aggregates. As shown in Fig. 6-1, each of the molecules is located on the lattice point of a 2D square grid. Now it is straightforward to define a cut-off radius where the excitonic couplings within the circle are defined as the short-range part, and the rest as the long-range part. For our purpose it is convenient to set the cut-off radius to unity. This is equivalent to setting only the nearest-neighbor interactions to the short-range part. We proceed to analyze the two parts separately below.

6.1.1 Short-Range Interactions

For nearest-neighbor interactions, the dispersion relation is simply two cosines from the two dimensions.

\[
E^{(s)}(k_x, k_y) = 2J_x(\theta) \cos(2\pi k_x) + 2J_y(\theta) \cos(2\pi k_y),
\]  

(6.1)
Figure 6-1: Two-dimensional square grid lattice of dipoles. We define $\theta$ to be the angle between any dipole with the $y$-axis. A cut-off radius of 1.5 lattice constant is indicated.

Figure 6-2: The dispersion relations for the short- (left) and long-range (right) parts with $\theta = 0$. The black lines are the analytical results Eqs. 6.1 and 6.2, while the colored continuous surfaces are those obtained by numerical diagonalization.

where $J_x(\theta) = J_0 \cos \theta$ and $J_y(\theta) = -2J_0 \sin \theta$ under our convention. Obviously this applies to arbitrary dimensionality. Since this is the exact, we find complete agreement between Eq. 6.1 (black lines and dots) with the numerical result (colored continuum) on the left hand side of Fig. 6-2.
6.1.2 Long-Range Interactions

For the long-range part, we intend to take advantage of the expressions for the dipolar interactions between parallel 1D chains as presented in earlier chapters. Since we are primarily interested in the long wavelength regime, we make use of the $k = 0$ limits of these expressions, namely Eq. 3.12. In addition, it is crucial to recognize that for the $k = 0$ cases there are no cross terms between the J- and the H-type chains, see Eq. 3.24. Consequently the full dispersion relation is simply the sum of the two contributions.

Now it is straightforward to carry out the final Fourier transforms and the final expressions are given by

$$E^{(l)}(k_x, k_y) = 2[1 - \cos(2\pi k_x)] + \log (1 - e^{2\pi k_y}) + \log (1 - e^{-2\pi k_y}) + 2\cos(2\pi k_y) - \pi(6.2)$$

Again the results are compared to the numerical exact ones on the right of Fig. 6-2. Despite with the continuum approximations assumed and a rather small cut-off radius, we obtained quantitative agreements.

Now we are at a position to understand the importance of such a divide-and-conquer approach. Due to the nature of the dipolar coupling, it is expected that the short-range part is the dominant contribution, as can be seen from the magnitude of $z$ values in Fig. 6-2. Thus, spectroscopic properties such as the location of the bright states, intricately dependent on the short-range contribution, are sensitive functions of minute geometric details. However, due to the scaling property of the cosine function at small $k$, one always expects van Hove singularity at the $\Gamma$ point, i.e. $(k_x, k_y) = (0, 0)$. This indicates that the final scaling of the system DOS at small $k$, which dominates the optical properties, is determined primarily by the long-range part. In other words, it can be said that the van Hove singularity at the $\Gamma$ point is opened up by the long-range contribution.

The above statement has a strong consequence in determining the spectroscopic properties that are only dependent on the long-wavelength scaling of the system DOS. From what we covered in the previous chapter, both the power-law exponent of the
T-dependent line shapes and the energy gap in case of a tubular aggregates belong to such category. We will return to this in the later sections where we consider multiple molecules per unit cell.

6.2 Dark States Brightening in Aggregates with Dark Band Edges

While it follows that excitonic aggregates with dark band edges are not emissive, as forecasted in the introductory chapters, for fluorescence emission the selection rules can be distorted given strong enough system-bath coupling. We emphasize this is the result of system-bath entanglement, from which the set of quantum numbers from diagonalizing the system Hamiltonian is no long a good reference in describing the system-bath composite’s coupling to the photon field.

In Fig. 6-3 we present the absorption and the emission spectra of a set of 2D aggregates calculated with the numerically exact stochastic path integral method[110]. For cases with \( \theta = 22.50^\circ, 33.75^\circ, \) and \( 45.00^\circ \) one have bright band edges and otherwise in the other two cases. The location of the bright state stays the same, given by

\[
E_b(\theta) = -\frac{J_0}{2} \sum_{x,y} \frac{1}{(x^2 + y^2)^{3/2}},
\]

where the summation runs through all lattice points except the origin. This is confirmed as shown in the similarity of the absorption spectra with varying \( \theta \).

On the other hand, qualitative differences can be seen from the emission spectra. This is due to the fact that an exciton state with energy \( E(k_x, k_y) = E(0.5, 0) = E(0, 0.5) = E_a \) given by

\[
E_a(\theta) = -\frac{J_0}{2} (B_0 + 3B_1 \cos 2\theta)
\]
becomes the ground state in the regime where $-13^\circ \lesssim \theta \lesssim 13^\circ$, where

\[
B_0 = \sum_{x,y} (-1)^y \frac{(x^2 + y^2)^{3/2}}{(x^2 + y^2)^{3/2}},
\]

\[
B_1 = \sum_{x,y} (-1)^y \frac{(x^2 - y^2)}{(x^2 + y^2)^{5/2}}.
\]

(6.5)

(6.6)

For aggregates with dark band edges as indicated, the rather strong system-bath coupling brightens up the dark, ground state of the system.

Figure 6-3: The numerically exact absorption and emission spectra of 2D aggregates with different $\theta$'s. We set $J_0=100$ cm$^{-1}$ and a Drude-Lorentz bath with $\lambda=100$ cm$^{-1}$ and $\gamma=53$ cm$^{-1}$.

### 6.3 Vibronic Progressions of 2D Aggregates with Dark Band Edges

If there is a relatively high-frequency, and in most cases intra-molecular, vibrational mode coupling strongly to the molecular excitons, vibronic progressions show up in the corresponding spectra. Spano et al.[99, 51] pioneered in describing the signature of excitonic aggregation in the changes of the vibronic progressions. In brief, the ratio of the heights of the $0-0$ peaks over the $0-1$ ones increases in the case of a J-aggregate, and vice versa for an H-aggregate. In addition, the spacings between adjacent peaks
also changes accordingly. Here we extend the analysis to the case of a generic 2D aggregate where there are nontrivial mixtures of J- and H-type aggregations.

### 6.3.1 Vibronic Progressions of Monomers

It is advantageous to remind ourselves the form of the vibronic progression of a monomer coupled to a high-energy vibration with frequency $\omega_0$. In this case the line shape function is simply a single oscillatory exponential and the corresponding spectrum is given by[116]

$$
\begin{align*}
g(t) &= \frac{\lambda}{\omega_0} e^{-\omega_0 t} \\
I(t) &= \int dt \cdot e^{-g(t)} = \sum_{n=0}^{\infty} e^{-i\lambda/\omega_0} \frac{1}{n!} \left( \frac{\lambda}{\omega_0} \right)^n \cdot \delta(\omega - n\omega_0).
\end{align*}
\tag{6.7, 6.8}
$$

The appearance of the progression of peaks follows from the equally spaced $\delta$ functions.

### 6.3.2 Vibronic Progressions of Dimers

It is most clear if we advance to the case of a dimer, coupled by a strength of $J$, where the system can be simply described by $\epsilon_k = \pm J$ with the in-phase and the out-of-phase combinations of site wavefunction magnitudes. In this case, following from the full cumulant expansion method by Ma et al.[17], the line shape function is given by

$$
\begin{align*}
2g(t) &= -\frac{\lambda}{\omega_0} e^{-\omega_0 t} + \frac{\lambda\omega_0}{(\omega_0 + 2J)^2} \left[1 + i(\omega_0 + 2J)t - e^{i(\omega_0 + 2J)t}\right] \\
&\approx -\frac{\lambda}{\omega_0} e^{-\omega_0 t} - \frac{\lambda\omega_0}{(\omega_0 + 2J)^2} e^{i(\omega_0 + 2J)t},
\end{align*}
\tag{6.9, 6.10}
$$

where we retain only the exponential terms contribute the most to the progressions.

Apparently the first term in Eq. 6.10 corresponds to the original progression of peaks. However, the effect of exciton states is reflected by the second term, where spacing and the peak of the envelope function for the progression change according
to \((\omega_0 + 2J)\) and \((\omega_0 + 2J)^2\), respectively. For an H-dimer one has \(J > 0\) and the aforementioned changes of spacing and peak heights come through, and vice versa for a J-dimer.

The extension from the case of a dimer to a generic aggregate is straightforward. Since only the exciton state energies are involved in Eq. 6.10, direct substitution of the system DOS into it would produce the desired results. Obviously for each additional exciton state considered one gets a term corresponding to the energy gap between the state and the bright state. Most importantly this happens in an additive fashion. Thus, for aggregates with dark band edges we predict that the progressions are blurred by the contributions from both sides of the bright states in the system DOS.

### 6.4 Davydov Splittings in Tubular Aggregates: Multiple Molecules per Unit Cell

Finally we address the case where there are multiple molecules per unit cell. In the language of condensed matter this adds to multiple bands to the system dispersion, and the splittings among the bands are referred to as the Davydov splittings. We extend our previous analysis on the parallel- and perpendicular-polarized peaks of tubular aggregates in this regard.

First of all, the expression for the ratio between the total intensities of parallel- and perpendicular-polarized absorption is generalized as follows.

\[
\frac{I_\perp}{I_\parallel} = \frac{\sum_i \sin^2 \theta_i}{\sum_i \cos^2 \theta_i},
\]

where the index \(i\) runs through all molecules in a unit cell, and \(\theta_i\) is the the angle that the transition dipole makes with the tube axis.

Again taking the advantage of the additivity of excitonic couplings in a system, we consider each molecule/transition in a unit cell and its interactions with the rest of the lattice separately from the other molecules/ transitions. Under this scenario,
the previous result concerning the energy gap between the two peaks of a tubular aggregate of Eq. 5.14 can be generalized. For the case of two molecules per unit cell, this results in

\[
\mathcal{J}^\perp - \mathcal{J}^\parallel = \begin{pmatrix}
J_{11}^\parallel & J_{12}^\parallel \\
J_{21}^\parallel & J_{22}^\parallel
\end{pmatrix} - \begin{pmatrix}
J_{11}^\parallel & J_{12}^\parallel \\
J_{21}^\parallel & J_{22}^\parallel
\end{pmatrix}
\]

\[
= \frac{4\rho^2}{\epsilon \Re} \left( \mathrm{Si}(\theta) - \frac{2}{\pi} \right) \begin{pmatrix}
\sin^2 \theta_1 & \sin \theta_1 \sin \theta_2 \\
\sin \theta_1 \sin \theta_2 & \sin^2 \theta_2
\end{pmatrix},
\]

(6.12)

where the coupling matrices \( \mathcal{J}^\parallel \) and \( \mathcal{J}^\perp \) are the block-diagonalized system Hamiltonian corresponding to \((k_\parallel, k_\perp) = (0, 0) \) and \((k_\parallel, k_\perp) = (0, \pm 1) \), respectively.

Notice that this alone is not useful in the sense that the coupling matrices are not directly observable. In experiments one can only detect the final outcomes of full diagonalizations of the system Hamiltonians. In the context of two molecules per unit cell there will be two pairs of perpendicular- and parallel-polarized peaks[6], with information including the peak heights and locations. Thus, one needs to infer the coupling matrices from therein. Specifically, from the quadruplets of peak locations \((E_+^\perp, E_+^\parallel)\) and peak intensities \((I_+^\perp, I_+^\parallel)\):

\[
\frac{|I_+ - I_-|}{I_+ + I_-} = \Delta I = \frac{4J_{12}}{\sqrt{(J_{11} - J_{22})^2 + 4J_{12}^2}},
\]

(6.13)

\[
E_\pm = \frac{J_{11} + J_{22}}{2} \pm \frac{1}{2} \sqrt{(J_{11} - J_{22})^2 + 4J_{12}^2}.
\]

(6.14)

We can then solve for the coupling matrix elements

\[
J_{12} = -\frac{1}{4} \Delta I (E_+ - E_-)
\]

(6.15)

\[
J_{11} + J_{22} = E_+ + E_-
\]

(6.16)

\[
J_{11} - J_{22} = (E_+ - E_-) \sqrt{1 - \Delta I^2},
\]

(6.17)

from which the intended parameters \((\theta_1, \theta_2)\) can be calculated.

Note that Eq. 6.12 becomes less useful when there are more than two molecules.
per unit cell. The reason is that while the number of observables increases linearly, the number of unknowns in the coupling matrices scales as the square of the number of molecules per unit cell.
Chapter 7

A Unified Theoretical Framework for Understanding Multiple Timescales of Carrier Relaxation in Organic Systems: Hot Exciton Relaxation in Conjugated Polymers

In this chapter we present a unifying theoretical framework to understand the relaxation dynamics of hot carriers in organic systems, with particular focus on hot excitons in ring-based conjugated polymers. Starting from the sub-picosecond dynamics observed in ultrafast spectroscopies, it has been repetitively demonstrated that excitons in emissive conjugated polymers pumped deep in the absorption band exhibit multiple timescales relaxing through the exciton manifold. On the basis of Frenkel exciton model, the fastest timescales on the order from sub-100 fs to a few ps can be attributed to the vertical relaxation of the excitons in the exciton band structure, typically understood as ultrafast localization, where the dynamics is modeled by master equations in the eigenbasis. After this first step of relaxation, the excitons mostly occupy local exciton ground states (LEGS). Horizontal exciton motion among
neighboring LEGS mediated by Förster energy transfer takes over from there which accounts for further energy relaxation on the timescale of tens of ps. Lastly, if the polymer backbone motion is enabled in the case of solvated samples, the backbone planarizes due to the feedback torque from the excitons and exciton-polarons form in approximately 100 ps before relaxing back to ground state. Analytical expressions for each of the processes are provided to explain dependence of the time constants on various experimental variables such as excitation/detection energy, chain length, and temperature.

7.1 Introduction

Conjugated polymers have been playing a central role in the development of organic electronics in the past few decades owing to the ease of processing, tunable electronic properties, and low manufacturing cost[117, 118, 119, 120, 121]. The discovery of electroluminescence of ring-based conjugated polymers (e.g. PPP and PPV) in the 90s[122] further enables the development of organic optoelectronics based on these materials such as organic light-emitting diodes, photovoltaics[123, 124], field-effect transistors[125]. Spectroscopic characterization with ultrafast and/or single-molecule resolution in the past decade reveals complicated relaxation dynamics of optical transitions therein[126, 127, 128, 129, 130, 1, 131, 132, 133]. This is particularly interesting in terms of the possibility to harvest hot energy carriers, which could potentially double the light-harvesting efficiency of photovoltaics [134, 135], if the relevant relaxation processes are understood and selectively controlled.

This contribution aims at providing a unifying and coherent theoretical scheme to understand and explain the various experimental findings. To facilitate our discussion, it is advantageous to summarize the key experimental results:

1. Sub-picosecond (ps) dynamics associated with ultrafast localization[128, 130, 136, 137, 132] or exciton formation[131, 138].

2. ps timescale, attributed to "hopping" in general[129, 130, 1, 131, 138, 132].
3. 10 ps component, attributed to later stages of hopping transport[129, 130, 1, 139].

4. 100 ps component, related to backbone-coupled dynamics, enabled in solutions and disabled in films [140, 141, 3].

5. Excitation/detection energy dependence: higher the energy, faster the timescales[127, 130, 131], while at the band edge the third timescale disappears[130].

6. Temperature dependence: higher the T, lesser the distinction between the first two time constants[127].

7. Chain length dependence in long chains[130, 141] and oligomers[133], or conjugation break dependence[126, 142].

We propose a unifying theoretical framework to coordinate and understand the above listed experimental observations. In our model, a ring-based conjugated polymer chain is represented by a 1D Frenkel exciton model with each monomer unit as a constituent site. While each site is coupled to one another through super-exchange (for nearest neighbors) and/or dipolar couplings[141, 3] resulting in an exciton band structure, scattering and relaxation among the excitonic states therein are introduced by couplings to local environmental degrees of freedom. This includes a fast dissipating bath characterized by a generic spectral density as well as a slowly varying torsional dynamics of the polymer backbone. The former is treated perturbatively to obtain Pauli master equations in the exciton basis. And the latter dynamics is simulated classically using Langevin equation under the influence of the torsional potential, the random torques exerted by solvent molecules, and the systematic feedback torque due to the presence of the exciton. We show that by successively accounting for these ingredients one can identify three separate timescales from sub-ps to tens of ps without the involvement of torsional dynamics, while an additional 100 ps timescale relaxation occurs in correlation with the torsional dynamics.

To help navigate our theoretical results covering timescales across four orders of magnitude, we provide a summarizing schematics Fig. 7-1 and Table 7.1 for the relax-
ation processes involved and their corresponding mathematical expressions. Following
the course of events illustrated in Fig. 7-1, an exciton is created in a high-lying ex-
cited state in the single exciton manifold (0). The exciton quickly relaxes vertically
through the manifold to states near the bottom that are more localized than those
in the middle of the band (1), corresponding to the ultrafast localization mentioned
above. These states have been referred to as the local exciton ground states (LEGS)
due to their nodeless feature that mimics the exciton ground state of a homoge-
neous chain[143]. Such relaxation is described in the master equation framework as
dominated by scattering events accompanied by spontaneous emissions of phonons,
therefore the dissipation rate of each state in the manifold can be accurately approx-
imated by the convolution of the density of states (DOS) lower in energy and the
spectral density of the fast bath, manifested in the form of Eq. (7.7) as a monotonic
increasing function of energy. During the earliest of the timescales covered, it suf-
fices to consider a first order expansion of the solution to the master equations that
conveniently picks up the dissipation rates of the initial states and those at the de-
tection energy window, as in Eq. (7.4). This naturally leads to the separation of the
first two timescales and their strong dependence on the excitation/detection energy,
that in essence one measures the accumulated dissipation rate counting up from the
bottom band edge. Also, at elevated temperatures scatterings accompanying stim-
ulated phonon absorption/emission events weigh in, diminishing the gradient of the
accumulated dissipation rate as a function of energy and bringing the two timescales
closer together.

Further relaxation in the low energy tail of the band is introduced by long-range
dipolar couplings, that Föster resonance energy transfer (FRET) thermalizes the ex-
citon population horizontally among strongly localized states occupying neighboring
segments (2). This is the third relaxation timescale in our framework. Notice in
linear configuration the long-range interactions account for up to 7% of the total ex-
citonic couplings that their separate treatment does not significantly affect the above
mentioned vertical relaxation scheme. Under current consideration the FRET rate
is predominately governed by the spectral lineshape, Eq. (7.14), and the DOS of the
LEGS, Eq. (7.12), both can be characterized by a single quantity: the average size of the LEGS. The energy dependence of the FRET rate, inherited from that of the DOS, agrees with that observed in experiment that the rate slows down with decreasing detection energy and eventually ceases to exist at the edge of the absorption band. We note that in case of a solid phase polymer sample, FRET serves as the main channel of exciton diffusion until reaching a trapping site and/or its spontaneous emission back to ground state.

However, in dilute solutions the polymer backbone is allowed to freely relax in response to random forces exerted by the solvent molecules and the presence of exciton itself. While the fast component of these nuclear movements has been accounted for, the slow-varying torsional angles between adjacent rings are seen as a source of static disorder in the course of the relaxation processes in the above framework. The co-evolution of exciton and torsional degrees of freedom can be treated by simultaneously propagating the master equations for the former and the Langevin equation for the latter, Eq. (7.17). At each step of the propagation a mapping between the old and the new sets of exciton states in a quasi-adiabatic fashion. As such, a unique feature of ring-based conjugated polymers, where the equilibrium positions of the torsional angles in electronic ground and excited states are different, stands out: Owing to steric hindrance, in the ground state the energy is minimized in the staggered conformation, while in the excited state the excitonic coupling is maximized in the planar conformation. As a consequence, at the later stage of the FRET dynamics the exciton develops correlation with the flattening of the local torsional angles and form an exciton-polaron (3). Assuming the polaron size to be comparable to the average size of LEGS and linearizing the excitonic feedback torque in Eq. (7.17), the polaron formation dynamics can be cast into that of a displaced damped harmonic oscillator, with the relaxation time given by Eq. (7.20). Since the magnitude of the excited state torque is inversely proportional to the spatial extent of the exciton, this explains the size dependence seen in oligomers[133] that the longer the chain the slower the exciton-polaron relaxation rate. The exciton-polaron then diffuses under the influence of the random solvent fluctuations in the steady state until emissive or
non-emissive recombination occurs (4).

Figure 7-1: Schematic representation of the hot exciton relaxation processes covered in this contribution. See text and Table 7.1 for details.

In the following sections we sequentially discuss each of the above mentioned relaxation processes in detail. Starting from the fastest, sub-ps vertical relaxation, we treat the exciton relaxation without invoking the dynamics of the backbone torsional angles in section 7.2. This is carried out first for a homogeneous, nearest-neighbor-coupled chain and then for a more realistic, disordered one. In section 7.3 we cover the FRET dynamics on the timescale of 10 ps hosted by LEGS in disordered chains. The backbone torsional dynamics that leads to the formation of exciton-polaron is treated explicitly next in section 7.4. We conclude in section 7.5.
Table 7.1: Relaxation processes covered in this work and the key expressions derived for the timescales.

<table>
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<th>timescale</th>
<th>1 ps</th>
<th>10 ps</th>
<th>100 ps</th>
<th>≥ 1 ns</th>
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<td>ultrafast localization, Eqs. (7.4) and (7.8)</td>
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<tr>
<td>Förster resonance energy transfer, Eq. (7.16)</td>
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<td>exciton-polaron formation, Eq. (7.20)</td>
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<td>natural decay lifetime</td>
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7.2 Sub-ps Vertical Relaxation: Ultrafast Localization

As mentioned in the Introduction, we start our consideration from a standard Frenkel exciton Hamiltonian in the local basis

\[ H_s = \sum_m \epsilon_m |m\rangle \langle m| + \sum_{m,n} J_{mn} |m\rangle \langle n|, \quad (7.1) \]

where \( \epsilon_m \) is the on-site exciton energy and \( J_{mn} \) is the exciton coupling between sites \( m \) and \( n \). Diagonalizing \( H_s \) gives rise to the excitonic states of the chains. Upon absorbing incoming photons, certain states are populated according to the excitation conditions, i.e. excitation energy and polarization. Relaxation of the initial population distribution within the exciton band occurs due to coupling to the phonon modes of the solvent environment or the backbone of the chain itself. We model the relaxation by the Redfield master equation[1]

\[ \frac{dP_\mu}{dt} = \sum_\nu [W_{\mu\nu} P_\nu(t) - W_{\nu\mu} P_\mu(t)]. \quad (7.2) \]
The scattering rates $W_{\mu\nu}$ are given by

$$W_{\mu\nu} = \sum_n \phi_{\mu n}^2 \phi_{\nu n}^2 D^{(b)}(E_{\mu}) n(E_{\mu}, T),$$

(7.3)

where $\phi_{\mu n}$ is the wavefunction amplitude of state $\mu$ at site $n$, $D^{(b)}(E)$ is the spectral density of the phonon bath, and $n(E, T) = (e^{E/T} - 1)^{-1}$ is the Bose-Einstein factor. We set the Boltzmann constant to unity. Given the initial excitation profile, the solution to Eq. (7.2) can be expressed in terms of series expansion

$$P_{\mu}(t) = P_{\mu}^{(0)}(t) + P_{\mu}^{(1)}(t) + \cdots$$

(7.4)

$$= P_{\mu}(0) e^{W_{\mu\mu} t} + \sum_{\nu} \frac{W_{\mu\nu} P_{\nu}(0)}{W_{\nu\nu} - W_{\mu\mu}} (e^{W_{\nu\nu} t} - e^{W_{\mu\mu} t}) + \cdots$$

where the first two terms in the expansion are given explicitly. An example demonstrating the convergence of the series is shown in Fig. 7.2(a). Note that the convergence is faster in the case where $E_{\mu}$ is near the excitation energy, since all higher order terms in Eq. (7.4) involve states with energies ranged between the excitation energy and $E_{\mu}$. In the current context, the fluorescence emission dynamics is characterized by the dissipation rates $W_{\mu\mu}$ of the states at the excitation energy $E_{\text{exi}}$ (population rising) and those at the detection energy $E_{\text{det}}$ (population decaying). We examine this assertion in the following.

### 7.2.1 Homogeneous Chain

For simplicity we start by considering a homogeneous, nearest-neighbor coupled chain[2], i.e. $\epsilon_m = 0$ and $J_{m,n} = -\delta_{m,n+1} \cdot J$, coupled to a bath with spectral density

$$D^{(b)}(E) = \frac{\pi \lambda}{(n_b - 1)!} \left( \frac{E}{\omega_c} \right)^{n_b} e^{-E/\omega_c},$$

(7.5)

where $\lambda$ is the reorganization energy and $\omega_c$ is the cutoff frequency. Since the typical magnitude of the exciton coupling is on the order of eVs, much larger than the thermal energy at room temperature, we can safely assume that the dominant contribution
to the scattering rates arises from the spontaneous phonon emission term. In other words, the diagonal terms of the scattering rate matrix $W_{\mu\mu}$ can be well approximated by

$$W_{\mu\mu} \approx -\sum_{\nu} D^{(b)}(|E_{\mu\nu}|) H(E_{\mu\nu}),$$  \hspace{1cm} (7.6)

where $H(E)$ is the step function. In the continuum limit

$$W(E) = -\int_{E_0}^{E} dE' \cdot D^{(b)}(E - E') D^{(s)}(E'),$$  \hspace{1cm} (7.7)

where $D^{(s)}(E)$ is the system DOS and $E_0 = -2J$ is the location of the lower band edge. The wavefunction overlap is constant and can be included in the DOS. For the 1D chain under investigation we take $D^{(s)}(E) = \frac{2\pi}{E - E_0}$ to arrive at

$$W(E) = 2\pi^2 \lambda \sqrt{\omega_c} \left[ (2x^2 + 1)F(x) - x \right],$$  \hspace{1cm} (7.8)

where $F(x) = e^{-x^2} \int_{0}^{x} e^{t^2} dt$ is the Dawson integral and $x = \sqrt{(E + 2J)/\omega_c}$. It is worth noting that under the low temperature assumption, $-W(E)$ is a monotonic increasing function characterizing the dissipation rate at the given energy level and vanishes at the lower band edge $E = E_0$. As shown in Fig. 7-2(b), Eq. (7.8) follows closely with the exact results until the simple $1/\sqrt{E - E_0}$ scaling law of 1D DOS fails at around $E = -J$. Also the exact rate near the lower band edge $E = -2J$ converges to a nonzero value owing to the stimulated phonon absorption term neglected in the derivation of Eq. (7.8).

As mentioned in the previous section, the first-order term predominates the early relaxation dynamics as in Eq. (7.4), characterized by two time constants $-W(E_{\text{exi}})^{-1}$ and $-W(E_{\text{det}})^{-1}$. In Fig. 7-2(c) we compare these two components to those from a double exponential fit of the results of numerically propagating Eq. (7.2). While the slower of the two timescale ($t_2$) is always dominated by $W(E_{\text{det}})^{-1}$ as seen from the close agreement, the faster timescale $t_1$ deviates from Eq. (7.8) as $E_{\text{det}}$ approaches the lower band edge. Since the larger $E_{\text{exi}} - E_{\text{det}}$ is, the larger the contribution from
the higher order terms becomes. The dissipation rates of these intermediate states are larger than the rate of the detected state and smaller than the one of the initial state.

We identify the two time components seen here to the fastest timescales observed in experiments[127, 130, 131]. The separation of them stems from the accumulated downward scattering rate $W(E)$ accompanied by spontaneous emission of phonons that involves the two largest energy scales in conjugated polymers: $J$, which gives rise to the exciton band[144], and $\lambda$, which characterizes strong coupling to a phonon environment[145]. The validity of this picture is corroborated by looking at the dependencies of the timescales on, e.g., $E_{\text{det}}[130]$, $E_{\text{exi}}$, and $T[127]$. This will be discussed in details in the following sections.

Figure 7-2: Redfield dynamics of a homogeneous chain with 300 sites. The following parameters were used: $J = 1 \text{ eV}$, $T = 300 \text{ K}$, $n_b = 1$ (Ohmic bath), $\lambda = 0.05 \text{ eV}$, and $\omega_c = 1 \text{ eV}$. The parameters are chosen to roughly match the steady state linear spectra of typical conjugated polymers[1, 2]. (a) The population dynamics of the state with energy closest to $-1.5 \text{ eV}$ with the initial state being the nearest to $-1.0 \text{ eV}$. The circles correspond to solving Eq. (7.2) exactly, while the lines represent truncating the series expansion Eq. (7.4) to various degrees. (b) The diagonal dissipation rate $W(E)$ as a function of energy. (c) Comparison of fitted time constants to the analytical expression, Eq. (7.8).

7.2.2 Disordered Chain

In realistic polymer samples, static disorder localizes the exciton wavefunctions. We expect the above mentioned two timescales to hold since the exciton structure of a disordered chain is very similar to a homogeneous one with some effective chain
length, while all essential ingredients in deriving the above theory carry on. To validate this conjecture, we introduce disorder to the excitonic Hamiltonian using the parametrization of the couplings by Barford et al.[141, 3]

$$J_{mn} = -J^{(s)}(\delta_{m,n+1} \cos^2 \theta_{m-1} + (\delta_{m,n-1} \cos^2 \theta_m) - J^{(d)} \frac{1}{|m-n|^3}, \quad (7.9)$$

with $J^{(s)} = 1.0$ eV being the super-exchange and $J^{(d)} = 0.4$ eV the dipole-dipole contribution to the exciton transfer integral. $\theta_m$ is the dihedral angle between the ring normals of neighboring sites. The dihedral angles can be sampled from the thermal distribution of the torsional potential of the conjugated polymer of interest[146]. Here for simplicity we assume the potential to be harmonic with equilibrium angle $\theta_0$ and force constant $K$. The variance of the torsional angles at temperature $T$ is $T/K$. Taking all the dihedrals to the equilibrium value would reduce the situation to a homogeneous chain. We note that adding diagonal disorder in the Hamiltonian would lead to similar localization effect and the same conclusion to be elaborate in later sections[147]. For simplicity we restrict ourselves to off-diagonal disorder only.

Under the influence of disorder, the exciton states are localized onto individual segments. In Fig. 7-3(a) the exciton states of a representative disordered chain having significant overlap with a particular nodeless LEGS are shown. A definition of LEGS has been provided by Malyshev et al. [143], define

$$\alpha_\mu = \left\lvert \sum_m \phi_{\mu m} |\phi_{\mu m}| \right\rvert, \quad (7.10)$$

and that exciton states with $\alpha_\mu > 0.95$ are recognized as LEGS. Localization is most salient at the two band edges while the states with intermediate energies are more delocalized. We also show all of the LEGS of the same chain in Fig. 7-3(b) for comparison. For each of the individual and mutually exclusive segments occupied by a LEGS, we found that the same physics can be deduced comparing to the homogeneous chain studied earlier with an effective system DOS. In other words, the two timescales, on the order of ps and faster for typical conjugated polymers, based on Eq. (7.2) are
We now attempt a further theoretical analysis of the above observations. The disorder enters our scheme in two ways. First, in Eq. (7.3), the wavefunction overlap factor selects states that are occupying the same localization segments. As such, in the continuum limit taken in Eq. (7.7), the connectivity-averaged system DOS gains dependence on the energy of the exciton state where its scattering rate is of interest:

$$D^{(s)}(E', E) = \left( \sum_{\mu, \nu} \delta(E' - E_\mu) \delta(E - E_\nu) \sum_m \phi_{\mu m}^{2} \phi_{\nu m}^{2} \right)$$  \hspace{1cm} (7.11)$$

where the bracket represents disorder average. This is the case since the states closer to the band edges are more localized and see a different effective DOS than those in the middle of the band. Secondly, disorder broadens and shifts the DOS as has been well documented in the study of Anderson localization problems[148]. For 1D systems Halperin derived an expression for the disordered DOS

$$D^{(s)}(E) = \frac{\sigma}{\pi^2} \frac{d}{dE} \left[ \text{Ai} \left( -2 \frac{E - E_0}{\sigma} \right)^2 + \text{Bi} \left( -2 \frac{E - E_0}{\sigma} \right)^2 \right]^{-1}$$  \hspace{1cm} (7.12)$$

where $\sigma$ is the disorder strength, and $\text{Ai}(x)$ and $\text{Bi}(x)$ are the Airy functions. Interestingly, we found the first complication to be less concerning. By ignoring the additional energy dependence of the DOS and substituting Eq. (7.12) into Eq. (7.7), we obtain results in quantitative agreement with the numerically exact ensemble averaged Eq. (7.3), see Fig.7-4(b). This can be explained by an error cancelling effect: Exciton states near the band edge, for example, are distributed more sparsely due to stronger localization, compared to those closer to the middle of the band. Nevertheless the sparsity is precisely countered by overlap factor itself that more localized pair of states on the same segment are more strongly coupled.
7.3 10 ps Relaxation: FRET

In addition to the two timescales inherited from the master equation framework, disorder and localization introduce new physics in the low energy regime. Under the prescribed initial excitation condition, 70% and more of the total exciton population has relaxed onto LEGS that have direct overlap with the initial state(s) [1] within the first ps. The dynamics that follows the initial vertical relaxation is then dominated by spatial diffusion among LEGS, mediated by long-range interactions, i.e. FRET [1, 149, 139]. To better quantify the contribution of FRET, we separate the exciton Hamiltonian Eq. (7.9) into the nearest neighbor terms and the long-ranged ones. The latter is then treated with standard generalized FRET theory [17] for the LEGS in the eigenbasis that diagonalizes the nearest neighbor terms. The obtained exciton states are essentially identical to those from the full diagonalization since the long-ranged terms amount to less than 7% of the full Hamiltonian. The expressions of FRET...
rates and the spectral lineshape are listed in the following.

\[ k_{\mu\nu} = \frac{J_{\mu\nu}^2}{2\pi} \int d\omega \cdot I_{\mu}^{(a)}(\omega)I_{\nu}^{(e)}(\omega), \]  

(7.13)

where \( J_{\mu\nu} \) is the long-range coupling in the eigenbasis of nearest neighbor coupling and

\[ I_{\mu}^{(x)}(\omega) = \int dt e^{-i\omega t} e^{i(\varepsilon_{\mu} \pm \lambda) t - \xi_{\mu} W_0 t}, \]  

(7.14)

with the minus sign \((x = e)\) corresponding to the emission lineshape functions and vice versa for the absorption \((x = a)\). \( \xi_{\mu} = \sum_m |\phi_{\mu m}|^4 \) is the participation ratio and \( W_0 = T \cdot \lim_{\omega \to 0} D^{(b)}(\omega)/\omega \) is the pure dephasing rate, see our earlier report for details[17, 90]. Note that the independent bath assumption of FRET theory is justified by exclusivity among the LEGS[143]. The generalized FRET rates \( k_{\mu\nu} \) are then added to the Redfield rate matrix \( W_{\mu\nu} \), and the exciton dynamics is numerically solved according to the same master equation framework Eq. (7.2).

With the augmented model accounting for the disorder-induced localization, we proceed to demonstrate a third timescale that is dominated by FRET among LEGS at the low energy region of the exciton band. In Fig.7-3(c) we show the time constants of tri-exponential fitting to the relaxation dynamics compared to those directly sampled from the rate kernels Eqs. (7.6) and (7.13). For the latter, the fastest time constant is obtained in the same manner as in Fig.7-2(c), which is simply \( W(E) \) averaged over the initial excitation profile. The characterization of the slower two time constants is similarly carried out over the detection profiles, with one \((t_2)\) being the average of the original Redfield rate Eq. (7.6) and the other \((t_3)\) the generalized FRET rate Eq. (7.13). The third timescale that we assign as dominated by intra-chain FRET is mostly on the order of ps. We attribute the systematic deviation of the numerically fitted \( t_3 \) to variable degree of mixing of the generalized FRET rate with the original Redfield rate, in which strong detection energy dependence is predicted.

We proceed to develop a quantitative expression for the FRET rate as well. The coupling matrix element between two adjacent and collinear LEGS of length \( N^* \) can
be written as[129, 69]

$$\bar{J}(N^*) = \frac{\pi^2 J^{(d)}}{N^*^2} \left[ S(\pi) - S\left(\frac{2\pi}{N^*}\right) \right]$$  \hspace{1cm} (7.15)

for $N^*$ being the average LEGS size and $S(x) = [x \cos x - \sin x + x^2 \sin(x)]/2\pi x^2$, where $\sin(x)$ is the sine integral function. For typical ring-based conjugated polymers at room temperature we estimate $N^* \approx 10$ and $J^* \approx 5$ meV. Similar to the earlier section, we take the continuum limit of Eq. (7.13) and replace the excitonic coupling $J_{\mu\nu}$ and the spectral overlap with their averages, i.e. ignoring the correlation between the two in disordered chains. The resulting rate expression becomes

$$k_{\text{FRET}}(E) = \bar{J}(N^*)^2 \cdot \int dE' \cdot d\omega \left\langle \sum_{\mu} I_{\mu}^{(e)}(\omega)\delta(E - E_{\mu}) \right\rangle \left\langle \sum_{\nu} I_{\nu}^{(a)}(\omega)\delta(E' - E_{\nu}) \right\rangle D_{\text{LEGs}}(E')$$

$$= \bar{J}(N^*)^2 \cdot \frac{2W_0}{(2W_0)^2 + (E - E' - \frac{2\lambda}{N^*})^2} \cdot D_{\text{LEGs}}(E'). \hspace{1cm} (7.16)$$

As shown in Fig.7-4(a), we further assume the LEGS DOS to be normally distributed at the band edge with width $\sigma_{\text{LEGs}} \approx 3\pi^2 J/N^*^2[143]$. This leads to the expression

$$k_{\text{FRET}}(E) = \bar{J}(N^*)^2 \cdot V(E - E_0 - 2\lambda/N^* \cdot \sigma_{\text{LEGs}}, W_0),$$

where $V(x, a, b)$ is the Voigt profile with Gaussian width $a$ and Lorentzian width $b$. See Fig.7-4(c) for the comparison of the above analytical expressions with the numerical results. While FRET timescale plateaus within the range of LEGS DOS on the order of 10 ps, Eq. (7.16) underestimates the rate on the high energy end of the LEGS DOS. This deviation is understood by the neglect of the dependence of $\bar{J}$ on energy, assumed in the derivation of Eq. (7.16).

We are now in a position to understand the experimental observations regarding the dependence of hot exciton relaxation timescales on numerous control variables. Firstly, the dependence on the excitation and detection energy in the time-resolved fluorescence emission spectroscopy can be predicted by the current framework straightforwardly. While the fastest sub-picosecond timescale is inherited from the accumulated dissipation rate of the exciton states at the excitation energy[127], the second timescale measures that of the states at the detection energy[130]. Also, since
we are concerned with the accumulated rate, the acceleration of the relaxation as the chain length increases[130] can be explained by the increase in the exciton states accessible. This is especially the case considering the high-energy exciton states that are more delocalized and effectively confined by the finite chains. Lastly, recall that in deriving Eq. (7.6) we neglected the contribution from stimulated phonons events, which guarantees the monotonicity of the dissipation rate as a function of energy. At elevated temperature this approximation becomes less accurate. The energy dependence is particularly affected for states close to the band edge where stimulated phonon absorption is the major component to the rate. This reduces the timescale separation between states with different energies[127].

![Figure 7-4: Disordered DOS and its influence on the Redfield and FRET timescales. All parameters are the same as in Fig.7-3. (a) Total DOS of averaged over 10^4 torsionally disordered chains (blue circles) and that of the LEGS (red circles). Eq. (7.12) is shown in blue line and a Gaussian fit to the LEGS DOS is in red line. (b) The results of substituting Eq. (7.12) into Eq. (7.7) (circles) compare to exact Redfield rates (line). (c) The exact FRET rates (circles) compared to the results from Eq. (7.16). The red line represents the FRET rates calculated using the exact DLEGs(E) as (the red circles) in part (a) and the black line uses the fitted Gaussian profile (red line in (a)).](image)

7.4 100 ps Exciton Relaxation Coupled with Torsional Dynamics: Exciton-Polaron Formation

In the earlier sections we are concerned with polymers with fixed backbones, \( i.e. \) a constant set of \( \{\theta_m\} \) in Eq. (7.9). Such constraint can be relaxed when considering
polymers solvated in solution, a method which a large set of experiments has been adopting[130, 131]. An elegant experiment carried out by Friend and Sundström et al. demonstrated that further energetic relaxation is possible when comparing the transient absorption spectra of a spin-cast film with the same polymer in solution[140]. Numerous studies have found strong couplings between exciton dynamics and torsional motion of the polymer backbone[145], as is evident from the form of the super-exchange contribution to $J_{mn}$ in Eq. (7.9). In this section we explicitly treat the torsional dynamics simultaneously with the exciton relaxation in a quasi-adiabatic fashion, since the exciton wavefunction dynamics can be seen as instantaneous compared to the torsional motions. The exciton states are mapped to ones having largest overlap in the next time step. This method has been devised by Yaron et al. [141] and Barford et al.[31], which is slightly modified and described in the following.

To characterize the torsional motion of the backbone in solution, the dynamics of dihedral angles $\{\theta_m\}$ of individual monomers is modeled by Langevin equation

$$\ddot{\theta}_m = -\gamma \dot{\theta}_m + \frac{1}{I} \left[ \Gamma_m^{(s)}(t) + \Gamma_m^{(r)}(t) \right], \quad (7.17)$$

where $I$ is the moment of inertia, $\gamma$ is the friction coefficient, $\Gamma_m^{(s)}(t)$ is the instantaneous systematic torque, and $\Gamma_m^{(r)}(t)$ is the random torque generated by collisions with solvent molecules. $\gamma$ and $\Gamma_m^{(r)}$ is related by the fluctuation-dissipation theorem

$$\langle \Gamma_m^{(r)}(t_1) \Gamma_m^{(r)}(t_2) \rangle = 2I\gamma T \delta_{mn} \delta(t_2 - t_1), \quad (7.18)$$

where the bracket represents thermal averaging, the delta functions indicate the random torques being spatially and temporally uncorrelated Gaussian noise.

The systematic torque $\Gamma_m^{(s)}$ is divided into two components: the restoring torque $\Gamma_m^{\text{res}}$ proportional to the derivative of the torsional potential and the contribution arising from coupling to exciton $\Gamma_m^{\text{exc}}$. The former can be directly calculated from potentials obtained by high-level quantum chemistry simulations[146]. Here we simply take the harmonic expansion centered at the equilibrium angle $\theta_0$ such that the restoring torque is $\Gamma_m^{\text{res}} = -K(\theta - \theta_0)$, where $K$ is the spring constant[3]. The latter
is derived from the Hellmann-Feynman theorem

\[
\Gamma_m^{\text{exc}}(t) = -\left\langle \Psi(t) \left| \frac{\partial H_s}{\partial \theta_m} \right| \Psi(t) \right\rangle = 2J^{(s)} \sum_{\mu} \phi_{\mu m} \phi_{\mu, m+1} \sin 2\theta_m. \tag{7.19}
\]

Given an initial excitation profile and assuming thermal distribution of \(\{\theta_m(t = 0)\}\) as in the previous section, one can propagate Eq. (7.2) for a short time step and calculate the instantaneous torques Eq. (7.17) to obtain a new set of torsional angles. This process is iterated to obtain the full dynamics of the exciton dynamics coupled with torsional motions. One such trajectory is presented in Fig.7-5(a).

We note that there are two types of energetic relaxation when considering the coupling to torsional dynamics. Firstly the variation of the torsional angles opens up additional channels that accelerate the equilibration among the instantaneous exciton states[131, 138]. This is sometimes referred to as the surfing or crawling motion of excitons on a polymer chain[150, 151]. Second, in most of the ring-based polymers the torsional potential is minimized at a nonzero value owing to steric hindrance[146, 3] in the ground state. However, in the excited state the potential is found to be steeper and minimized at \(\theta_m = 0[145]\), as is implicit from the form of the super-exchange coupling Eq. (7.9). It is thus expected that the exciton-polaron would form where the exciton carries the lattice distortion while diffusing on the chain[3].

The nature of the exciton crawling motion is closely related to the FRET contribution discussed in the previous section. Firstly they both concern the horizontal movement of the excitons on a polymer chain, detectable by fluorescence anisotropy decay experiments[130, 1]. This is in contrary to the faster timescales discussed above and the formation of exciton-polaron, which exist even in short chains containing only one LEGS where such horizontal relaxation is not possible. Secondly, while this relaxation pathway translates to that the fluctuations of torsional angles rendering the very definition of LEGS fluid, exciton states higher in energy and more delocalized than LEGS are less affected by such fluctuations. Thus, the FRET dynamics couples more strongly to the backbone fluctuations than that that of the Redfield relaxation
described in the above framework. Experimentally it could be possible to distinguish FRET from the exciton crawling motion by comparing the relaxation dynamics in partially conjugated chains in solution to those fully conjugated[126, 128]. Given that the average conjugation length comparable to the length of LEGS, the FRET dynamics is predicted to resemble that found in the fully conjugated counterpart since the long-range dipole interactions giving rise to it is unaffected. However, the exciton crawling across the breaks is forbidden.

Similarly, the relaxation dynamics of the formation exciton-polaron can be separately identified. As mentioned, the exciton-polaron forms regardless of the conjugation breaks in the previous example. For simplicity, we start our consideration with short conjugated oligomers comparable supporting one LEGS individually. At low temperature, the random torques are suppressed and the ground state of the single exciton manifold can be well approximated by nodeless sine wave with or without the polaron dressing[152]. Under such premise the feedback of torsional dynamics upon the exciton state is broken, rendering the dynamics more tractable mathematically. Further linearizing the excitonic torque $\Gamma^{(exc)} \approx 4 J^{(s)} (\theta - \theta_0) / N$, where $N$ is the chain length, reduces the problem into that of a displaced damped harmonic oscillator. The rate of the relaxation of the oscillator can be written as

$$k_{pol} = \frac{1}{2} \left[ \gamma - \sqrt{\gamma^2 - \frac{4 K + 4 J^{(s)} / N}{I}} \right]$$

$$\approx \frac{K + 4 J^{(s)} / N}{\gamma I}, \quad (7.20)$$

where in the second line we truncate the expansion of square root at the first order since for realistic parameters the first term in the square root dominates. This approximation is most valid in cases with long side chains. The results is shown in Fig.7-5(b). As expected, Eq. (7.20) overestimates the relaxation rate due to the linearization approximation that overestimates the excitonic torque. For realistic parameters relevant in the current context, the exciton-polaron time is estimated to be on the order of tens of ps and beyond. This is assigned to be the fourth and the
slowest timescale covered in this contribution.

Iyoda and Kim et al.[133] have recently examined the hot exciton relaxation for a series of oligothiophenes with chain lengths ranging from four to ten monomers. They have found that the relaxation is characterized by two timescales. The slower of the two varies significantly as a function of chain length, the time constant increases from 24 (tetramer) to 45 (decamer) ps, while the faster one remains relatively static at 9 ps. Additionally, the peak of the fluorescence emission shifts in the course of the relaxation for tens of meVs, in agreement with the results of Westenhoff et al.[140]. The magnitude of the shift reduces as the chain length increases. Both of these observations can be explained by the above theory: Due to the lack of horizontal degree of freedom, the faster timescale corresponds to the vertical relaxation within the band. The slower timescale is associated with the exciton-torsional polaron formation, which shows strong size dependence as indicated by Eq. (7.20). The larger energy shifts for shorter chains originate from the fact that the excitonic torque $\Gamma^{\text{exc}}$ is more concentrated in shorter chains, shifting the exciton-polaron equilibrium toward the planar configuration.

In real systems at ambient temperature the random thermal noise comes into play. However, the average timescale should be unaffected as the thermal contribution vanishes by taking the noise average of Eq. (7.17). The existence of disorder, in addition, gives grounds for the premise of static exciton wavefunction in the above simplified model, since the starting point of exciton-polaron formation is in fact the LEGS, whose size has been estimated to be on the order of 10 monomers. To fully justify this assertion, we provide an estimation of the size of the exciton-polaron $N_{\text{pol}}$ by considering the variational treatment for the ground state of a 1D Gaussian well: $V(x) = -\epsilon_0 \exp(-ax^2)$, where $\epsilon_0$ is the depth of the well and $a \propto N_{\text{pol}}^{-2}$. Using a Gaussian ansatz for the wavefunction $\phi(x) \propto \exp(-bx^2/2)$ and equating the widths of the well and the wavepacket[153], one arrives at $a = b = \epsilon_0/\sqrt{2}$. We then associate the well depth $\epsilon_0$ with the relative displacement $(\theta_{eq} - \theta_0)/\theta_0$, where $\theta_{eq}$ is the equilibrium
position of the torsional angle in Eq. (7.17). The final expression can be written as

\[
N_{\text{pol}} = \frac{1}{2C} \left[ \frac{K}{4J^{(s)}} + \sqrt{\left( \frac{K}{4J^{(s)}} + 4C \right)^2} \right],
\]

(7.21)

where \( C \) is the constant factor relating the relative displacement to the well depth. Eq. (7.21) agrees quantitatively with the results from numerically solving Eq. (7.17). The typical exciton-polaron size is indeed comparable to the size of the LEGS in the relevant parameter regime \((K/J^{(s)} \approx 1)\). This result corroborate our earlier identification of the slowest fourth timescale as the formation of exciton-polaron as seen in numerous experimental studies[130, 131, 133].

Figure 7-5: Exciton relaxation coupled to backbone torsional motion. The relevant parameters are chosen to resemble those of P3HT with \( I = 208 \) ps and \( \gamma = 30 \) ps\(^{-1}\).
(a) Additional energy relaxation enabled with dynamic torsional angles, compared to the Redfield/FRET dynamics only (black dashed line). The red line represents results from solving Eq. (7.17) and the blue dash-dotted line corresponds to setting the exciton torque \( \Gamma^{(\text{exc})} \) to zero. The difference between the latter two is attributed to the binding energy of exciton-polaron. (b) The shifted damped oscillator model (red line) as approximation to numerically solving Eq. (7.17) at \( T = 0 \) (circles). The dashed line is the equilibrium angle satisfying \( \Gamma^{(\text{exc})} + \Gamma^{(\text{res})} = 0 \). (c) The estimation of exciton-polaron size with the 1D Gaussian well model. The constant factor \( C \) in Eq. (7.21) is determined to be 0.05 to best fit the numerical exact result of Eq. (7.17) at \( T = 0 \), where we identify the exciton-polaron size to be the inverse participation ratio of the equilibrium ground state wavefunction \( N_{\text{pol}} \equiv 1/\sum_n \phi_n^4 \).
7.5 Conclusion

We present a unifying theoretical framework and numerical schemes to analyze the multiple timescales of hot exciton relaxation in conjugated polymers found in experimental studies. For polymers in solid state samples, the initial vertical relaxation to LEGS gives rise to the first two timescales on the order of ps and faster seen in numerous experiments that reflect the cumulative scattering rates of the exciton band in the low temperature limit. The dynamics then transitions to mostly horizontal movement among LEGS through intra- or inter-chain FRET, depending on the sample configuration. For ring-based polymers in solution the torsional degrees of freedom strongly coupled to the excitons come into play. Further energetic relaxation can be achieved in cases where the polymer is solvated in solution by the formation of exciton-polaron, involving the planarization of conjugation backbone leading to stronger excitonic coupling. We discuss in detail how the time constant of each of these processes can be quantified, and their dependence on numerous control parameters including temperature, chain length, and the pumping/probing frequencies in spectroscopic measurements. Our study contributes to deeper understanding of hot carrier relaxation in organic systems in general and helps in exploring potential design principles aiming at harvesting these hot carriers for device energy efficiency.
Appendix A

Applying FFT algorithm in the
calculation of bath autocorrelation
functions on the complex plane

A.1 Bath Autocorrelation Function

A.1.1 Real Time

In calculating the effect of Gaussian environment on the subsystem of interest, we
often need to calculate the autocorrelation function of the bath coordinates. For
example, in the eigenbasis of the subsystem, the scattering rates among the states
due to interaction with the bath depend on such correlation functions. Assuming
that the bath couples linearly to the system through its generalized coordinate, the
correlation function can be written as

\[ C(t) = \sum_k \langle x_k(t)x_k(0) \rangle_b = \sum_k \sum_{n_k=0}^{\infty} \rho_{k,n} \langle k, n|x_k(t)x_k(0)|k, n \rangle. \] (A.1)

Here we assume the bath comprises numerous harmonic oscillators labelled by \( k \),
\( x_k \) its generalized coordinate, \( |k, n \rangle \) its \( n \)th state, and \( \rho_{k,n} \) the Boson distribution func-
tion. The time dependence comes from the interaction picture, where by transforming
to the creation and the annihilation operators this can be written as

$$x_k(t) = \frac{1}{2}(b^\dagger_k(t) + b_k(t)) = \frac{1}{2}(e^{i\omega_k t}b^\dagger_k + e^{-i\omega_k t}b_k).$$  \hfill (A.2)

Substituting the above relation to the correlation function expression, one can obtain the textbook working formula

$$C(t) = \frac{1}{4} \sum_k \coth \left( \frac{\beta \omega_k}{2} \right) \cos(\omega t) - i \sin(\omega t)$$ \hfill (A.3)

$$= \int_0^\infty \frac{d\omega}{\pi} J(\omega) \left[ \coth \left( \frac{\beta \omega}{2} \right) \cos(\omega t) - i \sin(\omega t) \right],$$ \hfill (A.4)

where we have inserted the continuous distribution of phonon modes, the spectral density $J(\omega)$. In our convention we take the reorganization energy to be expressed as $\pi \lambda = \int d\omega J(\omega)/\omega$.

### A.1.2 Complex Time

For the calculation of properties after system-bath relaxation, e.g. equilibrium reduced density matrix or emission spectrum, the argument of the bath correlation function can be complex or even purely imaginary. In such cases the analytic-continued expression can be used.

$$C(t - i\tau) = \int_0^\infty \frac{d\omega}{\pi} J(\omega) \frac{\cosh \left( \frac{\beta \omega}{2} - i\omega(t - i\tau) \right)}{\sinh \left( \frac{\beta \omega}{2} \right)},$$ \hfill (A.5)

$$= \int_0^\infty \frac{d\omega}{\pi} J(\omega) \left[ \cosh \left( \frac{\beta \omega}{2} \right) \cos(\omega t) + i \sinh \left( \frac{\beta \omega}{2} \right) \sin(\omega t) \right].$$ \hfill (A.6)

### A.2 FFT Algorithm

#### A.2.1 Real Time

In practice, there is only a handful of spectral densities where analytical formula of the correlation functions can be given. In general, one resorts to carrying out the frequency integration numerically, which in many known cases converges very slowly
(except for the purely imaginary contour, or in general, when \(|t|\) is small). In light of the fact that the time contour where the correlation functions needed to be evaluated is usually linearly spaced, FFT can be invoked to efficiently calculate them. Starting from the real-time expression, we have

\[
C(t) = \int_0^\infty \frac{d\omega}{\pi} J(\omega) \left[ \coth \left( \frac{\beta \omega}{2} \right) \cos(\omega t) - i \sin(\omega t) \right]
\]

(A.7)

\[
= \int_0^\infty \frac{d\omega}{\pi} J(\omega) \left( \frac{e^{-i\omega t}}{1 - e^{-\beta \omega}} - \frac{e^{i\omega t}}{1 - e^{\beta \omega}} \right).
\]

(A.8)

This form can be cast into the summation of an FFT and an iFFT series. In Matlab syntax, a working routine goes like this.

```matlab
nt=length(t);            % total number of time steps
dt=t(2)-t(1);           % step size
nn=le1;                % fine-meshing the frequency grid
N=nt*nn;               % total number of Fourier terms
dw=2*pi/N/dt;          % total number of time steps
w=(1:N)*dw;
C1=fft(J(w)./(1-exp(-b*w)));
C2=ifft(J(w)./(1-exp(b*w)));
C=(C1(1:nt)-C2(1:nt)*N)*dw/pi;
```

The artificial mesh-grid parameter nn can be increased to converge the summation.

### A.2.2 Complex Time

When calculating along a complex time contour, special care is needed to implement the FFT scheme. In this case each of the Fourier terms is multiplied by a different scaling factor \(e^{\pm i\omega \tau}\), which makes direct implementation impossible. Here we expand the hyperbolic functions in terms of the Matsubara frequencies \(\nu_k = 2\pi k/\beta\). (See Tanimura (2014): JCP.141.044114)
\[
\frac{\cosh \left( \frac{\beta \omega}{2} - \omega \tau \right)}{\sinh \left( \frac{\beta \omega}{2} \right)} = \frac{2}{\beta} \sum_{k=-\infty}^{\infty} \frac{\omega e^{i\nu_k \tau}}{\omega^2 + \nu_k^2} \tag{A.9}
\]
\[
\frac{\sinh \left( \frac{\beta \omega}{2} - \omega \tau \right)}{\sinh \left( \frac{\beta \omega}{2} \right)} = \frac{2}{\beta} \sum_{k=-\infty}^{\infty} \frac{-i\nu_k e^{i\nu_k \tau}}{\omega^2 + \nu_k^2}. \tag{A.10}
\]

So
\[
C(t - i\tau) = \int_0^\infty \frac{d\omega}{\pi} J(\omega) \frac{\cosh \left( \frac{\beta \omega}{2} - i\omega(t - i\tau) \right)}{\sinh \left( \frac{\beta \omega}{2} \right)} \tag{A.11}
= \frac{2}{\beta} \int_0^\infty \frac{d\omega}{\pi} J(\omega) \left\{ \frac{1}{\omega} + \sum_{k=1}^{\infty} 2\omega \frac{\nu_k}{\nu_k^2 + \omega^2} \cos(\nu_k \tau) \right\} \cos(\omega t) - i \sum_{n\nu_k=1}^{\infty} \frac{2\nu_k}{\nu_k^2 + \omega^2} \sin(\nu_k \tau) \sin(\omega t) \right\}. \tag{A.12}
\]

Making use of the product-to-sum formula of trigonometric functions and convert to exponential functions, one can again cast the above expressions into Fourier series. The essential difference made by invoking the Matsubara expansion is that the contribution from the imaginary time is now simply a phase shift for each of the Matsubara frequencies, which can then be taken out of the series. A working Matlab code is as follows.

```matlab
tr=real(t); ti=imag(t);
dt=tr(2)-tr(1);
nn=1e2;
N=nt*nn;
dw=2*pi/N/dt;
w=(1:N)*dw;

% zeroth order term
ttt=bath.spec(w)./w;bl=fft(ttt);b2=ifft(ttt);
C0=(bl(1:nt)+b2(1:nt)*N)*dw/2;clear ttt bl b2
```
Note that this only works when the real time $t$ is nonzero. For the purely imaginary case $C(-i\tau)$ direct integration converges fairly fast.

### A.3 Drude-Lorentz Spectrum

For the record, the analytical expressions of the bath correlation functions for Drude spectrum $J(\omega) = 2\lambda\omega_c/\omega_c^2 + \omega^2$ are as follows.

\[ C(t) = \lambda\omega_c \left[ \cot \left( \frac{\beta\omega_c}{2} \right) - i \right] e^{-\omega_c t} + \frac{4\lambda\omega_c}{\beta} \sum_{k=1}^{\infty} \frac{\nu_k e^{-\nu_k t}}{\nu_k^2 - \omega_c^2} + \frac{4i\lambda\omega_c}{\beta} \sum_{k=1}^{\infty} \frac{\nu_k e^{\nu_k t}}{\nu_k^2 - \omega_c^2} \]  \hspace{1cm} (A.13)

\[ C(t - i\tau) = \frac{4\lambda\omega_c}{\beta} \left[ \frac{1}{2\omega_c} e^{-\omega_c t} + \sum_{k=1}^{\infty} \cos(\nu_k \tau) \frac{\omega_c e^{-\omega_c t} - \nu_k e^{-\nu_k t}}{\omega_c^2 - \nu_k^2} - i \sum_{k=1}^{\infty} \nu_k \sin(\nu_k \tau) \frac{e^{-\omega_c t} - e^{-\nu_k t}}{\omega_c^2 - \nu_k^2} \right] \hspace{1cm} (A.14) \]
Bibliography


