Dephasing and Dissipation in a Source–Drain Model of Light-Harvesting Systems

Shi-Jie Xiong,[a,b] Lipeng Chen,[a] and Yang Zhao*[a]

The energy transport process in natural-light-harvesting systems is investigated by solving the time-dependent Schrödinger equation for a source–network–drain model incorporating the effects of dephasing and dissipation, owing to coupling with the environment. In this model, the network consists of electronically coupled chromophores, which can host energy excitations (excitons) and are connected to source channels, from which the excitons are generated, thereby simulating exciton creation from sunlight. After passing through the network, excitons are captured by the reaction centers and converted into chemical energy. In addition, excitons can reradiate in green plants as photoluminescent light or be destroyed by nonphotochemical quenching (NPQ). These annihilation processes are described in the model by outgoing channels, which allow the excitons to spread to infinity. Besides the photoluminescent reflection, the NPQ processes are the main outgoing channels accompanied by energy dissipation and dephasing. From the simulation of wave-packet dynamics in a one-dimensional chain, it is found that, without dephasing, the motion remains superdiffusive or ballistic, despite the strong energy dissipation. At an increased dephasing rate, the wave-packet motion is found to switch from superdiffusive to diffusive in nature. When a steady energy flow is injected into a site of a linear chain, exciton dissipation along the chain, owing to photoluminescence and NPQ processes, is examined by using a model with coherent and incoherent outgoing channels. It is found that channel coherence leads to suppression of dissipation and multie exciton super-radiance. With this method, the effects of NPQ and dephasing on energy transfer in the Fenna–Matthews–Olson complex are investigated. The NPQ process and the photochemical reflection are found to significantly reduce the energy-transfer efficiency in the complex, whereas the dephasing process slightly enhances the efficiency. The calculated absorption spectrum reproduces the main features of the measured counterpart. As a comparison, the exciton dynamics are also studied in a linear chain of pigments and in a multiple-ring system of light-harvesting complexes II (LH2) from purple bacteria by using the Davydov D1 ansatz. It is found that the exciton transport shows superdiffusion characteristics in both the chain and the LH2 rings.

1. Introduction

In photosynthetic systems, solar photons are absorbed to produce electronic excited states (excitons) in the light-harvesting molecular chromophores (antennas). The excitation energies are subsequently transferred to the reaction centers (RCs) and converted into chemical energy.[1] In the case of high light intensity, however, the energy absorbed from the solar light by the antennae may well exceed the capacity of RCs to convert it into chemical energy. In the presence of oxygen, the excess excitations remaining in antennas can result in the generation of highly reactive and harmful molecular species. To avoid this, a strategy that emerged during the evolution of plants is to harmlessly and nonradiatively convert the excess excitations into heat. This process is commonly called nonphotochemical quenching (NPQ) of excitons.[2] In spite of the adaptability of converting the excess excitations into heat in the case of high light radiation, in ordinary situations the transport of energy from antennas to RCs has a high efficiency with a near unity quantum yield, and shows robust quantum coherence.[3–16]

To fully understand the features and mechanisms of coherent transport and NPQ processes, extensive theoretical and experimental investigations have been carried out. The properties of the coherent transport have been studied with various models,[17–22] Excitation energy transfer from antennas to RCs is usually modeled by the semiclassical Förster theory, which considers incoherent hopping between sites.[17,18] The coherence in the energy transport is accounted for by the Redfield theory, in which the exciton dynamics is captured by a master equation in the limit of weak exciton–phonon coupling and under the Born–Markov approximation.[19] Based on this theory, Silbey and co-workers developed an approach to exciton diffusion.[20,21] Haken and Strobl used a stochastic model,[22] and Kenkre and Knox established a generalized master equation formalism[24,25] to investigate the coherent and incoherent aspects of the excitonic transfer. To make the models more realistic, Zhang et al. introduced a modified Redfield equation to include static disorder in the exciton system,[26] which was used to simulate the energy-transfer dynamics in light-harvesting systems.

[a] Prof. S.-J. Xiong, L. Chen, Prof. Y. Zhao
Division of Materials Science, Nanyang Technological University
50 Nanyang Avenue, Singapore 639798 (Singapore)
E-mail: yzhao@ntu.edu.sg
[b] Prof. S.-J. Xiong
National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing (China)
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complexes of green plants.\cite{27} Silbey and co-workers proposed a generalized theory that includes coherent transport effects only within donors and acceptors while treating interactions between them according to the standard Förster model.\cite{28, 29}

A comparison between Förster, Redfield, and other models is given by Yang and Fleming in ref.\cite{30}. By using a master equation approach coupled with the Born–Markov and secular approximations, Mohseni et al. carried out computer simulations and found that the energy transport efficiency can be enhanced by modulating environmental noise.\cite{31} To explore the mechanism of the NPQ processes, solutions of light-harvesting complexes from oxygen-evolving photosystem II (LHCII) in various solvents and of different densities are widely used, and have been proved as excellent in vitro systems for studies of NPQ mechanisms.\cite{32} It was found in many experiments that a drastic decrease of the fluorescence yield and lifetime is induced by in vitro aggregation of isolated LHCII antenna complexes.\cite{33–35} This may suggest that dimerization and oligomerization of LHCII in the aggregation play an important role in the formation of NPQ trapping centers. From the analysis of the spectroscopic measurements on LHCII aggregates, a number of mechanisms for NPQ processes have been proposed. Despite tremendous efforts, contention still surrounds the precise locations of quenchers in the antenna and their microscopic quenching mechanisms. It has been proposed that the quenching occurs in the charge-transfer states\cite{36} or in excimeric states\cite{37} of a strongly coupled chlorophyll dimer. One possible channel for NPQ, as proposed by Holt et al., is through a localized cation radical state of the xanthophyll from a charge-transfer state between chlorophyll and xanthophyll\cite{38} and another, by Bode et al., is coupling of chlorophyll to a short-lived xanthophyll excited state.\cite{39} The direct transfer of energy from the chlorophyll pool to a particular carotenoid is also proposed as a possible mechanism of NPQ.\cite{40}

Optimal conditions for energy transfer and their scaling behavior in light-harvesting systems have been studied taking into account dissipative effects of the surrounding environments.\cite{41–46} In addition, dissipative quantum dynamics of an anharmonic oscillator coupled to a spin bath and to a harmonic bath has been studied with the surrogate Hamiltonian approach.\cite{40} Combined effects of disorder, noise, and interactions on the diffusion of a wave packet have also been investigated experimentally by employing ultracold atoms in a quasi-periodic lattice with tunable parameters, and accompanying numerical simulations have been performed using a generalized Aubry–André model.\cite{46}

In this work we study the energy transfer in photosynthetic light-harvesting systems by solving the time-dependent Schrödinger equation of a source–network–drain model, which takes into account a number of considerations such as the quantum coherence, the noise influence of the environment, the energy dissipation of photoluminescence quenching, and NPQ due to the coupling with the environment. Electronic energy excitations (excitons) are hosted by a coupled pigment network, and exciton creation by incident solar photons, their annihilation due to the absorption in RCs, the photochemical quenching, and NPQ are modeled with virtual semi-infinite source and drain channels, which connect to relevant sites in the network on one end and extend to infinity on the other. These virtual chains allow incoming and outgoing channels through which a continuous energy flow can be established. With those virtual drain chains the Hamiltonian is still Hermitian but the energy flow through the channels is irreversible as there are only outgoing waves but no reflecting waves from their infinitely far ends, thus capturing the irreversible nature of the dissipation. The decay rate of a dissipation channel can be well parameterized by the hopping integral of the corresponding virtual chain. With this model the process of energy transport in the presence of dissipation can be treated fully quantum mechanically. We include the dephasing effect by introducing phase uncertainties in the time-dependent wave functions. Dynamics simulation of a wave packet in a linear chain demonstrates that without dephasing, the exciton movement remains superdiffusive, with full quantum characteristics, despite strong energy dissipation. By increasing the dephasing rate, the motion of the exciton is changed from being superdiffusive to diffusive. As a quantitative study of the effect of quantum coherence, we investigate exciton propagation following the injection of a steady energy flow in the presence of incoherent and coherent outgoing channels for photoluminescence and NPQ processes. It is found that channel coherence makes feasible the suppression of dissipation and multie exciton super-radiance. Using this model, we investigate the energy-transfer process in the Fenna–Matthews–Olson (FMO) complex by taking into account the dephasing, and the photochemical and nonphotochemical quenching. The site population evolution obtained demonstrates robust coherent oscillations during the exciton lifetime. Calculated energy flows of outgoing channels under a steady radiation point to the dissipation paths of the excitons. The energy-transfer efficiency is decreased significantly by increasing the rates of the nonphotochemical and photochemical quenching, and is slightly increased by increasing the dephasing rate.

2. Model and Formalism

We consider the following Hamiltonian for the exciton transport in a photosynthetic energy-transfer system [Eq. (1)]:

$$H_e = H_s + H_p + H_n + H_R$$

where $H_s$ is the Hamiltonian of a pigment network for exciton transport connecting the antennas with the RCs, such as the light-harvesting LH1 and LH2 photosynthetic complexes in the membrane of *Rhodospirillum (Rsp.) photometricum*\cite{47, 48} and the FMO protein complex in green sulfur bacteria.\cite{49} $H_s$ can be written as [Eq. (2)]

$$H_s = \sum_n E_n a_n^\dagger a_n + \sum_{n,m} J_{n,m} a_n^\dagger a_m$$

in which $a_n^\dagger$ is the creation operator of an exciton on site $n$, $E_n$ is the corresponding site energy, and $J_{n,m}$ is the hopping inte-
eral for excitons from site \( n \) to site \( m \). One has \( J_{n,m} = J_{m,n}^* \) as the Hamiltonian is Hermitian. A site may represent a single chromophore or a cluster of chromophores. For the former, \( J_{n,m} \) originates from the nearest-neighbor transfer integrals and Förster dipole–dipole interactions between well-separated pigments, both of which are strongly dependent on the distance between the pigments.\textsuperscript{[11,17,50–52]} For the latter, \( \varepsilon_n \) is the resonance level to host an exciton in the \( n \)th cluster of chromophores, whereas \( J_{n,m} \) labels the effective transfer integral between \( n \)th and \( m \)th clusters with a distance dependence that differs from that in the Förster theory.\textsuperscript{[28]} \( H_n, H_m \), and \( H_b \) are tight-binding sub-Hamiltonians describing a semi-infinite virtual chain connected to a site in the pigment network as pathways for the radiative exciton–photon transition, for the annihilation of excitons due to the NPQ, and for the converting into chemical energy in the RCs, respectively. The general form of \( H_n \) with \( \alpha = P, N, \) or \( R \) is given in Equation (3):

\[
H_n = \sum_{l=0}^{\infty} \sum_{j=1}^{\infty} \left[ g_{l,n,j}^a a_{l,n,j}^a a_{l-1,0,j} + g_{l,n,j}^b a_{l,n,j}^b a_{l-1,0,j} \right] + \varepsilon_n a_{l,n,j}^a a_{l,n,j}^b,
\]

in which a semi-infinite chain is labeled by the index \( n \) of a network site to which it is connected and the index \( \alpha = P, N, \) or \( R \) denotes the type of pathway. \( \alpha \) denotes the position on the chain counting from the pigment network, so the starting site of every semi-infinite chain is also the corresponding site in the network, implying \((n,0,P) = (n,0,N) = (n,0,R) = (n,0)\). \( g_{l,n,j}^a \) is the nearest-neighbor hopping integral in the chain of type \( \alpha \) and connected to the network site \( n \). The site energy in a chain is the same as that of the network site to which it is connected. We note that a network site can be connected to two or more virtual chains as it may simultaneously belong to two or more pathways of differing types. The tight-binding Hamiltonian of chain \((n,\alpha)\) yields a transition exciton band of width \( 4g_{l,n,j}^a \) centered at \( \varepsilon_n \), which specifies the maximum exciton flow through the channel. We can thus determine the parameters \( g_{l,n,j}^a, g_{l,n,j}^b \), and \( g_{l,n,j}^c \) from the maximum exciton–photon transition rate in antennas, the maximum NPQ rate, and the maximum rate of conversion to chemical energy by an RC, respectively. The exciton flow actually realized will, however, be determined by the occupation status of the channels, because an exciton can be injected from a chain only if there are excitons in the chain, whereas it can exit to a chain only if empty states are available.

In this model, the dissipation processes, which correspond to the quenching of the excitons, are described by the exciton outflow through the semi-infinite chains. The quenching rate of excitons in a chain is specified by \( 4g_{l,n,j}^c \). This description provides a direct quantum-mechanical treatment to include both coherent and dissipation effects. Particle and energy exchanges with the environment are also captured by boson-bath models, such as the famed spin-boson model. However, the exciton exit in the current model is described with the exciton outflow through various channels towards infinity whereas in the boson-bath models there is a static boson bath. The exciton flow is a natural candidate to capture the continuous energy loss leading to the exciton quenching, whereas the exchanges with a static bath often result in a system–bath equilibrium at variance with quenching processes. For example, for significant initial system excitations, the bath will soon reach saturation in its capacity to digest energy, as shown in ref.\textsuperscript{[45]}. In the present model, the spectrum of a single tight-binding channel may be insufficient to simulate complicated bath spectra. This difficulty can be readily overcome by introducing multiple channels.

With this model we can investigate the energy-transfer dynamics in photosynthetic systems by solving the time-dependent Schrödinger equation [Eq. (4)]:

\[
i \frac{\partial}{\partial t} |\psi(t)\rangle = H_b |\psi(t)\rangle
\]

in which the wave function can be expressed as a linear superposition [Eq. (5)]:

\[
|\psi(t)\rangle = \sum_n \sum_{l=1}^{\infty} c_n(t) a_{l,n}^a |0\rangle + \sum_{n,M} \sum_{l=1}^{\infty} c_{n,M}(t) a_{l,n,M}^a |0\rangle
\]

with \( |0\rangle \) being the vacuum. The first sum in Equation (5) is the part of the wave function in the pigment network, and the second sum, in the semi-infinite chains. Usually the time-dependent coefficients \( c_n(t) \) and \( c_{n,M}(t) \) can be solved from the Schrödinger equation with a specific initial condition. We note that the sub-Hamiltonians in the channels are regular tight-binding Hamiltonians, which yield the part of the wave function in these chains as [Eq. (6)]:

\[
c_{n,M}(t) = u_{n,M}(t) e^{ik_{n,M}(E)(t-\delta t)} + v_{n,M}(t) e^{-ik_{n,M}(E)(t-\delta t)}
\]

in which \( k_{n,M}(E) \) and \( k_{n,M}(E) \) satisfy Equations (7) and (8):

\[
g_{n,M}(E) e^{-ik_{n,M}(E)} + \varepsilon_n = E + \frac{i}{u_{n,M}(t)} \frac{du_{n,M}(t)}{dt}
\]

\[
g_{n,M}(E) e^{ik_{n,M}(E)} + \varepsilon_n = E + \frac{i}{v_{n,M}(t)} \frac{dv_{n,M}(t)}{dt}
\]

The first and second terms in Equation (6) represent the outgoing and incoming components in channel \((n,M)\), respectively. For the RC channels \((\alpha = R)\) and the NPQ channels \((\alpha = N)\), there is only an outgoing component, so \( v_{r,p}(t) \equiv v_{n,M}(t) \equiv 0 \). For the antenna channels \((\alpha = P)\), the amplitudes of incoming channels, \( u_{r,p}(t) \), are determined by the incident light intensity, whereas the amplitudes of the outgoing channels, \( u_{p,0}(t) \), which can be obtained from the Equation (6), give a measure of the photoluminescence emitted from the corresponding sites. For every chain there is only one unknown amplitude, whereas for the pigment network there are \( N \) unknown amplitudes \( c_n(t) \). Thus, there are a total of \( N + M \) unknowns, in which \( N \) and \( M \) are the number of network sites and the number of chains, respectively. The unknown amplitudes can be obtained from the N Schrödinger equations for the \( N \) components of the network.
The variance in this time interval is given by Equation 13:

\[ \left< \delta\phi^2 \right> = \frac{(\Delta\phi)^2}{3} \]  

and the \( M \) equations for the \( M \) components of \( \psi_{n,0}(t) \) are:

\[ \frac{d}{dt} \psi_{n,0}(t) = i [H_{n,0}, \psi_{n,0}(t)] + \sum_{m} J_{n,m} \psi_{m,0}(t) + \sum_{i} g_{n,i} \psi_{i,1,0}(t) \]  

with \( g_{n,i} \) being the amplitude of the incoming wave determined by the light radiated on site \( n \).

There are still two important issues that are not explicitly described in this Hamiltonian:

1) In the wave function that follows the Schrödinger equation, there is no dephasing effect. As the phases in the incoming and outgoing channels, especially those in the NPQ channels, are affected not only by the evolution of the wave function in the pigment network, but also by the environment, the dephasing effect should be described by the phase uncertainty in these components. We will include the dephasing effect in the calculation by introducing a dephasing rate \( \eta \) with [Eq. (12)]:

\[ \Delta \phi(t) = \eta \Delta t \]  

in which \( \Delta \phi(t) \) is the phase variance, which quantitatively specifies the phase uncertainty of amplitude \( \psi_{n,0}(t) \) produced by the environment during the time interval from \( t \) to \( t + \Delta t \). In the numerical integration of the time-dependent Schrödinger equation, such phase uncertainties are included by adding random deviations to the phases of \( \psi_{n,0}(t) \) at every time step by calling a random-number generator. If the added random phase deviation \( \Delta \phi \) in a time step is generated according to a uniform distribution in the range \( [-\Delta \phi, \Delta \phi] \) of phase variance in this time interval is given by [Eq. (13)]:

\[ \left< \delta \phi^2 \right> = \frac{(\Delta \phi)^2}{3} \]  

If such a phase deviation is included at each of \( N \) successive time steps, the phase variance in the time interval from \( t \) to \( t + N\Delta t \) is [Eq. (14)]:

\[ N \frac{(\Delta \phi)^2}{3} \]

Thus, the resultant dephasing rate is \( \eta = (\Delta \phi)^2/(3 \Delta t) \). In photosynthetic systems with a protein environment, the dephasing processes are usually caused by interactions with environmental phonons. In fact, a bath of phonons will be used to capture the dissipative effect of the environment on exciton dynamics in a LH2 ring in Section 6. In a stochastic model, these interactions are often described by dynamic fluctuations of the chromophore transition energies. [53] In solving the time-dependent Schrödinger equation, the inclusion of the fluctuations will lead to the random phase changes as considered in our calculations.

2) The noisy environment can also produce additional uncertainties to the system. One example is static disorder. We will consider the disorder in the site energy as [Eq. (15)]:

\[ P(e_n) = \begin{cases} 1/W & \text{for } |e_n - e_0| \leq W/2 \\ 0 & \text{otherwise} \end{cases} \]  

in which \( P(e_n) \) is the probability of finding the site energy \( e_n \), and \( W \) is the degree of the disorder. In the following sections, we will investigate the effects of dephasing and disorder on the exciton transport properties. Despite the fact that the temperature effect is not explicitly included in the model, both the dephasing and NPQ rates are temperature dependent, and a higher temperature often induces larger dephasing and NPQ rates.

3. Exciton Diffusion in a Chain in the Presence of Dissipation, Dephasing, and Disorder

We first consider the exciton diffusion in the presence of dissipation, dephasing, and disorder, which is modeled here by an infinite chain with the site index \( n \) running from \(-\infty \) to \( \infty \). Only the nearest-neighbor coupling is considered with \( J_{n-1,n} = J_0 \) for \( |n - m| = 1 \). Photon–exciton transition and NPQ occur on every site and no RCs are included, that is, \( g_{n} = g_{0} \) and \( g_{n} = 0 \), for all \( n \). Before \( t = 0 \), there are no excitons in the system. An exciton is created on site \( n = 0 \) at \( t = 0 \) and we investigate its subsequent evolution from the time-dependent Schrödinger equation.

In Figure 1 we plot the evolution of the population distribution of the exciton in the presence of dissipation but without dephasing and disorder. It is found that the wave packet spreads out from the initial site in both directions, whereas its total amplitude is decreased due to the radiative damping and the NPQ. The decay of the amplitude on a site begins with the arrival of the wave-packet front. As a result, the amplitudes near the site \( n = 0 \), where the exciton first enters, may be vanishing while the remaining wave packet is still spreading farther away from \( n = 0 \). At the same time, the amplitudes exhibit both temporal and spatial oscillations, thus implying robust quantum coherence in the absence of dephasing, but in the presence of energy dissipation due to the radiative damping and the NPQ. The combination of coherence and dissipation leads to a “nonclassical” envelope of the wave packet: the highest peaks are on the edges rather than at the center. Al-
though the dissipation only partially wipes out the excitation in the wave packet, the coherence is preserved in the remaining part.

In Figures 2 and 3 we plot the evolution of the exciton profile with initial excitation on site \( n = 0 \) in the presence of dephasing and disorder, respectively. It is demonstrated in Figure 2, that due to dephasing, the envelope of the wave packet is changed from a "nonclassical" (see Figure 1) to a "classical" profile, exhibiting the high peaks at the center, rather than on the edges. This provides us with a hint about how the quantum effect is destroyed. On the other hand, as shown in Figure 3, site energetic disorder can localize the wave packet. According to the scaling theory, a tiny static disorder can cause all the states to be localized in one dimension. Wave-packet localization is a result of the quantum interference of all randomly scattered waves. It is thus also a quantum effect and is different from the effect of dephasing in nature.

To verify the above point, we calculated the mean square displacement (MSD) \( \langle x^2(t) \rangle \) as a function of time. Usually, the MSD shows a power-law dependence on the time, that is, \( \langle x^2(t) \rangle \propto t^{\gamma} \) in which the exponent \( \gamma \) is an important property of exciton diffusion. In classical diffusion, one has \( \gamma \approx 1 \), with \( 2 > \gamma > 1 \) and \( \gamma < 1 \) corresponding to the superdiffusion and sub-diffusion regimes, respectively. On the other hand, in the ballistic regime of the quantum transport, \( \gamma \geq 2 \). In Figure 4 we plot the time dependence of the MSD of the exciton diffusion in
a chain with the dissipation but without the static disorder for various degrees of dephasing. We note that for zero dephasing rate, $\eta = 0$, the curve shows a ballistic behavior with $\gamma \geq 2$, in spite of the existence of strong dissipation, $g_1 = 8$ meV. This implies again that the dissipation alone cannot change the quantum nature of the transport. The dissipation can reduce the exciton amplitudes in the chain because some exciton components exit through the outgoing channels, but this cannot change the behavior of MSD as it is a quantity averaged over the components within the chain. By increasing the dephasing rate, however, a clear transition from the quantum superdiffusive behavior with $\gamma \approx 2$ to the classical diffusive behavior with $\gamma \approx 1$ is obtained. These results indicate the important role of the dephasing in such a transition.

In the presence of static disorder, all the states are localized. Thus, in principle, MSD should deviate from the power-law dependence on time and should saturate after a long time. In Figure 5 we show the time dependence of the MSD of the exciton diffusion in a chain with both the dissipation ($g_1 = 8$ meV) and the static disorder ($W = 12$ meV) for different values of dephasing rate. Other parameters are the same as those in Figure 1.

4. Stationary Flow of Energy in a Chain with Incoherent and Coherent Outgoing Channels

It is interesting to study how the stationary energy flow is distributed when constant-intensity sunlight is incident on a photosynthetic chain. In this section, we demonstrate that this issue can be resolved within the framework of the source–network–drain model. Instead of modeling energy flow in a realistic photosynthetic system, we examine an extended system to gain insights into the general features of excitonic energy transfer. If constant-intensity sunlight is incident on the system, the excitons will be created continuously on site $n = 0$ before spreading out in both directions. In this process, the energy transfer is subjected to photochemical and nonphotochemical quenching. As a result, in the stationary state, the exciton population flows from the site $n = 0$. In our source–network–drain model, the photochemical quenching and the NPQ are expressed with the outgoing channels with the decay rates specified by $4g_0h^{-1}$ and $4g_1h^{-1}$, respectively.

First, we assume that the outgoing channels are attached independently to the sites without quantum interference, that is, the photoluminescence and NPQ processes occur inherently among the pigments. The steady exciton inflow on site $n = 0$ is quantified by $4g_0d_0h^{-1}$, in which $d_0$ is the amplitude of the incoming exciton wave. The stationary solution can be obtained by solving Equations (9) and (10) and setting $dv_{in}(t)/dt = dv_{in}(t)/dt = 0$ for all $n$ and $\alpha$. For a uniform chain with $\epsilon_n = \epsilon_0$ and $J_{n,n+1} = J_0$ for all $n$, one can obtain an analytical solution [Eq. (16)]:

$$c_n = \frac{-2id_0g_0\sin k_0(E)}{g_1e^{-\frac{\hbar k_0}{2J_0}} - 2J_0g_1^2(E) - g_0e^{\frac{\hbar k_0}{2J_0}}} [\chi(E)]^n$$

in which $c_n$ is the amplitude of the exciton state at site $n$, $d_0$ is the amplitude of the incident exciton wave, $k_0(E) = \arccos[(E - \epsilon_0)/2g_0]$, $E$ is the energy of the incident excitons, and $\chi(E)$ follows Equation (17):

$$\chi(E) = \begin{cases} \frac{\pi^2}{2} \left( \frac{\sqrt{p(E) + \sqrt{p(E)^2 - 4}}}{2} \right) & \text{if} \ |p(E) + \sqrt{p(E)^2 - 4}| < 2 \\ \frac{\pi^2}{2} \left( \frac{\sqrt{p(E) + \sqrt{p(E)^2 - 4}}}{2} \right) & \text{otherwise} \end{cases}$$

where $p(E) = [g_0e^{-\frac{\hbar k_0}{2J_0}} - g_1e^{\frac{\hbar k_0}{2J_0}}]/J_0$.

It is clear that the solution given by Equation (16) exhibits exponential decay on both sides of the central site $n = 0$. The decay length depends upon the bandwidths and wave vectors in the channels of the photochemical quenching and the NPQ. Especially, if the exciton energy matches the band center, that is, $E = \epsilon_0$ and $k_0(E) = k(E) = \pi/2$, one has the decay length [Eq. (18)]:

$$L_0 = \left[ \ln \left( \frac{2J_0}{\sqrt{(g_0 + g_1)^2 + 4J_0^2 - g_0 - g_1}} \right) \right]^{-1}$$

Figure 5. Log–log plot of the time dependence of MSD of the exciton diffusion in a chain with both the dissipation ($g_1 = 8$ meV) and the static disorder ($W = 12$ meV) for different values of dephasing rate. Other parameters are the same as those in Figure 1.
in units of the lattice spacing. It can be observed that the photochemical quenching and the NPQ play the same role in the decay process. Apart from the decay of the wave function amplitude, its phase also varies while moving along the chain. The super-radiance may occur if the phases of different sites within a segment match, and the photoluminescence from this segment is detected coherently. In this case, the detected intensity is $M^2$ times, rather than $M$ times, that of a monomer, in which $M$ is the number of pigments in the segment.\(^{[3,4]}\) In the uniform chain with the exciton energy at the band center, however, the phase is changed by $\pi/2$ on moving to the neighboring site, which makes it difficult to observe the super-radiance effect. The phase variation with respect to sites may be slowed if one moves the exciton energy away from the band center, but this can cause a suppression of the total intensity as can be seen from the prefactor $\sin k_0$ in Equation (16).

In the presence of static disorder, the decay of the wave function may exhibit drastic changes. Although disorder-induced localization may suppress the spreading of the excitonic state, channels of photochemical quenching and NPQ may also get blocked by the disorder. In Figure 6 we plot the stationary population profile when a steady flow of excitons is injected on site $n=0$ in the presence of the static disorder of various strengths. The effect of disorder is certainly complicated: on the one hand, it may facilitate the spreading of the exciton wave, but on the other hand, this trend is countered by the localization effect as the strength of disorder becomes large.

Next, we investigate the stationary exciton profile and the distribution of photoluminescence intensity along the chain in the presence of quantum coherence among outgoing channels when a steady energy inflow is injected into site $n=0$. As mentioned earlier, in the propagation of the exciton wave function along the chain, its phase varies. Thus, the outgoing components can be either suppressed due to the destructive interference among the channels, or enhanced by constructive interference, depending on the phase variation within the realm of excitonic coherence. Generally, if the coherence size encompasses several periods of phase variation, the destructive interference will dominate, and the dissipation induced by the outgoing channels is suppressed. In Figure 7 we plot the stationary exciton profile along the chain for two values of the coherence size $L$. This behavior is completely different from the exponential decay expressed in Equation (16) and shown in Figure 6 in the absence of coherence: the amplitudes oscillate along the chain, and the maximum amplitudes remain almost unchanged up to $n=\pm 300$. The amplitude oscillation is attributed to the boundary-induced standing wave, and the period of the oscillation is the de Broglie wavelength of the exciton along the chain independent of the coherent size. The sustained oscillation can be viewed as a consequence of suppressed dissipation due to imposed quantum coherence. In Figure 8 we plot the distribution of photoluminescence intensity along the chain. There also appears to be an oscillation along the chain due to alternating constructive and destructive interference within the coherence size. The oscillation period in Figure 8 is different from that of the standing wave shown in Figure 7. Interestingly, the intensity approaches unity (the intensity of the incident wave) at $n=0$, thanks to the constructive interference in the vicinity of $n=0$.

Figure 6. Stationary population distribution with various degrees of static disorder when a steady exciton flow is injected at site $n=0$ with intensity $d_0 = 1$. The parameters are: $e_0 = 1.5 \text{ eV}$, $J_0 = 0.013 \text{ eV}$, $g_x = 0.002 \text{ eV}$, and $g_y = 0.003 \text{ eV}$.

Figure 7. Stationary population distribution of the chain with coherent outgoing channels when a steady exciton flow is injected at site $n=0$ with intensity $d_0 = 1$. The coherence is modeled by merging the $L$ outgoing channels together, where $L$ is the coherent length. The parameters are: $e_0 = 1.5 \text{ eV}$, $J_0 = 0.013 \text{ eV}$, $g_x = 0.002 \text{ eV}$, and $g_y = 0.0015 \text{ eV}$. Two values of the coherence size are used: $L=9$ (black) and $L=18$ (red).

Figure 8. Distribution of photoluminescence intensity along the chain with coherent outgoing channels when a steady exciton flow is injected at site $n=0$ with intensity $d_0 = 1$. The parameters are the same as those in Figure 7. Two values of the coherence size are used: $L=9$ (black) and $L=18$ (red).
5. Dynamics of Energy Transfer in the Fenna–Matthews–Olson Complex

As an application of our model, in this section we investigate the energy-transfer dynamics in the FMO pigment–protein complex,[49,55–58] commonly found in green sulfur bacteria adapted to low-light conditions, and assigned to the task of transferring to the RC complex solar-generated excitation energy in the peripheral antenna chlorosome. Due to its relatively small size and simple structure, the FMO complex has been extensively investigated both experimentally[13, 15, 55] and theoretically.[14, 49, 59–65] The FMO complex is a trimer of three identical subunits, each of which contains seven bacteriochlorophyll (BChl) molecules. Every BChl can be regarded as an excitation-hosting site. The seven BChls in a subunit form a network described by Hamiltonian $H_0$ of Equation (2) for which the site energies and the coupling strengths between sites are given in ref.[62]. The semi-infinite virtual chains described by sub-Hamiltonians $H_{\nu}, H_{\mu}$, and $H_\nu$ in Equation (3) are connected to the sites in the network to take into account the annihilation pathways of excitons due to radiative recombinations, NPQ processes, and chemical energy conversions in RCs. The dephasing effect can be included by introducing the phase uncertainty of the wave function components in corresponding virtual semi-infinite chains as illustrated in Section 2.

As BChl 3 is in the vicinity of the RC,[20] to investigate the dynamics of energy transport we can take site 3 as the excitation donor to the RC by connecting the virtual chain of $H_\nu$ to it. The transfer rate is specified by the hopping integral $g^\nu$ in this chain as $\Gamma_{RC} = 4g^\nu/\hbar$. If initially an exciton is created at site $i$, the evolution of the exciton can be obtained by solving the time-dependent Schrödinger equation, and the energy-transfer efficiency can be calculated as [Eq. (19)]:

$$Q_i = \Gamma_{RC} \int_0^\infty dt |c_i(t)|^2$$  \hspace{1cm} (19)

Figures 9 and 10 depict the time evolution of the exciton population on the seven pigments of the FMO complex after an exciton is created on site 1 and on site 6, respectively, while the RC is attached to site 3. It can be seen that the population reaches the RC in approximately 50 fs before entering an oscillation phase. Regular oscillations are visible on all sites up to 0.5 ps, which reflects the existence of quantum coherence at this timescale in agreement with 2D electronic spectroscopic measurements.[15] Figures 9 and 10 point to likely energy-transfer pathways from site 1 via 2 to 3 and from site 6 via 5, 7, and 4 to 3, respectively, as demonstrated by Cho et al. using 2D electronic spectroscopy.[66] Within 1 ps, only the initial site of excitation and its nearest neighbors (sites 1 and 2 in Figure 9, and sites 6 and 5 in Figure 10) show population decay, whereas the rest of the sites only exhibit a trend of population growth. Our results here are in agreement with those of Ishizaki and Fleming using the hierarchical equations of motion[65] and those of Skochdopole and Mazziotti using the Lindblad formalism.[63] The parameters used in this work strongly depend on temperature, the radiation intensity, and protein or solvent environments. In Figure 11 we show the effect of the dissipation rates and the dephasing rate on the energy-transfer efficiency. It can be seen that the efficiency decreases almost linearly with the dissipation rates, but increases marginally with the dephasing rate.

By using our model, we can also investigate the stationary energy flow with excitons generated continuously on the pigments in the FMO complex by constant radiation. In Figure 12 we show a chart of energy dissipation percentages by individual pigments in the FMO complex when a steady exciton flow is injected on a certain pigment. The largest portion of dissipation occurs on site 4, whereas only weak dissipation occurs on sites 1 and 2. The sum of dissipated energies on all sites and drained ones in the RC corresponds to the absorption of the injected energy, which allows for an estimation of the absorption by the FMO complex. Shown in Figure 13 is the calculated absorption spectrum with a steady exciton inflow from the antenna injected into site 1 and an outflow leaving site 4 to the RC. The main feature of the measured spectrum[68] has been re-

![Figure 9](https://example.com/figure9.png)  \hspace{1cm} Figure 9. Time evolution of site populations in the FMO complex. Initially, the exciton is created on site 1 and the outgoing channel leading to the RC is connected to site 3 with rate $g^\nu = 8$ meV. The dissipation rates are $g^\nu = g^\mu = 3$ meV and the dephasing rate is $\gamma = 0.05 \text{ fs}^{-1}$ for all sites. The evolution is obtained by averaging over 30 random phase configurations.

![Figure 10](https://example.com/figure10.png)  \hspace{1cm} Figure 10. Time evolution of site populations in the FMO complex with parameters adopted from those in Figure 9. Initially the exciton is created on site 6.
The seven sites of the FMO complex is given in the inset to show the relative positions of the energy used by the RC connected to site 3. Dissipation on various sites, whereas the green column denotes the percentage of energy. Columns marked with site numbers correspond to the percentages of energy injected into site 1 (main panel) and into site 4 (inset). The seven pigments of the FMO complex are indexed along the x axis such that the pink columns marked with site numbers correspond to the percentages of energy fluctuating in the range of 1 meV.

In this section, as a comparison to the source–drain model, we produce here, and our result is also consistent with those calculated in ref. [59] and ref. [60].

6. Excitonic Diffusion in LH2 Complexes of Purple Bacteria

In this section, as a comparison to the source–drain model, we use the Davydov D1 ansatz to study the exciton dynamics in a linear chain of pigments and in a multiple-ring array of light-harvesting complexes in purple bacteria. The LH2 complex of Rsp. molischianum [56] has a highly symmetric ring structure that is constructed by an eight-unit circular aggregate built from αβ heterodimers. Each unit contains a pair of α and β peptides, three bacteriochlorophyll a (BChl-a) molecules, and a caroteneoid. The BChl-a molecules form two rings named as B800 and B850 rings, according to peaks at 800 and 850 nm, respectively, in the LH2 absorption spectrum. In the B850 ring, there are 16 tightly positioned BChl-a molecules in which the Mg to Mg distance is about 9.36 Å for the 1α–2β dimer and about 8.78 Å for the 1β–2α dimer. [51] The exciton dynamics in a one-dimensional chain and a multiring LH2 system can be studied using the Davydov D1 ansatz and the Lagrangian formalism of the Dirac–Frenkel time-dependent variational method. [57, 58] The D1 trial states can be written as Equation (20):

$$|\psi_D(t)\rangle = \sum_a \alpha_a(t)|\tilde{U}_a(t)|0\rangle_{ex}|0\rangle_{ph}$$

and its multiple-ring version takes a similar form with an extra ring index r [Eq. (21)]:

$$|\psi_D(t)\rangle = \sum_{r,h} \alpha_{r,h}(t)|\tilde{U}_{r,h}(t)|0\rangle_{ex}|0\rangle_{ph}$$

Here, $\alpha_a(t)$ are the variational parameters representing exciton amplitudes for a chain (a multiple-ring system), and $\tilde{U}_a(t)$ is the corresponding Glauber coherent operator [Eqs. (22) and (23)]:

$$\tilde{U}_a(t) = \exp\left\{ \sum_q [\lambda_{a,q}(t)\hat{b}_a^\dagger - H.c.] \right\}$$

$$\tilde{U}_{r,h}(t) = \exp\left\{ \sum_q [\lambda_{r,h,q}(t)\hat{b}_{r,h}^\dagger - H.c.] \right\}$$

where H.c. stands for Hermitian conjugate. Detailed derivations of equations of motion for exciton dynamics in a chain and a multiple-ring LH2 system can be found in the Supporting Information. After solving the coupled equations of motion for the variational parameters, we obtain the single-exciton density matrix $\rho_{mn}(t)|\rho_{mn}(t)\rangle$ for the chain (the multiple-ring system) [Eqs. (24) and (25)].
the unit of the characteristic phonon frequency \(\omega\).

\[
\rho_{nm}(t) = \alpha_n^*(t)\alpha_m(t)S_m(t)
\]

(24)

\[
\rho_{nm}^{0\omega}(t) = \alpha_n^{0\omega}(t)\alpha_m^{0\omega}(t)S_m^{0\omega}(t)
\]

(25)

where \(S_m(t)\) and \(S_m^{0\omega}(t)\) denote the Debye-Waller factors, which are defined in the Supporting Information by Equations (A15) and (A22), respectively. Next, we can calculate the MSD defined for a chain as Equation (26):

\[
\langle x^2(t) \rangle = \sum_{n=1}^{N/2} (nd)^2 \rho_{nm}(t)
\]

and for a multiple-ring system as Equation (27):

\[
\langle x^2(t) \rangle = \sum_{r=1}^{N_{ring}/2} (rD)^2 \rho_r(t)
\]

(27)

Here, \(d (D)\) is the center-to-center distance between two adjacent pigments (LH2 rings), and we set \(d = 9.0 \text{ Å} (D = 8.0 \text{ nm})\), consistent with the structural data of natural photosynthetic membranes.\(^{19,22}\) \(\rho_{nm}(t)\) is the exciton population of the \(r\)th pigment (the \(r\)th ring) at time \(t\), and \(N_{ring}\) is the total number of pigments (rings).

In Figure 14a,b, we display log–log plots of \(\langle x^2(t) \rangle\) versus time for a linear chain for various values of the Huang–Rhys factor \(S\) and the exciton transfer integral \(J\). Given \(J = 0.3557\) (in the unit of the characteristic phonon frequency \(\omega_0\) as defined in the Supporting Information), the slopes in the log–log plot of MSD versus \(t\) for \(S = 0.2, 0.5, 0.8, \text{ and } 1.0\) are 2.01, 2.12, 2.16, and 2.16, respectively, which demonstrates quantum behavior of the exciton transfer dynamics. For \(S = 1.5\) and 2.0 and the same value of \(J\), the exciton is found to be much less mobile. Dependence on the transfer integral \(J\) is shown in Figure 14b in which all the curves indicate the quantum nature of the exciton dynamics. In general, the larger the value of \(J\), the faster the exciton transfer.

Figure 15a shows the log–log plot of \(\langle x^2(t) \rangle\) versus time for a one-dimensional array of LH2 rings with a center-to-center spacing \(D\). For systems of nine to 15 LH2 rings, a slope of approximately 1.5 is found for the short-time portion of the curves \((t < 1 \text{ ps})\), thus demonstrating superdiffusive characteristics. To further elucidate the coherent nature of energy transfer in LH2 rings, we calculated exciton coherence size \(L_p\), characterizing the size of a domain within which the chromophores emit coherently.\(^{15,4}\) Making use of the inverse participation ratio commonly found in the theory of quantum localization, the coherence size \(L_p\) can be defined as Equation (28):

\[
L_p(t) = \left( \sum_{n,m} |\rho_{nm}^{0\omega}(t)|^2 \right)^2 \left( \sum_{n,m} |\rho_{nm}(t)|^2 \right)^{-1}
\]

(28)

in which \(L\) is the total number of pigments in the system. The coherence size \(L_p\) as a function of time can be utilized to characterize the extent of excitonic coherence. Figure 15b depicts the long-time evolution of the coherence size \(L_p\) for multiple-ring systems. It is found that for various system sizes, \(L_p\) oscillates between 56 and 88 pigments, or between 3.5 and 5.5 rings with an average of 4.5 rings, which points to the superdiffusive behavior of exciton transport in the LH2 rings.

7. Conclusions

We have investigated the energy transport and dissipation in a chain of light-harvesting systems by using a source–network–drain model, which incorporates the effects of quantum coherence, dephasing, photoluminescence quenching, and NPQ, owing to the coupling to the environment and the environmental noise. In this model, the creation of excitons due to the absorption of sunlight and their annihilation, owing to photochemical quenching and NPQ are considered by adopting semi-infinite source and drain channels that connect to pigments in the chain. Simulations of the wave-packet dynamics in the chain show that, without dephasing, the exciton motion remains superdiffusive and with full quantum characteristics. This behavior is found in the short-time trajectory and is robust for a wide range of parameter values. By increasing the dephasing rate, the motion changes from superdiffusive to diffusive. From the investigation of the stationary processes following the injection of a steady energy flow on a pigment in the presence of incoherent and coherent outgoing channels of the photoluminescence and the NPQ processes, it is found...
that channel coherence leads to suppression of dissipation and multie exciton super-radiance. By using this model to investigate the energy-transfer processes in the FMO complex, we find that rapid and coherent energy transfer occurs within a FMO subunit despite the existence of dissipation and dephasing. The energy-transfer efficiency decreases linearly with increasing dissipation rate, but increases slightly with an increasing dephasing rate. Assuming the same dissipation rates for all sites, BChl 4 is found to have the largest contribution to dissipation. These are not the final page numbers!


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Exciton dynamics: Energy transport processes in natural-light-harvesting systems have been investigated using a source–network–drain model incorporating the environmental effects of dephasing and dissipation (see figure; \( \eta \) = dephasing rate, \( \langle x^2(t) \rangle \) = mean square displacement, \( \gamma \) = property of exciton diffusion).