

The role of intramolecular vibrations in photosynthetic exciton energy transfer



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Theses of the Ph.D. dissertation

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1 Introduction

1.1 Context and motivation

In the microscopic world, phenomena that contradict our experience obtained in everyday life are ubiquitous: particles can occur at a place to the reach of which they do not have enough energy classically (this effect is called quantum tunneling), they can be in different states simultaneously (quantum superposition) and can behave as if they were connected—even if they are far away from each other (quantum entanglement). Surprisingly, increasing amount of data suggests that these quantum effects also play a role in certain physiological processes [11]–[14], taking place in the vibrant medium of living matter at high ($\gg 0$ K) temperature.

In the research field called quantum biology, the most intensely studied topic is probably the exciton energy transfer occurring in the first stage of photosynthesis. During this process, the energy of the photons absorbed by the light-harvesting complexes (also called antenna complexes) is transported by pigment (chromophore) molecules to the reaction center with a strikingly high efficiency: depending on the type of the antenna complex and on the light conditions, 50–90% of the energy of an absorbed photon is converted into the energy of a pair of separated charges in the reaction center [15] (Fig. 1). The comprehension of the process is of great importance from the engineering point of view as well, since the design principles learned from biological systems might also be exploited in new types of solar cells and bionic sensors.

The energy transfer was explained for long by the Förster theory [17], according to which the exciton hops from pigment to pigment incoherently [18], [19]. The first decade of the present century nevertheless brought surprising findings: quantum states maintaining their coherence for a long time were observed experimentally in photosynthetic systems [20], even at physiological temperature [21], [22]. Shortly thereafter, it was also reported that such states play a part in the energy transfer [23].

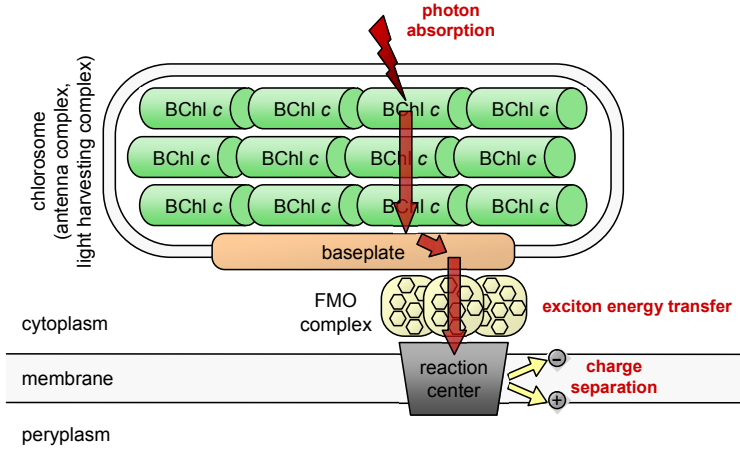


Figure 1: The light-harvesting apparatus of green sulfur bacteria. The sunlight is absorbed by the BChl-*c* molecules of the chlorosome. Then the captured energy is transferred through the baseplate and the Fenna–Matthews–Olson (FMO) complex to the reaction center, where it provokes a charge separation process. Adapted from Refs. [13] and [16].

1.2 Objectives

Former models of the photosynthetic exciton energy transfer focused exclusively on the electronic states of the participating molecules. In recent years, however, the role of intramolecular vibrations attracted increasing interest, and numerous papers concluded that these vibrations can enhance the exciton energy transfer [24]–[33], although there were also a few reports which inferred that the enhancement is small if the system interacts with its environment [30], [34]. On the other hand, I have found only scarce and conflicting statements on how the damping of the intramolecular vibrational modes affects the energy transfer.

In my dissertation, I examine the role of intramolecular vibrational modes in photosynthetic exciton energy transfer. I present a general approximate model formulated as a Lindblad-type master equation. Based on this model, I implemented a simulator program, by means of which I investigated dimer and heptamer model arrangements varying several parameters in a systematic

manner. (The new model and the simulation results have also been presented in a journal article, accepted for publication in *AIP Advances* [1].)

2 Theoretical background

The Schrödinger equation provides a general description of the behavior of non-relativistic atomic systems. However, its practical applicability is fundamentally limited by two factors: on the one hand, the dimension of the state space increases exponentially with the number of particles, and on the other hand, the equation is valid only for closed quantum systems, which do not interact with their environment¹, nevertheless, strictly speaking, the only closed system is the universe itself. Consequently, *ab initio* modeling of the exciton energy transfer is utterly hopeless. Instead, we have to lean on approximate models of open quantum systems.

According to this approach, the explicitly treated system is restricted to a small number of molecules, characterized by a few states, whereas the rest of the molecules (or rather, degrees of freedom) are considered to be the part of the environment, which is described in a simplified, averaged manner, for instance, as a heat-bath.

The Lindblad master equation is commonly used to model exciton energy transfer. It can be derived from the Liouville–von Neumann equation, which is in turn the generalization of the Schrödinger equation to systems being in a mixed quantum state. In the course of the derivation, three major approximations are made. The Born and Markov approximations assume that the system–bath coupling is weak and thus they neglect the changes of the bath. The third, so called secular or rotating wave approximation, in turn, ignores the off-resonant, fast oscillating terms of the state dynamics assuming that they do not influence the dynamics substantially on the time scale of inter-

¹ I distinguish open and closed quantum systems depending on whether they do or do not interact with their environment. Note, however, that some authors call a system closed even if it is exposed to external drives provided that the system dynamics can be described by a time-dependent Hamiltonian, and they use the term isolated for systems governed by a time-independent Hamiltonian [35]. Other authors, in turn, define closedness and openness with the reversibility and irreversibility of the system–environment interaction, respectively, while referring to systems not interacting with the environment at all as isolated [36].

est. The Lindblad master equation treats the system–bath interaction in a second-order approximation, and in general it takes the form

$$\begin{aligned} \frac{d}{dt} \hat{\rho}_S(t) = & -\frac{i}{\hbar} [\hat{H}, \hat{\rho}_S(t)] + \sum_j \gamma_j \left(\hat{A}_j \hat{\rho}_S(t) \hat{A}_j^\dagger \right. \\ & \left. - \frac{1}{2} \hat{A}_j^\dagger \hat{A}_j \hat{\rho}_S(t) - \frac{1}{2} \hat{\rho}_S(t) \hat{A}_j^\dagger \hat{A}_j \right), \end{aligned} \quad (1)$$

where $\hat{\rho}_S$ is the density matrix representing the state of the system, \hat{H} is the Hamiltonian operator of the system, \hbar stands for the reduced Planck constant, and the bracket denotes the commutator of the two operators, which is defined as $[\hat{H}, \hat{\rho}_S] = \hat{H}\hat{\rho}_S - \hat{\rho}_S\hat{H}$. The Lindblad operators \hat{A}_j together with the rate constants γ_j represent the system–bath coupling [35].

3 Summary of new scientific results

Thesis 1a: I have constructed a general quantum model that describes photosynthetic exciton energy transfer taking intramolecular vibrational modes explicitly into account.²

The new model describes a system built up of N pigment molecules (sites) (Fig. 2) considering two electronic states and an explicitly treated intramolecular vibrational mode at each site (Fig. 3(a)). In addition, the model contains an extra site, representing the reaction center. The couplings between the sites are calculated by means of the Franck–Condon overlap integrals. The time-evolution of the model system is described by a Lindblad-type master equation, in which the interaction with the memoryless environment is expressed phenomenologically through Lindblad operators. (See Figs. 3(b)–(e) for the transitions included in the model.)

² Elaborated in Chapter 3 of the dissertation.

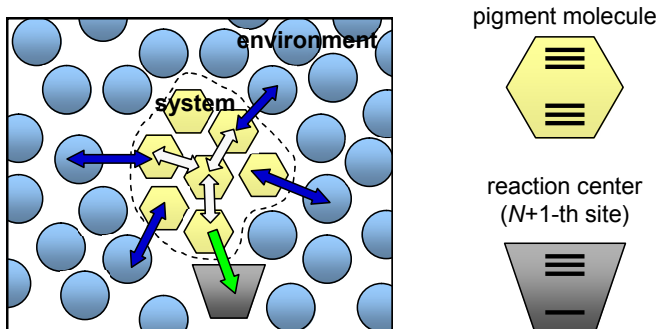


Figure 2: General scheme of the model arrangement. The system is built up of N pigment molecules (sites) (yellow hexagons), which are coupled to each other, to the reaction center ($N + 1$ -th site) (gray trapezoid), and to the surrounding molecules (blue circles).

Thesis 1b: Based on the new model, I have implemented a simulator program.³

According to the particular model system, the implemented simulator program constructs the corresponding Lindblad master equation, which is then solved numerically by means of the built-in functions of *Quantum Toolbox in Python (QuTiP)* [37], [38].

Thesis 2: I have surveyed in a uniform study how undamped and damped intramolecular vibrational modes influence the exciton energy transfer and especially its efficiency.⁴

To reveal the role of intramolecular vibrational modes, I have compared various scenarios. In the well-known case of the homodimer, the exciton coherently oscillates back and forth between the two sites, being present periodically with unit probability at site 1 and then at site 2. However, the detuning of the electronic energy levels of the sites decreases the probability of the “dislocation” of the exciton. I have confirmed that this deterioration of the

³ Elaborated in Chapter 4 of the dissertation.

⁴ Elaborated in Chapters 5 and 6 of the dissertation.

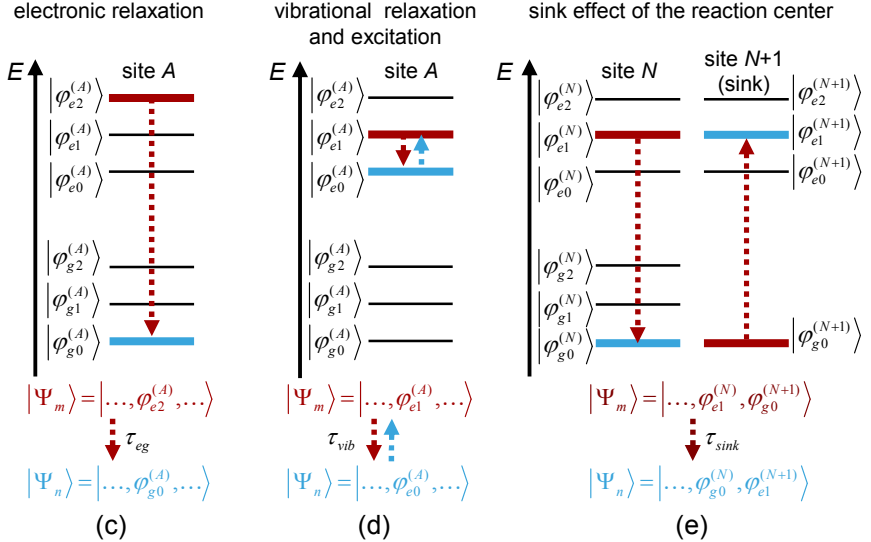
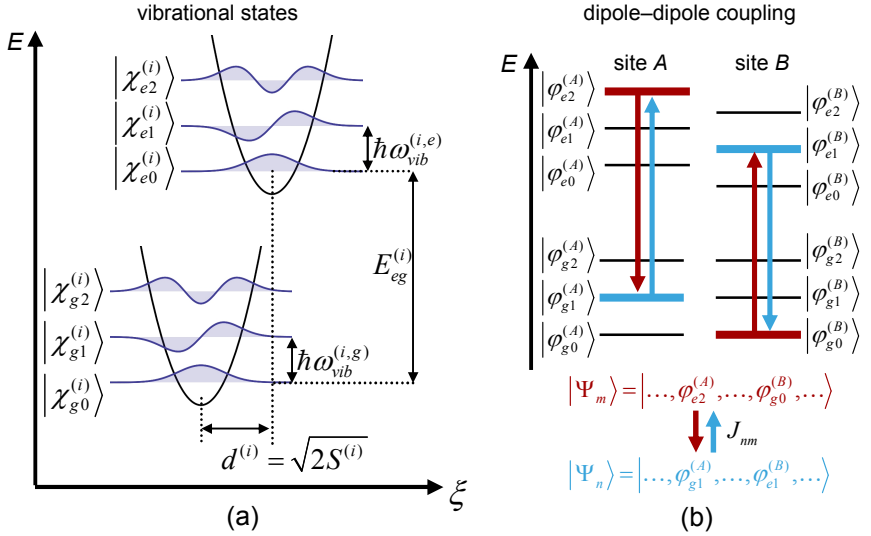


Figure 3: (a): the vibrational states of a molecule (b)–(e): transitions included in the model (pure dephasing is not depicted). [1]

transfer can be compensated by the presence of intramolecular vibrational modes [24]–[33] that create resonant energy states at the two sites, provided that the Huang–Rhys factors are sufficiently large to couple these levels. In addition, I have demonstrated that the damping of these vibrational modes can considerably enhance the energy transfer further (Fig. 4). The latter result is in accordance with Refs. [26], [28], [39], but it contradicts the findings of Refs. [31], [33].

The reason for the improvement of the efficiency is that vibrational relaxation can take the exciton to a state that is energetically detuned from all the states of the site from where the exciton arrived, which impedes the propagation of the exciton back to the previous site (Fig. 5). Vibrational relaxation can thus unidirect the energy transfer and, moreover, trap the exciton at sites connected to the reaction center, resulting in a higher efficiency. I refer to this kind of transport process as *vibrational-relaxation-enhanced exciton energy transfer (VREET)*.

Thesis 2a: I have demonstrated that the relative enhancement of the energy transfer caused by vibrational relaxation is multiple times larger than the relative enhancement caused by pure dephasing.⁵

By omitting the population transferring effect of vibrational relaxation (and excitation), I introduced pure dephasing in the model. I demonstrated that this process can also increase the efficiency of the energy transfer (as it had been formerly described in Refs. [40], [41]); however, the enhancement caused by pure dephasing is notably surpassed by the one caused by vibrational relaxation (both in the dimer model at 0 K and in the heptamer model of the Fenna–Matthews–Olson (FMO) complex at 0 K and at 300 K) (Fig. 6).

⁵ Elaborated in Secs. 5.4, 6.2, and 6.3 of the dissertation.

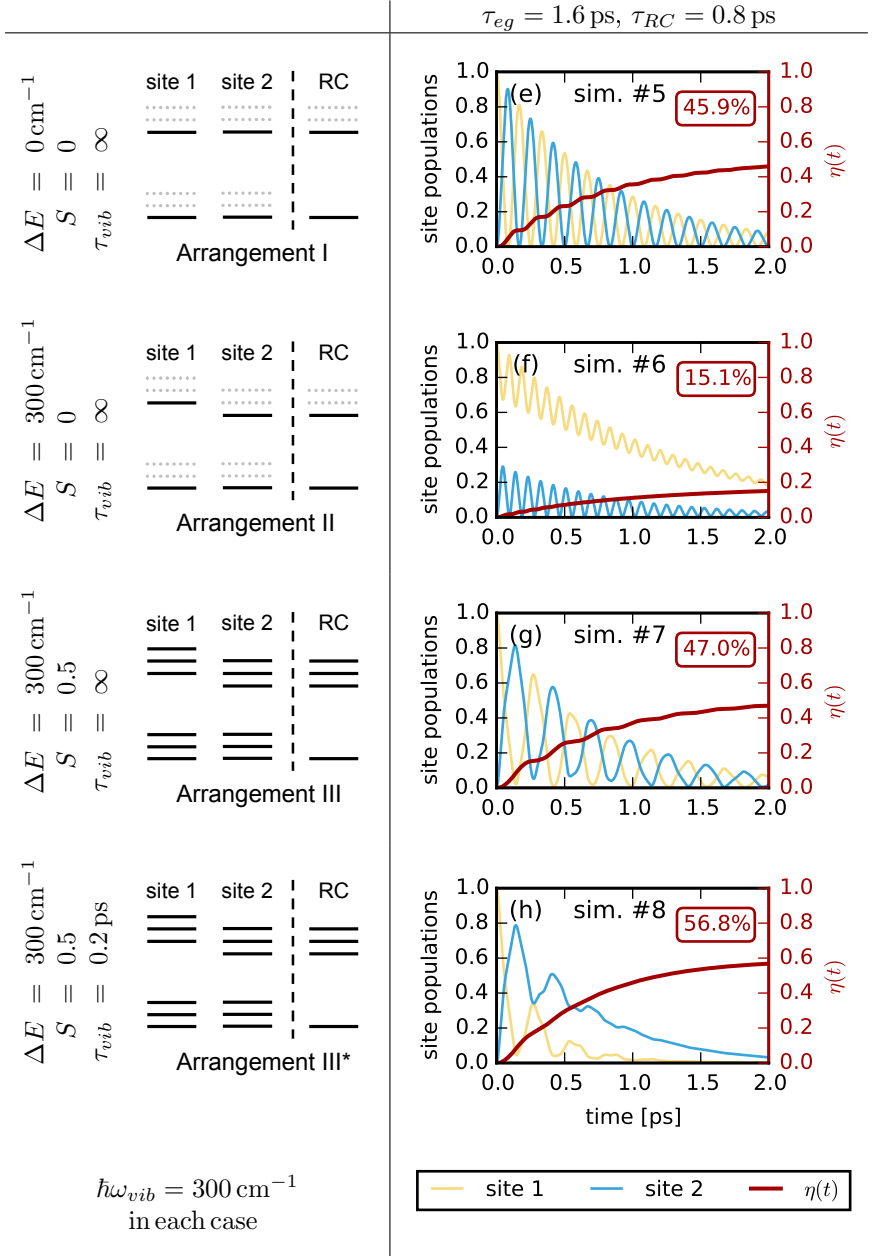


Figure 4: Dynamics of the exciton energy transfer in various dimer model systems. [1]

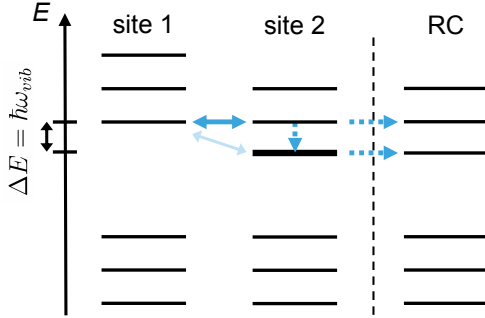


Figure 5: The path of vibrational-relaxation-enhanced exciton energy transfer (VREEET) from site 1 to the reaction center (RC) in the dimer model. There is dipole–dipole coupling between energetically resonant states $|\varphi_{e0}^{(1)}\rangle$ and $|\varphi_{e1}^{(2)}\rangle$; thus, the exciton can oscillate among them. Vibrational relaxation, however, gets site 2 from $|\varphi_{e1}^{(2)}\rangle$ to $|\varphi_{e0}^{(2)}\rangle$ (the latter state is denoted by the thick line), from where the propagation of the exciton back to site 1 (along the thin double arrow) is impeded because of the energy mismatch. In effect, the exciton is trapped at site 2 in state $|\varphi_{e0}^{(2)}\rangle$, from where the reaction center absorbs its energy. [1]

Thesis 2b: I have demonstrated that vibrational relaxation can considerably and robustly enhance the exciton energy transfer in wide ranges of several parameters.⁶

I have examined the dependence of VREEET on several simulation parameters. Running simulations on dimer model systems at 300 K, I have shown that VREEET is robust both against the parallel change of electronic energy levels of the sites and against the alteration of the strength of the inter-pigment coupling. I demonstrated that faster vibrational relaxation produces larger enhancement of the energy transfer and also that the slower the sink effect of the reaction center, the higher the relative increment of the transfer efficiency. In addition, I have revealed that VREEET exhibits the highest efficiency if the energy detuning between the electronic levels of the neigh-

⁶ Elaborated in Secs. 5.5 and 6.3 of the dissertation.

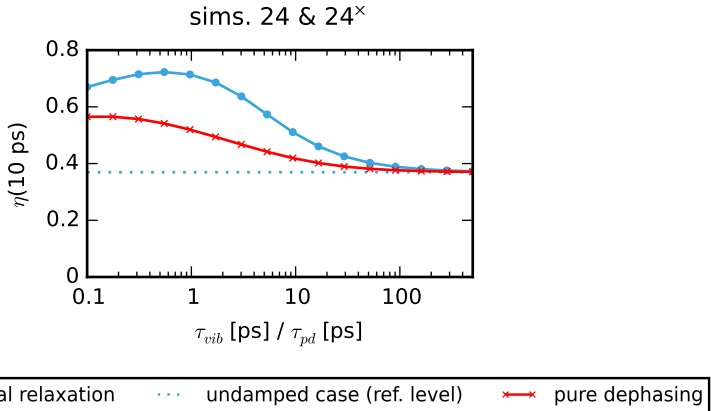


Figure 6: Energy transfer efficiency in the heptamer model of the FMO complex if the system is exposed to vibrational relaxation of time constant τ_{vib} or to pure dephasing of time constant τ_{pd} . (The exciton starts from site 6; $T = 300$ K.)

boring sites is intermediate, the vibrational mode is quasi-resonant with this energy detuning, and the Huang–Rhys factors of the sites are large enough to couple the corresponding vibronic states. I found that the energy transfer efficiency declines with increasing temperature, but the enhancement caused by vibrational relaxation remains considerable at higher temperatures as well. I demonstrated that the increase of the frequency of the vibrational modes (together with the detuning of the electronic levels of the coupled sites so that they remain resonant) reduces the temperature-dependence of the efficiency, since it lowers the occupation probability of higher vibrational levels, through which the backward propagation of the exciton can take place.

The results that I obtained for the heptamer model of the FMO complex at 300 K show trends which are similar to those obtained for the dimers, and they demonstrate that vibrational relaxation can enhance the exciton energy transfer in more complex systems as well, even at room temperature, also if the vibronic levels are not strictly resonant (Figs. 7 and 8(a)). This corroborates that the directionality of the exciton transfer is provided by thermalization [26], [42]–[44]. I got values up to 96% for the relative gain caused by vibrational relaxation. Fixing the frequency of the intramolecular vibrational mode

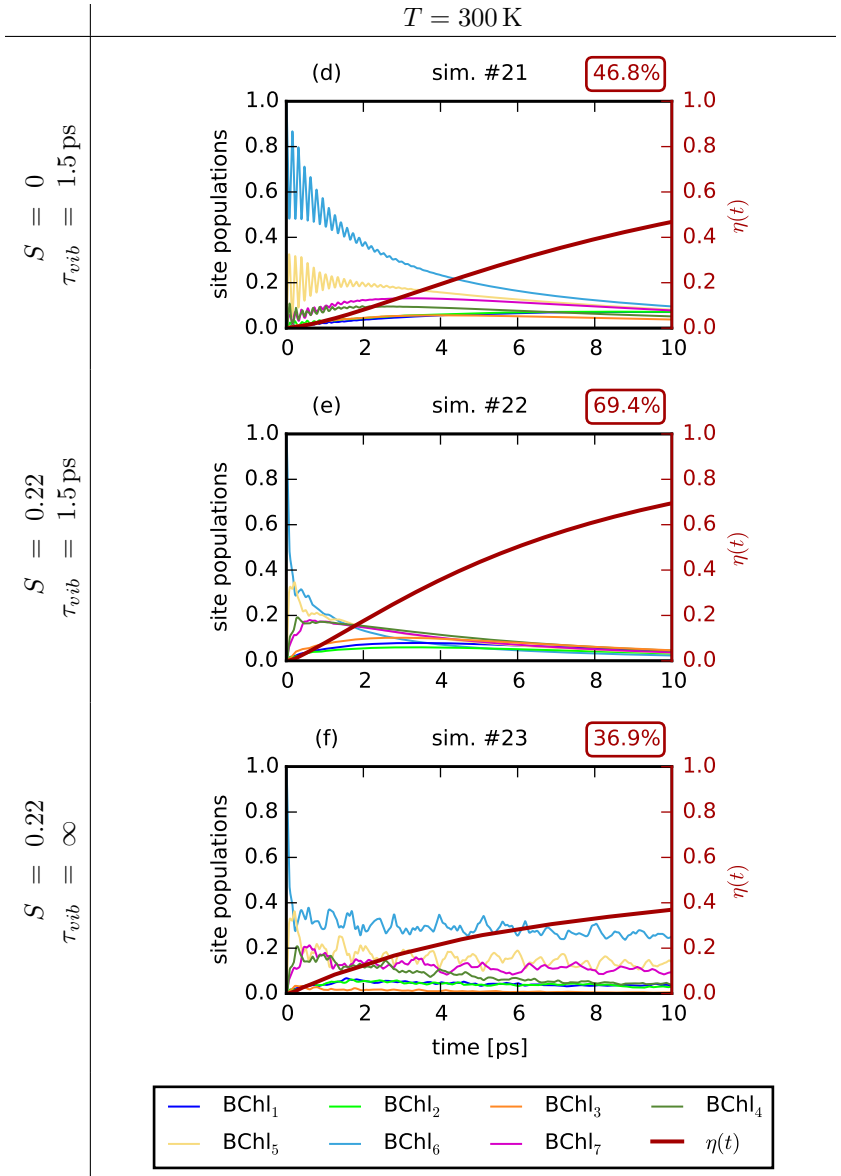


Figure 7: Population dynamics in the heptamer model of the FMO complex at 300 K if the exciton is initially at site 6. [1]

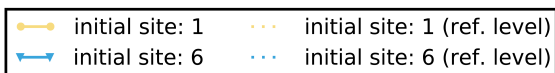
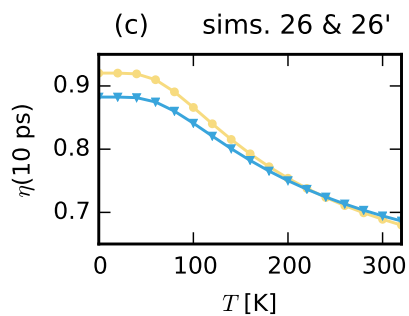
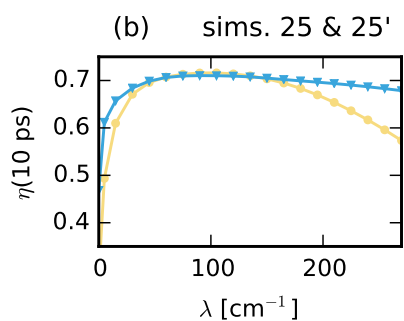
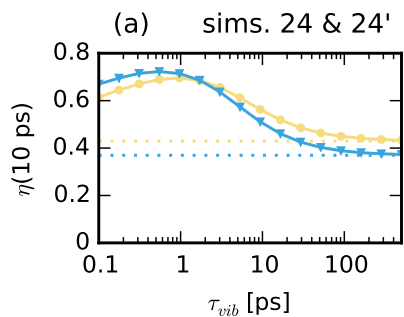


Figure 8: Dependence of the energy transfer efficiency in the heptamer model of the FMO complex on various system parameters. [1]

and sweeping the Huang–Rhys factor, I found that the energy transfer efficiency of the FMO complex at 300 K depends strongly on the reorganization energy and reaches its maximum at some intermediate value of the reorganization energy (Fig. 8(b)), which trend is characteristic of the results provided by non-Markovian models [45], [46]. Finally, I found that the energy transfer efficiency declines monotonically with increasing temperature in the case of both energy pathways of the FMO complex (Fig. 8(c)). This corresponds to data published previously on the energy pathway starting at site 6 [45], but differs from former results on the energy pathway starting at site 1 [45], [46].

VREEET occurred in wide ranges of the investigated parameters both in the simple, “constrained” dimer model systems and in the more complicated, “disordered” heptamer model of the FMO complex. This—presuming that the presented mechanism also works in real systems, built up of molecules with numerous vibrational modes—suggests that VREEET might be prevalent in light-harvesting complexes, and it can contribute to the high efficiency of the exciton energy transfer occurring during the initial stage of photosynthesis.

4 Applications

The potential inherent in newly emerging quantum technologies has its root primarily in quantum coherence, that is, in the possibility of the coexistence of various states. Therefore, the comprehension of coherence and environment-induced decoherence is of key importance. The operation of quantum computers requires long-lasting quantum coherence; in other words, the noise of the environment is to be eliminated in their case. On the other hand, the interaction between a quantum system and its environment can also be beneficial, and nature seems to exploit it, for instance, in photosynthesis. The underlying mechanisms—among them those discussed in this thesis—might also be applied in artificial light-harvesting systems [47] and in sensors during the unfolding second quantum revolution.

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The Author's Publications

Journal articles

- [1] **I. B. Juhász** and Á. I. Csurgay, “Impact of undamped and damped intramolecular vibrations on the efficiency of photosynthetic exciton energy transfer”, *AIP Advances*, accepted for publication.
- [2] **I. B. Juhász** and Á. I. Csurgay, “Fluorescence in two-photon-excited diffusible samples exposed to photobleaching: A simulation-based study”, *Journal of Biomedical Optics*, vol. 20, no. 1, p. 015 001, 2015.
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- [4] **I. B. Juhász** and Á. I. Csurgay, “Simulation-based investigation of the three-dimensional distribution of fluorescence and photobleaching in multi-photon excited samples”, in *Proceedings of SPIE*, F. Wyrowski, J. T. Sheridan, J. Tervo, and Y. Meuret, Eds., vol. 9131, Brussels, 2014, 91310S.
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