

Foreword

„Learning from Nature“ is a common theme in the natural sciences. The ingenious machinery of photosynthesis is particularly attractive as it has evolved to efficiently convert the sun light into chemically usable energy. Can we mimic natural photosynthesis to open the door to an unlimited energy source? Do we need to copy just structural elements into man made supramolecular architectures? How important is the interplay between structure and dynamics for the realization of function? Finally, did Nature restrict itself to the classical laws of Physics or did Quantum Mechanics provide some advantage? In fact it has been the last question which triggered most interest in the Physics community recently. Initiated by sophisticated nonlinear optical experiments, which revealed signatures of quantum coherent evolution at physiological temperatures, the first step of photosynthesis, i.e. the harvesting of sunlight, has been in the focus of broad research efforts.

A quantum dynamical description of a system as complex as a light-harvesting antenna protein provides quite a challenge. Models have to be developed, flexible enough to incorporate results from experiments as well as from atomistic simulations. Density matrix theory is the method of choice for dynamics simulations in condensed phases. With the recent development of efficient non-Markovian and non-perturbative approaches one is in the position to follow the quantum dynamics of the electronic excitations numerically exactly, which facilitates a test of models without invoking further approximations.

The present thesis is concerned with the dynamics and spectroscopy of electronic energy transfer in three model systems capturing different aspects of photosynthetic light harvesting. The simplest one, a molecular heterodimer, allows for a very detailed investigation of coherent oscillations in the dynamics. Here, it is possible to identify

those quantum states, which are at the origin of these oscillations. In particular a scheme is devised, that enables discriminating between pure electronic and coupled electron-vibrational processes. This is of relevance since these types of coherences are affected differently by the protein environment, what might help to explain the observed long lasting oscillations. The second model mimics an energy funnel, a fundamental principle in photosynthesis. Special emphasis is devoted to the interplay between the energy level structure and relaxation and decoherence dynamics. The basic features of both models come together in the third application to the so-called Fenna-Matthews-Olson complex, which is part of the light-harvesting apparatus of green sulfur bacteria. This heterogeneous complex hosts different energy transfer pathways as well as coherent oscillations, which could be identified as being of electron-vibrational origin. Key to the success of this thesis has been the development of a numerical program package for the propagation of the density matrix and the extraction of linear and nonlinear spectroscopic signals.

The prospective reader of this thesis will benefit from the combination of mathematical derivations, numerical implementation, and specific applications to current problems in excitation energy transfer research in natural and artificial systems.

Prof. Dr. Oliver Kühn

Preface

Photosynthesis was studied intensively during the last decades by biologists, chemists, and physicists. Although the general process is well understood nowadays, the details, especially those concerning the effects leading to the high efficiency of the photosynthetic apparatus of plants, bacteria, and algae, require further investigations.

In the present work, an intermediate step in photosynthesis, that is the energy transfer from the light-absorbing antenna complexes to the photosynthetic reaction center is investigated from the perspective of theoretical physics. The concepts of dissipation theory and exciton dynamics are applied to a set of model aggregates to study various aspects, like transfer efficiency and spectral features, of the energy transfer in light-harvesting systems.

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Complexes

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