Nanotechnology tries to build up systems with basic functional units having even the size of single molecules. To get an idea of what is possible on this length-scale, different types of theoretical studies are mandatory. Numerical simulations are of huge significance which give a view on the spatial structure of the respective nanosystem. But calculations on the electronic energy level scheme are also very helpful. And often, simulations may become necessary which highlight the dynamic behavior of nanostructures related, e.g. to the action of external fields. The present article reports on the description of ultrafast laser pulse driven dynamics in specific molecular nanostructures called light-harvesting antennae. They are found in the photosynthetic apparatus of bacteria and higher plants. Such photosynthetic antennae represent perfect objects for studying dynamics in nanosystems because of their very precise defined spatial structure and the possibility to isolate them from the cell membrane. And, it is a specialty of these antennae that a quantum dynamical description of the internal energy motion is inevitable.

I. Introduction

It is a strong challenge for modern research to elucidate the functionality of systems on an atomic scale, i.e. in the nanometer range (1 nm = 10^-9 m). The new field of applied research called nanotechnology tries to profit from the detailed understanding of everything that happens on this tiny length-scale. For example, modern electronics dream upon scaling down basic device units to the spatial extension of molecules (design of a molecular electronics). Obviously biological systems represent functional nanotechnology for millions of years. Every part of a living system on a subcellular level is governed by functional units having a spatial extension in the nanometer range. Therefore, it is of huge importance not only for biology to uncover the functionality of biological systems on a nanometer scale. This is often called clarification of structure-function relationship since the knowledge of the atomic and molecular structure represents the preconditions of achieving a complete understanding of the functionality.

Infobox A: Photosynthetic Antenna Complexes

The storage of solar energy in energetically rich organic compounds and the accompanying release of oxygen represents the basis of life on earth and the related process is called photosynthesis. The photochemistry of photosynthesis starts with a primary charge separation in the photosynthetic reaction center. It results in a transmembrane potential which drives biochemical reactions leading finally to the release of oxygen and the fixation of carbon. In most cases the initial excitation is supplied by light-harvesting antennae, which surround the reaction center to enlarge the cross section for the capture of sunlight. If the antennae have absorbed sunlight the excitation energy is efficiently transferred as excitons to the reaction center [11]. The active pigments are different forms of chlorophyll (as well as of bacteriochlorophyll and carotenoid molecules). There is a huge diversity of antenna complexes in bacteria and higher plants. For some of them the structure is known with an atomic resolution. The present article concentrates on the cyanobacterial PS1 (Fig. 1), the so-called FMO-complex of green bacteria (Fig. 2), and the LH2 of purple bacteria (Fig. 4).

Infobox B: The Exciton Concept

To describe electronic excitations in solid state systems or molecular systems the concept of excitons represents a very successful approach. If energy in terms of light quanta (photons) is absorbed by a single atom or molecule an excited state of the related electrons may be formed. In semiconductors like Si every atom is strongly bound to its neighbor. After photoabsorption the excited electron is positioned far away from the excited Si-atom (the so-called hole). Then, the excited electron feels the attractive electrostatic force of the hole leading to a bound state called exciton (it is similar to the hydrogen atom with the hole replacing the proton). Considering instead of the Si-atoms (forming a regular lattice) the arrangement of chlorophyll molecules in a photosynthetic antenna the excited electron remains in the molecule from which it was promoted out of the ground-state. However, such a local excitation may move from one chlorophyll molecule to the other forming again a delocalized state also called exciton [10] (cf. also Fig. 2). It is just this type of excitons (named after the Russian physicist Y.I. Frenkel, 1894–1952) which is found in photosynthetic antenna systems.
One example where such an understanding has been achieved to an enormous extent is the way bacteria and higher plants use sunlight to gain energy. Our present day knowledge of all the involved processes represents the results of decades of research work done by biologists, chemists, and physicists, just giving an example of interdisciplinary work with theoretical physicists involved. Studies in this field are not only concerned with phenomena taking place on fractions of nanometers but also on time-scales extending down to the femtosecond region (= 10^{-15} \text{s}). It is this and also the fact that these systems absorb sunlight within the visible range that let come into play ultrafast optical spectroscopy. The correct interpretation of spectroscopic data and the improvement of our understanding of the functionality, however, asks for a proper description of the observations. This can be attained by using methods and techniques of Quantum Physics which include the development of specific models and the performance of numerical simulations. And possibly, with all that in mind one may take a step forward from such a basic research work into the field of applied research. Hence, the attempt to understand the details of the excitation energy transfer in photosynthetic antenna systems may be considered prototypical for practical use of dynamic phenomena in nanosystems.

II. Theoretical Models for Photosynthetic Antenna Systems

Long before any part of a photosynthetic antenna has been known with atomic resolution it was believed that an exciton mechanism was responsible for the excitation energy transport to the reaction center (see Infobox B). Having data at hand which give a detailed spatial arrangement of the chlorophyll molecules with a resolution of few Ångström (1 Å = 0.1 nm) one may try to develop a quantum mechanical model of the energy level structure of the photosynthetic antenna as well as a quantum dynamical description of the exciton motion. (It is typical that these processes need modern theoretical tools of quantum physics to be correctly interpreted.)

Fig. 2

Energy level scheme related to the monomeric part of the FMO-complex (see Infobox A). Every chlorophyll molecule (green) is described by two electronic levels (upper and lower edge of the purple stripes). Excitation into the upper level (yellow arrow) becomes possible by light absorption (yellow wavy line). This excitation may move from one chlorophyll molecule to the other by a de-excitation-excitation process (blue arrows connected by a blue wavy line). If the interaction between different chlorophyll molecules is strong an energy level scheme valid for the whole antenna complex is formed with collective excitations called excitons (right part, see also Infobox B). Now, photoabsorption directly leads to an excitation of these spatially delocalized states (right part, yellow arrow and yellow wavy line). Since the chlorophyll molecules are embedded in proteins the whole structure of the antenna fluctuates according to thermal fluctuations of the protein. This leads to a modulation of the energy level scheme with the result that a certain portion of the excitation energy is dissipated into the surroundings.
understood.) There have been attempts to compute the electronic energy level structure for the complex of chlorophyll molecules (for example [2, 3]). However, such a quantum chemical approach has been successful only in part since the consideration of the whole protein which carries the antenna is beyond present day computational capabilities. Moreover, direct computation of the coupling of the electronic excitations (excitons) to vibrations of the chlorophyll molecules and to the surrounding protein (necessary for a description of excitation energy dissipation) also seems to be hopeless at the moment. Consequently, an approach has to be chosen which is based on additional assumptions mainly related to the energy level structure of the chlorophylls and their mutual interaction. Concrete parameter values are fixed by a comparison of this model with different experimental results. A particular type of such a model is explained in Fig. 2. It is applied here to a complex of seven chlorophyll molecules but more complex antenna systems can be described in a similar way. The result of the parameter adjustment within such a model is demonstrated in Fig. 3 for the PS1 antenna system (cf. Fig. 1). It includes the calculation of the absorption spectrum based on the known spatial structure of the PS1 and a search for the optimal set of the 96 chlorophyll excitation energies.

The usefulness of such an exciton model for the understanding of nonlinear optical experiments is described in more detail in the following section. In Section IV a control of excitation energy motion in antenna complexes by ultrafast laser pulses is suggested.

III. Nonlinear Spectroscopy of Femtosecond Dynamics

A number of excitation energy transfer processes in photosynthetic antenna systems take place on a timescale below one picosecond (= $10^{-12}$ s). Respective techniques of ultrafast optical spectroscopy are neces-
ecessary to follow them. Pump-probe spectroscopy represents one commonly used method, where one laser pulse (the pump pulse) excites the system and the other laser pulse (the probe pulse) probes the excited state. If the duration of both pulses are shorter than the dynamics of excitation energy transfer one may trace the dynamics by varying the time delay between both pulses. To achieve a proper interpretation of the measured data accompanying calculations become necessary. Fig. 4 displays respective results together with the structure of the described antennae, the LH2 of purple bacteria (see Infobox A).

In order to obtain a detailed understanding of such laser pulse induced ultrafast dynamics the model introduced in Fig. 2 has to be extended to the case that the pump pulse may excite two excitons simultaneously in the antenna complex (formation of the two-exciton state). Furthermore, it is not sufficient to compute the probability for the excitation of a particular exciton level. Instead, to get a correct quantum mechanical description of the dynamics it is of basic importance to include cross correlations between different energy levels (via the so-called density matrix). The complex temporal behavior of the cross correlations is shown in the upper left panel of Fig. 4. The various boxes (with black background) display different time-steps during and after the pump pulse excitation. «0» stands for the ground state of the complex, «1» for all exciton levels, and «2» for the double excitations (two-exciton levels). The respective energy of all levels increases from the left to right as well from top to bottom. The probability that an energy level has been excited is given by the spots on the diagonal of the «1–1» and «2–2» box. The contributions of the off-diagonal regions in these boxes as well as all contributions in boxes like «0–1», «1–2», etc. are induced by the optical excitation and vanish mainly due to the thermal fluctuations of the carrier protein. The scheme demonstrates the complex quantum dynamical behavior of the antennae which is found when describing the spectroscopic data (see lower panel of Fig. 4).

IV. Laser-Pulse Control of Excitation Energy Motion

The idea of laser pulse control dates back to the eighties. It aims at driving the motion of a molecule into a particular quantum mechanical state guided by a respectively tailored laser pulse. Since such quantum dynamics are strongly disturbed by thermal fluctuations of the molecule itself and of its environment the control should proceed in the femtosecond time-region. To tailor a laser pulse appropriately, here, means to change its intensity and frequency on a time-scale much shorter than the overall duration of the pulse. Then, the quantum mechanical state may be excited and modified in such a fast way that it really moves into the chosen target state (cf. [8–10]).

The discussion related to laser pulse control of exciton dynamics is somewhat speculative. However, when putting this in a broader context it should be of huge interest to manipulate the transfer of excitation energy in nanostructures. Indeed, the structural robustness of antenna systems favors these systems when compared, for example, with dye aggregates. Fig. 5 shows the results of some computational studies carried out for the FMO-complex (see Infobox). It was the aim of these studies to demonstrate the possibility to localize the excitation energy on a single molecule against the tendency of forming delocalized exciton
states (drawn in the right part of Fig. 2). In fact, after 600 femtoseconds nearly 80% of the overall excitation was concentrated on the chlorophyll molecule in the center of the complex. All other chromophores were much less populated. The laser pulse which realized such an excitation energy concentration followed from the solution of an optimization problem and is also shown in Fig. 5.

As already mentioned such studies are not mainly undertaken to get a deeper insight into the biological function of antenna systems, but rather to demonstrate the basic possibility to manipulate transport processes on an Ångström length-scale and a femtosecond time-scale. This might be of huge importance for any further development in the field of nano-systems either as a tool for investigation or as a strategy to achieve a certain functionality.

References