

Chapter 1

Introduction

1.1 Motivation

With the development of quantum mechanics in the nineteen–twenties the principal tools to calculate the exact properties of molecular systems were developed. Quantum mechanics managed to explain many of the previously mysterious properties of the microworld, especially in the field of spectroscopy, and therefore prompted the famous statement by Dirac in 1929, that “... *the underlying physical laws necessary for the mathematical theory of the large part of physics and the whole of chemistry are thus completely known*”[1].

The application of quantum mechanics in the fields of physics and chemistry, and in recent years biology, led to an enormous dynamics in the experimental and theoretical understanding of the way nature works. Especially on the experimental side, the development of lasers with the capability to generate laser pulses with durations on the timescale of femto–seconds, led to new possibilities [2]. With these extremely short pulses it became feasible to study the reaction dynamics of molecules and individual molecular bonds directly. The extremely short laser pulses allow the resolution of molecular motions on the scale of a few Ångströms, giving insight into internal reorganizations of single atoms within molecules and the breaking of individual bonds [3].

The properties of the ultra–short pulses triggered the development of new spectroscopic techniques [4], which rely on the high time resolution and the fact, that a short pulse will, according to the Heisenberg principle, have a high frequency uncertainty. This allows the excitation of a coherent super–position of several molecular eigenstates, i.e. a molecular wavepacket, close to the center frequency of the pulse. The time evolution of this wavepacket corresponds to a movement of a molecular degree of freedom, which then can be probed with a second, time–delayed laser pulse, as schematically shown in Fig. 1.1. This so called pump–probe spectroscopy allows to take “snapshots” of the molecular dynamics induced by a laser pulse. From this dynamics it is then possible to draw conclusions about the shape of the intramolecular potentials of the system [5, 6, 7].

One process, which is of great importance in all fields of chemistry, especially in bio-

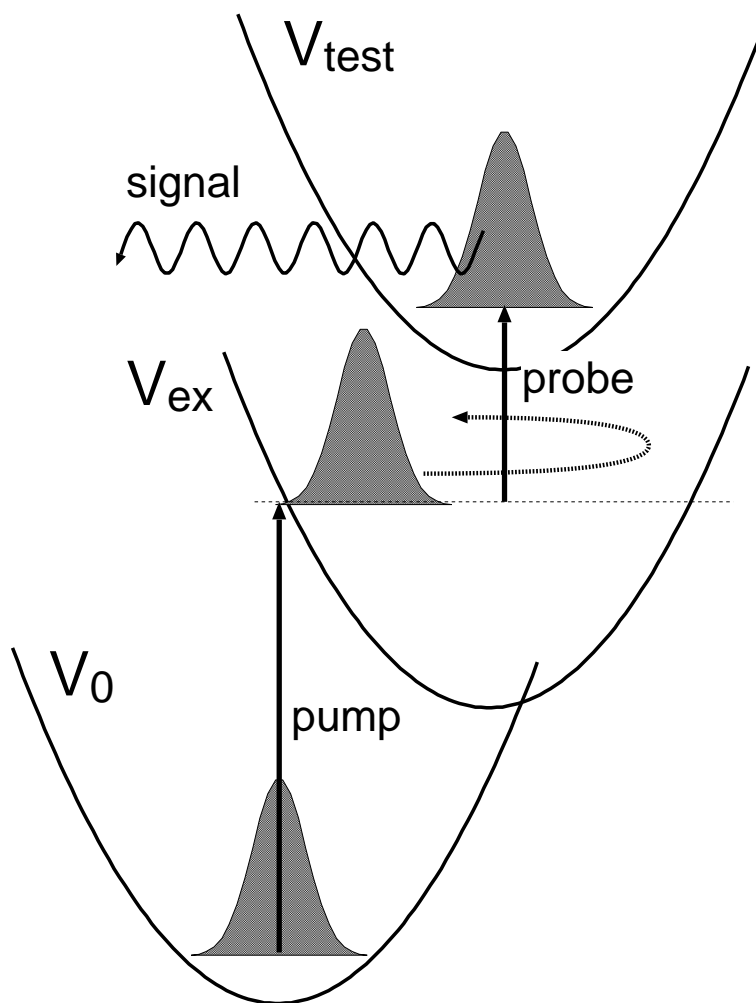


Figure 1.1: Schematic view of the pump–probe technique. The stationary state in the ground state potential V_0 is excited by a pump laser pulse to an energetically higher electronic state V_{ex} . The wavepacket in this state is built from a superposition of coherent eigenstates and therefore is not static, but oscillates. The following probe pulse is tailored to excite the moving wavepacket from a certain position in V_{ex} to a test state V_{test} from which it can be observed experimentally (e.g. via fluorescence).

chemistry, is the inter- or intramolecular proton transfer (PT) [8, 9, 10, 11, 12, 13, 14]. For instance, PT is one of the central processes in photosynthesis, where a PT across a membrane stores the solar energy in form of an electrochemical potential [15, 16]. The structure and dynamics of the hydrogen bond are also an important factor for the geometry of a molecule, as the proton can form bonds to different parts of a molecular complex. This can lead to different shapes, depending on the location of the bond. For instance the α -helix and other helical conformations in proteins is defined via intramolecular H-bonds [17]. The folding and final shape of most other biomolecules is also closely connected to the strength of the different H-bonds. While the strength of these bonds is not higher than the one between other molecular groups, their directive power is more pronounced, as the missing inner shell electrons allow for larger changes in electron density, which is the cause of this strong influence. As small changes in this bonds in a molecule can lead to large scale reorganizations of the remaining atoms and is normally accompanied by strong shifts in the charge distribution, these processes are also prime candidates for the development of molecular switches, e.g. in the field of molecular electronics [18, 19].

In smaller molecules, PT is one of the central processes in most acid-base reactions and is the most important factor in the behavior and spectral properties of liquid water [20, 21, 22]. This again is of great importance for biological processes, as biological reactions take place mostly in aqueous solutions. In biological membranes, charge transfer reactions can take place along so called “water wires” in protein channels [23]. Due to the relative lightness of the proton in contrast to all other molecular components, the PT process exhibits strong effects of quantum nature, which cannot be explained with classical molecular dynamics [12]. Additionally, it can also be strongly influenced by movements of the scaffold modes in the system. This coupling can be observed experimentally with the pump-probe spectroscopy mentioned above. For experimentalist these systems are also interesting, as with ^2H (D) and ^3H (T) hydrogen has two isotopes which exhibit extremely strong isotope effects, due to the high relative mass differences. As an additional complexity, all of the above processes normally take place in an large environment and not isolated in the gas phase. The biomolecules are either large enough by themselves to act as an environment to the small region where the PT takes place, or are embedded in a liquid environment [11, 24, 25].

With these complicated effects influencing the absorption line shape of the molecules, linear spectroscopy is no longer sufficient to unravel the microscopic processes and their timescales. Nonlinear [4] and, more recently, multidimensional [26, 27] spectroscopic methods have been developed to study these complex systems. One of the standard methods is the pump-probe approach described above [3, 28], which allows to observe the couplings of the proton motion to the scaffold as modulations in the spectral signal. This has been demonstrated for the electronic ground state [29, 30] as well as for the electronic excited state proton transfer [31, 32].

In recent years, the goal of the field has also shifted away from the passive role of an

observer toward the active role of reaction control in systems of increasing complexity. For this the laser spectroscopic techniques are no longer used to probe the properties of a molecule, but to drive the reaction in an already known molecule along a desired pathway. Extensive reviews of this approach can be found in the recent literature [2, 33, 34, 35, 36]. An especially interesting approach is the use of self-learning (genetic) algorithms to determine a control field with minimal knowledge of the system, as presented by Gerber *et al.* [37].

The multitude of effects and methods discovered and under development in the field of experimental proton dynamics pose a great challenge to the theoretical side of the field. While in principle, all the observed processes can be described with the Schrödinger equation, it is in practice often not possible to model the problem exactly, as not all the internal molecular properties are known (i.e. the inter- and intra-molecular potentials). This makes it necessary to develop additional theories and approximations, to enable the understanding of the molecular behavior.

As shown in [12], the movement of the proton in a hydrogen bond has to be treated within a quantum mechanical model. While it is often sufficient to describe the movement of the heavier atoms of the scaffold with classical mechanics, recent studies have shown that the quantum nature of the most strongly coupled heavy atom modes can also play a crucial role in influencing the proton dynamics and in particular the reaction rates [38]. To model these effects, it is necessary to develop theoretical methods, which allow for the treatment of high dimensional quantum systems. In addition to this, the fact that all these systems also interact with an environment makes them prime candidates to develop models including dissipation or to combine quantum and classical descriptions [11, 14, 24, 25, 39, 40, 41, 42].

The complex mathematical equations, resulting even from the approximate descriptions of multidimensional quantum dynamics, are only solvable analytically for simple systems like the harmonic oscillator or the hydrogen atom. Exact numerical solutions are available for systems like H_2^+ [43, 44]. The approximate numerical solutions necessary for more complex problems are always limited by the amount of available computer resources. Even though the advances in the speed of available hardware in the last two decades were enormous, the largest quantum systems one is able to treat without any approximations (beyond the necessary discretization to treat the mathematics numerically) are on the order of six dimensions [45]. All systems containing more degrees of freedom have to be treated within some kind of approximation, e.g. the time dependent Hartree (TDH) method or its extension, the multiconfigurational time dependent Hartree (MCTDH) approach [46, 47, 48, 49, 50, 51, 52, 53]. With these methods it is possible to calculate models of higher dimensionality, e.g. the 24-dimensional study of pyrazine presented in [54] or the calculation of rate constants for the reactions $\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$ and $\text{D}_2 + \text{OHD} + \text{DOH}$ [55]. Due to the limitations imposed by the maximum number of degrees of freedom, the theory has been lagging behind the experiment in this field for the most parts, as calculations for larger molecules or systems interacting with the environment required the

development of more refined models and approximations to reduce the complexity to a level manageable by the currently available computer capacity. An extensive collection of the techniques used in computational chemistry can be found in [56].

For the PT process in large systems the field of condensed phase theory is of special importance. In contrast to the modeling of a closed system, this approach needs to include the effects of energy dissipation and relaxation into the quantum systems. These effects are important, if one wants to explain the connection of a small system to a bath which is large enough to be treated with statistical methods. For the treatment of these couplings methods using a description in terms of a reduced statistical operator have been developed [39, 57, 58, 59], which continue to be refined, as larger computers become available and a better understanding of the processes connected to the redistribution of energy among a large number of degrees of freedom is gained [60, 61]. While it is still necessary, to use these statistical approximations for macroscopic systems, the increasing power of the CPUs makes it possible to develop numerical methods for the treatment of ever larger systems in an exact representation. This then leads to a hierarchical description of the PT process, where a small subsystem (usually just the proton) is modeled using the full Schrödinger equation. The neighboring parts of the system, which couple directly to the proton are then treated within an approximation like MCTDH, which in turn is coupled to the large environment. This then has to be handled with statistical methods. For the modeling the coupling between the classical and the quantum systems and the interaction of them with the laser field is of prime importance [14, 35, 62, 63].

An added difficulty is the fact that the calculations for the PT system are only exact in the sense that the Schrödinger equation is solved without approximations for the available potential characterizing the transfer. As this normally is also calculated within a limited quantum chemical model, one can quickly see the problems a theoretical approach to this field will have. The goal of not only calculating the dynamics, but also to model reaction control increases the difficulty of the calculations further. Now one also has the additional task to find good methods for determining optimize laser fields achieving this control. The development of optimal control strategies [64, 65, 66], which allow one to determine the laser field needed for the control of a system by only specifying an initial and final state and the potential surface characterizing the system, is the most interesting development in this direction.

As one can see from this list, the theoretical description of PT is an area where much work remains to be done. Especially the calculation of accurate, high dimensional potentials, the effects of dissipation on model systems, methods to generate optimal laser fields for reaction control and understanding the emerging ultrafast IR spectroscopic data are topics of continuing interest.

1.2 The Scope of this Work

In this thesis several of the areas mentioned in the section above are examined. The aim is to gain a deeper understanding of PT processes inside molecular systems coupled to a dissipative environment. The work is split into two main parts: In the following section (Chapter 2) the theories used and developed are presented in detail. Within this chapter the first Section (2.1) describes the quantum chemical methods employed to generate the potential surfaces necessary for the dynamical calculations. In this part the standard techniques used for this purpose are briefly described, starting from the Born–Oppenheimer (BO) approximation and then giving an overview over the Hartree–Fock (HF) theory, Møller–Plesset (MP2) method and density functional methods. In the final part of this section the special requirements for treating the hydrogen bond with these methods are given.

The next Section (2.2) takes a detailed look at the properties of the potential resulting from the *ab initio* calculations. Different approaches to reduce the dimensionality of the molecular system are presented and the concept of the Cartesian reaction surface Hamiltonian is developed. While the concept behind this approximation was already introduced by Miller *et al* [67, 68] in the eighties, in this work the method is applied to a medium sized molecule (PMME, see Section 3.3) to model the proton dynamics in a fully *ab initio* potential and in high dimensionality.

The following Section (2.3) gives a review over the theory of quantum dynamics. In this part the approximations needed to treat a quantum system in a dissipative environment are described in detail.

The next part (Section 2.4) introduces the numerical methods used to implement the theories presented before. Special focus is given to the implementation of the CRS Hamiltonian within the MCTDH method, which is one of the main developments of this thesis.

The final Section (2.5) of the theory chapter details the different theories used in the field of laser control of chemical reactions. After making some remarks about the coupling of the quantum system to the laser field, the different methods to generate a control field for a specific reaction are described. This starts with the guessing of analytical laser pulses for pump–dump schemes, and then continues with genetic algorithms, local tracking control and finally the optimal control method.

After the theoretical background used in this work is introduced, the different approximations and control schemes are tested on model systems and *ab initio* potentials in Chapter 3. This chapter is again split into three main parts.

In the first Section (3.1) different model systems are used to test the performance of the control approaches presented in Section 2.5, applied to isolated systems as well as to the dissipative case. In this part a reaction pathway previously developed in our group for the isomerization in a double minimum potential transferring the population through the barrier, is discussed in detail. This reaction path uses laser driven tunneling to move the hydrogen through the barrier instead of above it. Following this are tests of the

various control methods on one- and two-dimensional model potentials to gain a better understanding of the dynamics in these potentials.

The next Section (3.2) describes the *ab initio* calculations made to generate a potential surface for the proton transfer in the 8-hydroxyimidazo[1,2-*a*]pyridine (HIP) molecule. In addition the first calculations to construct a CRS Hamiltonian are introduced.

In the final Section (3.3) of the chapter, the method of the CRS Hamiltonian is applied to a different molecule – phthalic acid monomethylester (PMME) – and the dynamics of this system is studied with the MCTDH method. Additionally the CRS model is supplemented by including the solvent bath via molecular dynamics simulations.

In Chapter 4 the results are summarized and a personal outlook over the future work necessary in this field is given.

