Chapter 4

Summary and Outlook

This work presents an overview over several theoretical aspects of the important problem of proton dynamics in small molecules. It focuses on the quantum mechanical description of these systems and investigates the possibilities of control of the proton transfer reaction with laser fields using numerical simulations. Beginning with a 1d double well potential, which is modeled to represent a malonaldehyde molecule, to quantum chemical calculations for the potential energy surface of HIP and to the deuterium dynamics in PMME, different approaches to the complicated many-body problem of intramolecular proton transfer are described.

The design of external control fields to steer this reaction to achieve high transfer efficiency is then the goal of the simulations. For the 1d double well model this is done by using three different methods to optimze the parameters of the laser pulse, namely optimal control, genetic algorithms and inverse control. The method of optimal control, which uses only minimal knowledge of the system (i.e. only initial and final state are known), resulted in a control field which initiates a tunneling transfer through the potential barrier, rather than the naively expected reaction path leading over the barrier. The same holds true for a higher barrier system, where the algorithm produces a combined pump–tunnel scheme. If one starts with the knowledge of these reaction paths from the optimal control, it then is possible to design analytical pulses reproducing this process very efficiently.

Effects of a dissipative environment have to be included into the calculation when the investigated molecule is not isolated but located in a solvent. The model calculations for the 1d double well model show, that the control efficiency reached for the small, isolated system is lowered considerably when coupling to a bath is included. This shows that the approach of designing optimal laser pulses for an isolated system and then adding dissipation will not lead to very efficient control. The same pattern is observed with the laser fields generated by the other two control methods, namely genetic algorithms and local tracking control.

Local tracking works both for isolated and dissipative systems with the same algorithm, which relies on the inversion of the quantum dynamical equations to give a relatively simple

analytical expression for the calculation of a laser pulse for the reaction control. In contrast to optimal control, it does not require an iterative scheme to generate the laser field, so it is much faster than this approach. Its application is limited because it needs tightly localized wavepackets to work properly. If these cannot be maintained during the dynamics, the method will not produce useful results. But even with this limitation its speed and the fact, that dissipative systems can be handled by the same approach make this algorithm very useful for the generation of control fields. However, further work is required to see how the definition of the reaction path and the use of different observables influence the results. In this work only position tracking was examined, which had difficulties moving the wavepacket across the anharmonic potential region around the barrier. Further studies could focus on the control of different expectation values, like the energy or the population of certain levels, as recently shown in [116].

In contrast to the local tracking and the optimal control methods, genetic algorithms do not rely on any analytical properties of the system, but on random mutation and evolution of the most effective laser pulse from a population of individuals. The method has shown some potential in recent experiments by generating laser pulses optimizing the generation off specific fragments in a dissociation reaction. The evolutionary algorithms were quite successful producing optimized laser fields for small model systems with a limited number of parameters to search. However, this approach is not well suited to a "black box" approach, i.e. using it without any constraints on the parameter space, for more complicated models. The random search and the large population sizes required for these lead to lots of "useless" calculations (i.e. ones, which have been made before or will definitely not produce good results), which in turn quickly hits the limit of todays computers already for two dimensional systems. Despite its experimental success, from the theoretical point of view this method is therefore either useful for small systems, where the large ensembles can be handled in reasonable time, or for systems where the reaction path is already known approximately. In this case, the method can be used to refine the parameters of the approximate path to produce even better reaction efficiency. As found for the small model systems, this approach produces an efficient laser field much faster than the calculation with unrestricted parameter space, allowing for larger systems to be handled as well. A further advantage of the method is, that it can be applied to all problems for which a "fitness" of an individual can be defined, without any further analytical effort required. Therefore these methods will continue to become more interesting with the ever increasing computer power, in particular as it is well suited for parallel computing, and with the development of more efficient methods for the calculation of reaction dynamics. These developments will allow one to evaluate the fitness of a laser pulse in shorter time, making larger populations and more generations possible.

The study of the different control schemes for proton transfer in model potentials has shown, that the "dumb" algorithms can generate important information about the possible reaction dynamics by uncovering new reaction pathways and that it is necessary to include

the effects of dissipation into the methods to find optimal control pulses. Two of the methods presented in this work include dissipation, of these the local tracking control was not able to handle the double well model, while the genetic algorithms were, with the currently available computers and propagation methods, not able to handle larger systems. The method of optimal control is up to now not suited to handle larger molecules, as it requires a lot of computational effort. Methods to include dissipation into this algorithm are also not trivial, and are still under development [123]. With the investigations presented, a step toward the development of general methods to generate optimal laser fields for reaction control has been made.

Furthermore, for the first time application of a CRS Hamiltonian build completely from *ab initio* data in combination with the MCTDH propagation method has been demonstrated. The basic requirements for building the CRS Hamiltonian were studied on HIP, which turned out to be not well suited to ultra-fast reaction control in the ground state. This experience was then used to build a CRS Hamiltonian for PMME, in which laser induced dynamics could be studied. These studies resulted in a interesting discovery. They showed, that it is not so important to include the maximum number of degrees of freedom into the model calculation, but rather to identify the most important contributions and simulate them with improved accuracy. In contrast to a TDH simulation for all degrees of freedom [151], the MCTDH calculations for the nine most important modes showed effects of IVR not observed in the model with more dimensions, but less accuracy. This makes the CRS Hamiltonian an interesting tool for further applications in this directions. The *ab initio* data needed to build it automatically give information about the coupling strength of the different modes and allow one to include them up to a required accuracy into the calculations. The MCTDH method is well suited to deal with the resulting Hamiltonian, as it can handle lots of weakly coupled modes very efficiently and the accuracy can be tuned for each mode according to the available computing power.

An expansion of the CRS Hamiltonian approach to other systems and inclusion of flexible reference geometries [90] in future calculations with refined MCTDH methods therefore is promising. What has also been shown is, that the effects a solvent has on the intramolecular dynamics greatly influences the structure of the resulting spectrum and therefore they have to be taken into account in the calculations. Even the high dimensional methods used here for isolated PMME were not able to explain the fast decay times observed in the pump–probe spectra. First studies of the solvent effects on this system with classical MD simulations showed, that couplings of the low frequency normal modes to the environment can account for the fast energy dissipation. The calculations made in this work were using a relatively simple approach, leaving as a future challenge the more elaborate study of the coupling between the environment and the CRS Hamiltonian.

As one sees from the models presented in this work, nowadays the theories and computing resources exist to handle small systems with dissipation or large systems with no dissipation, and a goal should be to merge the existing theories to enable the treatment of

large, dissipative systems. The examination of the different schemes to calculate optimal control fields revealed the problems these methods have, when larger systems are to be examined or dissipation is included into the picture. The further goal therefore should be the continuing development of the algorithms used in this work, putting special focus on the CRS Hamiltonian, which seems to be very well suited to study proton dynamics within larger molecules using the MCTDH approach. The fast dynamic simulations possible with this method, even for larger systems, will improve the efficiency of all the control approaches, as they all need to calculate the evolution of the systems they have to control. So a combination of the methods of optimal control with MCTDH could result in a program which can make efficient predictions of optimal laser fields even on large systems. An additional field for future study is the molecular dynamics of the solvent, and its interaction with the molecule. This requires the development of effective classical or semiclassical models and methods to couple the results to the quantum dynamics model, and would then result in a toolkit of algorithms, which could be applied to the simulation of a variety of quantum systems of widely varying complexity, not limited to proton transfer alone.