Chapter 1

Introduction

1.1 Overview

The birth of quantum mechanics in the beginning of this century signified the dawn of a new era in chemistry and physics. This theory shed light at the hitherto mysterious world of atoms and molecules, providing an explanation of many important empirical laws and relationship. The development of the quantum mechanics in its early years has been explosive, prompting the statement of one of its founding fathers, 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].

This encompassing statement did not, however, take into account the difficulties lying ahead. The mathematical machinery of quantum mechanics is complex, allowing analytical solutions only for the simplest models of physical phenomena. The concepts introduced by this theory were defying the conventional scientific intuition, giving rise to numerous paradoxes. And finally, many interesting phenomena in the world of atoms and molecules occur on the time scales, unthinkable at that time for the experimentalists to approach, as summarized by the president of the Faraday

Society, Sir Melville in 1947 [2]:

> “The direct physical methods of measurement simply cannot reach these magnitudes, far less make accurate measurements in a limited period of time, for example 10^{-3} s.”

These difficulties proved to be a temporary obstacle. The development of computers and the resulting rapid advance in numerical mathematics made the previously insurmountable problems tractable. The introduction of amplified stimulated emission light sources, or lasers, in the second half of the century provided the experimentalists with necessary tools. The unique properties of the laser light – its coherence, monochromaticity, intensity, and not the least the possibility to generate very short light pulses make the lasers ideally suitable for investigation of the quantum mechanical effects in nature.

However, many processes of fundamental significance for the chemistry, e.g. the fast elementary reactions, molecular vibrations, rotations, making and breaking of chemical bonds, proceed on the time scales of pico- and femtoseconds, and pulses of such durations for many years were beyond the possibilities of laser systems.

When the developments in laser technology, especially in the field of ultrashort pulse generation, made it possible to produce light pulses of sub-picosecond duration, a new exciting field was born - the *femtosecond chemistry*.

Femtosecond chemistry was pioneered by A.H. Zewail and coworkers [3], and it is now a rapidly developing field of great promise. The ultimate recognition of its importance was the award of the Nobel Prize in Chemistry to Zewail in 1999. For a broad overview of the current status of the subject the reader is referred to the following reviews and collections [4–9].

The goal of the femtosecond chemistry is to monitor, influence, and eventually control the fundamental processes in molecules or clusters on the time scales of nuclear motion. These include, but are not limited to, monitoring the intramolecular vibrational redistribution (IVR) [10, 11], formation and breaking of chemical bonds

[12–14], selective excitation and preparation of molecular quantum states [15–21]. Understanding the ultrafast behaviour of molecules, and influencing it with the help of laser fields may lead to the ultimate goal of controlling the flow and outcome of chemical reactions [22,23], and steering them along the paths which are inaccessible by conventional chemical means.

The progress in the femtosecond chemistry was boosted by the discovery of new active medium for laser generation - sapphire crystals activated with titanium ions [24,25]. The remarkable properties of this medium made it possible to generate powerful, tunable laser pulses in the femtosecond time domain (the theoretical limit for the pulse duration with Ti:sapphire crystals is 8 fs!). These lasers are nowadays used in almost all experiments in the femtosecond time domain.

On the theoretical side, the core of femtosecond chemistry is the quantum mechanical description of the system under consideration, most commonly a single molecule or cluster, by means of a Schrödinger equation for the time-dependent wave functions (wave packets), or Liouville-von Neumann equation for the density matrices [4]. The system is subject to a time dependent perturbation by an electromagnetic field, which is treated by means of classical electrodynamics. The electromagnetic field in question consists typically of one or more laser pulses, defined by their shapes, amplitudes, durations, delay times, relative phases, frequencies and frequency modulations (e.g. chirping). By choosing the appropriate parameters of the laser field, the molecular motions are stimulated, probed, prepared and controlled [15,22,26].

One of the difficulties encountered by the quantum theoretical simulations in femtosecond chemistry is the so-called exponential scaling of the computational effort with respect to the number of system degrees of freedom. While solving exact quantum mechanical equations for systems with one degree of freedom (e.g. vibrating diatomic molecules) is not a task especially demanding computationally, the computational effort increases sharply when additional variables are taken into account, to the extent that the three-dimensional [1] problems require state-of-the-art

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[1] Within the Schrödinger equation formalism. For density matrix propagation the number of “numerical” degrees of freedom is twice the number of “physical” degrees of freedom

computational facilities, and there have been only very few examples of quantum dynamics in a reactive system with more than three degrees of freedom. [2] To treat the systems with even higher dimensionality, one has to employ other methods, such as classical trajectories [32, 33], mixed quantum-classical methods [34–40], which do not follow the rule of exponential scaling. However, the breakthrough comes at the cost of neglecting some quantum mechanical aspects of molecular behaviour. A possible way to treat multidimensional systems quantum mechanically is making use of the modern computer hardware, namely the massively parallel distributed memory supercomputers, adapting the programs for quantum mechanical propagation to their hardware.

1.2 The structure of the thesis

This work is intended as a contribution to the theory of femtosecond chemistry, and is dealing with the fundamental dynamical processes induced by the ultrashort (picosecond and femtosecond) laser pulses in isolated small molecules and clusters. The motivation is to offer a close look into the important processes of intramolecular dynamics, and to demonstrate the possibilities of the control of these processes, taking into account all relevant system degrees of freedom.

The thesis is organized as follows:

The next chapter presents the results on the first three-dimensional quantum dynamical *ab initio* simulations of the large amplitude vibrational dynamics of Ag_3 clusters in the gas phase, monitored by femtosecond pump-probe NeNePo spectroscopy. A close look on the microscopic quantum dynamics of the silver mini-clusters is offered, and the influence of vibrational temperature of the initial cluster ensemble is investigated. The results of quantum dynamical simulations are compared with the previously published semiclassical simulations, as well as with the experiment.

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[2] There have been reports on quantum dynamical simulations in four [27,28], and, with carefully introduced approximations, five [29], six [30], and even 24 (*sic!*) dimensions [31].

In Chapter 4 a novel three-dimensional model of an asymmetric triatomic molecule is presented, where the derived three-dimensional vibrational Hamiltonian does not contain unphysical singular terms. The model is then applied to the studies of a nitric acid ($HONO_2$) molecule in the gas phase, on the example of which the processes of restricted IVR and efficient photoinduced dissociation have been investigated.

Chapter 5 is dedicated to the studies of a rotating diatomic molecule (HF), where the possibility of efficient control of excitation and dissociation of a molecule in presence of rotation is demonstrated.

The conclusion and outlook of the thesis are offered in Chapter 6, followed by the appendices. Appendix A addresses the issues of parallel computation in application to wave packet propagation. In the Appendix B a discrete variable representation technique suitable for the solution of the time-independent Schrödinger equation is presented, together with the extension thereof, allowing easy evaluation of complicated kinetic energy operators. Appendix C offers a discussion on the origins of the singular terms in widely known 3-D Hamilton operators in internal molecular coordinates.