Chapter 6

Conclusions

The subject of this work is the exploration of the quantum wave packet dynamics of small molecules and clusters in the gas phase, induced and driven by ultrashort laser pulses on a femtosecond or picosecond time scale. This dynamics has been treated by models of full dimensionality, where all relevant degrees of freedom have been taken into account. The studies concentrated on the issues of the development of models for photoinduced dynamics, investigation of the IVR, and problems of control.

The introductory part of the thesis, Chapter 1, discusses the problems and issues being addressed in this work, together with a historical perspective of the development of the field of femtosecond chemistry, and outlines the structure of the thesis.

In Chapter 2 the techniques and methods of the solution of both time-dependent and time-independent Schrödinger equations, which are of relevance to the applications considered in the work, are reviewed. These include the split-operator technique for the wave packet propagation, the direct relaxation technique for the solution of the eigenvalue problem of the Hamilton operator. Also, the issues of the analysis of time-dependent wave functions are addressed.

Chapter 3 is dealing with the application of the time-dependent wave packet

techniques to the NeNePo pump-probe investigation of the large amplitude vibrational dynamics of neutral silver trimers. The results of the first application of the techniques of parallel programming to the three-dimensional quantum mechanical wave packet study of Ag_3 are presented. These simulations proved to be very demanding with respect to computational power employed (the size of propagation grids exceeded 8,000,000). To make the problem tractable, a simplified model of the phenomena has been developed, which nevertheless did not lead to the loss of relevant physical information. The results of the quantum mechanical wave packet propagation have been compared with the corresponding semiclassical propagation results and the microscopic-level differences between the two approaches and their signatures in the observed signals have been discussed [99].

Silver trimers in their ground electronic state, due to the large vibrational excess energy and high density of quantum states in the region where dynamics takes place, offers a good example of dissipative IVR [97, 144]. The processes of emergence and completion of the IVR have been considered quantum mechanically, and signatures of weak recurrences, or fractional revivals have been found.

In order to investigate the effects of the initial temperature of the cluster ensemble, a new approach has been developed and applied, which employs a Boltzmann-weighed superposition of the NeNePo-ZEKE signals of several low-lying vibrational eigenstates of Ag_3^-. The contributions of the individual quantum states forming the ensemble to the observed signals have been investigated, and it has been shown, how the features of wave packet evolution can be identified in the signals. The results obtained were compared with newest experimental data of Wöste group [94, 109], and excellent correspondence to the experiment has been established.

In Chapter 4 the ultrafast dynamics of the nitric acid molecule in the gas phase has been considered in three dimensions. A general model for the investigation of nuclear dynamics of asymmetric triatomic molecules interacting with a laser field has been proposed, which differs from the other widely accepted models in the respect, that the quantum mechanical equation of motion is free of singular terms in the vicinity of the linear configuration, allowing the studies of large amplitude bending motions.

To illustrate the potential of the model, it has been applied to two exemplary problems. As a first application, the restricted IVR in $HONO_2$ has been studied, which emerges in the process of preparation and evolution of vibrational zeroth-order states. The emergence of the characteristic in- and out-phase oscillations, or quantum beats, has been demonstrated in a three-dimensional wave packet simulation. The structure of the emerging multi-level quantum beats has been analyzed, and the dominant contributions to the beat pattern have been established.

The low-lying zeroth-order state under consideration has also been prepared selectively by means of a subpicosecond laser pulse, demonstrating the feasibility of the zeroth-order states as intermediate steps for laser control. The character of quantum beats in the process of selective preparation by laser light proved to be different from the artificial free evolution case, due to the coherent nature of the excitation process.

Another application of the model was the problem of the laser-driven breaking of the ON single bond of $HONO_2$, where it has been shown that efficient (93% yield) dissociation can be achieved by means of a single picosecond laser pulse. The efficient vibrational redistribution between the bending and the ON stretching modes during the process of dissociation proves the importance of the bending degree of freedom for the dynamics of triatomics, and underscores the need of its correct physical description.

Chapter 5 is dedicated to the studies of vibrational-rotational excitation of a diatomic HF molecule by ultrashort laser pulses. When linear-polarized laser light is used, the magnetic quantum number is conserved in the process of excitation, leading to the azimuthal symmetry of the three-dimensional molecular Hamiltonian, and the dynamics can be described by a two-dimensional model. It has been shown, that even in presence of rotation, the quantum states of the HF molecule can be prepared with selectivity close to 100%, which amounts to efficient laser control. The highly efficient dissociation, with close to 100% probability, has also been demonstrated.

An interesting phenomenon in the process of selective preparation of the molecule has been observed, namely that the quantum states can still be prepared very ef-

ficiently, even if the direct one photon transition to these states is forbidden by the selection rules. In this case, the excitation proceeds simultaneously via two interfering multiphoton excitation pathways, involving allowed transitions.

The control schemes employed in this study, based on the careful consideration of the physical processes occuring in the molecule, have led to very high state selectivity of the processes studied, and this degree of selectivity has not been obtained by application of the optimal control theory to the same system [121], where the selectivities of about 25% were achieved. This indicates that the optimization techniques of Ref. [121] should be used with care, taking into account the specific features of the process. The relative simple character of the laser pulse sequence used for the purposes of control in this work make the experimental realization of proposed control schemes feasible with the development modern laser techniques [145, 146].

In the Appendix A the issues of parallelization of quantum dynamical algorithms are discussed. The SIMD parallel programming paradigm has been used in this work, and the heart of the method is the parallelization of a three-dimensional fast Fourier transformation by means of slab decomposition. The computational effort scales almost linearly with the increase in the number of processing elements used.

Appendix B offers a brief description of a Fourier basis discrete variable representation technique for solution of the time-independent Schrödinger equation. An attractive feature of this method is the possibility to obtain an analytical expression for the matrix elements of the kinetic energy operatior in the Fourier basis. In the literature, such expressions have been derived for the operators of the kind $\partial^2/\partial x^2$ (square of the momentum operator). More complex Hamilton operators, such as the one derived in Chapter 4, also require the evaluation of first order coordinate derivatives. For this purpose, an analytical expression for the DVR matrix elements of the $\partial/\partial x$ operator has been derived.

The kinetic energy part [Equation (4.15] of the Hamilton operator of Chapter 4 is markedly different from the ones widely used in the literature in the fact, that the singular terms in the vicinity of linear configuration are absent. Appendix C offers an attempt to elucidate the origin of the discrepancy. The emergence of the singular

terms has been attributed to the limitations of the technique of Podolsky [147], which is normally used for derivation of the vibrational-rotational Hamilton operators.

6.1 Outlook

The main motivation behind the present work has been the application of existing methods of time-dependent wave packet propagation to small systems in full dimensionality. Although these methods, due to their *ab initio* character yield accurate information on the ultrafast dynamics of small systems, there exists a need for the ability to treat larger systems, with number of degrees of freedom greater than three, in order to keep up with the developments in the fields like the ultrafast spectroscopy and reaction dynamics of biomolecules [148–154].

One line of overcoming these difficulties is the development of approximate models, which nevertheless are able to adequately describe the effects of interest. Steps in this direction have already been undertaken, and results of simulations of wave packet dynamics in four [27, 28], five [29], six [30], nine [155] and even 24 [31] dimensions have been reported.

Another promising direction of research is concerned with the development of mixed quantum-classical models, where a few selected degrees of freedom are treated quantum mechanically, and the rest is described by semiclassical means [156]

It seems, however, that the potential of the new techniques of parallel computation is far from being exhausted. The progress made in the field of application of parallel programming to the quantum chemistry problems suggests that with the development of better algorithms and new computer hardware, *ab initio* quantum dynamics could be performed in at least four dimensions.

Also, the reexamination of certain widely accepted "practical" ways of implementation of the concepts of quantum mechanics may yield the unexpected results, which also can contribute to the decrease of the computational effort, the examples

from this work being the supposed unsuitability of the normal coordinates for the large amplitude dynamics, and presence of the singular terms in the rovibrational Hamilton operator of a triatomic molecule.

Finally, the techniques of laser control appear to function well in systems with high dimensionality, hinting at the possibility of reliable control of the systems with at least three degrees of freedom. The need to extend the theoretical machinery of laser control to more complex molecules is highlighted by the recent experiment of G. Gerber and coworkers [157] on successful control of the polyatomic organometallic complexes. This experiment offers a challenge to extend and perfect the existing control schemes, either the ones described in this work, or numerous others, in order to make them applicable also for very large, biologically and chemically relevant molecules.