Non-adiabatic quantum molecular dynamics:

- Benchmark systems in strong laser fields
- Approximate electron-nuclear correlations

Dissertation
zur Erlangung des
Doktorgrades der Naturwissenschaften
(Doctor rerum naturalium)

vorgelegt von
Michael Fischer
geboren am 31. Januar 1985 in Görlitz

Dresden 2014
Eingereicht am 13. Dezember 2013

1. Gutachter: Prof. Dr. Rüdiger Schmidt
2. Gutachter: Prof. Dr. Paul-Gerhard Reinhard

Verteidigt am 04. Juli 2014
Abstract

The non-adiabatic quantum molecular dynamics (NA-QMD) method couples self-consistently classical nuclear motion with time-dependent density functional theory (TDDFT) in basis expansion for the electron dynamics. It has become a versatile approach to study the dynamics of atoms, molecules and clusters in a wide range of scenarios. This work presents applications of the NA-QMD method to important benchmark systems and its systematic extension to include quantum effects in the nuclear motion.

Regarding the first objective, a complete study of the strong-field ionization and dissociation dynamics of nature’s simplest molecule H$_2^+$ is performed. By including all electronic and nuclear degrees of freedom and all reaction channels, molecular rotation is shown to play an important role in the ionization process. In addition, strong orientation effects in the energy deposition process of the Buckminster fullerene C$_{60}$ in short intense laser pulses are surprisingly found in full dimensional calculations. Their consequences on the subsequent nuclear relaxation dynamics shed new light on available experimental data and future experiments are proposed to confirm the detailed predictions.

Regarding the second objective, the NA-QMD formalism is basically extended to take electron-nuclear correlations into account. This extension is achieved by means of a trajectory surface hopping scheme in the adiabatic Kohn-Sham framework. First studied examples from collision physics and photochemistry illustrate the relevance and importance of quantum effects in the nuclear dynamics.
Contents

1 Introduction ........................................................................................................... 7

2 Theory ................................................................................................................... 11
  2.1 Mixed quantum-classical molecular dynamics methods ............................... 11
  2.2 Non-adiabatic quantum molecular dynamics (NA-QMD) ....................... 17
  2.3 Non-adiabatic quantum molecular dynamics with trajectory surface hopping
      (NA-QMD-H) ................................................................................................. 24
  2.4 Adiabatic quantum molecular dynamics (QMD) ........................................ 31
  2.5 Summary ......................................................................................................... 32

3 NA-QMD: Complete dynamics of H$_2^+$ in strong laser fields .................... 35
  3.1 Introduction ..................................................................................................... 35
  3.1.1 Preliminary considerations ...................................................................... 37
  3.1.2 Computational details ............................................................................. 38
  3.2 Multiphoton Dissociation of H$_2^+$ in strong laser fields ......................... 41
      3.2.1 Theory: Field-dressed nuclear quantum dynamics (FBO) ................. 41
      3.2.2 Computational details: FBO ............................................................ 43
      3.2.3 Total angular distributions of fragments and dissociation probabilities 43
      3.2.4 Adiabatic Floquet surfaces and multiphoton channels .................... 45
      3.2.5 Role of nuclear rotation in multiphoton dissociation ......................... 48
  3.3 Ionization and dissociation of H$_2^+$ in strong laser fields .......................... 54
      3.3.1 Total ionization and dissociation probabilities .................................. 54
      3.3.2 Angular distributions of fragments ................................................... 56
      3.3.3 Towards comparison with experiment .............................................. 57
  3.4 A simplified model for the laser-induced dynamics of H$_2^+$ ....................... 62
      3.4.1 Theoretical approach ....................................................................... 62
      3.4.2 Preliminary Considerations ............................................................. 64
      3.4.3 Comparison with experiment ......................................................... 66
  3.5 Summary ......................................................................................................... 69
4 NA-QMD: Orientation dependence of energy absorption and nuclear relaxation of C_{60} in fs-laser pulses .................................................. 71
  4.1 Introduction .............................................................. 71
    4.1.1 Computational details ............................................ 73
    4.1.2 Ground state and optical properties ............................. 73
  4.2 Orientation dependence of energy absorption .......................... 75
  4.3 Laser-induced nuclear relaxation dynamics of C_{60} ..................... 80
    4.3.1 Pulse length dependence of normal mode excitation ............... 80
    4.3.2 Orientation dependence of nuclear relaxation dynamics .......... 81
    4.3.3 Intensity dependence of nuclear relaxation dynamics ........... 85
  4.4 Summary ................................................................. 86

5 NA-QMD-H: Case study and applications .................................... 89
  5.1 Electron-nuclear correlations in atomic collisions ..................... 89
    5.1.1 Case study: model system of H^+ + H collisions .................. 89
    5.1.2 Atom-molecule and atom-cluster collisions ..................... 96
    5.1.3 Comparison with experiment: He + H_2 and He + He collisions .... 102
  5.2 Electron-nuclear correlations in the laser-induced dynamics of organic molecules 106
    5.2.1 Electronic relaxation of the methaniminium cation ............... 106
    5.2.2 Excitation and electronic relaxation of ethylene ............... 110
  5.3 Summary and open questions ........................................... 117

6 Conclusions and outlook ..................................................... 119

Appendix A ................................................................. 121
  A.1 Instantaneous Floquet states ...................................... 121
  A.2 Assignment of multiphoton channels in NA-QMD ...................... 122

Appendix B ................................................................. 125
  B.1 Normal mode analysis ............................................. 125

Appendix C ................................................................. 127
  C.1 Separate spin treatment within Tully hopping ...................... 127

Bibliography ............................................................... 129
1 Introduction

During the last decades, large progress has been made in the understanding of non-adiabatic phenomena in atoms, molecules and clusters, which represent the basis for many important processes occurring in different fields of physics, chemistry and related areas. Non-adiabatic processes are basically characterized by collision- or light-induced electronic excitations coupled to the nuclear dynamics in molecules or clusters [1]. Triggered by the availability of powerful laser sources working in the femto-second [2,3] and even atto-second regime [4–6], experiments have been able to uncover a variety of fascinating phenomena, among them above-threshold ionization (ATI) [7] and dissociation (ATD) [8], high harmonic generation (HHG) [9], charge resonance enhanced ionization (CREI) [10], molecular alignment [11], ultrafast internal conversion [12], and Coulomb explosion [13]. Present-day pump-probe techniques allow to observe the nuclear and electron dynamics in laser-induced processes in real-time. On the other side, refined scattering experiments have delivered detailed insight into reaction mechanisms in ion-cluster and cluster-cluster collisions such as electronic and vibrational excitation, charge transfer, and fragmentation [14–17].

The theoretical description of non-adiabatic processes is a very challenging task, as in principle the solution of the time-dependent Schrödinger equation (TDSE) for the atomic many-body system is required for this purpose. Such a full quantum mechanical description is, at present, limited to only a small number of degrees of freedom: The world record up to now seems to be the full numerical solution of the seven-dimensional time-dependent Schrödinger equation for the H$_2$ molecule, however, aligned along the laser polarization direction [6]. Approximations are therefore inevitable in order to treat larger systems.

Most commonly, the quantum mechanical solution of the full problem is circumvented by means of a (non-adiabatic) mixed quantum-classical description, i.e coupling classical molecular dynamics for the nuclei to a – mostly time-independent – quantum mechanical description of the many-electron system. The latter requires the solution of the electronic structure problem, for which a large variety of ab-initio approaches, popular especially in chemistry, exist, among them Hartree-Fock theory (HF), multi-configurational self-consistent field theory (MCSCF) or the coupled-cluster method (CC) [18]. All these methods rely on the many-electron wave function in some way. This is necessarily connected to limitations in their range of applications due to the large numerical effort of these methods, especially in molecular dynamics applications. An alternative for dealing with the electronic structure problem is given by density functional theory (DFT) [19], which deals with the electronic
one-particle density instead, consequently reducing the computational effort dramatically. This approach has become a standard tool in chemistry and material science [20]. All these methods are nowadays routinely used in quantum chemistry codes like GAUSSIAN [21], GAMESS [22], and MOLPRO [23], to name but a few.

An explicitly time-dependent description of the non-adiabatic electron dynamics, in particular in the presence of an external laser field, is more difficult. Above all, time-dependent density functional theory (TDDFT) [24] is in the first line combining efficiency and accuracy. The non-adiabatic quantum molecular dynamics method (NA-QMD) developed in our group couples self-consistently electronic excitations within TDDFT to classical nuclear motion in atomic many-body systems. The original version by Saalmann and Schmidt [25] marked the first attempt to generalize adiabatic QMD theories existing until then, thereby providing a microscopic description of non-adiabatic processes, e.g. excitation and relaxation mechanisms in collisions of atoms with metal clusters, charge transfer and Coulomb explosion in ion-cluster collisions. Moreover, a first idea to take electron-nuclear correlations into account has been developed and applied to a simple one-electron system, namely the Na$^+_2$ + He collision [26]. Two important limitations were inherent in the original NA-QMD method: first it was restricted to conservative systems only, second it was approximate (not ab-initio) due to the representation of the exchange-correlation potential in the Kohn-Sham equations as a sum of atomic potentials. The present ab-initio version of the NA-QMD method has been developed by Kunert and Schmidt [27] overcoming the original limitations, amongst others, by including external laser fields. Later, it was generalized to describe ionization in many-electron systems [28].

In contrast to grid-based implementations of TDDFT like the octopus project [29], the NA-QMD approach is based on a finite basis expansion which reduces the computational effort considerably. A corresponding systematic estimate of the basis set expansion error has been given in [30]. Up to now, a large variety of molecular processes has been investigated successfully by means of the NA-QMD method ranging from dimers up to clusters with hundreds of electronic and nuclear degrees of freedom. This concerns laser-induced dynamics of H$_2$ and H$^+_2$ [31,32], the isomerization of small organic molecules like ethylene and diimide [33,34] as well as the excitation of the giant breathing mode in C$_{60}$ [35], ion-cluster collisions [36,37] as well as fullerene-fullerene collisions [38]. For further applications see [39].

In particular, two benchmark systems are of outstanding importance: nature’s simplest molecule H$_2^+$ and the Buckminster fullerene C$_{60}$. In spite of the increase of computer power, no full-dimensional description including all degrees of freedom and all fragmentation channels under the influence of a laser field has been achieved so far for these systems, not even for the hydrogen molecular ion. In particular, previous experiments have indicated the importance of molecular rotation or orientation for laser-induced fragmentation of H$_2^+$ [40]. Due to its highly symmetric structure - resembling a soccer ball - orientation effects of the laser-induced phenomena like fragmentation in the Buckminster fullerene C$_{60}$ are intuitively
expected to be of minor relevance. Consequently, to the best of our knowledge, no work has been done in that direction up to now.

The first of the two main objectives of this thesis is to contribute to closing these gaps. This is achieved, on the one hand, by a complete study of the strong-field ionization and dissociation dynamics of H$_2^+$, i.e. including all electronic and nuclear degrees of freedom and all reaction channels (Chapter 3) [41–43]. On the other hand, we investigate the orientation dependence of energy absorption of C$_{60}$ in short intense laser pulses (Chapter 4) [44].

From a fundamental point of view, the basic problem of the mixed quantum-classical description of an atomic many-body system concerns the way the coupling between the classical and quantum subsystems is treated [45]. The most straightforward way to realize this coupling results naturally in the mean-field approximation for the nuclear dynamics [25,27,29,46,47], often called Ehrenfest method [45,48–50]. In this approximation, the nuclei propagate purely classically on an effective time-dependent potential energy surface which is an average over the electronic subsystem. It is therefore successfully applicable to describe situations where the quantum nature of the nuclear motion is negligible (e.g. in high-energy atom-cluster collisions [36,37]) and/or to the calculation of mean observables which are not largely affected by quantum effects of the nuclear dynamics (e.g. the mean absorbed energy within a molecule exposed to an intense laser field [35]). In other words, the Ehrenfest dynamics fails to treat processes which are dominated by the wave packet dynamics of the nuclei (e.g. in chemical reactions [51]) and/or to obtain differential experimental quantities which are a priori determined by the inherent quantum nature of the nuclei (e.g. the kinetic energy release (KER) of the products resulting from laser- or collision-induced fragmentation of a molecule [15]). Overcoming the limitations of the mean-field or Ehrenfest dynamics represents a challenging and ongoing field of the time-dependent theory of finite atomic many-body systems [45]. Thereby, the ultimate goal consists in the development of a (in any case still approximate) theory which describes self-consistently the coupled electron-nuclear dynamics on full quantum mechanical footings. To realize this, very different attempts have been proposed so far. Among them, a rigorous reformulation of the TDSE by means of a two-component (nuclei and electrons) time-dependent density functional theory (TDDFT) [52], an ab-initio multiple spawning molecular dynamics [53], a moment expansion of the density matrix in the exact Ehrenfest equations [54] as well as a number of ab-initio molecular dynamics methods based on TDDFT [24] and Tully’s surface hopping mechanism [55] to include electron-nuclear correlations [56–58].

In its present state the NA-QMD method is based on a purely classical, i.e. mean-field or Ehrenfest, treatment of the nuclei. As the second objective of this work, we present (Chapter 2) and apply (Chapter 5) an extended formalism of the NA-QMD, which includes electron-nuclear correlations by coupling self-consistently the non-adiabatic equations of motion for the electrons with a trajectory surface hopping scheme in the adiabatic framework for the nuclei, termed non-adiabatic quantum molecular dynamics with hopping ("NA-
QMD-H") [59–61].

This thesis is organized as follows:

In Chapter 2, we first present a general overview over the present NA-QMD version and develop its extension to take electron-nuclear correlations approximately into account [59]. The resulting new method is termed NA-QMD-H for reasons of differentiation. The connection of these methods and their reduction to the adiabatic limit (QMD) are outlined as well.

In Chapter 3, we present a detailed study of the fragmentation dynamics of H$_2^+$ under intense short laser pulses using the NA-QMD method [41, 42]. Complementarily, nuclear quantum dynamics calculations aid the interpretation of respective phenomena, and a simplified classical model for the strong field dynamics of H$_2^+$ is proposed allowing the comparison with data obtained under realistic experimental conditions with a feasible computational cost [43].

In Chapter 4, the NA-QMD approach is utilized to shed light on the role of molecular orientation effects in the energy absorption and relaxation dynamics of C$_{60}$ in femto-second laser pulses [44]. Corresponding results contribute to the understanding of already existing experimental data and propose future experiments to confirm the detailed predictions.

In Chapter 5, systematic case studies for the NA-QMD-H method are performed focusing on the relevance of electron-nuclear correlations and the need to consider them explicitly for a variety of scenarios, utilizing examples from collision physics [60] and photochemistry [61].

Atomic units are used throughout this thesis ($\hbar = m_e = e = 1$) unless stated otherwise.
2 Theory

In this chapter we present the theoretical approach used to describe the time evolution of atomic many-body systems including all electronic and nuclear degrees of freedom. After an excursion to the general background of molecular dynamics approaches, we review the non-adiabatic quantum molecular dynamics (NA-QMD) method, developed in our group [25, 27, 28, 30], in Section 2.2. This approach treats simultaneously and self-consistently electronic excitations (quantum mechanically) and nuclear motion (classically). Subsequently, in Section 2.3, we develop an extension of this method in order to include electron-nuclear correlations in the formalism, which we term NA-QMD-H [59]. Finally, we summarize the essential idea of adiabatic quantum molecular dynamics (QMD), which represents the limiting case of both NA-QMD and NA-QMD-H, if electronic transitions are negligible.

2.1 Mixed quantum-classical molecular dynamics methods

Driven by the desire to study the interactions and dynamics of atoms, molecules and clusters in real-time, eventually in the presence of an external laser field, a large variety of methods has been developed in the last decades for this purpose. In this Section, we review the essential ingredients, most of these approaches are based on (see e.g. [62]), in particular their classification into adiabatic and non-adiabatic molecular dynamics approaches.

From a fundamental point of view, these systems demand a full quantum mechanical description, i.e. conventionally in terms of the (non-relativistic) time-dependent Schrödinger equation for the composed system of $N_e$ electrons and $N_i$ nuclei/ions

$$i\frac{\partial}{\partial t} \Psi(r, R, t) = H(r, p, R, P, t) \Psi(r, R, t)$$

(2.1)

where $r = \{r_1 \ldots r_{N_e}\}$, $p = \{p_1 \ldots p_{N_e}\}$, $R = \{R_1 \ldots R_{N_i}\}$, and $P = \{P_1 \ldots P_{N_i}\}$ represent the collective variables for the respective coordinates and momenta. The full Hamiltonian
is given by

\[ H(r, p, R, P, t) = \sum_{A=1}^{N_i} \frac{p_A^2}{2M_A} + \sum_{i=1}^{N_e} \frac{p_i^2}{2} + \sum_{i=1}^{N_e} \sum_{A=1}^{N_i} \frac{-Z_A}{|r_i - r_A|} + \sum_{i<j}^{N_e} \frac{1}{|r_i - r_j|} \]

\[ + \sum_{A<B}^{N_i} \frac{Z_A Z_B}{|R_A - R_B|} + \sum_{A=1}^{N_i} Z_A |R_A| \cdot E(t) + \sum_{i=1}^{N_e} -r_i \cdot E(t) \]  

(2.2)

with the kinetic energies of the nuclei \( T_i(P) \) and electrons \( T_e(p) \), the electron-nuclear attraction \( V_{e,i}(r, R) \), electron-electron repulsion \( V_{e,e}(r) \), and nuclear-nuclear repulsion \( V_{i,i}(R) \) (with nuclear masses \( M_A \) and charges \( Z_A \)). The latter two terms in (2.2) describe the interaction with the external laser field, i.e. nuclear-laser interaction \( V_{i,las}(R, t) \) and electron-laser interaction \( V_{e,las}(r, t) \), which are included using the dipole approximation and length gauge. In the presence of an external laser electric field \( E(t) \), this Hamiltonian becomes explicitly time-dependent. The time-independent electronic terms represent the electronic Hamiltonian

\[ H_e(r; R) = T_e(p) + V_{e,i}(r, R) + V_{e,e}(r) + V_{i,i}(R) \]  

(2.3)

where the Coulomb repulsion of the nuclei is included here as well, as it is just a constant for a fixed nuclear configuration.

Conveniently, the so-called Born-Oppenheimer expansion is utilized in order to simplify (2.1) and reads

\[ \Psi(r, R, t) = \sum_I \Omega_I(R, t) \Phi_I(r; R) . \]  

(2.4)

The Born-Oppenheimer states \( \Phi_I(r; R) \) are solutions of the time-independent electronic eigenvalue problem

\[ H_e(r; R) \Phi_I(r; R) = E_I(R) \Phi_I(r; R) \]  

(2.5)

and form a complete orthonormal basis. The eigenvalues \( E_I(R) \) are the Born-Oppenheimer surfaces. Note that the nuclear coordinates \( R \) only appear as a parameter in (2.5), i.e. the electronic structure problem (2.5) is solved for a fixed nuclear configuration. After inserting (2.4) in (2.1), one derives the coupled time-dependent Schrödinger equations for the evolution of the nuclear wave functions \( \Omega_I(R, t) \) as

\[ i \frac{\partial}{\partial t} \Omega_I(R, t) = \left[ T_i(P) + E_I(R) + V_{i,las}(R, t) \right] \Omega_I(R, t) \]

\[ - \sum_{J=1}^{N_i} \frac{1}{M_A} D_{ij} \frac{\partial}{\partial R_A} \Omega_J(R, t) - \sum_{J=1}^{N_i} \frac{1}{2M_A} G_{ij}^A \Omega_J(R, t) \]

\[ - \sum_{J} E(t) \cdot L_{\Omega} \Omega_J(R, t) \]  

(2.6)
The first line of (2.6) describes the *adiabatic* evolution of the nuclear wave function in the electronic state $I$, while the second line describes *non-adiabatic* transitions from or to other states $J$ via the first-order and second-order non-adiabatic derivative couplings $D_{IJ}^A$ and $G_{IJ}^A$ given by

$$D_{IJ}^A = \langle \Phi_I(R) | \frac{\partial}{\partial R_A} \Phi_J(R) \rangle , \quad (2.7)$$

$$G_{IJ}^A = \langle \Phi_I(R) | \frac{\partial^2}{\partial R_A^2} \Phi_J(R) \rangle . \quad (2.8)$$

Such transitions typically occur due to the presence of avoided crossings or conical intersections between the potential energy surfaces. The third line in (2.6) contains the *diabatic* transitions due to the presence of the laser electric field, which are *non-adiabatic* transitions as well, with the respective dipole matrix elements

$$L_{IJ} = \langle \Phi_I(R) | \sum_{i=1}^{N_e} r_i \Phi_J(R) \rangle . \quad (2.9)$$

The scalar product in (2.7), (2.8), and (2.9) is taken with respect to the electronic coordinates only.

Consequently, *adiabatic* molecular dynamics means that the system evolves in one (fixed) electronic state, i.e. the ground state or an excited state of the system, whereas in *non-adiabatic* molecular dynamics electronic transitions are taken into account.

Various approaches for solving the time-dependent Schrödinger equation (2.1) with different approximations have been developed so far. Among these full quantum mechanical methods is the multi-configuration time-dependent Hartree approach (MCTDH) [63], where nuclear wave packets are propagated on one or several coupled potential energy surfaces. These surfaces, however, have to be parameterized in some way for computational efficiency. In ab-initio multiple spawning (AIMS) [64], nuclear wave functions for each electronic state are represented by Gaussian basis functions which travel along classical trajectories. This allows "on-the-fly" propagation, as this method only requires local information about the underlying energy surfaces, usually calculated with high-level quantum chemistry methods.

Alternatively, multi-component density functional theory [52] builds upon a density functional theory for both electrons and nuclei. Finding an adequate exchange-correlation correlation functional, however, represents a severe difficulty of this approach.

Due to the prohibitive computational effort for systems with a large number of atoms and/or potential energy surfaces, mixed quantum-classical methods have been developed, where the "light" electrons are treated quantum-mechanically, whereas the nuclei are treated classically. This relates to a partial classical limit, "$\hbar \to 0$", for the nuclear degrees of freedom replacing the nuclear wave packet by an ensemble of independent point particles,
i.e. classical trajectories $R_A(t)$, which can be written roughly as

$$|\Omega(R, t)|^2 \rightarrow \prod_{A=1}^{N_i} \delta(R_A - R_A(t)) . \quad (2.10)$$

Among the various related molecular dynamics methods, we give an overview over some of the most prominent "on-the-fly" trajectory-based approaches (see [62, 65]), where we consider the case without an external laser field for convenience (i.e. neglecting the electron-laser and nuclear-laser interactions in the previous equations).

**Born-Oppenheimer molecular dynamics**  Born-Oppenheimer molecular dynamics is based on the adiabatic and classical limit of (2.6), i.e. neglecting transitions to other potential energy surfaces by neglecting the coupling elements (2.7) and (2.8), also called Born-Oppenheimer approximation. The motion of the nuclei is determined by classical motion on one potential energy surface $E_I(R)$, which is given by the solution of the electronic structure problem (2.5), according to Newton’s equations of motion

$$M_A \ddot{R}_A = -\frac{\partial E_I}{\partial R_A} . \quad (2.11)$$

Hence, the electrons do not evolve dynamically, but are assumed to follow the nuclear motion instantaneously. These adiabatic dynamics, or the Born-Oppenheimer approximation, are valid in the case of large energy gaps and small nuclear velocities (characterized in terms of the so-called Massay parameter [65]). This approximation, however, breaks down in the vicinity of avoided crossings or conical intersections, and non-adiabatic treatments are needed.

**Ehrenfest molecular dynamics**  The simplest non-adiabatic approach is the *Ehrenfest* method [66], which starts from a single-configuration ansatz for the total wave function

$$\Psi(r, R, t) = \Omega(R, t)\Phi_I(r, t) \exp\left[i \int dt' E_e(t')\right] . \quad (2.12)$$

Note, that this differs from (2.4), as the electronic state is now explicitly time-dependent. After taking the classical limit, this leads to the equations of motion of Ehrenfest molecular dynamics

$$i\frac{\partial}{\partial t} \Phi(r, t) = H_e(r; R)\Phi(r, t) \quad (2.13)$$

$$M_A \ddot{R}_A = -\frac{\partial}{\partial R_A} \langle \Phi_I(t)|H_{el}(R)|\Phi_I(t) \rangle . \quad (2.14)$$

This method represents a mean-field description, as the effective potential energy surface for the nuclei is given by the average over the electronic subsystem in (2.14). In contrast to
2.1 Mixed quantum-classical molecular dynamics methods

Born-Oppenheimer molecular dynamics, the electrons evolve dynamically. Expanding the electronic wave function in Born-Oppenheimer states

$$\Phi(\mathbf{r}, t) = \sum_I c_I(t) \Phi_I(\mathbf{r}; \mathbf{R})$$

(2.15)

leads to

$$i\frac{\partial}{\partial t} c_I(t) = E_I(\mathbf{R}) c_I(t) - i \sum_J \sum_A \mathbf{R}_A \cdot \mathbf{D}^A_{IJ} c_J(t)$$

(2.16)

$$M_A \ddot{\mathbf{R}}_A = -\sum_I |c_I(t)|^2 \frac{\partial}{\partial \mathbf{R}_A} E_I(\mathbf{R}) - \sum_{IJ} c^*_I(t) c_J(t) \left[ E_I(\mathbf{R}) - E_J(\mathbf{R}) \right] \mathbf{D}^A_{IJ}$$

(2.17)

and one recognizes that electronic transitions are taken into account due to the presence of the non-adiabatic coupling vector $\mathbf{D}^A_{IJ}$ in (2.16) and (2.17). The drawback of this approach is that electron-nuclear correlations are missing due to the mean-field nature of the nuclear dynamics, i.e. the nuclear dynamics proceed purely classically on a time-dependent effective potential. The Ehrenfest method is known to fail in cases when potential energy surfaces exhibit a very different behavior, which cannot be captured by means of a mixed trajectory [65]. Unphysical admixtures of energetically inaccessible states may also be present in the average potential energy surface.

**Trajectory surface hopping molecular dynamics** An alternative non-adiabatic approach, called trajectory surface hopping method, combines excited state molecular dynamics with a stochastic scheme for non-adiabatic transitions. It builds upon the expansion (2.15) with the equations of motion

$$i\frac{\partial}{\partial t} c_I(t) = E_I(\mathbf{R}) c_I(t) - i \sum_J \sum_A \mathbf{R}_A \cdot \mathbf{D}^A_{IJ} c_J(t)$$

(2.18)

$$M_A \ddot{\mathbf{R}}_A = -\frac{\partial E_I}{\partial \mathbf{R}_A}$$

(2.19)

where the nuclei evolve on some potential energy surface $E_I(\mathbf{R})$ and quantum mechanical expansion coefficients $c_I(t)$ are used to define a surface switching scheme, allowing sudden jumps to other surfaces. One of the most popular trajectory surface hopping methods is Tully’s fewest switches algorithm [55], minimizing the number of transitions between different electronic states. Electron-nuclear correlations are approximately taken into account, i.e. quantum effects for the nuclear motion in terms of non-adiabatic transitions. The stochastic nature of this approach, however, demands an ensemble of trajectories for each initial state of the system in contrast to Ehrenfest molecular dynamics. In addition, it is worthwhile to mention that methods have been suggested, that combine Ehrenfest and surface hopping molecular dynamics [50, 67].
Besides the molecular dynamics techniques outlined so far, a large variety of alternative methods exists. To name but a few, path-integral molecular dynamics [68], semiclassical methods [69, 70], and Bohmian mechanics or quantum hydrodynamics [71, 72] have been developed as well, essentially designed to go beyond the classical description of the nuclei more rigorously, e.g. by including coherence and tunneling. Many of these are, however, merely applicable to model systems, and thus difficult to couple to "on-the-fly" electronic structure methods.

A crucial point in mixed quantum-classical molecular dynamics is the way in which the quantum mechanical part is treated. Ab initio wave function based quantum chemical methods (see e.g. [18]), including post Hartree-Fock approaches like CI, CASSCF, MCSCF, MRCI, are known to give high-accuracy potential energy surfaces as well as the couplings between them. The drawback, however, is their large computational effort. Semi-empirical quantum chemical approaches offer a cheap alternative, but are less general, as they rely on empirically approximated interactions and are thus applicable only to systems which differ not too much from the system which has been used to derive the empirical parameters. As an alternative for this, density functional theory (DFT) as well as its time-dependent counterpart (TDDFT) have become very popular over the last two decades [20]. According to its basic theorems, all observables of the system can be expressed as a functional of the electronic single-particle density [19, 24]. This point marks the key for the comparably low computational cost at reasonable accuracy.

In the following, we outline the mixed quantum-classical non-adiabatic quantum molecular dynamics methods used in this work, i.e. the conventional non-adiabatic quantum molecular dynamics (NA-QMD) [25, 27, 28, 30], which combines TDDFT (or TDHF) in basis expansion with Ehrenfest dynamics for the nuclei, as well as an extension to take electron-nuclear correlations into account in the spirit of surface hopping dynamics ("NA-QMD-H").
2.2 Non-adiabatic quantum molecular dynamics (NA-QMD)

The non-adiabatic quantum molecular dynamics method in its present form represents a coupled description of a quantum mechanical treatment of the electrons with time-dependent density functional theory (TDDFT) or Hartree-Fock (TDHF) in basis expansion with classical dynamics for the ions. The respective equations of motion are derived from a generalized mixed quantum-classical action principle. In this section, we review the basic steps (for details see [27, 33]), including its extensions to take ionization into account [28].

General approach

We consider a mixed quantum-classical polyatomic many-electron system, i.e. the $N_e$ electrons are described by a many-electron wave function $\Psi(r_1, \sigma_1, \ldots, r_{N_e}, \sigma_{N_e})$ and the $N_i$ ions (or nuclei) by classical trajectories $R(t) = \{R_1(t) \ldots R_{N_i}(t)\}$. Its total action

$$A = A_{\text{cl}} + A_{\text{qm}}$$

consists of a classical part

$$A_{\text{cl}} = \int_{t_0}^{t_f} \text{d}t \left[ \sum_{A=1}^{N_i} \frac{M_A}{2} \dot{R}_A^2 - U(R, t) \right]$$

and a quantum mechanical part

$$A_{\text{qm}} = \int_{t_0}^{t_f} \text{d}t \langle \Psi | \frac{\partial}{\partial t} - H | \Psi \rangle .$$

The classical action (2.21) contains the classical interaction potential

$$U(R, t) = \sum_{A<B}^{N_i} \frac{Z_A Z_B}{|R_A - R_B|} + \sum_{A=1}^{N_i} Z_A R_A \cdot E(t)$$

which describes the Coulomb repulsion of the ions (with masses $M_A$ and charges $Z_A$) as well as the interaction of the ions with a possible external laser electric field $E(t)$.

The quantum mechanical action (2.22) contains the many-electron Hamiltonian [cf. (2.2)]

$$H = T_e + V_{e,i} + V_{e,e} + V_{e,\text{las}}$$

as well as the many-electron wave function $\Psi$, which is represented by a Slater determinant in the framework of TDDFT or TDHF. The scalar product in (2.22) denotes integration
over the electronic coordinates and summation over the electronic spins. This allows us to rewrite (2.22) as

$$A_{qm} = \int_{t_0}^{t_1} dt \int d^3 r \sum_{\sigma = \uparrow, \downarrow} \sum_{j=1}^{N_e} \Psi^{j\sigma*}(r, t) \left[ i \frac{\partial}{\partial t} + \frac{\nabla^2}{2} \right] \Psi^{j\sigma}(r, t) - A_{pot} ,$$

(2.25)

where $\Psi^{j\sigma}(r, t)$ are the time-dependent single-particle Kohn-Sham (KS) or Hartree-Fock (HF) functions $j$ for spin $\sigma$ ($\sigma = \uparrow, \downarrow$). We stress that $r$ denotes the one-electron coordinate in this context, whereas $R$ represents the collective ionic coordinate. The potential term in (2.25) reads

$$A_{pot} = \int_{t_0}^{t_1} dt \int d^3 r \rho(r, t) \left[ V(r, R, t) + \frac{1}{2} \int d^3 r' \rho(r', t) \frac{1}{|r - r'|} \right] + A_{xc}[\rho^\uparrow, \rho^\downarrow]$$

(2.26)

and is a functional of the electronic (single-particle) spin densities $\rho^\sigma$ given by

$$\rho^\sigma(r, t) = \sum_{j=1}^{N_e} \Psi^{j\sigma*}(r, t) \Psi^{j\sigma}(r, t) .$$

(2.27)

Correspondingly, the total electronic (single-particle) density is just given by the sum of the two spin contributions

$$\rho(r, t) = \sum_{\sigma = \uparrow, \downarrow} \rho^\sigma(r, t) .$$

(2.28)

The external potential $V(r, R, t)$ in (2.26) includes the electron-nuclear attraction and the electron-laser interaction potential (in dipole approximation with length gauge)

$$V(r, R, t) = - \sum_{A=1}^{N_i} \frac{Z_A}{|R_A - r|} - r \cdot E(t)$$

(2.29)

and $A_{xc}$ is the exchange correlation term which – in the spirit of DFT and HF – can be assumed to be a functional of the single-particle spin density.

The equations of motion for the time-dependent Kohn-Sham or Hartree-Fock functions $\Psi^{j\sigma}(r, t)$ and the classical trajectories $R_A(t)$ follow from the variational principle applied to the total action (2.20). By variation with respect to the time-dependent Kohn-Sham functions $\Psi^{j\sigma}(r, t)$ one derives the time-dependent Kohn-Sham equations

$$i \frac{\partial}{\partial t} \Psi^{j\sigma}(r, t) = \left[ -\frac{\nabla^2}{2} + V_s^{\sigma}(r, R, t) \right] \Psi^{j\sigma}(r, t)$$

(2.30)

with the effective single-particle potential

$$V_s^{\sigma}(r, R, t) = V(r, R, t) + \int d^3 r' \rho(r', t) \frac{1}{|r - r'|} + \frac{\delta A_{xc}[\rho^\uparrow, \rho^\downarrow]}{\delta \rho^\sigma(r, t)} .$$

(2.31)
Note, that the effective potential (2.31) is a functional of the density (2.28), where the exchange-correlation part is unknown in general, and thus has to be approximated in practical calculations. The present implementation dymol [39] uses the adiabatic local spin-density approximation (ALSDA) for the exchange-correlation term or the exact non-local Hartree-Fock exchange (for details see [73]). Thus, the equations (2.30) represent either the time-dependent Kohn-Sham or Hartree-Fock equations and the operator on the right-hand side of (2.30) is the Kohn-Sham or Hartree-Fock Hamiltonian

\[ H^\sigma = -\frac{\nabla^2}{2} + V^\sigma_s(r, R, t) . \] (2.32)

The classical equations of motion result from variation with respect to the classical trajectories \( R_A(t) \) as

\[ M_A \ddot{R}_A = -\frac{\partial U(R, t)}{\partial R_A} + \sum_{\sigma=\uparrow, \downarrow} \sum_{j=1}^{N_e^\sigma} \int d^3r \Psi_j^{\sigma*}(r, t) \frac{\partial V(r, R, t)}{\partial R_A} \Psi_j^{\sigma}(r, t) . \] (2.33)

In principle, the coupled EOM (2.30) and (2.33) have to be solved simultaneously with appropriate initial conditions. However, the direct solution of (2.30) and (2.33) on a numerical grid would restrict the range of applications of the theory drastically, e.g. it would be impossible to consider molecular collisions, laser-induced ionization or fragmentation, owing to the unrealizable numerical effort. Therefore, the core part of the NA-QMD method is a local basis expansion of the single-particle orbitals, as outlined in the next section.

**Local basis expansion**

The NA-QMD method is built upon a basis expansion in order to simplify the coupled equations of motion (2.30) and (2.33). The Kohn-Sham functions are expanded into a set of local, i.e. ion-centered, basis functions \( \phi_\alpha \)

\[ \Psi_j^{\sigma}(r, t) = \sum_\alpha a_j^{\sigma*}(t) \phi_\alpha(r - R_A) . \] (2.34)

The time-dependent electronic density (2.28) in the local basis reads

\[ \rho(r, t) = \sum_{\sigma=\uparrow, \downarrow} \sum_{j=1}^{N_e^\sigma} a_j^{\sigma*}(t) a_j^{\sigma}(t) \phi_\alpha^*(r - R_A) \phi_\beta(r - R_A) . \] (2.35)

It is convenient to define a variety of matrix elements corresponding to this basis expansion:

- overlap matrix

\[ S_{\alpha\beta} = \langle \phi_\alpha | \phi_\beta \rangle \] (2.36)
- (Kohn-Sham) Hamilton matrix

\[ H_{\alpha\beta}^\sigma = \langle \phi_\alpha | H^\sigma | \phi_\beta \rangle \]  

(2.37)

- non-adiabatic coupling matrix

\[ B_{\alpha\beta} = \langle \phi_\alpha | \frac{d}{dt} \phi_\beta \rangle \]  

(2.38)

- as well as the vector matrices

\[ B_A^{\alpha\beta} = \langle \phi_\alpha | \frac{\partial}{\partial R} \phi_\beta \rangle \]  

(2.39)

\[ B_A^{\alpha\beta+} = \langle \frac{\partial}{\partial R} \phi_\alpha | \phi_\beta \rangle \]  

(2.40)

\[ C_A^{\alpha\beta} = \langle \frac{d}{dt} \phi_\alpha | \frac{\partial}{\partial R} \phi_\beta \rangle \]  

(2.41)

\[ C_A^{\alpha\beta+} = \langle \frac{\partial}{\partial R} \phi_\alpha | \frac{d}{dt} \phi_\beta \rangle \]  

(2.42)

- and the combined force matrix

\[
K_A^{\alpha\beta} = \sum_{\gamma\delta} \left( B_A^{\alpha\beta+} S_{\gamma\delta}^{-1} H_{\beta\delta}^\sigma + H_{\alpha\gamma}^\sigma S_{\gamma\delta}^{-1} B_{\delta\beta}^A \right) \\
+ i \left[ C_A^{\alpha\beta+} - C_A^{\alpha\beta} + \sum_{\gamma\delta} \left( B_A^{\alpha\gamma} S_{\gamma\delta}^{-1} B_{\delta\beta}^A - B_A^{\alpha\gamma} S_{\gamma\delta}^{-1} B_{\delta\beta}^A \right) \right].
\]  

(2.43)

The first term in (2.43) contains the non-adiabatic derivative couplings \( B_A^{\alpha\beta} \), whereas the second term gives rise to the force corrections due to the finiteness of the basis set (see below). Due to the dependence of the KS-Hamiltonian (2.32) on the electronic density (2.35), the Hamilton matrix (2.37) depends implicitly on the time-dependent expansion coefficients \( a_{\alpha}^{\sigma}(t) \).

**Equations of motion in basis expansion**

With the basis expansion (2.34) and the corresponding matrix elements defined above the time-dependent Kohn-Sham or Hartree-Fock equations (2.30) follow from variation of the total action with respect to the time-dependent expansion coefficients as [27]

\[
\dot{a}_\alpha^{\sigma}(t) = - \sum_{\beta\gamma} S_{\alpha\beta}^{-1} \left( i H_{\beta\gamma}^\sigma + B_{\beta\gamma} \right) a_\gamma^{\sigma}(t)
\]  

(2.44)

and, analogously, the classical equations of motion (2.33) are derived by variation of the total action with respect to the classical trajectories as

\[
M_A \dot{R}_A = - \frac{\partial E(t)}{\partial R_A} + \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_{\sigma}} a_{\alpha}^{j\sigma+}(t) K_A^{\alpha\beta} a_{\beta}^{j\sigma}(t),
\]  

(2.45)
where the effective time-dependent potential energy surface $E(t)$ is defined below in (2.47). This set of equations has to be solved self-consistently, as the matrix elements in (2.44) depend on the classical coordinates and the force in (2.45) on the nuclei depends on the quantum mechanical expansion coefficients. We note that the matrix element $K_{\sigma\alpha\beta}^A$ [see (2.43)] contains the non-adiabatic couplings and a velocity-dependent correction term that appears in the forces due to the finiteness of the local basis set. A transparent interpretation of these complicated force corrections has been given in [27].

As can be seen from the classical equations of motion (2.45), the NA-QMD method represents a mean-field or Ehrenfest approach, as the force is given by an average over the quantum mechanical subsystem. Nuclear dynamics proceeds fully classically on one effective explicitly time-dependent potential energy surface and, thus, electron-nuclear correlations are not taken into account by this approach.

**Energy balance**

The total energy of the mixed quantum-classical system is

$$E_{\text{tot}}(t) = \sum_{A=1}^{N_e} \frac{M_A}{2} \dot{\mathbf{R}}_A^2 + E(t).$$

The second term $E(t)$ in (2.46) defines the effective time-dependent potential energy surface for the nuclear dynamics and is given by

$$E(t) = E_{\text{kin}}(t) + E_{\text{ext}}(t) + E_Q(t) + E_{\text{xc}}[\rho^\uparrow, \rho^\downarrow](t) + U(\mathbf{R}, t)$$

(2.47)

where the individual terms given in Kohn-Sham representation and basis expansion are

- the electronic kinetic energy
  $$E_{\text{kin}}(t) = \int d^3 r \sum_{\sigma=\uparrow, \downarrow} \sum_{j=1}^{N_e} \Psi^j\sigma^*(\mathbf{r}, t) \left[ -\frac{1}{2} \nabla^2 \mathbf{r} \right] \Psi^j\sigma(\mathbf{r}, t) = \sum_{\sigma=\uparrow, \downarrow} \sum_{j=1}^{N_e} \sum_{\alpha\beta} a_{\alpha}^{j\sigma\ast}(t) T_{\alpha\beta} a_{\beta}^{j\sigma}(t)$$

(2.48)

- the external interaction energy
  $$E_{\text{ext}}(t) = \int d^3 r \rho(\mathbf{r}, t) V(\mathbf{r}, \mathbf{R}, t) = \sum_{\sigma=\uparrow, \downarrow} \sum_{j=1}^{N_e} \sum_{\alpha\beta} a_{\alpha}^{j\sigma\ast}(t) V_{\alpha\beta} a_{\beta}^{j\sigma}(t)$$

(2.49)

- the Coulomb energy
  $$E_Q(t) = \frac{1}{2} \int d^3 r \int d^3 r' \frac{\rho(\mathbf{r}, t) \rho(\mathbf{r'}, t)}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{2} \sum_{\sigma'\sigma} \sum_{j,j'} \sum_{\alpha\beta\gamma\delta} a_{\alpha}^{j\sigma\ast}(t) a_{\gamma}^{j'\sigma'}(t) Q_{\alpha\beta\gamma\delta} a_{\beta}^{j\sigma}(t) a_{\delta}^{j'\sigma'}(t)$$

(2.50)
• and the exchange correlation energy \( E_{xc}[\rho^\uparrow, \rho^\downarrow](t) \). This contribution implicitly depends on the Kohn-Sham functions or the time-dependent expansion coefficients.

The last term in (2.47) is the nuclear potential \( U(R, t) \) given in (2.23).

The additional matrix elements are

\[
T_{\alpha\beta} = \langle \phi_\alpha \left| -\frac{1}{2} \nabla_r^2 \right| \phi_\beta \rangle \tag{2.51}
\]

\[
V_{\alpha\beta} = \langle \phi_\alpha | V(r, R, t) | \phi_\beta \rangle \tag{2.52}
\]

\[
Q_{\alpha\beta\gamma\delta} = \int d^3r \int d^3r' \frac{\phi^*_\alpha (r - R_{A_\alpha}) \phi_\beta (r - R_{A_\beta}) \phi^*_\gamma (r' - R_{A_\gamma}) \phi_\delta (r' - R_{A_\delta})}{|r - r'|} \tag{2.53}
\]

Starting from (2.46) one derives the energy balance as

\[
\frac{dE_{\text{tot}}}{dt} = -\dot{E}(t) \cdot \int d^3r \rho(r, t) r + \dot{E}(t) \cdot \sum_A N_A Z_A R_A \tag{2.54}
\]

and one recognizes that the total energy is conserved only in the field-free case as expected.

**Description of ionization**

The NA-QMD method so far allows, in principle, to account for ionization of many-electron systems, but two basic problems arise here. First, a realistic description of ionization requires the inclusion of highly excited or continuum states. In the framework of the local basis set defined in (2.34), this would mean a large number of basis functions to include. Second, a finite basis set only allows for a finite spread of electronic motion in space and, correspondingly, in order to avoid unphysical reflection of electronic density far away from the nuclei, an absorber potential has to be defined. The treatment of ionization within NA-QMD has been developed in [28, 31].

The first of these issues is dealt with by extending the local ion-centered basis set in (2.34) by a space-fixed grid of Gaussians centered at the grid points. This allows the use of a rather small ion-centered basis set for the description of the molecular properties, while the spread of the electronic density far away from the nuclei is enabled by the grid.

The second problem is solved by the inclusion of an imaginary absorber potential, in analogy to grid-based approaches, and it is not defined in space but in energy domain. This absorber potential for spin \( \sigma \) is given by

\[
V^\sigma_{\text{abs}} = \sum_a f(\epsilon^\sigma_a) \langle \chi^\sigma_a(t) \rangle \langle \chi^\sigma_a(t) \rangle \tag{2.55}
\]

The adiabatic states \( |\chi^\sigma_a(t)\rangle \) defined as eigenstates of the Kohn-Sham Hamiltonian (see 2.37)

\[
H^\sigma |\chi^\sigma_a(t)\rangle = \epsilon^\sigma_a(t) |\chi^\sigma_a(t)\rangle \tag{2.56}
\]
are explicitly time-dependent as well as the respective eigenenergies $\epsilon_a^\sigma(t)$, if electron-laser interaction (see 2.29) is included in $H^\sigma$ in (2.56). It is also convenient to define the absorber potential based on the field-free Kohn-Sham Hamiltonian, i.e. without inclusion of the electron-laser interaction term in (2.56). The adiabatic states and respective eigenenergies are then explicitly time-independent. Further details about adiabatic states are given in Section 2.3. In either case, after expansion of adiabatic states in the full basis set of ion-centered and grid basis functions

$$|\chi_a^\sigma(t)\rangle = \sum_{\alpha} U_{a\alpha}^\sigma(t) |\phi_\alpha(t)\rangle$$

one derives the matrix elements for the absorber potential

$$V_{\text{abs,}\alpha\beta}^\sigma = \sum_a f(\epsilon_a^\sigma) \sum_{\gamma\delta} S_{\alpha\gamma}^a U_{a\gamma}^\sigma U_{\delta\alpha}^{\sigma+} S_{\delta\beta}^{\sigma+} .$$

Using this, the time-dependent Kohn-Sham equations (2.44) are extended to

$$\dot{a}_{\alpha}^{j\sigma} = -\sum_{\beta\gamma} S_{\alpha\beta}^{\sigma-1} \left( iH_{\beta\gamma}^\sigma + V_{\text{abs,}\beta\gamma}^\sigma + B_{\beta\gamma} \right) a_{\gamma}^{j\sigma}. $$

The absorber function $f(E)$ in (2.55) and (2.58) determines the strength of the absorber at energy $E$ and is connected to the lifetimes of the adiabatic states. In the case of the absorber including the laser electron-interaction it is chosen as

$$f(E) = \begin{cases} \frac{1}{2\tau_{\min}} \sin^2 \left( \frac{\pi E}{2E_{\text{ref}}} \right) & E < 0 \\ \frac{1}{2\tau_{\min}} \sin^2 \left( \frac{\pi}{2} \right) & 0 < E < E_{\text{ref}} \\ \frac{1}{2\tau_{\min}} & E_{\text{ref}} < E < E_{\max} \\ \infty & E_{\max} < E \end{cases}$$

whereas for the field-free absorber it is set as

$$f(E) = \begin{cases} \frac{1}{2\tau_{\min}} \left( \frac{E}{E_{\text{ref}}} \right)^\beta & E < 0 \\ \frac{1}{2\tau_{\min}} \left( \frac{E_{\text{ref}}}{E} \right)^\beta & 0 < E < E_{\max} \\ \infty & E_{\max} < E \end{cases}$$

Consequently, the absorber acts only on adiabatic states with energy $\epsilon_a^\sigma > 0$, i.e. ionized or continuum states. After expansion of the time-dependent Kohn-Sham functions in the adiabatic states

$$|\Psi_j^\sigma(t)\rangle = \sum_a a_{a}^{j\sigma}(t) |\chi_a^\sigma(t)\rangle$$

it follows that the norm $N_j^\sigma(t) = \langle \Psi_j^\sigma(t) | \Psi_j^\sigma(t) \rangle$ decreases in time if these continuum states are populated

$$\frac{d}{dt} N_j^\sigma(t) = -2 \sum_a f(\epsilon_a^\sigma) |a_{a}^{j\sigma}(t)|^2.$$
2.3 Non-adiabatic quantum molecular dynamics with trajectory surface hopping (NA-QMD-H)

In this section, we go beyond the mean-field version of NA-QMD presented in Section 2.2, and extend the theory in order to take electron-nuclear correlations approximately into account by means of a trajectory surface hopping scheme [59]. The basic idea of Tully’s surface hopping approach consists in approximating the nuclear wave packet dynamics by an ensemble of classical trajectories moving on randomly chosen and suddenly changing potential energy surfaces. The transition (hopping) probabilities between these surfaces are determined by the non-adiabatic couplings between the corresponding states. In doing so, the same initial state leads to an ensemble of different trajectories representing a classically sampled wave packet disregarding, however, all interference effects. The general approach to realize Tully’s concept within TD-DFT coupled to MD has been presented and applied first in [26], where the earlier (not ab-initio) version of the NA-QMD formalism [25] has been combined with the surface hopping approach. Here, we present in detail the novel "hopping extended" formalism of the ab-initio version of the NA-QMD [27] which, also in extension to [26], allows to take into account explicitly a possible external laser field. The corresponding techniques have been added to the present NA-QMD implementation dynmol [39].

Adiabatic basis expansion

The first step is to represent the time-dependent Kohn-Sham functions in an alternative basis (see also Figure 2.1) set by expanding them into adiabatic single-particle states $\chi^\sigma_a(r; R)$ as

$$\Psi^{j\sigma}(r, t) = \sum_a a^j_a(t) \chi^\sigma_a(r; R)$$

which are solutions of the generalized (time-independent) ground state eigenvalue problem

$$\left[ -\frac{\nabla^2}{2} + V_{gs,s}^\sigma(r; R) \right] \chi^\sigma_a(r; R) = \epsilon^\sigma_a(R) \chi^\sigma_a(r; R) .$$

The effective single-particle potential in the ground state is given by

$$V_{gs,s}^\sigma(r, R) = V(r, R) + \int d^3r' \rho_{gs}(r') \frac{\partial A_{xc}[\rho_{gs}, \rho_{gs}^{\uparrow \downarrow}]}{\delta \rho_{gs}^\sigma(r)}$$

which is a functional of the ground state electronic density

$$\rho_{gs}(r) = \sum_{\sigma = \uparrow \downarrow} \sum_a N^\sigma_a \chi^\sigma_a(r; R) \chi^\sigma_a(r; R)$$
and defines the ground state Kohn-Sham Hamiltonian

$$H_{gs}^\sigma = \frac{-\nabla^2}{2} + V_{gs,s}^\sigma(\mathbf{r}, \mathbf{R}).$$  \hfill (2.68)

The adiabatic single-particle states themselves are expanded in the same local basis set (2.34) as in NA-QMD

$$\chi_a^\sigma(\mathbf{r}; \mathbf{R}) = \sum_\alpha U_{a\alpha}^\sigma(\mathbf{R})\phi_\alpha(\mathbf{r} - \mathbf{R}_A),$$  \hfill (2.69)

and the eigenvalue problem (2.65) then transforms to the local basis set representation

$$\sum_\beta \left[ H_{gs,a\beta}(\mathbf{R}) - \epsilon_a^\sigma(\mathbf{R})S_{\alpha\beta}(\mathbf{R}) \right] U_{a\beta}^\sigma(\mathbf{R}) = 0$$  \hfill (2.70)

with $H_{gs,a\beta}^\sigma(\mathbf{R}) = \langle \phi_\alpha | H_{gs}^\sigma | \phi_\beta \rangle$.

Note, that in eqs. (2.69), (2.70) and consistently in all following formulas, the Greek indices $\alpha, \beta$ belong to the local atomic basis set $\{\phi_\alpha\}$, whereas the Latin index $a$ belongs to the adiabatic molecular basis $\{\chi_a^\sigma\}$. For a compact overview, we have summarized in Figure 2.1 the relevant notations of and transformations between both basis sets, including those of the time-dependent case.

The above eigenvalue problems (2.65) respectively (2.70) have to be solved iteratively, as the Hamiltonian itself depends on the ground state (2.67) density resp. the expansion coefficients $U_{a\beta}^\sigma(\mathbf{R})$. Note, that this Hamiltonian differs from the one used in the time-dependent Kohn-Sham equations (2.30) and (2.44). Here we calculate the field-free ground state at a fixed classical configuration $\mathbf{R}$ and, thus, the energies $\epsilon_a^\sigma(\mathbf{R})$ represent (field-free) single-particle energies in the (ground state) Kohn-Sham framework for the respective spin. These are essentially the same adiabatic states that have been used to define the field-free absorber potential in NA-QMD in Section 2.3.

As the key ingredient for the trajectory surface hopping formalism, we treat the two spins ($\sigma = \uparrow \downarrow$) separately. The above expansion of Kohn-Sham functions into adiabatic single-particle states can then be generalized to the expansion of the underlying many-particle Slater determinant for the respective spin

$$\Psi^\sigma(\mathbf{r}_1, \ldots, \mathbf{r}_{N_e}, t) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \Psi^\sigma_1(\mathbf{r}_1, t) & \cdots & \Psi^\sigma_1(\mathbf{r}_{N_e}, t) \\ \vdots & \ddots & \vdots \\ \Psi^\sigma_{N_e}(\mathbf{r}_1, t) & \cdots & \Psi^\sigma_{N_e}(\mathbf{r}_{N_e}, t) \end{vmatrix}$$  \hfill (2.71)

into adiabatic Slater determinants

$$\Xi_{a_1^\sigma, \ldots, a_{N_e^\sigma}}^\sigma(\mathbf{r}_1, \ldots, \mathbf{r}_{N_e}; \mathbf{R}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \chi_{a_1^\sigma}(\mathbf{r}_1; \mathbf{R}) & \cdots & \chi_{a_1^\sigma}(\mathbf{r}_{N_e}; \mathbf{R}) \\ \vdots & \ddots & \vdots \\ \chi_{a_{N_e}^\sigma}(\mathbf{r}_1; \mathbf{R}) & \cdots & \chi_{a_{N_e}^\sigma}(\mathbf{r}_{N_e}; \mathbf{R}) \end{vmatrix}$$  \hfill (2.72)
The time-dependent many-particle expansion coefficients \( C_{\sigma^1...\sigma^N_{\sigma_e}}(t) \) are determinants of the time-dependent expansion coefficients in (2.64)

\[
C_{\alpha_1^\sigma...\alpha_{N_{\sigma_e}}^\sigma}(t) = \begin{vmatrix}
\alpha_1^{\sigma_1}(t) & \cdots & \alpha_{N_{\sigma_e}}^{\sigma_1}(t) \\
\vdots & \ddots & \vdots \\
\alpha_1^{\sigma_{N_{\sigma_e}}}(t) & \cdots & \alpha_{N_{\sigma_e}}^{\sigma_{N_{\sigma_e}}}(t)
\end{vmatrix}.
\]

(2.74)

An adiabatic many-particle state is determined by the occupied single-particle states, i.e. the set of indices \( \{\alpha_1^{\sigma_1}...\alpha_{N_{\sigma_e}}^{\sigma_{N_{\sigma_e}}}\} \) for each spin or, equivalently, both adiabatic Slater determinants \( \Xi_{\alpha_1^\sigma...\alpha_{N_{\sigma_e}}^\sigma}^\uparrow \) and \( \Xi_{\alpha_1^\sigma...\alpha_{N_{\sigma_e}}^\sigma}^\downarrow \). It remains to specify the adiabatic energy corresponding to an adiabatic many-particle state. For this, we need the transformation

\[
c_{\alpha^\sigma}(R) = \sum_a U_{a\alpha}^{\sigma}(R)c_a^{j\sigma}
\]

(2.75)

which connects adiabatic single-particle occupations with the corresponding time-independent expansion coefficients \( c_{\alpha^\sigma}(R) \) in the local basis set in (2.34). The occupied single-particle

**Figure 2.1:** Overview about notations, transformations and representations of single-particle functions belonging to the atomic basis \( \{\phi_\alpha(r - R_{\alpha_{\sigma}})\} \) (left) and to the molecular basis \( \{\chi_\alpha^\sigma(r; R)\} \) (right).

Throughout the paper, the Greek indices \( \alpha, \beta, \gamma, \delta \) correspond to the atomic basis, whereas the Latin indices \( a, b \) belong to the molecular basis.

First row: Transformations between both basis functions.
Second row: Expansions of the time-dependent KS functions in both basis sets.
Third row: Transformations between the time-dependent expansion coefficients.
2.3 Non-adiabatic quantum molecular dynamics with trajectory surface hopping

states in \( \Xi_{a_1^{\sigma_1} \ldots a_N^{\sigma_N}} \) are characterized by

\[ c^\sigma_a = \delta_{a, a^\sigma_j} , \quad (2.76) \]

i.e. they contribute if the adiabatic single-particle energy level \( a \) is included in the adiabatic Slater determinant (i.e. \( a = a^\sigma_j \)). In contrast to (2.35) the corresponding electronic density is now explicitly time-independent and reads

\[ \rho(r) = \rho^\uparrow(r) + \rho^\downarrow(r) = \sum_{\sigma = \uparrow, \downarrow} \sum_{j=1}^{N^\sigma} c^{j\sigma*}_a(R) c^{j\sigma}_\beta(R) \phi^\sigma_\alpha(r - R_{A_a}) \phi^\sigma_\beta(r - R_{A_\beta}) . \quad (2.77) \]

We note that the electronic ground state density (2.67) is a special case of (2.77) with \( c^{j\sigma}_a = \delta_{j, a^\sigma} \) in (2.75), where \( j = 1 \ldots N^\sigma \), i.e. only the lowest adiabatic single-particle energy levels are occupied. With this, the adiabatic state energy is given by

\[ E_{a_1 \ldots a_N}(R) = \sum_{\sigma = \uparrow, \downarrow} \sum_{j=1}^{N^\sigma} \sum_{a \alpha \beta} c^{j\sigma*}_a(R) \left[ T_{\alpha\beta} + \tilde{V}_{\alpha\beta} + \frac{1}{2} \sum_{\sigma' = \uparrow, \downarrow} \sum_{j'=1}^{N^{\sigma'}} \sum_{\gamma \delta} Q_{\alpha\beta\gamma\delta} c^{j'\sigma'*}_{\gamma}(R) c^{j'\sigma'}_{\delta}(R) \right] c^{j\sigma}_\beta(R) \\
+ \tilde{E}_{xc}[\rho^\uparrow, \rho^\downarrow] + U(R) \quad (2.78) \]

where the quantity \( \tilde{V}_{\alpha\beta} = \langle \phi^\alpha | V(r, R) | \phi^\beta \rangle \) is the matrix element (2.52) without the laser field and the exchange correlation energy \( \tilde{E}_{xc}[\rho^\uparrow, \rho^\downarrow] \) belongs to the field-free case as well, i.e. depends implicitly on the \( c^{j\sigma}_a(R) \) due to the functional dependence on the electronic density (2.77). In (2.78), \( U(R) \) is the field-free classical interaction potential, i.e. the nuclear-nuclear repulsion (eq. (2.23) without the laser field).

**Equations of motion**

The equations of motion are now set as follows: the electrons are still propagated according to the time-dependent Kohn-Sham equations (2.44), while the ions are propagated classically on the potential energy surface \( E_{a_1 \ldots a_N}(R) \) [see (2.78)] corresponding to the presently occupied adiabatic many-particle state. We thus have

\[ \dot{a}^{ij\sigma}_\alpha(t) = - \sum_{\beta \gamma} S^{-1}_{\alpha\beta} \left( iH^{\sigma}_{\beta\gamma} + B_{\beta\gamma} \right) a^{ij\sigma}_\gamma(t) \quad (2.79) \]

\[ M_A \ddot{R}_A = - \frac{\partial E_{a_1 \ldots a_N}(R)}{\partial R_A} . \quad (2.80) \]

The electronic equations of motion (2.79) are obviously formally the same as in the NA-QMD case (2.44). Their solution, however, is different from that of (2.44), because the nuclear trajectories \( R(t) \) are now given by (2.80) instead of (2.45).

The nuclear equations of motion (2.80) are formally different from that given in [25] for the adiabatic quantum molecular dynamics (QMD) case (eq. (A12) in ref. [25]), where they
are explicitly expressed in local basis set representation. However, one can easily show that 
eq (2.79) over the classical time step \( \Delta t \). The transition probability 
\( g(a) \) via the transformation (see also Figure 2.1) 
\( E \) at time \( t \). For this, the time-dependent coefficients 
the Tully hopping 
procedure [55] for both spins. For this, the time-dependent coefficients 
(2.74) via the transformation (see also Figure 2.1)

\[
a^\sigma_{a}(t) = \sum_{\alpha\beta} U_{\alpha\sigma}^{\sigma}(R) S_{\alpha\beta} a^\sigma_{\beta}(t). 
\]

(2.81)

The transition probability \( g_\sigma(a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}) \) from a given state \( \Xi_\sigma(a^\sigma_{1}...a^\sigma_{N_e}) \), i.e. the actual surface \( E_{a1...aNe}(R) \) in the nuclear equations of motion (2.80), at time \( t \) to an arbitrary state \( \Xi_\sigma(b^\sigma_{1}...b^\sigma_{N_g}) \) at time \( t + \Delta t \) is defined as

\[
g_\sigma(a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}) = \frac{B^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}}}{A^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}}} \Delta t
\]

(2.82)

with

\[
A^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}} = C^\sigma_{a^\sigma_{1}...a^\sigma_{N_e}} C^\sigma_{b^\sigma_{1}...b^\sigma_{N_g}}
\]

and

\[
B^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}} = -2Re \left( A^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}} D^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}} + 2Im \left( A^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}} L^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}} \right) \right).
\]

(2.84)

The many-electron non-adiabatic derivative coupling \( D^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}} \) and laser-induced diabatic coupling \( L^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}} \) given by

\[
D^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}} = \left\langle \Xi_{a^\sigma_{1}...a^\sigma_{N_e}} | \frac{d}{dt} \Xi_{b^\sigma_{1}...b^\sigma_{N_g}} \right\rangle = \hat{R} \cdot \left\langle \Xi_{a^\sigma_{1}...a^\sigma_{N_e}} | \frac{\partial}{\partial R} \Xi_{b^\sigma_{1}...b^\sigma_{N_g}} \right\rangle
\]

(2.85)

\[
L^\sigma_{a^\sigma_{1}...a^\sigma_{N_e} b^\sigma_{1}...b^\sigma_{N_g}} = \left\langle \Xi_{a^\sigma_{1}...a^\sigma_{N_e}} | \mathbf{r} \cdot \mathbf{E}(t) \Xi_{b^\sigma_{1}...b^\sigma_{N_g}} \right\rangle = \mathbf{E}(t) \cdot \left\langle \Xi_{a^\sigma_{1}...a^\sigma_{N_e}} | \mathbf{r} \Xi_{b^\sigma_{1}...b^\sigma_{N_g}} \right\rangle
\]

(2.86)

are nonzero only in the case of a one-particle transition, i.e. when the states \( \Xi_{a^\sigma_{1}...a^\sigma_{N_e}} \) and \( \Xi_{b^\sigma_{1}...b^\sigma_{N_g}} \) differ in exactly one orbital. The hopping criterion is then formulated as a

**Trajectory surface hopping**

The switching between different adiabatic states is accomplished via the Tully hopping procedure [55] for both spins. For this, the time-dependent coefficients \( a^\sigma_{a}(t) \) are propagated according to (2.79) over the classical time step \( \Delta t \) and lead to the many-electron coefficients (2.74) via the transformation (see also Figure 2.1)
2.3 Non-adiabatic quantum molecular dynamics with trajectory surface hopping

comparison with a uniform random number ζ (0 ≤ ζ ≤ 1): A hop for spin σ from state \( \Xi_{a_1}^{\sigma}...a_N^{\sigma} \) to state \( \Xi_{b_1}^{\sigma}...b_N^{\sigma} \) occurs, if

\[
\sum'_{b_1^{\sigma} < ... < b_N^{\sigma}} g_{a_1^{\sigma}...a_N^{\sigma} b_1^{\sigma}...b_N^{\sigma}} < \zeta < \sum_{b_1^{\sigma} < ... < b_N^{\sigma}} g_{a_1^{\sigma}...a_N^{\sigma} b_1^{\sigma}...b_N^{\sigma}}, \tag{2.87}
\]

where the primed sum denotes summation over all energy levels below (excluding) the total adiabatic many-particle energy \( E_{b_1^{\sigma}...b_N^{\sigma}} \) and the full sum denotes summation over all energy levels up to (including) the total adiabatic many-particle energy \( E_{b_1^{\sigma}...b_N^{\sigma}} \) accessible via one-particle excitations from the initial state \( \Xi_{a_1^{\sigma}...a_N^{\sigma}} \). In consequence, many-particle transitions are realized as successive one-particle transitions (for an illustration see Figure 2.2).

When a hop for spin σ occurs in the absence of the laser field, the kinetic energy has to be adapted in order to guarantee total energy conservation, otherwise – in the presence of the laser field – not. In the simplest way, this can be done by rescaling all classical velocity components by a common factor connected to the ratio of the kinetic energy after and before the hop. A more common, but computationally much more demanding way is to rescale the classical velocity components along the non-adiabatic coupling vector in (2.85)

\[
D_{a_1^{\sigma}...a_N^{\sigma} b_1^{\sigma}...b_N^{\sigma}} = \left\langle \Xi_{a_1^{\sigma}...a_N^{\sigma}} \left| \frac{\partial}{\partial \mathbf{R}} \Xi_{b_1^{\sigma}...b_N^{\sigma}} \right. \right\rangle. \tag{2.88}
\]

If the energy is not sufficient in order to perform a transition, the hop is rejected.

We term this approach, which consists of the electronic equations of motion (2.79), the nuclear equations of motion (2.80), the hopping probabilities (2.87) as well as the chosen velocity rescaling method, NA-QMD-H ("H" denotes hopping in order to distinguish from the Ehrenfest-type NA-QMD). In consequence, this method represents a trajectory surface hopping approach for atomic many-body systems. The dynamics proceeds not purely classically in contrast to the conventional NA-QMD method due to non-classical, probabilistic transitions to other potential energy surfaces.

**Remarks and comparison to other approaches**

In this section a critical discussion of the approximations, assumptions, advantages and restrictions of the presented method is given, also in comparison with existing ab-initio MD procedures based on TDDFT combined with Tully hopping [56–58].

(i) The electronic excitation energies (2.78) and, thus, the forces on the nuclei (2.80) are based on bare KS excitations, as used also in [57]. These excitation energies have been shown to be well-defined approximations [74] to the real excitation energies, calculated e.g. within linear response TDDFT [58]. A detailed discussion of this point has been given also in [75].

In addition, the KS excitations allow the inclusion of an in principle unlimited number
Figure 2.2: Schematic representation of the surface hopping procedure in the adiabatic many-electron picture. Initially, at time $t_1$, the system is in its ground state. At some later time $t_2$, a hop occurs, leading to a singly excited state. Even later, another hop occurs, and the system ends up in a doubly excited state. In this way, many-particle transitions are realized as successive one-particle transitions. Defining the single-particle occupation configuration for each spin as $p^\sigma_a = \sum_{j=1}^{N_e} c_{ja}^\sigma$ [cf. (2.76)] we get a simple representation of the adiabatic many-electron states: $\{p^\uparrow\}$ = (111000) and $\{p^\downarrow\}$ = (111000) at $t_1$, $\{p^\uparrow\}$ = (101010) and $\{p^\downarrow\}$ = (111000) at $t_2$, $\{p^\uparrow\}$ = (101010) and $\{p^\downarrow\}$ = (011001) at $t_3$, etc.

of excited states overcoming the limitations of restricted open-shell KS excitations [56], capable to treat only the lowest lying states. As another advantage, multiply excited states, which are e.g. important in the photoisomerization of ethylene [33, 53], can be treated by KS excitations, whereas linear response TDDFT only allows to treat one-particle excitations.

From the numerical point of view, the calculation of the non-adiabatic (2.85) and diabatic couplings (2.86) is very efficient with KS excitations, as those between adiabatic Slater determinants are nonzero only in the case of one-particle transitions. Thus, the NA-QMD-H method should allow to treat rather large systems at relatively moderate computational cost.

We also note, that it is crucial to keep track of the adiabatic states between successive time steps. This will be done using a sign consistency procedure based on the maximal delayed overlap of the adiabatic states in analogy to [76].

(ii) As in all approaches [56–58], we take the electronic ground state of the system as reference for the adiabatic states (2.72) and the Tully hopping procedure (2.87), which minimizes the number of hops for a single trajectory ("fewest switches algorithm", [55]). However, this choice will limit the application of the theory to short laser pulses
which indeed may induce electronic excitations via (2.86), but, on the other side, must be short enough to do not affect the nuclear motion considerably. For longer pulses, the explicit inclusion of the laser field requires an improved treatment, e.g. the use of time-dependent Floquet states [77] instead of the adiabatic surfaces, used also in [78].

(iii) As a peculiarity of our method, we treat both spins separately, as usually done also in conventional HF or LSDA calculations. Nevertheless, the separate hopping procedure for both spins represents an approximation, as the action (2.25) is not separable with respect to the spin contributions. Note, however, that both spin systems are still coupled via the total many particle energies (2.78) which depend on both spins and build the foundation for the hopping criterion (2.87).

Needless to say, that an explicit treatment of a possible time-dependent magnetic field requires a coupled treatment of both spin contributions in the hopping algorithm.

(iv) Instead of a classical path approximation [57], we treat electronic and nuclear dynamics self-consistently coupled. This will allow to study, besides electronic relaxation processes and/or isomerization mechanisms, a large variety of further non-adiabatic phenomena on this level of approximation. This concerns, e.g., large amplitude vibrational motion [35], scattering between complex particles [36, 37], fragmentation in laser fields [42], etc.

The validity and accuracy of all these assumptions and approximations will depend on the system under study. Despite that, however, the NA-QMD-H method offers a simple and straightforward extension of the NA-QMD approach, which, in principle, allows to take into account quantum effects in the nuclear motion for systems with a large number of atoms and electrons.

2.4 Adiabatic quantum molecular dynamics (QMD)

By definition, adiabatic QMD describes classical nuclear motion on the Born-Oppenheimer ground state surface calculated by any ab-initio, quantum electronic structure method, i.e. time-independent DFT or HF in our case. The NA-QMD method includes electronic excitations, but still treats the nuclei classically moving on an effective, explicitly time-dependent potential ("Ehrenfest dynamics"). The NA-QMD-H approach, in addition, accounts approximately for quantum effects in the nuclear dynamics by Tully’s surface hopping procedure. Thus, all three molecular dynamics (MD) methods represent a kind of hierarchy of ab-initio MD approaches with increasing complexity and generality (see Fig. 2.3).

On the other side, both non-adiabatic approaches should automatically contain the adiabatic QMD limit, if electronic transitions are unlikely or unimportant. In [25] we have explicitly shown that the equation of motion of the QMD can be derived from that of the
NA-QMD method (2.45) if the time scales of electronic and nuclear dynamics are very different (right arrow in Fig. 2.3). Evidently, the NA-QMD-H formalism (2.79),(2.80),(2.87) reduces to the QMD limit, if all hopping probabilities (2.82) vanish (left arrow in Fig. 2.3).

The circumstances in which this is the case can be entirely recognized by considering the quantities entering the non-adiabatic and diabatic matrix elements (2.85),(2.86) which determine the hopping probabilities (2.82). This concerns the nuclear velocities $\dot{\mathbf{R}}$ in (2.85) and the electric field $\mathbf{E}$ in (2.86) (as external dynamical parameters for the electrons) as well as the non-adiabatic coupling vector in (2.85) and the dipole transition matrix element in (2.86) (as inherent electronic structure properties). Thus, electronic transitions can be suppressed by four reasons:

1. If the nuclear velocities $\dot{\mathbf{R}}$ in (2.85), and, thus, the kinetic energy of the nuclei, are too small, electronic excitations are forbidden by energy conservation as an inherent part of the hopping procedure.

2. Energetically allowed hops are strongly suppressed if the non-adiabatic coupling matrix elements (2.85) vanish, i.e. avoided crossings or conical intersections in the adiabatic potential energy surfaces (2.78) are lacking.

3. A laser field induces transitions only, if the field strength $\mathbf{E}$ (or intensity) is large enough to create finite hopping probabilities (2.82) via (2.86), because the field is described classically in the formalism.

4. Even strongest field strength $\mathbf{E}$ are not enough to create transitions as long as the dipole matrix elements in (2.86) vanish owing to symmetry reasons.

Thus, the NA-QMD-H formalism also provides a physical transparent picture of the complex non-adiabatic mechanisms.

2.5 Summary

In this chapter, we have outlined the theoretical basis of this work (for an overview see Figure 2.3). The conventional non-adiabatic quantum molecular dynamics (NA-QMD) method [25, 27, 28, 30] represents an *Ehrenfest* or *mean-field* approach to non-adiabatic dynamics of atomic many-body systems (in the presence of an external laser field), being able to describe ionization as well. Here, we have presented an alternative formulation within an adiabatic many-electron framework augmented with Tully’s fewest switches algorithm, which we term NA-QMD-H [59]. This approach takes quantum effects for the nuclear motion approximately into account, more precisely electron-nuclear correlations, as a *trajectory surface hopping* method.
We added a detailed and critical discussion of the basic assumptions and possible improvements or extensions of the NA-QMD-H method. Differences and similarities of the approach as compared to other state-of-the-art MD approaches are outlined as well. We presented a systematic hierarchy of ab-initio MD approaches with increasing complexity and generality and discussed under which circumstances any non-adiabatic MD merges into the adiabatic QMD limit.

Going from bottom to the top in Fig. 2.3, this hierarchy also shows that the present formalism of the NA-QMD-H method is the result of a continuous and systematic extension of the basic QMD.
3 NA-QMD: Complete dynamics of $\text{H}_2^+$ in strong laser fields

In this chapter, we present a complete study of the laser-induced dynamics of $\text{H}_2^+$, i.e. including all electronic and nuclear degrees of freedom as well as all fragmentation channels (dissociation and ionization) using the mixed quantum-classical NA-QMD method. After a short introduction into the field and a description of the technical details for the calculations in Section 3.1, we study the dissociation channel in detail in Section 3.2 [41]. The underlying multiphoton nature of dissociation is analyzed rigorously in a time-dependent Floquet picture. In the central part (Section 3.3), the ionization channel is in the center of interest and we examine the dynamical relevance of molecular rotation for ionization [42]. Finally, in Section 3.4 we introduce a rigorously simplified model for the dissociation and ionization of $\text{H}_2^+$, which allows the comparison with data obtained under realistic experimental conditions with a feasible computational effort [43].

3.1 Introduction

The interaction of small molecules with intense laser fields has been of growing interest over the last two decades triggered by the rapid progress in laser technology [79, 80]. As one reason, the availability of ultra-short strong light pulses provides the potential for controlling and manipulating physical and chemical processes. With the aid of sophisticated experimental techniques based on time-of-flight spectroscopy and fragment imaging, complete measurements of simple physical mechanisms have become possible [40, 81–84]. A detailed theoretical understanding of these, however, is the key to apply optimal control schemes efficiently. Despite intense theoretical research and the massive increase in computer power, no full-dimensional quantum mechanical approach has been devised which can describe the complete interaction of diatomic molecules with short intense laser pulses.

As nature’s simplest molecule, $\text{H}_2^+$ is of fundamental interest as a benchmark system [85]. Due to the prohibitive computational expense of a full-dimensional quantum mechanical description of dissociation ($\text{H}_2^+ \rightarrow \text{H} + \text{H}^+$) and ionization ($\text{H}_2^+ \rightarrow \text{H}^+ + \text{H}^+ + \text{e}^-$) even in this case, calculations were limited to certain degrees of freedom or reaction channels in the past. As one approximation, only a few electronic bound channels have been taken into account, which allows to study nuclear dynamics and consequently dissociation fully quan-
tum mechanically, neglecting the ionization channel completely [86–88]. Theoretical (and experimental) studies have uncovered a variety of phenomena that govern the photodissociation dynamics of H$_2^+$ in strong laser pulses such as bond softening (BS) and hardening (BH) [8,89,90], above threshold dissociation (ATD) [91] as well as centrifugal fragmentation (CF) [77]. The nuclear rotational degree of freedom with respect to the polarization direction of the laser field has turned out to be of fundamental importance for these mechanisms even for laser pulses much shorter than the free rotational period of H$_2^+$ ($\approx 556$ fs) [77,88].

As another approach, including dissociation and ionization in a full quantum mechanical description, nuclear rotation has been neglected by assuming the molecule to be aligned with the laser polarization direction [92,93]. On this basis, the crucial role of the vibrational degree of freedom in the ionization process of H$_2^+$ has been established. Prominent effects include the washout of charge resonance enhanced ionization (CREI) [94,95] at specific internuclear distances [84,96] as well as Lochfraß (internuclear separation dependent ionization) [97,98]. Much less is known about the influence of the nuclear rotational degree of freedom on the ionization mechanism. From a previous key experiment [40] it can be concluded that rotation and/or orientation are relevant for ionization. Resolving this issue requires a complete study of the strong field dynamics, i.e. calculations including all degrees of freedom (nuclear and electronic) as well as all fragmentation channels (dissociation and ionization).

In the course of this chapter, we present the first complete study of the strong field dynamics of H$_2^+$ on the basis of the mixed quantum-classical NA-QMD method [41,42]. We therefore focus on the fragmentation probabilities (dissociation and ionization) and the corresponding angular distributions of the fragments as function of the initial vibrational level $\nu$ of the molecule. In a first step (Section 3.2), we study the photodissociation of H$_2^+$ for laser parameters where ionization is negligible, and evaluate the accuracy of our method by comparison of the respective results to those of a full quantum mechanical approach for the nuclear dynamics [41]. The latter allows us to go beyond a purely qualitative understanding of the dissociation mechanisms within the conveniently utilized Floquet picture and, instead, follow the nuclear dynamics on each Floquet surface in real-time. This sheds new light on the alignment behavior of the molecule in dependence on the initial vibrational state by including the rotational degree of freedom in a Floquet-like propagation method. A one-dimensional analysis of multiphoton processes based on such a method has been performed in [99]. Acknowledging how useful the Floquet picture is to understand the dynamics qualitatively, we present a novel scheme to extract multi-photon branching ratios from the NA-QMD results. In a second and main step (Section 3.3), the results for ionization and dissociation are presented for a range of experimentally relevant laser parameters with the focus on the role of nuclear rotation in the ionization process [42]. In addition, we suggest a simple model for the strong field dynamics of H$_2^+$, which allows us to study ionization and dissociation at low computational cost and a reasonable level of accuracy (Section 3.4).
This allows the calculation of intensity- and (in principle) temperature-averaged quantities for the comparison with data obtained under realistic experimental conditions [43].

### 3.1.1 Preliminary considerations

The investigations in this chapter are motivated by previous experimental research and the laser conditions are chosen accordingly. The laser electric field is assumed to be linearly polarized along the z-axis (see Figure 3.1 for the definition of the coordinates)

\[
E(t) = e_z E_0 \sin^2 \left( \frac{\pi t}{T} \right) \cos(\omega t) = E_0(t) \cos(\omega t)
\]  

(3.1)

where \( E_0 \) is the amplitude, \( \omega \) the photon frequency, and \( T = 2T_{\text{FWHM}} \) the total pulse length. The laser wavelength used in this study is \( \lambda = 800 \text{ nm} \) corresponding to \( \hbar \omega \approx 1.57 \text{ eV} \) in (3.1). We study dissociation and ionization for experimentally relevant peak intensities\(^1\) \( I_0 = 2 \cdot 10^{14} \text{ W/cm}^2 \) and \( I_0/2 \) and pulse lengths (\( T = 25 \text{ fs}, 50 \text{ fs} \) and \( 100 \text{ fs} \)).

\[\text{Figure 3.1: Sketch of H}_2^+ \text{ in a laser field linearly polarized along the z-axis of the coordinate system: internuclear distance vector } R = R_2 - R_1 \text{ and nuclear rotational (alignment) angle } \theta \text{ with respect to the laser polarization axis.}\]

The physical observables of interest, i.e. the angular distributions of dissociated and ionized fragments as well as the corresponding total dissociation and ionization probabilities, are calculated via trajectory statistics within our mixed quantum-classical NA-QMD method. For this, we define the angular interval

\[ I_k = [k \Delta \theta, (k + 1) \Delta \theta] \]  

(3.2)

The angular distributions are the probability densities of the dissociated (D) or ionized (I) fragments. Thus, only those trajectories which are fragmented (denoted by the index \( j_F \)),

\(^1\)Note that intensity and electric field amplitude are connected by \( I = \frac{2 \pi c}{3} E^2 \). Correspondingly, in atomic units the amplitude is connected to the peak intensity (in \( \text{W/cm}^2 \)) by \( E = \sqrt{\frac{3.31 \text{ W/cm}^2}{I}} \) [100].
i.e. $R > R_{D}$ at final time $t_{f}$, are taken into account. This final time has to be chosen, in general, larger than the total pulse length in order to allow for post-pulse alignment of the molecule. The angular distributions (at rotational angle $\theta_{k} = (k + \frac{1}{2})\Delta \theta \in I_{k}$) then read

$$P_{D}(\theta_{k}) = C \sum_{j_{F}: \theta_{j_{F}}(t) \in I_{k}} \frac{\sin \theta_{j_{F}}(t) N_{j_{F}}(t_{f})}{\sin \theta_{k}}$$  \hspace{1cm} (3.3)

$$P_{I}(\theta_{k}) = C \sum_{j_{F}: \theta_{j_{F}}(t) \in I_{k}} \frac{\sin \theta_{j_{F}}(t_{0})(1 - N_{j_{F}}(t))}{\sin \theta_{k}}$$  \hspace{1cm} (3.4)

with

$$C = \frac{1}{\Delta \theta \sum_{l} \sin(\theta_{l}(t_{0}))}. \hspace{1cm} (3.5)$$

Here, $N_{j}(t)$ is the norm of the electronic wave function, which may decrease due to the presence of the absorber potential [cf. (2.63)] and, thus, is a measure for ionization. The factor $\sin \theta_{j}(t_{0})$ in (3.3) and (3.4) is a weight factor which appears due to the initial uniform angular sampling (see Section 3.1.2 for details). Accordingly, the total dissociation and ionization probabilities are given by

$$P_{D} = \tilde{C} \sum_{j_{F}} \sin \theta_{j_{F}}(t_{0}) N_{j_{F}}(t_{f}) = \sum_{k} P_{D}(\theta_{k}) \sin \theta_{k} \Delta \theta$$  \hspace{1cm} (3.6)

$$P_{I} = \tilde{C} \sum_{j_{F}} \sin \theta_{j_{F}}(t_{0})(1 - N_{j_{F}}(t)) = \sum_{k} P_{I}(\theta_{k}) \sin \theta_{k} \Delta \theta$$  \hspace{1cm} (3.7)

with

$$\tilde{C} = \frac{1}{\sum_{l} \sin(\theta_{l}(t_{0}))}. \hspace{1cm} (3.8)$$

### 3.1.2 Computational details

In order to describe ionization with NA-QMD (Sec. 2.2), we need to specify the details about the extended basis set and the absorber potential. We use a basis set consisting of 125 basis functions in expansion (2.34), where 33 Gaussian basis functions are centered at each nucleus (parameters are collected in Table 3.1) and 59 s-type Gaussians with width $\sigma = 5.156$ a.u., which are centered at $R_{A_{\alpha}} \equiv R_{kl}$ on a hexagonal grid. The latter is defined by

$$R_{kl} = d(k\mathbf{e}_{1} + l\mathbf{e}_{2}); \; k, l = -5, \ldots, 5; \; |k - l| \leq 4,$$  \hspace{1cm} (3.9)

where the distance is $d = 3.869$ a.u. and $\mathbf{e}_{1,2} = \pm \frac{\mathbf{e}_{y}}{2} \pm \frac{\sqrt{3}}{2} \mathbf{e}_{z}$.

The absorber potential is set as follows. For the field-free absorber (2.61) we use $\tau_{\text{min}} = 5.0$ a.u. and $\beta = 0.1$, whereas in the case of the absorber explicitly including the laser field
Table 3.1: Parameters of the nuclei-centered Gaussian basis set with the width given by $\sigma_k = \sigma_1 \cdot f^{k-1}$ ($k = 1, \ldots, N$). For the functional form of the basis functions see [28].

<table>
<thead>
<tr>
<th>f</th>
<th>$\sigma_1$ [a.u.]</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.7</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>1.7</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>1.7</td>
<td>3</td>
</tr>
</tbody>
</table>

(2.60) we use $\tau_{\text{min}} = 4.76$ a.u. The reference and the maximal energy are $E_{\text{ref}} = 0.3$ a.u. respectively $E_{\text{max}} = 2.0$ a.u.

The quality of the absorber potential is evaluated by comparison with grid-based results calculated using the OCTOPUS code [29] as benchmark which allows, in principle, convergence to the exact result. This is shown in Figure 3.2 for the fixed-nuclei ionization of $\text{H}_2^+$ (fixed internuclear distance $R$ and alignment angle $\theta$) in a laser field with peak intensity $I_0$ and pulse length $T = 50$ fs. Both absorber types agree quite well with the reference results for small internuclear distances ($R < 10$ a.u.): the field-free absorber seems to be more accurate in that $R$-region, whereas some fluctuations in the ionization probability occur for the absorber including the laser field. For higher internuclear distances at small alignment angles the latter fails completely, as the ionization probability approaches 1, whereas in the field-free type the ionization probabilities roughly converge to the atomic hydrogen limit ($R \rightarrow \infty$). Thus, in general, the absorber based on the field-following adiabatic states poses a problem when the nuclei reach high internuclear distances while the laser field is present and strong enough to induce ionization. This may definitely be the case for very long laser pulses. For the laser pulse durations used in this study, however, the absorber including the laser field has been checked to be sufficient. It is important to mention that the field-free absorber requires a higher numerical accuracy and is thus computationally more demanding. We therefore use the field-based absorber (2.60) with the parameters given above for our investigations.

In order to solve the coupled NA-QMD equations of motion including electronic and nuclear motion, i.e. (2.44) and (2.45), the initial internuclear distances and vibrational momenta are sampled according to a microcanonical distribution attributed to the vibrational level $\nu$. The alignment angle $\theta$ is sampled uniformly in the interval $[0^\circ, 90^\circ]$ and initial angular momentum is set to zero, i.e. the molecule is assumed to be initially rotationally cold. For each initial state, we use a total of 480 trajectories for the full-dimensional and 250 trajectories for the laser-aligned calculations. The time step for the classical motion is chosen as $\Delta t = 1$ a.u.

The threshold value for fragmentation, which is needed for the calculation of the angular distributions of fragments for ionization and dissociation as well as the corresponding total
Figure 3.2: Fixed-nuclei ionization probabilities of $\text{H}_2^+$ in a laser pulse with peak intensity $I_0$ and pulse length $T = 50$ fs: absorber based on field-free or field-following states as well as grid-based OCTOPUS [29] results. The ionization probabilities of the hydrogen atom are indicated by the blue (for the field-free absorber) or red dot (for the field-based absorber) at large $R$. The OCTOPUS results are calculated with an absorber potential given by $V(z) = 0.04 \cdot (|z| - 20)^2$ with $20$ a.u. $\leq |z| \leq 30$ a.u. The molecule is placed in a cylinder around the z-axis (radius $r = 14$ a.u. and height $h = 60$ a.u.); the grid spacing is $d = 0.5$ a.u. We use a time step given by $\Delta t = 0.04$ a.u. for the propagation.

probabilities, is set to $R_D = 10$ a.u.
3.2 Multiphoton Dissociation of H$_2^+$ in strong laser fields

In this section we study the dissociation dynamics of H$_2^+$ exposed to short intense laser pulses with 800 nm wavelength [41]. We lay the focus on vibrationally resolved angular distributions of dissociated fragments for two reasons. On the one hand, these quantities are highly differentiable and, thus provide a sensitive test for the NA-QMD calculations. On the other hand, dissociation in a parameter regime where ionization is negligible can be described fully quantum mechanically. Therefore, we employ a field-dressed Floquet-like propagation method for the nuclear quantum dynamics, which allows direct interpretation of the multiphoton characteristics of the dissociation process in terms of two-dimensional adiabatic Floquet surfaces. A scheme, which allows to extract the contribution of different photon channels from the NA-QMD calculations, is presented as well.

3.2.1 Theory: Field-dressed nuclear quantum dynamics (FBO)

In order to properly define the angular distribution of dissociated fragments and the corresponding total probabilities based on the nuclear quantum dynamics calculations, we shortly outline the field-dressed Floquet-like propagation method. A one-dimensional version of this approach has been given in [99, 101]. Here, we present the full-dimensional method, which includes the nuclear rotational degree of freedom (see also [102] for details in the derivation).

The full time-dependent Schrödinger equation for H$_2^+$ in a laser field in the center of mass frame reads

$$i \frac{\partial}{\partial t} \Psi(R, r, t) = [T_R + H_e(r; R) - r \cdot E(t)] \Psi(R, r, t),$$

where $T_R = -\nabla^2_R / (2\mu)$ is the kinetic energy for the relative motion of the nuclei and $H_e(r; R)$ is the electronic Hamiltonian. Here, $\mu$ is the reduced mass, $r$ is the electronic coordinate and $R$ the internuclear distance vector (see Figure 3.1).

In order to capture multiphoton effects, we expand the wave function $\Psi(R, r, t)$ in diabatic field-dressed Born-Oppenheimer (FBO) states [cf. (2.4)]

$$\Psi(R, r, t) = \sum_I \sum_{n=-\infty}^{\infty} \frac{1}{R} \Omega_{I,n}(R, t) e^{in\omega t} \Phi_I(r; R),$$

where $\Phi_I(r; R)$ are Born-Oppenheimer states and $\Omega_{I,n}(R, t)$ is the nuclear wave function on BO-surface $V_I(R)$ dressed by photon number $n$. In this framework, $n > 0$ can be interpreted as emission and $n < 0$ as absorption of $n$ photons from the laser field [103]. Note that the basis expansion (3.11) is overcomplete. Using (3.11) and neglecting the non-adiabatic
derivative couplings, the nuclear time-dependent Schrödinger equation reads as [cf. (2.6)]

\[
\sum_n i \frac{\partial \Omega_{I,n}(\mathbf{R}, t)}{\partial t} e^{i n \omega t} = \sum_n \left[ \frac{1}{2 \mu} \frac{\partial^2}{\partial R^2} + \frac{L^2}{2 \mu R^2} + (V_I(R) + n \omega) \right] \Omega_{I,n}(\mathbf{R}, t) e^{i n \omega t} \\
- \sum_{J,n} \frac{1}{2} \mathbf{E}_0(t) \cdot \mathbf{L}_{IJ}(\mathbf{R}) \left[ e^{i n \omega t} + e^{-i n \omega t} \right] \Omega_{J,n}(\mathbf{R}, t) e^{i n \omega t}
\]

(3.12)

where \( L \) is the angular momentum operator. If \( \tilde{\Omega}_{I,n}(\mathbf{R}, t) \) is a solution of (3.12), then \( \tilde{\Omega}_{I,n}(\mathbf{R}, t) = \Omega_{I,n}(\mathbf{R}, t) + k(\mathbf{R}, t) e^{i k \omega t} \) is a solution of (3.12) as well. Although \( \tilde{\Omega}_{I,n}(\mathbf{R}, t) \) is different from \( \Omega_{I,n}(\mathbf{R}, t) \), it leads to the same total wave function (3.11). This arbitrariness can be alleviated by the additional constraint that (3.12) has to hold for every Fourier component \( e^{i n \omega t} \). This leads to the FBO Schrödinger equation

\[
i \frac{\partial}{\partial t} \Omega_{I,n}(\mathbf{R}, t) = \left[ \frac{1}{2 \mu} \frac{\partial^2}{\partial R^2} + \frac{L^2}{2 \mu R^2} + (V_I(R) + n \omega) \right] \Omega_{I,n}(\mathbf{R}, t) \\
- \sum_J \frac{1}{2} \mathbf{E}_0(t) \cdot \mathbf{L}_{IJ}(\mathbf{R}) \left[ \Omega_{J,n+1}(\mathbf{R}, t) + \Omega_{J,n-1}(\mathbf{R}, t) \right]
\]

(3.13)

We observe that only the slowly varying electric field envelope enters (3.13).

With this, we define the angular distribution of dissociated fragments \( P_D^n(\theta) \) corresponding to the \( n \)-photon channel as

\[
P_D^n(\theta) = \sum_I \int_{R_D} dR \int_0^{2\pi} d\phi \left| \Omega_{I,n}(\mathbf{R}, t_f) \right|^2 .
\]

(3.14)

Correspondingly, the total \( n \)-photon dissociation probability is given by

\[
P_D^n = \pi \int_0^{\pi} d\theta \sin \theta P_D^n(\theta) .
\]

(3.15)

In addition we note, that the total angular distribution for dissociation and dissociation probability are given as sum over all photon channel contributions, i.e. \( P_D(\theta) = \sum_n P_D^n(\theta) \) and \( P_D = \sum_n P_D^n \).

For comparison, the bare time-dependent Schrödinger equation according to (3.13), i.e. the one derived without photon resolution, is given by [cf. (2.6)]

\[
i \frac{\partial}{\partial t} \Omega_I(\mathbf{R}, t) = \left[ -\frac{1}{2 \mu} \frac{\partial^2}{\partial R^2} + \frac{L^2}{2 \mu R^2} + V_I(R) \right] \Omega_I(\mathbf{R}, t) \\
- \sum_J \mathbf{E}(t) \cdot \mathbf{L}_{IJ}(\mathbf{R}) \Omega_J(\mathbf{R}, t)
\]

(3.16)

and contains the full oscillating electric field in contrast to (3.13). The corresponding dissociation probability and angular distribution of fragments are defined analogously to (3.15) and (3.14).
3.2 Multiphoton Dissociation of $H_2^+$ in strong laser fields

3.2.2 Computational details: FBO

The FBO Schrödinger equation (3.13) is solved numerically using the WavePacket code [104]. For this, the nuclear wave function is expanded in plane waves (radial part) and spherical harmonics (angular part). The FBO expansion (3.11) is restricted to $5\,\sigma_g$ and $6\,\sigma_u$ dressed state Born-Oppenheimer surfaces. This has been checked to be sufficient to obtain converged angular distributions of photofragments with the FBO method by comparison of the results to the bare propagation method (3.16). Within the latter, we have also checked that the two lowest $1s\sigma_g$ and $1s\sigma_u$ Born-Oppenheimer states are sufficient under the laser conditions used in this chapter, by inclusion of the lowest $\pi_u$ state, which has given essentially the same results. The Born-Oppenheimer surfaces as well as their corresponding dipole transition matrix elements are calculated via QMD ground state calculations.

We use the following numerical setup or parameters. For the radial part of the nuclear wave function, an equally-spaced radial grid ranging from $0.2$ a.u. to $200.0$ a.u. with $2000$ grid points is utilized. Spherical harmonics with angular momenta up to $l = 59$ are used for the angular part. The propagation time step is set to $\Delta t = 0.4$ a.u.

The initial state for the propagation is a product of a vibrational eigenstate $\nu$ and a spherical harmonic according to the rotational ground state starting from the $\sigma_g + 0\omega$ surface:

$$\Omega_{\sigma_g,0}(R, \theta, \phi; \nu; t = 0) = \frac{1}{4\pi}\chi_{\nu}(R).$$

The lower boundary of the dissociated region of space has been set to $R_D = 10$ a.u. as for the NA-QMD calculations.

3.2.3 Total angular distributions of fragments and dissociation probabilities

We first present the NA-QMD results for the total angular distribution of dissociated fragments $P_D(\theta)$ in comparison with those obtained from nuclear quantum dynamics. The laser parameters are set to $T = 25$ fs and peak intensity $I_0$. Under these conditions, our NA-QMD results reveal that the ionization probabilities for each vibrational level do not exceed 20 percent. Accordingly, the fragmentation dynamics is dominated by dissociation, which allows to use our full quantum results, explicitly excluding ionization, as test of the accuracy of the NA-QMD approach.

The angular distributions according to the dissociation channel are presented in Figure 3.3 for initial vibrational levels from $\nu = 1 - 14$ as well as the corresponding Franck-Condon average (with the Franck-Condon factors taken from [105]). The latter refers to an incoherent summation over the initial vibrational levels which is appropriate for experimental ion-beam setups [99]. As can be seen clearly, the mixed quantum-classical and the full
Figure 3.3: Angular distribution $P_D(\theta)$ of dissociated $H_2^+$ for single initial vibrational levels $\nu$ as well as Franck-Condon average: quantum mechanical (straight black lines) and NA-QMD results (red bars).

Quantum results show a good qualitative agreement. In the case of the vibrational ground state ($\nu = 0$) the NA-QMD results (not shown) display negligible dissociation, a fact that has been observed already in the laser-aligned case [93]. We mention, that this originates from the microcanonical sampling and can be alleviated by using more sophisticated initial conditions based on the Wigner distribution (for details see [106]). Three characteristically different types of dissociation dynamics can be concluded from Figure 3.3:

- For low vibrational excitation ($\nu \leq 4$) the probability densities decrease as a function of the angle.

- In contrast, for intermediate $\nu$ the distributions exhibit a double-humped shape with a secondary maximum around $\theta = 30^\circ - 60^\circ$.

- At high initial vibrational levels, the angular distributions tend to be almost uniform, most clearly visible for the highest vibrational excitation $\nu = 14$.

In the Franck-Condon case, low $\nu$ are dominating the average leading to a forward peaked distribution.
3.2 Multiphoton Dissociation of $H_2^+$ in strong laser fields

![Figure 3.4: Comparison of full quantum mechanical with NA-QMD results for total dissociation probabilities of $H_2^+$ as a function of initial vibrational excitation. Left: laser-aligned case, taken from [93]; right: full-dimensional dynamics.](image)

The reasons for this non-trivial dependence on the rotational angle of the angular distribution of dissociated fragments will be uncovered in the remainder of this section guided by detailed analysis within the FBO approach.

Evaluating the accuracy of the NA-QMD approach further, we compare the corresponding total dissociation probabilities for the different initial vibrational levels to those obtained fully quantum mechanically in Figure 3.4. We observe an almost perfect agreement of the two types of results up to $\nu = 10$. The deviations above $\nu = 10$ are likely related to the Ehrenfest treatment (see Sec. 2.1), which can lead to an overestimation of the dissociation probability. Furthermore, large dissociation probabilities of about 0.8 are observed around $\nu = 10$, which is unprecedented in the aligned case ($\theta = 0$, see dotted lines in Figure 3.4) [93], where maximal dissociation probabilities were around 60 percent.

3.2.4 Adiabatic Floquet surfaces and multiphoton channels

The aim of the following is to understand the characteristic shapes of the angular distributions of dissociated fragments in Figure 3.3. To this end we first explain the different multiphoton character of the distributions in the regime of low, medium and high initial vibrational states in terms of a few relevant two-dimensional adiabatic Floquet surfaces (for the definition of the Floquet surfaces see Appendix A.1). Subsequently, we compare the contributions to the angularly resolved dissociation probability from the relevant photon channels in the FBO and NA-QMD description. The scheme used to extract the different photon channel contributions from the NA-QMD results is explained in Appendix A.2.

For low initial vibrational levels, the angular distributions are peaked in forward direction (see Figure 3.3) with a maximum at $\theta = 0^\circ$. For these initial states ($\nu = 1 - 5$), the photodissociation occurs mainly via the $2\omega$-dissociation channel as can be concluded from
the relative location of these vibrational levels [see Figure 3.5 (d)]. As can be seen in Figure 3.5 (c), in this case the relevant Floquet surface shows a ridge (indicated by solid line in the figure) between $\theta = 30^\circ$ and $\theta = 60^\circ$ for $R \geq 4.0$ a.u. This leads to an alignment behavior of the dissociating wave packet on the $2\omega$-Floquet surface. At the beginning of the laser pulse and also for higher angles during the laser pulse, the dynamics is mainly governed by the diabatic pathways of the Floquet surfaces for low $\nu$, which results from the fact that the avoided crossings in these cases are very small. Only at low angles, the Floquet barrier of the $2\omega$-surface is lowered enough at high intensities allowing for a dissociation on this surface, leading to a forward peaked angular distribution. In Figure 3.6 (a,b) the respective results of the full quantum mechanical and NA-QMD calculations are shown and confirm this interpretation.

For higher vibrational levels, 1-photon dissociation plays the dominant role, maximally present for initial $\nu = 9$, as this vibrational level is located directly at the 1-photon crossing
3.2 Multiphoton Dissociation of $H_2^+$ in strong laser fields

Figure 3.6: Multiphoton contributions to the total angular distribution in the dissociation of $H_2^+$ for $\nu = 4$ (a,b), $\nu = 9$ (c,d), and $\nu = 14$ (e,f) calculated with the FBO method (left) and NA-QMD (right).

[see Figures 3.5 (b,d), 3.6 (c,d)]. In these cases the initial wave packet already spreads to higher $R$, i.e. a growing part of the wave packet is already on the $1\omega$-Floquet surface at the beginning of the laser pulse (the outer classical turning point for $\nu = 9$ is located at $R \approx 5.1$ a.u.). When the laser pulse reaches its maximum strength, this Floquet surface has a trench, which is directed to higher angles for increasing $R$ and is indicated by a line in the corresponding figure. For that reason, the wave packet shows a counter-intuitive or anti-alignment behavior [107]. For increasing vibrational level, a large part of the wave packet is located at higher $R$. Thus, this alignment forcing works at higher angles, leading to a secondary peak in the total angular distributions, which moves to higher angles for higher $\nu$ (see also Figure 3.3). The NA-QMD angular distributions for the $1\omega$- and $2\omega$-channels show the same alignment and anti-alignment behavior as in the quantum dynamical case [see Figures 3.6 (c,d)].

Starting with $\nu = 9$, 0-photon dissociation represents an additional influence on the angular distribution of photofragments. As can be seen in Figs. 3.3 and 3.6 (e,f), a broadening of the angular distribution due to the 0-photon contribution occurs. This results from the fact that a relevant part of the wave packet is located at internuclear distances which are far away from the avoided crossing that forms between the $0\omega$- and $1\omega$-surface [see Figures 3.5...
(a,b)]. For high $\nu$ the initial wave packet extends beyond the beginning of the ridge on the $0\omega$-surface (the outer classical turning point for $\nu = 14$ is located at $R \approx 7.2$ a.u.) and parts of the wave packet can slide to higher angles leading to a slight anti-alignment behavior, i.e. a finite dissociation contribution at $\theta \approx 90^\circ$, as shown in Figures 3.6 (e,f). Again, the NA-QMD calculations reproduce these alignment features.

In addition, we stress that our 2D Floquet interpretation is not only based on kinetic energy spectra, but on direct propagation on various field-dressed Born-Oppenheimer surfaces, allowing a time-resolved analysis of dissociation dynamics, which is impossible on the basis of bare kinetic energy spectra [87]. This will be demonstrated in the subsequent section.

### 3.2.5 Role of nuclear rotation in multiphoton dissociation

![Figure 3.7](image)

**Figure 3.7:** Dominant 2-photon dissociation of H$_2^+$ for $\nu = 4$ including (left) and neglecting (right) nuclear rotation. Also shown are the nuclear densities at the laser peak intensity, $t = 12.5$ fs, and shortly afterward, $t = 19.0$ fs, according to the 2-photon dissociation channel.

The FBO approach allows us to perform a detailed time-resolved analysis of the dissociation dynamics and, hence, follow the motion of the nuclear wave packet on each Floquet surface (see Appendix A.1). Therefore, in this section we compare the full dimensional nuclear quantum dynamics calculations to those obtained with frozen nuclear rotation (i.e. isotropically orientated but non-rotating), in order to evaluate the role of nuclear rotation in the multiphoton dissociation process.
3.2 Multiphoton Dissociation of $H_2^+$ in strong laser fields

Figure 3.8: Dominant 1-photon dissociation of $H_2^+$ for $\nu = 9$ including (left) and neglecting (right) nuclear rotation. Also shown are the nuclear densities at the laser peak intensity, $t = 12.5$ fs, and shortly afterward, $t = 19.0$ fs, according to the 1-photon dissociation channel.

We lay the focus here on the same initial vibrational levels as in Figure 3.6, i.e. $\nu = 4, 9, 14$, as they represent the "optima" for the multiphoton processes in question [see also Figure 3.10 (g)]. For low $\nu$, dissociation dynamics is governed by alignment towards the laser polarization axis, which has been attributed to the ridge of the relevant 2-photon Floquet surface. The snapshots of the nuclear densities at laser peak intensity and shortly afterwards, shown in the left part of Figure 3.7, confirm this assessment. Only the part of the wave packet at low alignment angles is enabled to dissociate by circumventing the ridge on the $2\omega$ surface, leading to a forward peaked angular distribution. Without nuclear rotation, this dynamical pathway is blocked and, thus, $2\omega$ dissociation becomes less effective. The corresponding angular distribution is clearly broadened compared to the one including nuclear rotation (see the right part of Figure 3.7).

In the previous section, we attributed the dissociation process for intermediate $\nu$ to the $1\omega$ channel. The respective time-dependent nuclear densities are shown in Figure 3.8. The trench of the $1\omega$ Floquet surface leads to a counter-intuitive or anti-alignment behavior [107] of the wave packet, which is obvious from the angular spread of the wave packet with increasing $R$. This dynamics produces the characteristic side peak in the corresponding angular distribution. Without nuclear rotation, the wave packet preferentially dissociates

We lay the focus here on the same initial vibrational levels as in Figure 3.6, i.e. $\nu = 4, 9, 14$, as they represent the "optima" for the multiphoton processes in question [see also Figure 3.10 (g)]. For low $\nu$, dissociation dynamics is governed by alignment towards the laser polarization axis, which has been attributed to the ridge of the relevant 2-photon Floquet surface. The snapshots of the nuclear densities at laser peak intensity and shortly afterwards, shown in the left part of Figure 3.7, confirm this assessment. Only the part of the wave packet at low alignment angles is enabled to dissociate by circumventing the ridge on the $2\omega$ surface, leading to a forward peaked angular distribution. Without nuclear rotation, this dynamical pathway is blocked and, thus, $2\omega$ dissociation becomes less effective. The corresponding angular distribution is clearly broadened compared to the one including nuclear rotation (see the right part of Figure 3.7).

In the previous section, we attributed the dissociation process for intermediate $\nu$ to the $1\omega$ channel. The respective time-dependent nuclear densities are shown in Figure 3.8. The trench of the $1\omega$ Floquet surface leads to a counter-intuitive or anti-alignment behavior [107] of the wave packet, which is obvious from the angular spread of the wave packet with increasing $R$. This dynamics produces the characteristic side peak in the corresponding angular distribution. Without nuclear rotation, the wave packet preferentially dissociates
Figure 3.9: Multiphoton dissociation of $H_2^+$ for $\nu = 14$ including (left) and neglecting (right) nuclear rotation. Also shown are the nuclear densities at the laser peak intensity, $t = 12.5$ fs (upper block), and shortly afterward, $t = 19.0$ fs (lower block), according to the contributing multiphoton dissociation channels.

at higher angles (see right part of Figure 3.8 at $t = 12.5$ fs) on the corresponding $1\omega$-Floquet surface, as the laser-aligned 1-photon dissociation probability is higher at lower effective intensities [see Figure 3.10 (a)], which is equivalent to higher alignment angles. This results in a broad angular distribution, peaked farther away from the laser polarization direction compared to the full dimensional results [Figure 3.8 (b)].

Finally, for high $\nu$ multiphoton dissociation dynamics takes place as all (0,1,2) photon channels give a relevant contribution. A large part of the initial wave packet extends beyond the beginning of the ridge on the $0\omega$-surface as can be seen at the nuclear density at the time of laser peak intensity. On this surface, dissociation proceeds nearly uniform with respect to the alignment angle with a finite dissociation contribution at $\theta \approx 90^\circ$ in the final angular distribution as shown in Figure 3.9 (left part). Switching off nuclear rotation in this case again leads to suppressed alignment and anti-alignment (as discussed before for $\nu = 4$ and
3.2 Multiphoton Dissociation of $H_2^+$ in strong laser fields

$\nu = 9$). As the coupling between the $\sigma_g$ and $\sigma_u$ surface vanishes perpendicular to the laser polarization direction, there is no dissociation contribution at $\theta \approx 90^\circ$.

After we have seen the connection between the final multiphoton angular distributions and the time-dependent nuclear dynamics on the time-dependent Floquet surfaces, we now want to characterize the multiphoton dissociation of $H_2^+$ from a wider perspective to prepare the investigations in Section 3.3. Therefore, on the one hand, we compare the multiphoton dissociation probabilities for different peak intensities and pulse length in dependence on the initial vibrational state. On the other hand, we evaluate the importance of the rotational degree of freedom and a full-dimensional description by comparison of the results for laser-aligned $H_2^+$ with those of isotropically orientated $H_2^+$, the latter with and without nuclear rotation. This is shown in Figure 3.10. At first, we consider the laser-aligned case (upper part of Figure 3.10), which leads us to the following observations:

- In the regime of intensities and pulse lengths under investigation, the dissociation dynamics is governed by 2-photon dissociation at low $\nu$ (maximal at $\nu = 2 - 4$) and 1-photon dissociation at intermediate $\nu$ (maximal around $\nu = 9$). At high $\nu$ (above $\nu = 8$), 0-photon dissociation contributes significantly to the total dissociation yield.

- By increasing the pulse length at fixed peak intensity, multiphoton channels separate, i.e. while for the shortest pulse all multiphoton channels overlap over a wide region of $\nu$, for the longest pulse regions of nearly pure 1--- or 2---photon dissociation show up. This is due to the fact that the dynamics become more adiabatic for longer pulses, i.e. the wave packet adapts to the adiabatic Floquet surface, which is relevant for the initial vibrational level under consideration. The maximal multiphoton dissociation probabilities increase together with the total dissociation probabilities with growing pulse duration with nearly complete maximum 1- and 2-photon dissociation for $T = 100$ fs.

- Comparing the probabilities for different intensities at fixed pulse length reveals that 2-photon dissociation mainly increases and 1-photon as well as 0-photon dissociation mainly decreases by doubling the peak intensity. In consequence, the total dissociation probabilities increase with intensity for low $\nu$, but are reduced for high $\nu$.

- A minimum in the dissociation probability occurs around $\nu = 5$ for the longest pulse ($T = 100$ fs), originating from the overlap of comparably weak 2$\omega$- and 1$\omega$-dissociation. This suppressed dissociation at $\nu = 5$ cannot be understood in terms of reduced dipole couplings accessible via perturbation theory (as done in [108]), as we are faced with the strong field regime here.

Most of these observations hold for isotropically orientated $H_2^+$ as well (lower part of Figure 3.10), but with the important difference that 2-photon dissociation is much smaller than in
the laser aligned case. This originates from the fact that most of the molecules feel a lower effective intensity $\sim \cos^2 \theta$. More importantly, the role of nuclear rotation clearly exhibits itself in the pulse length dependence of the multiphoton dissociation probabilities. While nuclear rotation has minor impact on the multiphoton dissociation probabilities for short laser pulses, neglecting nuclear rotation for the longer pulses leads to a strong reduction of $2\omega$-dissociation, especially at low $\nu$, and $1\omega$-dissociation, especially at higher $\nu$. In contrast, the $0\omega$-channel appears to be enhanced, if nuclear rotation is switched off. Nevertheless, the total dissociation probabilities decrease without nuclear rotation for all $\nu$. 
3.2 Multiphoton Dissociation of $H_2^+$ in strong laser fields

Laser-aligned $H_2^+$

<table>
<thead>
<tr>
<th>$I_0$</th>
<th>$F_D$</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25 fs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 fs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 fs</td>
</tr>
</tbody>
</table>

Isotropically orientated $H_2^+$

<table>
<thead>
<tr>
<th>$I_0$</th>
<th>$F_D$</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25 fs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 fs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 fs</td>
</tr>
</tbody>
</table>

Figure 3.10: Dissociation probability $P_D$ (black) at peak intensity $I_0 = 2 \cdot 10^{14}$ W/cm$^2$ and $I_0/2$. Also shown are the $2\omega$- (blue), $1\omega$- (green), and $0\omega$- (red) contributions. The upper part shows the results using the laser-aligned approximation, whereas the lower part shows the results for initially isotropically orientated $H_2^+$; with (full, squares) and without (dotted, circles) nuclear rotation.
3.3 Ionization and dissociation of H\(_2^+\) in strong laser fields

In this section, we perform a complete study of the laser-induced dynamics of H\(_2^+\) using the NA-QMD method, i.e. we include all nuclear and electronic degrees of freedom as well as all reaction channels, i.e. dissociation and ionization [42]. After we have shown that the NA-QMD approach accurately describes fixed-nuclei ionization (Section 3.1.2) as well as multiphoton dissociation (Section 3.2), our main aim in the following is to evaluate the dynamical relevance of nuclear rotation for the ionization channel and study the competition between ionization and dissociation in dependence on experimentally relevant laser parameters.

3.3.1 Total ionization and dissociation probabilities

We first turn our attention to the total dissociation and ionization probabilities as a function of the initial vibrational state (\(\nu = 0 \ldots 14\)) of the molecule. The corresponding results are shown in Figure 3.11 for different peak intensities (\(I_0 = 2 \cdot 10^{14}\) W/cm\(^2\) and \(I_0^2\)) as well as different pulse lengths (\(T = 25\) fs, 50 fs and 100 fs) for isotropically orientated H\(_2^+\) (lower part of Figure 3.11) including and excluding nuclear rotation. Also shown are the probabilities for the laser-aligned case (upper part of Figure 3.11). Panels (g) to (i) of Figure 3.11 reveal that by increasing the pulse length, while keeping the intensity fixed at \(I_0\), ionization is enhanced gradually and tends to become the dominant fragmentation mechanism. Reducing the intensity by a factor of 2 decreases ionization dramatically, as can be seen in panels (j) to (l). At this point we note, that these trends are apparent in the laser-aligned case as well. Ionization responds to an increase in pulse length or intensity in a similar way, but the ionization probabilities are clearly enhanced compared to the full dimensional case. Accordingly, the relative contribution of the two competing fragmentation channels may differ qualitatively as well [see panel (b), where ionization exceeds dissociation above \(\nu = 4\) in contrast to panel (h)]. Returning to the full-dimensional results we recognize that with increasing relevance of ionization also the role of nuclear rotation grows (cf. the dashed lines in Figures 3.11 (g-l)). The role of rotation, however, is much more intricate. In the case of high vibrational excitation rotation plays virtually no role. Furthermore, including nuclear rotation may also lead to reduced dissociation compared to rotationally frozen molecules, a behavior which is in clear contrast to the expectations from dissociation-only calculations (Sec. 3.2.5).

These at first glance surprising findings can be understood by considering the orientation dependence of ionization together with the relevant time scales for ionization and rotation. For fixed nuclei, ionization, which is most effective at laser peak intensity reached at \(\frac{T}{2}\), depends on the orientation of the molecule with respect to the laser polarization direction.
3.3 Ionization and dissociation of $H_2^+$ in strong laser fields

[see Figure 3.12 (a)]. It is clearly seen that strong ionization takes place when the molecular axis is in the vicinity of the laser polarization axis, i.e. $\theta \leq 15^\circ$ and $R \approx 4$ a.u. and 10 a.u. but also for intermediate angles up to $\theta \approx 40^\circ$ at internuclear distances around 8 a.u. This is in agreement with the well-known fact that laser-aligned molecules ionize much more easily. Second, the effective laser-induced dipole moment generates a torque on the molecule, which tends to align the molecule with respect to the laser polarization direction within at most one-quarter of the rotational period

$$\tau_\nu = \frac{\pi J_\nu}{2L_\nu}$$

(3.18)

with the moment of inertia $J_\nu = \mu R_{\nu}^3$, where $R_{\nu}$ is the equilibrium distance for the respective $\nu$, and angular momentum $L_\nu$, which is acquired during the laser pulse and depends on the laser parameters in a non-trivial way. The alignment times corresponding to the NA-QMD results in Figure 3.11 are shown in Figure 3.12 (b). In addition to the time scale for ionization ($\tau_\nu$) and rotation ($\tau_\nu$), fragmentation saturation (FS), i.e. $P_I + P_D \approx 1$, represents an additional influence on the dissociation and ionization probabilities.

We first note from Figure 3.12 (b) that for $\nu = 14$ in all cases shown the rotational time scale is distinctly larger than the ionization time scale. This explains why the full ionization probabilities agree with those for frozen rotation: nuclear rotation is so slow that the molecule is ionized before it can rotate appreciably. The dissociation process, on the other hand, is not limited by a narrow time frame around the laser peak intensity as in the case of ionization, and, thus, a small difference between the "rotating" and "frozen" dissociation probabilities exists. The latter observation has already been made in the calculations excluding the ionization channel (cf. Figure 3.10). In some cases, however, the rotationally frozen and full results agree nevertheless, but this is an indirect effect of FS, i.e. $P_D(14) = 1 - P_I(14)$, and to the agreement of the respective probabilities for ionization.

We also mention that in the case of $T = 100$ fs, where the rotational and ionization time scales differ least for $\nu = 14$ as compared to the shorter pulses, the negligible influence of rotation on ionization is additionally supported by the near isotropic orientation dependence of ionization at large $R$ [see Figure 3.12 (a)].

Around $\nu = 4$ and for $T \gtrsim 50$ fs there is sufficient time for the molecule to rotate towards the laser polarization direction before ionization reaches its maximum [$\tau_\nu < T/2$, see Figure 3.12 (b)]. This leads to a considerable enhancement of ionization and dissociation compared to rotationally frozen molecules. The strong dependence of dissociation on rotation for $\nu = 4$ has been attributed to the 2-photon dissociation channel in Section 3.2.5. Accordingly, it is this channel and the structure of the underlying Floquet surface which are responsible for the short rotation time scales. The strong enhancement of both channels has another important consequence: FS may be reached for lower $\nu$ than for rotationally frozen molecules. Therefore, in the regime of saturated full but not yet saturated rotationally frozen dynamics, the large $P_I$ in the full dynamics may push the corresponding probabilities
\[ P_D \] below those of frozen molecules, since the latter are not subject to FS [see the region around \( \nu = 7 \) in Figure 3.10 (i)].

For \( T = 100 \text{ fs} \) and small \( \nu \), the rotational time scales are shorter than those for ionization. Therefore we expect a considerable rotational enhancement of dissociation and ionization for low vibrational states, i.e. \( \nu = 1 - 4 \). Since the absolute probabilities in these cases are small, they are summarized in Table 3.2. The enhancement can reach almost one order of magnitude for ionization from \( \nu = 1 \), whereas a factor of 2 remains for \( \nu = 4 \).

\[
\begin{array}{ccccc}
\nu & P_I & & & P_D \\
& \text{frozen} & \text{rotating} & \text{aligned} & \text{frozen} & \text{rotating} & \text{aligned} \\
1 & 0.02 & 0.18 & 0.37 & 0.07 & 0.43 & 0.46 \\
2 & 0.12 & 0.39 & 0.69 & 0.14 & 0.46 & 0.29 \\
3 & 0.28 & 0.56 & 0.81 & 0.22 & 0.41 & 0.19 \\
4 & 0.31 & 0.65 & 0.86 & 0.24 & 0.33 & 0.14 \\
\end{array}
\]

Table 3.2: Ionization (\( P_I \)) and dissociation (\( P_D \)) probabilities for selected initial vibrational \( \text{H}_2^+ \) levels and laser parameters corresponding to Figure 3.10 (i). “rotating” refers to full dimensional results, “frozen” to an ensemble of rotationally frozen molecules and “aligned” to molecules aligned with the laser polarization axis. The latter scenario implies dimensionally reduced calculations.

Table 3.2 also reveals that the ionization probabilities for laser-aligned \( \text{H}_2^+ \) are distinctly higher compared to the full results, whereas dissociation becomes rather weak with increasing \( \nu \) due to FS. This is due to the fact that in this case the molecules are subjected to the strong ionization region along the laser polarization direction [see Figure 3.12 (a)]. It is thus clear, that a dimensionally reduced description is not sufficient in order to produce realistic results.

In addition we note that rotation has minor impact on the total probabilities for the shortest pulse and a small vibrational excitation, i.e. \( T = 25 \text{ fs} \) and \( \nu \leq 4 \), in agreement with respective ratio of rotation and ionization time scale \( [\tau_\nu > T/2] \), see Figure 3.12 (b)]. Furthermore, we observe a decrease of ionization and an increase of dissociation in the regime of FS for the longest pulse (see Figures 3.10 (k,l) for \( \nu \gg 8 \)). Under these conditions the majority of molecules is already outside the strong ionization region at high \( R \) when the laser reaches its maximum strength and, correspondingly, ionization is less efficient.

### 3.3.2 Angular distributions of fragments

After we have examined the total probabilities in the previous Section, we now turn our attention to the angularly resolved fragment distributions. The results shown in Figure 3.13 reveal that even for the short pulse of 25 fs the rotating molecules tend to align in contrast to the rotationally frozen molecules (grey circles). This observation appears as
a surprise, especially for the ionization channel, on the basis of the integral probabilities, where the role of nuclear rotation is diminished due to angular integration with the volume element proportional to \( \sin \theta d\theta \) suppressing contributions near \( \theta = 0^\circ \). This alignment effect survives Franck-Condon (FC) averaging. In addition we note, that while the dissociation channel exhibits the characteristic multiphoton features as discussed in Section 3.2, a similar behavior is also found in the ionized fragment distribution, with anti-alignment for the higher \( \nu \). This is connected to the fact, that the latter distributions are influenced by both the nuclear motion on the respective Floquet surface and the orientation dependent ionization rates.

For the long pulse of 100 fs we expect from our previous discussion a strong alignment effect for low vibrational excitation. This is indeed the case as becomes clear from Figure 3.14: Nuclear rotation enhances ionization by a factor of almost 30 in \( P_I(\theta \approx 0) \) compared to frozen rotation. The latter approximation fails completely to reproduce the full dimensionally calculated angular distributions for low \( \nu \), see \( \nu = 4 \) in Figure 3.14. For \( \nu = 9 \), where fragmentation is almost saturated for frozen and full dynamics, the respective distributions clearly differ as well. Correspondingly, the drastic influence of rotation prevails in the FC averaged angular distributions.

### 3.3.3 Towards comparison with experiment

In order to compare our results for dissociation and ionization to the experiment, several factors have to be taken into account. First, measuring vibrationally resolved fragmentation yields is difficult, thus Franck-Condon (FC) averaging over initial vibrational levels is required. Second, focal volume averaging is necessary due to the spatial dependence of the laser intensity profile, as many molecules are exposed to low intensities in the wings of the intensity distribution, typically assumed to be of Gaussian shape. In principle, also (thermal) averaging over initial rotational states [86] has to be performed. While the first requirement is easily met, the latter two depend on the exact conditions of individual experiments, which are not trivial to quantify.

In Table 3.3 we provide an overview over the effect of molecular rotation on Franck-Condon (FC) averaged probabilities. As can be seen, rotation increases the ionization and dissociation probability for all laser parameters considered, up to a factor of 2 for the longest pulse with \( T = 100 \) fs. Owing to the focal volume in the experiment, the results for \( I_0/2 \) are included as well. As is evident from Table 3.3, ionization and dissociation exhibit a fundamentally different dependence on intensity. The ionization probability depends crucially on the laser intensity. At half peak intensity the ionization probability is reduced by almost one order of magnitude for all pulse lengths. Such a dramatic intensity dependence of ionization is known already from the hydrogen atom and \( \text{H}_2^+ \) with fixed internuclear distance [109]. The dissociation probability, on the other hand, decreases \( (T = 25 \) fs) or even
increases \((T = 100 \text{ fs})\) by a factor less than 2, where the latter is connected to fragmentation saturation.

The pulse length of 45 fs FWHM in the experiment [40] corresponds roughly to our “long” pulse of 100 fs (total length). Due to the spatial intensity profile and the width of the ion beam used there, mainly low laser intensities contribute considerably to the fragment signal. With this in mind, our calculation for the 100 fs pulse using \(I_0/2\) given in Table 3.3 should be closer to the experimental situation than using the peak intensity \(I_0\). Indeed, for \(I_0/2\) our results corroborate the experimental finding that ionization \((P_I = 0.066)\) is largely suppressed as compared to dissociation \((P_D = 0.48)\). A more detailed discussion dealing with the competition of ionization and dissociation and the role of focal volume averaging is given in Section 3.4.

<table>
<thead>
<tr>
<th>probability</th>
<th>(T [\text{fs}])</th>
<th>(I_0)</th>
<th>(I_0/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T = 25, 50, 100 \text{ fs})</td>
<td>frozen</td>
<td>rotating</td>
</tr>
<tr>
<td>(P_I)</td>
<td>25</td>
<td>0.024</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.25</td>
<td>0.48</td>
</tr>
<tr>
<td>(P_D)</td>
<td>25</td>
<td>0.23</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.29</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.18</td>
<td>0.32</td>
</tr>
</tbody>
</table>

**Table 3.3:** Franck-Condon averaged ionization \((P_I)\) and dissociation \((P_D)\) probabilities as a function of pulse length \((T = 25, 50, 100 \text{ fs})\) and intensity \((I_0 = 2 \cdot 10^{14} \text{ W cm}^{-2} \text{ and } I_0/2)\) calculated excluding rotation (frozen) and full dimensionally (rotating).
3.3 Ionization and dissociation of $H_2^+$ in strong laser fields

Figure 3.11: Ionization probability $P_1(\nu)$ (red circles) and dissociation probability $P_D(\nu)$ (green squares) as a function of the initial vibrational state $\nu$ for different pulse lengths and peak intensities of $I_0 = 2 \cdot 10^{14}$ W/cm$^2$ and $I_0/2$. The upper part shows the results using the laser-aligned approximation (a-f), whereas the lower part shows the results for initially isotropically orientated $H_2^+$ (g-l). The dashed lines represent results for fixed nuclear orientation (frozen rotation).
Figure 3.12: Part (a): Calculated ionization probability \( P_I(R, \theta) = 1 - N[R, \theta](T) \) for fixed nuclear positions with the parallel and perpendicular component \( R_{||} = R \cos \theta \) resp. \( R_{\perp} = R \sin \theta \) \( (T = 50 \, \text{fs}, I_0; \text{Figure taken from [42]}) \). Part (b): Alignment time \( \tau_\nu \) as a function of pulse length \( T \) and peak intensity \( I_0 \) (filled symbols) and \( I_0/2 \) (open symbols) for vibrational states \( \nu = 1 \) (circles), \( \nu = 4 \) (squares) and \( \nu = 14 \) (diamonds). The solid line is the time scale of ionization, \( T/2 \).

Figure 3.13: Angular distributions of the dissociated \( (P_D(\theta)) \) and ionized fragments \( (P_I(\theta)) \) corresponding to Figure 3.10 (g) \( (I_0 = 2 \cdot 10^{14} \, \text{W/cm}^2, \, T = 25 \, \text{fs}) \), for the vibrational levels \( \nu = 4, 9, 14 \) as well as Franck-Condon averaged. The results calculated with frozen rotation are given by gray circles. Note that the total probabilities in Figure 3.10 are given by \( P_I = \int d\theta \sin \theta P_I(\theta) \).
Figure 3.14: Same as in Figure 3.13, but for $T = 100$ fs (corresponding to Figure 3.10 (i)). The insets show the corresponding angular distributions of fragments on a smaller scale.
3.4 A simplified model for the laser-induced dynamics of $H_2^+$

In this section, we introduce a model for the laser-induced dynamics of $H_2^+$, which avoids the explicit description of the electronic dynamics [43]. This enables us to study ionization and dissociation at low computational cost, and perform the focal volume averaging directly, which is necessary for comparison with experiment.

3.4.1 Theoretical approach

In the following, we provide the theoretical basis of our model, which consists of two main ingredients. First, the dissociation channel is described by a mixed quantum-classical mean-field approach according to the general equations of motion given by (2.16) and (2.17). In principle, these have to be solved by including a sufficient number of Born-Oppenheimer surfaces. Here we take into account only the two lowest $1s\sigma_g$ and $1s\sigma_u$ Born-Oppenheimer states [with Born-Oppenheimer surfaces $V_{g,u}(R)$ and dipole coupling $L_{gu}(R)$], because these are the most important states to capture the essential dynamics under the laser conditions used in this chapter (cf. Section 3.2). Neglecting the respective non-adiabatic couplings leads to the coupled equations of motion

$$i\dot{c}_g(t) = V_g(R)c_g(t) + e_z \cdot E(t) \cos \theta L_{gu}(R)c_u(t)$$

$$i\dot{c}_u(t) = V_u(R)c_u(t) + e_z \cdot E(t) \cos \theta L_{gu}(R)c_g(t)$$

(3.19)

and

$$\dot{R} = \frac{P_R}{\mu}$$

$$\dot{\theta} = \frac{P_\phi}{\mu R^2}$$

$$\dot{\phi} = \frac{P_\phi}{\mu R^2 \sin^2 \theta}$$

$$\dot{P}_R = \frac{P_R^2}{\mu R^3} + \frac{P_\phi^2}{\mu R^3 \sin^2 \theta} - \frac{\partial V}{\partial R}$$

$$\dot{P}_\phi = \frac{P_\phi^2 \cos \theta}{\mu R^2 \sin^2 \theta} - \frac{\partial V}{\partial \theta}$$

$$\dot{P}_\phi = 0$$

(3.20)

with the time-dependent mean-field potential energy surface

$$V(R, \theta, t) = |c_g|^2V_g(R) + |c_u|^2V_u(R) + (c_g^*c_u + c_u^*c_g)e_z \cdot E(t) \cos \theta L_{gu}(R).$$

(3.21)

Second, ionization is coupled to the dissociation dynamics via trajectory surface hopping of the system to the Coulomb surface, i.e. $V(R) = \frac{1}{R}$, on the basis of fixed-nuclei ionization rates. For this purpose, the ionization probability is defined as

$$P_{\text{ion}} = 1 - e^{-\Gamma(R, \theta, t)\Delta t}.$$

(3.22)
where $\Delta t$ is the classical time step, and compared to a uniform random number $\zeta \in [0, 1]$. If $P_{\text{ion}} > \zeta$, the trajectory hops to the Coulomb surface, otherwise it remains in the dissociation channel. Here, for computational efficiency, we approximately assume

$$\Gamma(R, \theta, t) = \Gamma_{\text{par}}(R, E_0(t)) \cos^2 \theta + \Gamma_{\text{perp}}(R, E_0(t)) \sin^2 \theta,$$

for the angular dependence of the fixed-nuclei ionization rate as in [110]. $\Gamma_{\text{par}}(R, E_0(t))$ and $\Gamma_{\text{perp}}(R, E_0(t))$ are the fixed-nuclei ionization rates for the laser electric field parallel and perpendicular to the molecular axis.

Our model differs from the one developed in [110] in the way dissociation dynamics is treated. In [110] a perturbational approach corresponding to the lowest order Floquet perturbation theory [102] has been used, i.e. the nuclear dynamics proceeds according to potential energy surfaces given by

$$V_{g,u}(R, \theta) = V_{g,u}(R) - \frac{E_0(t)^2}{4} (\alpha_{g,u}^{\text{par}}(R) \cos^2 \theta + \alpha_{g,u}^{\text{perp}}(R) \sin^2 \theta),$$

(3.24)

in contrast to the effective potential energy surface we use here. The drawback of (3.24) is that it is valid only for low laser intensities and can only account for 1-photon effects [102]. Our model, however, is not based on perturbation theory. Hence, we can study the dynamics of $H_2^+$ in strong laser fields including multiphoton effects.

In order to solve the classical equations of motion from above, we have to define initial conditions corresponding to the quantum mechanical initial state $(\nu, l, m)$. As the Born-Oppenheimer surfaces of $H_2^+$ are spherically symmetric, we can treat the vibrational and rotational degrees of freedom separately within a microcanonical sampling. The vibrational initial conditions $(R_0, P_{R_0})$ are chosen at random times according to a classical orbit under the condition

$$H_{\text{vib}} = \frac{P_R^2}{2\mu} + V_g(R) + \frac{l(l+1)}{2\mu R^2} = E_{\nu,l},$$

(3.25)

where $E_{\nu,l}$ is the energy of the ro-vibrational state $(\nu, l)$. On the other hand, the rotational initial conditions $(\theta_0, P_{\theta_0})$ are chosen according to a classical orbit at random times under the condition

$$L_{\text{rot}}^2 = P_\theta^2 + \frac{m^2}{\sin^2 \theta} \equiv l(l+1).$$

(3.26)

The quantum number $m$ is identified with $P_\phi$ based on the comparison with the corresponding quantum mechanical Hamiltonian. Note that $\phi$ is a cyclic variable in the classical equations of motion. The trajectory is started with zero momentum as for the vibrational part. We note that this kind of sampling allows, in principle, for thermal averaging of probabilities and probability densities in complete analogy to the quantum mechanical case, i.e. by incoherent sum over the $m$-contributions corresponding to each $l$ and subsequent weighting of these $l$ by a Boltzmann distribution according to a desired temperature. In this section, however, we restrict our considerations to initially rotationally cold molecules, i.e. $l = 0$. 

3.4 A simplified model for the laser-induced dynamics of $H_2^+$
3.4.2 Preliminary Considerations

Here, we give some details about the calculations in this Section and evaluate the accuracy of our model by comparison of the model to full quantum as well as NA-QMD results. The essential computational ingredients for the model are summarized as follows:

1. The ionization rates $\Gamma_{\text{par}}$ and $\Gamma_{\text{perp}}$ in (3.23) have been calculated for fixed nuclei using NA-QMD. For this purpose, a cw-laser with a $\sin^2$-shaped switching on within $t_{\text{on}} \approx 10$ fs is applied parallel and perpendicular to the molecular axis. The corresponding ionization rates are then obtained by fitting the norm to $N(t) = \exp(\alpha - \Gamma t)$, where $\alpha$ is some offset, in the time interval of constant field strength envelope. The corresponding rates are tabulated for different internuclear distances $R \in [0.1, 30.0]$ a.u. and laser intensities $I \in [0.01, 4.2] \cdot 10^{14}$ W cm$^{-2}$; the time-dependent rates (3.23) are extracted from these via cubic spline interpolation.

2. The $\sigma_g$ and $\sigma_u$ Born-Oppenheimer surfaces as well as their corresponding dipole transition matrix element $L_{\text{gu}}(R)$ are calculated via an NA-QMD ground state calculation.

3. The equations of motion (3.19) and (3.20) are propagated using a 4th-order Runge-Kutta scheme with a time step of $\Delta t = 0.1$ a.u.

4. For each set of initial parameters, i.e. $(I, T, \nu)$, 10000 trajectories are propagated with the initial conditions for the respective $\nu$ as described in Sec. 3.4.1 in order to guarantee a good statistics for the desired quantities, i.e. dissociation and ionization probabilities.

It remains to analyze the parameterization of the ionization rates (3.23) before application of the model to actual problems. The results are shown in Figure 3.15 for two intensities, comparing the parameterization with the full NA-QMD rates. The first peak around $R \approx 5$ a.u. is connected to the $1\omega$-resonance, while we attribute the strong ionization region at higher internuclear distances to charge-resonance enhanced ionization (CREI) [94,95]. In addition, the ionization rate depends dramatically on the laser intensity as discussed before: doubling the laser intensity increases the ionization rate by nearly one order of magnitude. We observe an overall good performance of the parameterized ionization rates in comparison to the NA-QMD ones. Some minor deviations, however, manifest themselves in the angular dependence of the rates, i.e. an increase of the rate towards $\theta = 90^\circ$ in the NA-QMD results around $R \approx 9$ a.u. for the higher intensity [see Figure 3.15 (a)]. The simple parameterization (3.23) neglects these more complicated angular dependencies.

With this, we benchmark the model against more sophisticated dynamical calculations, i.e. nuclear quantum mechanical and NA-QMD calculations.
3.4 A simplified model for the laser-induced dynamics of $H_2^+$

Figure 3.15: Fixed-nuclei ionization rates (multiplied by a factor of 1000) in a cw-laser with $\lambda = 800$ nm and intensity $I = 2 \cdot 10^{14} \text{ W cm}^{-2}$ (a,b) and $I = 1 \cdot 10^{14} \text{ W cm}^{-2}$ (c,d): full NA-QMD calculation and parameterization according to (3.23). Note the strong dependence of ionization on laser intensity, i.e. the ionization rate changes by one order of magnitude, when the laser intensity is doubled.

Comparison with exact quantum mechanical results The comparison of the model results without ionization to nuclear quantum dynamics is shown in Figure 3.16 for the peak intensities and pulse lengths, which we have considered in this chapter before. The agreement of the dissociation probabilities is very good for nearly all vibrational levels despite the classical approximation for the nuclei. The model thus clearly captures all the relevant multiphoton effects due to the non-perturbational treatment of nuclear dynamics as well as the correct intensity and pulse length dependence of dissociation. The multiphoton contributions can be extracted approximately via the scheme given in Appendix A.2.

Comparison with NA-QMD results We also compare the full FC-averaged NA-QMD results given in Section 3.3.3 to our model. This is shown in Figure 3.17 for the two peak intensities $I_0 = 2 \cdot 10^{14} \text{ W cm}^{-2}$ and $I_0/2$ in dependence on the pulse length. The model reproduces the correct pulse length dependence for dissociation and ionization at both peak intensities, where the agreement is nearly perfect for the lower intensity. For the higher peak intensity, however, the dissociation probability is underestimated and the ionization probability overestimated to some extent. The trend is nevertheless reproduced correctly. In addition we mention that the interplay of ionization and rotation time scales, which has been discussed in Section 3.3.1, is reproduced correctly by the model as well.

In consequence, despite the approximations made in the construction of the model, it appears to be quite accurate in comparison to the full calculations. This is true in particular
Figure 3.16: Model (blue circles) and nuclear quantum dynamics results (black squares) for vibrationally resolved dissociation probabilities $P_D(\nu)$ at peak intensities $I_0 = 2 \cdot 10^{14} \text{ W cm}^{-2}$ (a-c) and $I_0/2$ (d-f).

Figure 3.17: Classical model (straight lines) and NA-QMD results (squares) for Franck-Condon averaged ionization probabilities $P_I$ (red) and dissociation probabilities $P_D$ (green) at peak intensities $I_0/2$ (a) and $I_0 = 2 \cdot 10^{14} \text{ W cm}^{-2}$ (b).

for lower laser intensities, which dominate the focal volume intensity average. In this case, the model even reaches a reasonable quantitative accuracy.

3.4.3 Comparison with experiment

In the experiment [40], dissociation and ionization of $H_2^+$ ($\lambda = 800$ nm) have been studied for two different pulse lengths, i.e. a "short" pulse with 45 fs FWHM and a "long" pulse with 135 fs FWHM, at a peak intensity of approximately $2.5 \cdot 10^{14} \text{ W cm}^{-2}$. Key observations include the absence of ionization for the longer pulse as well as a small dissociation-to-ionization ratio, i.e. ionization has been found to be an order of magnitude smaller than dissociation in that experiment. In the following, we contrast these findings with our model results under these laser conditions.
First, we analyze the behavior of dissociation and ionization in dependence on the laser peak intensity for the two pulse lengths. The corresponding total FC-averaged probabilities are presented in Figure 3.18. Both dissociation and ionization depend strongly on intensity, the latter more dramatically (note the logarithmic scale for $P_I$). In the regime of high laser intensities, the dissociation probability has a maximum and decreases for larger intensities due to the competition with the ionization channel. The position of this maximum as well as the maximum dissociation probability depend on the pulse length: the maximum is located at a higher intensity for the shorter pulse, as competing ionization is smaller, and maximum dissociation is larger for the short than for the long laser pulse. For the largest intensities shown, $P_I$ nearly reaches 1, whereas dissociation disappears. Consequently, also the dissociation-to-ionization ratio decreases dramatically.

<table>
<thead>
<tr>
<th>$I[10^{14} \text{ W/cm}^2]$</th>
<th>$P_I$</th>
<th>$P_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 fs 135 fs</td>
<td>45 fs 135 fs</td>
<td>45 fs 135 fs</td>
</tr>
<tr>
<td>1 0.006 0.025</td>
<td>0.096 0.124</td>
<td></td>
</tr>
<tr>
<td>2 0.033 0.081</td>
<td>0.122 0.127</td>
<td></td>
</tr>
<tr>
<td>4 0.099 0.155</td>
<td>0.120 0.117</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4: Intensity-averaged ionization and dissociation probabilities for some selected peak intensities according to Figure 3.18.

The results in Figure 3.18 are calculated for fixed laser peak intensities. A serious
comparison with the experiment [40] requires to take into account the spatial intensity profile of the laser, i.e. focal volume averaging. Under the assumption of a spatial Gaussian distribution, which is consistent with the measurement, intensity averaging of a probability \( P \) for our model reads (see e.g. [83])

\[
\bar{P} = \frac{\int \frac{dI}{\bar{I}} P(I)}{\int \frac{dI}{\bar{I}}} = \frac{\int dx P(x)}{\int dx} \tag{3.27}
\]

with \( x = \ln(I) \). The intensity (and FC-) averaged ionization and dissociation probabilities for different focal peak intensities corresponding to Figure 3.18 are given in Table 3.4. We first notice that ionization increases dramatically with intensity for the shorter pulse, where the rate of increase goes down at higher peak intensity in agreement with experimental observations [40]. Dissociation, on the other hand, varies rather slowly and decreases for the highest peak intensity. This shows an opportunity for optimization of the dissociation yield as a function of the laser parameters. For the longer pulse, ionization is stronger than for the short pulse. This observation appears natural from simple intuition and has also been reported in the literature [111] (for different laser conditions), but is in clear contrast to the experiment [40] where no ionization at all has been measured for the long pulse. One may speculate about the reason for this discrepancy, possibly the experimental difficulty of determining the focal peak intensity together with the strong intensity dependence of ionization might represent one factor; this can be \( \sim \pm 50\% \) as discussed in [83]. The finite resolution in the measurement of KER spectra might also play a role. The total absence of ionization, however, remains a mystery. Nevertheless, we can conclude that ionization is much smaller than dissociation for the short pulse. Furthermore, our results indicate a maximum ionization yield at a KER of \( \sim 6 \) eV and a maximum dissociation yield at a KER of \( \sim 0.5 \) eV for the short pulse in reasonable agreement with the experiment [40].

In conclusion, we have been able to confirm the dominance of dissociation over ionization observed experimentally [40] using a simple classical model by calculating the corresponding focal volume average directly which extends the discussion in Section 3.3.3. While this has been possible at low computational cost, the simple model has some drawbacks. Minor limitations are the classical description of the nuclei as well as the rough description of geometric alignment due to the parameterization (3.23). The most severe limitation is the mean-field description of dissociation, which prohibits the calculation of accurate KER spectra for the dissociation channel and, consequently, for the ionization channel as well. Despite that, the model has been shown to be accurate for the calculation of total dissociation and ionization probabilities.
3.5 Summary

In this chapter, we presented a complete study of laser-induced ionization and dissociation of $\text{H}_2^+$ including all degrees of freedom using the NA-QMD method [41, 42]. By comparison of the results to nuclear quantum dynamics, we have shown that the NA-QMD approach allows for a good description of the angular distributions of dissociated fragments and the total dissociation probabilities as a function of the initial vibrational excitation [41]. A scheme to resolve multiphoton contributions in the probabilities within NA-QMD has been introduced as well. This and the time-dependent field-dressed quantum mechanical approach (FBO) have allowed for a direct connection of the initial vibrational level to the final Floquet channel. Whereas for low initial $\nu$, the $2\omega$ Floquet surface is needed to explain the dissociation dynamics, for intermediate $\nu$ the $1\omega$ surface and for high $\nu$ the $0\omega$ surface plays the decisive role. The FBO approach also enabled us to follow the wave packet on each time-dependent Floquet surface directly and evaluate the role of nuclear rotation in multiphoton dissociation.

The central finding in this chapter is the intricate and important role of nuclear rotation in the ionization of $\text{H}_2^+$ [42]. Ionization was enhanced up to an order of magnitude in the parameter regime we have investigated. The effect of rotation was determined by the competition of the optimum time scales for ionization, strongest at half pulse length, and rotation, i.e. the time it takes to align a molecule with the polarization axis where ionization is most effective.

The experimentally observed dominance [40] of dissociation over ionization manifested itself in the strong intensity dependence of the two fragmentation channels already in the NA-QMD results. We also introduced a simple but accurate model, which allowed us to confirm experimental observations directly by performing the focal volume intensity averaging, necessary due to the spatial intensity profile of the laser in the experiment, at a feasible computational cost [43].
4 NA-QMD: Orientation dependence of energy absorption and nuclear relaxation of C$_{60}$ in fs-laser pulses

In this chapter, we present a full-dimensional study of the energy deposition process of C$_{60}$ in a short laser pulse as a function of the molecular orientation with respect to the laser polarization direction [44]. We utilize the mixed quantum-classical NA-QMD method for this purpose. After a short introduction into the field, we describe the computational details for our calculations in Section 4.1 and provide a basis set capable of accurately reproducing important ground state and optical properties of C$_{60}$. With this, we investigate the orientation dependence of energy absorption in Section 4.2. Finally, in Section 4.3, the consequences of this orientation dependence on the subsequent energy redistribution process among the nuclear degrees of freedom are analyzed.

4.1 Introduction

Since its discovery in 1985 [112], the Buckminster fullerene C$_{60}$ has been investigated intensively in many fields of physics, chemistry and related areas. With its well defined, highly symmetric structure and the large number of nuclear and electronic degrees of freedom, C$_{60}$ has become an ideal model system to study structural, electronic and dynamical properties of complex atomic many-body systems, such as electron transport in molecular systems [113–115], collisions between complex particles [116], cluster physics on surfaces [117] or laser-finite matter interaction [118]. Thereby, due to the nearly spherical symmetry, one would intuitively expect a minor impact of orientation effects on the underlying mechanisms or observed phenomena. And indeed, many laser and collision induced phenomena have been explained successfully within the spherical jellium approximation [119–127] or the infinitely conducting sphere model [128, 129].

In contrast, Gutierrez et al [115] found that the conductance across a C$_{60}$ junction between two carbon nanotubes changes with the orientation of the molecule with respect to the tubes over several orders of magnitude. Furthermore, it has been observed experimentally [130], that the fusion cross section in fullerene-fullerene collisions is several orders of magnitude smaller than that of the expected geometrical one. This is due to the fact
that only very few and specific relative orientations between pentagons and hexagons of
the colliding clusters contribute to fusion, as theoretically explained by quantum molecular
dynamics calculations [16, 131, 132]. A recent experiment by Daughton et al. [117] suggests
that the charge transfer to C$_{60}$ at surfaces depends on the molecular orientation as well. To
what extent the molecular orientation plays a role in the laser-induced fullerene dynamics
is still an open question.

The response of C$_{60}$ to short intense laser pulses is a subject of great current interest.
Due to the availability of powerful laser sources, experiments were able to uncover a variety
of interesting phenomena determining laser induced fragmentation and ionization dynamics
[133–136]. As a key laser parameter, the laser pulse length compared to the electron-phonon
timescale ($\sim 150–300$ fs) influences the competition between ionization and fragmentation.
For long laser pulses (in the ns-regime), bimodal mass spectra have been measured, featuring
fullerene-like C$_{60-2m}$ and smaller C$_n$ fragments, which has been understood as statistical
(thermal) process, as enough time is available for energy transfer to the vibrational degrees of
freedom. This process is characterized by emission of carbon dimers and may proceed on long
time scales (ns, $\mu$s or even ms) [134]. In contrast, the dynamics in short laser pulses (sub-ps)
is much more intricate as different relaxation channels overlap: single and multiple ionization
as well as thermal and non-thermal fragmentation. Furthermore, above threshold ionization
(ADI) [137] and the excitation of Rydberg states [138] have been observed, which manifest
themselves as multi-electron mechanisms. On the theoretical side, different approaches
have been utilized in order to gain insight into these experiments. E.g., Beu et al. [139, 140]
have shown by means of tight-binding molecular dynamics calculations, that the amount
of energy deposited into the system clearly decides about the shape of the final fragment
size distribution. In [35] it was shown that the period and the amplitude of the laser-
excited $A_g(1)$ "breathing" mode depends strongly on the energy absorbed by the C$_{60}$ molecule.
Consequently, the amount of absorbed energy can be viewed as a key quantity which decides
about the subsequent nuclear relaxation mechanism.

The most striking feature of fs-pulses (in contrast to ps-pulses) concerns the lack of small
fragments and the predominant abundance of intact, multiply charged fullerene ions in the
experimental mass spectra of the photofragments [141]. It has been argued [141] that most
of the absorbed energy remains in the electronic system preventing fragmentation even at
intensities as large as $I \approx 10^{14}$ W cm$^{-2}$. This argument has been supported by pump-probe-
control experiments where the excitation of the giant $A_g(1)$ "breathing" mode has been
identified as one of the nuclear relaxation pathways [35]. This vibrational mode assimilates
only a few 10 eV of the total amount of electronically absorbed energy of several 100 eV [35].
However, a comprehensive understanding of the whole mechanism is still far from being
reached.

In this chapter we study the energy deposition process and subsequent nuclear relaxation
dynamics of C$_{60}$ in a laser pulse with the focus on the orientation of the molecule with respect
to the laser field's polarization direction [44]. The investigation and the corresponding demanding numerical calculations are performed on the basis of the Non-Adiabatic Quantum Molecular Dynamics (NA-QMD) method with the computational details outlined in Section 4.1.1. The energy absorption into the electronic system is studied in Section 4.2. The orientation dependence of the absorbed energy has dramatic consequences on the energy redistribution among the nuclear degrees of freedom, which is the topic of Section 4.3. In addition, based on the amount of energy deposited into C\(_{60}\), an interpretation of mass spectra in previous fs-regime experiments [134,135] is discussed and future experiments are proposed.

### 4.1.1 Computational details

The fullerene C\(_{60}\) is a prototype of a large finite system with a large number of degrees of freedom. It has 174 vibrational degrees of freedom and 240 valence electrons, where 180 of these are localized structure-defining \(\sigma\)-electrons and the remaining 60 are delocalized \(\pi\)-electrons giving rise to complex photophysical processes [134]. In its equilibrium geometry, it has the shape of a truncated icosahedron and belongs to the \(I_h\) point group.

In order to perform the investigations in this chapter, we use the NA-QMD method with the adiabatic local density approximation (ALDA) for the exchange correlation term in (2.31). The local basis set we utilize is build upon modified versions of the cc-pVDZ (here: 9s,4p) and DeMon Coulomb Fitting (here: 8s) Gaussian basis sets [142–144] for the description of the carbon atoms and their density. These Gaussian basis sets are used to construct atomic basis sets of different size, i.e. including 4 (2s,2p), 8 (2s,2p,3s,3p) and 12 (2s,2p,3s,3p,4s,4p) atomic orbitals. Note, that the 1s atomic orbital is kept frozen (frozen core approximation). In addition, an attractive potential \(V(r) = \left(\frac{r}{r_0}\right)^2\) with \(r_0 = 2.8\) a.u. is applied, which describes a pseudo atom and leads to a more accurate description of the molecular properties [73].

### 4.1.2 Ground state and optical properties

With the basis set provided in Section 4.1.1, we calculate the main ground state and optical properties of C\(_{60}\). Table 4.1 shows the results for the equilibrium C\(_{60}\) radius \(R\), the two bond lengths \(a_5\) (hexagon-pentagon single bond) and \(a_6\) (hexagon-hexagon double bond) as well as periods of important vibrational normal modes (see also Appendix B.1): the two totally symmetric \(A_g\) modes, i.e. breathing mode \(A_g(1)\) and pentagonal-pinch mode \(A_g(2)\), and the oblate-prolate mode \(H_g(1)\). The first optically allowed excitation energy is also contained in Table 4.1. The calculated values agree very well the experimental ones and those obtained with the quantum chemistry program GAMESS [22]. Increasing the basis set size obviously leads to more accurate values for the vibrational normal mode periods and the first dipole allowed optical transition energy.
In [27], an approach to calculate the optical spectrum by a real-time NA-QMD propagation has been suggested. Therefore, a very short laser pulse \( \mathbf{E} = E_0 \delta(t) \) is applied to the molecule. The optical dipole spectrum is calculated from the imaginary part of the Fourier transform of the time-dependent electronic dipole moment \( \mathbf{d}_\text{el}(t) = \int d^3r \rho(r) \) and reads

\[
S(E) \sim E \Im \int dt e^{iEt - \kappa t} \mathbf{d}_\text{el}(t) \tag{4.1}
\]

where \( \kappa \) is a damping factor, which gives a minimum width of the peaks and represents an approximate way to account for peak broadening connected with vibrational motions [151].

Experimentally, the photoabsorption cross section \( \sigma(E) \) is measured, which is proportional to the dipole strength function \( S(E) \). In our calculations, we use a numerically short \( \sin^2 \)-shaped laser pulse with total length \( T = 0.2 \) a.u. to mimic the \( \delta \)-pulse, and propagate (2.44) to a final time \( t_f = 14000 \) a.u. (\( \approx 338 \) fs) with the nuclei kept fixed in the ground state equilibrium geometry. The optical absorption spectrum of \( C_{60} \) is shown in Figure 4.1. In the low energy region [panel (a)], the experimental excitation energies are reproduced quite well with increasing basis set size except for a small downshift in energy, which is probably connected to the experimentally present electron-phonon coupling [150]. The resonances for the smallest basis set (4 AO) are shifted towards higher energies compared to those obtained from the larger basis sets, however, they exhibit comparable dipole strength, especially in the optical regime. The spectrum shows an intense peak region around 20 eV [panel (b)], which has been attributed to the plasmon resonance (see also [152, 153]). Also in this case, the overall shape of the experimental spectrum is reproduced well by the NA-QMD approach.

**Figure 4.1:** Optical absorption spectrum of \( C_{60} \) in dependence on basis set size (4, 8, 12 AO) as well as experimental values [149,150] of the lowest optically allowed transition energies (a) where the dotted curves represent the absorption spectra scaled by a factor of 200 for the low energy region (\( \kappa = 0.001 \) a.u.). Panel (b) shows the absorption spectrum including higher dipole excitations above the ionization threshold up to 40 eV (\( \kappa = 0.01 \) a.u.); experimental curve taken from [152].
4.2 Orientation dependence of energy absorption

The first dipole-allowed transition of C$_{60}$, i.e. from the highest occupied molecular orbital HOMO to the lowest unoccupied molecular orbital LUMO+1, can be excited by a laser pulse with wavelength $\lambda \approx 400$ nm (see Section 4.1.2). We therefore focus on the energy deposition process of C$_{60}$ in a resonant ($\lambda = 400$ nm) and a non-resonant ($\lambda = 800$ nm) laser pulse in order to reveal a possible wavelength dependence. In the remainder of this chapter, we use a linearly polarized laser pulse with varying polarization direction given by

$$E(t; \theta, \phi) = E_0 \sin^2 \left( \frac{\pi t}{T} \right) \cos \omega t \left[ \cos \phi \sin \theta \, e_x + \sin \phi \sin \theta \, e_y + \cos \theta \, e_z \right] \quad (4.2)$$

with amplitude $E_0$, pulse length $T$, fundamental frequency $\omega$. The polarization angles $\phi$ and $\theta$ describe the polarization direction of the electric field with respect to a fixed molecular position or, equivalently, the different orientations of the molecule in a settled linearly polarized laser field (see sketch on the top of Fig. 4.2).

The absorbed energy in a short laser pulse with pulse length $T = 10$ fs in the weak field regime, i.e. $\mu$eV respectively meV energy absorption, in dependence on the laser polarization direction is shown in Figures 4.2 (a,b) for the non-resonant and resonant case. The results are calculated using the smallest basis set (4 AO) with fixed nuclei, which is a valid approximation, as nuclear motion is negligible in the presence of the short laser pulse. It can be seen clearly that the energy absorption depends on the orientation angles in a quite regular way connected with the molecular structure in both cases with maximal absorption in hexagons and minimal absorption in pentagons. The extent of this orientation dependence, however, appears to be quite different. By looking at the relative absorbed energy, i.e. the absorbed energy normalized to the maximum absorbed energy, we see that the molecular orientation is crucial in the non-resonant case with even up to $\sim 30\%$ reduction with respect to maximum absorbed energy, whereas it is negligible in the resonant case with just maximally $\sim 0.5\%$ reduction with respect to maximum absorbed energy. In the strong field regime [Figures 4.2 (c,d)], i.e. typical energy absorption in the eV-range, these features survive. Again they are significant in the non-resonant case only with up to $\sim 30\%$ reduction with respect to maximum absorbed energy. As the orientation dependence is much stronger in the non-resonant case, we only focus on this one in the following.

In order to verify the quality of these observations, we also analyzed the energy absorption pattern in dependence on the basis set size. This is shown in Figure 4.3 for an intensity $I = 2.0 \cdot 10^{13}$ W/cm$^2$. Evidently, the orientation dependence holds for the larger basis sets. However, the magnitude of total absorbed energy is different which can be understood in the weak-field regime on the basis of the dipole response in Figure 4.1 (a). At an energy of 1.55 eV, which corresponds to $\lambda = 800$ nm, the dipole strength is much larger for the basis sets with 8 AO or 12 AO than for the smallest one with 4 AO. Correspondingly, this translates into the behavior of the absorbed energies.
While this orientation dependence is observed and verified by basis set studies, the physical reason behind it is intricate. First of all, the HOMO is 5-fold and the LUMO+1 is 3-fold degenerate, which already leads to a total of 15 dipole matrix elements of these orbitals within the bare Kohn-Sham framework. These may overlap in a complicated way under an actual laser field. Perturbation theory did not help to draw a clear picture of neither absorption pattern nor difference between resonant and non-resonant excitation. At this point we mention that we observed a weak variation of the dipole response in the resonant ($\sim 1\%$) and a stronger variation in the non-resonant case ($\sim 10\%$) based on the real-time calculation of the optical spectrum (as in Section 4.1.2). The angle-dependent pattern, however, suffers from poor statistics, a problem which is not present when studying the absorbed energy in the weak-field regime.
4.2 Orientation dependence of energy absorption

Table 4.1: Ground state properties of C_{60} and first optically allowed excitation energy in dependence on basis set size as well as experimental values. The respective normal modes are indicated above the Table by arrows for the nuclear displacements: breathing mode A_g(1), pentagonal-pinch mode A_g(2), and oblate-prolate mode H_g(1). The Table also contains results calculated with GAMESS using the 6-31G basis set and LDA for the exchange-correlation part, where the excitation energy has been determined by LR-TDDFT.
Orientation dependence of the absorbed energy $E_{\text{abs}}$ normalized to its maximum value $E_{\text{abs}}^{\max}$ (given in each figure) in a linearly polarized laser field $\mathbf{E}(t; \theta, \phi)$ with different laser parameters ($T = 10$ fs in all cases): (a) $\lambda = 800$ nm and $I = 1.0 \cdot 10^{13}$ W cm$^{-2}$, (b) $\lambda = 400$ nm and $I = 1.0 \cdot 10^{13}$ W cm$^{-2}$, (c) $\lambda = 800$ nm and $I = 1.2 \cdot 10^{14}$ W cm$^{-2}$, (d) $\lambda = 400$ nm and $I = 1.2 \cdot 10^{14}$ W cm$^{-2}$. The black dots indicate the positions of the carbon atoms (view on yz-plane, cf. sketch on the top of the Figure, where we have slightly rotated the molecule for a complete definition of the polarization and orientation angles). The results have been calculated using the smallest basis set (4 AO) and the fixed-nuclei approximation.
Figure 4.3: Orientation dependent absorbed energy of C$_{60}$ in a linearly polarized laser field with $T = 10$ fs and $I = 2 \cdot 10^{13}$ W/cm$^2$ calculated using a basis set with 4 AO (a), 8 AO (b) and 12 AO (c). The black dots indicate the positions of the carbon atoms.
4.3 Laser-induced nuclear relaxation dynamics of $^{60}$C

The question in the following is what impact the orientation dependence of energy absorption for a non-resonant laser pulse ($\lambda = 800$ nm) as discussed in Section 4.2 can have on subsequent nuclear relaxation dynamics. We use $\Delta t \approx 0.24$ fs as classical time step and the smallest basis set with 4 AO for the investigations including nuclear motion, as this basis set has shown to give qualitatively correct results concerning the orientation dependence of energy absorption (see Section 4.2). Initially, $^{60}$C is in its ground state equilibrium geometry.

4.3.1 Pulse length dependence of normal mode excitation

We first analyze the connection between energy absorption and nuclear dynamics for a fixed polarization direction, which is chosen parallel to the $C_5$ symmetry axis of $^{60}$C for computational efficiency.

![Figure 4.4: Total kinetic energy and selected normal mode contributions for different laser pulse length.](image)

Therefore, we study the laser-induced normal modes (see also Appendix B.1) in dependence on the pulse length of the laser and the absorbed energy. We choose a "short" ($T = 10$ fs), "medium" ($T = 54$ fs) and "long" pulse ($T = 80$ fs). This choice is motivated by previous research [154], where it has been shown that vibrational normal mode excitation in the weak field regime can be controlled by the pulse length. According to that work, the "short", "medium" and "long" pulse correspond to dominant $A_g(2)$, $A_g(1)$ and $H_g$ normal mode excitation, respectively. In Figure 4.4, the total kinetic energy and selected normal modes are shown for different laser intensities and the three pulse lengths. In the weak field...
regime, we indeed observe the three normal modes appearing dominantly for the respective pulse lengths, which confirms the findings of [154]. In contrast, for strong laser pulses, the $A_g(1)$ mode is dominant for all pulse lengths considered. Thus, no control of vibrational normal mode excitation is possible in the strong field regime. In [35] it has been shown that the period of the $A_g(1)$ mode increases with the energy deposited into the molecule by the laser pulse. This also holds for the $A_g(2)$ and $H_g(1-5)$ modes as can be seen clearly in Figure 4.5: The periods of these normal modes increase with the absorbed energy, i.e. the $A_g(1)$ period from 63 fs to 80 fs, the $A_g(2)$ period from 21 fs to 25 fs, and the $H_g(1)$ period from 114 fs to 170 fs. Above an absorbed energy of $E_{abs} \approx 500$ eV the molecule fragments in any case.

![Figure 4.5](image)

**Figure 4.5:** Periods of the $A_g(1)$, $A_g(2)$ and $H_g(1)$ vibrational normal modes in dependence on absorbed energy for different laser pulse length.

### 4.3.2 Orientation dependence of nuclear relaxation dynamics

After we have connected the absorbed energy with normal mode excitation in dependence on the pulse length, we now focus on the role of the molecular orientation with respect to the laser polarization direction in the nuclear relaxation dynamics. We choose a long and strong laser pulse with total pulse length $T = 54$ fs and peak intensity $I = 6.2 \cdot 10^{14}$ W cm$^{-2}$, which corresponds to the "medium" pulse length in Section 4.3.1. With this choice, nuclear motion will massively affect the energy deposition mechanism and may lead to fragmentation in the after-pulse nuclear dynamics.
Figure 4.6: Laser polarization direction dependent absorbed energy of C$_{60}$ normalized to its maximal value (given in each figure) in a linearly polarized laser field with (a) fixed and (b) moving nuclei ($T = 54$ fs, $I = 6.2 \cdot 10^{14}$ W cm$^{-2}$, $\lambda = 800$ nm). The black dots indicate the positions of the carbon atoms.

At first we inspect the energy absorption pattern, comparing the results without and with nuclear motion in Figure 4.6. The energy absorption pattern changes clearly when increasing the pulse length from $T = 10$ fs (Section 4.2) to $T = 54$ fs [see Figure 4.6 (a)]. A change in the energy absorption pattern is maybe no surprise, as this is known qualitatively already from a simple two-level system, where the population transfer between the two energy levels and, thus, energy absorption depends on the ratio between the pulse length and the intrinsic Rabi period. We also clearly see that nuclear motion is not negligible anymore during energy deposition by the laser field [compare Figures 4.6 (a,b)], as the absorption pattern changes and the absorbed energy increases: the maximum values of $E_{\text{abs}}$ are increased from $E_{\text{abs}}^{\text{max}} \approx 400$ eV [Fig. 4.6 (a)] up to about $E_{\text{abs}}^{\text{max}} \approx 600$ eV [Figure 4.6 (b)]. The latter can be understood from the optical spectrum, which is shifted towards larger polarizabilities with increasing cluster radius due to $A_g(1)$ mode excitation, leading to a larger amount of absorbed energy. The total effect of the orientation dependence in this case is an up to $\sim 50\%$ reduction with respect to maximum absorbed energy.

This strong orientation dependence may have dramatic consequences for the subsequent, i.e. after-pulse, nuclear relaxation dynamics. In Figure 4.7 the average C$_{60}$ radius is shown on the sub-ps timescale for selected orientations corresponding to the blue, green and red colored regions in Fig. 4.6 (b) and, thus, different absorbed energies ranges. It can be seen clearly, that in the presence of the laser pulse ($t \leq 54$ fs) the C$_{60}$ radius increases in all cases. Based on the normal mode analysis, we attribute this to the first quarter of the $A_g(1)$ breathing mode. The initial excitation of the breathing mode, observed in all our calculations independent of the orientation of the molecule, is the key feature of the earliest stage of the electron-vibration coupling mechanism in C$_{60}$. 

4.3 Laser-induced nuclear relaxation dynamics of C\textsubscript{60}

The long time behavior ($t \gtrsim 50$ fs) of the relaxation dynamics, however, depends on the orientation and on the amount of absorbed energy, with three main channels (see also Fig. 4.7):

(1) **breathing:** For orientations with relatively low energy absorption (blue areas and blue dotted lines in Figs 4.6 and 4.7, respectively) the breathing mode survives with amplitude and frequency depending on the actual electronic energy (cf. different dotted blue lines) in accord with our previous studies and experiment [35]. The present investigations deliver, in addition, a natural explanation for the weak pump-probe signal of this mode in the experimental spectra: For a given laser pulse and C\textsubscript{60} in the gas phase, all orientations of the cage will contribute simultaneously and, thus, all nuclear relaxation channels will do so.

(2) **isomers:** At intermediate absorbed energy (green) highly deformed but still stable complexes are formed with a nearly constant average C\textsubscript{60} radius $\sim 7.5$ a.u. (cf. the equilibrium C\textsubscript{60} radius $\sim 6.7$ a.u.). These electronically excited isomeric states of C\textsubscript{60} are characterized by dominant excitations of vibrational “surface” modes which conserve the volume of the complexes. As in the former case (1), these isomers are also very stable on the sub-ps timescale, because only about one tenth of the total absorbed energy is transfered into vibrational energy (not shown). However, on longer, i.e. ps (or ns), timescales one expects fragmentation, mainly via C\textsubscript{2} evaporation.

(3) **fission:** For orientations with highest energy absorption (red), the cluster fragments basically into two, nearly equally sized large pieces (Fig. 4.7). As seen from the behavior of $R(t)$ in Fig. 4.7 the fission events are the direct consequence and continuation of the initially excited giant breathing mode. Evidently, the (nearly) symmetric fission channel is the energetically favored pathway of the nuclear relaxation. The strongly deformed cap-like fission fragments (Fig. 4.7) are highly unstable and are expected to decay into many small fragments C\textsubscript{n} ($n \lesssim 13$) on a ps timescale. As a fingerprint of fission and the most important feature for its experimental verification, our calculations show that this process evolves along the laser polarization direction (see Fig. 4.7).

In addition we note that the observed nuclear relaxation channels are connected to highly non-adiabatic multi-electron dynamics: many electrons are excited during the laser pulse and most of the absorbed energy remains in the electronic system ($200$ eV $- 400$ eV), while only a small amount of energy is contained in the vibrations ($10$ eV $- 80$ eV). Consequently, fragmentation proceeds as a non-thermal process in our results (see also discussion in Section 4.3.3).
Figure 4.7: $C_{60}$ radius $R$ as a function of time $t$ for different molecular orientations (dotted lines) in the same laser field ($T = 54$ fs, $I = 6.2 \cdot 10^{14} \text W \text{cm}^2$, $\lambda = 800$ nm) as used before (cf. Fig. 4.6). The colors (blue, green, red) correspond to typical orientations within the same colored regions of Fig. 4.6 (b) and, thus, belong to different energy absorption intervals given in the Figure. The full lines are the corresponding mean values of $R(t)$ and summarize the three different relaxation channels: (1) excitation of breathing modes (blue), (2) formation of non-breathing isomeric states (green), and (3) ultrafast almost symmetric fission (red). Typical snapshots of the dynamics at $t \approx 240$ fs corresponding to the three relaxation channels are shown on the top of the Figure using the same colors. The black arrows indicate the laser polarization axis [cf. Fig. 4.6 (b)]. Note, the fission process proceeds along the laser polarization direction.
4.3.3 Intensity dependence of nuclear relaxation dynamics

The laser intensity determines the amount of absorbed energy as well. In accordance with this, we observe different nuclear relaxation channels for different laser intensities (at a fixed molecular orientation and for pulse length $T = 54$ fs) as shown in Figure 4.8. As in the case of the orientation dependence, the absorbed energy decides about the relaxation channel in the after-pulse dynamics, i.e. fragmentation into two pieces, formation of a highly deformed stable complex, or dominant breathing motion. Figure 4.8 also reveals that the energy is deposited by the laser pulse mainly into the electronic system and only a small amount into vibrations, equivalently to the case of changing laser orientation (see Section 4.3.2).

![Figure 4.8](image)

**Figure 4.8:** $C_{60}$ radius $R$ (a), electronic excitation energy $E_{ex}^{el}$ (b) and vibrational kinetic energy $E_{vib}^{el}$ (c) for different laser intensities in a laser field with $T = 54$ fs. The laser polarization is set parallel to the $C_5$ symmetry axis.

Based on the different relaxation channels together with the varying amount of energy absorbed by $C_{60}$, one may speculate about later stages of the nuclear relaxation dynamics on the above-ps timescale. A relatively low amount of absorbed energy leads to stable $C_{60}$ on the sub-ps timescale and might be followed by $C_2$ evaporation at larger timescales \([155–157]\), which would be connected to typical fullerene-like fragments $C_{60−2m}$ in previous experiments, or no fragmentation at all. On the other hand, the fragmentation into two pieces may be seen as a transient to multi-fragmentation, leading to small $C_n$ fragments in experimental mass spectra. This interpretation is also in close correspondence with
tight-binding simulations by Li et al [157], which featured fullerene-like fragments for low and multi-fragmentation patterns for high energy absorption. Although ionization is not included in our calculations, this interpretation is consistent with previous experimental results (Figure 16 in [134]) taking into account the effects of focal volume and orientation dependence on the energy deposition process as well: using a laser pulse with $\lambda = 800$ nm and $T = 50$ fs, no fragmentation has been observed at laser intensities $I = 3.8 \cdot 10^{13} \text{ W cm}^{-2}$, while strong fragmentation together with the occurrence of small fragments $C_n$ with $n \lesssim 13$ is observed at a peak intensity $I = 6.0 \cdot 10^{14} \text{ W cm}^{-2}$. In our calculations, the former case corresponds to energy absorption $E_{\text{abs}} < 1$ eV, while the latter case (with $E_{\text{abs}} \approx 500$ eV) corresponds indeed to the fragmentation scenario discussed in this section. Obviously, a decrease of the intensity would necessarily lead to the absence of the fission (and thus final multi-fragmentation) channels. We also mention that transient carbon clusters as a precursor for the small $C_n$ fragments (with $n = 1, 2, 3$) have also been measured in [135].

4.4 Summary

In this chapter, we have investigated the orientation dependence of the excitation and relaxation mechanism of $C_{60}$ in a linearly polarized laser field [44]. Using the NA-QMD method we found surprisingly:

(i) The energy deposition depends strongly on the molecular orientation with respect to the laser polarization axis. In particular, the total effect of this orientation dependence concerning the variation of the energy absorption is strong in case of a non-resonant laser pulse with $\lambda = 800$ nm, whereas it is negligible for the resonant case with $\lambda = 400$ nm.

(ii) The initial stage of the electron-vibration coupling is overwhelmingly dominated by a blow-up of the cage radius (corresponding basically to the excitation of the first quarter of the giant $A_g(1)$ breathing mode), independent of orientation and laser parameters. Therefore, selective normal mode excitation, as it can be controlled in the weak-field regime, is not possible in the strong-field regime.

(iii) The long-time nuclear relaxation mechanism is determined (mainly) by the absolute amount of absorbed energy and, thus, depends (for a fixed laser peak intensity) dramatically on the molecular orientation. We see three scenarios: (1) excitation of the long-living breathing modes, (2) formation of stable, non-breathing isomers, and (3) ultrafast fragmentation processes by splitting of the cage into two pieces on the sub-ps timescale.

Having identified the amount of absorbed energy as key quantity for subsequent nuclear relaxation, we have also provided an interpretation of mass spectra measured in previous experiments using short laser pulses in the fs-range.

The orientation dependence of the absorbed energy (i) can hardly be verified experimentally with $C_{60}$-targets in the gas phase. However, if $C_{60}$ is oriented on a surface (similar as in the experiments of Daughton et. al. [117]), we predict strong orientation dependent mass
spectra of the ablated fragments as a function of the laser polarization axis with respect to the surface.

The initial blow-up mechanism (ii) and the relaxation channels (iii) should be directly observable in future gas phase experiments. In particular, our calculations predict that the small fragments $C_n$ ($n \lesssim 13$) resulting from the fission channel will be preferentially emitted along the laser polarization axis. Thus, the fission channel can be identified by measuring the angular distribution of these fragments. Furthermore, the characteristic blow-up mechanism should be detectable in pump-probe experiments similar to that used to identify the breathing mode [35].

Finally, we mention that the investigations in this chapter are also the basis of experiments at the LCLS facility at SLAC planned for the future [158].
5 NA-QMD-H: Case study and applications

In this chapter, we focus on the relevance of electron-nuclear correlations and their need to be considered explicitly for a variety of scenarios on the basis of the novel NA-QMD-H approach developed in Section 2.3. First, we present a case study, where a minimal model system of $\text{H}^+ + \text{H}$ collisions is considered and full quantum mechanical calculations are available for comparison [59]. Second, we apply the new NA-QMD-H approach to atom-atom, atom-molecule and atom-cluster collisions, and will elaborate the electronic and vibrational excitation patterns also in comparison with existing, still unexplained experimental data [60]. Third, we consider the laser-induced dynamics of small organic molecules with the focus on the electronic and nuclear relaxation dynamics and compare our calculations with other methods [61].

5.1 Electron-nuclear correlations in atomic collisions

5.1.1 Case study: model system of $\text{H}^+ + \text{H}$ collisions

In order to obtain a first insight into the mechanism and consequences of the electron-nuclear correlations in non-adiabatic dynamics, we consider here the simplest case – an idealized model of $\text{H}^+ + \text{H}$ collisions, described in detail below [59]. The fundamental one-electron system, $\text{H}^+ + \text{H}$ respectively $\text{H}_2^+$, which served already as a case study in our previous work [25, 27], is in particular well-suited to deliver a transparent and pedagogically useful insight into the complex non-adiabatic mechanisms. Here, we will focus in particular on the basic differences of and the general similarities between the NA-QMD and NA-QMD-H formalisms, to reveal some principal effects of electron-nuclear correlations in atomic collisions. In addition, we will compare the predictions of both methods with those of exact quantum mechanical calculations.
Collision model

In order to make the approach as transparent as possible we apply the simplest atomic collision model for the H$_2^+$ system (see also [25]): Only central collisions are considered and a minimal (atomic and molecular) basis set is used that allows for non-adiabatic transitions.

In this case, the classical equations of motion of the NA-QMD (2.45) and NA-QMD-H (2.80) reduce to a one-dimensional problem for the internuclear distance \( R = |\mathbf{R}_1 - \mathbf{R}_2| \). The corresponding time-dependent KS-equations (2.44) or (2.79) reduce to the time-dependent Schrödinger equation (TDSE) for the expansion coefficients of the one-particle wave function \( \Psi^{\sigma}(\mathbf{r}, t) \equiv \Phi(\mathbf{r}, t) \) in the atomic basis expansion (2.34). However, here we use an adiabatic molecular basis expansion (2.64) for the representation of \( \Phi(\mathbf{r}, t) \).

This allows to perform exact quantum mechanical, NA-QMD and NA-QMD-H calculations on an equal footing.

The adiabatic molecular states \( \chi_a^{\sigma}(\mathbf{r}; R) \equiv \Phi_n(\mathbf{r}; R) \) and corresponding energy levels \( E_n^{\sigma}(R) \equiv E_n(R) \) in (2.65) are obtained from the solution of (2.70) using intentionally the smallest possible set of atomic hydrogen orbitals \( \phi_\alpha \) in (2.69) that may lead to excitations, i.e. the 1s- and 2s-functions centered on both nuclei, generating the four molecular states 1s\( \sigma_u \) \((n = 1)\), 2s\( \sigma_u \) \((n = 2)\), 1s\( \sigma_g \) and 2s\( \sigma_g \). Both \( \sigma_g \) states are then excluded from our model for two reasons: first, the \( \sigma_g \) states are essentially decoupled from the \( \sigma_u \) states; second, the \( \sigma_g \) states exhibit only a small non-adiabatic coupling. Consequently, the primary non-adiabatic mechanism remains unaffected by this choice, while the model is kept as simple as possible. The potential energy surfaces \( E_n(R) \) are shown in panel (a) of Figure 5.1 (black curves). These states exhibit an avoided crossing at \( R \approx 0.8 \) a.u. which is connected with a large non-adiabatic coupling \( D_{12}(R) \) as shown by the black curve in Figure 5.1 (b). This gives rise to the following non-adiabatic mechanism: starting initially on the lower potential energy surface (1s\( \sigma_u \) state) at large \( R \), the system moves towards the non-adiabatic transition region in the course of the collision dynamics, where the avoided crossing may give rise to non-adiabatic transitions to the 2s\( \sigma_u \) surface connected with a conversion of kinetic into electronic excitation energy.

The corresponding diabatic molecular basis set \( \{ \tilde{\Phi}_n(\mathbf{r}; R) \} \) provides the convenient framework for exact quantum mechanical calculations and is derived from the adiabatic basis set \( \{ \Phi_n(\mathbf{r}; R) \} \) by the so-called Smith rotation [159]

\[
\begin{pmatrix}
\tilde{\Phi}_1(\mathbf{r}; R) \\
\tilde{\Phi}_2(\mathbf{r}; R)
\end{pmatrix} = \begin{pmatrix}
\cos \theta(R) & \sin \theta(R) \\
-\sin \theta(R) & \cos \theta(R)
\end{pmatrix} \begin{pmatrix}
\Phi_1(\mathbf{r}; R) \\
\Phi_2(\mathbf{r}; R)
\end{pmatrix}
\]

(5.2)

under the condition of vanishing derivative couplings

\[
\left\langle \tilde{\Phi}_1(\mathbf{r}; R) \left| \frac{\partial}{\partial R} \right| \tilde{\Phi}_2(\mathbf{r}; R) \right\rangle = 0 .
\]

(5.3)
Correspondingly, the Smith rotation angle $\theta(R)$ is given by
\[
\theta(R) = \int_{R}^{\infty} dR' D_{12}(R') .
\] (5.4)

According to the orthogonal transformation (5.2), the corresponding diabatic potential energy surfaces $V_{mn}(R)$ and their respective coupling $V_{12}(R)$ are connected with the respective adiabatic quantities by
\[
V_{11}(R) = \cos^2 \theta(R) E_1(R) + \sin^2 \theta(R) E_2(R) \quad (5.5)
\]
\[
V_{22}(R) = \sin^2 \theta(R) E_1(R) + \cos^2 \theta(R) E_2(R) \quad (5.6)
\]
\[
V_{12}(R) = V_{21}(R) = [E_1(R) - E_2(R)] \cos \theta(R) \sin \theta(R) . \quad (5.7)
\]

The diabatic energy levels $V_{mn}(R)$ and their coupling $V_{12}(R)$ are also shown in Figure 5.1 (green curves). In contrast to the adiabatic energy levels $E_n(R)$, the diabatic potential energy surfaces cross in the non-adiabatic transition region (Fig. 5.1 (a)), whereas their coupling rather spreads over a large $R$-region in contrast to the strongly localized coupling $D_{12}(R)$ in the adiabatic framework (Fig. 5.1 (b)).

We will consider two quantities (observables): First, the mean total kinetic energy loss $\Delta E$ of the colliding system as a function of the center-of-mass impact energy $E_{cm}$, which in this case is equal to the mean transferred electronic excitation energy at a given $E_{cm}$ due to the lack of internal vibrational degrees of freedom; second, the differential kinetic energy spectra of both nuclei $P(E)$, i.e. the probability of measuring the relative kinetic energy $E$ between the nuclei in the exit channel.

![Figure 5.1: Energy levels of $H_2^+$ in the adiabatic and diabatic representation (a) as well as the respective couplings (b) in dependence on the internuclear distance $R$. They are obtained from QMD ground state calculations using the d-aug-cc-pV6Z Gaussian basis set [142–144] for numerical construction of the 1s and 2s atomic orbitals of hydrogen. Only the 1s$_{\sigma_u}$ and 2s$_{\sigma_u}$ states are considered, as discussed in the text.](image-url)
**Exact quantum mechanical calculations**

The one-electron nature of the collision model allows to perform relatively easy exact quantum mechanical calculations for the whole collision system. For this purpose, the diabatic representation is the convenient and practical framework (see above). Therefore, we expand the total wave function into the diabatic basis

$$\Psi(r, R, t) = \sum_{n=1}^{N} \Omega_n(R, t) \Phi_n(r; R).$$

Using this, we derive the coupled time-dependent Schrödinger equations for the nuclear wave function $\Omega_n(R, t)$

$$i \frac{\partial}{\partial t} \Omega_n(R, t) = \left[ -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{1}{R} \right] \Omega_n(R, t) + \sum_{m=1}^{N} V_{nm}(R) \Omega_m(R, t)$$

with the reduced mass $\mu = 918.0$ a.u.

The initial state is chosen as a traveling Gaussian starting from the $1s\sigma_u$ surface

$$\Omega_1(R, t=0) = \left( \frac{\pi \sigma^2}{2} \right)^{\frac{1}{4}} e^{i(R-R_0)P_{R_0} - \frac{(R-R_0)^2}{4\sigma^2}}$$

with width $\sigma = 0.7$ a.u., $R_0 = 20.0$ a.u. and an initial momentum $P_{R_0} = -\sqrt{2\mu E_{cm}}$ corresponding to a mean impact energy $E_{cm}$ of the wave packet.

Equation (5.9) is then solved numerically using the code WAVEPACKET [104] by expanding the wave function in a basis of plane waves and applying the split operator scheme [160]. We use an equally spaced radial grid with 2000 grid points ranging from 0.06 a.u. to 32.0 a.u. The time step is $\Delta t = 0.1$ a.u. The final time is set to $t_f \approx \frac{E_{cm}}{\sqrt{2\mu E_{cm}}} \cdot 40.0$ a.u., which represents an estimate of the return of the wave packet to its initial center.

The mean kinetic energy loss

$$\Delta E = \bar{E}_{\text{kin}}(t=0) - \bar{E}_{\text{kin}}(t_f)$$

is calculated from the expectation values of the kinetic energy

$$\bar{E}_{\text{kin}}(t) = \sum_{n} \int_{R=0}^{\infty} dR \Omega_n^*(R, t) \left[ -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} \right] \Omega_n(R, t)$$

with $\bar{E}_{\text{kin}}(t=0) \equiv E_{cm}$. The differential kinetic energy spectrum $P(E)$ of the nuclei is obtained from the momentum representation of the nuclear wave function at $t = t_f$ as

$$P(E) = \frac{1}{2\pi} \sum_{n} \left| \int_{R=0}^{\infty} dR e^{i\sqrt{2\mu E}R} \Omega_n(R, t_f) \right|^2.$$
5.1 Electron-nuclear correlations in atomic collisions

NA-QMD calculations

In contrast to the exact quantum mechanical approach (see above), the nuclear degrees of freedom are treated classically in NA-QMD and NA-QMD-H. In these methods, the adiabatic basis expansion (2.64) of the electronic wave function reads

$$\Phi(r, t) = \sum_{n=1}^{2} a_n(t) \Phi_n(r; R)$$  \hspace{1cm} (5.14)

with the adiabatic expansion coefficients $a_{n\sigma}^j(t) \equiv a_n(t)$. In the case of NA-QMD approach, this leads to the mixed quantum-classical equations of motion

$$\dot{a}_n(t) = -i E_n(R) a_n(t) - \sum_{m=1}^{2} \dot{R} \cdot D_{nm}(R) a_m(t)$$ \hspace{1cm} (5.15)

$$\dot{P}_R = -\frac{\partial E_{\text{surf}}(t)}{\partial R}$$

$$- \sum_{n,m=1}^{2} a_n^*(t) a_m(t) [E_n(R) - E_m(R)] D_{nm}(R)$$ \hspace{1cm} (5.16)

$$\dot{R} = \frac{P_R}{\mu}$$ \hspace{1cm} (5.17)

with the effective time-dependent potential energy surface [see (2.47)], but now in the adiabatic representation,

$$E(t) \equiv E_{\text{surf}}(t) = \sum_{n=1}^{2} |a_n(t)|^2 E_n(R) + \frac{1}{R}.$$ \hspace{1cm} (5.18)

The initial state is an ensemble of classical trajectories starting from the 1s$\sigma_u$ surface, i.e. $a_1(t = 0) = 1$. The initial internuclear distances $R$ and momenta $P_R$ are chosen randomly according to the Wigner distribution $W(R, P_R)$ of the quantum mechanical initial state (5.10)

$$W(R, P_R) = \frac{1}{2\pi} e^{-\frac{(R-R_0)^2}{2\sigma^2}} e^{-2\sigma^2 P_R - P_{R_0})^2}.$$ \hspace{1cm} (5.19)

corresponding to a central impact energy $E_{cm} = \frac{P_R^2}{2\mu}$, a mean initial distance $R_0 = 19.0$ a.u. and $\sigma = 0.7$ a.u. as in (5.10). This allows a meaningful comparison of the differential kinetic energy spectra $P(E)$ with the quantum mechanical spectra (5.13).

Equations (5.15)-(5.17) are integrated using a 4th-order Runge-Kutta scheme with a time step $\Delta t = 0.01$ a.u. The final time $t_f$ is defined by $R(t_f) = R_0$, i.e. the return of the trajectory to its starting point after scattering. For convergence, a total of $N_{\text{traj}} = 1000$ trajectories with different initial conditions $R$ and $P_R$ for each impact energy $E_{cm}$ is sufficient.

The kinetic energy loss is given by

$$\Delta E = E_{cm} - \bar{E}_{\text{kin}}(t_f)$$ \hspace{1cm} (5.20)
where $\bar{E}_{\text{kin}}(t_f) = \frac{1}{N_{\text{traj}} \cdot \text{trajectories}} \sum P_R(t_f)^2$ is the mean kinetic energy in the exit channel. The kinetic energy spectrum $P(E)$ is obtained from a smoothed histogram of the final kinetic energies $E = \frac{P_R(t_f)^2}{2\mu}$ corresponding to different initial conditions.

**NA-QMD-H calculations**

Analogously, starting from the basis expansion (5.14), the equations of motion for the NA-QMD-H method are

$$\dot{a}_n(t) = -iE_n(R)a_n(t) - \sum_{m=1}^{2} \hat{R} \cdot D_{nm}(R)a_m(t)$$  \hspace{1cm} (5.21)

$$\dot{P}_R = -\frac{\partial E_{\text{surf}}^n(R)}{\partial R} \text{ with } n = 1 \text{ or } 2$$  \hspace{1cm} (5.22)

$$\dot{\hat{R}} = \frac{P_R}{\mu}$$  \hspace{1cm} (5.23)

with the *actual time-independent* potential energy surface [see (2.78)]

$$E_{a_1...a_{N_e}} \equiv E_{\text{surf}}^n(R) = E_n(R) + \frac{1}{R}.$$ \hspace{1cm} (5.24)

The change of the surface is enabled via Tully hopping and the general quantities (2.82), (2.83) and (2.84) reduce to

$$g_{nm} = \frac{B_{mn}}{A_{mn}} \Delta t$$ \hspace{1cm} (5.25)

$$A_{mn} = a^*_n a_m$$ \hspace{1cm} (5.26)

$$B_{mn} = -2 \text{Re}(A_{mn} D_{mn} \cdot \dot{\hat{R}})$$ \hspace{1cm} (5.27)

The system switches from $E_{\text{surf}}^n(R)$ to $E_{\text{surf}}^m(R)$, if two conditions are fulfilled [cf. (2.87)]:

(i) $\zeta < g_{nm}$, where $\zeta$ is a uniform random number ($0 \leq \zeta \leq 1$),

(ii) there is a sufficient amount of kinetic energy, i.e. $\frac{P_R(t_f)^2}{2\mu} > E_{\text{surf}}^m(R) - E_{\text{surf}}^n(R)$.

In case of a switch, the kinetic energy is adapted by momentum rescaling.

The initial conditions, numerical parameters for solving equations (5.21)-(5.23) as well as the definition of the kinetic energy loss $\Delta E$ and kinetic energy spectra $P(E)$ are the same as in the NA-QMD calculations (see above). For convergence, however, a total of $N_{\text{traj}} = 10000$ trajectories for each impact energy $E_{cm}$ is necessary because for each initial condition $R$ and $P_R$ an ensemble of trajectories has to be considered, in addition.
5.1 Electron-nuclear correlations in atomic collisions

Results and discussion

Due to the simplicity of the model (two states with the lower state as the initial one, one avoided crossing passed twice, no internal vibrational degrees of freedom), the results, shown in Figure 5.2, can be interpreted and understood in detail.

In Figure 5.2 (a), the mean kinetic energy loss $\Delta E$ as a function of the impact energy $E_{\text{cm}}$ is presented. Evidently, the results obtained in all three methods are qualitatively and quantitatively the same. At low impact energy $E_{\text{cm}} \lesssim 35$ eV, the collision proceeds elastically with zero energy loss and, thus, no electronic excitation. With increasing $E_{\text{cm}}$, non-adiabatic transitions to the higher potential energy surface $E_{\text{surf}}^2(\infty)$ become important and the energy loss reaches a maximum at $E_{\text{cm}} \approx 74$ eV with $\Delta E \approx 9$ eV corresponding almost to the asymptotic difference in the potential energy surfaces $E_{\text{surf}}^2(\infty) - E_{\text{surf}}^1(\infty) \approx 10$ eV (see Figure 5.1 (a)), and, thus, to the maximal possible energy loss. Hence, this maximum appears due to a constructive interference of electronic transitions of the first and second passing of the non-adiabatic coupling region (with final state populations $|a_2(t_f)|^2 \approx 1$ and $|a_1(t_f)|^2 \approx 0$) and can be qualitatively understood already within Landau-Zener-Stückelberg theory [25, 161]. At larger impact energies $E_{\text{cm}} \gtrsim 74$ eV, the optimal conditions for this constructive interference disappear, leading to a natural decrease of $\Delta E$ with increasing $E_{\text{cm}}$ [161]. Summarizing this part, from the present analysis one can conclude that electron-nuclear correlations do not show up as long as integral quantities (like $\Delta E$) are considered.

The situation is changed drastically when more differential quantities, like the kinetic energy spectra of the nuclei $P(E)$, are considered. In Figure 5.2 (b), these spectra are shown for three impact energies ($E_{\text{cm}} = 50, 80,$ and $129$ eV). The (correct) quantum mechanical results generally exhibit a double peak structure (corresponding to the two possible reaction channels within the model), with one peak centered at $E_{\text{cm}}$ (elastic scattering) and the second one at $E_{\text{cm}} - (E_{\text{surf}}^2(\infty) - E_{\text{surf}}^1(\infty)) \approx E_{\text{cm}} - 10$ eV (inelastic scattering). Thereby, the relative peak heights measure the degree of inelasticity: In the weakly non-adiabatic region I (with $E_{\text{cm}} = 50$ eV and $\Delta E \approx 2.8$ eV), the elastic peak dominates over the inelastic one, whereas the opposite is the case in the optimal transfer region II (with $E_{\text{cm}} = 80$ eV and $\Delta E \approx 8.6$ eV). In the high-energetic region III (with $E_{\text{cm}} = 129$ eV and $\Delta E \approx 4.5$ eV) again the elastic peak height exceeds the inelastic one.

In contrast (and as expected), the NA-QMD results exhibit generally only one (average) peak with peak positions, however, corresponding to the mean values of the double-humped quantum mechanical distributions. The spectra obtained within the NA-QMD-H approach reproduce (somewhat surprisingly) quantitatively the exact quantum mechanical results, demonstrating that for this toy model the surface hopping mechanism accounts completely for the quantum nature of the nuclear motion.
Figure 5.2: Kinetic energy loss $\Delta E$ (a) in dependence on the impact energy $E_{\text{cm}}$ and kinetic energy spectra $P(E)$ (b) taken at the three impact energies indicated in (a): 50 eV (I), 80 eV (II) and 129 eV (III).

5.1.2 Atom-molecule and atom-cluster collisions

In atom-atom collisions the amount of electronic excitation determines the dynamics, as we have demonstrated for the simplest case in Section 5.1.1. As an additional influence, ro-vibrational excitation in the molecular target may affect the scattering process in atom-molecule collisions. In this section, we investigate simple atom-molecule collisions ranging from the diatomic one-electron to the polyatomic multi-electron case, namely $\text{He}^+ + \text{Na}_2^+$, $\text{He} + \text{Na}_2$, $\text{He} + \text{N}_2$, and $\text{He} + \text{Na}_9^+$ [60]. In order to evaluate the importance of electron-nuclear correlations in these scattering scenarios, the study is performed in a comparative way using the QMD, NA-QMD and NA-QMD-H methods. The QMD method does not include electronic excitations and therefore allows only for ro-vibrational excitations in the molecular target. The NA-QMD method additionally includes electronic excitations without electron-nuclear correlations. The latter are accounted for only when using the NA-QMD-H approach, and their manifestation will depend on the specific physical observable taken into consideration.

Computational details

Our focus in this case study is the relevance of electronic excitation in the molecular target. Therefore, we only take the valence electrons of Na and N into account, while the remaining electrons, in particular those of the He projectile, are treated using the frozen core approximation. In all cases, atomic basis sets are constructed from Gaussian basis sets [142–144] using an additional attractive potential $V(r) = \left(\frac{r}{r_0}\right)^2$, which describes a pseudo-atom and gives a better description of the molecular properties when using small basis sets [73]. The details are summarized in Table 5.1
5.1 Electron-nuclear correlations in atomic collisions

<table>
<thead>
<tr>
<th>atom</th>
<th>Gaussian basis set (atom)</th>
<th>atomic orbitals</th>
<th>$r_0$ [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>6-31G</td>
<td>2s</td>
<td>3.5</td>
</tr>
<tr>
<td>Na</td>
<td>6-31G</td>
<td>3s,3p</td>
<td>5.8</td>
</tr>
<tr>
<td>N</td>
<td>d-aug-cc-pV6Z ($s,p$-only)</td>
<td>2s,2p,3s,3p</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 5.1: Basis set used to describe the respective atoms. The atomic density is described in all cases using the DeMon Coulomb Fitting basis set ($s,p$-type Gaussians only).

The calculations are performed within time-dependent density functional theory (TDDFT) using the adiabatic local density approximation (ALDA) for the exchange-correlation potential in the case of the many-electron targets ($\text{Na}_2$, N$_2$, Na$_9^+$), where we treat both spins equally here, i.e. spin-restricted.

Initially, the whole system is in the electronic ground state and the target molecules in their ground state equilibrium geometry with a fixed initial orientation with respect to the projectile. At this point we mention that the respective equilibrium internuclear distances of the target molecules in our calculations are 6.9 a.u. for Na$_9^+$, 6.4 a.u. for Na$_2$, 2.2 a.u. for N$_2$, whereas the cluster-radius for Na$_9^+$ is 6.6 a.u. The He atom starts 20 a.u. away from the molecular target with impact parameter zero, i.e. we consider only central collisions. The classical time step is chosen to be $\Delta t = \frac{0.01 \text{ a.u.}}{|v_{\text{He}}^0|}$, where $v_{\text{He}}^0$ is the initial velocity of the projectile in the laboratory frame (target at rest). The NA-QMD-H results are averaged over 250 trajectories for dimer and 100 trajectories for Na$_9^+$ targets for each impact energy.

Results

One observable, which reveals important information about the excitation mechanisms in a collision and can be measured in experiments [14, 15], is the kinetic energy loss $\Delta E$ in the center-of-mass frame

$$\Delta E = E_{\text{cm}} - E_{\text{cm}}(t \to \infty)$$

with $E_{\text{cm}}(t) = \frac{\mu}{2}v_{\text{rel}}(t)^2$, where $v_{\text{rel}}(t)$ is the relative velocity of projectile and target in the center-of-mass frame and $\mu$ their reduced mass. The impact energy is $E_{\text{cm}} = E_{\text{cm}}(t = 0)$.

The He projectile represents a perturbation potential, which induces excitations in the target molecule mainly in the time frame of the collision, i.e. closest approach, while the relaxation dynamics of the target molecule proceeds on much longer time scales. In this case, we can consider the NA-QMD method as a computationally cheap benchmark for the NA-QMD-H method when considering the kinetic energy loss, as discussed also in the end of Section 5.1.1. We therefore compare the kinetic energy loss using the QMD, NA-QMD and NA-QMD-H method for the different examples in dependence on the impact energy. The results are shown in Figure 5.3 together with the entrance channels.
**He** + **Na$_2^+$** and **He** + **Na$_2$** collisions  

As first examples for an atom-molecule collision we investigate the He+Na$_2^+$ and He+Na$_2$ scattering with the collision geometry shown in Figure 5.3 (a,b). The former case, which simply represents a one-electron system, has already been investigated by means of an NA-QMD-H approach in [26] under different conditions. Here, this well-understood system serves as a comparative basis for the physically very similar He + Na$_2$ collision, which represents an *effective* one-electron system, as we treat both electrons with opposite spin equally (spin-restricted). The corresponding kinetic energy losses in dependence on the impact energy are shown in Figures 5.3 (a,b). Indeed, the Na$_2^+$ and Na$_2$ cases are very similar. We are faced with two different regimes: for $E_{cm} < 0.2$ keV the collision dynamics is governed by ro-vibrational excitations, whereas for large impact energies electronic excitations are dominant. In accordance, all methods, i.e. QMD, NA-QMD and NA-QMD-H give the same results in the vibrational regime. In contrast, in the electronic regime, the energy loss due to vibrations is negligible, as can be seen by comparing the QMD results with those of NA-QMD and NA-QMD-H. Taking a closer look, different collision mechanisms manifest themselves as a function of the impact energy $E_{cm}$ in both examples (the different scattering dynamics refer to the laboratory frame):

(I) The He atom is scattered dominantly by the "front" Na atom with a scattering angle below 90° (forward-scattering with reflection).

(II) The He atom is scattered by both Na atoms with similar effect with a scattering angle below 90° (forward-scattering with reflection) resulting in a translation of the target as a whole and minimum ro-vibrational excitation.

(III) The He atom is scattered by both Na atoms, but dominantly by the "rear" Na with a scattering angle above 90° (back-scattering with reflection). At even larger $E_{cm}$ a direct hit of both target atoms is possible connected with a "zig-zag" scattering through the target molecule which leads to a maximum in the energy loss (passing through).

(IV) With further increase of the impact energy, the He atom passes through the target molecule with a small scattering angle inducing mainly electronic but negligible ro-vibrational excitation.

As the main observation we see, that the NA-QMD-H method reproduces the kinetic energy loss calculated with the NA-QMD approach very well. While electron-nuclear correlations are of minor importance in the kinetic energy loss, they become important for the molecular relaxation dynamics, i.e. fragmentation. As we only use a single trajectory at a selected impact energy within QMD and NA-QMD, different relaxation channels are taken into account within the NA-QMD-H approach only. This is demonstrated in Figure 5.4 for the fragmentation probabilities in dependence on the impact energy. In the vibrational regime
all three methods give essentially the same results, while in the electronic regime the NA-QMD-H method delivers a finite fragmentation probability \(0 \leq P_F \leq 1\) for both examples. This agrees with physical intuition, as one expects a smooth transition in the fragmentation probability when the NA-QMD and QMD trajectories start to behave differently at \(E_{cm} \approx 1\) keV.

**He + N\(_2\) collision**  A simple example for a "real" many-electron problem is given by the He + N\(_2\) scattering (five active electron pairs). The collision geometry and the kinetic energy loss are shown in Figure 5.3 (c). In the chosen range of impact energies, one is faced with the electronic regime, as the QMD results representing ro-vibrational excitation deliver only a small kinetic energy loss. Again it can be seen clearly that the NA-QMD-H method reproduces the NA-QMD results quite well. The internuclear distances of N\(_2\) corresponding to QMD and NA-QMD for selected impact energies are shown in the left panel of Figure 5.5. Excluding electronic excitation leads to a bound trajectory showing vibration (green curves). In contrast, while no fragmentation is observed for low \(E_{cm}\), the N\(_2\) molecule fragments at large \(E_{cm}\) within NA-QMD. Taking a closer look on the NA-QMD results, we observe delayed fragmentation at \(E_{cm} = 7.2\) keV and immediate fragmentation at \(E_{cm} = 18.3\) keV. We again expect a smooth transition from a relatively small to a large fragmentation probability when taking electron-nuclear correlations into account. This expectation is indeed fulfilled within the NA-QMD-H results, as summarized in the right panel of Figure 5.5.

**He + Na\(_9^+\) collision**  Finally, we consider the example of a poly-atomic many-electron problem, namely the He + Na\(_9^+\). The corresponding results for the kinetic energy loss are shown in Figure 5.3 (d). The energy losses for this collision geometry are small in comparison to our previous examples. Nevertheless, the collision is dominated by electronic excitations, as the QMD energy losses are about one order of magnitude smaller except around \(E_{cm} \approx 0.5\) keV connected with a very small energy loss. Although the He penetrates the cluster for all impact energies in Figure 5.3 (d), the Na\(_9^+\) becomes "transparent" [36] in this particular impact energy range. The NA-QMD results are again reproduced with reasonable accuracy by the NA-QMD-H method.

In consequence, we have demonstrated with increasing many-electron nature, that the NA-QMD-H method is quite accurate in the case of atom-molecule collisions and delivers the correct fragmentation behavior in contrast to NA-QMD, which allows only for a single outcome at some selected initial geometry.
Figure 5.3: Kinetic energy loss $\Delta E$ in dependence on the impact energy $E_{\text{cm}}$ for collisions of He with different targets calculated with QMD (green), NA-QMD (black) and NA-QMD-H (red): Na$_2^+$ (a), Na$_2$ (b), N$_2$ (c) and Na$_9^+$ (d). The entrance channels are sketched in the right part of the Figure.
5.1 Electron-nuclear correlations in atomic collisions

Figure 5.4: Fragmentation probabilities $P_F$ in dependence on impact energy $E_{cm}$ for the collision of He with Na$_2^+$ (a) respectively Na$_2$ (b): QMD (green), NA-QMD (black) and NA-QMD-H (red). A trajectory is considered fragmented, if the internuclear distance $R$ exceeds $R_F = 12.8$ a.u. (Na$_2^+$) respectively $R_F = 12.4$ a.u. (Na$_2$) within a propagation time of 500 fs.

<table>
<thead>
<tr>
<th>$E_{cm}$ [keV]</th>
<th>QMD</th>
<th>NA-QMD</th>
<th>NA-QMD-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.48</td>
<td>0</td>
<td>0</td>
<td>0.38</td>
</tr>
<tr>
<td>7.2</td>
<td>0</td>
<td>1</td>
<td>0.50</td>
</tr>
<tr>
<td>18.3</td>
<td>0</td>
<td>1</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Figure 5.5: Left panel: Internuclear distance $R$ of N$_2$ calculated using the QMD (green) and NA-QMD (black) for selected impact energies. Right panel: Fragmentation probabilities for the He + N$_2$ collision calculated using the QMD, NA-QMD and NA-QMD-H method for selected impact energies. A trajectory is considered as fragmented, if the internuclear distance $R$ exceeds $R_F = 8$ a.u. within a propagation time of 50 fs.
5.1.3 Comparison with experiment: He + H\textsubscript{2} and He + He collisions

On the basis of fundamental atom-atom and atom-molecule collisions in the previous sections, the NA-QMD-H method has revealed physically reasonable results. In this section, we consider simple collisions of these types, namely He + H\textsubscript{2} and He + He scattering [162], which were investigated experimentally by means of energy loss spectroscopy (ELS). ELS is an experimental method, which delivers insights into interactions occurring in collisions, i.e. ro-vibrational and electronic excitations as well as charge transfer and electron capture processes [162, 163]. Basically, the kinetic energy loss of the He projectile in dependence on the scattering angle has been measured in the experiment [162] for both targets and the corresponding spectra exhibited quite characteristic patterns: three dominant peaks were present in the energy loss spectra. The first peak at small energy loss was connected to electronically elastic scattering, while the two higher-energy peaks were attributed to electronic excitations, more precisely one- and two-electron excitations within the H\textsubscript{2} molecule and He atoms, respectively. In the following, we contrast these experimental findings with a comparative theoretical study on the basis of QMD, NA-QMD and NA-QMD-H calculations.

Computational details

The basis sets we use for the calculations in this section are summarized in Table 5.2. In the case of He + H\textsubscript{2} collision, the electrons of the He projectile are treated using the frozen core approximation, motivated by the experimental conclusion that excitations in the H\textsubscript{2} target dominate the spectra. The atomic basis sets are constructed from Gaussian basis sets [142–144], where we use an additional attractive (pseudo-atom) potential \( V(r) = \left( \frac{r}{r_0} \right)^2 \) for the He atom (see also Section 5.1.2).

<table>
<thead>
<tr>
<th>collision</th>
<th>atom</th>
<th>Gaussian basis set (atom)</th>
<th>atomic orbitals</th>
<th>( r_0 ) [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He + H\textsubscript{2}</td>
<td>H</td>
<td>d-aug-cc-pV6Z (s, p-only)</td>
<td>1s,2s,2p,3s,3p</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>6-31G</td>
<td>2s</td>
<td></td>
</tr>
<tr>
<td>He + He</td>
<td>He</td>
<td>d-aug-cc-pV5Z (s, p-only)</td>
<td>1s,2s,2p,3s,3p</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 5.2: Basis sets used for the atoms in the He + H\textsubscript{2} and He + He collisions. The atomic density is described in all cases using the DeMon Coulomb Fitting basis set (s, p-type Gaussians only).

All calculations are performed within spin-restricted, time-dependent Hartree Fock theory (TDHF). In order to allow for single-electron excitations in this framework within the NA-QMD-H method, we additionally invoke a half-electron (HE) approximation in the spirit of [164]. Originally, this idea was used to allow for the description of open-shell systems, such as hydrocarbon radicals and radical ions, using a modified closed-shell, i.e. spin-restricted, method. In its heart, the unpaired electron of the radical is replaced by
two half-electrons of opposite spin. Here, we extend this approach by replacing all electron pairs by two half-electron pairs, which are treated as if they were electrons of opposite spin. With this mathematical trick we are able to account for single-electron transitions in our spin-restricted calculations approximately, avoiding the spin contamination, which appears in spin-unrestricted calculations and may cause severe problems in the adiabatic state tracking procedure (see Section 2.3).

![Energy level diagrams](image)

**Figure 5.6:** Excitation energies constructed from bare KS-excitations from the ground state: H$_2$ (a) and He (b).

The energy level diagrams, constructed from bare KS-excitations from the ground state, are shown in Figure 5.6, where we compare the spin-unrestricted and spin-restricted methods. The energy levels separate into two distinct regions: one-electron (I) and (mainly) two-electron excitations (II). As can be seen clearly in Figure 5.6, the HE approximation merely leads to a small shift of the excitation energies and correspondingly provides a reasonable description of the excitations.

Initially, the system is in the electronic ground state. The He atom starts 20 a.u. away from the target with impact parameters chosen between 0 a.u. and 4 a.u. The classical time step is chosen to be $\Delta t = 0.1$ a.u. for the He + H$_2$ and $\Delta t = 0.01$ a.u. for the He + He collision. In addition, for the molecular target initial orientations were chosen randomly, thereby keeping the initial internuclear distance fixed at its ground state equilibrium value.
Results

As the central quantity, we calculate the kinetic energy loss $Q$ of the He projectile in dependence on the scattering angle $\theta$ in the laboratory frame defined as

$$Q = \frac{M_{\text{He}}}{2} \left[ v_{\text{He}}^2(t = 0) - v_{\text{He}}(t \to \infty) \right]. \quad (5.29)$$

At first, we consider the energy loss spectra calculated with QMD and NA-QMD, shown in Figure 5.7 (a,b). The QMD results for the He + He scattering [Figure 5.7 (a)] deliver just one peak connected to adiabatic scattering, whereas for He + H$_2$ [Figure 5.7 (b)] two types of adiabatic peaks are present: one connected with small energy losses corresponding to large impact parameters, i.e. "distant" scattering, and a "jet" giving large energy losses at small scattering angles corresponding to collisions at small impact parameters, where the He passes through the H$_2$ molecule between the two H atoms. The energy loss for "distant" scattering increases for larger scattering angles due to smaller impact parameters and, thus, more violent collisions. The NA-QMD calculations essentially deliver the same qualitative result of roughly one peak, which is shifted to higher energy losses in comparison to the adiabatic peak by some average amount of electronic excitation.

In contrast, the experimentally observed three-peak structure in the energy loss spectra is reproduced by the NA-QMD-H calculations, as is shown for both examples in Figure 5.7 (c,d). The peak energy losses corresponding to the NA-QMD-H results are compared with the experimental ones in Table 5.3. Despite the approximations used for these calculations, we derive quite a good estimate of the peak energies for the one- and two-electron excitations in comparison to the experiment [162].

Consequently, electron-nuclear correlation are essential for the calculation of realistic energy loss spectra, which we have demonstrated here for the He + H$_2$ and He + He collisions by comparison to experiment [162]. While NA-QMD fails completely, the NA-QMD-H method successfully delivers the correct features in these spectra.

<table>
<thead>
<tr>
<th>excitation</th>
<th>He + He</th>
<th>He + H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>theory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 electron</td>
<td>24 eV</td>
<td>14 eV</td>
</tr>
<tr>
<td>2 electrons</td>
<td>52 eV</td>
<td>30 eV</td>
</tr>
<tr>
<td>experiment [162]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 electron</td>
<td>20 eV</td>
<td>12 eV</td>
</tr>
<tr>
<td>2 electrons</td>
<td>42 eV</td>
<td>30 eV</td>
</tr>
</tbody>
</table>

Table 5.3: Rough estimate of the (central) peak energies for one- and two-electron excitations (above the adiabatic peak) corresponding to the energy loss spectra for the He + H$_2$ and He + He scattering in Figure 5.7.
Figure 5.7: Energy loss spectra for the He + He (a,c) and He + H\textsubscript{2} (b,d) collisions calculated with QMD (a,b), NA-QMD (a,b) and NA-QMD-H (c,d). The NA-QMD-H results for He + H\textsubscript{2} (d) collision, calculated for selected initial conditions which lead to final scattering angles in the range $\theta \in [1.0^\circ, 4.0^\circ]$ within NA-QMD calculations, have been smoothed with Gaussians for better visibility of the relevant features. The dotted blue lines in panels (c) and (d) indicate the experimental peak energies (cf. Table 5.3).
5.2 Electron-nuclear correlations in the laser-induced dynamics of organic molecules

In this section, we investigate the relevance of electron-nuclear correlations in the laser-induced dynamics of organic molecules on the basis of our novel NA-QMD-H method [61]. Therefore, we consider two important benchmark systems, namely the methaniminium cation and ethylene, which attracted much attention especially in photochemistry [33,64,165,166], as these molecules belong to the smallest systems that can undergo cis-trans isomerization and exhibit a rich variety in the electronic relaxation process. Thereby, we extend previous NA-QMD-based investigations of the laser-induced dynamics of ethylene [33].

5.2.1 Electronic relaxation of the methaniminium cation

The methaniminium cation (CH$_2$NH$_2^+$) represents a minimal model for retinal [165], which plays a fundamental role in the photo-activity of proteins and photoinduced cis-trans isomerization responsible for the primary process of vision. For this reason, it has attracted much attention in previous studies to shed light on the dynamics of retinal. On the other hand, due to its simplicity it has served as a benchmark system to test new computational methods [58, 165, 166]. Despite its smallness, it exhibits an interesting complexity in the electronic structure and connectedly excited state relaxation dynamics: while excitation to the first excited state S$_1$ is followed by torsional motion around the CN double bond leading to decay back to the ground state S$_0$, in contrast, excitation to the second excited state S$_2$ results in a two-step decay process characterized by a fast decay to the S$_1$ state via CN bond stretching and re-population of the ground state at later stages of the dynamics [166]. In this section, we use this qualitatively quite different relaxation behavior depending on the initial electronic state as a comparative basis for a study utilizing the NA-QMD and NA-QMD-H methods, evaluating the importance of electron-nuclear correlations in the non-radiative decay dynamics of the methaniminium ion.

Computational details

The aim of our investigations is to achieve a reasonably accurate description of the methaniminium cation at a relatively low computation effort. For this reason, we use a small basis set for our calculations including the 1s,2s atomic orbitals of hydrogen as well as the 2s,2p atomic orbitals of carbon and nitrogen, where the two innermost electrons are treated with the frozen core approximation in the latter two cases. The atomic and the corresponding density basis sets are constructed from the 6-31G and DeMon Coulomb Fitting basis sets [142–144] (s, p-type Gaussians only). All calculations are performed within
5.2 Electron-nuclear correlations in the laser-induced dynamics of organic molecules

The molecules are assumed to be initially in the desired excited state, i.e. $S_1$ or $S_2$, after a vertical transition from the ground state. The corresponding positions and momenta of the nuclei have been sampled microcanonically according to the vibrational ground state of the methaniminium ion within the classical normal mode approximation, where the results are averaged over 50 trajectories for NA-QMD and 500 trajectories for NA-QMD-H. We use a time step $\Delta t = 1$ a.u. in our calculations.

**Ground and excited state properties**

We first analyze important ground state equilibrium and optical properties of the methaniminium cation summarized in Table 5.4, where we compare our NA-QMD(-H) results\(^1\) to RHF/CIS calculations using GAMESS as well as more sophisticated quantum chemical results from the literature. As is clear from the Table, the corresponding bond lengths and bond angles are described quite well despite some deviations of the CN bond length and the $S_0/S_1$ excitation energy, which is slightly underestimated in NA-QMD-H.

![Figure 5.8: Definition of the geometry parameters for the methaniminium cation in its (planar) ground state equilibrium geometry.](image)

The potential energy surfaces corresponding to the torsional degree of freedom for the ground and the lowest singly excited states are shown in Figure 5.9 calculated using the NA-QMD-H method and GAMESS. The $S_0$ and $S_1$ states agree quite well qualitatively, exhibiting a maximum of the ground state respectively minimum of the first excited state at the twisted orthogonal structure ($\theta = 90^\circ$). The $S_2$ (and $S_3$) state, however, agree qualitatively only around the ground state equilibrium geometry ($\theta \approx 0^\circ$) and disagree for larger $\theta$. This is expected to be a minor problem, however, as the decay from the $S_2$ state proceeds very fast mainly via CN bond stretch (see also [166]) and, thus, these larger $\theta$ regions are unlikely to be accessed as the system evolves on this state. The essential steps in the relaxation dynamics can be concluded as follows: while decay from $S_2$ to $S_1$ may be triggered by CN bond stretch rather than torsion, decay from $S_1$ to $S_0$ is connected with torsional motion in the $S_1$ state which drives the system towards the avoided crossing

\(^1\)More precisely, the ground state properties are obtained by QMD ground state calculations and the excitation energies are constructed from bare KS-excitations from the ground state.
Table 5.4: Ground state properties of the methaniminium cation as well as first optically allowed excitation energy calculated with NA-QMD(-H) and GAMESS. The latter results have been determined on the spin-restricted Hartree Fock (RHF) level of theory using the 6-31G basis set. The excitation energies are based on KS excitations in NA-QMD-H (see Section 2.3) and CIS in the GAMESS results. The Table also contains accurate quantum chemical results taken from [165]. The geometry parameters are defined in the sketch given in Figure 5.8. In its ground state equilibrium geometry the methaniminium cation is planar, i.e. $\theta = 0^\circ$.

<table>
<thead>
<tr>
<th>approach</th>
<th>$R_{CN}$ [a.u.]</th>
<th>$R_{CH}$ [a.u.]</th>
<th>$R_{NH}$ [a.u.]</th>
<th>$\phi(C)$ [$^\circ$]</th>
<th>$\phi(N)$ [$^\circ$]</th>
<th>$\Delta E$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA-QMD(-H)</td>
<td>2.60</td>
<td>2.04</td>
<td>1.86</td>
<td>118.8</td>
<td>120.7</td>
<td>7.86</td>
</tr>
<tr>
<td>GAMESS</td>
<td>2.40</td>
<td>2.03</td>
<td>1.89</td>
<td>120.2</td>
<td>122.2</td>
<td>8.82</td>
</tr>
<tr>
<td>QC [165]</td>
<td>2.41</td>
<td>2.04</td>
<td>1.91</td>
<td>119.4</td>
<td>121.5</td>
<td>8.47</td>
</tr>
</tbody>
</table>

Figure 5.9: Potential energy surfaces of the methaniminium cation for the ground state $S_0$ and the lowest excited states - $S_1$, $S_2$, $S_3$ - in dependence on the torsion angle $\theta$ (all remaining geometry parameters are kept frozen according to the ground state equilibrium values) calculated using NA-QMD-H (a) and GAMESS (b).

Excited state relaxation

In the following, we focus on the radiationless decay of the methaniminium ion starting from the $S_1$ and $S_2$ state in a comparative way using the NA-QMD and NA-QMD-H methods. The respective results are shown in Figure 5.10 for initial excitation to the $S_1$ state and Figure 5.11 for initial excitation to the $S_2$ state.

In the first case (initial $S_1$ state), the state population decays directly from the $S_1$ state to the ground state in both NA-QMD and NA-QMD-H as shown in Figure 5.10 (c,d).
5.2 Electron-nuclear correlations in the laser-induced dynamics of organic molecules

Based on this observation, one might draw the conclusion, that both approaches describe the relaxation process correctly. Taking a closer look on the $S_0$ populations (black curves), however, one recognizes that the ground state re-population stops in the NA-QMD results after 100 fs and reaches a final value of 70% [see Figure 5.10 (c)]. This means that some excitation of higher states is artificially present in the NA-QMD results. Correspondingly, the electronic excitation energy

$$E_{\text{ex}}(t) = E(t) - E_{\text{gs}}(t)$$

(5.30)
does not converge to zero for the NA-QMD approach [see blue curve in Figure 5.10 (a)], i.e. the system does not decay back to the ground state in this case. In contrast, the NA-QMD-H method describes the one-step decay behavior from $S_1$ to $S_0$ correctly, as ground state re-population is connected with a decrease in the electronic excitation energy [see blue curve in Figure 5.10 (b)].

A more complex decay pattern appears, when the system starts from the $S_2$ state. The state populations in Figure 5.11 (c,d) indicate, again for both NA-QMD and NA-QMD-H, a fast decay from the $S_2$ mainly to the $S_1$ state within the first 20 fs. Afterwards, recovery of the ground state dominates and the intermediate $S_1$ state decays on a longer time scale. As in the previous case, excitation of higher states hinders a ground state recovery within NA-QMD with a non-relaxing electronic excitation energy, whereas the relaxation proceeds correctly in NA-QMD-H [see blue curves in Figures 5.11 (a,b)].

Consequently, electron-nuclear correlations are correctly accounted for within the NA-QMD-H approach, whereas NA-QMD fails. The two types of relaxation dynamics, which we observe here with NA-QMD-H, reproduce on a qualitative level previous findings [58, 165, 166], where higher level quantum chemical methods were used. For better comparison, we estimated the ground state recovery times by exponential fitting of the $S_0$ population to a function $f(t) = 1 - \exp\left(-\frac{t}{\tau}\right)$. The results are summarized in Table 5.5. By means of the NA-QMD-H approach we reproduce the correct trend, that ground state recovery proceeds faster with initial $S_1$ than initial $S_2$ excitation. Although we do not gain the accurate ground state recovery time within our framework, however, we get at least a rough estimate.

<table>
<thead>
<tr>
<th>Initial state</th>
<th>NA-QMD-H</th>
<th>QC [166]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>40 fs</td>
<td>72 fs</td>
</tr>
<tr>
<td>$S_2$</td>
<td>62 fs</td>
<td>97 fs</td>
</tr>
</tbody>
</table>

Table 5.5: Estimated ground state recovery times according to Figure 5.10 (c,d) for initial $S_1$ and Figure 5.11 (c,d) for initial $S_2$ state. The quantum chemistry results have been extracted from [166].
Figure 5.10: Excited state relaxation of CH$_2$NH$_2^+$ after vertical excitation to the S$_1$ state: NA-QMD (a,c) as well as NA-QMD-H (b,d) results for electronic excitation energy $E_{\text{el}}^\text{ex}(t)$ (a,b) defined in (5.30) and state occupations (c,d). Panels (a,b) also contain the excited state energies with respect to the ground state energy for better comparison.

5.2.2 Excitation and electronic relaxation of ethylene

Ethylene (C$_2$H$_4$) is one of the simplest systems that can undergo cis-trans isomerization and ultrafast energy conversion via conical intersections, which plays a fundamental role in the context of biochemistry for the conversion of light into mechanical energy [64]. The photo-induced dynamics of ethylene are conveniently understood in a three state picture including the ground state S$_0$, the first excited state S$_1$ and second excited state S$_2$: Upon absorption of a photon and excitation to the S$_1$ state, the system evolves on this state via torsion. Non-adiabatic transitions to the other surfaces are possible, where relaxation to the ground state is enabled via a S$_1$/S$_0$ conical intersection. Much work has been devoted to the understanding of the dynamics of ethylene and its excited state lifetime. The long existing discrepancy between the theoretically calculated lifetime of $\tau \approx 89 - 180$ fs and the experimentally measured one of $\tau \approx 50$ fs has been shown recently [167, 168] to originate from the impact of the instantaneous ionization potential of the molecules in the pump-probe experiments on the measured lifetimes. Ethylene is very similar in its structure to the methaniminium cation considered in Section 5.2.1 and provides an alternative benchmark system, which we use here in the same spirit for a comparative study utilizing the NA-QMD
and NA-QMD-H methods. In this section, however, we go one step further by including the laser field explicitly.

**Computational details**

As for the methaniminium cation (Section 5.2.1), we want to achieve a reasonably accurate description of ethylene at a relatively low computational effort. Therefore, we use a small basis set for our calculation including the 1s,2s atomic orbitals of hydrogen as well as the 2s,2p atomic orbitals of carbon, treating the two innermost electrons of the latter with the frozen core approximation. These atomic and the corresponding density basis sets are constructed from the 6-31G and DeMon Coulomb Fitting basis sets [142–144] (s, p-type Gaussians only). All calculations are performed within spin-unrestricted, time-dependent Hartree Fock theory (TDHF).

Our investigation is performed in two parts: first without laser-field and second taking the laser field into account explicitly. Correspondingly, the molecules are assumed to be initially in the desired state, i.e. $S_1$ in the first and $S_0$ in the second case. The corresponding positions and momenta of the nuclei have been sampled microcanonically according to the vibrational ground state of the ethylene within the classical normal mode approximation, where the results are averaged over 50 trajectories for NA-QMD and 500 trajectories for NA-QMD-H. The classical time step is chosen as $\Delta t = 1$ a.u.
Ground and excited state properties

Essential (planar) ground state equilibrium and optical properties of ethylene are summarized in Table 5.6, where the corresponding geometrical parameters are defined in Figure 5.12. The NA-QMD(-H) results\(^2\) are compared to those calculated with GAMESS (RHF/CIS, 6-31G basis set) as well as accurate quantum chemical and experimental ones taken from the literature. The corresponding bond lengths and bond angles are described quite well despite some deviations of the CC-bond length and the \(S_0/S_1\) excitation energy. We also note that the NA-QMD-H excitation energy is closer to the exact result than expected from the GAMESS calculation with similar basis set size.

![Figure 5.12: Definition of the geometry parameters for ethylene in its (planar) ground state equilibrium geometry.](image)

<table>
<thead>
<tr>
<th>approach</th>
<th>(R_{CC}) [a.u.]</th>
<th>(R_{CH}) [a.u.]</th>
<th>(\phi) [°]</th>
<th>(\Delta E) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA-QMD(-H)</td>
<td>2.63</td>
<td>2.03</td>
<td>120.9</td>
<td>7.20</td>
</tr>
<tr>
<td>GAMESS</td>
<td>2.50</td>
<td>2.03</td>
<td>121.9</td>
<td>8.82</td>
</tr>
<tr>
<td>QC [169]</td>
<td>2.53</td>
<td>2.05</td>
<td>121.5</td>
<td>7.8</td>
</tr>
<tr>
<td>Experiment (see refs. in [170])</td>
<td>2.53</td>
<td>2.05</td>
<td>121.2</td>
<td>7.66</td>
</tr>
</tbody>
</table>

Table 5.6: Ground state properties of ethylene as well as first optically allowed excitation energy calculated with NA-QMD(-H) and GAMESS. The latter results have been determined on the spin-restricted Hartree Fock (RHF) level of theory using the 6-31G basis set. The excitation energies are based on KS excitations in NA-QMD-H (see Section 2.3) and CIS in the GAMESS results. The Table also contains accurate quantum chemical results taken from [169] as well as experimental data. The geometry parameters are defined in the sketch given in Figure 5.12. In its ground state equilibrium geometry ethylene is planar, i.e. \(\theta = 0°\).

Photoisomerization of ethylene proceeds via rotation around the CC-double bond by the torsion angle \(\theta\). The corresponding potential energy curves in dependence on the torsion angle for the ground and excited states are compared in Figure 5.13 for NA-QMD-H and

\(^2\) More precisely, the ground state properties are obtained by QMD ground state calculations and the excitation energies are constructed from bare KS-excitations from the ground state.
5.2 Electron-nuclear correlations in the laser-induced dynamics of organic molecules

GAMESS. At first we note the good qualitative agreement of the $S_0$ and $S_1$ states, exhibiting a maximum of the ground state respectively minimum of the first excited state at $\theta = 90^\circ$. The energy gap at $\theta = 90^\circ$ is, however, missing in NA-QMD-H and too small in the GAMESS results as compared to quantum chemical ones [169]. We also note that the $S_2$ state is missing in the CIS results due to its doubly excited character but included in the NA-QMD-H approach. This partly contradicts the original concern [171] that bare KS excitations are inferior compared to CIS and LR-TDDFT, as doubly excited states might be important for the dynamics as well.

**Figure 5.13:** Potential energy curves of ethylene in dependence on the torsion angle $\theta$ (all remaining geometry parameters are kept frozen according to the ground state equilibrium values) calculated using NA-QMD-H (a) and GAMESS (b).

From the electronic structure properties we can already draw conclusions about essential steps of excited state dynamics: after excitation of ethylene to the $S_1$ state the system is driven to the conical intersection at $\theta = 90^\circ$ by torsional motion and CC-bond stretching (due to minimum of $S_1$ surface at a larger $R_{CC}$, not shown). Quenching to the ground state occurs via non-adiabatic transitions and the vibrational energy is redistributed among the nuclear degrees of freedom.

**Excited state relaxation and laser-induced dynamics**

First, we focus on the excited state relaxation of ethylene after a vertical transition from the ground to the first excited state. The results for the electronic excitation energy and the individual state populations are shown in Figure 5.14, comparing NA-QMD and NA-QMD-H. The initial stages (first $\sim 15$ fs) of the $S_1$ state dynamics proceeds via CC-bond stretching and torsional motion, which is reproduced comparably well in NA-QMD and NA-QMD-H, as the dynamics proceed completely adiabatically [compare the blue curves in Figure 5.14 (a,b)]. After accessing the conical intersection, different dynamical pathways are followed as manifestation of electron-nuclear correlations, which is captured by NA-QMD-H only. As
in the case of the methaniminium cation (Section 5.2.1), the system remains excited and does not decay in NA-QMD, whereas the excitation energy decreases to zero in accordance with the re-population of the ground state, thus giving excited state relaxation correctly within NA-QMD-H. We estimate a decay time $\tau \approx 160$ fs from an exponential fit of the $S_1$ population to $f(t) = \exp \left( -\frac{t}{\tau} \right)$, which lies in the region of decay times reported in other theoretical studies ($\tau \approx 50 - 180$ fs, see [64,172–174]).

Second, by explicit inclusion of the laser field, optimization of the laser parameters is necessary in order to transfer a large amount of population from the ground to the target excited state. We use a $\sin^2$-shaped laser field with pulse length $T = 10$ fs, where we choose the peak intensity as $I = 3 \cdot 10^{12} \text{ W cm}^{-2}$ and fundamental frequency $\omega = 0.26$ a.u. (this corresponds to an excitation energy of 7.07 eV) in order to transfer much population to the $S_1$ state, but little population to the $S_2$ or other excited states. The results are shown in Figure 5.15. In the presence of the laser field, the $S_1$ and $S_2$ states are populated, which proceeds in a similar way in NA-QMD and NA-QMD-H. After switching off the laser field, only those trajectories, which are in an excited state, may evolve via CC-bond stretching and torsional motion accessing the conical intersection. When the conical intersection is
5.2 Electron-nuclear correlations in the laser-induced dynamics of organic molecules

Figure 5.15: Laser-induced excited state relaxation of C\textsubscript{2}H\textsubscript{4}: NA-QMD (a,c) as well as NA-QMD-H (b,d) results for electronic excitation energy \( E_{\text{el}}^2(t) \) (a,b) defined in (5.30) and state occupations (c,d). The molecules are initially in the ground state and excited by a \( \sin^2 \)-shaped laser pulse (\( \omega = 0.26 \) a.u., \( I = 3 \cdot 10^{12} \text{ W cm}^{-2} \text{, } T = 10 \text{ fs} \)). Panels (a,b) also contain the excited state energies with respect to the ground state energy for better comparison.

reached, quenching to the ground state may occur. Again, the excited state relaxation is reproduced correctly in NA-QMD-H, where the electronic excitation energy decays to zero, in contrast to NA-QMD, where the system remains excited. The state populations confirm this, as in NA-QMD-H the system is in the \( S_0 \) state after 250 fs, whereas a finite excitation of \( \sim 12\% \) remains in NA-QMD. Trajectories, which remain in the ground state, just show vibrational dynamics around the equilibrium geometry.

In addition, we note that hydrogen-migration and H\textsubscript{2} elimination, which have been reported in the literature as relevant dynamical pathways [169,175,176], are observed in the NA-QMD-H but not in the NA-QMD calculations. Some representative snapshots of such a trajectory are shown in Figure 5.16.
Figure 5.16: Typical trajectory for the excited state relaxation of ethylene calculated with NA-QMD-H: the system is initially in the ground state $S_0$ with a near-planar geometry (1st snapshot, $t = 0$ fs) and, after laser-excitation, evolves via torsional motion and CC bond stretching (2nd snapshot, $t = 19$ fs) in the $S_1$ state. At later times, hydrogen migration might occur to form ethylidene-like structures (3rd snapshot, $t = 191$ fs), which is a potential precursor for subsequent $H_2$ elimination.
5.3 Summary and open questions

In this chapter, we demonstrated the need to take electron-nuclear correlations into account in a variety of scenarios by comparing the results calculated with the novel NA-QMD-H scheme to NA-QMD calculations. In the case of collisions (Section 5.1), the NA-QMD-H approach delivers the same average kinetic energy loss as the NA-QMD method demonstrating the accuracy of the NA-QMD-H method and the minor importance of electron-nuclear correlations for this observable. Differential quantities such as fragmentation probabilities or energy loss spectra are reproduced physically reasonably with the NA-QMD-H scheme only, whereas the NA-QMD method fails completely. In the case of excited state relaxation of organic molecules (Section 5.2), only the NA-QMD-H approach is able to capture the correct relaxation dynamics, even in the presence of an external laser field, including important reaction pathways. This shows that despite its approximate nature, the NA-QMD-H method developed in this thesis captures the essential physics of these processes and, therefore, marks an advancement of the NA-QMD method in the description of the dynamics of poly-atomic many-electron systems.

As an open question for future work, the interplay between the use of time-dependent orbitals for the quantum mechanical propagation and the adiabatic Slater determinant description remains to be investigated. The former may produce an effectively time-dependent electronic structure, which is inherent in all methods that are based on time-dependent orbitals like (multi-configurational) TDHF and TDDFT. This may lead to new challenges concerning the realistic description of state-to-state transitions required for optimal control scenarios, as pointed out recently [177].
6 Conclusions and outlook

The aim of this thesis is twofold: First, we presented applications of the non-adiabatic quantum molecular dynamics (NA-QMD) method to important benchmark systems and, second, we extended basically the NA-QMD formalism to include quantum effects in the nuclear motion (NA-QMD-H).

First, we demonstrated the universality of the NA-QMD method by the investigation of the smallest and the largest atomic system, nature’s simplest molecule H$_2^+$ and the Buckminster fullerene C$_{60}$, exposed to short intense laser pulses. This allowed to contribute to present research in closing important gaps in the understanding of the dynamics of these important systems.

In the case of H$_2^+$ (Chapter 3), we presented a first complete study of strong-field ionization and dissociation including all electronic and nuclear degrees of freedom under experimentally relevant laser conditions [41, 42]. On this basis, it was shown that molecular rotation plays an important role in the laser-induced dynamics and may enhance ionization up to an order of magnitude in the parameter regime under consideration. The relevance of rotation was determined by a criterion based on the competition of the optimum time scales for ionization, strongest at half pulse length, and rotation, i.e. the time it takes to align a molecule with the polarization axis where ionization is most effective. The NA-QMD study enabled us to clarify the experimentally observed dominance of dissociation over ionization [40], which has its origin in the strong intensity dependence of the two fragmentation channels, and to construct a simple model for direct calculation of experimentally relevant focal volume intensity averaging at low computational cost [43].

In the case of C$_{60}$ (Chapter 4), we studied the orientation dependence of the excitation and relaxation mechanism in a linearly polarized laser field [44]. Surprisingly, the energy deposition was found to depend strongly on the molecular orientation with respect to the laser polarization axis leading to different pathways in the subsequent nuclear relaxation: (1) excitation of the long-living breathing modes, (2) formation of stable, highly deformed complexes (isomers), and (3) ultrafast fragmentation processes by splitting of the cage into two pieces on the sub-ps timescale. With the amount of absorbed energy identified as the key quantity for the subsequent nuclear relaxation mechanism, mass spectra measured in previous experiments using short laser pulses in the fs-range could be ascribed to these different pathways. Future experiments have been proposed to confirm the detailed predic-
Conclusions and outlook

These investigations are also the basis of experiments at the LCLS facility at SLAC planned for the future [158].

Second, we extended basically the NA-QMD method in order to overcome the hitherto existing limitation of a purely classical description of the nuclei and take electron-nuclear correlations approximately into account (Chapter 2). This was achieved by means of a trajectory surface hopping scheme in the adiabatic Kohn-Sham orbitals ("NA-QMD-H") [59]. We demonstrated the relevance of electron-nuclear correlations in comparison to the NA-QMD approach in a variety of studies concerning collision physics [60] and photochemistry [61].

It was shown that electron-nuclear correlations are of fundamental importance for the realistic description of energy loss spectra and excited state relaxation processes in polyatomic many-electron systems and are considered in a physically reasonable and accurate way within the NA-QMD-H scheme only (Chapter 5). With this, we could shed light on previous experimental kinetic energy loss spectra for atomic collisions and give a rough estimate of excited state decay times of organic molecules.

The investigations in this work offer a fruitful basis for future research. The complete study performed in this work for H$_2^+$ could be extended to larger molecules, e.g. H$_3^+$, in order to study the interplay of laser-induced ionization and dissociation in a "real" polyatomic many-electron system. Ground-breaking experimental results exist in this case [178], but theoretical calculations beyond purely classical ones [179] do not exist up to now. On the other hand, with the inclusion of electron nuclear correlations in the dynamics of atomic-many body systems within the NA-QMD-H method, a wide range of applications in collision- and laser-induced dynamics opens naturally. Limitations of the mean-field NA-QMD method may now be circumvented with this novel scheme. E.g., re-examination of the pump-probe dynamics of C$_{60}$ [35], where only one periodicity could be identified using the NA-QMD approach, might shed new light on the other observed frequencies in the experimental signal. Furthermore, connecting the NA-QMD-H scheme with the description of ionization might provide a general way for the separation of ionization and dissociation dynamics in extension to previous solely NA-QMD based schemes restricted to the one-electron case only [180].
Appendix A

A.1 Instantaneous Floquet states

Adiabatic Floquet surfaces provide an appropriate picture for the interpretation of multi-photon effects in the dissociation of H$_2^+$. Therefore, we briefly summarize the main ideas of Floquet theory [181] and give a definition of the instantaneous adiabatic Floquet surfaces used in Section 3.2.

Staring from the time-dependent Hamiltonian

$$\tilde{H}(\mathbf{R}, \mathbf{r}, t) = H(\mathbf{R}, \mathbf{r}) - \mathbf{r} \cdot \mathbf{e}_z E_0 \cos(\omega t) ,$$  \hspace{1cm} (A.1)

which is strictly periodic in time with period $T = \frac{2\pi}{\omega}$ (cw laser), the solutions of the corresponding time-dependent Schrödinger equation can be written as

$$\chi_k(\mathbf{R}, \mathbf{r}, E_0, t) = e^{-i\epsilon_k(\mathbf{R},E_0)t} \cdot u_k(\mathbf{R}, \mathbf{r}, E_0, t)$$  \hspace{1cm} (A.2)

with the Floquet states $u_k$, which are periodic in time with period $T$ according to $u_k(\mathbf{R}, \mathbf{r}, E_0, t) = u_k(\mathbf{R}, \mathbf{r}, E_0, t + T)$, and the corresponding quasi-energies respectively Floquet surfaces $\epsilon_k$. After insertion of (A.2) into (A.1) we arrive at the eigenvalue problem

$$H_F(\mathbf{R}, \mathbf{r}, t)u_k(\mathbf{R}, \mathbf{r}, E_0, t) = \epsilon_k(\mathbf{R}, E_0)u_k(\mathbf{R}, \mathbf{r}, E_0, t)$$  \hspace{1cm} (A.3)

where we have introduced the Floquet-Hamiltonian $H_F(\mathbf{R}, \mathbf{r}, t) = \tilde{H}(\mathbf{R}, \mathbf{r}, t) - i \frac{\partial}{\partial t}$. This Hamiltonian is defined on the composite Hilbert space $\mathcal{F} = \mathcal{H} \otimes \mathcal{T}$, where $\mathcal{H}$ is the usual Hilbert space of all square-integrable functions $h(\mathbf{r}; \mathbf{R})$ and $\mathcal{T}$ the space of time-dependent functions $a(t)$ with period $T$. The corresponding scalar product is given by

$$\langle f_1 | f_2 \rangle_{\mathcal{F}} = \frac{1}{T} \int_0^T \langle f_1 | f_2 \rangle_{\mathcal{H}} dt .$$  \hspace{1cm} (A.4)

The eigenvalue problem (A.3) is solved in analogy to (3.11) by expansion of the Floquet states in Born-Oppenheimer states and Fourier components (field-dressed Born-Oppenheimer states)

$$u_k(\mathbf{R}, \mathbf{r}, E_0, t) = \sum_I \sum_{n=-\infty}^{\infty} c_{I,n}^k(\mathbf{R}, E_0) \Phi_I(\mathbf{r}; \mathbf{R}) e^{in\omega t} .$$  \hspace{1cm} (A.5)
Inserting (A.5) in (A.3) and multiplication of the eigenvalue equation with $\Phi^*_I(r; R)e^{-i\omega t}$, which are the basis functions of $\mathcal{F}$, yields after integration over the set of electronic coordinates and time, i.e. applying the scalar product (A.4),

$$[V_I(R) + n\omega] c_{I,n}^k(R, E_0) + \sum_j \frac{E_0}{2} \mathbf{e}_z \cdot \mathbf{L}_{I,J}(R) \left[ c_{J,n-1}^k(R, E_0) + c_{J,n+1}^k(R, E_0) \right]$$

$$= \epsilon_k(R, E_0)c_{I,n}^k(R, E_0).$$

(A.6)

Here, we have used $\langle \phi_m(R)|\phi_j(R)\rangle = \delta_{m,j}$ as well as $\frac{1}{T} \int_0^T e^{i(l-n)\omega t} dt = \delta_{n,l}$. The Floquet surfaces $\epsilon_k(R, E_0)$ and the corresponding state vectors $c_{I,n}^k(R, E_0)$ are defined for a cw laser with amplitude $E_0$. Correspondingly, they can be understood to be given instantaneously at some fixed field strength envelope at time $\hat{t}$, i.e. $E_0 \equiv E_0(\hat{t})$, and used for projection of the time-dependent field-dressed nuclear wave functions onto the adiabatic Floquet surfaces. This procedure is utilized for the calculation of the Floquet-surfaces and the nuclear wave packets on the Floquet surfaces in Section 3.2.

### A.2 Assignment of multiphoton channels in NA-QMD

In this section, we outline the scheme for extracting the contributions of the different photon channels to the angular distribution of dissociated fragments from the NA-QMD results.

In order to split the angular distribution of fragments into multiphoton channels within the NA-QMD method, where the nuclear motion is governed by the Ehrenfest (mean-field) force (2.45), the occupation probabilities of the bare Born-Oppenheimer states, i.e. the $\sigma_g$ and $\sigma_u$ states, are calculated for each trajectory. The final population is used as criterion to attribute each trajectory to the respective bare BO state: if the final population of the bare BO state differs at most 10 percent from the total final population $N_{j_F}(t_f)$, then the trajectory indexed by $j_F$ is regarded to be of $\sigma_g$- respectively $\sigma_u$-type. This procedure is visualized in Fig. (A.1), showing three different trajectories in the upper panel. MF (mean-field) here corresponds to a trajectory that cannot be assigned to one specific BO surface whereas this is possible for the trajectories ending on the $\sigma_g$, respectively $\sigma_u$ surface.

It remains to assign the photon number to the bare BO channel. This is accomplished on the basis of the nuclear kinetic energy release (KER) spectrum $P_D(E)$ which can be extracted from NA-QMD via trajectory statistics (see also Section 3.2.1) according to an energy interval

$$I_n = [n\Delta E, (n+1)\Delta E].$$

(A.7)

The (unnormalized) KER spectrum (at an energy $E_n = n\Delta E \in I_n$) is

$$P_D(E) = \sum_{j_F: E_{j_F}(t_0) \in I_n} \sin(\theta_{j_F}(t_0))N_{j_F}(t_f)$$

(A.8)
A.2 Assignment of multiphoton channels in NA-QMD

\[ E_{j\nu}(t_f) = \mu \frac{\dot{R}(t_f)^2}{2} \]  

(A.9)

where \( \mu \) is the reduced mass.
Appendix B

B.1 Normal mode analysis

In order to study vibrational excitations in the dynamics of polyatomic molecules, the instantaneous vibrational normal mode analysis is a common method [182, 183], which we summarize in this section. For this purpose, we start from the total energy of the system with \( N \) nuclei \( \mathbf{x} = \{x_1, \ldots, x_{3N}\} \) given by

\[
E = E_{\text{kin}} + V
\]  

(B.1)

with kinetic energy

\[
E_{\text{kin}} = \sum_{i=1}^{3N} \frac{M_i}{2} \dot{x}_i^2
\]  

(B.2)

and the ground state potential energy surface \( V \). For small displacements \( \mathbf{y} \) from the ground state equilibrium geometry \( \mathbf{x}_0 \), i.e. \( \mathbf{x} = \mathbf{x}_0 + \mathbf{y} \), the potential can be expanded approximately to second order as

\[
V(\mathbf{x}) \approx V(\mathbf{x}_0) + \sum_{ij} \left[ \frac{\partial V(\mathbf{x})}{\partial x_i \partial x_j} \right]_{\mathbf{x}=\mathbf{x}_0} y_i y_j .
\]  

(B.3)

Typically, mass scaled coordinates are used, i.e. \( \tilde{y}_i = \sqrt{\frac{M_i}{\omega_i}} y_i \). This leads to the eigenvalue problem

\[
\sum_j \tilde{V}_{ij} \xi_{jn} = \omega_n^2 \xi_{in}
\]  

(B.4)

with \( \tilde{V}_{ij} = \frac{1}{\sqrt{M_i M_j}} \left[ \frac{\partial V(\mathbf{x})}{\partial x_i \partial x_j} \right]_{\mathbf{x}=\mathbf{x}_0} \). In (B.4), the eigenvectors \( \xi_{in} \) are the eigenmode vectors and \( \omega_n \) are the eigenfrequencies of the eigenmodes \( (n = 1, \ldots, 3N) \). In the case of a nonlinear molecule, the six lowest (near-zero) eigenfrequencies are connected to translation and rotation. The remaining \( 3N - 6 \) eigenmodes are the vibrational modes. For the arbitrary motion of a molecule, the harmonic approximation (B.3) is not valid anymore, as the molecule might evolve far away from its equilibrium geometry.

The kinetic energy is quadratic in the velocity, and can thus be expanded exactly in terms of normal mode contributions corresponding to the ground state equilibrium geometry.
Therefore, we define the eigenmode coordinates by the transformation

\[ \eta_n = \sum_i U_{in} \sqrt{M_i} (x_i - x_{i0}) \]  \hspace{1cm} (B.5)

where \( U \) is a unitary matrix consisting of the eigenmode vectors from (B.4), i.e. \( U = (\xi_1, \ldots, \xi_{3N}) \). The coordinates \( \eta_n \) represent the amplitudes and therefore the strengths of the distinct normal modes. Using this, the kinetic energy can be decomposed as

\[ E_{\text{kin}} = \sum_n E_{\text{kin}}^n \]  \hspace{1cm} (B.6)

where \( E_{\text{kin}}^n = \frac{\eta_n^2}{2} \) is the kinetic energy of normal mode \( n \).

Within vibrational normal mode analysis, we calculate the kinetic energy of each (ground state equilibrium) vibrational normal mode \( n \) from the vibrational kinetic energy (without rotation and translation) at each time step via the transformation (B.5).
Appendix C

C.1 Separate spin treatment within Tully hopping

In this section, we focus on the performance of the separate spin treatment within the NA-QMD-H theory outlined in Section 2.3. This is done by exciting simple molecules with a sin^2-shaped laser field and keeping the nuclei frozen.

<table>
<thead>
<tr>
<th>Test case</th>
<th>(N = 100)</th>
<th>(N = 1000)</th>
<th>(N = 5000)</th>
<th>NA-QMD</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (\text{H}_2^+)</td>
<td>3.30 eV</td>
<td>3.74 eV</td>
<td>3.81 eV</td>
<td>3.78 eV</td>
</tr>
<tr>
<td>(b) (\text{C}_2\text{H}_4) (TDHF)</td>
<td>5.85 eV</td>
<td>6.68 eV</td>
<td>6.49 eV</td>
<td>6.40 eV</td>
</tr>
<tr>
<td>(c) (\text{C}_2\text{H}_4) (TDDFT)</td>
<td>3.80 eV</td>
<td>4.32 eV</td>
<td>4.44 eV</td>
<td>4.73 eV</td>
</tr>
</tbody>
</table>

*Table C.1:* Absorbed energy for the different test cases in Figure C.1.

The results for the ground state occupation are shown in Figure C.1. The first case, \(\text{H}_2^+\), represents a simple one-electron system, and accordingly the ground state occupation converges to the exact ground state occupation for an increasing number of NA-QMD-H "trajectories". In the many-electron case, we define the ground state occupation within NA-QMD by the (uncorrelated) product of the populations for the two spin components for comparison with NA-QMD-H. The results are shown for \(\text{C}_2\text{H}_4\) calculated with TDHF and TDDFT, where we observe a reasonably good agreement reproducing the correct qualitative trend in both cases. Some deviations occur, however, within TDDFT.

The quality of the NA-QMD-H results is quantified by the absorbed energies, tabulated in Table C.1. Comparing with the NA-QMD results, we recognize a good convergence within NA-QMD-H (in dependence on the size of the sample). Thus, despite the approximate nature of the separate treatment of both spins within NA-QMD-H, the results deliver the correct physics.
Figure C.1: Ground state occupation for different test cases within a $\sin^2$-shaped laser field ($T = 10$ fs, $\omega \approx 0.3$ a.u.) calculated with fixed nuclei: $\text{H}_2^+$ (a, $I = 1 \cdot 10^{13} \text{ W cm}^{-2}$) and $\text{C}_2\text{H}_4$ ($I = 2 \cdot 10^{13} \text{ W cm}^{-2}$) calculated with TDHF (b) respectively TDDFT (c). The full lines are the NA-QMD results, whereas the dotted lines denote the NA-QMD-H results calculated with different numbers of "trajectories".
Bibliography


[134] I.V. Hertel, T. Laarmann, and C.P. Schulz, *Ultrafast excitation, ionization, and fragmentation of C\textsubscript{60} 50*, 219–286 (2005), ISSN 1049-250X.


[141] Ihar Shchatsinin, Tim Laarmann, Nick Zhavoronkov, Claus Peter Schulz, and Ingolf V. Hertel, *Ultrafast energy redistribution in C\textsubscript{60} fullerenes: A real time study by two-color femtosecond spectroscopy*, The Journal of Chemical Physics 129(20), 204308 (2008).

[142] *Extensible computational chemistry environment basis set database*.


Danksagung

An dieser Stelle möchte ich meinen Dank an alle richten, die mich bei der Erstellung dieser Arbeit unterstützt haben.
Mein ganz besonderer Dank gebürt Herrn Prof. Rüdiger Schmidt, der mir die Möglichkeit gab, auf diesem interessanten Gebiet zu promovieren.
Dr. Jan Handt danke ich für viele hilfreiche Diskussionen und die Unterstützung bei zahlreichen Computerfragen.
Sebastian Krause danke ich für die Zusammen- und Vorarbeit zu den Untersuchungen von Wasserstoff im Laserfeld.
Des Weiteren danke ich dem Max-Planck-Institut für Physik komplexer Systeme (MPI-PKS) bzw. der International Max Planck Research School for "Dynamical Processes in Atoms, Molecules and Solids" für die finanzielle Unterstützung und die Bereitstellung von Rechnerkapazitäten.
Ebenfalls danke ich dem Zentrum für Informationsdienste und Hochleistungsrechnen (ZIH) an der TU Dresden für die Bereitstellung von Rechnerkapazitäten.
Außerdem vielen Dank an die übrige Arbeitsgruppe, namentlich Frank Großmann, Max Buchholz und Tobias Fiedelschuster sowie die ehemaligen Mitglieder Christoph Goletz, Werner Koch, Sebastian Krause, Frank Mulansky für die vielen Diskussionen zur Physik, Computerfragen und anderes.
Für das Korrekturlesen der Arbeit danke ich insbesondere Jan Handt, Martin Winter, Max Buchholz und Claudia Zerbe. Weiterhin möchte ich mich bei allen Mitarbeitern des Instituts für Theoretische Physik für die angenehme Arbeitsatmosphäre bedanken.
Nicht zuletzt danke ich meinen Eltern, meiner Freundin und meinen Freunden.
Erklärung

Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.


Michael Fischer