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DISSERTATION

Ultrafast Dynamics in the Strong Laser Field Ionization of Atoms and Molecules

ausgeführt zum Zwecke der Erlangung des akademischen Grades

eines Doktors der technischen Wissenschaften unter der Leitung

von

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387

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Abstract

This thesis presents a theoretical investigation of ultrafast dynamics during strong laser field ionization with atoms and molecules. For that a new method for solving the time-dependent Schrödinger equation was developed and implemented, where a hybrid discretization was used with cylindrical coordinates with a finite element method for the radial ρ coordinate and a pseudo-spectral technique for the *z* coordinate. The main results of the thesis are:

- Orientation dependence, orbital symmetry dependence of molecular field ionization was studied with a two-dimensional model molecule. To get the information of rescattering electrons, an analytical probing of rescattering electrons was implemented. By studying the momentum distribution of rescattering electrons during strong field ionization of molecules, we found that the rescattering process is strongly dependent on the orientation and symmetry of the molecule.
- 2. Sub-cycle dynamics during laser field ionization of molecules was investigated. With a two-dimensional diatomic molecule model, we found that the laser induces sub-laser-cycle dynamics during field ionization and the field-induced sub-cycle dynamics modifies the time structure of rescattering electrons. Such dynamics may modify the time-frequency structure of high-order harmonic response, or lead to the appearance of even harmonics with certain laser intensities.
- 3. An extreme-ultraviolet (XUV) probing method with attosecond resolution has been applied to study ionization dynamics of a hydrogen atom in a strong infrared laser field. Distortion of ground state and electron excitation during strong field ionization influence the total XUV photon ionization yield. We found the total XUV photon ionization yield follows electron density near the nucleus.

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Notation

- *H* Hamiltonian
- Ψ wavefunction
- \mathscr{E} electric field
- *A* vector potential
- ω laser frequency
- τ pulse duration (full with at half maximum)
- *I* laser intensity
- *I_p* ionization potential
- E_g ground state energy
- E_e excited state energy
- U_p ponderomotive energy
- Γ ionization rate
- c speed of light
- *i* imaginary unit

Overview

With the advance of the Kerr-lens mode-locking [1, 2], the duration of laser pulse has reached the scale of few laser optical cycles (e.g. the 800 *nm* laser has the optical cycle of 2.67 *fs*). On the other hand, chirped pulse amplification (CPA) [3] led to ultrahigh intensity of laser pulses (up to $10^{18} W/cm^2$ with intensity fluctuation of 1% [4]). In laboratories, table-top femtosecond laser systems with pulse durations of a few ten femtosecond and intensities larger than $10^{14} W/cm^2$ are widely available at wavelength in the visible and infrared range (from 400 nm to $2 \mu m$) [5]. Several research groups have achieved sub-5-fs pulses in visible and near infrared range [6, 7, 8]. By using the technique of gas-filled single hollow fiber with spatial light modulator, the Yamashita group achieved 2.8 *fs* pulses, the shortest pulse duration at present in visible range [9]. Furthermore, with a so-called "carrier-envelope phase stabilization" technique, the electric field of the laser pulse can be highly reproduced with shot to shot phase fluctuations of less than 100 attosecond ($1 as = 10^{-18} s$), which is only a small fraction of the laser optical period [10].

In recent years, in several experiments the barrier of femtosecond was broken and sub-femtosecond or attosecond duration was reached with such few-cycle laser pulses. It was demonstrated that the electron motion in atoms or molecules (typical time scale is a few hundred attosecond) can be controlled by a few-cycle lase pulse [11] and even can be employed to image a molecular orbital [12], or to produce extreme-ultraviolet(XUV) pulses with durations of a few hundred attosecond [10], or to directly characterize the electric field of a laser pulse [13]. With the generated XUV attosec-

ond pulse, the door was opened to a new regime, which is named "attosecond physics" [14].

In a strong laser field, electrons in atoms or molecules will be ionized through tunneling ionization or above-threshold ionization, and then be accelerated in the field, and part of them will be guided back to the parent ions and rescatter with the ions approximately in the next half cycle of the laser field. If the rescattering is elastic, one can obtain a snapshot of the ion's nuclear position [12] from electron diffraction patterns. If the rescattering is inelastic, further electrons might be kicked out from the ion, which provides information of electron dynamics at that time [15, 16]. Such process is called nonsequential multiple ionization [17, 18]. In the inelastic scattering case, electrons may also recombine with their parent ions and emit high-order harmonic radiation with energies generally equal to the sum of kinetic energy of the electron at the time of recombination and the ionization potential of the atom or the molecule. High-order harmonic radiation is normally in the XUV or soft X-ray regime. As the electron energy varies rapidly during rescattering, the high-order harmonic radiation is broadband with an intrinsic chirp. By compensating the intrinsic chirp and applying a spectral filter, attosecond XUV pulse trains or even an isolated single attosecond XUV pulse can be produced [19]. Presently, single attosecond pulses can be produced with a duration of 170 as at $\sim 100 \, eV$ by filtering the cutoff of high-order harmonic radiation generated by a 5 fs laser pulse [20], or with a duration of 130 as at $\sim 36 eV$ with the so-called polarization gating method [21]. The durations of such isolated attosecond XUV pulses are less than 1/15 of the optical period of the fundamental femtosecond laser.

The new born attosecond XUV pulse normally propagates with its fundamental infrared laser pulse, and the time-delay between the XUV pulse and the infrared pulse can be controlled with an accuracy of a few ten attoseconds, which makes it an excellent candidate for pump-probe measurements. The pump-probe technique is the most direct method to trace fast dynamics in the time domain. With a single isolated attosecond XUV pulse and a precisely timing controlled infrared laser pulse, the so-called

streak-camera scheme can be used for sampling the emission of Auger electrons. The experiment was described in Ref. [22]. An isolated 650*as* XUV pulse excites a core electron and produces a inner-shell vacancy with a very short lifetime. This vacancy is rapidly filled by an electron from the outer shell, and the energy lost by the electron is carried away by a photon or a secondary electron, the Auger electron. The emission time of the Auger electron corresponds directly to the life time of the inner-shell vacancy. Therfore, sampling the Auger electron emission in the same way the photoelectron emission is sampled, this gives us direct time-domain access to inner-shell atomic process with attosecond resolution.

When an atom or a molecule is exposed to a strong laser pulse, one electron or more electrons will leave the nucleus through tunneling ionization or above-threshold ionization. The strong field ionization process is essential to understand strong field effects, such as high-order harmonic generation and nonsequential multiple ionization. A very recent experiment was performed by using a XUV-IR-pump-probe scheme to measure tunneling ionization with attosecond resolution [23]. The attosecond time-scale of the tunneling process was demonstrated by using multiple excitation and relaxation processes. In the experiment, the infrared pulse was chosen such that it cannot ionize the atoms by itself. In the experiment, the atoms were first excited by the XUV pulse, with which some of the electrons are sent to the excited states of the atom, and then tunneling ionization can be induced by the infrared laser pulse. By controlling the time delay between XUV pulse and infrared pulse, the tunneling process during infrared laser cycles can be measured with attosecond resolution in the time domain. The light-induced tunneling technique may now be used to provide further observations of electron dynamics.

Because high-order harmonic radiation is emitted due to the recombination of electrons that are guided back to their mother ions by the laser field, the spectrum and the phase of harmonic radiation contain information of the electronic orbital that is ionized. The shape of highest occupied molecular orbital (HOMO) can be imaged in three dimensions under certain conditions. By changing the relative angle between molecular orientation and the polarization of the probe laser, one can obtain a set of projections of the molecular orbital. This can be transformed into an image of the molecular orbital by using an algorithm based on computer tomography [24]. It has been done [25] for di-nitrogen (N_2) with a reference of argon. Experimental high-order harmonic spectra were taken at 19 angles of the molecular orientation axis to the laser polarization axis. With such spectra, the $3\sigma_g$ orbital was well reconstructed. Such a rescattering image of molecular orbitals is based on the assumption that the rescattering wavepacket of the molecule is well known and does not depend on the orbital structure of the molecule.

Several other techniques are being used both in spatial dimension to improve spatial resolution and temporal domain to gain insight into the bound electrons and even nuclei with extremely short time scale. Laser-induced electron diffraction is one of them. Efforts to image molecular dynamics with a sub-picosecond electron beam by watching the time dependence of diffraction pattern by electron pulse [26, 27] have been made. The typical electron energy is between 50 keV to 300 keV, which corresponds to de Broglie wavelength from 0.05Å to 0.02Å. To compare with the typical bond length in range of 1 Å, they are more than one magnitude smaller, which makes spatial reconstruction from diffraction pattern easy and accurate. The main limitation of the technique is that electrons naturally disperse due to mutual repulsion and velocity dispersion. The time resolution of the conventional diffraction technique is around the time scale of a few hundred femtoseconds. An electron diffraction pattern of a molecule can also be obtained from recollision of electrons with their parent molecules in a strong laser pulse, with about 1 Å spatial resolution and 1 fs temporal resolution [12, 28, 29, 30]. As we mentioned before, during a strong laser pulse, detached electrons can be guided back to rescatter with their parent ions, and elastic scattering will lead to generation of a diffraction pattern, with which one can image the molecule. The temporal resolution will be approximately the time between electron releasing and rescattering, which is about half an optical period of the laser field. The merit of such technique is that the temporal resolution of electron diffraction is about 1 fs for infrared laser pulse (half an optical cycle of laser pulse with wavelength 800 nm is 1.3 fs), even in sub-femtosecond regime for laser pulses with shorter wavelengths (e.g. 400 nm).

Another goal in attosecond science is to achieve XUV-pump XUV-probe studies on ultra-fast dynamics. Due to extremely small two-photon cross sections, nonlinear optics experiments in the XUV range are particularly hard. With current high-order harmonic radiation, autocorrelation measurement was performed only with rather long harmonic wavelength (around 13 eV) for the two-photon ionization of helium [31]. The method has a limitation as photon energies need to be less than the ionization potential of the chosen atom. In another experiment, it was reported that such limitation can be avoided because of small cross-section for above-threshold ionization [32]. Up to now, purely XUV pump-probe experiments still can not be performed with present XUV pulse intensities. This is one of the main reason why we need more intense XUV pulses [33]. Once such pulses become available, the whole range of methods based on pump-probe technique can be applied to a rather short time scale. In particular, specific inner-shell excitation can be addressed and the distortion of the initial system by the probing field can be significantly reduced. A door will be opened to gain insight into the fastest process in chemistry and atomic physics or even nuclear physics.

The motivation of this thesis is based on recent experiments with few-cycle laser pulses and attosecond XUV pulses. Rescattering electron wavepacket is crucial for its application in molecular tomography, which should not depend on the mother molecule. Therefore, a question appears: is electron rescattering universal for all species molecules? Does it depend on the initial state of the molecule? The momentum distribution over time of rescattering electrons should be carefully studied before one can use it.

Moreover, as attosecond XUV pulse has become a brand new and powerful tool to probe ultrafast dynamics by exciting or ionizing electrons in atoms or molecules with attosecond time scale, one essential question should be answered: what is really probed by such an XUV attosecond probing method? In other words, which quantities of atoms or molecules will determine or affect the output from the XUV probing method.

Both questions will be investigated in this thesis. The momentum and time structures of rescattering electrons will be studied for initial states with different symmetry and orientation during strong field ionization. For the XUV probing method, we calculated the XUV probing of strong laser field ionization to identify the quantity that determines the total XUV ionization yield.

In the first chapter, a short review over strong field theory is presented, especially numerical methods for solving time-dependent Schrödinger equation. Time propagators, spatial and temporal discretization and gauges used to solving the TDSE are discussed. Moreover, numerical simulations of high-order harmonic generation from single particle response and its propagation effects are presented.

In the second chapter, orientation dependence and orbital symmetry dependence of laser field ionization were studied with a two-dimensional diatomic molecule model. To get the information of rescattering electrons, a method to determine the rescattering part of the electronic wavefunction was developed. By studying the momentum distribution of rescattering electrons during laser field ionization, we found that rescattering process during strong field ionization of molecules is strongly dependent on the orientation and orbital symmetry of its initial state.

In the third chapter, sub-cycle dynamics during laser field ionization of molecules was investigated. With a two-dimensional diatomic molecule model, we found that the strong laser induces sub-cycle dynamics during field ionization due to Rabi-like oscillations, and such dynamics modifies the time-structure of rescattering electrons. The field-induced dynamics can be observed in the time-frequency structure of high-order harmonic response, which has inherited the effect from electrons recombination with their parent ions. Further, in additional to harmonics with odd multiples of the fundamental laser frequency, even harmonics can appear at certain laser conditions.

In the fourth chapter, an XUV probing method with attosecond resolution has been applied to study ionization dynamics of hydrogen atoms in a strong infrared laser field. A hybrid discretization was used to the solving time-dependent Schrödinger equation of the hydrogen atom with two-dimensional cylindrical coordinates. The finite element method is applied in the radial coordinate while a pseudo-spectral technique is employed in z-coordinate. Distortion of the ground state and electron excitation of the atom in the strong laser field influence the total XUV photon ionization yield. It was found that the total XUV photon ionization yield neither follows the population of ground state nor total unionized population, but follows the electron density near the nucleus.

Chapter 1

Numerical simulations of atoms and molecules in a strong laser field

1.1 Introduction

In a strong laser field, which is comparable to the electric field inside in the atom or the molecule, electrons will be ionized and accelerated in the external field. Part of these electrons can be guided back to their parent ions and scatter from them. During such process, there is a rather complex interplay between laser force and atomic force. Fortunately, most of phenomena in strong field physics can be explained under following approximation: the dynamics can be separated into two parts, one part "inside" the atom where atomic force dominates and the other part "outside" the atom where the laser force dominates. Based on such a picture, numerical calculations can be performed with models in a classical, semi-classical or fully quantum mechanical frame. In many cases, the classical picture can essentially explain the phenomena and quantum mechanical calculations are only needed to achieve quantitatively correct results.

1.1.1 Strong field approximation (SFA)

Strong field approximation is the most used analytical method to investigate strong field phenomena, such as above-threshold ionization, high-order harmonic generation and non-sequential double ionization. It assumes that the initial bound states of atoms or molecules are unaffected by the external laser field while the final state, which is in the continuum, cannot feel the Coulomb potential. With the strong field approximation, the unbound part of the electron wavepacket has the general form [34]

$$\Psi(\mathbf{r},t) = \int d^3k \int_{-\infty}^t dt' \exp\left(-i\Phi(\mathbf{k},t')\right) \exp(i\mathbf{k}\cdot\mathbf{r})\chi(\mathbf{k},t), \qquad (1.1)$$

where

$$\Phi(\mathbf{k},t') = -\frac{1}{2} \int_{-\infty}^{t'} d\tau \left[\mathbf{k} - \frac{1}{c} \mathbf{A}(\tau) \right]^2, \qquad (1.2)$$

is the so-called Volkov phase and $\mathbf{A}(\tau)$ is the vector potential of the external field in Coulomb gauge ($\nabla \cdot \mathbf{A} = 0$) and *c* is the speed of light in vacuum. Atomic units $\hbar = e = m_e = 1$ are used all through the thesis, where \hbar is reduced Plank constant, -e and m_e the electron charge and mass, respectively. The Volkov solution of a free electron in a laser field is just a plane wave times the Volkov phase. The "release amplitude" $\chi(\mathbf{k}, t)$ depends on the ionization process. It can simply be given by

$$\boldsymbol{\chi}(\mathbf{k},t) = \vec{\mathcal{E}}(t) \cdot \mathbf{d}(\mathbf{k}) \exp(iI_p t)$$
(1.3)

where $\vec{\mathscr{E}}(t)$ is the field strength of the laser field, $\mathbf{d}(\mathbf{k})$ is the field-free bound-continuum dipole moment and I_p is the ionization potential of the system.

The equation (1.1) has a simple interpretation. The "release amplitude" $\chi(\mathbf{k},t)$ describes how the electron wavepacket is driven to the continuum and gives the initial quantum mechanical phase of the wavepacket. The Volkov phase describes the free evolution of the wavepacket from that time on and determines how contributions add up from all times. The laser is assumed to only influence the free electron motion through the vector potential in the Volkov phase, but it has no effect on the release amplitude.

The strong field approximation is very suitable to describe propagation after electron release. This allows one to reconstruct electron spectra and high-order harmonic spectra in great detail. However, tunneling ionization is not correct in the strong field approximation, because of neglecting the atomic potential, which is a crucial factor on laser ionization. There are several techniques to correct the influence of the atomic potential [35, 36], with which one can get quantatively correct high-order harmonic spectra [37]. For a correct description of the ionization process, solving full timedependent Schrödinger equation is required.

1.1.2 Strong field ionization

Ionization is the essential process to understand strong field phenomena, such as highorder harmonic generation, above-threshold ionization and nonsequential double ionization. The Keldysh parameter [38] determines whether multiphoton or tunneling ionization or barrier-suppression ionization dominates the ionization processes, which is defined as

$$\gamma = \sqrt{\frac{I_p}{2U_p}} \tag{1.4}$$

where I_p is the ionization potential of the system. U_p is the ponderomotive energy, given by

$$U_p = \frac{\mathscr{E}_0^2}{4\omega_0^2}$$
(1.5)

where ω_0 and \mathscr{E}_0 are the central frequency and the peak field strength of the field, respectively. For $\gamma \gtrsim 1$, multiphoton ionization dominates, which is a process that extends over several electric field cycles with interference between electron wavefunctions which are produced during each field cycle. On the other hand, for $\gamma \lesssim 1$, ionization is dominated by tunneling ionization or barrier-suppression ionization, in which regime interference between electron wavefunctions from different time plays a minor role for the ionization yield. Tunneling ionization or barrier-suppression ionization can be well described by static-field ionization models. The quasi-static ionization yield Y_q is given by

$$Y_q = 1 - \exp\left\{-\int \Gamma[\mathscr{E}(t)]\,dt\right\}$$
(1.6)

where $\Gamma[\mathscr{E}(t)]$ is the ionization rate for static field $\mathscr{E}(t)$. The tunneling ionization strongly depends on the electric field strength and the ionization potential of the system. For the hydrogen atom, the tunneling ionization rate for static field \mathscr{E} is given by [39]

$$\Gamma(\mathscr{E}) = \frac{4}{\mathscr{E}} \exp\left[-\frac{2}{3\mathscr{E}}\right].$$
(1.7)

For general atoms, the Ammosov, Delone, and Krainov (ADK) formula is widely used to get the tunneling ionization rate, which is given by

$$\Gamma_{ADK} = C_{n^*l}^2 f(l,m) \left(\frac{3\mathscr{E}}{\pi (2I_p)^{3/2}}\right)^{1/2} \left(\frac{2(2I_p)^{3/2}}{\mathscr{E}}\right)^{2n^* - |m| - 1} \exp\left(-\frac{2(2I_p)^{3/2}}{3\mathscr{E}}\right)$$
(1.8)

with

$$C_{n^*l} = \left(\frac{2e}{n^*}\right)^{n^*} (2\pi n^*)^{-1/2}, \qquad (1.9)$$

$$f(l,m) = \frac{(2l+1)(l+|m|)!}{2^{|m|}|m|!(l-|m|)!}$$
(1.10)

where n^* is an effective quantum number, and l and m are angular and magnetic quantum numbers, respectively, and e is the Euler number. Recently, the ADK formula was successfully extended to molecules [40]. In the tunneling regime, the ionization rates formulae show the exponential dependence of ionization rate on the inverse of the field strength. Consequentially, electron emission dominantly happens at a very narrow time when the field reaches its peak.

For barrier-suppression ionization, there are no reliable analytic formulae to estimate the ionization rate. Generally, the ionization rate in this regime is obtained by numerical calculations [41, 42]. The dependence of field strength is much weaker in this regime, which leads a broader time-distribution of electron emission.

1.1.3 Electron recollision

Generally speaking, the idea of electron rescattering plays a central role in the theoretical description of the interaction of intense laser pulses with atoms and molecules: an electron is released from a bound system usually by tunnel ionization, then it travels as a free, basically classical particle in the laser field, and then it scatters with its parent system, if it is guided back there by the field [43, 44]. This is so-called threestep model, which was first used to explain the generation of high-order harmonics. There is overwhelming and rather detailed experimental and theoretical evidence that rescattering dominates the atomic dipole response at high frequencies and similarly compelling evidence is being accumulated that it is also responsible for enhanced double ionization of atoms and molecules [17, 18].

Recently it was proposed that the rescattering electrons can be used like a (coherent!) microscopic electron beam to provide images of the parent system, e.g. of the nuclear positions of a molecule by double-ionizing a molecule at a well defined time after initial tunnel ionization [12], by providing a diffraction image of the parent system [28], and even by mapping the bound part of the electronic wave function into the high harmonic spectra, from where it could be recovered by tomographic methods [25].

As electron detachment and recollision occupy only a fraction of the whole cycle, time-structures are on the scale of a few hundred attosecond. These extremely rapid processes can be manipulated by controlling the laser field which is being exploited in an increasing number of experiments. From high harmonic radiation attosecond pulses can be extracted and efforts are directed to obtaining higher harmonic intensities and detailed control of the time structure. Harmonic radiation also serves to diagnose recollision itself and to extract information about structure [25] and dynamics of the target [45, 46]. The early focus of recollision experiments was on ionization and harmonic generation with noble gases, where the recollision picture has become firmly established. The chirp of the harmonics can be linked to recollision times [47], and control

of the recollision through laser polarization [48, 49] and two-color fields [50] was demonstrated. Now attention is increasingly shifting towards molecules, because of their more complex structure and richer dynamics.

1.1.4 High-order harmonic generation

High-order harmonics are generated from recombination of rescattering electrons with their parent ions. The recombination energy is given by the sum of the ionization potential and the electron kinetic energy when it recombines, which is normally in extreme-ultraviolet (XUV) or soft X-ray range. The maximum harmonic energy is produced by electrons which are released at about 0.05 optical cycles after peak electric field strength and recombine about a half cycles later. The maximum energy of harmonic radiation, so-called cutoff energy, is evaluated by the three-step model as

$$\omega_{cutoff} \approx I_p + 3.17U_p \tag{1.11}$$

where I_p is the ionization potential of the system and U_p is the ponderomotive energy (Eq. (1.5)).

In case of a symmetric system in a multi-cycle laser pulse, the electron release and recombination process is repeated each half laser cycle and harmonic radiation emits as well. The corresponding harmonic spectrum consists of a series of narrow peaks at odd multiples of the frequency of the driving field. In case of a few-cycle laser pulse, the release and recombination time as well as the cutoff energy become dependent on the carrier-envelope phase of the laser pulse. A single high frequency attosecond radiation can be filtered out when the pulse has some certain carrier-envelope phase [51].

The simple semi-classical picture of high-order harmonic generation as given by the three-step model accurately predicts the range of photon energies of high-order harmonic generation, and also fully explains the time-structure of the radiation. However, a quantum mechanical treatment is needed for a more complete picture of the high-order harmonic process. A fully quantum mechanical and analytical theory of high-order harmonic radiation, derived by Lewenstein et al.[52], has been extremely successful in describing the general characteristics of high-order harmonic radiation, which will be discussed later on.

1.2 Solving the time-dependent Schrödinger equation

1.2.1 Time-dependent Schrödinger equation (TDSE)

In this section, we concentrated on the method for numerically solving the TDSE, which will be used in the following chapters of the thesis. The three-dimensional TDSE has a form as

$$i\frac{\partial}{\partial t}\Psi(t) = H(t)\Psi(t) \tag{1.12}$$

where *H* is the Hamiltonian of the system and $i = \sqrt{-1}$ is the imaginary unit. Normally, the Hamiltonian is given by

$$H(\mathbf{r};t) = -\frac{1}{2}\nabla^2 + V(\mathbf{r};t)$$
(1.13)

where the first part is the kinetic energy operator and the second part is the potential operator.

If the initial state is know as $\Psi(t_0)$, the formal solution of Eq. (1.12) can be expressed as

$$\Psi(t) = U(t, t_0)\Psi(t_0) \tag{1.14}$$

where the time propagator $U(t, t_0)$ is given by

$$U(t,t_0) = \hat{T} \exp\left[-i \int_{t_0}^t H(t') dt'\right]$$
(1.15)

In Eq. (1.15), \hat{T} is time ordering operator and H(t') is time-dependent Hamiltonian. If the Hamiltonian is time independent, the formal solution of Eq. (1.15) is

$$U(t,t_0) = \exp[-i(t-t_0)H].$$
(1.16)

If Hamiltonian is time dependent, this solution (1.16) is approximate. When the time step $(\Delta t = t - t_0)$ is chose sufficiently small, the time propagator can be replaced by an approximate propagator with a certain accuracy.

1.2.2 Time propagators

Various schemes have been proposed to approximate the time propagator [53, 54]. The simplest Euler scheme expands the propagator with first order of $H\Delta t$, which reads as

$$\exp(-iH\Delta t) = 1 - iH\Delta t + O(\Delta t^2).$$
(1.17)

This is a explicit scheme, which means matrix inversion is not needed, but it is unstable. Moreover, it is no unitary, that is, the norm of the wavefunction is not preserved during time propagation, which will lead to unphysical results. To numerically study a time-dependent process with TDSE, it is important to get a unitary time propagator. There are several frequently used propagators, which have higher accuracy, such as Crank-Nicholson (CN) method, Peaceman-Rachford (PR) method, Runge-Kutta (RK) method, and split-step (SS) method.

The CN propagator is presented as the so-called Cayley form [55]

$$\exp(-iH\Delta t) = \frac{1 - iH\Delta t/2}{1 + iH\Delta t/2} + O(\Delta t^3)$$
(1.18)

which is an implicit scheme. Appealing features of the CN method are that it is unitary and the energy is constant, and most importantly, it is unconditionally stable and consistent [56, 57]. The accuracy of CN method is order of Δt^3 . A serious drawback of the CN method is that each time step requires the inversion of a matrix, which makes the efficiency of computation rather poor, especially for two-dimensional or higher dimensional systems.

To avoid solving a linear system in two-dimension, one can split the time propagator as $\exp(-i(A+B)\Delta t)$, where *A* and *B* are arbitrary operators. This is the main idea of PR method [58, 59], by which the time propagator is approximated by

$$\exp[-i(A+B)\Delta t] = \frac{1}{1+iA\Delta t/2} \frac{1-iB\Delta t/2}{1+iB\Delta t/2} (1-iA\Delta t/2) + O(\Delta t^3).$$
(1.19)

By introducing an intermediate state $\Psi_{n+\frac{1}{2}}$, the propagator can be separated into two implicit schemes,

$$(1 + iB\Delta t/2)\Psi_{n+\frac{1}{2}} = (1 - iA\Delta t/2)\Psi_n,$$

$$(1 + iA\Delta t/2)\Psi_{n+1} = (1 - iB\Delta t/2)\Psi_{n+\frac{1}{2}}.$$

$$(1.20)$$

With a two-dimensional problem, one can choose the operators such that A contains differential operators of one coordinate and B contains those of the other coordinate. Then PR method has reduced the computation problem from solving one two-dimensional linear equation to solving two one-dimensional linear equations for each time step. The accuracy of PR method is also order of Δt^3 .

The Runge-Kutta (RK) method is one of the most used integrator for ordinary differential equations, by which high accuracy can be achieved and adaptive step control can be easily implemented [60]. The basic idea of the RK method is using a trial step at the midpoint of an interval to cancel out lower-order error terms. The second-order formula is

$$k_{1} = \Delta t f(t_{n}, \Psi_{n}),$$

$$k_{2} = \Delta t f(t_{n} + \frac{1}{2}\Delta t, \Psi_{n} + \frac{1}{2}\Delta k_{1}),$$

$$\Psi_{n+1} = \Psi_{n} + k_{2} + O(\Delta t^{3}),$$
(1.21)

where $f(t_n, \Psi_n) = -iH(t_n)\Psi_n$. It has an accuracy with order of Δt^3

The fourth-order RK method, which is the mostly used one, has an accuracy with order Δt^5 . The formulae are read as

$$k_{1} = \Delta t f(t_{n}, \Psi_{n})$$

$$k_{2} = \Delta t f(t_{n} + \frac{1}{2}\Delta t, \Psi_{n} + \frac{1}{2}\Delta k_{1})$$

$$k_{3} = \Delta t f(t_{n} + \frac{1}{2}\Delta t, \Psi_{n} + \frac{1}{2}\Delta k_{2})$$

$$k_{4} = \Delta t f(t_{n} + \Delta t, \Psi_{n} + k_{3})$$

$$\Psi_{n+1} = \Psi_{n} + \frac{1}{6}k_{1} + \frac{1}{3}k_{2} + \frac{1}{3}k_{3} + \frac{1}{6}k_{4} + O(\Delta t^{5}).$$
(1.22)

The general idea of split-step (SS) method is to make use of the special structure of an equation, in which the time evolution operator can be separated into two easily solvable parts (H = A + B), which, however, do not commute with each other. It will produce a splitting error due to the non-commutativity of separated parts. The Baker-Campbell-Hausdorf formula [61, 62] is very useful to reduce noticeably the splitting error. The second-order SS method can be presented based on Baker-Campbell-Hausdorff formula,

$$\exp[-i(A+B)\Delta t] \approx SS_2(\Delta t) = \exp(-iA\Delta t/2)\exp(-iB\Delta t)\exp(-iA\Delta t/2) \quad (1.23)$$

which has an accuracy of $O(\Delta t^3)$.

The fourth-order SS method is given in the form

$$SS_4(\Delta t) = SS_2(\omega \Delta t)SS_2[(1 - 2\omega)\Delta t]SS_2(\omega \Delta t)$$
(1.24)

where $\omega = (2 + 2^{1/3} + 2^{-1/3})/3$. The accuracy of the fourth-order SS method is the same as the fourth-order RK method.

Note that the number of products of exponential operators increases with the order of decay of splitting error. In general, the operators A and B in Eqs. (1.23) and (1.24) may be interchanged without affecting the accuracy order of the method.

1.2.3 Time discretization

The straight forward discretization of time is a uniform step grid. A good time propagator should exert some adaptive control over its own progress, making changes in its step-size as needed. Usually the purpose of this adaptive step-size control is to achieve some predetermined accuracy in the solution with minimum computational efforts. Implementation of adaptive step-size control requires that the stepping algorithm signals information about its performance, most importantly, an estimate of its truncation error. Obviously, the calculation of this information will add to the computational overhead, but the investment will generally be repaid handsomely. With fourth-order Runge-Kutta, the most straightforward technique by far is two-step method (e.g. [63]). We take each step twice, once as a full step, then, independently, as two half steps. Then we compare the results of both calculation and estimate the accuracy to determine the step-size (one can find a detailed description in "Numerical Recipes" [60].) The two-step method can also used for other propagators.

1.2.4 Coordinates, spatial discretization and derivatives

The three-dimensional TDSE in velocity gauge of hydrogen atom in a strong laser field with dipole approximation has the form

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[\frac{1}{2}(\mathbf{p} - \frac{1}{c}\mathbf{A}(t))^2 - \frac{1}{r}\right]\Psi(\mathbf{r},t)$$
(1.25)

where $\mathbf{A}(t)$ is the vector potential of the external laser field in Coulomb gauge and $-\frac{1}{r}$ is the Coulomb potential.

Spatial discretization directly depends on the coordinates in which to represent the wavefunction. Usually used coordinates are spherical coordinates, cylindrical coordinates and Cartesian coordinates. In the thesis, cylindrical coordinates and Cartesian coordinates will be used to study the sub-cycle dynamics during laser field ionization of hydrogen atoms and molecules, respectively.

Cylindrical coordinates

We assumed that laser field is linearly polarized and the polarization direction is parallel to z axis. Because of the symmetry, cylindrical coordinates ρ , z, ϕ (x= $\rho \cos \phi$, y = $\rho \sin \phi$, z = z) are introduced with an ansatz

$$\Psi(\rho,\phi,z;t) = \frac{1}{\sqrt{2\pi}} \Psi(\rho,z;t) \exp(im\phi)$$
(1.26)

and TDSE of hydrogen atom in length gauge with dipole approximation has the form

$$i\frac{\partial}{\partial t}\Psi(\rho,z,\phi;t) = \left[\frac{1}{2}p_{\rho}^{2} + \frac{m^{2}}{2\rho^{2}} + \frac{1}{2}(p_{z} - \frac{1}{c}A(t))^{2} - \frac{1}{\sqrt{\rho^{2} + z^{2}}}\right]\Psi(\rho,z,\phi;t) \quad (1.27)$$

where A(t) is the vector potential of the external laser field and *m* is the magnetic quantum number. In our calculations, the ground state of hydrogen atom is used,

which implies m = 0. The TDSE turns into

$$i\frac{\partial}{\partial t}\psi(\rho,z;t) = \left[\frac{1}{2}p_{\rho}^{2} + \frac{1}{2}(p_{z} - \frac{1}{c}A(t))^{2} - \frac{1}{\sqrt{\rho^{2} + z^{2}}}\right]\psi(\rho,z;t)$$
(1.28)

and the normalization condition is

$$\int_{0}^{\infty} \rho d\rho \int_{-\infty}^{\infty} dz |\psi(\rho, z; t)|^{2} = 1.$$
 (1.29)

As presented in Ref. [64], a scaled coordinate method was applied to solving the TDSE in cylindrical coordinates. The singularity in the origin can be avoided and the differential operators can be conveniently applied with finite difference method. It was implemented as follows. The scaled cylindrical coordinates are defined as

$$x = \xi^{\lambda} \cos \phi, y = \xi^{\lambda} \sin \phi, z = z, \qquad (1.30)$$

and the wavefunction was determined by

$$\Phi(\xi, z) = \sqrt{\lambda} \xi^{\lambda - 1/2} \psi(\rho, z).$$
(1.31)

The wavefunction was propagated by using PR method. It turned out the best choice is $\lambda = 3/2$, both for stability and accuracy.

Cartesian coordinates

The Hamiltonian of the system in three-dimensional coordinates with velocity gauge for the hydrogen atom in a linearly polarized field is

$$H(x, y, z; t) = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}(p_z - \frac{1}{c}A(t))^2 - \frac{1}{\sqrt{x^2 + y^2 + z^2}}.$$
 (1.32)

Because coordinates x and y are symmetric, one can take a cut in x - y plane which turns Eq. (1.32) into an equation in two-dimensional Cartesian coordinates,

$$i\frac{\partial}{\partial t}\psi(x,z;t) = \left[\frac{1}{2}p_x^2 + \frac{1}{2}(p_z - \frac{1}{c}A(t))^2 - \frac{1}{\sqrt{x^2 + z^2}}\right]\psi(x,z;t).$$
 (1.33)

To avoid the singularity of the potential, a screened potential is usually employed to model the system, which is defined as

$$V(x,z) = -\frac{1}{\sqrt{x^2 + z^2 + a^2}}$$
(1.34)

where *a* is the screening parameter, which can be adjusted to get the correct ionization potential of the system.

For two-dimensional Cartesian coordinates, the Hamiltonian is given by

$$H(x,z;t) = \frac{1}{2}p_x^2 + \frac{1}{2}(p_z - \frac{1}{c}A(t))^2 + V(x,z).$$
(1.35)

With the split-step method, one can separate Hamiltonian into kinetic energy part $\frac{1}{2}p_x^2 + \frac{1}{2}(p_z - \frac{1}{c}A(t))^2$ and potential part V(x,z). Before applying kinetic energy part, the wavefunction is transformed into momentum space numerically by Fourier transform

$$\tilde{\Psi}(p_x, p_z; t) = \int dx \int dz \Psi(x, z; t) \exp(-ixp_z) \exp(-izp_z).$$
(1.36)

After that, wavefunction is brought back to configuration space by backwards fast Fourier transform, and then the potential part is applied. This is one variant of the pseudo-spectral method.

To present spatial discretization and evaluation of spatial derivatives, Cartesian coordinates are used as an example. Spatial discretization for Cartesian coordinates mostly is used as equally spaced mesh with finite box size

$$\begin{cases} x_j = j\Delta x, \quad j = -N_x, ..., N_x - 1, \\ z_k = k\Delta z, \quad k = -N_z, ..., N_z - 1, \end{cases}$$
(1.37)

where Δx and Δz are step sizes in *x* and *z* coordinates, respectively. The box ranges are $[-N_x\Delta x, (N_x - 1)\Delta x]$ and $[-N_z\Delta z, (N_z - 1)\Delta z]$ in *x* and *z* coordinates, respectively.

If the time propagator is performed in configuration space, spatial derivatives need to be calculated. Usually, Spatial derivatives are obtained by using finite difference method. The finite difference method is one of the simplest ways of approximating a differential operator, and is extensively used in solving differential equations. First order differential of the wavefunction with three-point finite difference method is given by

$$\frac{d\Psi(x_n)}{dx} = \frac{\Psi(x_{n+1}) - \Psi(x_{n-1})}{2\Delta x},$$
(1.38)

and second order differential of the wavefunction is read as

$$\frac{d^2\Psi(x_n)}{dx^2} = \frac{\Psi(x_{n+1}) - 2\Psi(x_n) + \Psi(x_{n-1})}{\Delta x^2}.$$
(1.39)

1.2.5 Eigenstates and eigenenergies

To study a system, one first needs to know its initial state, usually the ground state. For TDSE, we need the eigenstates of the Hamiltonian. There are many numerical methods to obtain eigenstates of the system.

The straight forwards method to get eigenvalues and eigenstates is diagonalizing the Hamiltonian. It is convenient to get all eigenvalues and eigenstates of Hamiltonian when the matrix size is not too large.

The power iteration is a very simple algorithm to get eigenstates. It does not compute a matrix decomposition, and hence it can be used when the Hamiltonian H is a very large matrix. However, it will find only one eigenvalue (the one with the greatest absolute value) and it may converge very slowly. Therefore, it is not suitable to get eigenstates of our Hamiltonian.

Based on power iteration, the inverse iteration method [65, 66] improves on its performance, which is a very fast and efficient way to get an eigenstate. Whereas the power method always converges to the largest eigenvalue, inverse iteration also enables the choice of which eigenvalue to converge to. For an approximation μ to the eigenvalue we are interested in, if μ is closer to λ than any other eigenvalue of H, then $\lambda - \mu$ is the smallest eigenvalue of the matrix $(H - \mu \mathbf{I})$ (**I** is the unit matrix). By iterational calculating

$$\Psi_{n+1} = (H - \mu \mathbf{I})^{-1} \Psi_n, \qquad (1.40)$$

where initial vector Ψ_0 is a guess state, we can find the eigenstate corresponding to

this eigenvalue. Once we have a suitable eigenstate approximation, we can use the Rayleigh quotient to find the eigenvalue.

Imaginary time propagation is also a usually used method to get lowest few eigenstates and eigenvalues [67]. The imaginary time propagation method is based on the TDSE propagated in imaginary time ($t \rightarrow -it$). Then TDSE turns into

$$\frac{\partial \Psi(t)}{\partial t} = -H\Psi(t). \tag{1.41}$$

The formal solution then becomes

$$\Psi(\tau) = \exp(-H\tau)\Psi(0). \tag{1.42}$$

If $\Psi(\tau)$ is represented using Hamiltonians eigen wavefunctions

$$\Psi(\tau) = \sum_{j} c_j \exp(-E_j \tau) \phi_j, \qquad (1.43)$$

where ϕ_j are eigen wavefunctions with eigenenergy E_i , it is easy to see that the ground state decays the slowest and after a sufficiently long period of time there are no other eigen wavefunctions present in the wavefunction than the ground state. To solve for the excited states one just needs to project out all the lower states from the wave function. The choice of the initial guess for the ground wavefunction is not critical but only effects the time need for convergence.

In the thesis, we solved TDSE in two dimensions, where the Hamiltonian matrix is quite large. Therefore, the imaginary time propagator method was selected to get the ground state and the first excited state.

1.2.6 Boundary conditions

In a numerical simulation, it is impossible and unnecessary to simulate in the whole space. Generally we choose a region of interest in which we conduct a simulation. The interesting region has a certain boundary with the surrounding environment. Numerical simulations also have to consider the physical processes in the boundary region. In most cases, the boundary conditions are very important for the simulation regional physical processes. Different boundary conditions may cause quite different simulation results. Improper sets of boundary conditions may introduce nonphysical influences on the simulation system, while a proper set of boundary conditions can avoid that. Therefore, arranging the boundary conditions for different problems becomes very important. The frequently used boundary conditions for solving TDSE are periodic boundary and absorption boundary.

Periodic boundary is a simplest and convenient way to avoid boundary reflections. It implements for the first order differentials of wavefunctions at boundary as

$$\frac{d\Psi(x_{N_x})}{dx} = \frac{\Psi(x_{-N_x}) - \Psi(x_{N_x-1})}{2\Delta x},$$
(1.44)

$$\frac{d\Psi(x_{-N_x})}{dx} = \frac{\Psi(x_{-N_x+1}) - \Psi(x_{N_x})}{2\Delta x},$$
(1.45)

and the second order differentials of wavefunctions at boundary are read as

$$\frac{d^2\Psi(x_{N_x})}{dx^2} = \frac{\Psi(x_{-N_x}) - 2\Psi(x_{N_x}) + \Psi(x_{N_x-1})}{\Delta x^2},$$
(1.46)

$$\frac{d^2\Psi(x_{-N_x})}{dx^2} = \frac{\Psi(x_{N_x}) - 2\Psi(x_{-N_x}) + \Psi(x_{-N_x+1})}{\Delta x^2}.$$
 (1.47)

With periodic boundary, the wavefunction reenters from the other side of the space. Therefore, one should also be cautious with the box size to avoid unphysical interference by the reentering wavepacket. The fast Fourier transform methods also imply periodic boundary conditions.

In the numerical simulation of strong field interaction, the electron wavepacket after ionization will accelerate and expand, reach box boundary and be reflected or reenter, in case of periodic boundary conditions. The numerical reflections may cause undesired and unphysical effects. As the remote parts of the wave function are not needed to determine typical observables such as ionization yield or dipole response, the spatial domain where the wave function is calculated can be limited to some inner part. Doing that one must ensure that no unphysical reflections occur at the boundary of that domain. To avoid such unphysical reflections and reentering from box boundary, as described in [68, 69, 70], absorption boundary condition is needed. It is implemented

by adding an imaginary potential near boundary. The addition of a "complex absorbing potential" -iW(r) to the potential $\mathbf{V}(r)$ can provide nearly reflectionless absorption. The function W(r) is zero in some sufficiently large inner domain and smoothly grows to a certain magnitude W_a at the boundary. The absorption strength W_a and the absorption extension L_a are adjusted empirically to ensure sufficient absorption and to avoid reflections for a given physical situation. We defined the "complex absorbing potential" as

$$-iW(r) = \begin{cases} \frac{W_a}{2} \left[1 - \cos(\pi \frac{r - R_a}{L_a}) \right], & r > R_a, \\ 0, & r \leqslant R_a, \end{cases}$$
(1.48)

where R_a is the distance to start absorption. The artificial imaginary potential will destroy unitary time propagation and thus lead to dissipation of the wavefunction. The decreasing norm $\langle \Psi(t) | \Psi(t) \rangle$ can be used to evaluate the total ionization probability.

An alternative approach to removing outgoing flux is to multiply the wavefunction by a mask function $M(\mathbf{r})$, where $M(\mathbf{r})$ equals 1 in the inner domain and becomes small at the boundary.

1.2.7 Gauges

Formally, quantum mechanics is gauge invariant and therefore evaluating physical quantities must lead to the same result regardles of the selected gauge. However, such evaluations involve operations on the variables which may be gauge dependent. Therefore, in numerical simulations, the choice of gauge is important. Velocity and length gauges are two of the mostly used ones in strong field theory.

In velocity gauge, the Hamiltonian is given by

$$H_{\nu}(\mathbf{r};t) = \frac{\left(\mathbf{p} - \frac{1}{c}\mathbf{A}(t)\right)^2}{2} + \mathbf{V}(\mathbf{r}).$$
(1.49)

where $\mathbf{A}(t)$ is the vector potential of the external field. The Hamiltonian in length gauge has a form as

$$H_l(\mathbf{r};t) = -\frac{\nabla^2}{2} - \mathscr{E}(t) \cdot \mathbf{r} + \mathbf{V}(\mathbf{r}), \qquad (1.50)$$

where $\mathscr{E}(t)$ is the field strength of the external electric field. The electric field is defined by

$$\mathscr{E}(t) = -\frac{1}{c} \frac{\partial \mathbf{A}(t)}{\partial t}.$$
 (1.51)

The transform between the wavefunction in length and velocity gauge is given by

$$\Psi_l(t) = e^{-i\mathbf{A}(t)\cdot\mathbf{r}}\Psi_v(t). \tag{1.52}$$

The only difference between length gauge and velocity gauge are the external field term. For length gauge, the external field term is given by $-\mathscr{E}(t) \cdot \mathbf{r}$, while for velocity gauge, it is given by $-\frac{1}{c}\mathbf{p}\cdot\mathbf{A}(t) + \frac{1}{2c^2}\mathbf{A}^2(t)$. Depending on the problem, either length or velocity gauge may be advantageous. For example, high-order above threshold ionization is treated in velocity gauge at lower computational cost than that in length gauge [71]. On the other hand, ionization of heavy ions is more conveniently evaluated in length gauge [72]. In our calculations, we found that the velocity gauge is more efficient than the length gauge, but the results from both gauges are equivalent. Therefore, the velocity gauge is chosen to solve TDSE in this thesis.

1.3 Numerical simulations of high-order harmonic generation

1.3.1 Single particle response

Numerically, the high harmonic spectrum of single particle is calculated from the Fourier transform of the dipole acceleration:

$$P(\omega) = \left| \int \ddot{d}(t) e^{-i\omega t} dt \right|^2.$$
(1.53)

The dipole matrix acceleration in length gauge can be written in three different form [73] length form (Eq. (1.54)), velocity form (Eq. (1.55)) and acceleration form (Eq.

(1.56)):

$$\ddot{\mathbf{d}}_{l}(t) = \frac{d^{2}}{dt^{2}} \langle \boldsymbol{\psi}(t) | \mathbf{r} | \boldsymbol{\psi}(t) \rangle, \qquad (1.54)$$

$$\ddot{\mathbf{d}}_{\nu}(t) = \frac{d}{dt} \langle \boldsymbol{\psi}(t) | -i \nabla | \boldsymbol{\psi}(t) \rangle, \qquad (1.55)$$

$$\ddot{\mathbf{d}}_{a}(t) = \langle \boldsymbol{\psi}(t) | - \nabla V | \boldsymbol{\psi}(t) \rangle + \mathscr{E}(t), \qquad (1.56)$$

where *V* is the potential. All forms will give the same result, but will be different if the wavefunctions are not exact solutions of the TDSE of the system.

With Lewenstein model, the dipole high harmonic response is obtained as a product of three probability amplitudes [52]:

$$d(t) = \operatorname{Re}\left[\sum_{t_b} \frac{1}{\sqrt{i}} a_{ion}(t_b) a_{pr}(t_b, t) a_{rec}(t)\right],$$
(1.57)

where t_b stands for a particular birth time of the electron, which recollides with its parent ion at the moment t. The "ionization", "propagation", and "recombination" probability amplitudes in Eq. (1.57) are given by

$$a_{ion}(t_b) = \sqrt{\frac{dn(t_b)}{dt}},\tag{1.58}$$

$$n(t) = n_0 \left(1 - \exp\left[-\int_{-\infty}^t dt' \Gamma\{\mathscr{E}_l(t')\} \right] \right), \tag{1.59}$$

$$a_{pr}(t_b,t) = \left(\frac{2\pi}{t-t_b}\right)^{3/2} \frac{(2I_p)^{1/4}}{\mathscr{E}_l(t_b)} \exp[-iS(t_b,t)],$$
(1.60)

$$S(t_b,t) = \int_{t_b}^t dt' \left(\frac{1}{2} [p(t_b,t) - A_l(t')]^2 + I_p \right),$$
(1.61)

$$a_{rec}(t) = \frac{p(t_b, t) - A_l(t)}{\left[2I_p + \{p(t_b, t) - A_l(t)\}^2\right]^3},$$
(1.62)

$$A_l(t) = -\int_{-\infty}^t dt' \mathscr{E}_l(t'), \qquad (1.63)$$

$$p(t_b, t) = \frac{1}{t - t_b} \int_{t_b}^t dt' A_l(t'), \qquad (1.64)$$

where n(t) is the free-electron density, $\Gamma\{\mathscr{E}_l\}$ is the ionization rate at the electric field \mathscr{E}_l , n_0 is the initial concentration of neutral atoms, I_p is the ionization potential, p is the classical momentum of the electron. The instant of birth t_b as a function of time t

is determined by solution of the equation

$$p(t_b, t) - A_l(t_b) = 0. (1.65)$$

For a fixed time t this equation can have several solutions, which are included into the sum in Eq. (1.57).

1.3.2 Propagation effects

Propagation effects are an important issue for high-order harmonic generation. The most important propagation effects are absorption of the harmonics, dephasing between the harmonics and the fundamental, and defocusing of the fundamental, which are the main limitations for high harmonics to achieve high efficiency. When high frequency harmonic radiation propagates through gas, it will be absorbed by exciting core electron states [74]. The difference between phase velocities of fundamental laser and high harmonic radiation will lead to phase mismatching, which limits the accumulation of high harmonic radiation. Moreover, during high harmonic generation, the fundamental laser pulse will create free electrons in a channel with peak electron density at the center and a sharp decrease towards the pulse wings. Such a free-electron density profile will defocus the laser pulse, which will reduce the laser intensity and terminate the generation of high harmonics. Since the first observation of high harmonics in experiments [75], numerous efforts were made to increase the intensity of harmonics emission by optimizing propagation effects [76, 77, 78, 79]. Efficiency is critical to generate a detectable signal, and also the spectral properties are important.

A three-dimensional model with cylindrical symmetry was usually implemented to simulate propagation of an ultrashort laser pulse together with high harmonic radiation. Simulations are performed with slowly-evolving wave approximation [80]. Harmonics absorption and diffraction are taken into account, as well as the geometrical phase shift, dispersion induced by free electrons, energy losses and the delay due to the refractive index of neutral atoms. The equations were solved for the electric
field, because the concept of envelope is not important for few-cycle laser pulses. The equation used for laser field \mathscr{E}_l is the one derived in Ref. [81], which has a form in CGS units,

$$\frac{\partial \mathscr{E}_{l}(\rho,\xi,\tau)}{\partial \xi} = \frac{c}{2} \nabla_{\perp}^{2} \int_{-\infty}^{\tau} \mathscr{E}_{l}(\rho,\xi,\tau') d\tau' - \frac{1}{2c} \int_{-\infty}^{\tau} \omega_{p}^{2}(\rho,\xi,\tau') \mathscr{E}_{l}(\rho,\xi,\tau') d\tau' - \frac{2\pi I_{p}}{c\mathscr{E}_{l}(\rho,\xi,\tau)} \frac{\partial n_{e}(\rho,\xi,\tau)}{\partial \tau} - \frac{1}{c} \frac{\partial}{\partial \tau} \left\{ \Delta n^{(a)}(\rho,\xi,\tau) \mathscr{E}_{l}(\rho,\xi,\tau) \right\}. \quad (1.66)$$

The equation for the harmonic pulse \mathcal{E}_h in the slowly-evolving wave approximation is

$$\frac{\partial \mathscr{E}_{h}(\rho,\xi,\tau)}{\partial \xi} = -\alpha(\omega_{h})\mathscr{E}_{h}(\rho,\xi,\tau) + \frac{c}{2}\nabla_{\perp}^{2}\int_{-\infty}^{\tau}\mathscr{E}_{h}(\rho,\xi,\tau')d\tau' - \frac{2\pi}{c}\frac{\partial}{\partial\tau}\{n_{a}(\rho,\xi,\tau)d_{h}[\mathscr{E}_{l}(\rho,\xi,\tau)] + \text{c.c.}\}. \quad (1.67)$$

In equations (1.66-1.67) \mathscr{E}_l and \mathscr{E}_h are the electric fields of laser and harmonic pulse, respectively, ρ is the distance to the beam axis, ξ and τ are the co-moving coordinates:

$$\xi = z, \tag{1.68a}$$

$$\tau = t - z/c, \tag{1.68b}$$

where c is the speed of light in vacuum. ω_p is the plasma frequency, which is given by

$$\omega_p(\rho,\xi,\tau) = \sqrt{\frac{4\pi e^2 n_e(\rho,\xi,\tau)}{m_e}}.$$
(1.69)

 I_p is the ionization potential. α is the XUV absorption coefficient, which depends XUV photon energy. d_h is the single-atom dipole response given by Eq. (1.57) n_e is the concentration of free electrons, and $\Delta n^{(a)}(\rho, \xi, \tau)$ is the contribution of neutral atoms to the refractive index of the plasma. Static-field ionization rates $\Gamma[\mathscr{E}_l]$ were calculated by ADK formula [82] in our calculations. Using these rates the concentration of neutral atoms can be calculated as

$$n_a(\rho,\xi,\tau) = n_0 \exp\left(-\int_{-\infty}^{\tau} \Gamma[\mathscr{E}_l(\rho,\xi,\tau')]d\tau'\right),\tag{1.70}$$

where n_0 is the initial concentration of atoms (before the laser pulse appeared). The concentration of free electrons is correspondingly equal to

$$n_e(\rho,\xi,\tau) = n_0 - n_a(\rho,\xi,\tau) = n_0 \cdot \left(1 - \exp\left(-\int_{-\infty}^{\tau} \Gamma[\mathscr{E}_l(\rho,\xi,\tau')]d\tau'\right)\right). \quad (1.71)$$

The contribution of neutral atoms to the refractive index is taken to be proportional to n_a :

$$\Delta n^{(a)}(\rho,\xi,\tau) = sn_a(\rho,\xi,\tau) = sn_0 \exp\left(-\int_{-\infty}^{\tau} \Gamma[\mathscr{E}_l(\rho,\xi,\tau')]d\tau'\right), \quad (1.72)$$

where *s* is a coefficient depending on gas species.

1.3.3 Time-frequency analysis of the high-order harmonic response

Time-frequency analysis is a powerful tool to gain insight into the characters of high harmonic spectrum. It is implemented as following: multiply a time-window function at time t' with window width T to the dipole acceleration and then Fourier transform it, which reads in formule as,

$$D(\omega,t) = \left| \int dt' \ddot{d}(t') e^{-(t-t')^2/T^2} e^{-i\omega t'} \right|^2$$
(1.73)

As an example, Fig. 1.1 shows us a typical time-frequency analysis result of high-order harmonic response from an atomic system in a gaussian shape pulse with pulse duration 5 fs (full width at half maximum, FWHM), peak intensity $3.5 \times 10^{14} W/cm^2$ at wavelength 800*nm*. In the figure, harmonic intensities are presented as a distribution over emission time and harmonic energy, which gives us the time when harmonics are emitted and with which energies. The green curves on the figure are harmonic radiation sign energy over emission time from a classical trajectory calculation. It intuitively shows us harmonics radiate every half laser cycles. Moreover, harmonic radiation from so-called "short trajectory" and "long trajectory" [Appendix A.2] can been well distinguished. The quantum mechanical results of high-order harmonic energy over emission time basically follows the classical one, except for with some extra width and structures due to quantum expansion and interference of electron wavepackets. It shows that the photon energies generated over time are well predicted by the classical recollision model.



Figure 1.1: Time-frequency analysis of harmonic response from an atomic model interaction with a gaussian shape pulse with pulse duration 5 *fs* (FWHM), peak intensity $3.5 \times 10^{14} W/cm^2$ at wavelength 800*nm*, where the dashed green curve presents the sum of electron recollision energies and the ionization potential of the atom as a function of recollision time from classical trajectory calculations [Appendix A.2].

Chapter 2

Time and momentum distributions of rescattering electrons

2.1 Introduction

Orientation of the molecule relative to the laser field is an important experimental parameter with which, e.g., the ionization yield varies significantly. Basic features of the orientation dependence of total ionization are predicted by the molecular ADK theory of tunnel ionization [40], which only depends on the asymptotics of the field-free electronic wave function in field direction.

To determine the momentum distribution of the emitted electrons during strong field ionization, knowledge of the wave function in a fixed direction is insufficient: in the simplest case of a diatomic molecule, electrons are released from around both centers leading to three-dimensional interference patterns that depend on the relative phases and positions of the two centers [83]. More generally, the emission depends on the nodal structure of the outer electronic orbitals [84].

For imaging of molecules a much more detailed understanding of the rescattering process is required as compared to high harmonic generation and double ionization using atoms. We need to be able to clearly distinguish between the "beam" of rescattering electrons and its coherent target, usually considered as the orbital $|0\rangle$ from which the electron was removed in the first place. For high harmonic generation, according to the Lewenstein model [52], the measured spectra are determined by a time-dependent matrix element of the form

$$\int d^{(3)}k\langle 0|z|\vec{k}\rangle a(\vec{k},t), \qquad (2.1)$$

where $|\vec{k}\rangle$ is a suitable set of scattering states, e.g. the Volkov solutions for a free electron in the laser field, with respect to which the amplitudes $a(\vec{k},t)$ of the rescattering electron are defined. For the reconstruction of $|0\rangle$ we need to know amplitude and phase of *a* as a function of momentum \vec{k} and time *t*. It was noted earlier [85, 86] that harmonic spectra of molecules will in general show structures that depend on the orientation of the molecular axis relative to the laser polarization due to the double-center shape of the orbital $|0\rangle$ because of interferences comparable to a double slit experiment. Clearly, analogous effects must be expected already in the electron detachment process if there is some non-trivial structure in the initial wave function.

Considering its importance, little attention has been paid to the structure of an electron wave function produced by tunnel ionization in the laser field. The reason may be a conceptual one, as in a strong field there is no rigorous distinction between bound parts of the wave function and the wave function "after" tunneling. The Hamiltonian with a (dc) field has a strictly continuous spectrum and all eigenfunctions including the approximate bound states are infinitely extended and not normalizable. When the field is strong, approximate bound states cease to by clearly identifiable. If one decomposes an exact solution of the time-dependent Schrödinger equation (TDSE) with a field into field-free bound and scattering states, one observes transitions between bound and scattering states, a large part of which is reversible. Depending on the system parameters, these virtual transitions may largely exceed the final ionization. They can be partly associated with adiabatic distortions of the wave function in the field, but their ultimately unphysical nature is betrayed by their gauge dependence. The discussion about the "correct" gauge for the strong field approximation [87] derives from this

ambiguity. In the strong field approximation, the bound part of the wave function is chosen as the field free initial electron orbital, but the physical meaning of this orbital in presence of the laser field depends on the gauge. As the reversible bound-continuum transitions appear generally less pronounced in length as compared to velocity gauge, length gauge is considered the better choice for an approximate decomposition.

In this chapter, we investigated the time and momentum structure of the rescattering electron wave function for simple molecular models. We first discussed the concept of a "rescattering wave function" and give a pragmatic definition in the context of the two-dimensional TDSE. Using numerical solutions of the TDSE we then studied the effects of orientation of the molecular axis, and gerade and ungerade symmetry of the outer electronic orbital on the rescattering electron wave function.

2.2 Method

2.2.1 Description

The physical reason for the difficulties to spectrally distinguish bound from rescattering electrons is the coherence of the two parts of the wave function: where they overlap, amplitudes add up and merge into a single, indistinguishable entity. This difficulty does not arise, when one "observes" electrons at a distance from the bound system, where all more strongly bound parts are exponentially damped. This amounts to taking the rescattering picture seriously and counting only those electrons that had been removed to a large distance before they reappear near the bound electrons.

We implemented this idea as follows: at time t_0 the solution $\Psi(\vec{r},t)$ of the TDSE is multiplied by a probe function

$$M_{z_0}(\vec{r}) = \exp\left[-\left(\frac{x^2}{w_{x0}^2} + \frac{(z-z_0)^2}{w_{z0}^2}\right)\right],\tag{2.2}$$

which has its carrier at a distance z_0 from the bound system with width w_{z0} measured in polarization direction. This probe function approximates a plane where we measure intensity and momenta of the electrons as a function of time. The criteria for the choice of M_{z0} will be discussed below. An example is shown in Fig. 2.1. In the left panel, we can clearly see the electron emission in the laser field, and on the right panel, masked wavepacket contains part of emitted electrons.



Figure 2.1: Electron density distributions of the wavefunction (left panel) at a certain time during laser field ionization and that of its masked wavefunction (right panel) at probe distance $z_0 = 15 a.u.$ with probe width $w_{z0} = 3 a.u.$

The probed wave function part $M_{z_0}(\vec{r})\Psi(\vec{r},t_0)$ can then be propagated further by the TDSE

$$\chi_{\vec{r},t_0}(t_0) = M_{z_0}(\vec{r})\Psi(\vec{r},t_0), \qquad (2.3)$$

$$i\frac{\partial}{\partial t}\chi_{t_0}(\vec{r},t) = H(\vec{r},t)\chi_{t_0}(\vec{r},t)$$
(2.4)

or it can be converted to a Wigner distribution and propagated classically:

$$W_0(\vec{r},\vec{p}) = \frac{1}{2\pi} \int d^3\xi \, \chi_{t_0}^*(\vec{r} - \frac{\vec{\xi}}{2}) \chi_{t_0}(\vec{r} + \frac{\vec{\xi}}{2}) \exp\left(i\vec{p}\cdot\vec{\xi}\right),\tag{2.5}$$

$$\frac{\partial W_0}{\partial t} = \frac{\partial W_0}{\partial \vec{p}} \cdot \frac{\partial V}{\partial \vec{r}} - \vec{p} \cdot \frac{\partial W_0}{\partial \vec{r}}, \qquad (2.6)$$

where V is the potential.

By integrating over all probe times t_0 one obtains the rescattering part of the wave function for quantum mechanical forward propagation,

$$\Phi_r(\vec{r},t) = \int dt_0 \chi_{t_0}(\vec{r},t),$$
(2.7)

from which time, space, and momentum distributions "on target", i.e. at z = 0 are calculated.

For classical propagation, the electron density can be obtained as

$$D_r(\vec{r},t) = \int dt_0 \int d\vec{p} W_{t0}(\vec{r},\vec{p},t).$$
 (2.8)

2.2.2 Parameter dependence

The probe distance z_0 , the probe width w_0 and the shape of the mask function are unphysical parameters on which our conclusions must not depend.

Probe distance

First, we investigate the dependence of the rescattering electron density on the probe distance z_0 The probes are taken during the first half cycle of a sin² shape laser pulse, with peak field strength of 0.3 a.u.. With this pulse, the first electron recollision will be studied. The vector potential of laser field is taken to be

$$A(t) = \frac{c\mathscr{E}_0}{\omega_0} \sin^2\left(\frac{\pi t}{2\tau}\right) \sin(\omega_0 t), \qquad (2.9)$$

where $\tau = 207 a.u.(5 fs)$ is the full width at half maximum (FWHM) of the sin² pulse and the center frequency $\omega_0 = 0.057 a.u.(800 nm)$. *c* is the speed of light. The electric field (Fig. 2.2) of the laser pulse is taken from the derivative of its vector potential

$$\mathscr{E}(t) = -\frac{1}{c} \frac{\partial A(t)}{\partial t}.$$
(2.10)

For checking the probe parameters, a model atom system was used with the onedimensional screened Coulomb potential

$$V(x) = -\frac{1}{\sqrt{x^2 + a^2}}$$
(2.11)



Figure 2.2: Electric field with a \sin^2 shape laser pulse and peak field strength of 0.3 a.u. in the rising edge of the pulse.

with a = 1.59 a.u. ($I_p = 0.452 a.u.$ similar to that of neon atom).

Fig. 2.3 presents the time-dependent electron densities obtained with three different probe distances $z_0 = 10, 15$, and 20a.u.. The strong decreasing of the density with increasing probe distance arises because not all electrons reach each barrier. Fig. 2.4 shows the rescattering electron momentum as a function of maximum excursion amplitude for a classical electron in the same field (for calculation details see Appendix. A.2): only the fastest electrons will pass through all three barriers. When we take electrons with momentum $p_z > 1.8a.u$. (see panel a in Fig. 2.5), currents on target are quite different for different probe distance. But when we include only electrons with momenta $p_z > 2.8a.u$, the three barriers give very similar electron densities on target (see panel c in Fig. 2.5). It coincides with classical trajectory calculation(Fig. 2.4). In other words, the rescattering electron behaves classically. For a certain probe distance, only electrons with high momentum will be included, which is the most interesting part for applications of rescattering. The minimal requirement for the probe distance is that the probe should at least be reached by the electrons needed for a given application.



Figure 2.3: Rescattering electron density as obtained with probes placed at three different distances z_0 . The differences arise because slower electrons do never reach the more distant probes. For model and laser parameters see the text.

Probe width

The probe width is another important parameter for the method. The weak dependence of the current on probe width is demonstrated in Fig. 2.6 for the range of width from w = 2a.u. through 5a.u.: the overall shape of the current is nearly independent on probe width. The slight difference in densities for different probe widths can be explained by the fact that more electrons are included for larger probe width.

For a two-dimensional system, in the direction perpendicular to the laser polarization the probe function can be chosen rather broad or even infinite without causing overlap with the bound system, thus obviating the need for an unphysical restriction.

The unphysical nature of the probe function also introduces gauge-dependence into the present procedure: the Fourier-transform of M_{z_0} refers to the *canonical* momentum, which coincides with the physical momentum in length gauge but contains a time-



Figure 2.4: The rescattering momentum of a classical electron released with momentum 0 as a function of its maximum distance from the atom. Only electrons with recollision momentum > 2.8 a.u. reach distances > 20 a.u.. Laser parameters are given in the text.



Figure 2.5: Rescattering electron density as obtained with probes placed at three different distances z_0 with momentum restriction. All momenta $p_z > 1.8 a.u.$ (a), $p_z > 2.4 a.u.$ (b) and $p_z > 2.8 a.u.$ (c) are included.



Figure 2.6: Dependence of the rescattering electron density on probe width w with probe position $z_0 = 15 a.u.$ Probe widths w = 2a.u., 3a.u., 5a.u. are presented as magenta dotted curve, hashed blue curve and solid red curve.

dependent boost in velocity gauge. The gauge-dependence of our method, however, is on the same scale as the dependence on the probe width.

2.2.3 Comparison between quantum mechanical and classical propagation

By choosing between quantum mechanical or classical propagation of the probed wave packet, we can judge how classically the rescattering electrons behave. In Fig. 2.7 it is shown that the electron densities on target obtained by quantum mechanical (Eq. (2.4)) or classical (Eq. (2.6)) propagation nearly coincide, corroborating the basically classical nature of the rescattering motion. This agrees with what we get from probe distance study.



Figure 2.7: Comparison of quantum mechanical (hashed blue curve) and classical (solid red curve) definition of the rescattering density.

2.3 Molecular orientation and orbital symmetry dependence

2.3.1 Model

To study the effect of orientation and orbital symmetry on the rescattering electrons for a molecule, a two dimensional diatomic model is employed under single active electron approximation.

The Hamiltonian of the system has a form in velocity gauge

$$H(t) = \frac{1}{2} \left[\frac{1}{i} \frac{\partial}{\partial z} - \frac{1}{c} A(t) \right]^2 - \frac{1}{2} \left[\frac{\partial}{\partial x} \right]^2 - V(x, z)$$
(2.12)

with the potential defined as

$$V(x,z) = -\frac{0.5}{\sqrt{a^2 + (x + R\sin\theta)^2 + (z + R\cos\theta)^2}} - \frac{0.5}{\sqrt{a^2 + (x - R\sin\theta)^2 + (z - R\cos\theta)^2}},$$
(2.13)

where the parameter *a* was adjusted for an ionization potential of 0.3 a.u. and the internuclear separation was fixed at 2R = 3a.u. θ is the molecular orientation angle, which is the angle between molecular axis and laser polarization. Laser field is applied in *z* direction, with the same parameters as those used in previous section [Section 2.2]. Electrons are ionized by the first peak of the laser pulse, and then driven back when laser field changes its direction. In our calculation, probe is taken with the probe width $w_0 = 3a.u$ and the probe distance $z_0 = 15a.u$.

2.3.2 Momentum distribution of rescattering electrons

First, the ground state is chosen as the initial state. The electron density distributions of the gerade initial states with different orientations are presented in Fig. 2.8. Electron momentum distribution is defined from the Fourier transform of masked wavefunction

$$M(p_x, p_z) = \left| \int dx dz M_{z0}(x, z) \Psi(x, z, t_0) \exp(-ip_x x) \exp(-ip_z z) \right|^2.$$
(2.14)

The the rescattering electron momentum distribution in parallel and perpendicular directions are calculated as

$$M_{z} = \int dp_{x} M(p_{x}, p_{z}), M_{x} = \int dp_{z} M(p_{x}, p_{z}).$$
(2.15)

Fig. 2.9 shows the rescattering electron momentum distribution as probed at a distance $z_0 = 15 a.u.$ for the orientations $\theta = 0^\circ, 45^\circ$ and 90° at time t_0 when electron density reaches its peak. In qualitative agreement with the molecular ADK theory [40], the ionization rates decrease with increasing angle. The overall shapes of the parallel and perpendicular momentum distributions remain similar and smooth, although in the perpendicular momentum distribution a slight asymmetry appears at 45° .

This picture changes drastically, when we ionize from an excited rather than the ground state. To facilitate comparison with the previous case, we adjusted the potential parameter a in the Hamiltonian (Eq. (2.13)) such that the first excited state has a binding energy of 0.3 a.u.. Fig. 2.10 presents electron density distributions of the ungerade initial states with different orientations. Fig. 2.11 shows the probed spectra for the excited state with ungerade symmetry.



Figure 2.8: Electron density distributions of the initial state with gerade orbital for different orientations.



Figure 2.9: Dependence of the rescattering electron momentum distributions at $z_0 = 15$ on the molecular orientation. The initial state is the gerade ground state of the system. Both, parallel (a) and perpendicular (b) momenta show a smooth distribution that decreases from parallel $\theta = 0^{\circ}$ to perpendicular $\theta = 90^{\circ}$ alignment of the molecular axis. The perpendicular distribution becomes slightly asymmetric for $\theta = 45^{\circ}$.



Figure 2.10: Electron density distributions of the initial state with ungerade orbital for different orientations.



Figure 2.11: Dependence of the rescattering electron momentum distributions at $z_0 = 15 a.u.$ on the molecular orientation with an ungerade initial state. The decrease of the density for perpendicular alignment is more pronounced and a node appears in the perpendicular momentum distribution.

In this symmetry, the ionization yield drops more strongly when going from parallel to perpendicular orientation. More importantly, the distribution of perpendicular momenta strongly changes its shape from a smooth bell-shaped distribution to a double hump distribution with a node for perpendicular momentum $p_{\perp} = 0$. The appearance of this node can be explained in the strong field approximation using simple symmetry arguments.



Figure 2.12: Electron density distributions of rescattering electrons on target over perpendicular coordinate and over time for 0° (left) and 90° (right) alignment.

Density distributions of rescattering electrons over perpendicular direction and over time "on target" are presented in Fig. 2.12 for 0° and 90° alignments. The distribution for 0° has a well defined shape only due to wavepacket expansion, while that for 90° has a node, which origins from its parent system. By integration over time, Fig. 2.13 presents electron density over perpendicular coordinate. It is obvious that most electrons will not recollide with our target — the molecule, which has a size of 2R = 3a.u..

The suppression of zero perpendicular momentum leads to strong suppression of recollision and high harmonic generation in addition to the suppression of total ionization. The effect must also be taken into account for a correct interpretation of the



Figure 2.13: Electron density of rescattering electrons on target over perpendicular coordinate for 90° alignments.

experiments [88, 89], where double-ionization by recolliding electrons was used as a measure of orientation dependent ionization rates. Some of the molecules investigated there have exact anti-symmetries and all have nodal planes which will lead to strong variations of momentum distributions of the recolliding electrons with molecular orientation. The observed double ionization therefore depends not only on total ionization, but also on the fraction of the returning electrons that contribute to double ionization. E.g., while for our model \sim 50% of the returning electrons pass through a region around the molecule of twice size of the internuclear distance, this fraction is only \sim 10% for perpendicular orientation.

2.3.3 Time-structure of rescattering electrons

Finally, we calculated the time-distribution of the electron density at the probe. Here we have chosen an internuclear separation of 2R = 6a.u. in order to enhance the effect. Fig. 2.14 shows the very dramatic effect of molecular orientation on the timing of the electron "beam": the maximum of the current may move by as much as 0.3 fs. The

mechanism of this effect will be discussed in details in the next chapter.



Figure 2.14: Time-dependence of the rescattering electron density at $z_0 = 15 a.u.$ for different molecular orientations. An ungerade initial state for a system with internuclear separation 2R = 6 a.u. is chosen.

2.4 Conclusions

We have demonstrated that one can, with some approximation, define the rescattering part of the electron wave function by probing the wavefunction at sufficient distance from the bound system. The procedure is not rigorous, but it depends only weakly on unphysical parameters and gauge.

However, the dependence on orientation and symmetry of the active electron's orbital may be dramatic. In particular, with the molecular axis aligned perpendicular to the laser polarization, an initial ungerade symmetry of the the orbital causes a node at the perpendicular rescattering momentum $p_{\perp} = 0$ and, depending on laser parameters, only a very small part of the wave function rescatters from the parent system. Not only momentum distribution, but also the time-structure of the rescattering electrons

strongly varies with orientation: for larger molecules, peak flux may change by as much as 0.3 fs.

Our studies strongly indicate that the time and momentum structure of rescattering electrons is by no means universal. Attempts to establish the rescattering wave function for an unknown system by simple comparisons with noble gas atoms appear futile. As a minimum requirement, the specific symmetry properties of the orbitals of the active electrons must be taken into account when determining the rescattering wave function. If that orbital is what is to be determined as in the experiment [25], one possible procedure would be an iterative fit to the measured data, rather than a direct tomographic reconstruction. While this seems possible in principle, such a reconstruction must strongly rely on an adequate and efficient theoretical description. For experiments where nuclear rather than electronic motion is measured [12] at least the time-structure of the rescattering wave function must be well understood. The observed variations of 0.3 fs are for the integral over all momenta. As the rescattering double ionization probability is expected to strongly depend on the rescattering momentum, the time-dependence must be analyzed in relation to the (as yet unknown) momentum dependence of rescattering double ionization.

Chapter 3

Sub-cycle dynamics in the laser field ionization of molecules

3.1 Introduction

To define a time of ionization and an electron spectrum at that time one needs to distinguish between bound and unbound electrons while the field is present. This is discussed in detail in Ref. [90], where an approximate bound-unbound distinction was introduced. This distinction is applicable in the case of strong fields, while at weaker fields it becomes dependent on details of the approximation, in particular on the gauge used to describe the interaction with the field. One finds "virtual continuum population" that can significantly exceed ionization found after the pulse because large part of it relapses into bound states. From such data it is impossible to tell "when" ionization really happens. These difficulties arise, because the concept of ionization is asymptotic in time and only for time-independent Hamiltonians states it can be associated with the bound or unbound property at any given time. Except possibly when the system evolves adiabatically, a spectral classification into bound and unbound states in presence of an electric field is impossible. For the present chapter we avoid this problem by adopting the original idea of the classical re-collision model for the timedependent Schrödinger equation. Electron detachment is determined from the wave function amplitude that we find at distances where the laser force dominates over the molecular potential. We can associate that amplitude with a time of electron emission by propagating it back to near the ion. In this way we can discuss electron re-collision without the need for deciding whether the electronic wave function ever became unbound or just strongly distorted.

For the time of electron release, electronic dynamics during the emission process must be taken into consideration. In its usual form, the re-collision picture assumes that ionization is a quasi-stationary process, where at any time the rate is proportional to the tunnel ionization rate for the instantaneous field strength. Because of a strongly non-linear dependence of ionization on field strength this implies a sharp maximum of emission at the peak of the laser field. However, ionization can only be quasi-stationary when the time-scales of electronic motion in the system are well-separated from the laser time scale. In atoms, this assumption can well describe electron emission, but in molecules, this is not generally the case.

In this chapter we investigate the influence of sub-cycle field-induced internal electronic dynamics of molecules on electron emission and re-collision. For two-dimensional model molecules, we found pronounced effects of field-induced intra-molecular dynamics during strong field ionization. The sub-cycle field-induced dynamics is caused by Rabi-like oscillation between the ground state and the first excited state. Moreover, it leads to a modulation of emission wavepacket which sequentially modulates the recollision wavepacket and further modulates high-order harmonic generation from the molecule. Such dynamics information can survive through three-dimensional propagation of high-order harmonics, which makes the sub-cycle field-induced dynamics is the appearance of even harmonics under certain conditions.

3.2 Method and model

The same single electron diatomic model is used as in the previous chapter [Section 2.3.1] with the parameter *a* in Eq. (2.13) was adjusted for an ionization potential of 0.51 a.u. and the internuclear separation was fixed at 2R = 4.38 a.u. (parameters similar as for the CO_2 molecule). The orientation of the molecule is given by the angle θ between the molecular axis and the polarization direction of the field. In this chapter, we will concentrate on orientation $\theta = 0^\circ$. Laser field is applied in parallel direction (*z* coordinate) with vector potential $A(t) = \frac{c\mathscr{E}_0}{\omega_0} \cos(\omega_0 t)$ with peak field strength \mathscr{E}_0 and center frequency $\omega_0 = 0.057a.u.$ ($\lambda = 800 nm$). The TDSE (Eq. (2.12)) was solved by a fast Fourier transform method with box sizes 60 a.u. in perpendicular direction and 120 a.u. in parallel direction.

To get the emission current and the rescattering current, we used the same method that was introduced in the previous chapter [Section 2.2]. We chose the probe function at probe distance $z_0 = 6a.u$. with probe width $w_0 = 3a.u$. and we quantum mechanically forward propagated the probed wavefunction to get rescattering electron wavepacket.

In our calculations, we neglected nuclear motion, as electron release and re-collision happen during about a laser half-cycle of 1.3 fs, which should be compared to typical vibrational periods of 15 - 25 fs for molecules like CO_2 . Although the two-dimensional model precludes quantitative comparisons with experimental data, we will argue below that the mechanism underlying the release dynamics is universal and not specific for our model. The ground and the first excited states of our model were obtained by imaginary time propagation, where for the excited state orthogonality with respect to the previously calculated ground state was imposed.

3.3 Sub-cycle dynamics induced by internal oscillations

3.3.1 Rabi-like oscillations of a two-level system in a laser field

When a strong field is applied on a two-level system with a dipole transition allowed, the electric field will excite the system. At some point when the system is completely in its excited state, the field actually goes on to de-excite the atom again ("stimulated emission"). This cycle of absorption-emission is called Rabi oscillations, and it proceeds at a frequency depending on the strength of the electric field. During the optical cycle the system is usually in a superposition of ground and excited state. The population transfer between the two states is as referred to a Rabi flopping.

Under the rotating wave approximation [91], Rabi flopping between the levels of a two-level system in laser field of the resonant frequency will occur at the Rabi frequency Ω_R , which is proportional to external field strength \mathscr{E} and dipole moment μ between the two states

$$\Omega_R = \mu \mathscr{E}.\tag{3.1}$$

The frequency of modulations for population in a detuned field, which is named generalized Rabi frequency, depends on Rabi frequency and the detuning parameter. The relation between generalized Rabi frequency and Rabi frequency can be written as

$$\Omega = \sqrt{\Omega_R^2 + \Delta^2},\tag{3.2}$$

where the detuning parameter is $\Delta = (E_e - E_g) - \omega_{field}$. E_g and E_e are energies of the ground and the excited state, and ω_{field} is the frequency of the external field.

In case of a few-cycle intense laser pulse, rotating wave approximation is no longer valid. The oscillation frequency can not be simply given by Eq. (3.2), which will be time dependent. To get the Rabi-like oscillation between the two states, we use an ansatz for the simple two-level system as

$$|\Psi(t)\rangle = c_g(t)|g\rangle e^{-iE_g t} + c_e(t)|e\rangle e^{-iE_e t},$$
(3.3)

where $|g\rangle$ and $|e\rangle$ are the ground and the excited states, and $c_g(t)$ and $c_e(t)$ are the amplitudes, and E_g and E_e are energies of the ground and the excited state of the two states, respectively.

With this ansatz, the TDSE of the model in a linear polarized external field have the form

$$i\frac{\partial}{\partial t}\left[c_g(t)|g\rangle e^{-iE_g t} + c_e(t)|e\rangle e^{-iE_e t}\right] = H(t)\left[c_g(t)|g\rangle e^{-iE_g t} + c_e(t)|e\rangle e^{-iE_e t}\right],\quad(3.4)$$

where Hamiltonian is defined as $H(t) = H_0 - \mathscr{E}(t)z$ and $\mathscr{E}(t)$ is the external field. The time-independent part Hamiltonian is given by

$$H_0 = \frac{p^2}{2} + V(r), \qquad (3.5)$$

where V is the potential.

The system obeys the following relations:

$$\langle g|e\rangle = 0,$$

$$\langle g|z|e\rangle = \mu,$$

$$H_0|g\rangle = E_g|g\rangle,$$

$$H_0|e\rangle = E_e|e\rangle,$$

$$(3.6)$$

where μ is the dipole momentum.

By closing Eq. (3.4) with $|g\rangle$ and $|e\rangle$, equations for the amplitudes read

$$\begin{cases} i\dot{c}_g(t) = -\mu \mathscr{E}(t)c_e(t)\exp(-i(E_e - E_g)t), \\ i\dot{c}_e(t) = -\mu \mathscr{E}(t)c_g(t)\exp(-i(E_g - E_e)t). \end{cases}$$
(3.7)

The Rabi-like oscillation between the two involved states can be obtained by numerically solving Eq. (3.7).

As an example, populations of the two states are presented in Fig. 3.1 with $\mu = 2a.u.$ and $\Delta E = 0.1a.u.$. A Gaussian shape cosine-pulse is used with FWHM 5 fs at wavelength 800nm and peak intensity $3.5 \times 10^{14} W/cm^2$ (shown as magenta dashed curve in Fig. 3.1). It is shown that the oscillation frequency strongly depends on the field strength of the external field. The modulation frequency of the population of the

first excited state increases when field strength increases. Moreover, when the field is gone, the system stays at some point with a superposition of the ground state and the first excited state.



Figure 3.1: Populations of the ground state (solid red curve) and the first excited state (dotted green curve) of a two-level system. The dashed magenta curve indicates absolute value of laser field strength (with different scale).

3.3.2 Field-induced internal oscillations in molecules

Due to the Rabi-like oscillation, the populations of the ground state and the first excited state will be modulated when a strong field is applied. To compare with a two-level system, populations of the ground state and the first excited state of our diatomic model are calculated by solving the two-dimensional TDSE. For our system, dipole momentum μ is 2.28 *a.u.* which is calculated directly from result of TDSE and the energy gap ΔE between the ground state and the first excited state is 0.03 *a.u.*, and the ground state is chosen as the initial state.

In Fig. 3.2, it is shown that modulations in state populations for different laser intensities closely follow the evolution of a two-level system except depletion due to

ionization. The modulations strongly depend on the laser intensity. For all intensities, the time structure of the modulations for the two-level system is very similar to the TDSE results. On the other hand, one may ask whether this kind of modulations will have an effect on field ionization. The answer is yes. In the following sections, we investigated the effect of the internal dynamics on ionization, rescattering and even high harmonic generation.

3.3.3 Effect of internal sub-cycle dynamics on electron emission

To simplify numerical calculations, a 1.5 cycles pulse is applied to the molecule, with which electrons will be released during the first half cycle and re-collide with its parent system in the following cycle.

Fig. 3.3 shows the emission current on the probe with a probe distance 6a.u. for different laser intensities. Because the probe is taken close to the nucleus, the emission current should well follow the exact emission current from the system. Obviously, there are some modulations in emission current when laser field is strong enough. At intensity $6 \times 10^{13} W/cm^2$ peak emission approximately coincides with peak field strength, but at intensity $1.3 \times 10^{14} W/cm^2$ two emission peaks of different height appear that are separated by approximately 1/4 of an optical cycle, and at the largest intensity of $2.2 \times 10^{14} W/cm^2$ two roughly equal peaks with slightly smaller separation appear. Moreover, it is clear that the peak of the emission current increases when the laser intensity increases due to the increase in ionization rate.

Let's go back to check the populations of the ground state and the first excited state during the first half-cycle of the laser pulse, which are shown in Fig. 3.4. For different laser intensities, populations of the first excited states have different time-dependence due to Rabi-like oscillations. The emission current always follows the population of the first excited state except when the laser field is very weak and ionization stops. This means the electrons are emitted from the first excited state, where the ionization potential is less than that of the ground state.



Figure 3.2: Populations of the ground state for our model system (solid red curves) and a comparable two-level system (dotted blue curves) with different laser intensities. From top to bottom, laser intensities are $6 \times 10^{13} W/cm^2$, $1.3 \times 10^{14} W/cm^2$, and $2.2 \times 10^{14} W/cm^2$, respectively.



Figure 3.3: Emission current for different laser intensities in first half cycle. Solid red curve, dashed green curve and hashed blue curve are with laser intensity $6 \times 10^{13} W/cm^2$, $1.3 \times 10^{14} W/cm^2$, and $2.2 \times 10^{14} W/cm^2$, respectively. Dotted-dashed cyan curve shows laser field.

In summary, analyzing the electronic wavefunction during emission one finds that the variations are caused by intra-molecular electron dynamics induced by the ionizing field. The laser field induces pronounced Rabi-like oscillations of the populations of the ground and the first excited state. Electron emission predominantly happens when the excited state becomes populated at times when the field is strong. In that way emission itself becomes modulated by the oscillations between the bound states.

3.3.4 Effect of internal sub-cycle dynamics on rescattering electrons

The variations in the re-collision times match emission, if one takes into account that only emission times corresponding to classically re-colliding trajectories can significantly contribute. The correspond rescattering currents on the target are presented in Fig. 3.5. The rescattering current on the target is obtained by forward propagating



Figure 3.4: Populations of the ground state (dashed green curves) and the first excited state (hashed magenta curves) for different laser intensities (from top to bottom $6 \times 10^{13} W/cm^2$, $1.3 \times 10^{14} W/cm^2$, and $2.2 \times 10^{14} W/cm^2$) in first half cycle, while the solid curves are the emission currents on the probe. Dash-dotted cyan curves are profiles of the laser pulse.



Figure 3.5: Time-distributions of electron emission and re-collision for laser intensities $6 \times 10^{13} W/cm^2$, $1.3 \times 10^{14} W/cm^2$, and $2.2 \times 10^{14} W/cm^2$ (from top to bottom). The dot-dashed cyan curves indicate $|\mathscr{E}(t)|$. Emission (solid red curves) and re-collision (dashed green curves) distributions scaled to maximal values of 1 with the probe located at $z_0 = 6a.u$.

the probed rescattering wavepackets to the target. At the intensity $1.3 \times 10^{14} W/cm^2$ the variation of emission times leads to a strong emphasis of "long trajectories", i.e. re-collisions well after the node of the field. We also investigated the emission time structure for laser polarization perpendicular to the molecular axis where the first excited state is not dipole-reachable from the ground state. As expected, the emission time structure closely follows the field strength and very weakly varies with intensity, which is shown in Fig. 3.6.



Figure 3.6: Emission current of the molecule with perpendicular alignment for different laser intensities: solid red curve for intensity $6 \times 10^{13} W/cm^2$, dashed green curve for intensity $1.3 \times 10^{14} W/cm^2$, and dotted blue curve for intensity $2.2 \times 10^{14} W/cm^2$. The dot-dashed cyan curves indicate $|\mathscr{E}(t)|$.

The mechanism makes it clear that the modulation of electron emission by fieldinduced internal dynamics is a universal phenomenon, which is not bound to the specific model used here. In general, the dynamics modifies ionization times when (1) it occurs on a time scale that is comparable to the laser optical period and (2) the internal rates are significant compared to the ionization rate. Condition (1) means that there is an electronically excited state at most a few photon energies above the ground state. At a laser photon energy of $1.5 \, eV$ corresponding to the $\sim 800 \, nm$ wave length this condition becomes fulfilled at larger internuclear distance as we used them in our model. Condition (2) can always be met by reducing laser intensity. At fixed wave length that means that one approaches Keldysh parameters of $\gamma \sim 1$, which is, in fact, where many experiments are being performed.

Oscillations between the populations of bound states were reported also at very strong field [92], where, however, the oscillation frequency far exceeds the laser frequency and no observable modulation of the emission results.

3.4 Internal sub-cycle dynamics effect in high-order harmonic generation

3.4.1 Time structure of high-order harmonic generation

The most sensitive experimental signature of re-collision is in high harmonic emission, where re-collision momenta are closely linked to re-collision times [47, 46]. The experimental signature of field-induced intra-molecular dynamics, which depends on laser intensity and orientation of the molecular axis, should also be observed in the high-order harmonic spectrum of the molecule.

A time-frequency analysis of high-order harmonic response was performed to study the internal sub-cycle dynamics effect. Fig. 3.7 presents time-frequency distributions, which are calculated by Eq. (1.73), for high-order harmonic response with different laser intensities, as well as harmonic energy over recombination time from classical trajectory calculations. For laser intensity $6 \times 10^{13} W/cm^2$, distribution is continuous, which is similar to that of an atomic system. However, for higher laser intensities, distributions are not continuous and there appear additional dips due to the field-induced dynamics. For laser intensity $1.3 \times 10^{14} W/cm^2$, there is one dip in the short trajectory part, while for laser intensity $2.2 \times 10^{14} W/cm^2$, there are two dips, one near cutoff and the other one in the long trajectory part. Fig. 3.8 presents the time-frequency analysis of high-order harmonic response of a 90° aligned molecule, with the same laser pulse as that in the middle pattern of Fig. 3.7. The time-frequency structure well follows the classical trajectory results, which is similar to an atomic system. The modulated structures in high harmonic response are directly related to the field-induced dynamics of electron ionization. In other words, field-induced dynamics can be investigated through spectrum analysis of high-order harmonic generation.

A more direct insight into the field-induced dynamics is the time-structure of highorder harmonic generation near the cutoff. Time-structure of high harmonics near the cutoff is calculated as,

$$S(t) = \int_{\omega_F}^{\infty} D(\omega, t) d\omega$$
 (3.8)

where $D(\omega, t)$ is calculated by Eq. (1.73). The Fig. 3.9 shows that the single-atom harmonic response in the energy range above 80% of the harmonic cutoff energy ($\omega_F = 0.8\omega_{cutoff}$) closely follows the corresponding re-collision density distribution. The figures also contain the harmonic intensities for perpendicular oriented molecule, which remain independent of intensity. It is clear that for laser intensity $6 \times 10^{13} W/cm^2$, the time-structure of high-order harmonics for parallel aligned molecule is the same as that for perpendicular aligned molecule. However, for higher laser intensity, the time structures of high-order harmonics for parallel aligned molecules are shifted to the left ("short trajectory") or the right ("long trajectory") due to sub-cycle field-induced dynamics. The time shift between different intensities is as large as 0.3 optical cycle (800*as*).

Recent experimental work has revealed a similar change of the harmonic emission profile as a function of intensity and orientation of the molecular axis [93]. They found that to compare with atoms, different aligned CO_2 and N_2 molecules, the time structures of selected harmonic radiation are quite different. The time delay of harmonic radiation between 0° and 90° aligned CO_2 is about 160 *as*.


Figure 3.7: Time-frequency analysis of high harmonic response of the 0° aligned molecule for different laser intensity $(6 \times 10^{13} W/cm^2 \text{ (top)}, 1.3 \times 10^{14} W/cm^2 \text{ (middle)}, and <math>2.2 \times 10^{14} W/cm^2 \text{ (bottom)})$, while the green curves inside give harmonic energy over recombination time from classical trajectory calculations [Appendix A.2].



Figure 3.8: Time-frequency analysis of high harmonic response of the 90° aligned molecule for laser intensity $1.3 \times 10^{14} W/cm^2$ while the green curves inside give harmonic energy over recombination time from classical trajectory calculations [Appendix A.2].



Figure 3.9: Time structures of high order harmonics with different laser intensities ($6 \times 10^{13} W/cm^2$ (top), $1.3 \times 10^{14} W/cm^2$ (middle), and $2.2 \times 10^{14} W/cm^2$ (bottom)). The blue dashed curves indicate time-structure of high order harmonics from 90° alignment molecules, which has no field-induced dynamics during ionization.

3.4.2 Appearance of even harmonics

Another observable effect of the internal dynamics is the transient appearance of even harmonics. Between subsequent re-collisions, the system evolves according to the field-induced dynamics. In our case Rabi-like oscillations between the gerade ground and the ungerade excited state lead to variations of the electron density. At intensities where the ratio of the laser period to the field-induced internal oscillation period approaches an even number, the system returns to the same state at each subsequent re-collisions. Any asymmetry of this state will cause even harmonics. As the internal dynamics depends on laser intensity, the even harmonics show a resonance-like dependence on pulse intensity.

Harmonic spectra from our model system with parallel alignment are shown in Fig. 3.10 with different laser intensities, where even harmonics clearly show up around order 15. A laser pulse with duration of 15 fs (FWHM), and intensity of $6 \times 10^{13} W/cm^2$ is applied to the molecule. We find even harmonic peaks with up to 3-8% of the peak height of the neighboring odd harmonic peaks, which is on a scale that can be detected in the experiments. For perpendicular alignment there are no even harmonics, which are presented in Fig. 3.11 with the same laser pulse as that applied to the parallel aligned molecule. Such an orientation dependent effect is another experimental signature of field-induced dynamics.

3.5 Can internal sub-cycle dynamics survive propagation of high-order harmonic generation?

The field-induced internal sub-cycle dynamics can be a detectable effect in experiments only when information of the effect survives after harmonics propagation. It is important to understand whether the property of time-frequency structure is preserved after harmonics propagation in the gas when comparing with single particle response.



Figure 3.10: High-order harmonic spectra of parallel aligned molecule with different laser intensities. Even harmonics show up between odd harmonics around order 15, especially for laser intensity $6 \times 10^{13} W/cm^2$.



Figure 3.11: High-order harmonic spectra of perpendicular aligned molecule with different laser intensities. No even harmonics show up.

3.5.1 Method: generation and propagation

In the previous section, we have found that harmonics emission near cutoff will shift to the short trajectory part or long trajectory part due to field-induced sub-cycle dynamics. As described in Ref. [94], the phase matching conditions are different for harmonic radiation from long trajectories and short trajectories. Then we need to know whether such a behavior persists after propagation of the harmonics through medium.

To simulate harmonics propagation in the gas [Section 1.3], we used a code first developed by N. Milosevic and optimized by V. S. Yakovlev [95]. In the code, an extension Lewenstein model [52] is employed to calculate the single-particle dipole response. Simulations with such model are much more efficient than that solving the full TDSE.

As discussed in the previous section, the modulations of electron emission closely follows the population of the first excited state. The field-induced modulation happens during the strong field ionization, which is single-particle response. Therefore, we numerically implemented such field-induced dynamics into the ionization process. In practice, field-induced modulations can be introduced into emission part ("ionization" probability amplitudes $a_{ion}(t_b)$ (Eq. (1.59)) of the three-step model by modifying timedependent free-electron density:

$$n'(t) = c_e^2(t)n_0\left(1 - \exp\left[-\int_{-\infty}^t dt' \Gamma\{\mathscr{E}_l(t')\}\right]\right),\tag{3.9}$$

where $c_e(t)$ is the solution of Eq. (3.7) for a two-level system and $\Gamma\{\mathscr{E}_l(t')\}$ is the ionization rate for static field $\mathscr{E}_l(t')$. In the following part of the section, the modified Lewenstein model will be used to simulate the single particle response of the molecule with sub-cycle field-induce dynamics during strong field ionization.

3.5.2 Internal sub-cycle dynamics after harmonics propagation

First, the validity of the modified Lewenstein model was checked. The same laser pulse is used as that in previous section (1.5 cycles, 800 nm), as well as the same parameters

of the molecule as those used in Section 3.3 for the two-level system ($E_g = 0.51 a.u.$, $E_e = 0.54 a.u.$ and $\mu = 2.28 a.u.$). The laser pulse has a gaussian spatial profile with beam waist of $61 \mu m$. Laser pulse and harmonic radiation are propagated together through a 2mm gas tube at 100mbar with $I_p = 0.54 a.u.$, and the focus position was chosen at the center of gas volume. In our calculations, we chose XUV absorption coefficient of Argon. With such parameters, for an unmodified atomic system, propagation effect prefers short trajectory of harmonic generation.

The time-structures of high harmonics from this simplified single particle response are shown in Fig. 3.12 with different peak intensities. Harmonics with energy larger than 80% of the cutoff energy are selected. To compare with lowest laser intensity $6 \times 10^{13} W/cm^2$ (solid red curve), the peak of time-structure shifts to the right for laser intensity $1.3 \times 10^{14} W/cm^2$ (dashed green), but to the left for laser intensity $2.2 \times 10^{14} W/cm^2$ (hashed blue). This qualitatively agrees with the result of TDSE calculations of our model system (Fig. 3.9 in Section 3.4).



Figure 3.12: Time-structures of harmonic radiation near cutoff before propagation (Laser pulse peak intensities $6 \times 10^{13} W/cm^2$ (solid red), $1.3 \times 10^{14} W/cm^2$ (dashed green), and $2.2 \times 10^{14} W/cm^2$ (hashed blue)).

In Fig. 3.13, it shows the time-structures of on-axis high harmonics after propa-

gation through 2*mm* gas with the same harmonics selection. To compare with those before propagation, the positions of time-structure peak changed somewhat due to propagation effects. For laser intensity $6 \times 10^{13} W/cm^2$ (solid red), time-structure of high harmonics after propagation is quite similar to that before propagation. But with laser intensity $1.3 \times 10^{14} W/cm^2$ (dashed green) and $2.2 \times 10^{14} W/cm^2$ (hashed blue), the peaks shift to the left. That is because harmonic generation from long trajectories has been suppressed after propagation. Nevertheless, the differences between different laser intensities are still clear. The effect coming from field-induced internal sub-cycle dynamics is still detectable after propagation.



Figure 3.13: Time-structures of on-axis harmonic radiation near cutoff after propagation through 2mm gas (Laser pulse peak intensities $6 \times 10^{13} W/cm^2$ (solid red), $1.3 \times 10^{14} W/cm^2$ (dashed green), and $2.2 \times 10^{14} W/cm^2$ (hashed blue)).

With our simplified artificial pulse, the field-induced sub-cycle dynamics can survive through high harmonics propagation. But in experiments, more realistic pulse is used. A laser pulse with duration 5 fs (FWHM), gaussian-shape pulse at wavelength 800*nm*, which is available in laboratory now, was employed to redo the calculations.

The vector potential of the laser pulse is defined as

$$A_z(t) = \frac{c\mathscr{E}_0}{\omega_0} \exp\left(-2\ln 2\frac{t^2}{\tau_0^2}\right),\tag{3.10}$$

where \mathscr{E}_0 is peak field strength and ω_0 is center frequency and τ_0 is FWHM. The electric field strength is obtained from derivative of vector potential $\mathscr{E}(t) = -\frac{1}{c} \frac{\partial A(t)}{\partial t}$.

Time-frequency distributions of high-order harmonics have been investigated for a modulated system to compare with those of a system without modulations with different laser intensities. Besides the time-profile of the laser pulse, the other parameters are the same as those used for 1.5 cycles pulse. Laser intensity $9 \times 10^{14} W/cm^2$ is chosen which is much high to emphasize field-induced sub-cycle dynamics and with a higher ionization potential (Ip = 0.8 a.u.) to decrease the total ionization yield.

The time-frequency distributions of high-order harmonics before propagation are shown in Fig. 3.14. Modulations in time-frequency distributions are obvious for system with modified source. On the left hand of Fig. 3.14, the time-frequency structure of non-modulated system is smooth. However, for the modulated system shown on the right hand panel, the overall shape of time-frequency structure is similar to that of non-modulated system, but modulations appear in the structures. Fig. 3.15 presents the time-frequency distributions after propagation through 2mm gas. Except for that intensity distributions change between "short trajectory" and "long trajectory" slightly, the overall shapes of distributions are almost the same as those before propagation. Therefore, field-induced modulations of the single particle response is proven to survive high harmonics propagation for the modified system also for realistic pulse shape.

However in the laboratory, because the high harmonic signal can be only detected in the farfield, we need to further propagate harmonic radiation through a vacuum of certain distance before it reaches detector. In our calculations, harmonic radiations propagated through 1 meter vacuum after the gas volume. The time-frequency distributions of on-axis and off-axis (1*cm* from the center) in the farfield are shown in Fig. 3.16 and Fig. 3.17, respectively. From on-axis distributions, one can clearly see



Figure 3.14: Time-frequency distributions of harmonic response "before propagation". Panel (a) is for the system without modulations with laser intensity $9 \times 10^{14} W/cm^2$. Panel (b) is for the system with modulations with laser intensity $9 \times 10^{14} W/cm^2$.



Figure 3.15: Time-frequency distributions of "on-axis" harmonic response "after propagation".Panel (a) is for the system without modulations with laser intensity $9 \times 10^{14} W/cm^2$. Panel (b) is for the system with modulations with laser intensity $9 \times 10^{14} W/cm^2$.

harmonics from "long trajectory" have been strongly suppressed, while the modulations in the "short trajectories" hold their position. In the off-axis distributions, we noticed that harmonics have smaller cutoff energy which is due to weaker peak laser intensities from off-axis, and field-induced modulations (right panel) also have slightly different from those of on-axis. As described in Ref. [94], by changing the parameters of laser pulse focus and gas pressure, the propagation effect will prefer short trajectories or long trajectories. Therefore, sub-cycle field-induced dynamics information can be observed from measuring high-order harmonic radiation in experiments.



Figure 3.16: Time-frequency distributions of "on-axis" harmonic response in the "far field" (1*m*) after propagation. Panel (a) is for the system without modulations with laser intensity $9 \times 10^{14} W/cm^2$. Panel (b) is for the system with modulations with laser intensity $9 \times 10^{14} W/cm^2$.

3.5.3 Even harmonics after propagation

As described in previous section [Section 3.4.2], even harmonics may appear due to the internal sub-cycle dynamics. Fig. 3.18 presents high-order harmonic spectra of single particle response from our molecule system (left panel) and an atomic system (right panel) interaction with a gaussian laser pulse with duration 15 fs (FWHM) and intensity $1.5 \times 10^{14} W/cm^2$ at wavelength 800 nm. The atomic system has the same ionization potential as our molecule. For our molecule, even harmonics clearly show up near the cutoff, while no even harmonics appear for the atomic case. High-order



Figure 3.17: Time-frequency distributions of "off-axis" harmonic response in the "far field" (1*m*) after propagation. Panel (a) is for the system without modulations with laser intensity $9 \times 10^{14} W/cm^2$. Panel (b) is for the system with modulations with laser intensity $9 \times 10^{14} W/cm^2$.

harmonic spectra after propagation through a 2*mm* gas tube at 100*mbar* are shown in Fig. 3.19. They are quite similar to those before propagation presented in Fig. 3.18, except for intensities. Striking even harmonic appear in case of our molecule, and only odd harmonics show up for the atomic system. It is obvious that the even harmonics due to the internal sub-cycle dynamics can survive from harmonics propagation.

3.6 Conclusions

In this chapter, we numerically investigated the sub-cycle field-induced dynamics during strong field ionization of molecules. Such a sub-cycle dynamics coming from field-induced Rabi-like oscillations modulates electron emission during field ionization. It strongly depends on the laser intensities and dipole momentum between the ground state and the excited state of the molecule. The information of the dynamics will be carried by emitted electrons part of which will be guided by the laser field and rescatter with its mother ion. The recombination of modulated rescattering electron wavepacket with the ion will lead to radiation of high-order harmonics, which inherit modulations from rescattering electrons. As a result, the time-structure of high-order



Figure 3.18: High-order harmonic spectra of single particle response from our molecule (a) and an atomic system (b) with the same ionization potential.



Figure 3.19: High-order harmonic spectra of our molecule (a) and an atomic system (b) after propagation through a 2mm gas tube.

harmonics strongly depends on laser intensities due to field-induced dynamics. Another observable phenomena is appearance of even harmonics due the sub-cycle fieldinduced dynamics.

Moreover, the field-induced sub-cycle dynamics which modulates the time-frequency distribution of high harmonics can survive after propagation in media. In other words, propagation effects will not destroy the field-induced time-frequency information in high-oder harmonics, which makes field-induced sub-cycle dynamics an observable effect. With such an effect, one can estimate the time structure of rescattering electron, which is important for the application of rescattering process. Furthermore, it should also possible to be used as a tool to reveal other sub-cycle electron dynamics in molecules.

Chapter 4

Attosecond probing of strong field ionization dynamics: hydrogen atom

4.1 Introduction

Strong field ionization of atoms is an experimentally and theoretically accessible model process for the probing of electronic dynamics by extreme ultraviolet (XUV) attosecond pulses [96, 97]. In experiments so far the XUV pulses have been used to trigger atomic process [22, 13, 98], which were probed by a precisely synchronized strong infrared (IR) laser pulse. An important drawback of this scheme is the strong perturbation of the observed system by the probe pulse. A much extended range of ultrafast spectroscopy applications may be expected, when instead the XUV pulse is used as a weakly perturbative probe. Presently available XUV intensities preclude purely XUV pump-probe schemes, which is why the probed processes must be triggered by a strong laser pulse. Ionization may be the most general effect of a laser pulse on any system. Possible observables include the depletion of the initial ground state, the appearance of ionic states, as well as transient and permanent populations of excited states. These processes are reflected in the XUV part of the photoelectron emission spectrum and in total XUV photoelectron yields, as also photoemission *rates* depend on the system's state.

One complication of this idea is that in very strong fields with very fast ionization the notion of field free stationary states increasingly looses meaning, or, to put it differently, very many field free states states are needed for an adequate representation of the system. Even when it nearly adiabatically returns to the initial state after passage of the pulse, the electronic wave function *during* the pulse may resemble a wavepacket formed from a continuum of strongly dressed states.

A second complication on a more technical level is that little is known about what exactly is probed by a short XUV pulse. At typical XUV photon energies around 80 eV the radiation does not interact with free or weakly bound electrons. For an interaction, the close proximity of a third body — the nucleus — is needed, which is why one expects to probe predominantly electronic processes that occur near the nucleus.

XUV photoelectron spectra from field-free states are correctly described by perturbation theory and the interpretation of emission spectra poses no problem [99]. When a strong laser field is present, spectra get distorted by the laser after the electrons are set free, which leads to characteristic "streaking" of the momentum distribution [100]. Total yields, however, are assumed to remain unaffected by streaking and should exclusively depend on the interaction of the laser with the bound system prior to (and during) XUV photoelectron emission.

In the present chapter we investigated how the total XUV photoelectron yields vary during ionization by a strong few-cycle laser field. We will show that as a rule an interpretation of the XUV photoelectron yield in terms of populations of field free states is not possible, but that there is a close relation to the electron density near the nucleus. Our findings are based on numerical solutions of the time-dependent Schrödinger equation (TDSE) in three dimensions with a linearly polarized laser pulse. For the three-dimensional calculations we introduced a newly developed method using a representation in cylindrical coordinates and a combination of the finite elements method (FEM) with the Fast Fourier Transform (FFT) technique.

4.2 Method

An atom in a strong linearly polarized field gets distorted in polarization directions and the quiver amplitude of detached electrons may be by 10 to 100 times larger than the atomic size. For that reason it is advantageous to solve the TDSE of the hydrogen atom in cylindrical coordinates (Eq. (1.27)). A linearly polarized laser field is assumed with polarization direction parallel to *z*-axis. The interaction with the field is described in velocity gauge with the vector potential $A_z(t) = -\int_{-\infty}^t d\tau c \mathscr{E}_z(\tau)$. As in linear polarization the magnetic quantum number *m* is conserved, Eq. (1.28) is written for the case m = 0, assuming the atom is initially in its ground state.

For the numerical solution of Eq. (1.28) some care must be taken to obtain a *hermitian* discrete representation of the kinetic energy in ρ -direction and to correctly treat the Coulomb singularity. One solution to that problem is to scale coordinates as to soften the singularities near $\rho = 0$ [Section 1.2.4]. In our approach, we employed a hybrid discretization with a finite element basis in ρ -direction and an equidistant grid discretization in *z*-direction. By this procedure one easily constructs hermitian discrete operators and removes the explicit appearance of the Coulomb singularity in the discretized equations.

4.2.1 Finite element method

The finite element method [101] is a method for solving an equation by approximating continuous quantities as a set of quantities at discrete points, often regularly spaced into a so-called grid or mesh.

The ansatz for the wavefunction is chosen as

$$\Psi(\rho, z, t) = \sum_{n,m} c_m^n(z, t) h_m^n(\rho)$$
(4.1)

where h_m^n are m = 0, ..., M linearly independent polynomials of maximal degree M whose support is restricted to "finite elements" $[\rho_{n-1}, \rho_n]$

$$h_m^n(\rho) \equiv 0, \quad \rho \notin [\rho_{n-1}, \rho_n], \quad n = 1, \cdots, N.$$
(4.2)

In each interval, finite elements basis functions are constructed as

$$h_{1}^{n}(\rho_{n-1}) = 1$$

$$h_{2}^{n}(\rho_{n}) = 1$$

$$h_{m}^{n}(\rho_{n-1}) = h_{m}^{n}(\rho_{n}) = 0, m \neq 1, 2.$$
(4.3)

Continuity of Ψ in ρ -direction is enforced by a linear constraint on the coefficients c_m^n , which is implemented as

$$c_1^{n+1} = c_2^n \tag{4.4}$$

Further details of our implementation of the finite elements method can be found in Ref. [102].

Inserting the ansatz into Eq. (1.28), multiplying from the left by $h_{m'}^{n'}(\rho)$ and integrating over ρ we obtain a set of coupled equations for the linear coefficients $\vec{c}(z,t)$

$$i\vec{c}(z,t) = \left\{\frac{1}{2}\left[\frac{1}{i}\frac{\partial}{\partial z} - \frac{1}{c}A_z(t)\right]^2 + S^{-1}H^{\rho}(z)\right\}\vec{c}(z,t).$$
(4.5)

Here $\vec{c}(z,t)$ denotes the vector of coefficients c_m^n and $H^{\rho}(z,t)$ is given by

$$H^{\rho}_{n'm',nm}(z) = \int \rho d\rho h^{n'}_{m'}(\rho) \left[-\frac{1}{2\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} - \frac{1}{\sqrt{\rho^2 + z^2}} \right] h^n_m(\rho)$$
(4.6)

and S is the overlap matrix for the ρ -coordinate

$$S_{n'm',nm} = \int \rho d\rho h_{m'}^{n'}(\rho) h_m^n(\rho).$$
(4.7)

As the $h_m^n(\rho)$ are restricted to intervals $[\rho_{n-1}, \rho_n]$, *S* and H^{ρ} are banded matrices with the band width 2M + 1 (cf. Ref. [102]).

Eq. (4.5) was solved on an equidistant grid for the *z*-coordinate, where the derivatives $\partial/\partial z$ were calculated by Fast Fourier Transform (FFT) and time integration was performed by a self-adaptive, high order Runge-Kutta scheme. To avoid electrons reentering and reflections, absorption boundary conditions are used in both direction (cf. Section. 1.2.6).

4.2.2 Typical parameters

Note that the use of FFT method implies periodic boundary conditions in the *z*-direction. Most calculations were performed with N = 24 finite elements with an increasing element size and polynomial degree M = 4 on the interval [0, 20] in ρ -direction and 4096 equidistant points on the interval [-80, 80) in *z*-direction. For convergence checks, the box size was extended to $[0, 40] \times [-160, 160)$.

During the simulation a significant part of the wave function reaches the boundaries of the finite calculation volume. To avoid reflections in ρ -direction and unphysical reentry of the wave function from the opposite end in *z*-direction, we used absorbing potentials near the box boundaries as defined in Eq. (1.48), e.g. in ρ direction absorption starting from 16*a.u.* and in *z* direction starting from 72*a.u.* with absorption strength $W_a = 1$ (Eq. (1.48)). The ground state and the lowest few excited states were obtained by imaginary time propagation [Section 1.2.5].

4.2.3 Definition of the field

The vector potential of the external IR laser field was taken to be

$$A_L(t) = \frac{c\mathscr{E}_{L0}}{\omega_L}\sin^2\left(\frac{\pi t}{2\tau_L}\right)\sin\left(\omega_L t\right),\tag{4.8}$$

where $\tau_L = 207 a.u.(5 fs)$ is the full width at half maximum (FWHM) vector potential of the sin² pulse and the center frequency $\omega_L = 0.057 a.u.(800 nm)$ and the peak field strength \mathscr{E}_{L0} . *c* is the speed of light.

The vector potential of the XUV pulse has a gaussian shape as

$$A_X(t) = A_{X0}(t - t_X)\sin\left(\omega_X(t - t_X)\right) = \frac{c\mathscr{E}_{X0}}{\omega_0}\exp\left[-2\ln 2\left(\frac{t - t_X}{\tau_X}\right)^2\right]\sin\left(\omega_X(t - t_X)\right),$$
(4.9)

where A_{X0} is the envelope function, FWHM $\tau_X = 10.3 a.u. (250 as)$, center frequency $\omega_X = 3.0 a.u.$ and peak field strength $\mathscr{E}_{X0} = 0.01 a.u.$ (intensity $I_X = 3.5 \times 10^{12} W/cm^2$). t_X is the time delay between the IR lase pulse and the XUV pulse.

The field strength of the external field is the time derivative of the vector potential,

$$\mathscr{E}_{L,X}(t) = -\frac{1}{c} \frac{\partial A_{L,X}(t)}{\partial t}.$$
(4.10)



Figure 4.1: Electric field of IR laser pulse (bold red curve) at wavelength 800 nm and that of IR laser field with XUV pulse (photon energy 3a.u.) with a certain time delay (thin blue curve).

Fig. 4.1 presents a typical field of an IR laser pulse with a delayed XUV pulse. The IR field is a two-cycle pulse with peak field strength 0.12a.u. (intensity $5.1 \times 10^{14} W/cm^2$) at 800 nm and the XUV pulse has duration 250 as with peak field strength 0.01 a.u.(intensity $3.5 \times 10^{12} W/cm^2$) at 15.2 nm. The XUV pulse can be obtained from high-order harmonic generation of noble gas in experiments [10] and the IR pulse can provide by a commercial femtosecond laser system. With such an "IR + XUV" field, we probed ionization dynamics of hydrogen atom by varying the time delay between IR and XUV field in the next section.

4.3 **Results and Discussions**

4.3.1 XUV ionization yield

To study the results of such an IR-pump XUV-probe method, XUV single-photon ionization yield will be a valuable quantity, because it strongly depends on the state when XUV light is shining on. Numerically, the XUV ionization yield as a function of time delay t_X between the IR pulse and XUV pulse was calculated as

$$Y_X(t_X) = |\langle \psi_X(t_X) | \psi_X(t_X) \rangle|^2$$
(4.11)

where ψ_X is the additional wave function amplitude due to the XUV pulse

$$|\psi_X(t_X)\rangle = (1 - |\psi_L\rangle\langle\psi_L|)|\psi_{LX}(t_X)\rangle$$
(4.12)

and t_X is the time delay, and $\Psi_{LX}(t_X)$ is the wavefunction calculated with an XUV pulse, which is arrives at time t_X during the laser pulse, while Ψ_L is the wavefunction propagated with only the laser pulse. The normsquare of the additional wave function amplitude ψ_X gives us the photoelectron density produced by the XUV pulse. All time-dependent wavefunctions are obtained from results of solving the TDSE. The matrix element is evaluated at some time $t > t_X$ after the XUV pulse is over, where no further XUV single photon ionization happens.

We calculated XUV photoelectron yield Y_X for a hydrogen atom that is ionized by a strong laser pulse. The IR laser pulse was taken at wave length 800 nm ($\omega_L = 0.057 a.u.$), peak intensity $5.1 \times 10^{14} W/cm^2 (\mathcal{E}_L = 0.12 a.u.)$, and with a sine-square pulse envelope of 1 optical cycle FWHM. The IR pulse leads to about 50% ionization of the hydrogen atom.

As XUV photon energy ($\omega_X = 3a.u.$) is larger than the bound energy of ground state electron ($E_0 = -0.5a.u.$), single photon ionization is induced by XUV pulse. XUV photon ionization yield as a function of time delay is shown in Fig. 4.2. There are some large "wiggles" during the IR field and some small "wiggles" after the IR field. Therefore, some informations during IR laser field ionization has been encoded to the results, and the question is to find out which quantity determines XUV photon ionization.



Figure 4.2: XUV photon ionization yield Y_X (solid red curve) from hydrogen atom by a 250*as* XUV pulse during ionization of an IR laser with laser intensity $5.1 \times 10^{14} W/cm^2$. Hashed blue curve indicate the IR field ($|\mathscr{E}_L(t)|$).

4.3.2 Quasi-static bound states population

In Fig. 4.3, it is shown that $Y_X(t_X)$ roughly follows the evolution of the bound states population $P_{qb}(t)$ as given by the quasi-static depletion

$$P_{qb}(t) = 1 - \exp\left\{-\int_0^t \Gamma[\mathscr{E}(\tau)] d\tau\right\},\tag{4.13}$$

where $\Gamma[\mathscr{E}]$ are the ionization rates for static field \mathscr{E} , which is numerically calculated by the complex scaling technique [41]. There are, however, important deviations. Most prominently, the XUV photoelectron yield has local minima just before nodes of the electric field and rises to local maxima near the nodes. Moreover, after the pulse has passed, the XUV yield is not proportional to the quasi-static bound state population $P_{ab}(t)$.



Figure 4.3: The field-free ground state population (dashed green curve), the field-free bound states population (dash-dotted cyan curve) and the quasi-static bound state population (dotted magenta curve) compare with XUV photoelectron yield Y_X from hydrogen atom during ionization by a two-cycle laser pulse at wave length 800*nm* (solid red curve). All curves are normalized to 1 at time t = 0. The hashed blue line on the bottom indicates the electric field $|\mathscr{E}(t)|$.

4.3.3 Populations of field-free bound states

We also show the probability of finding the atom in the field free ground state

$$P_0(t) = |\langle \Psi(0) | \Psi(t) \rangle|^2.$$
(4.14)

As shown in Fig. 4.3, this quantity has similar characteristics as the XUV probe signal, but the modulations are less pronounced, which indicates that excited and continuum

states influence the XUV probing process. Note, however, that the effect of the excited state population after the pulse is rather small compared to the modulations of the XUV yield during the pulse. Therefore the participation of excited states in the ionization dynamics can only be of a transient nature, as in adiabatic distortions by the strong field.

The field-free bound states population is present as dash-dotted cyan curve in Fig. 4.3. It is calculated as

$$P_b(t) = \sum_n |\langle \phi_n | \Psi(t) \rangle|^2, \qquad (4.15)$$

where ϕ_n are the field-free bound states. In the Eq. (4.15), the ground state (1*s* state) and the first three excited states (2*p*, 3*p*, 4*p* states, to which the transition from 1*s* state are dipole allowed and easily obtained with imaginary time propagation) are included. The field-free bound states population roughly follows the quasi-static population, which tells that there are about 3% excitation after the IR laser. The present of excited states after the IR field leads to a beat in the electron density. It was shown in Ref. [103] how such a beat is reflected in modulations of *Y*_X as in Figure 4.2 at large times.

4.3.4 Electron density near the nucleus

As discussed in the introduction, one expects to probe by an XUV pulse the electrons near the nucleus. We define an electron density near the origin by

$$N_0(t) = \int_0^{\rho_0} \rho d\rho \int_{-z_0}^{z_0} dz |\Psi_L(\rho, z; t)|^2, \qquad (4.16)$$

where $\Psi_L(\rho, z; t)$ are wavefunctions during IR field ionization, without XUV pulse. The electron density near the nucleus during laser field ionization is shown in Fig. 4.4 as green curve, which has been normalized to 1 at time $t_X = 0$. The electron density is selected with parameters $\rho_0, z_0 = 0.1 a.u$. The normalized XUV photon ionization yield roughly follows electron density near nucleus, except that there has more striking oscillations for electron density near nucleus to compare with XUV photon ionization. The reason is that XUV pulse has its own duration which will determined the resolution of such XUV probing method.

Due to the influence of XUV pulse duration, time average should taken for the electron density to compare with XUV photon ionization yield. For a single photon ionization, the ionization yield is proportional the intensity of the field. Therefore, we take an averaged electron density as

$$N_0'(t) = \langle N_0(t) \rangle_{A_{X0}(t-t_X)} = \frac{\int dt_X A_{X0}^2(t-t_X) N_0(t)}{\int dt_X A_{X0}^2(t-t_X)}$$
(4.17)

where the time average is taken over the intensity profile of the XUV pulse $A_{X0}^2(t-t_X)$ (Eq. (4.9)). Figure 4.4 includes $N'_0(t)$ with the same parameters as $N_0(t)$ ($\rho_0, z_0 = 0.1 a.u.$). Y_X exactly follows $N'_0(t)$ when both curves are normalized to 1 at t = 0. In other words, the electron density near the nucleus is observed by this XUV probing method.

The electron density near the nucleus was studied with different integration parameters (z_0 and ρ_0), which is presented in Fig. 4.5. For integration range from 0.1 a.u. to 1.0 a.u., structures electron density are quite the same, and slight difference shows up for z_0 , $\rho_0 = 2.0 a.u.$.

4.3.5 Longer wavelengths and lower intensities

We find that the simple correspondence between N'_0 and Y_X is not only valid in a limited parameter range. It is preserved at lower intensities and at longer wave lengths, which are shown in Fig. 4.6, 4.7, 4.8, 4.9. XUV ionization yield, electron density near nucleus (taken with ρ_0 , $z_0 = 0.1 a.u.$) and ground state population are presented. In Fig. 4.6, wavelength 800 nm with intensity $1.3 \times 10^{14} W/cm^2$ are used, where ionization yield is much less than that of intensity $5.6 \times 10^{14} W/cm^2$. Longer wavelength 1600 a.u.with intensities $1.3 \times 10^{14} W/cm^2$ and $4.2 \times 10^{14} W/cm^2$ are presented in Fig. 4.7, 4.8, while Fig. 4.9 presents wavelength 3200 a.u. with intensity $1.3 \times 10^{14} W/cm^2$. The



Figure 4.4: XUV photoelectron yield Y_X from hydrogen atom during ionization by a two-cycle laser pulse at wave length 800 *nm* (solid red line) compares with the electron density near the nucleus (dashed gree curve). Hashed blue curve presents the electron density near the nucleus after averaging with the XUV intensity envelope. All curves are normalized to 1 at time t = 0.



Figure 4.5: Electron densities near nucleus with different integration parameters (from z_0 , $\rho_0 = 0.1 a.u.$ to z_0 , $\rho_0 = 2.0 a.u.$). All curves have been normalized to 1 at time t = 0.

XUV ionization yield never exactly follows the ground state population, but always follows the electron density near the nucleus. This observation neither depends on the laser wavelength nor the laser intensity.

4.3.6 Influence of XUV pulse parameters

To perform such XUV probing, one should consider the parameters of the probe — XUV pulse. XUV photon energy, pulse duration and intensity are three most important parameters to influent the XUV photon ionization yield.

XUV photon energy

First, XUV photon energy is studied. Other XUV pulse parameters are chosen as intensity $3.5 \times 10^{12} W/cm^2$, pulse duration (FWHM) 250*as*. The IR field is 800*nm* with intensity $5.3 \times 10^{14} W/cm^2$. We selected three different time delays, one at the very beginning of the IR pulse, one near the center of the IR field and the other at time



Figure 4.6: XUV photon ionization yield Y_X for wavelength 800 nm and intensities $1.3 \times 10^{14} W/cm^2$ is presented as red points. Electron density near nucleus ($\rho_0, z_0 = 0.1$) and ground state population are shown as blue and green curves, respectively. All curves are normalized to 1 at t = 0.



Figure 4.7: XUV photon ionization yield Y_X for wavelength 1600 nm and intensities $1.3 \times 10^{14} W/cm^2$ is presented as red points. The electron density near nucleus $(\rho_0, z_0 = 0.1)$ and the ground state population are shown as blue and green curves, respectively. All curves are normalized to 1 at t = 0.



Figure 4.8: XUV photon ionization yield Y_X for wavelength 1600 nm and intensities $4.2 \times 10^{14} W/cm^2$ is presented as red points. Electron density near nucleus ($\rho_0, z_0 = 0.1$) and ground state population are shown as blue and green curves, respectively. All curves are normalized to 1 at t = 0.



Figure 4.9: XUV photon ionization yield Y_X for wavelength 3200 nm and intensities $1.3 \times 10^{14} W/cm^2$ is presented as red points. Electron density near nucleus ($\rho_0, z_0 = 0.1$) and ground state population are shown as blue and green curves, respectively. All curves are normalized to 1 at t = 0.

when the IR has gone. Results are shown in Fig. 4.10 with data normalized to 1 for photon energy 2a.u.. For three different time delay, we get the same relation between XUV photon ionization yield and XUV photon energy. It is clear that XUV photon ionization yield strongly depends on the XUV photon energy, but the XUV photon ionization yield behavior during IR field ionization is preserved with different XUV photon energy. It also can be explained by that XUV photon energy is not critical to the method because XUV photon ionization for hydrogen atom is in single photon ionization regime.



Figure 4.10: XUV photon ionization yield with different XUV photon energy for three different time delay, red square for time delay at the beginning of the IR field, green circle for time delay during the IR field and blue cross for time delay after the IR field. All curves have been normalized to 1 at first points.

XUV pulse intensity

Intensity of XUV pulse will also directly influence the XUV photon ionization yield. In Fig. 4.11, it presents a linear dependence of XUV ionization yield on XUV pulse



Figure 4.11: XUV photon ionization yield with different XUV pulse peak intensity for three different time delay, red square for time delay at the beginning of the IR field, green circle for time delay during the IR field and blue cross for time delay after the IR field. All curves have been normalized to 1 at first points.

intensity for three different time delays. Time delays are chosen the same as those used in Fig. 4.10). Therefore, numerically the XUV pulse intensity is not an import issue for the method. It is due to that XUV photon ionization yield is proportional to XUV pulse intensity in single photon ionization regime.

XUV pulse duration

As the pulse duration will determine the resolution of XUV probing method, XUV pulse duration should be a critical parameters. To probe a sub-cycle dynamics, XUV

pulse duration should less than the time structure of the dynamics, otherwise the dynamics will be averaged out due to resolution problem.



Figure 4.12: XUV photon ionization yield (points) with different XUV pulse duration for time delays after the IR pulse when we got small "wiggles". Red filled squares present for pulse duration 150*as*, green circle for pulse duration 250*as*, blue filled circle for pulse duration 500*as* and magenta square for pulse duration 750*as*. Curves are electron densities near nucleus with related pulse duration averaging to the same color points.

After the IR field ionization, the excitation causes beating between ground and excited states which yields small but fast modulation for the electron density near nucleus. Fig. 4.12 presents XUV photon ionization yields (points) as a function of time deadly between the IR pulse and XUV pulse. XUV pulse duration varies from 150*as* to 750*as*. Also electron densities with related pulse duration averaging are presented in the figure. For XUV pulse duration 150*as* and 250*as*, we can get clear structures of electron density near nucleus due to states beating. When XUV pulse duration is too long, the structures disappear due to resolution problem. In Fig. 4.13, electron densities

near nucleus (ρ_0 , $z_0 = 0.1 a.u.$) are presented with different averaging durations. It is clearly shown that also the dip structure in electron density during the field strongly depends on the averaging durations. For the longest duration shown in Fig. 4.13, only ionization steps are left.



Figure 4.13: Electron density with different time duration (FWHM) averaging, solid red curve for no time averaging, dashed green curve for duration 150*as*, hashed blue curve for duration 250*as*, dotted magenta curve for duration 500*as* and dash-dotted cyan curve for duration 750*as*,

In summary, XUV pulse duration determines the resolution of the XUV probing method, while XUV photon energy and XUV pulse intensity only affect the total XUV ionization yield.

4.4 Conclusions

In conclusion, we presented a hybrid-discretization method to solving the TDSE of hydrogen atom in cylindrical coordinates. With such method, we show that truly dy-

namical effects occur during strong field ionization, even at parameters where the total ionization after passage of the pulse is well described by quasi-static depletion of the bound system. The XUV probing method can be used to measure the dynamics. We found that the XUV photon ionization yield never follows the population of field-free ground state and the total population of quasi-static bound state, but follows the electron density near the nucleus. The dips in the XUV photon ionization yield originate from the adiabatic distortions of the ground state and irreversible excited state dynamics. Both effects, in principle, are of an observable magnitude. In our examples, the major part of the the dynamics is due to ground state distortion which causes the local minima in the observed XUV ionization yield, while excitation introduces only some minor modulations and ground-excited state beatings after the end of the laser pulse.

XUV parameters for the XUV probing method were carefully studied. It is shown that XUV pulse duration determines the resolution of the XUV probing method, while XUV photon energy and XUV pulse intensity only affect the total XUV ionization yield. In principle, for an XUV probing experiment, one need an XUV pulse with short enough pulse duration to resolve the ultrafast dynamics and intense enough pulse intensity to make the effect detectable.
Appendix

A.1 Units relations for mostly used quantities

Quantity	atomic unit	SI	others
time	1 a.u.	2.42e-17 s	24.2 as
energy	1 a.u.	4.36e-18 J	27.2 eV

Table A.1: Units relation for time and energy.

Wavelength	Period (SI)	Period (a.u.)	Energy (eV)	Energy (a.u.)
800 nm	2.67 fs	110 a.u.	1.55 eV	0.057 a.u.
15.2 nm	50 as	2.09 a.u.	81.6 eV	3 a.u.

Table A.2: Units relations for wave quantities of infrared pulse and extreme-ultraviolet pulse.

A.2 Classical trajectory calculation for electron recollision

Here we briefly summarize the classical theory of electron recollision in a strong field which was first proposed in Ref. [104].

The vector potential of a linear polarized laser field is usually defined as

$$A(t) = A_0(t)\cos(\omega_0 t), \qquad (A.1)$$

where ω_0 is the center frequency and $A_0(t)$ is the envelope function, which mostly used as a gaussian function,

$$A_0(t) = \frac{c\mathscr{E}_0}{\omega_0} \exp\left(-2\ln 2\frac{t^2}{\tau^2}\right) \tag{A.2}$$

or sine-square function

$$A_0(t) = \begin{cases} \frac{c\mathcal{E}_0}{\omega_0} \sin^2(\frac{\pi t}{2\tau}), & 0 < t < 2\tau \\ 0, & otherwise \end{cases}$$
(A.3)

where \mathscr{E}_0 is the peak field strength and τ is the pulse duration (full width at halt maximum, FWHM), respectively. *c* is the speed of light.

In classical mechanics, the position of electron obeys Newton's second law, which reads with atomic units ($m_e = -e = 1$) as

$$\ddot{x}(t) = F = -\mathscr{E}(t) \tag{A.4}$$

where $\mathscr{E}(t)$ is the electric field of the laser pulse, which can derived from the vector potential,

$$\mathscr{E}(t) = -\frac{1}{c} \frac{\partial A(t)}{\partial t}.$$
(A.5)

where *c* is the speed of light.

Eq. (A.4) can simple solved by integration with certain initial condition, which is usually given by [105]

$$\dot{x}(t_i) = 0, \tag{A.6}$$

$$x(t_i) = 0. \tag{A.7}$$

For the classical electron rescattering, electron is released at time t_i with zero velocity and comes back to its origin position to recollide with the nucleus at time t_f . t_f should be solutions of the following equation.

$$x(t_f) = 0. \tag{A.8}$$

As an example, for a 5 *fs* (FWHM), 800*nm*, sine-square shape laser pulse, the relation between recollision time and recollision energy is presented in Fig. A.14. It is clear the recollision energy is a function of recollision time. For each half laser cycle, earlier recolliding electrons has low energy, and some point the recolliding energy reaches its peak and then decays with the increasing of recolliding time. The increasing slope is so-called "short-trajectory", which comes from recollision with a short electron trajectory, and the decreasing is called "longe-trajectory", that is, electron travels back from a longer trajectory but with the same recollision energy as that of "short-trajectory". The merging point of "short-trajectory" and "longe-trajectory" is named "cut-off". The cut-off energy is about $3.17U_p$, where $U_p = \frac{\delta_0^2}{4\omega_0^2}$ is the ponderomotive energy.



Figure A.14: Relation between recollision energy and recollision time presents with solid red curve, as well as electric field strength in dashed green curve.

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Acknowledgments

This project presented in this thesis would not be possible to be finished without the support of many people. First of all, I am grateful to my adviser, Dr. Armin Scrinzi, who leaded me through the project with educations on attosecond physics and exciting discussions, read my numerous revisions of the thesis and suggestions on scientific writing. I also acknowledge him and Ms. Xue Jie for friendly helping me to settle down and start my life in Vienna. Thanks to Dr. Vladislav S. Yakovlev and Dr. Markus Kitzler, who helped me with programming and fruitful discussions and cooperations in the project. I appreciated group members, Dr. Jeremie Caillat, DI Ede Christopher, DI Gerald Gordan, Dr. Marlene Wickenhauser, Dr. Volkmar Putz, Dr. Olga Smirnova, who provided me a great research environment. I would like to show acknowledgment to Prof. Dr. Georg Reider, Dr. Irina Sorokina, Prof. Dr. Ernst Wintner, Prof. Dr. Evgeni Sorokin, Prof. Dr. Karl Unterrainer, who contributed to my educations with interesting lectures. Thanks to Ms. Dietlinde Egger, who kindly gave me helps in my earlier life in Vienna and later guided me to prepare for the defense. I would like to thank secretaries of Photonics Institute and FWF, Ms. Elfriede Lohwasser, Ms. Eva Sturm, Ms. Angelika Wiesinger, Ms. Heike Höller, Ms. Barbara Weber, who were helpful for my daily scientific life. Acknowledgment would also addressed to FWF, who provided me financial support to complete this project. Thanks to all friendly colleagues in Photonics institute, and thanks numerous friends who endured this long process with me. Thanks to my family who always support and encourage me. Finally, grateful thanks to my wife, Wumei, always offering supports and endless love.

Curriculum Vitae

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Education

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Research interests

Interaction of strong laser field with atoms and molecules, HHG and attosecond pulses generation, measurement and applications, generation and applications of few-cycle laser pulses and coherent X-ray source

Journal publications

- 1. Xinhua Xie, A. Scrinzi, M. Wickenhauser, A. Baltuska, I. Barth, and M. Kitzler, Influence of bound electron dynamics on high harmonic generation: circularly polarized attosecond X-ray pulses, In preparation.
- 2. Ch. Ede, **Xinhua Xie**, M. Wickenhauser, A. Scrinzi, *Cross-talk in XUV-IR single and double photoionization*, In preparation.

- 3. M. Kitzler, **Xinhua Xie**, S. Roither, A. Scrinzi, A. Baltuska, *Angular encoding in attosecond recollision*, Submitted to New Journal of Physics.
- Xinhua Xie, M. Wickenhauser, W. Boutu, H. Merdji, P. Salières, A. Scrinzi, Subcycle dynamics in the laser ionization of molecules, Physical Review A, 76, 023426, 2007
- 5. M. Kitzler, **Xinhua Xie**, A. Scrinzi, A. Baltuska, *Optical attosecond mapping by polarization selective detection*, Physical Review A, 76, 011801(R), 2007
- Xinhua Xie, G. Jordan, M. Wickenhauser, A. Scrinzi, *Time and momentum distribu*tions of re-scattering electrons, Journal of Modern Optics, Vol.54, Iss.7, 999-1010, 2007
- J. Li, Z. Duan, Z. Zeng, Xinhua Xie, Y. Deng, R. Li, Z. Xu, S. L. Chin, *Time-resolved measurement of low-density plasma channels produced by a kHz fs laser in air*, Physical Review E, 72, 026412, 2005
- Y. Deng, Xinhua Xie, H. Xiong, Y. X. Leng, C.F. Cheng, H.H. Lu, R.X. Li, and Z. Z. Xu, Optical breakdown for silica and silicon with double femtosecond laser pulses, Optics Express, 13, 3096, 2005
- 9. Xinhua Xie, Y. Liu, P. Fan, R. Li, *Spectral focusing characteristics of a grazingincidence flat-field grating spectrometer*, Chinese Physics, Vol.13, No.11, 2004
- 10. Z. Zeng, R. Li, **Xinhua Xie**, Z. Xu, *High-intensity attosecond high-order harmonic* generation driven by synthesized laser field, Physical Review A 70, 053809, 2004
- 11. Xinhua Xie, Z. Zeng, et al, *Flat-top Phase-matched high-order harmonics in a gas-filled cell*, Chinese Optics Letters, Vol.2, No.6, 2004.
- Xinhua Xie, Z. Zeng, et al, *Phase-matched high-order harmonic generation by the interaction of argon atoms with high-repetition-rate low-energy femtosecond laser pulses*, Science in China-Series G, Vol.34, No.3, 2004.

 R. Li, Z. Zeng, Xinhua Xie, Z. Xu, Theoretical and experimental study on attosecond high-order harmonics radiation at Shanghai Institute of Optics and Fine Mechanics, Journal of Korean Physical Society, Vol.44(2), No.3, 2004

Conference contributions

- Xinhua Xie, C. Ede, M. Wickenhauser, A. Scrinzi, *Modulation of attosecond XUV* photo-ionization by an IR field(poster), International Workshop and 391.WE-Heraeus-Seminar on Attosecond Physics, Dresden, Germany, 2007
- M. Kitzler, Xinhua Xie, A. Scrinzi, A. Baltuska, *Optical attosecond mapping by polarization selective detection*(poster), International Workshop and 391.WE-Heraeus-Seminar on Attosecond Physics, Dresden, Germany, 2007
- Xinhua Xie, M. Wickenhauser, A. Scrinzi, Sub-cycle dynamics in the laser ionization of molecules(talk), German Physics Society Spring Meeting, Dsseldorf, Germany, 2007
- Xinhua Xie, M. Wickenhauser, A. Scrinzi, *Effects of molecular orientation in the laser ionization of molecules*(talk), International Conference on the Interaction of Atoms, Molecules and Plasma with Intense Ultrashort Laser Pulses, Szeged, Hungary, 2006
- Xinhua Xie, G. Jordan, C. Ede, A. Scrinzi, Molecular orientation, orbital symmetry, and electron correlation in the laser ionization of molecules(talk), SILAP 2006 Super Intense Laser Atom Physics, Salamanca, Spain, 2006
- G. Jordan, Xinhua Xie, C. Ede, A. Scrinzi Rescattering imaging of molecular orbitals(poster), Ultra-Fast Dynamic Imaging Workshop, Imperial College London, London, United Kindom, 2006
- 7. Xinhua Xie, M. Spanner, A. Scrinzi, *Attosecond probing of strong field ionization dynamics*(poster), 10th International Conference on Multiphoton Processes (ICOMP),

Orford, Quebec, Canada, 2005

- V. Yakovlev, Xinhua Xie, A. Scrinzi Modeling pump-probe ionization of a twoelectron system(poster), 10th International Conference on Multiphoton Processes (ICOMP), Orford, Quebec, Canada, 2005
- Xinhua Xie, M. Spanner, A. Scrinzi, Probing sub-cycle strong field ionization dynamics with an attosecond XUV pulse(Poster), 55th Austrian Physics Society Annual Meeting, Vienna, Austria, 2005
- J. Caillat, Xinhua Xie, M. Spanner, V. Yakovlev, A. Scrinzi, *Probing electronic dynamics with attosecond XUV pulses*(talk), International Symposium on Topical Problems of Nonlinear Wave Physics, St. Petersburg, Russia, 2005

Experimental skills

- Pump-probe technique, spectral analysis and X-ray spectrograph
- Measurement of ultra-short pulses (by SSA or SPIDER) and diagnosis of laser beam
- Vacuum technique and vacuum system maintenance

Computational skills

- Programming languages : Fortran 90/77, C/C++
- Analytic softwares : Gnuplot, Matlab, OriginLab, Winspec32
- Word Processing softwares: Latex, Open Office, MS Office

Language

Chinese (native), English (fluent), German (basic)