ATTOSECOND PULSE GENERATION AND APPLICATION TO THE STUDY OF ULTRAFAST ELECTRON DYNAMICS IN MOLECULES

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Abstract

This thesis describes the application of time-resolved techniques to the study of ultrafast electron dynamics in nitrogen molecules. Electron motion in molecules occurs on the attosecond \((10^{-18} \text{ s})\) time scale; for this reason it can be followed only by using light pulses with attosecond temporal duration. Attosecond pulses are produced exploiting a non-linear process called high-order harmonic generation (HHG). In HHG an intense infrared (IR) femtosecond pulse is focused in a gas target to produce odd harmonic frequencies of the IR fundamental frequency, thus creating new wavelengths extending into the extreme ultraviolet (XUV) \((10 – 100 \text{ eV})\) or even the soft x-ray \((100 – 200 \text{ eV})\) energy region. This comb of odd frequencies corresponds to a train of attosecond pulses (APTs) in the temporal domain. However, isolated attosecond pulses are more attractive as they allow the achievement of a better temporal resolution in pump-probe measurements. In order to isolate a single pulse, a gating technique on the HHG process must be applied. The first part of this thesis shows numerical results on three possible gating techniques: polarization gating (PG), double optical gating (DOG) and generalized double optical gating (GDOG). Simulations were carried out in order to optimize the experimental setup. Isolated pulses with a time duration of 200 as were generated and completely characterized. The second part of this thesis presents the experimental results of attosecond pump - femtosecond probe measurements performed on nitrogen molecules. The results demonstrate the possibility to observe and control the ultrafast electron dynamics occurring in photoexcited and photoionized diatomic molecules on a sub-femtosecond scale. Dissociation dynamics are initiated by ultrashort
APTs generated in argon or in xenon. In the case of xenon, XUV pulses can excite low excited states of the molecular cation $N_2^+$. In the case of argon, XUV photons can excite also highly excited electronic states of $N_2^+$ or low-excited states of the dication $N_2^{2+}$. In both cases, the measurements revealed the presence of sub-cycle oscillatory dynamics due to quantum interference between different dissociation paths.
Riassunto

Questo lavoro di tesi descrive l’applicazione di tecniche risolte in tempo allo studio di dinamiche ultraveloci in molecole di azoto. I moti elettronici che avvengono nelle molecole sono caratterizzati da scale temporali dell’attosecondo ($1 \times 10^{-18}$ s) e per questo motivo possono essere studiati solo mediante l’utilizzo di impulsi ad attosecondi. Tali impulsi vengono generati attraverso un processo non lineare di generazione di armoniche di ordine elevato, in cui un impulso infrarosso della durata di pochi femtosecondi viene focalizzato su di un getto di gas al fine di produrre uno spettro discreto, composto dalle sole frequenze dispari della fondamentale, che si estende fino alle regioni dell’ultravioletto estremo (XUV) ($10 – 100$ eV) o dei raggi X molli ($100$ eV – $5$ keV). Tale pettine di frequenze dispari corrisponde ad un treno di impulsi ad attosecondi (attosecond pulse train - APT) nel dominio del tempo. Tuttavia è più interessante disporre di impulsi isolati in quanto essi permettono di ottenere una migliore risoluzione temporale in misure di pump-probe. Per poter isolare un singolo impulso, il processo di generazione di armoniche di ordine elevato deve essere controllato da opportune tecniche di gating.

La prima parte di questa tesi presenta i risultati di simulazioni condotte su tre possibili tecniche di gating: il polarization gating (PG), il double optical gating (DOG) e il generalized double optical gating (GDOG). Tali simulazioni sono state svolte con l’obiettivo di ottimizzare l’apparato sperimentale. In un secondo momento è stata dimostrata la possibilità di generare impulsi isolati mediante la tecnica di PG; la completa caratterizzazione di essi ha portato a concludere che la loro durata temporale è di $200$ as.

La seconda parte della tesi presenta i risultati sperimentali ottenuti me-
diante misure di pump-probe su molecole di azoto. I risultati dimostrano la possibilità di osservare e di controllare con risoluzione inferiore al femtosecondo i moti elettronici ultraveloci che avvengono in molecole biatomiche foto-eccitate e foto-ionizzate. Le dinamiche di dissociazione vengono avviate da APTs ultrabrevi generati in xenon e in argon. Nel caso di impulsi XUV generati in xenon è stato possibile indagare gli stati del catione molecolare \( N_2^+ \) posti a bassa energia. Stati elettronici dell’\( N_2^+ \) posti ad energie maggiori e stati a bassa energia del dicatione molecolare \( N_2^{2+} \) sono stati invece eccitati a seguito dell’assorbimento di fotoni XUV generati in argon. In entrambi i casi, le misure hanno permesso di rivelare la presenza di dinamiche oscillatrici ultraveloci dovute ad interferenze quantistiche tra diversi cammini di dissociazione.
Introduction

In general any time-resolved experiment requires the generation and detection of wave packets, which are produced by coherent superposition of atomic or molecular eigenstates. The time dependence originates from the quantum mechanical phase factors $e^{-iE_n t/\hbar}$ associated with each eigenstate [1]. The generated electron wave packets present a temporal evolution on time scales which range from the microseconds to the attoseconds. For example, if the 1s electron of an hydrogen atom is partially excited to the 2s state, a coherent superposition of the two states can be generated. The corresponding electron density oscillates between the two states with a period $T = \hbar/\Delta E = 400 \text{ as}$, where $\Delta E = 10.2 \text{ eV}$ is the energy difference between the 1s and the 2s states.

A number of important chemical and physical processes in atoms, molecules, nanostructures and solids evolve on a sub-femtosecond temporal scale. The experimental investigation of these ultrafast processes requires the use of attosecond light pulses.

Attosecond extreme-ultraviolet pulses can be produced by implementing a non-linear process called high harmonic generation (HHG). In HHG an intense infrared (IR) femtosecond laser pulse is focused in a gas target to produce odd harmonic frequencies of the IR fundamental frequency, thus creating new wavelengths extending into the extreme ultraviolet ($10−100 \text{ eV}$) or even the soft X-ray regime ($100 − 200 \text{ eV}$). The possibility to generate attosecond pulse trains by HHG was first proposed by Farkas and Toth in 1992 [2]. The authors suggested that if the radiation related to each harmonic had an appropriate phase relationship, this would correspond to a train of
attosecond pulses in the time domain. In 2001, Paul et al. were able to experimentally demonstrate the generation of trains of 250 as pulses [3]. In the same year, Hentschel et al. experimentally demonstrated the possibility to generate isolated attosecond pulses by performing a suitable frequency filtering of the XUV radiation produced by HHG in a noble gas [4].

Since then tremendous progress has been achieved in the field of attosecond science, with the introduction of new techniques for the generation of isolated attosecond pulses and with the demonstration of various schemes for the application of these pulses. Outstanding results demonstrate that attosecond pulses can be successfully combined with femtosecond IR pulses in order to have enough energy to perform pump-probe measurements but still preserving the attosecond resolution. In the case of molecules, first pump-probe measurements with attosecond temporal resolution were performed on hydrogen molecules (H$_2$ and D$_2$) in 2006 [5]. An isolated attosecond pulse was used to ionize D$_2$ molecules; the subsequent electron dynamics was probed by a 6 fs IR pulse, with controlled electric field. The experimental results demonstrated the possibility to directly investigate the electron localization following molecular photoionization caused by the absorption of XUV photons. More recently, trains composed of two attosecond pulses were used in pump-probe measurements on the ammino acid phenylalanine [6], thus indicating the possibility to extend these spectroscopy techniques to more complex molecular systems. This study allowed to observe the evolution of the electron density distribution after the sudden photoionization of the neutral molecule. Indeed, after the removal of an electron, the molecule is in a non-stationary state, consisting in a superposition of electronic states of the cation. Afterwards, the molecule reaches a stationary state through a process called charge migration, in which the positive charge created after the photoionization migrates throughout the system on a timescale of a few femtosecond solely driven by the electron correlation and electron relaxation [7]. This ultrafast redistribution of the electron cloud can influence the nuclear dynamics and cause a reorganization of the molecular structure.

The purpose if this thesis work was the realization of a high photon flux attosecond source and its exploitation in pump-probe measurements with at-
to second temporal resolution. This study was carried out to observe electron dynamics in diatomic molecules and particular attention was devoted to the investigation of ultrafast dynamics of highly excited states. Various temporal gating techniques have been analyzed in order to confine the harmonic generation process in a single event (generation of isolated attosecond pulses) or to a pair of events. In particular, the design of the optical setup required for the implementation of three different temporal gating techniques (namely polarization gating (PG), double optical gating (DOG) and generalized double optical gating (GDOG)) has been performed. Isolated attosecond pulses with a time duration of 200 \textit{as} were generated and completely characterized. Ultrashort attosecond pulse trains were used to photoexcite and photoionize nitrogen molecules and the subsequent dissociation dynamics was probed by means of a time-delayed femtosecond infrared pulse. These measurements revealed the presence of ultrafast oscillatory dynamics due to quantum interference between different dissociation paths.

The thesis is organized as follows:

- the \textbf{first chapter} reports the theory of the high-order harmonic generation process. In the first part, the interaction between a single atom and few-cycle infrared pulses is described by means of a simplified semiclassical model. The second part will describe the same mechanism following the quantum treatment proposed by Lewenstein.

- the \textbf{second chapter} will present some techniques devised in order to generate and characterize isolated attosecond pulses. After a brief description of the known techniques implemented so far for the generation of isolated attosecond pulses, three temporal gating techniques will be discussed in detail. For each case, numerical results are presented. The second part of the chapter will describe a technique for the complete characterization of isolated attosecond pulses.

- the \textbf{third chapter} will focus on the description of the laser system and of the experimental setup. Particular attention is devoted to the description of the velocity map imaging (VMI) spectrometer and of
the Abel inversion algorithm used to retrieve the 3D momentum distribution of charged particles. A complete characterization of isolated attosecond pulses in terms of temporal intensity and phase will be shown.

- the fourth chapter will present the results of the attosecond pump-femtosecond probe measurements performed on nitrogen molecules. Experimental results demonstrating the possibility to observe and control the ultrafast electron dynamics occurring in photoionized and photoexcited diatomic molecules will be shown. In particular, a temporal mapping of dissociation and autoionization processes will be displayed. Experimental evidences of sub-cycle oscillatory dynamics will be shown and described in terms of quantum interferences between different dissociation paths.
High harmonic generation

Many physical processes are characterized by ultrafast timescales. Molecular rotations and intra-molecular vibrations occur on picosecond ($10^{-12}$ s) and femtosecond ($10^{-15}$ s) timescales, while the electron dynamics occurs on attosecond ($10^{-18}$ s) temporal scales. Therefore, sub-femtosecond pulses are of crucial importance for the investigation of electron motion in molecules.

In the last decade, the development of ultrashort laser sources operating in the visible - near infrared spectral range allowed to study physical processes in the femtosecond scale. Since the shortest pulse duration is determined by the laser wavelength, the pulse duration of visible light sources is limited to a few femtoseconds. In order to obtain attosecond pulses, it is necessary to devise some techniques to generate shorter wavelengths, ranging from the extreme ultraviolet (XUV) to the soft-X-rays spectral region.

This chapter will deal with the high harmonic generation (HHG) process, exploited to obtain XUV radiation.

High harmonic generation relies on an extremely non-linear mechanism induced in a medium, typically a noble gas, by a high intensity laser pulse. This non-linearity entails the generation of high-order harmonics of the fundamental laser frequency $\omega_0$.

The interaction between the laser pulse and the medium will be analyzed through two different approaches, described in the following sections:
a semiclassical theory, which attributes the harmonics emission to a three-step process, and a quantum theory, developed in order to account for some mechanisms neglected by the semiclassical description.

1.1 Three-step model

The HHG process occurring in a single atom can be described with a semiclassical picture, assuming the following approximations:

- single active electron (SAE) approximation;
- strong field approximation.

Under these approximations, high-order harmonic generation process can be described as a mechanism composed of three different steps [8] (fig. 1.1):

- Step 1: Ionization. When laser intensity reaches values between $10^{13}$ and $10^{14}$ W/cm$^2$, the electrons experience a force exerted by the electric field which is comparable with the binding energy of the external shells of the atom. As a result, the IR field can bend the coulombic potential of the atom, thus leading to quantum tunnel ionization.

- Step 2: Motion after liberation. Assuming that the IR field is sufficiently strong (Strong Field Approximation - SFA) to neglect the influence of the coulombic potential of the ion, the motion of the freed electron can be described by classic equations.

- Step 3: Recollision. Since the sign of the electric field changes every half optical cycle, for proper initial conditions the electron can be swept back to its parent ion. This causes the recombination and the consequent emission of an XUV photon of energy equal to the sum of the ionization energy of the atom and the kinetic energy acquired by the electron in the continuum. Since this mechanism occurs every half optical cycle of the incident radiation, the emitted XUV radiation is characterized by a discrete spectrum with odd harmonics of the fundamental laser frequency $\omega_0$. 
A detailed analysis of these three steps is reported in the next paragraphs.

1.1.1 Ionization

It is worth noting that, in this model, only the ionization step requires a non-classical description.

Depending on the values of the ionization potential $I_p$ of the atom and of the ponderomotive energy $U_p$, ionization can be attributed to two different phenomena: multi-photon absorption and tunnel ionization.

Ponderomotive energy is defined as the cycle-averaged kinetic energy acquired by the electron from the IR field:

$$U_p = \frac{e^2 E_0^2}{4m_e \omega_0^2},$$

(1.1)
where $e$ and $m_e$ are, respectively, the charge and the mass of the electron, while $E_0$ and $\omega_0$ represent the amplitude and the frequency of the electric field.

In order to estimate the relative contributions of the two possible mechanisms leading to ionization, the ponderomotive energy has to be compared to the value of the ionization energy of the atom. To this purpose, the Keldysh coefficient is used:

$$\gamma = \sqrt{\frac{I_p}{2U_p}}. \quad (1.2)$$

The obtained value gives an indication of which mechanism contributes predominantly to the ionization of the atom.

If $\gamma \gg 1$, the promotion of the electron to the continuum is caused by multi-photon absorption: in order to make a transition from the bound state to the continuum, the electron needs to simultaneously absorb $n$ photons, in order to have: $n\hbar\omega_0 > I_p$.

On the other hand, if the laser intensity is larger than $10^{13} W/cm^2$, $\gamma \ll 1$, and the ionization occurs via tunnel effect.

In this case, the ionization rate can be described as [9]:

$$W(E(t)) = \omega_s |C_{n^*l^*}|^2 G_{lm} \left( 4\frac{\omega_s}{\omega_t} \right)^{2n^*+l^*+1} \exp \left( -\frac{4N_s}{3\omega_t} \right) \quad (1.3)$$

where

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

$$\omega_s = \frac{\epsilon_s^0}{\hbar},$$

$$\omega_t = \frac{eE(t)}{\sqrt{2m_eE_s^0}},$$

$$n^* = \sqrt{\frac{\epsilon_t}{\epsilon_s^0}},$$

$$|C_{n^*l^*}|^2 = \frac{2^{2n^*}}{n^*\Gamma(n^* + l^* + 1)\Gamma(n^* - l^*)}.$$
1.1 Three-step model

$\epsilon_s^h$ is the ionization potential of hydrogen, $l$ and $m$ are the azimuthal and magnetic quantum numbers and $E(t)$ is the amplitude of the electric field. The effective quantum number is given by:

$$l^* = \begin{cases} 
0 & \text{for } l \ll n \\
n^* - 1 & \text{otherwise}
\end{cases}$$

The probability of ionization, $P(t)$, during a time interval $t + dt$ is:

$$P(t) = W(E(t))dt$$

where $E(t)$ is the amplitude of the electric field:

$$\vec{E}(t) = E_0 \cos(\omega t) \hat{e}_x + \alpha E_0 \sin(\omega t) \hat{e}_y.$$ (1.5)

This model describes the formation of a sequence of wavepackets, one near each peak of the laser field.

1.1.2 Motion after liberation

The evolution of the electron wavepacket in the continuum under the influence of the electric field of the laser can be described by a purely classical model.

The following calculation will neglect the influence of both the electric field of the parent ion and the magnetic field of the laser radiation.

Defining $t_0$ as the initial instant and assuming that the initial position and velocity of the electron are equal to zero, the motion after the tunneling event is described by the following equations:

$$x = x_0 \left[-\cos(\omega t)\right] + v_{0x} t + x_{0x}, \quad (1.6)$$

$$y = \alpha x_0 \left[-\sin(\omega t)\right] + \alpha v_{0y} t + y_{0y}, \quad (1.7)$$

$$v_x = v_0 \sin(\omega t) + v_{0x}.$$

$$v_y = \alpha v_0 \sin(\omega t) + v_{0y}.$$ (1.8)
\[ v_y = -\alpha v_0 \cos(\omega t) + v_{0y}, \quad (1.9) \]

where \( \alpha = 0 \) if the laser field is linearly polarized while \( \alpha = \pm 1 \) if the laser field is circularly polarized; \( v_0 = qE_0/m_e\omega, \ x_0 = qE_0/m_e\omega^2 \) whereas \( v_{0x}, v_{0y}, x_0, \) and \( y_0 \) are evaluated starting from the above cited initial conditions.

### 1.1.3 Recombination

For circularly polarized light, eq. 1.8 and eq. 1.9 show that the freed electrons will never return to position \( x = 0 \) occupied by the parent ion and, consequently, they will never recombine with it.

For linearly polarized light, eq. 1.3, 1.22 and 1.7 predict that half of the freed electrons return to the parent ion once during the first optical cycle after the ionization event. The other emitted electrons will never return to the vicinity of the ion.

Eq. 1.3 - 1.9 permit to find the probability \( P(\epsilon) \), per unity of energy and per laser period, of finding an electron passing the ion with energy \( \epsilon \). The retrieved probability distribution is shown in fig. 1.2.

![Figure 1.2: Probability distribution of energies owned by electrons at the time of their first encounter with the ion. The parameters used in the calculation are those of helium with light intensity of \( 5 \times 10^{14} \text{W/cm}^2 \) and wavelength 0.8\( \mu \text{m} \). The sharp cutoff in the electron energy occurs at 3.17U_p [8].](image)

As can be seen, the most likely and maximum velocity of an electron passing the nucleus corresponds to an instantaneous kinetic energy equal to...
3.17U_p. In particular, this energy is owned at the recombination instant by electrons emitted via tunnel effect, when \( \omega t \) is equal to 17, 197, etc., i.e. by electrons released at 0.05 optical cycles after the peak of the driving electric field and that recollide with the parent ion nearly three quarters of an optical cycle later.

As a consequence, the maximum energy of the photons emitted during the recombination is \( I_p + 3.17U_p \). This maximum energy corresponds to the maximum frequency in the emission spectrum, the so-called cut-off frequency:

\[
\omega_{\text{cut-off}} = \frac{I_p + 3.17U_p}{\hbar}
\]

By imposing the condition \( x(t) = 0 \), it is possible to retrieve the instants \( t \) at which the electron recombines with the parent ion and the corresponding kinetic energy.

The photon emitted as a consequence of the recombination has an energy \( \hbar \omega = I_p + E_k \). It can be shown that, for a fixed photon energy, there are different solutions to equation \( x(t) = 0 \). They are characterized by different return times \( \tau = t - t' \) spent by the electron in the continuum. These solutions describe two possible classical trajectories followed by electrons during their motion before recombination. While the shortest trajectory (short trajectory) is characterized by a return time \( \tau \) shorter than half of the optical cycle of the driving radiation, the time spent by an electron following a long trajectory is nearly a whole optical cycle.

### 1.1.4 XUV spectrum

Since the above described process is repeated every half optical cycle of the laser field, the emission of XUV pulses is periodic.

It is possible to describe the interaction between an ion and a field composed by \( N \) optical cycles, neglecting the depletion of the fundamental state [10]. If \( a_i(t) \) is the electric dipole moment associated with the \( i \)-th recollision event, all the contributes \( a_i \) are identical, but delayed in time and taken with opposite sign in order to account for the inversion of simmetry.
Thus, the total electric dipole moment becomes:

$$a(t) = \sum_{k=-N/2}^{N/2} \left\{ a_1(t - kT) - a_1 \left[ t - \left(2k - 1\right)\frac{T}{2}\right] \right\}, \quad (1.11)$$

where $T = 2\pi/\omega_0$ is the period of the driving laser field.

In order to calculate the emission spectrum, it is necessary to calculate the Fourier transform of the second time derivative of the total electric dipole moment:

$$\tilde{a}(\omega) = \int_{-\infty}^{+\infty} \ddot{a}(t)e^{i\omega t}dt =$$

$$= \omega^2 \tilde{a}_1(\omega) \sum_{k=-N/2}^{N/2} \left\{ e^{ik\omega T} - e^{i(2k-1)\omega T/2} \right\} =$$

$$= \omega^2 \tilde{a}_1(\omega) \left[ 1 - e^{-i\omega T/2} \right] \sum_{k=-N/2}^{N/2} e^{ik\omega T} \quad (1.12)$$

For $N \to \infty$, we find that:

$$\sum_{k=-N/2}^{N/2} e^{ik\omega T} \to \sum_{n=-\infty}^{+\infty} \delta(\omega - n\omega_0)$$

and thus the term $(1 - e^{-i\omega T/2})$ cancels the even harmonics from the emitted spectrum. The structure of an emitted spectrum is displayed in fig. 1.3 (a).

![Figure 1.3: XUV pulse trains in the frequency (a) and in the time (b) domain.](image)

The conversion efficiency does not decrease with the process order, but remains approximately constant over a large spectral range, called plateau,
before falling abruptly in the cutoff region. The discrete structure of the spectrum corresponds, in the time domain, to a train of sub-femtosecond XUV pulses spaced by half period $T_0/2$ of the driving field (fig. 1.3 (b)). The time duration of each pulse is inversely proportional to the spectral width.

## 1.2 Lewenstein model

Although the semiclassical model gives a good description of the HHG process, it neglects some important phenomena like the quantum diffusion of the wave packets, the elastic scattering from the parent ion and the quantum interference between wave packets generated in different temporal instants.

For this reason a quantum mechanical description has been provided by Lewenstein. Lewenstein theory is based on the single active electron approximation. The laser-atom interaction can be described by the following Schrödinger equation, in which atomic units ($m_e = e = \hbar = 1$) are used and energies are expressed in terms of the photon energy:

$$i \frac{\partial}{\partial t} |\Psi(x,t)\rangle = \left[ -\frac{1}{2} \nabla^2 + V(x) - E\cos(t)x \right] |\Psi(x,t)\rangle,$$

(1.13)

where $|\Psi(x,t)\rangle$ is the wave function describing the electron wave packet, $V(x)$ is the Coulomb potential and $\vec{E}(t) = E\cos(t)$ is an electric field linearly polarized along the x-direction.

The x-component of the time-dependent dipole moment is:

$$x(t) = \langle \Psi(t) | x | \Psi(t) \rangle.$$  

(1.14)

If the electronic wave packet is expressed as a superposition of the bound and continuum wave functions:

$$|\Psi\rangle = |\Psi_{bound}\rangle + |\Psi_{cont}\rangle,$$

(1.15)
a four-term expression for the dipole moment can be obtained:

$$x(t) = \langle \Psi_{\text{bound}} | x | \Psi_{\text{bound}} \rangle + \langle \Psi_{\text{cont}} | x | \Psi_{\text{cont}} \rangle +$$

$$+ \langle \Psi_{\text{cont}} | x | \Psi_{\text{bound}} \rangle + \langle \Psi_{\text{bound}} | x | \Psi_{\text{cont}} \rangle$$

(1.16)

The first term represents the static dipole moment of the atom, while the second term describes the emission of Bremsstrahlung radiation, due to the acceleration of the electrons. The third term takes into account the emission of an electron from the atom, while the last one expresses the recombination of the electron with the parent ion. As also seen previously, the HHG process is due to this last term.

In order to find a solution of eq. 1.13, it is necessary to make some assumptions and approximations:

1. initially the system is in its ground state $|0\rangle$, which is characterized by a spherical symmetry;

2. the contribution of all the other bound states can be neglected: only the ground state $|0\rangle$ and the continuum are relevant for the evolution of the system;

3. the intensity of the laser field is below the saturation intensity, therefore the depletion of the ground state is negligible;

4. in the continuum, the electron can be treated as a free particle moving in an electric field (i.e. the atomic potential $V(x)$ has no influence on the electron).

These assumptions hold when there are no intermediate resonances and when the Keldysh parameter $\gamma$ is smaller than one, which means that the ionization of the atom is caused by tunneling of the electron through the potential barrier.

Under these approximations, the bound and the continuum waveforms can be expressed as:

$$\Psi_{\text{bound}}(t) = e^{iH_0 t} a(t) |0\rangle,$$

(1.17)
where $|\vec{v}\rangle$ is a state describing an electron moving in the continuum with a kinetic momentum $\vec{v}$, $a(t) \simeq 1$ is the ground state amplitude and $b(\vec{v}, t)$ are the amplitudes of the continuum states. The overall wave function is:

$$
\Psi(t) = e^{iI_p t} \left( a(t) |0\rangle + \int d^3v \ b(\vec{v}, t) |\vec{v}\rangle \right)
$$

(1.19)

By using eq. 1.19 in the Schrödinger equation (eq. schroedinger) and setting $a(t) = 1$ a solution can be obtained:

$$
b(\vec{v}, t) = i \int_0^t dt' E \cos(t') \int d^3x \ (\vec{v} + \vec{A}(t) - \vec{A}(t')) \\
\times \exp \left\{ -i \int_{t'}^t dt'' \left[ \frac{(\vec{v} + \vec{A}(t) - \vec{A}(t''))^2}{2} + I_p \right] \right\}
$$

(1.20)

where $\vec{A}(t) = (-E \sin(t), 0, 0)$ is the vector potential of the laser field.

Using eq.1.19 and eq. 1.20 and considering only the transitions from the continuum back to the ground state, the x-component of the time-dependent dipole moment becomes:

$$
x(t) = \int d^3\vec{v} \ d^3x(\vec{v}) b(\vec{v}, t) + c.c.
$$

(1.21)

Using eq. 1.19 and eq. 1.20:

$$
x(t) = i \int_0^t dt' \int d^3p \ E \cos(t') \int d^3x (\vec{p} - \vec{A}(t')) \\
\times \ d^3x (\vec{p} - \vec{A}(t')) \exp [-iS(\vec{p}, t, t')] + c.c.,
$$

(1.22)

where $\vec{p} = \vec{v} + \vec{A}(t)$ is the canonic momentum and

$$
S(\vec{p}, t, t') = \int_{t'}^t dt'' \left( \frac{|\vec{p} - \vec{A}(t'')|^2}{2} + I_p \right)
$$

(1.23)

is the quasi-classical action.

The first term $E \cos(t') d_x(\vec{p} - \vec{A}(t'))$ represents the probability amplitude.
for an electron to make the transition to the continuum at time $t'$ with a canonical momentum $p$.

After ionization, the electron continues to propagate until the time $t$ of recombination with the parent ion. During its motion in the continuum, the electron acquires a phase factor expressed by the term $\exp[-iS(p, t, t')]$.

It is possible to show that, for $t - t'$ of the order of one period of the laser field, the quasi-classical action varies much faster than the other terms contained in Eq. 1.22. Thus, the major contribution to the integral over $p$ comes from the stationary points $(p_{st}, t, t')$ of the quasi-classical action, calculated by solving the following equation:

$$\nabla_p S(p, t, t') = 0. \quad (1.24)$$

$\nabla_p S(p, t, t')$ can be expressed as the difference between the positions of the free electron evaluated at the instants $t$ and $t'$:

$$\nabla_p S(p, t, t') = x(t) - x(t'), \quad (1.25)$$

This means that the dominant contribution to the harmonic emission comes from those electrons that, after their motion in the continuum, are able to recollide with the parent ion.

The integral of eq. 1.22 can be calculated using the saddle-point method, retrieving the following expression:

$$x(t) = i \int_0^{+\infty} d\tau \left( \frac{\pi}{\epsilon + i\tau/2} \right)^{3/2} \left[ d_x^r(p_{st}(t, \tau) - A_x(t)) \times d_x(p_{st}(t, \tau) - A_x(t - \tau)) \times E\cos(t - \tau) \times \exp[-iS_{st}(t, \tau)] + c.c. \right], \quad (1.26)$$

where the integration is performed on the so-called return time $\tau = t - t'$.

The term $\frac{\pi}{\epsilon + i\tau/2}^{3/2}$ (where $\epsilon \to 0$ is a positive constant introduced in order to eliminate the singularity for $\tau = 0$) takes into account the effects of the quantum diffusion and reduces the contribution of the trajectories characterized by a long return time. Indeed, the cross section of recombination
is reduced as the value of return time reaches higher values.

Using eq. 1.26, the harmonic emission rate can be retrieved from the square module of the Fourier transform of the dipole moment:

\[ W(\omega) \propto \omega^3 |x(\omega)|^2, \] (1.27)

with

\[ x(\omega) = \int_{-\infty}^{+\infty} dt x(t)e^{i\omega t}. \] (1.28)

Eq. 1.28 consists of a double integration performed over \( t \) and \( \tau \). Substituting eq. 1.22 into eq. 1.28, we obtain a three-dimensional integral, that can be solved by further applying the saddle-point approximation. The new saddle-point equations are:

\[
\left. \frac{\partial \Theta}{\partial t} \right|_{t_{st}} = \omega - \frac{[p_{st} - A(t_{st})]^2}{2} - I_p = 0 \] (1.29)

\[
\left. \frac{\partial \Theta}{\partial t'} \right|_{t'_{st}} = \frac{[p_{st} - A(t_{st})]^2}{2} + I_p = 0 \] (1.30)

where \( \Theta(p_{st}, t, \tau) = \omega t - S(p_{st}, t, \tau) \) is the Legendre transform of the semi-classical action. Eq. 1.29 and 1.30 express the energy conservation at the ionization and recombination times.

Due to the fact that \( I_p \neq 0 \), the saddle point solutions \((p_{st}, t_{st}, \tau_{st})\) are complex and for this reason also the trajectories associated with them are complex.

It is possible to further approximate the Fourier transform of the dipole moment \( x(\omega) \) with the coherent superposition of these quantum paths:

\[
x(\omega) = \sum_{st} |x_{st}(\omega)| e^{i\Phi_{st}(\omega)} = \sum_{st} \frac{i2\pi}{\sqrt{det(S''')} \left[ \frac{\pi}{\epsilon + i\tau_{st}/2} \right]^{3/2}} d_x [p_{st} - A(t_{st})] \times E(t_{st} - \tau_{st}) \cdot d_x [p_{st} - A(t_{st} - \tau_{st})] \exp \left[ -iS(p_{st}, t_{st} + 1\omega t_{st}) + i\omega t_{st} \right] \] (1.31)

where \( \Phi_{st}(\omega) \) is the phase of the complex function \( x_{st}(\omega) \) and \( det(S'') \) is the
High harmonic generation
determinant of the $2 \times 2$ matrix, containing the second derivatives of $\Theta$ with
respect to $t$ and $t'$ evaluated in correspondence of the saddle-point solutions.

A series of saddle-point solutions $(p_{st}, t_{st}, t'_{st})$ that differ by the time spent by the electron in the continuum is derived considering each photon energy. In particular, if considering only those trajectories characterized by $Re(\tau) < T_0$, with $T_0$ the period of the laser field, it is possible to divide them into two main categories: long and short trajectories. While short trajectories are characterized by a return time shorter than half of the optical cycle of the electric field, long trajectories are characterized by a return time around one optical cycle.

Eq. 1.31 can be approximated as the coherent superposition of short and long quantum paths:

$$x(\omega) \approx \sum_{\text{short}} |x_s(\omega)|e^{i\Phi_s(\omega)} + \sum_{\text{long}} |x_s(\omega)|e^{i\Phi_s(\omega)}$$

(1.32)

It is worth noting that the phase of dipole moment induced on an atom by a driving laser depends on the laser intensity and that the harmonic phase follows this intrinsic atomic phase ([12], [14]).

Since long and short trajectories have different ionizing and returning times, they are subjected to different electric fields and their harmonic phases behave differently. If the contribution of the two quantum paths were added together to generate high order emission, different harmonics would have randomly distributed harmonic phase values. Consequently, the selection of harmonics emitted from a single trajectory is required to obtain isolated attosecond pulses.

1.2.1 Phase matching

Harmonic generation is optimized when phase matching is achieved [15]. Let’s consider the $q$th-order harmonic and its wave vector $k_q$. Optimal phase matching will be obtained in direction $k_q$ in a region of space if the harmonic
fields generated at any points $r_1$ and $r_2$ interfere constructively:

$$\arg [P_q(r_1) \exp (ik_q \cdot (r_1 - r_2))] = \arg [P_g(r_2)], \quad (1.33)$$

where $P_q$ is the $q$th Fourier component of the atomic polarization in the medium. For $r_1$ and $r_2$ close enough, this results in:

$$k_q = \nabla \arg (P_g). \quad (1.34)$$

In a perturbative regime, the wave vector of the polarization for the $q$th harmonic is just $q$ times that of the incident plane wave: $k_q = qk_0^1$, where $k_0^1 = \omega/c$. Actually, two other phase factors are involved:

- an intrinsic phase term, which depends on the intensity of the driving field:

$$\Phi_{at}(r, z) = q\omega t_{st} - S(p_{st}, t_{st}, t'_{st}), \quad (1.35)$$

where, for each quantum path characterized by a return time $\tau_{st}$, the semi-classical action can be roughly approximated by $S \simeq -\tau_{s}U_p$.

- the phase induced by focusing of the fundamental beam (Gouy phase), which for a Gaussian beam can be expressed as:

$$\Phi_{foc}(r, z) = \arg \left[ \frac{1}{b + 2iz} \exp \left( -\frac{k_0^1 r^2}{b + 2iz} \right) \right], \quad (1.36)$$

where $b$ is the confocal parameter.

The total wave vector $k_1$ for the fundamental Gaussian beam is therefore space dependent and reads:

$$k_1(r, z) = k_0^1 e_z + \nabla \Phi_{foc}(r, z). \quad (1.37)$$

The effective wave vector $K$ related to the atomic phase is:

$$K(r, z) = \nabla \Phi_{at}(r, z). \quad (1.38)$$
Therefore, the condition for optimum phase matching becomes:

\[ k_q = qk_1 + K. \]  (1.39)

Maps of the Gaussian beam wave vector \( k_1(r, z) \) and of the effective atomic wave vector \( K(r, z) \) in the focal region show that the phase matching condition 1.39 is satisfied in two different cases:

- for points located on axis \( (r = 0) \) and after the focus \( (z > 0) \), where a collinear phase matching is achieved: harmonics are efficiently generated along the propagation direction of the laser, yielding a Gaussian structure of the emitted harmonic field;

- for points located off axis \( (r > 0) \) and before the focus \( (z < 0) \), where a non-collinear phase matching is achieved: harmonics are not generated along the polarization direction, yielding an anular structure to the emitted harmonic field.

These considerations highlight the strong influence of propagation effects on the features of the emitted harmonic field. Since the dipole phase term depends on the quantum path, the phase matching condition can favor or cancel the contribution of short or long quantum trajectories. In other words, for an appropriately chosen focusing geometry, the macroscopic harmonic signal contains only the contribution of a selected trajectory. For a Gaussian fundamental beam and for an atomic medium placed after the focus, the contribution of long quantum trajectories is eliminated.

![Figure 1.4: Selection of short trajectories](image)
Resulting pulses are characterized by an intrinsic chirp [16]: in the case of short trajectories, the chirp is positive because low energy photons are emitted before those owning a high energy.
2.1 Generation of isolated attosecond pulses

As stated in the previous chapter, during the HHG process, XUV radiation is periodically generated near the peaks of the IR driving field. For 800 nm laser radiation, electrons are emitted during a time window of about 300 as centered around each peak of the electric field. As a result, XUV bursts are produced every half optical cycle of the IR driving field, leading to the generation of attosecond pulse trains (APTs).

Even though attosecond pulse trains have been already exploited in the investigation of fast molecular dynamics, isolated attosecond pulses (IAPs) are more attractive as they allow the achievement of a better temporal resolution.

In order to reliably produce isolated attosecond pulses, the electric field waveform of the laser has to be reproducible from pulse to pulse. Therefore, it is of great importance to stabilize the so-called CarrierEnvelopePhase (CEP) $\varphi$, defined as the offset between the maximum of the electric field of the laser and the maximum of the laser pulse. The electric field of a laser pulse can be written as:

$$E_L(t) = E_0(t)\cos(\omega_L t + \Phi),$$

(2.1)
where \( E_0(t) \) is a slowly varying amplitude function representing the pulse envelope and \( \omega_L \) is the laser carrier frequency (see fig. 2.1).

![Figure 2.1: Representation of the electric field and of the envelope of a few-cycle pulse in the case of \( \Phi = -90^\circ \).](image)

In the case of few-cycle pulses, the temporal variation of the electric field strongly depends on the value of the CEP. Due to the fact that high harmonics generation process is very sensitive to the shape of the driving field, it is important to control precisely the evolution of the electric field underneath the pulse envelope. Presently, many well-developed methods based on both active or passive CEP stabilization exist, allowing a good control of nonlinear responses of matter to laser fields.

As mentioned before, the harmonic spectrum corresponds to a train of attosecond pulses in the temporal domain. In order to isolate a single attosecond pulse a gating technique on the HHG process must be applied. These techniques rely on two different methods:

- **spectral filtering**;
- **temporal gating**.

*Spectral filtering* is based on the bandpass filtering of the highest energy region of the XUV emission obtained by HHG in gases. Indeed, the analysis of the classical trajectories of the freed electrons shows that only those electrons
emitted during a short time interval near the peak of the electric field own the maximum instantaneous kinetic energy at the recollision instant. Thus, the emission of the highest energies happens only during a short time interval. As a consequence, if a bandpass filtering of the cutoff region is performed, the observed radiation is ascribable to the emission produced in a few hundreds of attoseconds. However, this method suffers from two serious disadvantages, that severely limit the process efficiency: it requires few-cycle driving laser pulses and selects only the cutoff region of the emitted spectrum.

Temporal gating exploits the strong dependence of high-order harmonics emission on the features of the driving IR radiation. Indeed, high-order harmonic generation is strongly affected by the ellipticity of the pump light and decreases rapidly as soon as the polarization departs from linear. A circular polarization displaces the emitted electrons and prevents them to recombine with their parent ion. Shaping the incident pulse in a way that only half cycle of the driving radiation is linearly polarized is a way to isolate only one attosecond pulse from the whole train. This means that the whole XUV spectrum can be used to generate isolated pulses.

In the following section three different methods, based on the temporal gating approach, will be described: the Polarization Gating (PG), the Double Optical Gating (DOG) and the Generalized Double Optical Gating (GDOG). Besides the theoretical description, also simulation results will be presented.

2.1.1 Polarization Gating

PG was first proposed by Corkum in 1994 [19] and demonstrated experimentally by Sola et al. in 2006 [20].

As already pointed out, the three-step model shows that XUV radiation is emitted only if the laser polarization is sufficiently linear. Electrons emitted via tunnel effect are at first separated from their parent ion and subsequently swept back to the $x = 0$ position, following an almost linear trajectory. On the other hand, a circularly polarized driving field would, in addition, displace the electrons so that, if the displacement is too large, they never reencounter
the ion and the XUV emission is prevented.

As a consequence, a suitable modulation of the driving laser ellipticity can confine the XUV emission to a temporal window where the polarization is very close to linear. If the gate of linear polarization is short enough, an isolated attosecond pulse is emitted.

The experimental setup, depicted in fig. 2.2, is a collinear configuration consisting of two quartz wave plates, conveniently selected in order to obtain a pulse with a suitable time-varying ellipticity.

Figure 2.2: Scheme of collinear polarization gating.

The first element is a birefringent delay plate that splits the incident IR field in two orthogonally polarized pulses propagating along the ordinary and the extraordinary axes of the crystal. The delay $\delta$ between the two components is proportional to the thickness of the plate and depends on the difference between the ordinary and extraordinary refraction indexes. The optical axis of the wave plate forms an angle $\alpha = 45^\circ$ with the polarization direction of the incident IR field. Due to the superposition of the two orthogonal components, the output pulse is characterized by linearly polarized leading and trailing edges and by a circularly-polarized central part. This pulse is subsequently sent through a zero-order $\lambda/4$ wave plate, placed at a variable angle $\beta$ with respect to the initial polarization direction of the incident laser pulse. This last wave plate changes the polarization of the incoming pulse from circular to linear and vice versa. Thus, the final pulse after the propagation through this collinear configuration exhibits a circular polarization (high ellipticity) in the leading and trailing edges and linear polarization (low ellipticity) in the central part.
2.1 Generation of isolated attosecond pulses

It is possible to control the width of the temporal gate of linear polarization by changing the thickness of the first wave plate and by varying the angle $\beta$ of the second plate.

Strelkov et al. [21] demonstrated that the width $\Delta$ of the gate can be calculated as:

$$\Delta = \frac{\xi_{tr} \tau^2}{\delta |\cos 2\beta| \ln 2},$$  \hspace{1cm} (2.2)

where $\xi_{tr}$ is the value of driving laser ellipticity for which XUV generation efficiency is decreased by half and $\tau$ is the IR pulse duration. Setting $\beta = 0^\circ$, the narrowest gate can be obtained by reducing the IR pulse duration or by increasing the delay $\delta$. However, for large delays, the efficiency is decreased because a dip in the temporal intensity profile appears.

**Numerical results**

In order to optimize the experimental setup, some simulations on the PG technique were carried out.

Calculations were performed taking into account an infrared pulse, linearly polarized along the y-axis, with a time duration equal to 6 $fs$ and central wavelength $\lambda = 790$ nm.

Simulations show that a suitable thickness for the first wave plate is $d_1 = 173$ $\mu m$. As can be seen from fig. 2.3, the output pulse is characterized by circularly polarized leading and trailing edges and by a central part linearly polarized along the same direction as the input IR pulse.

The gate of linear polarization has a width of about 1 $fs$ (see fig. 2.4).
Figure 2.3: 3D shape of the output pulse.

Figure 2.4: Ellipticity of the output pulse.
2.1.2 Double Optical Gating

The main limitation affecting PG technique is the depletion of the ground state of the atom caused by the leading edge of the laser pulse. This issue sets an upper limit on the duration of the driving IR pulses, which has to be less than 7 fs. Indeed, since the gate of linear polarization is located in the central part of the driving field, if the atoms of the medium are strongly depleted by the leading edge, no high harmonic generation can occur.

In order to overcome this issue, Chang [22] proposed and demonstrated a two-color technique, known as double optical gating (DOG), in which a weak second harmonic field is added to the polarization gating field [23]. Indeed, second harmonic can break the symmetry of the driving field, thus increasing the spacing between consecutive attosecond pulses. Consequently, the width of the polarization gate can be close to one optical cycle of the IR radiation (the double of the gate width required by the polarization gating) and the driving pulses can be two times longer than those used in polarization gating.

Double optical gating can be implemented using a collinear configuration, consisting of two quartz wave plates followed by a β-barium borate (BBO) crystal, which creates the second harmonic field.

![Diagram of collinear double optical gating](image)

**Figure 2.5:** Scheme of collinear double optical gating.

As in polarization gating technique, the first plate creates two delayed, orthogonally-polarized components. The second quartz plate is used in combination with a BBO crystal in order to form a quarter wave plate, thus changing the polarization of the pulse from circular to linear and vice versa, and to generate the second harmonic field. The BBO crystal is cut for a
type-I phase matching with an angle $\theta = 30^\circ$.

Since the XUV emission has a periodicity of one full optical cycle, the condition on the gate width can be relaxed and the temporal gate can be set close to one optical cycle.

**Numerical results**

In order to develop a double optical gating configuration, the following simulation was performed. The IR pulse, linearly polarized along the $y$-axis, is characterized by a duration of $8 \text{ fs}$ and a central wavelength of $790 \text{ nm}$. Even though DOG configuration would permit longer laser pulse durations, the choice of a temporal length equal to $8\text{ fs}$ was dictated by the requirement of short probe pulses for future pump-probe measurements. The first quartz plate, of thickness equal to $88 \mu m$, transforms the incident field into a pulse linearly polarized in the leading and trailing edges and circularly polarized in the central part. The second quartz wave plate and the BBO crystal have thicknesses equal to $366 \mu m$ and $100 \mu m$ respectively. These values have been selected because their combined action is the same as a quarter wave plate.

The simulated electric field amplitude is shown in figure 2.6. Fig. 2.7 shows the ellipticity of the output pulse as a function of the time. As can be seen from this figure, the width of the gate is equal to $2.4 \text{ fs}$. 
Figure 2.6: 3D shape of the output pulse.

Figure 2.7: Output pulse ellipticity.
2.1.3 Generalized Double Optical Gating

DOG was developed in order to loosen the requirement for the laser pulse duration by reducing the depletion caused by the leading edge of the pulse. In order to further increase the pulse duration technique called Generalized Double Optical Gating (GDOG) [25] must be implemented. Applying this technique, it is possible to generate driving pulses having a polarization which varies from elliptical to linear and then back to elliptical, with a chosen ellipticity $\epsilon$.

The setup is the same that for the DOG, with the addition of a Brewster window after the first wave plate, in order to reject part of the driving field (see fig. 2.8).

![Figure 2.8: Scheme of collinear generalized double optical gating.](image)

It can be shown that, in these conditions, the width of the polarization gate becomes:

$$\Delta \approx \epsilon \frac{\xi_{th}}{ln2} \frac{\tau^2}{\delta},$$  \hspace{1cm} (2.3)

where $\xi_{th}$ is the threshold ellipticity, $\tau$ the laser pulse duration and $\delta$ the delay introduced by the first wave plate.

Comparing eq. 2.3 with eq. 2.2 and applying the GDOG to a 20 $fs$ input pulse, it becomes evident that DOG requires a delay $\delta$ that is almost twice the one needed if GDOG was used and $\epsilon$ was set equal to 0.5. Consequently, because the field strength before the gate is lower for GDOG than for DOG, longer laser pulse durations can be used. In general, longer pulses can be used
for smaller $\epsilon$. However, if $\epsilon$ is too low, attosecond pulses can be generated outside the gate.

Fig. 2.9 shows a calculation performed applying the Ammosov, Delone, and Krainov (ADK) theory for the ionization of argon atoms from an oscillating laser field. As can be seen, if GDOG technique is applied, the depletion of the medium is strongly reduced even for a pulse duration of 25 fs.

![Figure 2.9: Ionization probability as a function of input laser pulse duration for polarization gating (PG, solid line), double optical gating (DOG, dashed line), and generalized double optical gating (GDOG, dot-dashed line). The peak intensity at the center of the gate was held constant at $1.9 \times 10^{14} \text{W/cm}^2$ for all cases. (Figure taken from [24]).](image)

Feng et al. [25] demonstrated the possibility to generate isolated attosecond pulses having a temporal duration equal to 148 as by driving the process with 28 fs laser pulses coming directly from the CPA system.

**Numerical results**

The following simulations consider a linearly polarized IR pulse of duration equal to 20 fs and a central frequency equal to $\lambda_c = 790 \text{nm}$. The laser field passes through a first quartz plate of thickness $d_1 = 796 \mu\text{m}$, whose optical axis forms an angle of 45° with the polarization direction of the incident field. The output pulse passes through a Brewster window placed at an angle of $\sim 50^\circ$ with respect to the plane normal to the pulse propagation.
direction. After the window, a second wave plate and a BBO are placed. Their thicknesses are $d_2 = 410 \, \mu m$ and $d_3 = 100 \, \mu m$, respectively. Also in this case, they create together a quarter wave plate. Fig. 2.10 illustrates the final shape of the output pulse.

![3D shape of the output pulse.](image1)

**Figure 2.10:** 3D shape of the output pulse.

![Output pulse ellipticity.](image2)

**Figure 2.11:** Output pulse ellipticity.
2.2 Characterization of attosecond pulses

Femtosecond metrology allows a complete characterization of ultrashort pulses in the visible and near-visible range and it is the basis from which attosecond metrology was developed. Due to the fact that the responses of the detectors are much slower than the timescales of interest, it is necessary to use a time-nonstationary filter with a bandwidth which is a fraction of that of the field to be characterized. Due to the large bandwidth required, the time-nonstationary filter is, typically, the unknown pulse itself. This is accomplished by exploiting non-linear effects. This implementation is suitable for the characterization of femtosecond pulses, but not for attosecond pulses, because of their low intensity and their spectral range. Therefore, attosecond metrology relies on a different approach.

An XUV pulse can efficiently ionize a gas by single photon absorption. The result is an attosecond electron wavepacket that, far from any resonance, is a perfect replica of the XUV pulse, i.e. has the same phase and amplitude of the XUV field. The trajectories of the ejected electrons, launched at different moments of time over the duration of the attosecond pulse, have a probability related to the envelope of the attosecond pulse and initial momenta depending on the chirp of the XUV pulse. Thus, the full characterization of the electron wavepacket provides all the information on the attosecond pulse. The photoionization occurs in the presence of an intense femtosecond IR pulse, which acts as an ultrafast phase modulator of the electron wavepacket. In this way, a time-nonstationary filter is realized. This phenomenon is usually known as streaking.

The evolution of the photoionization spectra as a function of the delay $\tau$ between the XUV pulse and the IR pulse allows a complete reconstruction, both in amplitude and in phase, of the attosecond pulse. This technique is known as Frequency-Resolved Optical Gating for Complete Reconstruction of Attosecond Bursts (FROG-CRAB).
2.2.1 Theory of atomic XUV photoionization in a laser field

Semiclassical model

The streaking process can be divided into two separate steps: the photoionization of the atom by the XUV pulse and the subsequent acceleration of the emitted electrons by the IR field (fig. 2.12). The latter can be described classically.

Figure 2.12: An XUV pulse (blue line) and an IR field (red line) are focalized on a gas jet. The XUV pulse ionizes the atoms (yellow spheres) and emitted electrons (violet spheres) are accelerated by the IR streaking field. A detector acquires the energy spectra of the electrons emitted for different values of the delay between the XUV and the IR pulse.

Let’s consider an electron promoted to the continuum with an initial kinetic energy equal to $W_0 = v_0^2/2 = \Omega_X - I_p$, where $v_0$ is the initial velocity. Assuming $\Omega_X \gg I_p$ and using the strong field approximation, the motion of the electron under the action of the IR field can be described by:

$$\mathbf{v}(t) = -\mathbf{A}(t) + [\mathbf{v}_0 + \mathbf{A}(t_i)].$$  \hspace{1cm} (2.4)

The first term in eq. 2.4 represents the quiver motion of the electron in the laser field and goes to zero as the IR pulse ends, while the constant term in square brackets is the final drift velocity $\mathbf{v} = \mathbf{v}_0 + \mathbf{A}(t_i)$ measured after the
2.2 Characterization of attosecond pulses

laser pulse. This means that the effect of the streaking field is a variation of the final electron velocity, which depends on the value of the vector potential at the time $t_i$ of ionization. In the absence of the streaking field, the distribution of the electron final velocities is independent of $\theta$ and is a circle of radius $|v_0|$ centered on $|v| = 0$. Otherwise, if the IR field is present, the distribution of the final velocities is still a circle of radius $|v_0|$, but shifted by $A(t_i)$. If the streaking field is linearly polarized, the displacement is parallel to the electric field (fig. 2.13). The circle thus oscillates back and forth along the polarization direction as the time of ionization $t_i$ varies.

![Figure 2.13: Semiclassical description of the streaking concept. Figure taken from [26]](image)

The drift kinetic energy $W = v^2/2$ can be calculated as follows:

$$W = W_0 + 2U_p \cos 2\theta \sin^2 \phi_i \pm \alpha (8W_0 U_p)^{1/2} \cos \theta \sin \phi_i,$$

(2.5)

where:

$$\alpha = \left\{1 - \frac{2u_p}{W_0} \sin^2 \theta \sin^2 \phi_i\right\}^{1/2}.$$  

(2.6)

For $U_p < W/2$, only the positive sign in eq. 2.5 has a physical meaning. Eq. 2.5 shows that the energy change $\delta W = W - W_0$ varies with the observation angle $\theta$ and the ionization time $t_i$. Therefore, the streaking field induces a modulation of the drift kinetic energy of the emitted electrons, in close correspondence with the streak-camera technique.

Since the attosecond electron wavepacket is a perfect replica of the XUV photon burst, the time duration of the XUV pulse can be evaluated by analyzing the evolution in time of the electron energy spectra. This method
is valid also in the case of chirped XUV pulses. Let us consider the case of positive chirp and analyze the energy spectrum for four delays between the electron pulse and the laser field (fig. 2.14):

- Delay $\tau_1$. Low and high frequencies of the chirped pulse interact with a positive value of $eA(t)$: the whole electron energy spectrum (blue) is shifted to higher frequency values with respect to the unshifted spectrum (green).

- Delay $\tau_2$. Low and high frequencies of the chirped pulse interact with a positive and a negative value of $eA(t)$ respectively; the high energy part of the spectrum is shifted to low energy values and the low energy part of the electron spectrum is shifted to high energy. Hence, the streaked spectrum (blue) is narrower and higher than the unstreaked electron spectrum.

- Delay $\tau_3$. Low and high frequencies of the chirped pulse interact with a negative value of $eA(t)$: the whole unstreaked electron energy spectrum (green) is shifted to low energy (blue).

- Delay $\tau_4$. Low and high frequencies of the chirped pulse interact with a negative and a positive value of $eA(t)$ respectively; the high energy part of the electron spectrum is shifted to high energy and the low energy part of the electron spectrum is shifted to low energy. Hence, the streaked spectrum (blue) is wider and lower than the unstreaked electron spectrum.

A FROG-CRAB trace clearly shows the presence of a chirp in the electron pulse. Indeed, a positive chirp leads to a decrement of the width of the electron spectrum and an increment of the intensity of the spectrum in the temporal regions characterized by a negative slope of the vector potential. If the electron pulse is unchirped, the trace merely follows the vector potential.
2.2 Characterization of attosecond pulses

Figure 2.14: Electron streak records for four delays. We consider the interaction between a positively chirped pulse of electrons (colored pulse) and the infrared laser field (the red line is the product between the electron charge and the vector potential of the laser field). For every delay, on the right part of the picture, are shown the electron energy spectra of the pulse without streaking (green) and the electron energy spectra produced by laser field streaking (blue). Figure taken from [27].
Quantum theory

Let us consider the ionization of an atom by an attosecond XUV pulse alone, using the single active electron approximation. In the framework of the first-order perturbation theory, the transition amplitude $a_{\mathbf{v}}$ of the electron from the ground state to the final continuum state $|\mathbf{v}\rangle$ can be expressed as:

$$a_{\mathbf{v}} = -i \int_{-\infty}^{+\infty} dt d\mathbf{v} E_{\text{XUV}}(t) e^{i(W+I_p)t}, \quad (2.7)$$

where $\mathbf{v}$ is the momentum of the freed electron, $E_{\text{XUV}}$ is the XUV electric field, $d\mathbf{v}$ is the dipole transition matrix element from the ground state to the continuum state $|\mathbf{v}\rangle$, $W = v^2/2$ is the kinetic energy of the electron after the transition and $I_p$ is the ionization potential of the atom. In this calculation, atomic units are used.

In the following description, strong field approximation (SFA) is applied: this means that the IR streaking field is strong enough to dominate the ionic potential. Defining $\tau$ the delay between the XUV and the IR pulses, the transition amplitude becomes:

$$a_{\mathbf{v}} = -i \int_{-\infty}^{+\infty} dt e^{i\phi(t)} d\mathbf{p}(t) E_{\text{XUV}}(t - \tau) e^{i(W+I_p)t}, \quad (2.8)$$

where $\mathbf{p}(t) = \mathbf{v} + \mathbf{A}(t)$ is the instantaneous momentum of the electron in the laser field, $\phi(t)$ is the temporal phase modulation induced by the IR field to the electron wavepacket and $\mathbf{A}(t)$ is the vector potential of the IR radiation in the Coulomb gauge, such that $E_L = -\partial \mathbf{A}/\partial t$.

The phase modulation $\phi(t)$ is given by:

$$\phi(t) = - \int_t^{+\infty} dt' \left[ \mathbf{v} \cdot \mathbf{A}(t') + \frac{\mathbf{A}^2(t')}{2} \right]. \quad (2.9)$$

Comparing eq. 2.7 and eq. 2.8 shows that the main effect of the IR field is a phase modulation on the electron wavepacket; therefore, the femtosecond pulse can be considered as an ultrafast electron phase modulator.

Assuming a linearly polarized IR field $E_L(t) = E_0(t) \cos(\omega_L t)$ and inte-
2.2 Characterization of attosecond pulses

grating the relation \( E_L(t) = -\partial A(t)/\partial t \), the vector potential is given by:

\[
A(t) = -\frac{E_0(t)}{\omega_L} \sin(\omega_L t).
\] (2.10)

Substituting eq. 2.10 into eq. 2.9 and applying the Slowly Varying Envelope Approximation (SVEA), \( \phi(t) \) can be expressed as the sum of three phase terms:

\[
\phi(t) = \phi_1(t) + \phi_2(t) + \phi_3(t),
\] (2.11)

where:

\[
\phi_1(t) = -\int_{t}^{+\infty} dt' U_p(t'),
\] (2.12)

\[
\phi_2(t) = \sqrt{\frac{8W}{\omega_0}} \cos\theta \cos(\omega_0 t),
\] (2.13)

\[
\phi_3(t) = \frac{U_p}{2\omega_0} \sin(2\omega_0 t).
\] (2.14)

In the previous equations, \( U_p \) represents the ponderomotive energy and \( \phi \) is the angle between \( \mathbf{v} \) and the laser polarization direction.

The phase term \( \phi_1(t) \) is related to the envelope of the field and varies slowly in time, while \( \phi_2(t) \) and \( \phi_3(t) \) oscillate at the fundamental and at the second harmonic frequency of the IR field, respectively. Around \( \theta = 0^\circ \), since \( \phi_2(t) \) is proportional to \( W^{1/2} \), and, in most cases, \( U_p \ll W \), this term predominates over \( \phi_1 \) and \( \phi_2 \) and induces a considerable modulation amplitude even for moderate laser intensities.

Connection between the quantum and the semiclassical models

If the XUV pulse is short compared to the laser field period, the two models are strictly equivalent. In fact, in this case, \( \phi \) can be linearly expanded with respect to time. This linear phase modulation on the electron wavepacket leads to a shift in its spectrum, given by \( \delta W = W - W_0 = -\partial \phi/\partial t \). Solving this equation for \( W \), the same expression as in 2.5 is retrieved. This means that the energy modulation \( W(t) \) given by the semiclassical model and the phase modulation \( \phi(t) \) given by the quantum description are related by a
time derivation.

The bandwidth of the phase modulator is equal to $|\partial\phi/\partial t|$, which corresponds to the maximum energy shift of the photoelectron spectrum produced by the electric field. In order to correctly characterize the XUV pulse, the bandwidth of the phase modulator should be a significant fraction of that of the attosecond pulse.

### 2.2.2 FROG-CRAB

The FROG-CRAB technique [28] is inspired from Frequency Resolved Optical Gating (FROG) method, a well-developed technique applied to the measurement and the characterization of visible femtosecond pulses. FROG technique is based on the decomposition of the pulse into many temporal slices, thanks to a temporal gate, and on the measurement of the spectrum of each slice. The field $E(t)$ and the gate pulse $G(t)$ are focalized into an instantaneously (or nearly so) responding non-linear medium, and the emitted spectrum, called spectrogram, is acquired. As the gate is scanned across the pulse in time, all the time-frequency information about the pulse is recorded:

$$S(\omega, \tau) = \left| \int_{-\infty}^{+\infty} dt G(t) E(t - \tau)e^{i\omega t} \right|^2. \quad (2.15)$$

The FROG method operates in an iterative way: a spectrogram $\tilde{S}$ is computed from an initial guess \{\(E(t), G(t)\)}:

$$\tilde{S}(\omega, \tau) = |\tilde{S}(\omega, \tau)|e^{i\tilde{\phi}(\omega, \tau)} = \int_{-\infty}^{+\infty} E(t)G(t)e^{i\omega t} dt. \quad (2.16)$$

In the subsequent step, the algorithm retains only the phase $\tilde{\phi}(\omega, \tau)$, while replaces the modulus $|\tilde{S}(\omega, \tau)|$ with that of the measured spectrogram. Consequently, the computed spectrogram becomes:

$$\tilde{S}(\omega, \tau) \rightarrow \tilde{S}'(\omega, \tau) = \sqrt{I(\omega, \tau)}e^{i\tilde{\phi}(\omega, \tau)}. \quad (2.17)$$
2.2 Characterization of attosecond pulses

This guessed spectrogram is then antitransformated and thus expressed in the time domain:

\[
\tilde{S}'(t, \tau) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{S}(\omega, \tau)e^{-i\omega t}d\omega.
\] (2.18)

This retrieved expression is the guessed cross-correlation \(E(t)G(t + \tau)\). At this point, the algorithm estimates a new pair \(\{E'(t), G'(t)\}\) so that their cross-correlation is equal to \(\tilde{S}'\) for all delays \(\tau\). The steps above described are iterated until convergence is reached and a final pair \(\{E(f), G(f)\}\) is obtained.

This method can be applied also for the characterization of attosecond pulses. Indeed, the photoionization spectrum, calculated as the square modulus of the transition amplitude \(a_V\):

\[
S(W, \tau) = \left| \int_{-\infty}^{+\infty} e^{i\psi(\tau)} d\mathbf{p} E_{\text{XUV}}(t - \tau)e^{i(W+I_p)t}dt \right|^2
\] (2.19)

is the same as a FROG spectrogram of the electron wavepacket generated by the attosecond pulse, with a phase gate \(G(t) = e^{i\phi(t)}\). Several algorithms, based on the FROG iteration, can extract the fields \(E(t)\) and \(G(t)\) from the streaking traces. One of the most reliable and efficient algorithms is the so-called Principal Component Generalized Projections Algorithm (PCGPA).

In this algorithm, the pulse and the gate are represented as \(N\)-components vectors:

\[
E_i = E(t_i) \quad G_i = G(t_i), \quad 1 \leq i \leq N.
\] (2.20)

The outer product of these two vectors forms the following matrix:

\[
O = \begin{bmatrix}
E_1G_1 & E_1G_2 & \cdots & E_1G_{N-1} & E_1G_N \\
E_2G_1 & E_2G_2 & \cdots & E_2G_{N-1} & E_2G_N \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
E_{N-1}G_1 & E_{N-1}G_2 & \cdots & E_{N-1}G_{N-1} & E_{N-1}G_N \\
E_{N}G_1 & E_{N}G_2 & \cdots & E_{N}G_{N-1} & E_{N}G_N
\end{bmatrix}
\]
A signal matrix $S$ is obtained from $O$ by circularly shifting its rows:

$$
S = \begin{bmatrix}
E_1G_1 & E_1G_2 & \cdots & E_1G_{N-1} & E_1G_N \\
E_2G_2 & E_2G_3 & \cdots & E_2G_N & E_2G_1 \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
E_{N-1}G_{N-1} & E_{N-1}G_N & \cdots & E_{N-1}G_{N-3} & E_{N-1}G_{N-2} \\
E_NG_N & E_NG_1 & \cdots & E_NG_{N-2} & E_NG_{N-1}
\end{bmatrix}
$$

The signal matrix represents the cross-correlation signal $E(t)G(t + \tau)$ and a Fourier transform of its columns produces a FROG spectrogram. It is important to notice that the outer product matrix $O$ has only one non-zero eigenvalue, associated to a single left-eigenvector $E$ and a single right-eigenvector $G$. After applying the 2.17, i.e. keeping the phase factor of the retrieved spectrogram and replacing its modulus with that of the measured spectrogram, the resulting matrix $O'$ actually possesses several non-zero eigenvalues and eigenvectors. However, the left and the right eigenvectors of $O'$ associated with the eigenvalue characterized by the largest absolute value give the largest contribution to $O'$ and can therefore be used as the new pulse and gate for the next iteration. The calculation is repeated until convergence is reached. Due to the high redundancy in the CRAB trace, the PCGPA algorithm is very robust against noise.
CHAPTER 3

Experimental setup

This chapter will focus on the description of the laser system and of the setup used in the experiments. Particular attention will be devoted to the description of the velocity map imaging spectrometer (VMI) and the Abel inversion algorithm used to retrieve the 3D momentum distribution of charged particles from the measured 2D projections. In addition, temporal characterization of the XUV attosecond source will be presented in section 3.2.4.

3.1 The laser source

Fig. 3.1 shows a schematic of the laser system used in the experiments. Laser pulses delivered by a CEP-stabilized Ti:sapphire oscillator and are subsequently amplified with a chirped pulse amplification (CPA) technique [32]. The 6 mJ, 25 fs pulses obtained from the amplified Ti:sapphire laser are compressed down to a pulse duration of 6 fs by using the hollow-fiber compression technique [33].

3.1.1 The amplified Ti:sapphire laser system

The laser source is based on a Kerr-lens mode-locked Ti:sapphire oscillator. The active medium is pumped by a continuous-wave, frequency-doubled
Nd:YLF laser. The oscillator produces femtosecond pulses at a 80 MHz repetition rate, with a central wavelength of 800 nm. The spectrum contains wavelengths spanning from \( \sim 650 \) nm to \( \sim 1000 \) nm.

The group and the phase velocity in the laser cavity are usually different, which leads to a phase shift between the carrier wave and its envelope. As discussed in the previous chapter, CEP stabilization is essential for a complete control of high-order harmonic generation. Therefore, the femtosecond source is provided with a phase stabilization system, based on the difference frequency generation approach [34].

The amplification of the CEP-stabilized seed pulses is achieved by using the CPA technique: first the pulses are stretched to a pulse duration which allows to avoid material damage, then amplified and finally compressed. Stretching is achieved by a prism system that introduces an almost linear chirp. The resulting pulse duration is 200 ps.

An acusto-optic modulator (Dazzler) is also used to accurately control the dispersion of the seed pulses.

The amplification is achieved by using two amplification stages: the preamplifier and the booster. The preamplifier is a multi-pass amplifier based on a Ti:sapphire crystal, cut at the Brewster angle in order to reduce...
the reflection losses. The active medium is pumped by a frequency-doubled Nd:YLF laser, operating in Q-switching regime at a repetition rate equal to 1 kHz and with a pulse energy of 40 mJ.

A high amplification is achieved only if the interaction length is relevant. For this reason, the stretched pulses undergo four passes through the Ti:sapphire crystal. The output consists of a pulse train modulated by the intensity of the pump laser. A Pockels cell placed between two crossed polarizers acts on the pulse train in order to select only the most intense pulse. For a suitably short time window, a high voltage is applied to a KDP crystal which rotates the polarization of the transmitted pulse for 90° (Pockels effect). In this way, only the most intense pulse of the amplified train is transmitted through the second polarizer and undergoes an additional amplification, achieved by other five passes through the active medium. The resulting pulses have an energy of about 2.5 mJ and 1 kHz repetition rate.

The booster is also based on a Ti:sapphire crystal, pumped by a frequency-doubled Nd:YLF laser, operating in Q-switching regime, with a repetition rate of 1 kHz and pulse energy of 60 mJ. After two passes through the amplifier, the output pulses still have a repetition rate of 1 kHz and pulse energy of 8 mJ.

After the amplification system, the pulses are compressed using a transmission grating compressor. After compression, the laser pulses have an energy of 6 mJ and a pulse duration of 25 fs.

### 3.1.2 The carrier envelope phase stabilization system

Instabilities induced by the amplification translate into a phase shift between the envelope and the carrier wave. Therefore, an $f - 2f$ interferometer is placed after the compressor, in order to detect the phase noise. The spectrum of the infrared radiation is broadened in order to cover more than an optical octave. Low frequencies of the broadened spectrum are frequency-doubled and interfere with the high frequency part. This leads to the generation of a radio frequency beating signal, which provides a measurement of the carrier-envelope phase drift.
A fraction ($< 1 \mu J$) of the output energy is focused on a 1 mm thick sapphire plate in order to achieve a spectral broadening, from the infrared ($\approx 1000 \text{ nm}$) to the blue ($\approx 500 \text{ nm}$) regions. A thin lens after the sapphire plate focuses the white light into a 0.5 mm thick BBO crystal, optimized for second harmonic generation around 980 nm. As the polarization directions of the fundamental and the harmonic beams are orthogonal, a rotatable beam-splitter cube is used to project them onto a common axis. As a result, it is possible to observe the fringe pattern produced by the interference between the second harmonic of the infrared part of the white light and the green components of the same spectrum. The fringe position on the wavelength axis depends on the carrier envelope phase. Therefore, the shift of the position of the interference fringes contains the information about the CEP drift. A computer performs a Fourier analysis of the interference pattern and determines the CEP drift from pulse to pulse. Acquiring for a time interval of few seconds, it is possible to trace the CEP drift. A feedback loop acts on two glass wedges placed before the preamplifier in order to suitably modify the optical path of the beam.

The result is a long-term CEP stability, with a root mean square phase noise of 100 mrad.

### 3.1.3 The hollow fiber compression system

The high-order harmonic generation processes and pump-probe experiments require few-cycle infrared pulses. In order to achieve additional compression of the pulses delivered by the amplification system, it is possible to exploit third order non-linear effects. Due to the third-order non-linearity, the IR pulses experience the so-called self-phase modulation effect, resulting from the temporal variation of the refractive index with the instantaneous intensity as $n = n_0 + n_2 I(r,t)$. This corresponds to the appearance of new frequencies in the spectrum of the pulses. Indeed, the instantaneous frequency is related to the pulse intensity with:

$$\omega_1(t) = -\frac{\partial \varphi}{\partial t} \sim \omega_0 - \frac{n_2 \omega_0}{c} z \frac{\partial I(r,t)}{\partial t},$$

(3.1)
where $\varphi$ is the phase of the pulse. From eq. 3.1 it is possible to conclude that the generation of new frequencies depends on the slope of the pulse $\partial \varphi / \partial t$, the propagation distance $z$ in the Kerr medium and the nonlinear coefficient $n_2$. In a purely Kerr medium, the leading edge of the pulse generates frequencies in the red and the trailing edge generates frequencies in the blue. The extension of the spectrum permits the achievement of shorter time durations. If the beam is focused inside a Kerr medium, the radial profile of a gaussian pulse would determine an inhomogeneous spectral broadening, preventing an effective recompression in the temporal domain. An homogeneous self-phase modulation can be achieved by means of propagation in a single mode fiber. However, the use of single mode optical fibers is limited to the nanojoule level, in order to avoid damages inside the guiding structure. To overcome this limitation, the employment of a hollow fiber filled with noble gas, acting as a Kerr medium, has been proposed in 1996 [33]. The advantages of this approach consist in a high damage threshold and in a non-linearity that can be simply changed by varying the gas type and pressure. Propagation inside the fiber is achieved not by total reflection, but by grazing incidence at the inner surface of the capillary. As a result, all modes have radiative losses. However, losses are lower for the fundamental hybrid mode $EH_{11}$, which is the only mode able to propagate for a sufficient length. By properly matching the Gaussian beam waist at the entrance of the hollow fiber, almost all the energy of the pulse is transferred to this fundamental mode. It is possible to demonstrate that if the diameter of the laser beam at the entrance of the fiber is the 64% of the diameter of the hollow core a coupling efficiency of 90% can be achieved. The output radial profile is a zero-order Bessel function.

In our setup, the hollow fiber has a length of 1 m and an inner diameter of 310 $\mu$m. The gas employed as a Kerr medium is helium, and its optimal pressure inside the capillary lowers as the intensity of the pulses reaches higher values. The hollow fiber is used with a pressure gradient configuration [35]. As shown in fig. 3.2, the hollow fiber is placed in a gas cell divided into two sections. A first cell is continuously pumped and the second cell is filled by gas. The gas flows to the input through the capillary, thus creating a pressure gradient inside the fiber.
Pressure gradient allows one to avoid non-linear phenomena, such as self-focusing and filamentation, at the entrance of the fiber. Filamentation is due to the fact that, near the focal point, the beam reaches high enough intensities to ionize the gas. The generation of plasma acts as a diverging lens, preventing the complete focusing of the beam [36]. Defocusing action balances self-focusing due to the Kerr effect inside the gas medium and this dynamic interplay causes a self-guided propagation leading to a filament. Filamentation causes a considerable reduction in the coupling efficiency of the laser beam inside the fiber.

Usually the pressure of the gas at the end of the hollow fiber is set to 1 bar, while the measured pressure at the entrance is around 1 mbar.

The beam position at the input entrance of the hollow fiber is stabilized by using a feedback control setup composed of a four-quadrant photodetector, an analog PID circuit and a piezo-driven mirror.

Chirped mirrors after the hollow fiber ensure a compression of the pulses down to a temporal duration of 6 fs. The energy at the output of the fiber is about 2.5 mJ.

### 3.2 The generation and detection setup

The generation and detection setup, shown in fig.3.3, consists of a generation chamber in which the HHG process takes place, a focusing chamber, an interaction chamber and a spectrometer.

Since XUV radiation is strongly absorbed by air, the whole system op-
3.2 The generation and detection setup

Figure 3.3: Scheme of the generation and detection setup. BS: Beam Splitter; WPs: Waveplates; FM: Focal Mirror; DM: Drilled Mirror.

The IR beam is split in two arms using a beam splitter with 50% transmission. The first beam (pump) is used to generate the XUV radiation. Two birefringent waveplates are used to modulate the polarization of the pulse, as required for polarization technique. The remaining part of the beam is sent through a delay line and then collinearly recombined with the generated XUV beam by using a drilled mirror.

3.2.1 The XUV generation chamber

The IR beam is focused by a 50 cm focal-length silver coated mirror inside the generation chamber. Here, the pulses interact with a noble-gas jet emitted by a piezo driven pulsed valve operating at 1 kHz, synchronized with the laser pulse train. A piezo electric disc (PZD) periodically opens and closes a 1 mm diameter pipe and the amount of released gas is controlled by the voltage applied to the PZD. The valve is mounted on a three-axis translation stage to align the position of the gas jet respect to the laser beam. During the experiments, the gas jet was positioned after the laser focus in order to select the short quantum trajectories by means of the phase matching
condition. The radiation is collected and analyzed using a high throughput grazing-incidence spectrometer, that will be described in section 3.2.3.

3.2.2 The recombination chamber

An aluminium filter is placed on the pump beam path in order to eliminate the low-frequency components. The probe beam is delayed using a piezoelectric translation stage characterized by 1 nm resolution, equivalent to 7 as resolution in the time domain. In order to obtain a collinear propagation of the XUV and the IR beams, the pump beam is sent through the hole of a drilled mirror, while the probe beam is reflected by the outer part of the mirror. Subsequently, the two beams incide with a grazing angle of 85.2° on a 80 cm focal-length gold coated toroidal mirror and are focused in the same spot inside the interaction chamber.

3.2.3 The XUV spectrometer

The XUV radiation is collected in order to analyze its spectral features. No entrance slit is present because of the limited spatial dimension of the source and because it reduces the photon flux of an unknown amount. As shown in figure 3.4(a), the XUV beam, focused on the spectrometer entrance point A, is steered by a second toroidal mirror and converges towards a variable line spaced (VLS) grating.

As shown in fig. 3.4 (b), such a configuration focuses the different frequencies on a Rowland circle. The radiation is detected by means of a Micro Channel Plate (MCP) photomultiplier that amplifies the photon signal and converts it into an electron signal. Electrons are accelerated towards a phosphor screen and the resulting image is acquired by a charge coupled device (CCD). This detector can measure only a fraction of the whole XUV spectrum, therefore the MCP, the screen and the CCD are mounted on a translation stage.
3.2.4 Time of flight spectrometer

The previous chapter reported a description of the streaking technique, required to obtain a temporal characterization of attosecond pulses. In order to perform this measurement, a time of flight spectrometer (TOF) for electrons is mounted in the interaction chamber. The spectrometer is shown in fig. 3.5.

The entrance of the spectrometer is placed at a distance of 3 mm from the laser beam. After passing through the entrance aperture, the electron beam
Experimental setup

is collimated using a lens module, called extraction module, and focalized inside a drift tube. A positive voltage is applied to the drift tube if the emitted electrons are characterized by low velocities. On the contrary, if electron velocity reaches high values, a negative voltage can be applied. The photoelectrons continue their propagation towards a positively charged MCP. Since they have different initial velocities, electrons impinge onto the detector at different time instants, creating a pulsed current signal. The output from the MCP is subsequently amplified and sent to a discriminator, to remove the background noise. A time to digital converter device turns the pulsed signal into a digital representation of the time of flight of the electrons. A start signal, taken as a time reference from which the time of flight is estimated, is obtained by measuring the IR pulses by means of a photodetector. The relation between the time of flight $t$ and the kinetic energy $E_k$ of an electron is expressed by the following formula:

$$E_k = \frac{1}{2} m_e v^2 = \frac{1}{2} m_e \frac{l^2}{v^2},$$

where $m_e$ is the mass of the electron and $l$ is the trajectory followed by the electron inside the TOF spectrometer. The time of flight is inversely proportional to the square root of the applied voltage $V$:

$$t = \frac{l}{\sqrt{2V}} \sqrt{\frac{m_e}{e}}.$$  

(3.3)

However, eq. 3.3 is a simplified result and can not be used to retrieve the distribution of the velocities at the TOF entrance. Indeed, electrons do not experience a constant electric potential difference because of the presence of the ion optics at the TOF entrance. Therefore, an accurate calibration is needed. This is achieved by photoionizing the target gas by means of attosecond pulse trains. The measured time of flight signal is composed of a series of peaks and resembles the XUV spectrum. Each peak visible in the electron energy spectrum corresponds to a single harmonic peak in the XUV spectrum. Therefore, energy owned by electrons contributing to each peak is calculated as the photon energy associated with the corresponding harmonic.
peak minus the ionization energy of the target atoms.

Figure 3.6: (a): spectrum of the XUV radiation. Harmonics from the 13th to the 29th order are visible. (b): electron energy spectrum. Each peak is labelled with the order of the corresponding peak in the XUV spectrum.

Therefore, a streaking measurement can be performed by using a TOF spectrometer and by varying the delay between the IR and the XUV pulses. The information encoded in the retrieved trace can be extracted by means of the PCGPA algorithm, achieving a complete characterization of the attosecond pulses.

**Temporal characterization of attosecond pulses**

Isolated attosecond pulses were created by driving the high-order harmonic generation process with few optical cycle IR pulses ($\tau = 6\ fs$, central wavelength $\lambda_c = 790\ nm$). The polarization of femtosecond pulses was suitably modulated by exploiting the polarization gating technique described in section 2.1.1. XUV pulses were generated in different gases such as xenon, kripton and argon. Fig. 3.7 reports the broadband and continuous spectrum of the XUV radiation generated in argon. The emission covers the energy range $16 - 42\ eV$ between the aluminium absorption edge and the cutoff.

The XUV and the IR beams were focused by the toroidal mirror onto a nitrogen gas jet inside the interaction chamber. The generated photoelectrons were collected by the time of flight spectrometer and the evolution of the photoelectron spectra was recorded as a function of the temporal delay.
Experimental setup

Figure 3.7: Spectrum of the XUV radiation produced by means of polarization gating technique.

between the XUV and the IR streaking pulses. The result is a CRAB trace, shown in fig. 3.8. The temporal structure of the attosecond pulses was re-

Figure 3.8: Experimental CRAB trace measured as a function of the temporal delay between the attosecond and the streaking IR pulses.

trieved by means of the PCGPA algorithm. Reconstruction was performed by selecting only optical cycles before the principal ones. Indeed, the high value of IR intensity in correspondence of the principal cycles prevents a correct convergence of the FROG-CRAB reconstruction algorithm. Fig. 3.9 compares the experimental trace (a) with the reconstructed CRAB trace (b), obtained after 10000 iterations of the algorithm.
3.2 The generation and detection setup

Figure 3.9: Experimental (a) and reconstructed (b) traces.

As can be seen, the reconstructed CRAB trace is very similar to the measured one. The CRAB error, evaluated as the root mean square per element of the trace, is $\sim 10^{-3}$. In the reconstructed temporal intensity profile and phase of the XUV pulse, shown in fig. 3.10, the pulse duration was 200 as, and the almost parabolic phase indicates the presence of a second-order dispersion, corresponding to a positive linear chirp. The measured CRAB trace and the corresponding reconstruction of the XUV pulses clearly demonstrate the generation of isolated pulses. In our experimental conditions, the positive chirp leads to a decrease of the electronic spectrum width (thus resulting in a spectral peak increase) in the temporal regions characterized by a negative slope of the vector potential, as visible in fig. 3.8.

In order to achieve almost Fourier-transform limited attosecond pulses it is required to compensate for the positive chirp. In our setup, we employed a 100 nm thick aluminium filter with a negative Group Delay Dispersion (GDD) in the spectral region from 20 to 60 eV. A thicker aluminium foil would further compress the XUV pulses, but would also reduce the XUV photon flux. To achieve the maximum photon flux, experiments have been performed also without PG. In this case we obtained short trains composed by 2 or 3 attosecond pulses. Spectra of short trains obtained by HHG in argon, kripton and xenon are shown in fig. 3.11. Spectra displayed in fig. 3.11 are characterized by different cutoff values. In particular, for APTs generated in argon, the spectrum extends to photon energy values beyond
Figure 3.10: Reconstruction of the temporal intensity profile and phase of the attosecond pulses obtained from the CRAB trace shown in figure 3.8.

50 eV, while XUV radiation produced in krypton presents a cutoff at about 45 eV. An even lower cutoff value affects the XUV spectrum associated with ATPs generated in xenon. The high-order harmonics generating medium is selected on the basis of energy values required in the experiments.
Figure 3.11: Spectra of attosecond pulse short trains generated by HHG in argon (a), kripton (b), and xenon (c).
3.2.5 Velocity map imaging spectrometer

Pump-probe experiments described in this thesis were performed using a velocity map imaging (VMI) spectrometer, depicted in fig. 3.12. The VMI spectrometer measures the 2D projection of the 3D momentum distribution of charged particles emitted by photoionization of the gas target.

The laser beam is focused in a molecular gas jet placed in the center of the spectrometer. In order to achieve high gas density in the interaction region, while keeping a low average gas density inside the chamber, a pulsed valve, locked to the laser pulses, is used. The time duration of the gas pulse is \( \approx 20 \, \mu s \). The extraction region of the spectrometer consists of a flat plate that acts as a repeller and a ring electrode that acts as an extractor for electrons or ions. Positively charged electrodes allow detection of ions while negatively charged electrodes allow detection of electrons. In our configuration, the repeller incorporates the gas valve as shown in fig. 3.13.

![Figure 3.12: Scheme of the whole VMI spectrometer.](image)

The repeller has a flat central part, with a diameter \( \phi = 1 \, mm \), that turns in a conical shape, with a 154° cone angle to accommodate the focusing of the laser in front of the capillary. The mechanical design of the integrated pulsed valve is shown in fig. 3.14.

Since the gas injection system is integrated in the repeller, it is important to accurately adjust the relative position of the laser focus and of the ion optics, composed by the repeller, the extractor and a ground plate. For this reason, the electrodes are mounted on translation stages. The repeller and the extractor geometry is based on the Eppink-Parker configuration, devised in order to cope with the loss of resolution due to the finite dimensions of the charge source. Indeed, the obtained electrostatic lens focuses the ions coming
3.2 The generation and detection setup

Figure 3.13: Ion optics of the VMI spectrometer with an integrated effusive gas jet in the repeller optics. The ion optics consists of a repeller, an extractor and a ground plate. The repeller electrode is electrically isolated from the housing by ceramic isolators. The laser beam propagates in between the repeller and the extractor electrodes. The position of the ion optics can be moved vertically and horizontally by motor controlled translation stages to ensure a good overlap of the gas beam and laser focus. Figure taken from [39].

Figure 3.14: Pulsed piezo valve integrated in the effusive repeller. The effusive repeller comprises a flat part of 1 mm with a laser-drilled nozzle in the center. The repeller takes a conical shape from the flat part on to accommodate the laser focus. Figure taken from [39].
form different regions of the charge source, but sharing the same velocity, to one spot on the detector, consisting of a MCP multiplier and a phosphor screen. A CCD camera acquires the images on the phosphor screen. The time required for the particles to reach the detection system depends on the three spatial components of their velocity. The left part of fig. 3.15 shows the velocity vector and its components projected onto a three-dimensional coordinate system. This 3D distribution is acquired by the detector as a 2D map (right part of fig. 3.15).

\[ V_{2D} \]

\[ \theta_{3D} \]

\[ \theta_{yz} \]

\[ R \]

\[ L \]

\[ V_{3D,y} \]

\[ V_{3D,z} \]

\[ V_{3D,x} \]

\[ \phi \]

\[ \theta \]

\[ V_{2D,y} \]

\[ V_{2D,z} \]

\[ \alpha \]

\[ \beta \]

\[ \gamma \]

\[ \delta \]

\[ \epsilon \]

\[ \zeta \]

\[ \eta \]

\[ \theta \]

\[ \phi \]

\[ \chi \]

\[ \psi \]

\[ \omega \]

\[ \kappa \]

\[ \lambda \]

\[ \mu \]

\[ \nu \]

\[ \xi \]

\[ \pi \]

\[ \sigma \]

\[ \tau \]

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\[ \sigma \]

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\[ \pi \]

\[ \sigma \]

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\[ \psi \]

\[ \omega \]

\[ \kappa \]

\[ \lambda \]

\[ \mu \]

\[ \nu \]

\[ \xi \]

\[ \pi \]

\[ \sigma \]

\[ \tau \]

\[ \upsilon \]

\[ \phi \]

\[ \chi \]

\[ \psi \]
impinging at a distance $R$ from the center of the distribution is characterized by an initial velocity vector $v_{3D}$ perpendicular to the x-axis. Therefore, the maximum radius can be calculated as: $R = v_{3D} \cdot t$, where $t$ is the time of flight. If the interaction region is placed at a static potential $V_S$ with respect to the potential applied to the detector, the final velocity of the particle will be: $v_x = \sqrt{2qV_S/m}$. If the length of the interaction region is small compared to the total time of flight length, the time of flight can be expressed as:

$$t \simeq \frac{L}{v_x} = L\sqrt{\frac{m}{2qV_S}}. \quad (3.4)$$

If $E_k$ is the initial kinetic energy of the particle, the maximum radius is:

$$R \simeq v_{3D} t = L\sqrt{\frac{E_k}{V_S q}}. \quad (3.5)$$

Particles sharing the same charge, mass and x-component of the initial velocity, but differing in the absolute value of $v_{3D}$, will impinge the detector at different positions. Particle with the same $v_{3D,yz}$ component, but with different initial $v_{3D,x}$ will arrive at the detector at different time instants. The TOF spread is defined as the time needed to change the sign of the x-component velocity of those particles emitted with the minimum value of $v_x = -v_{3D}$:

$$\Delta t = \frac{2mv_{3D}}{qE}, \quad (3.6)$$

where $E$ is the strength of the local electric field, assumed to be constant.

**Abel inversion of the 2D velocity map**

3D momentum distributions measured on a VMI detector are the result of photon-matter interactions. Lambropoulos et al. [38] demonstrated that angular distributions obtained in multi-photon ionization processes consist of a superposition of Legendre polynomials, where the highest-order polynomial involved is determined by the order of the multi-photon ionization process. As a result, it should be profitable to express the inversion problem in terms of a coordinate system where the angular distribution $P_{3D}(v_{3D}, \theta_{3D}, \phi_{3D})$ can
Experimental setup

be written as a superposition of a finite number of Legendre polynomials $P_l(\cos\theta_{3D})$:

$$P_{3D}(v_{3D}, \theta_{3D}, \phi_{3D}) = \sum_l a_l(v_{3D}) P_l(\cos(\theta_{3D})), \quad (3.7)$$

where $\theta_{3D}$ and $\phi_{3D}$ are angles describing the velocity direction with respect to the $y$-axis and the $x$-axis respectively, $v_{3D}$ is the absolute value of the initial velocity, and $P_l$ is the $l$-th order Legendre polynomial. The first few Legendre polynomials are:

- $P_0(x) = 1$
- $P_1(x) = x$
- $P_2(x) = \frac{1}{2}(3x^2 - 1)$
- $P_3(x) = \frac{1}{2}(5x^3 - 3x)$
- $P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$

By imposing the normalization condition:

$$\int \int \int P_{3D}(v_{3D}, \theta_{3D}, \phi_{3D}) v_{3D}^2 \sin\theta_{3D} d\theta_{3D} d\phi_{3D} dv_{3D} = 1 = \int \int P_{3D}(v_{3D}, \theta_{3D}) d\theta_{3D} dv_{3D}, \quad (3.9)$$

and by using eq. 3.7, the angular distribution can be expressed as:

$$P_{3D}(v_{3D}, \theta_{3D}) = 2\pi v_{3D}^2 \sum_l a_l(v_{3D}) P_l(\cos(\theta_{3D})) \sin\theta_{3D}, \quad (3.10)$$

or as:

$$P_{3D}(v_{3D}, \cos(\theta_{3D})) = 2\pi v_{3D}^2 \sum_l a_l(v_{3D}) P_l(\cos(\theta_{3D})). \quad (3.11)$$

The velocity distribution $P_{3D}(v_{3D}, \theta_{3D}, \phi_{3D})$, as a function of $\theta_{3D}$ (or $\cos(\theta_{3D})$), becomes constant when the angular distribution is isotropic.

The impingement point defines a projected velocity $v_{2D}$, that is related to the $y$ and $z$ components of the velocity $v_{3D}$:

$$\begin{align*}
v_{3D,y} &= v_{2D} \cdot \cos(\theta_{2D}) \\
v_{3D,z} &= v_{2D} \cdot \sin(\theta_{2D})
\end{align*} \quad (3.12)$$
The 3D distribution can also be expressed as a superposition of a finite number of Legendre polynomials:

\[ P_{2D}(v_{2D}, \theta_{2D}) = \sum_l b_l(v_{2D}) P_l(\cos(\theta_{2D})), \]  
(3.13)

where the array of elements \( b_l(v_{2D}) \) completely determines the 2D velocity distribution. In agreement with the assumed cylindrical distribution, the two 2D distributions with \( \theta_{2D} \in \langle 0, \pi \rangle \) and \( \theta_{2D} \in \langle \pi, 2\pi \rangle \) contain identical informations.

The Abel projection of the 3D momentum distribution onto the 2D detection plane suggests that the array of elements \( b_l(v_{2D}) \), organized into a vector \( \mathbf{b} \), can be obtained from the array \( a_l(v_{3D}) \), organized into a vector \( \mathbf{a} \), by means of a matrix multiplication:

\[ \mathbf{b} = \mathbf{M} \mathbf{a}. \]  
(3.14)

The unknown array \( a_l(v_{3D}) \) can be obtained by inverting the previous relation:

\[ \mathbf{a} = \mathbf{M}^{-1} \mathbf{b}. \]  
(3.15)

It is worth noting that, wheras arrays \( \mathbf{a} \) and \( \mathbf{b} \) vary with the particular velocity map imaging experiment, the matrix \( \mathbf{M} \) does not depend on the experimental conditions. Therefore, once \( \mathbf{M} \) and \( \mathbf{M}^{-1} \) have been calculated, they can be repeatedly used for the inversion algorithm. The derivation of the matrix \( \mathbf{M} \) has to be done analytically, considering the projection of a monoenergetic momentum distribution with an angular distribution described by a single Legendre polynomial \( P_l \). As can be seen from fig. 3.15, the radial velocity \( v_{2D} \) is related to the 3D velocity \( v_{3D} \) by the following expression:

\[ v_{2D} = v_{3D} \cdot \sin(\theta_z), \]  
(3.16)

where \( \theta_z \) is the angle of the 3D velocity with respect to the x-axis. The incremental flux detected on an infinitesimal area element around a point
defined by $v_{2D}$ and $\theta_{2D}$ is expressed by:

$$\delta S_{2D} = P_{2D}(v_{2D}, \theta_{2D}) \delta v_{2D} v_{2D} \delta \theta_{2D},$$

and the corresponding area on the 3D sphere emits a flux:

$$\delta S_{3D} = P_{3D}(v_{3D}, \theta_{3D}, \phi_{3D}) v_{3D} \delta \theta_{3D} \delta \phi_{3D}.$$  

Therefore, by equating the two fluxes, it is possible to write the following expression, that defines the matrix $M$:

$$P_{2D}(v_{2D}, \theta_{2D}) = v_{3D} \frac{\delta \theta_{x}}{\delta v_{2D}} P_{3D}(v_{3D}, \theta_{3D}, \phi_{3D}).$$  

Subsequently, the inverse matrix $M^{-1}$ can be calculated by using standard numerical algorithms. The obtained 2D distributions can be inverted by fitting the experimental angular distributions for each value of $v_{2D}$ to a superposition of Legendre polynomials and expressing the experimental results in the form of eq. 3.13. The 3D momentum distribution is then calculated by applying eq. 3.15.

From the retrieved 3D momentum distribution, a complete description of the outcome of the experiment can be obtained by averaging over the radius or the angle.

For example, the kinetic energy distribution $P(E)$ is obtained by means of the following condition:

$$\int P(E) dE = m \int P\left(v_{3D} = \sqrt{\frac{2E}{m}}\right) v_{3D} d\v_{3D} = 1 = \int \int \int P(v_{3D}, \theta_{3D}, \phi_{3D}) v_{3D}^2 d(\cos \theta_{3D}) d\phi_{3D} dv_{3D}. \quad (3.20)$$

Considering the orthogonality of the Legendre polynomials:

$$\int_{-1}^{1} P_n(x) P_m(x) dx = \frac{2\delta_{nm}}{2n + 1}, \quad (3.21)$$
3.2 The generation and detection setup

It is possible to derive that:

\[ P(E) = \frac{4\pi v_{3D}}{m} a_{l=0}(v_{3D}). \]  \hspace{1cm} (3.22)

In the dipole approximation, the angular distribution of the photoelectrons produced in the photoionization of gas atoms by linearly polarized radiation is represented by the differential cross-section:

\[ \frac{d\sigma(E, \theta)}{d\Omega} = \frac{\sigma}{4\pi} \left[ 1 + \sum_{n \geq 2} \beta_n(E) P_n(\cos \theta) \right], \]  \hspace{1cm} (3.23)

where \( \sigma \) is the total photoionization cross-section representing the probability associated with the photoionization process and \( P_n \) is the \( n \)th-order Legendre polynomial. It is possible to demonstrate that, for linearly polarized incident radiation, only even term contribute to the sum. Furthermore, for single photon ionization processes, only the second order Legendre polynomial is relevant. Therefore, in this case, the differential cross-section is:

\[ \frac{d\sigma(E, \theta)}{d\Omega} = \frac{\sigma}{4\pi} \left[ 1 + \frac{\beta_2}{2}(3\cos^2 \theta - 1) \right]. \]  \hspace{1cm} (3.24)

If only small values of \( \theta \) are considered, the angular distribution is corresponds to \( \beta_2 \) except for a constant value.
CHAPTER 4

Attosecond dynamics in molecular nitrogen

APPLICATION of attosecond pulses for time-resolved electron spectroscopy is expected to have a broad impact on many areas of science. This chapter will present the results of attosecond pump - femtosecond probe measurements performed on nitrogen molecules. Our results demonstrate the possibility to observe and control the ultrafast electron dynamics occurring in photoexcited and photoionized diatomic molecules on a sub-femtosecond scale.

4.1 Molecular states

This section will present a brief description of molecular electronic states, along with an explanation of their representation by means of a symbolic notation. Since experimental measurements reported in this chapter were performed on nitrogen molecules, the considerations will be limited to a qualitative description of biatomic homonuclear molecules.

When a molecule is formed, the inner shell electrons of the two atoms remain tightly bound to the original nucleus and are barely affected. On the other hand, the outermost loosely bound electrons are influenced by all the particles of the system. Therefore, their wavefunctions are significantly
modified when atoms are brought together and their distribution can be interpreted as a sharing of the electrons by both atoms. Each nucleus exerts a Coulomb repulsion on the other, and both exert a Coulomb attraction on the electrons. Additionally, electrons repel each other, giving rise to complicated correlation effects. The total energy of the system is the sum of all these contributions and the system will be bound if the total energy exhibits a minimum at some value of internuclear separation $R$. Even without actually solving the equations, it is easy to appreciate that, for bound states, the dependence of energy on $R$ must have the form shown in fig. 4.1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{potential_energy_curve.png}
\caption{Potential energy curve of a binding electronic state.}
\end{figure}

If the nuclear separation is very large ($R \to \infty$), the levels will obviously be the same as those of the single atom. If the separation $R$ is finite, then, as a result of the interaction between the atoms, the energy levels will be modified.

Shared electrons occupy molecular orbitals according to Pauli’s principle. Molecular orbitals can be qualitatively represented as a linear combination of atomic orbitals and are approximate solutions to the molecular Schrödinger equation. A specification of the occupied molecular orbitals is provided by the molecular configuration. For example, the molecular configuration of homonuclear $N_2$ in its ground state is:

$$N_2 : 1\sigma_g^2 \ 1\sigma_u^2 \ 2\sigma_g^2 \ 2\sigma_u^2 \ 2\pi_u^2 \ 2\sigma_g^2,$$

(4.1)
where molecular orbitals are categorized by the labels $\sigma$ and $\pi$, according to their symmetry. The first excited state is described by the following configuration:

$$N_2 : 1\sigma_g^2 \ 1\sigma_u^2 \ 2\sigma_g^2 \ 2\sigma_u^2 \ 2\pi_u^2 \ 2\pi_g^1 \ 2\pi_g^1,$$ (4.2)

A given configuration may have different states depending on how the electrons are arranged in the orbitals. A molecular term symbol is used to indicate these states and specifies the total spin and angular momentum of the molecule, along with its symmetries:

$$2S^1\Lambda^{(\pm/\mp)}_{(g/u)}$$ (4.3)

The various symbols have the following meanings:

- $S$ is the total spin angular momentum quantum number, calculated from the individual electrons’ spin quantum numbers ($s_i = \frac{1}{2}$). The term $2S + 1$ indicates the spin multiplicity. For an unpaired electron, the total spin angular momentum is the same as the spin of the single electron: $S = s_i = \frac{1}{2}$. Therefore, the multiplicity becomes $2S + 1 = 2$, since there are two possible different states (spin up or spin down), that are degenerate in absence of an external magnetic field. For two unpaired electrons, the possible values of the total spin angular momentum quantum number are $S = s_1 + s_2$ (parallel spins) and $S = s_1 - s_2$ (anti-parallel spins). They give rise to triplet ($2S + 1 = 3$) and singlet ($2S + 1 = 1$) states, respectively. A closed-shell configuration is necessarily a singlet state.

- $\Lambda$ is the quantum number for the total orbital angular momentum of the electrons about the internuclear axis. Since the strong electric field of the nuclei creates a cylindrical symmetry about the internuclear ($z-$) axis, the total electronic orbital angular momentum $\hat{L}^2$ and its components $\hat{L}_x$ and $\hat{L}_y$ do not commute with the electronic Hamiltonian $\hat{H}$. On the contrary, $\hat{L}_z$ commutes with $\hat{H}$. This is due to the fact that the electronic Hamiltonian of a diatomic molecule is invariant under rotations about the internuclear axis (the $z$-axis), but not under rotations
around the x- or y-axes. Therefore, Λ, defined as the projection of the total electronic angular momentum on the internuclear axis, becomes a "good quantum number" and it is calculated as:

$$\Lambda = \sum_i \lambda_i,$$

(4.4)

where \(\lambda_i\) is equal to 0 for a \(\sigma\) electron and \(\pm 1\) for a \(\pi\) electron. It is customary to associate code letters with the value of \(\Lambda\) according to the correspondence:

<table>
<thead>
<tr>
<th>value of (\Lambda):</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>code letter:</td>
<td>Σ</td>
<td>Π</td>
<td>Δ</td>
<td>Φ</td>
</tr>
</tbody>
</table>

It is easy to appreciate that only unfilled orbitals contribute to the term orbital and spin angular momentum.

- the \(g/u\) subscripts can be used only for molecules with a centre of symmetry and label the symmetry of the electronic wave function with respect to inversion through its centre;
- the \(+/-\) superscripts apply only to the \(\Sigma\) states, and label the symmetry of the electronic wavefunction with respect to reflection in a plane containing the nuclei.

A molecule can absorb a photon and the electron wavepacket can be projected to an excited state. For a transition to occur, not only the energy of the photon have to match the energy difference between the states, but in addition selection rules must be satisfied. For one-photon processes, electric dipole allowed transitions must follow the rules:

- \(\Delta \Lambda = 0, \pm 1\);
- \(\Delta S = 0\), in the absence of spin-orbit coupling;
- \(+ \Leftrightarrow +, - \Leftrightarrow -\);
- \(g \Leftrightarrow u\).
4.2 Ultrafast electron dynamics in nitrogen molecules

Nitrogen molecules were excited by using ultrashort attosecond pulse trains (APTs) generated in a gas cell filled with argon or xenon gas. The gas release is controlled by a piezo-driven valve, triggered at the repetition rate of the laser pulses.

Fig. 4.2 (b) shows the potential energy curves of some relevant electronic states of the cation $N_2^+$ and of the dication $N_2^{2+}$. The two dashed lines mark the first and the double ionization thresholds, at 15.5 eV and at 42.88 eV above the $N_2$ ground state minimum. Panels (a) and (c) of the same figure show spectra of the XUV pulses produced by HHG in xenon and argon respectively. For both the generating media, the spectrum extends far beyond the first ionization threshold. A comparison between the potential energy curves and the spectrum of the XUV radiation generated by HHG in argon shows that in this case it is possible to exceed the double ionization threshold and to access highly excited electronic states of $N_2^+$ or low-excited energy states of the molecular dication $N_2^{2+}$. On the contrary, due to the lower cutoff, XUV pulses produced in xenon can excite only low-excited energy states of
Attosecond dynamics in molecular nitrogen

\( N_2^+ \). The VMI does not allow a coincidence detection and, therefore, it is not possible to determine whether \( N^+ \) fragments result from the dissociation of the cation \( N_2^+ \) or of the dication \( N_2^{2+} \). In order to discriminate the two possible contributions, a comparison between the VMI maps obtained by photoionizing \( N_2 \) molecules with APTs generated in argon or in xenon has to be performed. Differences can be brought back to the contribution of highly excited \( N_2^+ \) states or \( N_2^{2+} \) states since they can be excited only by XUV radiation generated in argon.

The angular distribution of \( N^+ \) fragments resulting from the dissociation following the excitation by XUV light generated in xenon and in argon is presented in fig.4.3 (a). Fig.4.3 (b) shows the initial 3D momentum distribution of the \( N^+ \) fragments retrieved from the measured 2D projection by means of the Legendre-polynomials based Abel inversion procedure.

![Figure 4.3](image)

**Figure 4.3:** (a): angular distribution of \( N^+ \) fragments resulting from the dissociation following the excitation by XUV radiation generated in xenon (left part) and in argon (right part). (b): slice though the 3D momentum distribution calculated with the Abel inversion procedure.

The total \( N^+ \) yield as a function of the kinetic energy release (KER) is calculated by performing a full angular integration of the retrieved momentum distribution. Fig. 4.4 shows the comparison between the \( N^+ \) kinetic energy spectra obtained in the case of excitation by APTs generated in argon or xenon.
4.2 Ultrafast electron dynamics in nitrogen molecules

Figure 4.4: $N^+$ kinetic energy distributions in the case of XUV pulse trains generated in xenon (blue line) and in argon (red line).

In both cases, several closely spaced peaks appear at KER values below 1 eV. Baltzer et al. [40] assigned these features to the dissociation of vibrational levels $\nu \geq 3$ of the $N_2^+(C^2\Sigma_u^+)$ electronic state. Table 4.1 reports the theoretical KER values associated with the possible ionization limits. The main contribution to the signal arises from fragments produced via the first ionization limit $L_1: \ N^+(3P) + N^+(4S)$, that overcomes the signal coming from the predissociation via spin-orbit coupling to the second dissociation limit and the direct dissociation to the third dissociation limit. Indeed, peaks of the $C^2\Sigma_u^+ \rightarrow L_2$ and $C^2\Sigma_u^+ \rightarrow L_3$ dissociations are not clearly visible in the experimental data. An additional contribution to the signal at KER values below 1 eV arises from the dissociation of the $N^+(D^2\Pi_g)$ state. Both the kinetic energy distributions present a band peaked at $KER = 1$ eV. It originates from direct dissociation of the $N_2^+(F^2\Sigma_g^+)$ state to the third dissociation limit $L_3$. When $N_2$ is photodissociated by XUV photons generated in argon, the kinetic energy distribution is characterized by a broader band starting at a $KER$ value of 1.7 eV. In the case of APT generated in xenon, this band is replaced by a weak tail, extending up to $\sim 4$ eV. Therefore, electronic states responsible for this feature should lie at energies around the second ionization threshold, and both $N_2^+$ and $N_2^{2+}$ dissociative channels contribute (see tables 4.1 and 4.2). It has been found that fragments originating
from the dissociation of $N_2^+(4^2\Sigma_g^+)$, $N_2^+(5^2\Sigma_g^2)$ and $N_2^+(6^2\Sigma_g^2)$ states strongly contribute to this feature. Dissociation of the $N_2^+(4^2\Sigma_g^+)\) state gives rise to the emission in band G, whereas dissociation of $N_2^+(5^2\Sigma_g^2)$ and $N_2^+(6^2\Sigma_g^2)$ states contributes to the emission in band H. It is worth noting that the $N_2^+$ ground state, labelled as $X^1\Sigma_g^+$, cannot give any contribution to the $N^+$ yield since it is a metastable state with a lifetime of $\sim 15\,\mu s$. Indeed, dissociation from this state can not be measured during the 200 $ns$ time gate applied at the detector. Moreover, also the contribution from the $N_2^+$ triplet state $b^3\Sigma_g^-$ is negligible, since it implies a spin-nonconsering transition. Therfore, only $N_2^+(A^1\Pi_u)$ and $N_2^+(C^1\Sigma_g^+)$ states can produce $N^+$ fragments in the kinetic energy region of interest.
### Table 4.1: $N_2^+$ electronic states

<table>
<thead>
<tr>
<th>state</th>
<th>$\nu$</th>
<th>Vertical $E_B$ (eV)</th>
<th>Fragmentation pathway. Theoretical KER/Exp. $N^+ E_k$</th>
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<tr>
<td></td>
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<td>$L1 : N^+(3P) + N(4S)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$L2 : N^+(3D) + N(4S)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$L3 : N^+(3P) + N(2D)$</td>
</tr>
<tr>
<td>$C^2\Sigma_g^+$</td>
<td>3</td>
<td>24.331</td>
<td>0.19/0.018</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>24.576</td>
<td>0.1415/0.14</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>24.817</td>
<td>0.262/0.226</td>
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<tr>
<td></td>
<td>6</td>
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<td>0.3805/0.38</td>
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<tr>
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<td>7</td>
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<tr>
<td></td>
<td>8</td>
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<td>0.6105/0.61</td>
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<td>$3^2\Sigma_g^+$</td>
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### Table 4.2: $N_2^{2+}$ electronic states

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<th>state</th>
<th>Vertical $E_B$ (eV)</th>
<th>Fragmentation pathway. Theoretical KER</th>
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</thead>
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<td></td>
<td>$D1 : N^+(3P) + N(3P)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D2 : N^+(1D) + N^+(3P)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D3 : N^+(1D) + N^+(1D)$</td>
</tr>
<tr>
<td>$X^1\Sigma_g^+$</td>
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<td>42.9717</td>
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<tr>
<td></td>
<td>$E_{max}$</td>
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<td>$A^1\Pi_u$</td>
<td>FC$_c$</td>
<td>45.4623</td>
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<td></td>
<td>$E_{max}$</td>
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<tr>
<td>$b^3\Sigma_g^-$</td>
<td>FC$_c$</td>
<td>40.0653</td>
</tr>
<tr>
<td></td>
<td>$E_{max}$</td>
<td></td>
</tr>
<tr>
<td>$C^1\Sigma_g^+$</td>
<td>FC$_c$</td>
<td>47.0831</td>
</tr>
<tr>
<td></td>
<td>$E_{max}$</td>
<td></td>
</tr>
</tbody>
</table>

| $X^1\Sigma_g^+$ | $E_{max}$ | 42.9717 | 2.0658 | 1.1218 | 0.1778 |
| $A^1\Pi_u$     | $E_{max}$ | 45.4623 | 3.3116 | 2.3676 | 1.4236 |
| $b^3\Sigma_g^-$| $E_{max}$ | 40.0653 | 3.61265 | 2.6686 | 1.7246 |
| $C^1\Sigma_g^+$| $E_{max}$ | 47.0831 | 4.1215 | 3.1775 | 2.2335 |

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| $C^1\Sigma_g^+$| $E_{max}$ | 47.0831 | 4.1215 | 3.1775 | 2.2335 |

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| $b^3\Sigma_g^-$| $E_{max}$ | 40.0653 | 3.61265 | 2.6686 | 1.7246 |
| $C^1\Sigma_g^+$| $E_{max}$ | 47.0831 | 4.1215 | 3.1775 | 2.2335 |
4.2.1 Attosecond delay scans with XUV APTs generated in argon

Relaxation dynamics of \( \text{N}_2^+ \) and of \( \text{N}_2^{2+} \) excited states are very fast. Therefore, time-resolved experiments with sub-femtosecond resolution are required. In the first group of experiments, dissociation dynamics is initiated by attosecond pulse trains generated by HHG in argon. The subsequent ultrafast relaxation dynamics is probed using intense IR pulses, characterized by a time duration of 6 \( \text{fs} \).

Fig. 4.5 (a) shows a long delay scan of the dissociation dynamics obtained by plotting the \( \text{N}^+ \) kinetic energy distributions of \( \text{N}^+ \) fragments ejected at \( 0^\circ \pm 25^\circ \) with respect to the laser polarization direction as a function of the delay between the APT and the infrared probe pulse. Fig. 4.5 (b) shows the coefficient weighting the second-order Legendre polynomial plotted as a function of the delay \( \tau \) and of the \( \text{N}^+ \text{KER} \).

![Figure 4.5](image)

**Figure 4.5:** (a): \( \text{N}^+ \) kinetic energy distributions as a function of the delay between the APT generated in Ar and the infrared probe pulse for fragments ejected at \( 0^\circ \pm 25^\circ \). (b): coefficient weighting the second-order Legendre polynomial plotted as a function of the delay between the APT generated in Ar and the infrared probe pulse. Colour scale shows fragment yield in arbitrary units.

From the picture above it is possible to see that the presence of the IR pulse causes the appearance of a feature that extends about to 3.7 \( \text{eV} \) when the IR and the XUV pulses are overlapped. This signal moves toward lower
4.2 Ultrafast electron dynamics in nitrogen molecules

Figure 4.6: Schematic of the mechanism associated to the long relaxation dynamics leading to the population of the $N_2^+(C^1\Sigma_g^+)$ electronic state or the autoionizing state of the molecular ion $N_2^{++}$.

Energy values as the time delay between the pump and the probe pulses is increased. $N^+$ fragments contributing to this feature are ejected mainly at $0^\circ$, while a detection in the $90^\circ$ direction reveals only a weak signal. This dissociation dynamics can be explained in terms of a two-colour dissociation process (see fig.4.6).

The interaction with the XUV pulse brings the molecule from the ground level to a super-excited state of the molecular ion, $N_2^{++}$, which can have an energy above the double ionization threshold and is energetically unfavorable. Quantum calculations performed by taking into account electron correlations demonstrate that the autoionization of the molecule, i.e. the spontaneous emission of an electron, becomes energetically favorable for proper internuclear separations. After the ejection of the electron, the strong repulsive force between the two nuclei leads to dissociation of the molecule into two $N^+$ fragments. In the absence of the IR probe pulse, the electron wavepacket promoted to the $N_2^{++}$ state would evolve relaxing along the potential energy curve until the internuclear distance becomes large enough to allow the autoionization of the molecule. If the IR pulse arrives before autoionization takes place, it interrupts the relaxation process by promoting the molecule to a $N_2^{2+}$ electronic state. If the dication state is dissociative, two $N^+$ frag-
ments are produced and their energy can be measured. Since the kinetic energy of the $N^+$ fragments depends on the internuclear distance at which the transition to the dication state takes place, for longer delays the signal moves toward lower kinetic energies following the potential energy curve of the dication. By comparing the kinetic energy release of the $N^+$ fragments with the values reported in table 4.2, it is possible to conclude that the dication electronic state involved in this mechanism is the $N_2^+(C^1\Sigma^+_g)$ state, that dissociates to the D1: $N^+(3P) + N^+(3P)$ limit, located at 38.84 eV above the $N_2$ ground state minimum. It is worth noting that also the $N_2^+(A^1\Pi_u)$ could give rise to a signal in this kinetic energy range, but dissociation from this state results in the ejection of $N^+$ fragments mainly at 90°, while the signal of interest is mainly recorded at 0°.

It has been found that the relaxation dynamics corresponding to dissociation along the dication curve is intersecting the initial dissociative KER after 120 fs, thus indicating that autoionization becomes energetically allowed when the two nuclei are separated by 3.2 Å [42].

Clear evidence is found in figure 4.5 of a second relaxation dynamics, characterized by a faster time evolution, by lower KER values and by a few femtosecond delay with respect to zero. At zero time delay, the $N^+$ yield associated with the $N_2^+(F^2\Sigma^+_g)$ band is strongly reduced and at $\tau \simeq 7$ fs a band characterized by a KER value of $\simeq 2$ eV appears. This feature moves toward lower energies as the delay between the XUV and the IR pulses is increased. This retarded relaxation dynamics proved itself to be source of interesting informations. Fig. 4.7 reports a magnified view of this feature.

The magnified scan, obtained by performing a better sampling of the delay axis, reveals a fine periodic structure lying in the $N^+$ KER range between 2 and 3 eV.

The whole periodic structure appears tilted. Indeed, as shown in figure 4.8, intensity oscillations evaluated at different values of $N^+KER$ are characterized by a continuous phase shift.
4.2 Ultrafast electron dynamics in nitrogen molecules

Figure 4.7: Ultrafast oscillations observed in attosecond delay scans with APTs generated in argon. (a): $N^+$ kinetic energy distributions as a function of the delay between the APT and the infrared probe pulse for fragment ejected at $0^\circ \pm 25^\circ$. (b): coefficient weighting the second-order Legendre polynomial plotted as a function of the delay between the APT generated in Ar and the infrared probe probe pulse. Colour scale shows fragment yield in arbitrary units.

Figure 4.8: Intensity profiles recorded at different values of $N^+ KER$ as a function of the delay between the APT generated in argon and the IR probe pulse.
The origin of these ultrafast oscillations has not yet been explained theoretically. An accurate modelling of electron dynamics inside a nitrogen molecule can be developed only by taking into account instantaneous electron-electron interactions. Up to now, accurate estimates of electron correlations have been prevented by considerable computational difficulties. Presently, several theoretical groups are working toward a solution of these complex issues.

However, a possible explanation for these ultrafast dynamics might be an interference between different quantum paths. On the basis of the measured energy values and of the electric dipole selection rules, it is possible to infer that electron states involved in the process might be electronic states belonging to bands E and H. Fig. 4.9 shows the potential energy curves of $N_2^+(\Sigma_g^+)$ states and a schematic of the mechanism associated with the oscillations observed in fig. 4.7.

![Figure 4.9: Schematic of the mechanism associated with the oscillations in fig. 4.7. Potential energy curves of $N_2^+(\Sigma_g^+)$ states are taken from [41].](image)

XUV photons can directly populate the $N_2^+(4^2\Sigma_g^+)$ state. The molecule evolves along the potential energy curves and dissociates onto a dissociation limit higher than $L3$, contributing to the emission in band $E$, between 2
and 4 eV. However, $N_2^+(4^2\Sigma^+_g)$ state can also be populated by means of a two-color process. Initially, XUV photons project the electron wavepacket onto $N_2^+(5^2\Sigma^+_g)$ or $N_2^+(6^2\Sigma^+_g)$ states. If the IR pulse is present, the excited wavepacket may be perturbed and may relax to the $N_2^+(4^2\Sigma^+_g)$ state. Therefore, wavepackets can populate the $N_2^+(4^2\Sigma^+_g)$ state by following two different quantum paths. As they undergo dissociation, they interfere and produce the retarded oscillating dynamics shown in fig. 4.7.

### 4.2.2 Attosecond delay scans with XUV APTs generated in xenon

A second group of measurements was performed by using attosecond pulse trains generated in xenon. As before, dissociation dynamics are initiated by short APTs and probed by delayed IR pulses. Fig. 4.10 (a) shows a long delay scan of the dissociation dynamics obtained by plotting the kinetic energy distributions of $N^+$ fragments ejected between 70° and 90° with respect to the laser polarization direction as a function of the delay between the APT and the infrared probe pulse. Fig. 4.10 (b) shows the coefficient weighting the second-order Legendre polynomial plotted as a function of the delay $\tau$ and of the $N^+KER$.

As it was previously mentioned, the lower cutoff affecting the XUV radiation generated in xenon prevents the investigation of highly excited electronic states of $N_2^+$ and of low-excited states of $N_2^{2+}$. This is apparent by comparing fig. 4.10 with fig. 4.5. Indeed, the dissociation dynamics observed at high $N^+KER$ values in the case of APTs generated in argon is no more visible. This is due to the fact that XUV photons do not have enough energy to promote the electron wavepacket to a super-excited $N_2^{2+*}$ state and the two-color ionization mechanism previously described can not take place. Instead, maps in fig. 4.10 show a strong signal related to the vibrational progression of the $N_2^+(C^2\Sigma^+_g)$ electronic state and to the emission from B and D states.

Also in this case, ultrafast oscillations are clearly visible in fig. 4.10 (b). A magnified image of the region in which oscillations occur is provided in fig. 4.11.
Figure 4.10: (a): $N^+$ kinetic energy distributions as a function of the delay between the APT generated in Xe and the infrared probe pulse for fragments ejected between 70° and 90° with respect to the laser polarization direction. (b): coefficient weighting the second-order Legendre polynomial plotted as a function of the delay between the APT generated in Ar and the infrared probe pulse. Colour scale shows fragment yield in arbitrary units.

Figure 4.11: Ultrafast oscillations observed in attosecond delay scans with APTs generated in xenon.
These oscillations differ from those described in section 4.2.1 since they occur when the IR and the XUV pulses are overlapped and are visible at lower energy values. In particular, oscillations are present at \( N^+ KER \) values assigned to the vibrational progression of the \( N_2^+ (C^1\Sigma_u^+) \) electronic state. Fig. 4.12 shows the intensity profiles recorded at fixed values of the \( N^+ KER \), plotted as a function of the delay between the attosecond pulse train and the IR pulse.

![Intensity profiles recorded at different values of \( N^+ KER \) as a function of the delay between the APT generated in xenon and the IR probe pulse.](image)

From figure 4.12 it is apparent that oscillations occurring at \( N^+ KER \) values above 0.5 eV are phase-shifted with respect to those taking place at lower energies. The phase shift between the two groups is about 120°. Also for these oscillations, no theoretical explanation is available. A collaboration with Max Born Institut of Berlin has been established in order to investigate the physical processes underlying these oscillatory dynamics. A possible explanation for these ultrafast dynamics may be the interference between different quantum paths. The electronic states involved in the mechanism might be the \( N_2^+ (B\ 1^2\Sigma_u^+) \), the \( N_2^+ (D\ 1^2\Pi_g) \) and the \( N_2^+ (C\ 2^2\Sigma_u^+) \). Their potential energy curves are shown in figure 4.13.

Fragments contributing to the signal of interest seem to derive from the dissociation of the \( D\ 1^2\Pi_g \) state. Figure 4.14 shows two possible quantum paths leading to the population of this state.
Figure 4.13: Potential energy curves of $N_2^+(B \, 1^2 \Sigma_u^+)$, $N_2^+(D \, 1^2 \Pi_g)$ and $N_2^+(C \, 2^2 \Sigma_u^+)$ states. (Taken from [41])

Figure 4.14: Schematic of the mechanism associated with the oscillations observed when the XUV APT generated in xenon is overlapped with the IR probe pulse.
The first one consists of a direct transition, caused by multi-photon absorption. A nitrogen molecule can absorb an XUV photon and be excited to the $N_2^+(B \ 1^2\Sigma_u^+)$ state. If a simultaneous absorption of an IR photon takes place, the electron wavepacket is projected onto the $D \ 1^2\Pi_g$ state. The second quantum path consists of a sequential transition, in which the electron wavepacket is first promoted to the $N_2^+(C \ 2^2\Sigma_u^+)$ state by the absorption of a high-energy XUV photon. After the excitation, the wavepacket starts to evolve along the potential energy curve. If IR radiation is present, it interrupts the process by causing the relaxation of the molecule to the $N_2^+(D1^2\Pi_g)$ state. Therefore, wavepackets following the direct and the sequential pathways can interfere and produce the oscillating dynamics observed in the experimental measurements. The phase shift between oscillations occurring at low and high $N^+KER$ values are due to a phase difference between the interfering electron wavepackets. In particular, this phase difference is acquired by the wavepacket during its evolution along the potential energy curve of the $N_2^+(C \ 2^2\Sigma_u^+)$ state. It is worth noting that the transition from the $N_2$ ground state to the $N_2^+(D \ 1^2\Pi_g)$ state can take place only if XUV and IR photons simultaneously interact with the nitrogen molecule. This means that the transition is allowed only when XUV and IR pulses are overlapped. As a consequence, ultrafast oscillations take place only at zero time delay. This is consistent with experimental results since fig. 4.10 clearly shows that oscillations disappear as the APT and the IR pulse are temporally separated. This differs from the case of dissociation dynamics initiated by APTs generated in argon, which is characterized by ultrafast oscillations starting at $\tau \simeq 7 \text{ fs}$. Indeed, in this case, transitions do not require the co-presence of XUV and IR photons.

### 4.2.3 Fourier analysis

Additional analyses of oscillations reported in fig. 4.7 and fig. 4.11 were carried out in the frequency domain. Figures 4.15 (a) and (b) present 2D Fourier maps of $N^+$ kinetic energy distribution scans obtained by exciting $N_2$ molecules by APTs generated in argon and in xenon, respectively.
Figure 4.15: Fourier transform maps of attosecond delay scans with APTs generated in argon (a) and in xenon (b).

From figure 4.15 (a) it is apparent that, in the case of argon, oscillations at different $N^+KER$ values do not have the same periodicity. Indeed, the frequency signal depends on the value of $N^+KER$. In particular, oscillations occurring at $N^+KER$ values below 1.3 eV are characterized by a frequency of 0.81 $PHz$. This means that the period of oscillation is 1.23 fs. The peak in the frequency signal shifts toward higher values as the $N^+KER$ increases, indicating a decrease in periodicity. For a $N^+KER$ value of 2.5 eV, the period of oscillation becomes 1.04 eV.

On the contrary, if the dissociating dynamics is initiated by APTs generated in xenon, oscillations at zero-time delay have the same periodicity for all $N^+KER$ values. Indeed, fig. 4.15 (b) shows that the peak in the frequency signal does not shift as the value of $N^+KER$ increases.

In this case, oscillations have a frequency of 0.8 $PHz$, corresponding to a periodicity of 1.25 fs, exactly half the period of the electric field of the IR pulse. This periodicity characterizes also the variation of the intensity of sidebands observed in a Reconstruction of Attosecond Beating By Interference of Two-photon Transitions (RABBITT) measurement\(^\text{1}\). Indeed, the mechanism associated with ultrafast oscillations observed in fig. 4.11 is the same as that exploited in the RABBITT technique: the absorption of one XUV photon accompanied by the absorption or stimulated radiation of an

\(^1\)For further details refer to [3]
IR photon (see fig. 4.14).
Conclusions and future perspectives

The work discussed in this thesis described the realization of a high photon flux attosecond source and its exploitation in pump-probe measurements on diatomic molecules. In the first part of the work, various temporal gating techniques have been analyzed in order to confine the harmonic generation process to a single event (generation of isolated attosecond pulses) or to a pair of events. In particular, the design of the optical setup required for the implementation of three different gating techniques (namely polarization gating (PG), double optical gating (DOG) and generalized double optical gating (GDOG)) has been performed. Numerical results obtained from simulations allowed the optimization of the attosecond source. Isolated pulses with a temporal duration of 200 as were generated and completely characterized. Ultrashort attosecond pulse trains were used to photoexcite and photoionize nitrogen molecules and the subsequent relaxation dynamics was probed by means of a femtosecond IR pulse. The experimental results demonstrated the possibility to observe and control the ultrafast electron dynamics occurring in photoexcited and photoionized diatomic molecules on a sub-femtosecond timescale. In particular, these measurements revealed the presence of ultrafast oscillatory dynamics due to quantum interference between different dissociation paths. An accurate description of physical mechanisms underlying these ultrafast phenomena can be developed only by taking into account complex electron correlation effects. In order to improve the temporal resolution, time-resolved experiments will be carried out by using isolated
attosecond pulses instead of attosecond pulse trains.

The reported pump-probe technique can be applied even to complex molecules of biological and pharmacological interest. Preliminary results have been obtained on the amminoacid phenylalanine [6], thus indicating the possibility to extend these spectroscopy techniques to the biological field.
Bibliography


Giunta la termine della stesura della tesi, desidero ringraziare tutti coloro che hanno contribuito alla realizzazione di questo lavoro.

Vorrei ringraziare innanzitutto il Prof. Mauro Nisoli, relatore di questo lavoro di tesi magistrale, per avermi dato la possibilità di svolgere l’attività di laboratorio presso il Dipartimento di Fisica e per avermi guidato con pazienza e cordialità fino alla stesura finale della tesi.

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