

Harnessing
Attosecond Pulse Generation
for applications in spectroscopy of optoelectronics molecules



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Harnessing Attosecond Pulse Generation for applications in spectroscopy of optoelectronics molecules

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*Everyone in academia is smart.
Distinguish yourself for being nice.*

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Chapter 1

Introduction

Time is an extraordinary concept, elusive but yet so familiar and noticeable. Time is an unyielding clock, driving the change and leading the course of all things.

In our macroscopic reality, time manifests itself through motion. The Earth's motion around the Sun dictates the cycles of seasons, while its rotation demarcates the division between days and nights. Even the cadence of our heartbeat functions as a metronome, directing the grand musical symphonies and the quieter rhythms of our existence. It is through this beating that we crafted our own unit for measuring time: the second (1 s). As the dimensions of the system scale down, the ticking of reality speeds up. The capability of moving massive amounts of information and sharing images and data across the globe is possible thanks to tiny master clocks embedded in every microprocessor, whose beating occurs one billionth time faster than ours on the nanosecond time scale ($1 \text{ ns} = 10^{-9} \text{ s}$). As we descend deeper into the microscopic realm, to the size of molecules and atoms, the rules of Physics become fuzzy and bizarre. At this level, the ticking of time is defined by the motion of electrons. These electrons operate on incredibly fast timescales, ranging from femtoseconds ($1 \text{ fs} = 10^{-15} \text{ s}$) to attoseconds ($1 \text{ as} = 10^{-18} \text{ s}$).

This ultrafast beating is the playground of quantum mechanics.

Driving tiny currents through doped-silica circuits on the nanosecond (ns) scale has been a game-changer for our technology today. Looking forward, the ability to control electrons on ultrashort time scales is establishing the foundation of new and exciting quantum mechanics-driven technologies [1].

Just like in basic engineering theory, in order to control a system, we need, first, to understand how it works, and we need to find ways to track its time evolution. Thus, as a key step, it is paramount to create reliable tools that enable precise measurements of the femtosecond/attosecond ultrafast process of interest [2].

I.1 Measuring a time-dependent process in quantum mechanics: fundamentals of pump-probe spectroscopy

How to measure a time-dependent process in quantum mechanics?

In the context of textbook quantum physics, "time" is not a measurable quantity [3]. A quantum system can be described using the bra-ket representation of the wavefunction $|\Psi(t)\rangle$. The evolution of a non-relativistic wavefunction is described by the Schrödinger equation, here written in atomic units:

$$i\partial_t |\Psi\rangle = \hat{H} |\Psi\rangle \quad (\text{I.1})$$

The Hamiltonian operator, denoted by $\hat{H}$, encapsulates the entire physics of the system physics and carries information on its energy.

An isolated and stationary system is characterized by a time-independent Hamiltonian $\hat{H} = \hat{H}_0$. In this scenario, it is possible to find a complete and orthonormal set of states, called eigenstates $|\phi_j\rangle$ that satisfies the following equation:

$$\hat{H}_0 |\phi_j\rangle = \epsilon_j |\phi_j\rangle \quad (\text{I.2})$$

In this scenario, the generic solution of Eq. (I.1) can be written as a superposition of all the eigenstates multiplied by a proper phase factor:

$$|\Psi(t)\rangle = \sum_n a_n |\phi_n\rangle e^{-i\epsilon_n t} + \int_\delta a(\delta) |\phi_\delta\rangle e^{-i\epsilon(\delta)t} d\delta \quad (\text{I.3})$$

where $|\phi_n\rangle$ is a discrete basis set defined over the index n , with a_n being the individual weight of the eigenstate, and $|\phi_\delta\rangle$ is a continuous basis set defined over the continuous index δ , with $a(\delta)$ being the associated weight. As also shown in Eq. [I.2], each eigenstate is correlated to a specific eigenvalue, either $\epsilon(\delta)$ or ϵ_n , representing its energy. To observe actual changes¹ in the wavefunction $|\Psi(t)\rangle$ over time, a superposition of at least two states is necessary. The simplest example of such a time-varying system is a Hydrogen atom electron in a superposition between the 1s, $|1s\rangle$, and 2p, $|2p\rangle$ states [4].

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} |1s\rangle e^{-i\epsilon_{1s}t} + \frac{1}{\sqrt{2}} |2p\rangle e^{-i\epsilon_{2p}t} \quad (\text{I.4})$$

As shown in Fig. I.1, we can calculate the probability distribution of $|\psi(t)\rangle$ in the cartesian space, identified by the vector $\mathbf{r}$, as: $|\langle \mathbf{r} | \psi \rangle|^2 = |\psi(\mathbf{r}, t)|^2$. As "time" progresses, due to the overlapping of two distinct energy levels, the electronic distribution will oscillate as:

$$|\psi(\mathbf{r}, t)|^2 \propto \cos((\epsilon_{2p} - \epsilon_{1s})t) \quad (\text{I.5})$$

¹i.e., not purely phase changes

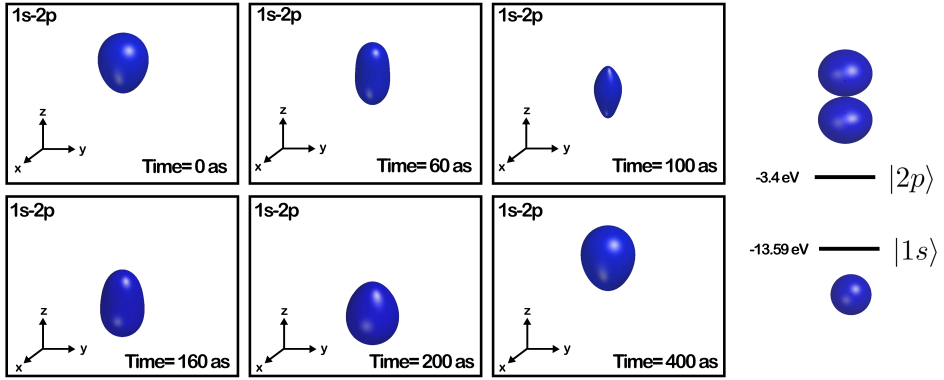


Figure 1.1: Representation of the iso-probabilistic surface of $|\langle r|\psi\rangle|^2 = |\psi(r, t)|^2$ for the superposition of 1s and 2p orbitals in an hydrogen atom. The different surfaces are reported for different times, showing a periodicity of about 400 as

Since for Hydrogen, $\Delta\epsilon = \epsilon_{2p} - \epsilon_{1s} \approx 0.367 \text{ a.u.}$ (10 eV), the period of this oscillation is about 400 as. This is a very elementary example showing how the natural timescale of a basic electronic motion in matter is the attosecond.

The dynamics of the wavefunction depicted in the previous case can produce tangible physical effects, such as spontaneous emission. Yet, in this context, "time", t , is largely insignificant because in an isolated system ² the initial point of this oscillation is completely undefined. Therefore, in this scenario, directly tracking the electronic motion is not only unfeasible but also an ill-posed task.

To re-introduce the concept of time and measure dynamics, an event defining a starting point of "time" is necessary; in other terms, a trigger that interacts with the system and initiates motion is required. This object, which is commonly referred to as "pump", is describable as an additional time-dependent Hamiltonian, denoted as $\hat{H}_I(t)$. In this new case, the total Hamiltonian can be written as $\hat{H} = \hat{H}_0 + \hat{H}_I(t)$. Since the eigenstates of the unperturbed system are still a complete basis set, the generic solution of Eq. 1.1 can still be written as:

$$|\Psi(t)\rangle = \sum_n a_n(t) |\phi_n\rangle e^{-i\epsilon_n t} + \int_\delta a(\delta, t) |\phi_\delta\rangle e^{-i\epsilon(\delta)t} d\delta \quad (1.6)$$

In this new framework, however, the eigenstates weights must exhibit time-dependence. This behaviour highlights the key role of the interaction Hamiltonian, which enables energy transfer between different states ³. At this point, the final objective is to solve

²The origin of spontaneous emission is, as well known, stochastic fluctuation of the electromagnetic vacuum. Therefore, our "strict" isolated system hypothesis and argument are a bit inadequate. For simplicity, I will avoid going into details. For clarity on this matter, see [5].

³In this context, even if H_I cannot be considered as a perturbation, we are assuming that the concept of the individual state of the system is still to some extent meaningful.

Eq. (1.1) and find the dynamics of these weights. Nevertheless, deriving an exact solution for this equation is a great challenge, and in many instances, it is even impossible. Consequently, as discussed in Appendix A, using advanced methodologies or clever approximations becomes essential.

To generally address equation (1.1) in this new scenario, it is necessary to introduce the so-called propagator formalism, as presented in [3]. In this regard, let us define an initial wavefunction, $|\psi(t_0)\rangle$. Then, we can express the evolution of the quantum system at subsequent times t as:

$$|\psi(t)\rangle = e^{-i \int_{t_0}^t \hat{H} dt'} |\psi(t_0)\rangle \quad (1.7)$$

where the operator $e^{-i \int_{t_0}^t \hat{H} dt'}$ is called time-propagator, or, simply, propagator.

In the most simple scenario, the Hamiltonian is equal to the isolated one, $\hat{H} = \hat{H}_0$, and the initial state at t_0 is equal to one of its eigenstates, $|\psi(t_0)\rangle = |\phi_j\rangle$, then, we have:

$$|\psi(t)\rangle = e^{-i \int_{t_0}^t \hat{H}_0 dt'} |\phi_j\rangle = e^{-i \epsilon_j (t-t_0)} |\phi_j\rangle \quad (1.8)$$

this result perfectly reconciles with the discussed picture of Eq. (1.3).

By exploiting this powerful method, see Appendix A.2 and Chapter 2, we can rewrite equation (1.7) more advantageously[6] as:

$$|\psi(t)\rangle = \left(-i \int_{t_0}^t e^{-i \int_{t'}^t \hat{H}(t'') dt''} \hat{H}_I(t') e^{-i \int_{t_0}^{t'} \hat{H}_0(t'') dt''} dt' + e^{-i \int_{t_0}^t \hat{H}_0(t'') dt''} \right) |\psi(t_0)\rangle \quad (1.9)$$

As discussed in [7] and sketch in Fig. 1.2, despite the apparent higher degree of complexity, Eq. (1.9) has, now, a straightforward meaning. Focusing on the left-hand side operator of Eq. (1.9), the system initially evolves without any external interaction, following the simplest time-propagator $e^{-i \int_{t_0}^{t'} \hat{H}_0(t'') dt''}$. At a specific moment, t' , the wavefunction interacts with our pump event, $\hat{H}_I(t')$. This interaction, depicted as a black dotted line in Fig. 1.2, serves as an 'instantaneous kick', after which the system progresses to the final time t under the influence of the full-propagator governed by the Hamiltonian $\hat{H}$. It is important to note that when the pump is restricted to a specific time window, the full propagator reverts to its unperturbed state once the interaction concludes; under this condition, it is justified the use of the unperturbed basis-set to describe the whole system dynamics and the energy transfer.

The mechanism described above is feasible at any given t' , within the temporal window in which the pump can act on the system. This picture allows us to interpret quantum mechanics following the path-integral formalism, as conceptualized by Feynman[8]. Following this vision, all the possible interaction instants are simultaneously possible, and their interference shapes the time evolution of the quantum system. Finally, the term on the right-hand side of Eq. (1.9) represents scenarios

where the system remains unaffected by the interaction, depicted as the continuous grey line in the figure. Equation (1.9) is called the second Dyson equation, and it inscribes the whole physics of a time-varying quantum system[3, 6].

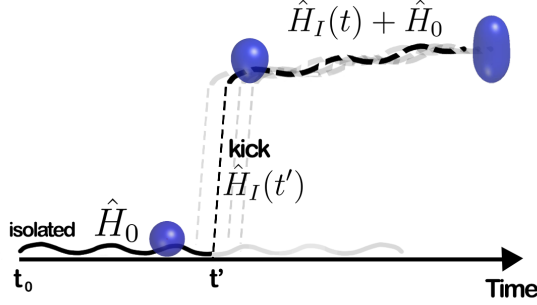


Figure 1.2: Sketch of the evolution of the quantum system, $|\psi(t)\rangle$, in the presence of a time-dependent Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_I(t)$, as in Eq. (1.9).

Figure 1.2 and, consequently, Eq. (1.9), pinpoint the role of the interaction Hamiltonian as a "pump-event", especially if it is temporally confined. Within the temporal window of its action, the pump Hamiltonian triggers a physical change in the system and its properties. For example, let us consider a generic hermitian operator $\hat{O}$, linked to a specific physical observable. As shown in Fig. 1.3, O_0 is the sub-space of possible outcomes for when measuring $\hat{O}$ on the initial unperturbed initial state $|\psi(t_0)\rangle$. In the simplest scenario, where $|\psi(t_0)\rangle$ is also an eigenstate of $\hat{O}$, we have:

$$\hat{O} |\psi(t_0)\rangle = o_0 |\psi(t_0)\rangle \quad (1.10)$$

As shown in Fig. 1.3 a), the interaction of the quantum system with the pump event leads to a significant alteration in its phase space, initiating specific dynamics of the physical observable $\hat{O}$.

Throughout its evolution, at each time point t , the system can produce varying outcomes upon measurement of the observable $\hat{O}$. However, due to the extremely rapid timescale of these dynamics, tracking the observable in real-time is not feasible. As a result, the measurement of our physical observable is practically confined to much later times, ideally as t approaches macroscopic time-scales ($t \rightarrow \infty$). This limitation confines the potential outcomes of the measurement to the final sub-space O_p , reached by the wavefunction at the end of its evolution. In the simplified picture, the measurement of the state $|\psi(t \rightarrow \infty)\rangle$ is thus represented as:

$$\hat{O} |\psi(t \rightarrow \infty)\rangle = o_P |\psi(t \rightarrow \infty)\rangle \quad (1.11)$$

Even with a proper time-axis for our quantum system, defined by a trigger-like event, the ultrafast evolution from O_0 to O_p remains elusive, covered by the integral in Eq.

(1.9) extended to $t \rightarrow \infty$. To investigate any ultrafast dynamics, we must introduce a second time-dependent element, a 'probe', which interacts with the system at a delayed time with respect to the pump event, expressed as:

$$\hat{H} = \hat{H}_0 + \hat{H}_{I_{pump}}(t) + \hat{H}_{I_{probe}}(t - \tau) \quad (1.12)$$

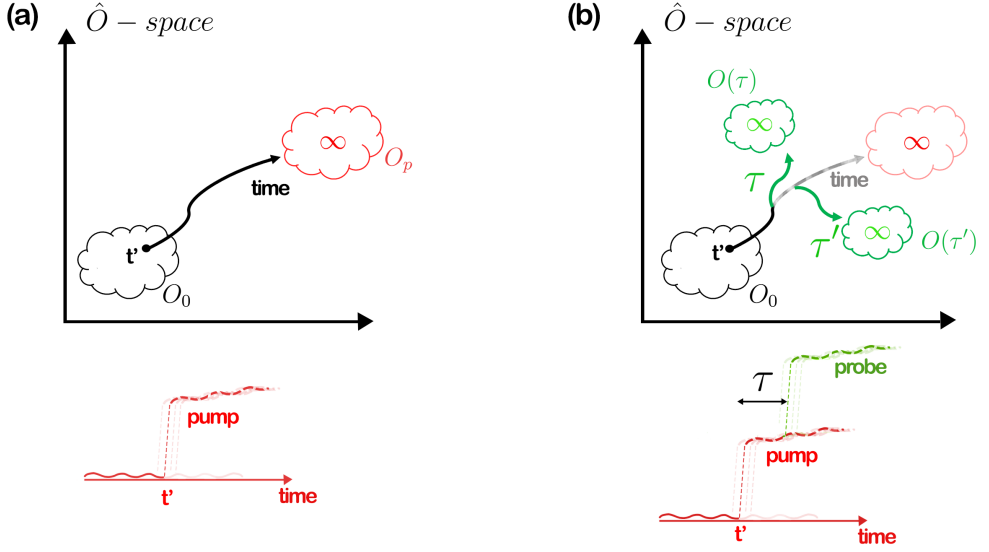


Figure 1.3: The diagram provides a visual explanation of a pump-probe experiment in quantum mechanics. a) a pump event, shown in red, triggers a specific physical process within the system. This event influences the dynamics of a particular physical observable $\hat{O}$. As a result, the observable transitions from an initial set of possible measurement outcomes, labelled O_0 , to a final set, denoted as O_P . b) after the introduction of a probe event, depicted in green, the final outcomes of the measurements related to the physical observable $\hat{O}$ are modified. The results, represented as $O(\tau)$, vary depending on the time delay, τ , between the pump and probe events. By employing the appropriate theoretical frameworks and by experimentally measuring $O(\tau)$ for different delays, we can effectively reconstruct the actual temporal evolution of the quantum system $|\Psi(t)\rangle$, gaining an understanding of its ultrafast response.

Figure 1.3 b) shows how the probe can impact the evolution of the quantum system, more specifically, how the probe modifies the behaviour of one of the system properties, $\hat{O}$. The timing between the probe event and the peculiar position of the system in the parameter space of the system plays a crucial role; specifically, by adjusting the delay, τ , between the pump and probe, we can change the final outcome of the measurement of the physical observable at $t \rightarrow \infty$. In the simple picture:

$$\hat{O} |\psi(t \rightarrow \infty, \tau)\rangle = o(\tau) |\psi(t \rightarrow \infty, \tau)\rangle \quad (1.13)$$

As discussed, directly accessing real-time phenomena in quantum mechanics is generally not possible. However, in an experiment, we can measure changes in a specific

physical observable, $o(\tau)$, as a function of a delay between two events. These events are the 'pump', which initiates the process, and the 'probe', which captures the system's evolution, imprinting the information onto an observable, still measured long after the event has occurred ($t \rightarrow \infty$). By conducting multiple experiments with different delays, we can ultimately decode the ultrafast dynamics. This idea is the foundation of the branch of Science called ultrafast spectroscopy, where ultrafast processes in nature are investigated from picosecond [9], femtosecond [10, 11] down to the attosecond [2, 12, 13, 14] time-scales.

As will be discussed later, the nature of the probe and the choice of the observable dictate the type of experiment and the theoretical framework required to interpret results and to access the temporal dynamics. Moreover, as highlighted by this discussion and by Eq. (1.9), to capture the time evolution of a quantum system, both the pump and probe events must be shorter than the process under investigation. Since electronic motion in matter occurs in the femtosecond/attosecond domain, bursts of electromagnetic radiation in the attosecond range are ideal candidates for pumping/probing these ultrafast dynamics of interest.

1.2 Attosecond pulses and electron dynamics in matter

Thanks to the advent of chirp-pulsed amplification[15], pulse compression and post-compression techniques[16, 17], and the great advancement of laser technologies, it is possible to generate intense femtosecond laser pulses in a reproducible manner.

When these intense femtosecond laser fields are focused on a noble gas target, a highly non-linear mechanism can lead to the generation of multiple-odd harmonics of the fundamental laser frequency. As sketched in Fig. 1.4a), this harmonic spectrum is characterized by a plateau region of harmonics and a cut-off extending into the extreme-ultraviolet (XUV) region [18]. Discovered in the late 1980s, this process, called High-order Harmonic Generation (HHG), forms the cornerstone for the creation of attosecond pulses [19, 20, 21].

In essence, as sketched in Fig 1.4b), generating attosecond pulses requires focusing ultrashort laser pulses, lasting from a few to hundreds of femtoseconds, into a gas medium, usually a noble gas. If the driving laser reaches intensities ranging from $10^{13} - 10^{16} \text{ W/cm}^2$, the Coulomb potential affecting the outer electron is significantly distorted, creating a potential barrier that allows the electron to tunnel through. This tunnel ionization is most likely to occur near the peaks of the driving electric field; hence, this process is localized within a specific time window. After ionization, the electron moves in the electromagnetic field, gaining substantial kinetic energy. With linearly polarized driving pulses, there is a slight chance that the electron will return to its parent ion and radiatively recombine, releasing its kinetic energy as an ultra-short light burst. The maximum kinetic energy these electrons can accumulate is directly proportional to the peak intensity and the square of the central wavelength of the

driving pulses ($E_{max} \propto \lambda^2 I_0$). As a result, under the right conditions, the spectrum of the emitted radiation can extend from the extreme ultraviolet into the soft-x-ray energy region. Since these processes occur every half-optical cycle of the driving laser field ($\approx 1\text{ fs}$ when $\lambda = 800\text{ nm}$, in the infrared (IR)) and are confined to a temporal window shorter than the half-optical cycle itself, a train of attosecond pulses is produced. This simplified picture, known as the three-step model [22, 23], enabled the scientific community to gain a fundamental understanding of the HHG process. As discussed in Chapter 2 e 3, it also laid the groundwork for proposing simple models that provide straightforward hints on how to engineer this process.

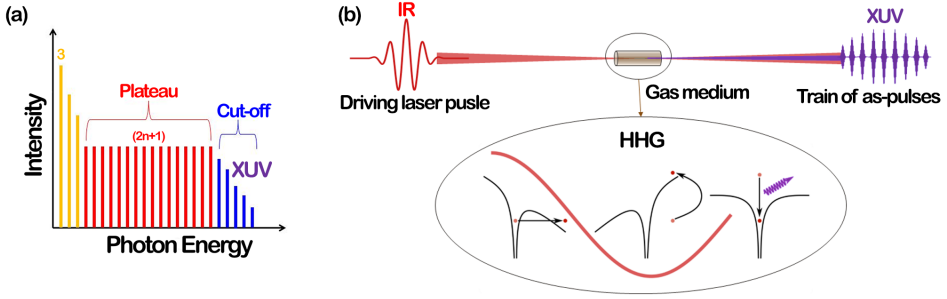


Figure 1.4: a) Spectrum generated by HHG in noble gas target b) Sketch of the three-step model mechanism at the basis of HHG. When an intense femtosecond laser pulse, in the infrared spectral region (IR), here called driving laser pulse, is focused on a gas medium, commonly a noble atom. The electron propagates in the continuum after tunnel ionization from its parent ion. When the electron recollides with the parent ion, every half-optical cycle, the extra kinetic energy accumulated during this journey can be emitted in the form of XUV radiation.

In 2001, the first pulse train of attosecond pulse, with each pulse lasting 250 attoseconds, was measured for the first time[24].

For several applications, isolated attosecond pulses are typically required; therefore, since the discovery of the HHG, great efforts have been invested to test and develop techniques to limit harmonic generation to a single event. As discussed in depth in the following chapters, the proposed techniques are primarily based on either the spectral selection of cutoff harmonics, temporal gating methods applied on the driving radiation, or a combination of both [25, 26].

Thanks to a collaboration between atomic physicists and laser scientists, already in the same year as the first measurement of the attosecond pulse train, a single pulse, showing a duration of 650 attoseconds, was isolated and characterized[27]. These two achievements marked the birth of the field of attosecond science[13].

Nowadays, the record for the shortest attosecond pulse amounts to 43 as [28], while the highest photon energy achieved is in the soft-x-ray, in the keV range[29]. Although gas-based high-order harmonics generation is still the most adopted technology for attosecond science, over the past two decades, ultrashort XUV pulses have also been generated using different media, including solids[30], liquids[31] and

plasma mirrors[32], as well as by employing different physical principle as in x-ray free-electron lasers (XFELs)[33]. Despite having significant interest and great potential, these methods are not the focus of this thesis.

Once the tools to generate attosecond radiation were available to a larger community, many experimental techniques were invented to use these pulses for measuring ultrafast processes occurring at time scales comparable to the duration of the pulse itself.

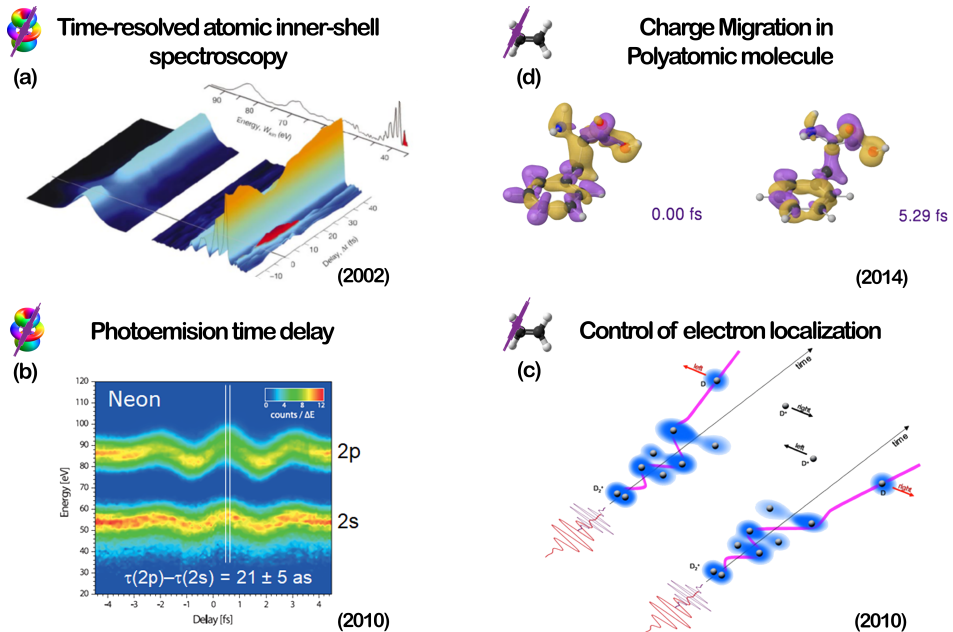


Figure 1.5: Example of physical processes observed thanks to attosecond technology in atoms and molecules: a) Auger decay in Krypton [34]. b) Photoemission time delay in Neon [35]. c) Charge Migration in Phenylalanine [36]. d) Control of electron localization in molecular hydrogen (H_2) and D_2 [37].

As sketched in Fig. 1.5, the advent of attosecond pulses opened up several unexplored research domains, enabling the "direct" observation⁴ and potential manipulation of electronic motion in atoms, molecules, liquids and solids.

The very first example of the application of attosecond pulses in matter was the measurement of a few-fs Auger decay in core-excited krypton (Kr) atoms [34] in 2002 (Fig. 1.4 a)). Since then, even more rapid phenomena have been investigated, such as the time delay in photoemission between different states of an atomic target. One of the first experiments on this topic was the investigation of the 2s-2p photoemission delay difference in neon (Ne), measured to be in the tens of attoseconds [35, 38]

⁴where here the word "direct" has the subtle meaning discussed in section 1.1.

(Fig. 1.4 b)). As attosecond technology advanced, the atomic physics community began exploring increasingly complex multielectron processes. This line of research has unveiled intriguing insights into phenomena such as autoionization [39], multichannel ionization [40], Fano resonances [41], up to the reconstruction of the quantum state and decoherence of photoelectron wavepackets [42, 43].

In 2010, the first attosecond experiment in molecules (H_2) was carried out (Fig. 1.4 c)), revealing the capability of controlling the localization of the electron in a dissociating hydrogen molecule on a few-fs time-scale [37]. A few years later, in 2014, the first observation of the charge migration process in a polyatomic molecule, phenylalanine, was obtained with a time-resolution of 250-as, showing ultrafast oscillation of the electronic charge in the molecule with a periodicity of about 4-fs [36] (Fig. 1.4 d)). Since then, the intricate interplay between electronic motion and subsequent nuclear responses has been extensively examined, paving the way to many new interesting avenues of research. A recent example highlighting this interplay is the revival of charge oscillation in silane (SiH_4), measured in 2022 [44]. The observed oscillations and coherent revival in the dynamics were attributed to a combination of adiabatic (purely electronic) and non-adiabatic (involving both electrons and nuclei) dynamics within the molecule excited states. A detailed discussion of the latest advancements in attosecond molecular physics and attosecond chemistry will be presented in the following section.

In recent years, attosecond techniques have also been applied to solids and liquids, yielding promising discoveries. In the case of solids, studies focusing on electron transport and band structure dynamics in insulators [45] and semiconductors [46, 47, 48] have been conducted, leading to a better understanding of inter- and intra- bands dynamics and advancing the control of ultrafast excitons, which could potentially redefine the speed limits of electronics [49]. For liquids, attosecond pulses have played a pivotal role in exploring the impact of a chemical environment on ultrafast electron dynamics. For instance, the photoemission time delay has been recently investigated in water [50] and ultrafast proton transfers have been observed in urea [51], deepening our comprehension on the influence of aqueous solution on electronic reactivity and chemical reactions. Applying attosecond technology in these areas will provide critical insights into the physics of complex systems in the future.

1.3 Applications of attosecond pulses to molecular physics: the birth of attochemistry

Since its early development, Physics has relied on studying prototypical systems to deduce fundamental information about the building blocks of reality.

While the study and control of complex systems are increasingly important, simple systems like atoms or small molecules, with just a few atoms, remain crucial for both

experimentalists and theoreticians. These simpler systems provide valuable insights into basic processes, such as matter-matter interaction (e.g. chemical reactivity) and light-matter interaction. Generally speaking, the long-term goal of these studies is to extend the knowledge acquired on the simple system to more complex ones, an approach traditionally closer to Chemistry. In essence, Chemistry begins when we use simplified models or approximations to explain a certain physical process, which, in its full complexity, would demand a computationally challenging, or even unfeasible, theoretical description.

Attosecond molecular physics and attosecond chemistry, or attochemistry, have focused on investigating electron-driven dynamics in molecules, where the interaction between the electronic degree of freedom and the ultrashort pulse guides, on a longer time scale, the nuclear rearrangement and determines the fate of the chemical reactivity [52]. Once the underlying physics of a particular photo-chemical process is fundamentally understood, the primary objective of attochemistry is to establish robust guidelines for optimizing the design of more advanced molecular systems or even to directly manipulate electron dynamics in a more natural environment, i.e. controlling chemical reactivity in solutions [53]. Numerous fundamental physical questions remain to be addressed to advance in this emerging field, which is still in its infancy. This necessity is coupled with the ongoing need to enhance both experimental and theoretical methodologies [2].

At the boundaries between attosecond molecular physics and attochemistry lies the investigation of the response to light of isolated molecules, i.e. molecules in the gas phase, where core light-matter interaction processes can still be studied in their simplest form, even if several approximations on their theoretical description are needed. In this framework, the most interesting and studied ones are charge migration and charge transfer [54].

1.3.1 Charge Migration and Charge Transfer in Molecules

The redistribution of charge within molecular systems is one of the most important photoinduced primary events, crucial in both chemical and biological systems, and pivotal in driving energy transfer [55]. The capability to precisely measure and control the core mechanisms responsible for charge transfer at their natural time scale is key to enhancing energy conversion in various applications. This research holds significant promise in developing more selective catalysts, improving energy storage solutions, and advancing photovoltaic or photosynthetic systems [56].

The theory of charge transfer was originally introduced in 1956 [57, 58] and later awarded with the Nobel Prize in Chemistry in 1992 [59]. This theory provides a framework for understanding how an electron can permanently move from one chemical site of the molecular system to another. While it has been successful in explaining various types of charge transfer in both organic and inorganic compounds, including

intermolecular and intramolecular processes, its initial development was limited to the classical domain. This limitation was due to the availability of only nanosecond pulses at that time, restricting the theory to thermodynamics and classical electromagnetism concepts.

The emergence of femtochemistry [10] and attosecond science has revolutionized our understanding of molecular processes, enhancing time resolution by nearly six orders of magnitude (10^6). This advancement allows for an in-depth exploration of these processes at the quantum level. Nowadays, the spatial redistribution of charge in a molecule is categorized into two distinct concepts: charge migration and charge transfer. This convention, as outlined in prior studies [54, 60], defines *charge migration* (CM) as a purely electronic phenomenon driven by the electronic coherence of superposed states. Whereas *charge transfer* (CT) is associated with the motion of electronic charge coupled to nuclear re-arrangement and ultimately results in a permanent transfer of charge.

Charge Migration and Electronic Coherence

Before the introduction of attosecond pulses in molecular spectroscopy, research on the fragmentation of small peptides raised an interesting query: *What causes peptides to dissociate at molecular sites distant from the initial ionization point?* [61]. This question stimulated extensive theoretical research [60, 62] on the existence of purely electronic processes occurring before any nuclear rearrangement. Such behaviour was attributed to an ultrafast, entirely electronic charge redistribution within the ionized species. This process, driven by electron correlation and maintained by coherence among various electronic states, was named charge migration.

As exemplified in Fig. 1.6, for the case of a hydrogen molecular ion (H_2^+), CM occurs when a coherent superposition of two (or more, in some cases) states is created. In our simple scenario, we assume a coherent superposition of the π and π^* orbitals of H_2^+ in a fixed-nuclei configuration, and we observe its evolution:

$$|\Psi_{H_2}\rangle = c_\pi |\psi_\pi\rangle e^{-i\epsilon_\pi t} + c_{\pi^*} |\psi_{\pi^*}^*\rangle e^{-i\epsilon_{\pi^*} t} \quad (1.14)$$

$$|\Psi_{H_2}(\mathbf{r}, t)|^2 \propto \text{Re}\{c_\pi c_{\pi^*}^* \psi_\pi \psi_{\pi^*}^* e^{i(\epsilon_\pi - \epsilon_{\pi^*})t}\} \quad (1.15)$$

If any nuclear motion is neglected, the superposition leads to a periodic (≈ 300 as) charge motion between the two hydrogen nuclei.

From this basic example, several key insights about charge migration can be deduced:

- i) CM is intrinsically periodic. Since nuclear motion has not yet occurred, the electronic states remain unchanged, allowing for free charge oscillation across the molecular system.
- ii) CM occurs exclusively when the orbitals are coherently populated, necessitating a wavefunction with clearly defined and balanced weights, c_π and c_{π^*} in Eq.(1.15).
- iii) The electronic states involved must exhibit spatial overlap, i.e. the

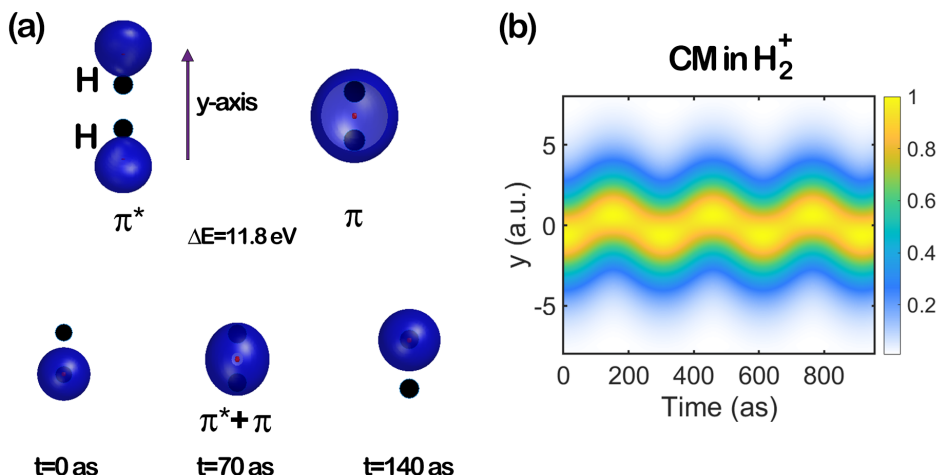


Figure 1.6: a) 2D visualization of the anti-bonding, π^* , and bonding, π , orbitals isosurfaces (at 0.99, red and 0.75, blue) in H_2^+ , calculated as a linear combination of hydrogen-like atomic orbitals. The energy distance between levels is estimated to be ≈ 11.8 eV. A coherent superposition of these states is simulated in the lower part of the figure, showing a periodic charge migration process between the two protons. b) Projection of the normalized probability distribution of the wavefunction (Eq. (1.15)) across the y-axis as a function of time during the charge migration.

product $\psi_\pi \psi_{\pi^*}$ is nonzero.

Due to these specific requirements, the experimental observation of charge migration took several years after its theoretical prediction. The first empirical evidence was obtained in 2014 with the detection of a 4-fs CM in phenylalanine [36], followed by the observation of a 2-fs CM in iodoacetylene in 2015 [63].

Two major challenges in these experiments are to select the appropriate pump-pulse, which starts the coherent superposition of states, and a physical observable that grants sub-femtosecond resolution. As a result, the preferred methods for tracking CM in molecules have been either isolated attosecond pulses [36, 64, 65] or short intense infrared pulses [44, 63]. Due to the nature of the pump pulses, the main focus of the community has been CM in ionized molecules. However, recent studies have also highlighted the feasibility of investigating CM in neutral species [66].

Another significant challenge in observing CM is decoherence (and/or dephasing), typically caused by nuclear motion [44, 67, 68], which often begins after just a few-fs. As a result, charge migration is often expected to gradually weaken as nuclear motion intensifies. However, it is interesting to note that under certain conditions, if coherence is sustained sufficiently long, one might observe a damped yet coherent revival of CM following the initial dephasing [44].

As nuclear rearrangement occurs, the electronic wavepacket may encounter a conical intersection [69], defined as regions on the molecular potential energy surface where two electronic states intersect at a point. In the vicinity of this singularity, electron dynamics decelerate to the femtosecond scale, facilitating a permanent en-

ergy exchange between states. This process can lead to a permanent redistribution of charge, which might also eventually cause molecular dissociation [70].

Thus, both nuclear motion and the permanent transfer of energy between electronic states play pivotal roles in linking charge migration with the crucial subsequent process of charge transfer.

Charge Transfer and Ultrafast Dynamics

Charge transfer, a fundamental process observed across various systems regardless of their size or nature, necessitates two key components: a donor site, with an electronic reservoir, and an acceptor site, where the electrons are pulled towards [54]. This movement of charge is typically triggered by excitation or ionization (i.e. removal of an electron). Following the trigger, the electronic charge is moved from the donor to the acceptor, where it is either stored or leads to molecular fragmentation. The diversity of charge transfer phenomena is shaped by the chemical characteristics of the donor and acceptor groups, as well as by factors such as the system size and its molecular environment. This variety in charge transfer types captures the interest of various interdisciplinary scientific communities, each focusing on different aspects and implications of these phenomena.

Intramolecular charge transfer (ICT) is the most basic example, where charge transfer is mostly defined by short-time-scale dynamics as the molecule typically evolves, after excitation/ionization, in the proximity of conical intersections, leading to rapid energy exchange. The study of ICT set the basis of molecular optoelectronics (e.g. molecular nano-wires)[71], fast electro-optical switches and photovoltaics [72].

Another example is the study of metal-to-ligand charge transfer (MLCT) in metal complexes [73]. In MLCT, excitation typically transfers an electron from an orbit primarily localized on a metal center to one primarily localized on a ligand. The absorption of light stimulates the transition of an electron from the metal d-orbital (the donor) to the ligand π^* orbital (the acceptor), creating an excited state where electron density shifts towards the ligand. This phenomenon plays a crucial role in photovoltaic applications [74], e.g. it can be used as the driving mechanism for charge injection in nanoparticles [75]. Conversely, the opposite process is also possible. In ligand-to-metal charge transfer (LMCT), the ligand acts as the donor and the metal center as the acceptor. LMCT mechanisms have important consequences in applications such as photo-catalysis[76].

As the system grows in size, intermolecular charge transfer in the presence of solvents, intermolecular charge transfer in proteins and photo-catalytic compounds also becomes possible and is the main line of research bridging the information gathered with ultrashort time-resolution with real-life applications [56, 77, 78].

In the following discussion, I will focus on ICT (CT, for simplicity) in isolated molec-

ular systems. In quantum mechanics, a molecule is a non-trivial entity [79]. The molecular wavefunction, within the Born-Oppenheimer approximation, can be expressed as:

$$|\Psi\rangle = |\psi_e(\mathbf{R}, \mathbf{r})\rangle \otimes |\chi_N(\mathbf{R})\rangle \quad (1.16)$$

where $|\psi_e(\mathbf{R}, \mathbf{r})\rangle$ is the electronic wavefunction, defined by the particular nuclear geometry $\{\mathbf{R}\}$, and $|\chi_N(\mathbf{R})\rangle$ is the nuclear wavefunction.

This approach facilitates the formulation of potential energy surfaces, $E(\mathbf{R})$, derived by solving the equation below for all possible electronic states at a given nuclear configuration (assuming fixed nuclei):

$$\hat{H}_{el} |\psi_e(\mathbf{R}, \mathbf{r})\rangle = E(\mathbf{R}) |\psi_e(\mathbf{R}, \mathbf{r})\rangle \quad (1.17)$$

In this context, $\hat{H}_{el}$ is the electronic Hamiltonian, accounting for all the interactions such as electron-nuclei and electron-electron, excluding the nuclei kinetic energy.

$E(\mathbf{R})$ is a multi-dimensional surface which can be described as a function of all the possible reaction coordinates ($\{q\}$), which essentially are linear combinations of the nuclei positions $\{\mathbf{R}\}$.

As sketched in Fig. 1.7a), the most basic molecular system suitable for charge transfer can be conceived as two offset parabolic curves (U_D and U_A) along a certain reaction coordinate, q .

In its most basic physical interpretation, see [55]; charge transfer is encoded in the transition rate of an initial molecular population, $P_D(t)$, from the donor electronic state(s) $|\psi_e(\mathbf{q}_D, \mathbf{r})\rangle_D$ to an acceptor state(s) $|\psi_e(\mathbf{q}_A, \mathbf{r})\rangle_A$. This transition represents the depletion of $P_D(t)$ describable using a rate equation:

$$\partial_t P_D(t) = -k_{CT} P_D(t) \quad (1.18)$$

where k_{CT} is the charge transfer rate.

Determining k_{CT} is a complex task. Nevertheless, under certain assumptions: i) the charge transfer initiates from the potential minimum of U_D , ii) U_D and U_A share the same vibrational frequency (ω_{vib}) and iii) the vibrational states follow a Maxwell-Boltzmann distribution, an analytical formula can be derived [55]:

$$k_{CT} \propto e^{-\frac{E_\lambda}{4k_B T} (1 - \frac{\Delta E}{E_\lambda})^2} \quad (1.19)$$

Here, as depicted in Fig. 1.7a), ΔE is the energy gap between the two minima⁵, and $E_\lambda = \frac{1}{2}\omega_{vib}(q_A - q_D)^2$ is the reorganization energy. Equation (1.19), which emerges from quantum mechanical principles[55], coincides with what the more intuitive chemical derivation followed in 1959[58].

⁵In Marcus theory [58], $\Delta E = -\Delta G$, with G being the Gibbs free energy, which is more appropriate in scenarios like molecules in a solution.

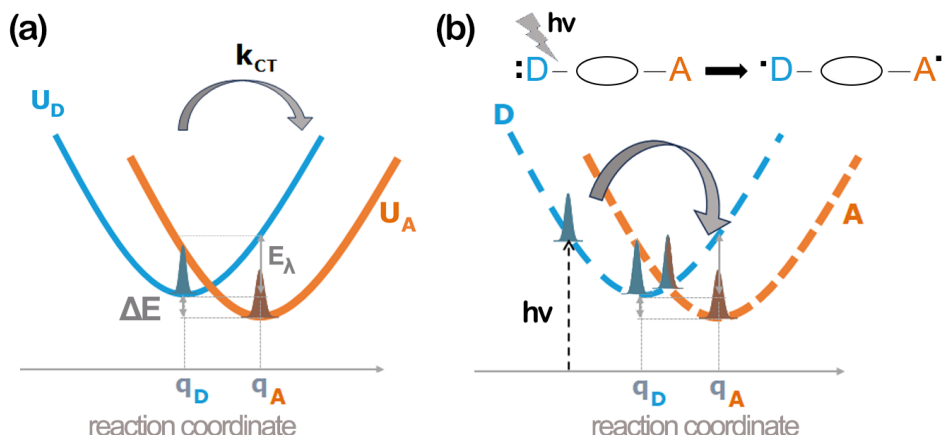


Figure 1.7: a) Sketch of the charge transfer process, showcasing the electronic wavefunction redistribution from the donor group versus toward the acceptor group. This transition occurs by moving across distinct potential energy surfaces: the donor curve in blue and the acceptor in orange. b) Visualization of photo-induced charge transfer, and the attempt of following the wavepacket dynamics across the surfaces. The figure highlights the limitations of the simple assumptions used in deriving Eq. (1.19).

While Eq. (1.19) holds significant practical value in various contexts, as recognized by the Nobel in 1992, its physical description of charge transfer primarily pertains to longer time scales where macroscopic reactions happen. Nonetheless, many key features of this process lie in its ultrashort dynamics, during which numerous assumptions of basic charge transfer theory become inapplicable.

In our ultrafast domain, we focus on the rapid evolution of the wavepacket in photo-induced charge transfer processes. As illustrated in Figure 1.7b), the donor wavefunction population is created by a vertical photo-ionization (or photo-excitation) event, thus making, for example, the assumption of a thermal distribution near the q_D minimum obsolete. Moreover, given that the electronic wavepacket can develop near conical intersections (in the figure, where the blue and red curves intersect), there is often a strong coupling between the nuclear and electronic degrees of freedom, breaking down the validity of the Born-Oppenheimer approximation.

Consequently, investigating the mechanisms that govern and direct charge transfer on such ultrashort timescales remains an essential task for the scientific community [54]. To unravel the ultrafast physics of charge transfer, new experiments with few-femtosecond resolution and innovative theoretical approaches are essential.

1.3.2 Experimental techniques: tr-PES, ATAS and ions-fragmentation

As highlighted in previous sections, accurately measuring time-dependent processes, such as charge transfer or charge migration in molecules, requires two key components: i) an appropriate "pump" event to initiate the dynamics and a suitable "probe"

for sampling the ultrafast process at specific points in time, and ii) an experimental technique that encode the information into a physical observable.

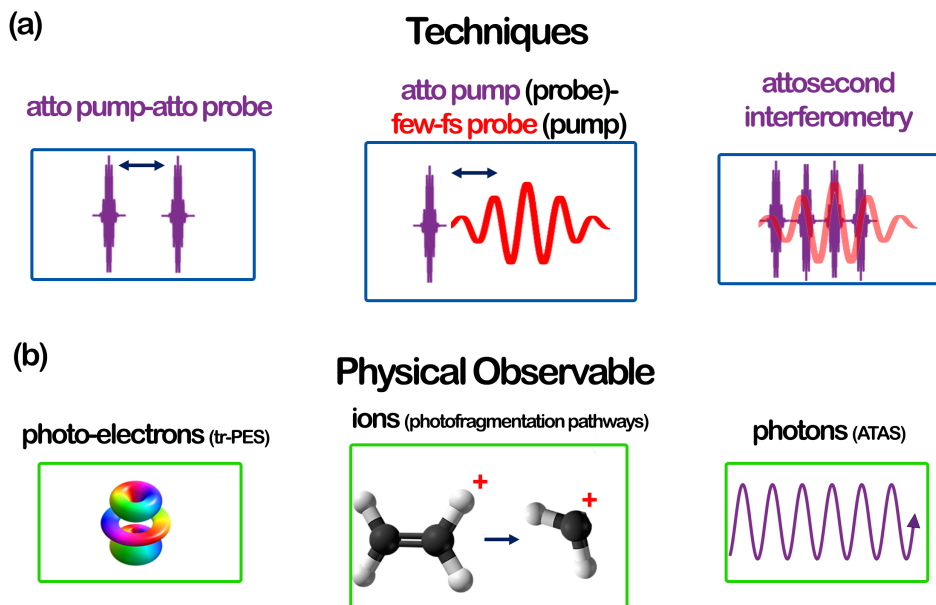


Figure 1.8: a) Sketch of possible pump-probe sources at the core of attosecond spectroscopy. b) Sketch of the basic set of physical observables used in attosecond experiments in molecular systems.

As depicted in Fig. 1.8, over the years, different combinations between pump/probe pulse configurations (extending from the attosecond to the femtosecond range) and physical observables (including photons, electrons, ions) have been chosen to conduct many experimental investigations on CT/CM in molecular systems, here few example:

- An increasingly popular method for examining these charge dynamics is attosecond transient absorption spectroscopy (ATAS) [80]. This technique involves exciting (pumping) the sample with few-femtosecond visible (VIS) or near-infrared (NIR) pulses, followed by probing the resulting dynamics with attosecond pulses, often with element-specific sensitivity. In this case, the physical observable is the transmitted spectrum of the attosecond radiation after the interaction. ATAS has been utilized to trace charge dynamics, whether CM or CT, through conical intersections in diatomic molecules like iodine monobromide (IBr) [81], in polyatomic molecules such as methyl bromide (CH_3Br) [82], and in cations like ethylene (C_2H_4^+) [83], methane (CH_4^+) [84], as well as in neutral silane (SiH_4) [44].
- High harmonic spectroscopy, an interferometric technique, resolves charge dynamics in molecules by using intense fs-laser pulses as the pump and the gen-

erated high-order harmonics as both the "probe" and the physical observable [63].

- As an alternative, also attosecond photoemission spectroscopy can offer key insights into both pure electronics (as in CM) and coupled electron-nuclear dynamics in molecules (as in CT). In this case, extreme-ultraviolet attosecond pulses initiate (pump) dynamics by removing an electron from the valence orbitals, while femtosecond VIS-NIR pulses control (probe) the subsequent dynamics, often in a non-perturbative way. Typical physical observables include the photoelectron kinetic energy, as in time-resolved photoemission spectroscopy (tr-PES), or the ion spectra (ion-photo fragmentation pathway), recorded as a function of the pump/probe delay. This technique has been applied to observe charge migration in aromatic amino acids such as phenylalanine and tryptophan [36, 85], the photodissociation dynamics (CT) of ethylene cation C_2H_4^+ [86, 87], and the rapid energy relaxation following ionization by 20-fs XUV pulses in planar polycyclic aromatic hydrocarbons (PAHs) of increasing sizes [88].

New techniques are currently explored using different pulse configurations, new detection schemes, or both. These include attosecond pump-attosecond probe spectroscopy, in either free electron laser facilities [33] or with high-order harmonic generation sources [89], which promise to achieve intrinsic attosecond time resolution. Additionally, methods employing few-fs-tunable ultraviolet pulses [90, 91] combined with an attosecond probe are currently under development to study, in the near future, the ultrafast charge dynamics in the neutral states of molecular sample. Finally, more advanced choices for observables, such as time-resolved coincidence ion-electron spectroscopy [92], are also currently being investigated.

1.4 Thesis overview

As outlined in the previous section, two key efforts are essential for progressing attochemistry: i) the development, or refinement, of attosecond tools to enhance the reliability and/or the resolution in measuring ultrafast dynamics, and ii) the combination of new experimental and/or theoretical approaches to deepen our understanding of ultrafast charge dynamics processes.

During my PhD, I addressed both aspects by improving the current knowledge on table-top attosecond sources and exploring charge transfer processes in prototypical donor-acceptor molecular systems. For each of these aspects, I attempt to summarize the motivation behind them as simple, straightforward inquiries. These questions are positioned at the beginning of each key section and are revisited and answered at the end of the same section.

Chapter 2 presents a thorough examination of the underlying physics of HHG. As elucidated, HHG arises from the intricate interplay between the response of a single atom to an intense driving field and the coherent response of a vast ensemble of individual emitters. Accordingly, this chapter delves into the fundamental aspects of the microscopic response, employing both classical models and *ab initio* quantum mechanical derivations, as well as exploring the macroscopic properties essential for the efficient generation of attosecond pulses.

Chapter 3 details our experimental and theoretical achievements in attosecond technology in three primary areas: i) optimizing the efficiency of high-order harmonic generation sources, ii) fine-tuning the spatial properties of HHG to minimize spatial aberrations, and iii) developing innovative and flexible methods for generating isolated attosecond pulses.

Chapter 4 presents our recent experimental and theoretical efforts in investigating the ultrafast photophysics of prototypical donor-acceptor systems. The aim is to unravel the key mechanisms at play in the initial stages of charge transfer, which ultimately influence the fate of subsequent dynamics. The findings contribute significantly to a more comprehensive understanding of the early-stage photo-physics of donor-acceptor molecules, which is highly relevant to fields such as photovoltaics and molecular optoelectronics.

Chapter 5 gives a summary of the results and a general outlook on future research direction.

Chapter 2

High-order Harmonics Generation

Within the complex domain of semiclassical light-matter interactions, our focus narrows to a specific phenomenon: the generation of attosecond pulses through High-order Harmonic Generation (HHG). As mentioned in Chapter 1, this process typically involves focusing an intense laser field onto a noble gas target. Although other targets (molecules, solids, liquids) are feasible, for historical and practical reasons, our analysis will consider only noble gases within the single active electron approximation, which remains a robust approximation in many scenarios.

HHG itself is an intricate process. Generating attosecond pulses effectively depends on two crucial aspects: firstly, the microscopic response of individual atoms, which must support the creation of ultrashort pulses via this highly non-linear process, and secondly, the macroscopic collective and in-phase participation of an ensemble of atoms to the process (i.e. generating medium). Thus, to describe HHG, we need to combine a microscopic description of matter with a macroscopic view of the generation of electromagnetic radiation from an extended gas medium.

From a microscopic perspective, the key to describing HHG is outlining the physics of the interaction between an intense laser field and an individual atom. This requires a quantum mechanical description of how a time-dependent electromagnetic field influences the time evolution of the atomic wavefunction. On the macroscopic level, the challenge is understanding how multiple emitters can coherently sum their radiation in an extended medium where the laser field, driving the HHG process at the microscopic level, varies spatially (and temporally). Indeed, in a standard HHG setup, the number of emitters is substantial, $> 10^{15}$; hence, phase matching is pivotal in harmonic generation.

In this chapter, after an initial overview of the fundamental elements of any light-matter interaction theory (Section 2.1), we will delve into the physics of both factors

impacting HHG: a complete description of the microscopic response to an intense laser field, both from a classical and quantum perspective (Section 2.2) and macroscopic phase-matching (Section 2.3).

The microscopic and macroscopic discussions are crucial for a comprehensive understanding of the key results of this dissertation presented in Chapter 3. Moreover, these models offer the possibility of engineering reliable attosecond pulse sources, a fundamental step if one wants to harness this radiation for attosecond chemistry experiments (Chapter 4).

2.1 Semiclassical laser-matter interaction

In semiclassical light-matter interaction theory, light is treated as a classical field, following microscopic Maxwell's equations (in SI units):

$$\begin{aligned}\nabla \times \mathbf{E} &= -\partial_t \mathbf{B} & \nabla \cdot \mathbf{E} &= \frac{\rho}{\epsilon_0} \\ \nabla \times \mathbf{B} &= \frac{1}{c_0^2} \partial_t \mathbf{E} + \mu_0 \mathbf{J} & \nabla \cdot \mathbf{B} &= 0 \\ \mathbf{E} &= -\nabla A_0 - \partial_t \mathbf{A} & \mathbf{B} &= \nabla \times \mathbf{A}\end{aligned}\tag{2.1}$$

where $(\mathbf{E}, \mathbf{B})$ represent the electromagnetic field, $(-\mathbf{A}, A_0)$ the four-vector potential, and $(\rho, \mathbf{J})$ are the density of charges and the density of current, respectively.

Matter, instead, within a single active electron picture, is described via the time-dependent Schrödinger equation (TDSE) (in SI units):

$$\hat{H} |\psi\rangle = i\hbar \partial_t |\psi\rangle \tag{2.2}$$

where $\hat{H}$ is the light-matter interaction Hamiltonian.

In a generic α -gauge (see Appendix A), $\hat{H}$ is expressed as:

$$\hat{H} = \frac{1}{2m} (\hat{\mathbf{p}} + e\mathbf{A}^{(\alpha)})^2 - eA_0^{(\alpha)} \tag{2.3}$$

with $\hat{\mathbf{p}}$ the momentum operator, $(-\mathbf{A}^{(\alpha)}, A_0^{(\alpha)})$ the electromagnetic four-vector potential, in the specific α -gauge, and e the *modulus* of the electron charge, or *elementary charge*.

2.1.1 Light-Matter interaction: From the perspective of light

From the perspective of light, its interaction with matter is bidirectional; light changes matter and matter can change light. Indeed, light can be absorbed, scattered, and generated. One of the processes at the core of generation of light is a time-varying charge distribution, e.g. an oscillating dipole [93].

Dipole radiation is a widely studied phenomenon that bridges the quantum description of matter, a single electron in our context, with the propagation and generation of electromagnetic radiation. The relation establishing the connection between the Schrödinger equation (Eq. (2.2)) and Maxwell's equations (Eq. (2.1)) is:

$$\rho(\mathbf{r}, t) = -e|\psi(\mathbf{r}, t)|^2 \quad (2.4)$$

where $\psi(\mathbf{r}, t) = \langle \mathbf{r} | \psi \rangle$ represents the electron wave function in space. According to classical electromagnetism:

$$\mathbf{d}(t) = \int_{\mathcal{R}^3} \mathbf{r} \rho(\mathbf{r}, t) d\mathbf{r} \quad (2.5)$$

Hence, combining Eq. (2.5) with Eq. (2.4), we find:

$$\begin{aligned} \mathbf{d}(t) &= -e \int_{\mathcal{R}^3} \mathbf{r} |\psi|^2 d\mathbf{r} = -e \int_{\mathcal{R}^3} \mathbf{r} \psi^*(\mathbf{r}, t) \psi(\mathbf{r}, t) d\mathbf{r} = -e \int \mathbf{r} \langle \psi | \mathbf{r} \rangle \langle \mathbf{r} | \psi \rangle d\mathbf{r} = \\ &= -e \int \langle \psi | \hat{\mathbf{r}} | \mathbf{r} \rangle \langle \mathbf{r} | \psi \rangle d\mathbf{r} = -e \langle \psi | \hat{\mathbf{r}} \left(\int |\mathbf{r}\rangle \langle \mathbf{r}| d\mathbf{r} \right) | \psi \rangle = -e \langle \psi | \hat{\mathbf{r}} | \psi \rangle \end{aligned}$$

where we have exploited the position operator $\hat{\mathbf{r}}$ and its property of completeness to derive the following trivial expression:

$$\boxed{\mathbf{d}(t) = -e \langle \psi(t) | \hat{\mathbf{r}} | \psi(t) \rangle} \quad (2.6)$$

This dipole expectation value is pivotal in our semi-classical framework, and it allows us to investigate the properties of many interesting mechanisms, such as the emission of high-order harmonics and attosecond pulse generation.

Single emitter

To model the generation of an electromagnetic field from a known oscillating dipole, $\mathbf{d}(t)$, the result of Eq. (2.6) has to be incorporated as a source term in Eq. (2.1). For example, for a single emitter (i.e. atomic antenna), within the dipole approximation, the electric field generated is given by [93]:

$$\mathbf{E}(\mathbf{r}, t) = \int_{-\infty}^{+\infty} d\omega \frac{\omega^2}{4\pi\epsilon_0 r} (\mathbf{n} \times \tilde{\mathbf{d}}(\omega) \times \mathbf{n}) e^{i\omega(t - \frac{r}{c_0})} + \text{c.c.} \quad (2.7)$$

where r denotes the modulus of the position $\mathbf{r}$, $\mathbf{n}$ is its normalized vector, and $\tilde{\mathbf{d}}$ is the Fourier transform of the *electric dipole*, defined as:

$$\tilde{\mathbf{d}}(\omega) = \int_{-\infty}^{+\infty} \mathbf{d}(t) e^{-i\omega t} dt \quad (2.8)$$

Multiple emitters: propagation equation

In a scenario with multiple emitters, we must rely on macroscopic equations to describe the medium where the electromagnetic field is collectively generated. The equation governing this process, derived from macroscopic Maxwell's equations, is the standard wave equation:

$$[\nabla^2 - \frac{1}{c^2} \partial_t^2] \mathbf{E} = \mu_0 \partial_t^2 \mathbf{P} \quad (2.9)$$

where $\mathbf{P}$ is the general medium polarization, encompassing all possible linear and non-linear processes. The polarization is locally defined by the individual electric dipoles, $\mathbf{d}(\mathbf{r}, t)$, within the medium, as well as their local density, $n(\mathbf{r}, t)$, following:

$$\mathbf{P}(\mathbf{r}, t) = n(\mathbf{r}, t) \mathbf{d}(\mathbf{r}, t) \quad (2.10)$$

2.1.2 Light-Matter interaction: From the perspective of matter

To give practical meaning to the dipole described in Eq. (2.6), it is crucial to solve quantum mechanics equations and assess the influence of an electromagnetic field on matter. Specifically, in the scenario of a single active electron, the Schrödinger equation, here expressed in atomic units (a.u.), has to be solved:

$$\boxed{\hat{H} |\psi\rangle = i \partial_t |\psi\rangle} \quad (a.u.) \quad (2.11)$$

As sketched in Chapter 1, the exact solution to Eq. (2.11) is given by:

$$|\psi, t\rangle = |\psi(t)\rangle = e^{-i \int_{t_0}^t \hat{H}(t') dt'} |\psi(t_0)\rangle \quad (2.12)$$

here, advanced time-propagator tools [94] are employed.

A detailed explanation of this peculiar exponential operator, which allows us to describe the complete temporal evolution of a quantum state, initialized in $|\psi(t_0)\rangle$, is reserved for Appendix A.

As observed, the semiclassical light-matter interaction Hamiltonian is gauge-dependent. Hence, under the dipole approximation, $\mathbf{E}(\mathbf{r}, t) \approx \mathbf{E}(0, t)$, the Hamiltonian shown in Eq. (2.3) can be expressed in two equivalent forms:

$$\hat{H}^{(l)} = -\frac{1}{2} \nabla^2 - \phi + \hat{\mathbf{r}} \cdot \mathbf{E}(t) \quad (2.13)$$

$$\hat{H}^{(v)} = \frac{1}{2} (\hat{\mathbf{p}} + \mathbf{A}(t))^2 - \phi \quad (2.14)$$

where the first equation represents the length gauge Hamiltonian, $\hat{H}^{(l)}$, and the second one denotes the velocity gauge Hamiltonian, $\hat{H}^{(v)}$, with ϕ being the Coulomb potential ($\propto +1/r$).

As detailed in Appendix A, the gauge-variance of Schrödinger equations is a fascinating subject; the main consequence is the gauge dependence of the wavefunction $|\psi\rangle^{(\alpha)}$. A useful outcome for the subsequent discussion is a simple rule for transitions between gauges:

$$\boxed{|\psi\rangle^{(l)} = e^{+i\hat{\mathbf{r}}\cdot\mathbf{A}} |\psi\rangle^{(v)}} \quad (2.15)$$

Thus, the wavefunction solving Eq. (2.13) differs from that in Eq. (2.14) by a global phase shift. This finding is essential for constructing a coherent gauge-invariant physical theory where physical observables remain unaffected by the choice of gauge.

In essence, the goal of our HHG discussion is to get direct insight into the time-dependence of the dipole matrix element $\mathbf{d}(t)$ (Eq. (2.6)) and use it to predict the properties of the HHG radiation from either a single emitter (microscopic models) or from an extended medium (microscopic and macroscopic models). This can be achieved by finding the proper time evolution of the wavepacket of Eq. (2.11) in the presence of an intense driving field.

2.2 Microscopic aspects of HHG

Quantum mechanics is fundamental to understanding high-order harmonic generation. Yet, sometimes, even intricate phenomena can be elucidated through "classical" arguments. In our case, HHG can be commonly explained using a straightforward ballistic model known as the three-step model [22, 23, 95]. Conceived between 1992 and 1993, this model, despite its simplicity, successfully captured essential aspects of HHG and paved the way to a more detailed quantum formalism developed in 1994 [21]. As illustrated in Fig. 2.1, HHG can be described as the consequence of three subsequent steps of light-matter interaction.

When an intense laser field ($\approx 10^{14} \text{ W/cm}^2$), typically in the infrared spectral region (IR), impinges on an atomic target, the Coulomb potential is bent, creating a potential barrier. One of the valence electrons can undergo *tunnel ionization*, and it is ejected into the continuum. Following ionization, the freed electron *propagates in the continuum*, driven by the laser electric field (Lorentz's force). As the electric field reverses, the electron trajectory also changes, bringing it back to its parent ion. The final stage in the HHG process is the *recollision* step, where the electron, having returned to the proximity of its initial ionization site, has a certain probability of recombining with the parent ion. During recombination, the kinetic energy accumulated by the electron during its motion in the continuum is released in the form of a high-energy photon, which, under the standard generation conditions, is typically in the XUV spectral range ($\approx 10 - 100 \text{ eV}$). Yet, by properly tuning the intensity and wavelength of the driving field, the photon energy can be even extended in the keV region.

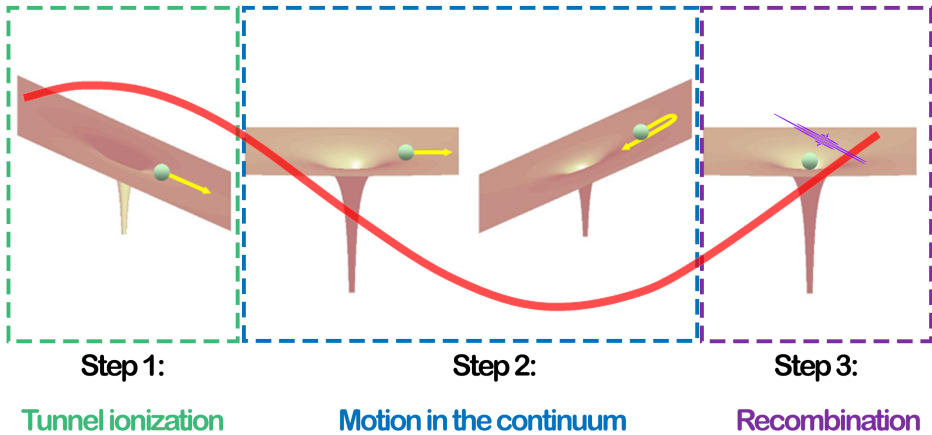


Figure 2.1: Sketch of the three-step model in HHG: i) tunnel ionization from the parent ion. ii) motion in the continuum driven by the IR field (continuous red line). iii) Recombination and emission of an attosecond burst of extreme ultraviolet light.

Since an electron is freed around each electric field maximum, the described process

reiterates every half-cycle of the driving field, leading to the generation of a train of attosecond pulses, as observed, for the first time, in 2001 [96].

The central focus of the three-step model is to analyze all possible electron trajectories as a function of the instant of recombination for different laser field conditions, intensity and wavelength. As detailed in the next paragraph, this simple model allows us to identify crucial properties of the HHG process, such as the maximum photon energy, i.e. cut-off, see Fig. 1.3.

An extension of the three-step model was proposed in 2018 [97, 98], which we will call γ -model from now on. The γ -model provides a more comprehensive analysis of the kinetic energy of the different trajectories as a function of the recombination instant and, therefore, gives more direct insight into the change of the emitted photon energies as a function of time. Starting from this model many crucial features of the harmonics can be predicted, such as the attosecond-chirp[98], spatio-temporal properties [99, 100, 101] and, even, general macroscopic phase matching trends [102].

A three-step model-based description is sometimes insufficient, and a quantum approach is needed. As detailed later in this section, the quantum framework used to describe HHG is more subtle and requires more advanced tools.

2.2.1 Three-step model and γ -model

In this paragraph, we derive the γ -model starting from standard three-step model considerations. These results will be used as the starting point for the discussion presented in Section 3.2.

Three-step model: Analysis of the kinetic energy of photoelectron trajectories

Let us consider an electron moving in the continuum after tunnel ionization. The Newton equation of motion for the free electron in the laser electric field $\mathbf{E}(t)$, assumed to be linearly polarized along the x-direction $\mathbf{E}(t) = E(t)\mathbf{u}_x$, is:

$$\ddot{x} = -\frac{e}{m_e}E(t) \quad (2.16)$$

where e and m_e are the absolute values of the electron charge and mass, respectively. By integrating Eq.2.16, the velocity $\dot{x} = v(t)$ of the electron can be written as:

$$\begin{cases} v(t) - v(-\infty) = \int_{-\infty}^t -\frac{e}{m_e}E(\tilde{t}) d\tilde{t} \\ x(t) - x(-\infty) = \int_{-\infty}^t v(\tilde{t}) d\tilde{t} \end{cases} \quad (2.17)$$

In our "quasi"-classical picture, tunnel ionization can happen at any instant, t' . Consequently, to describe a generic electron trajectory created at time, t' , and propagating

in the continuum until t , the previous system of equations has to be adapted as follows:

$$\begin{cases} v_{t'}(t) - v(t') = \int_{t'}^t -\frac{e}{m_e} E(t) dt \\ x_{t'}(t) - x(t') = \int_{t'}^t v(t) dt \end{cases} \quad (2.18)$$

In this way, $v_{t'}(t) = v(t, t')$ represents the time-evolution of the velocity for a specific electron trajectory created at the time t' .

For simplicity, we assume the driving laser as a monochromatic cosinusoidal field with angular frequency ω_0 (for a non-monochromatic field, simple numerical calculations can be pursued).

$$E(t) = E_0 \cos(\omega_0 t) \quad (2.19)$$

where E_0 is the electric field amplitude.

In the following, we adopt a reference frame centered at the parent ion, so that the photoelectron emitted at time t' , starts its motion from $x(t, t') = 0$. The final assumption is that each photoelectron has zero momentum, which implies $v(t, t') = 0$ for every trajectory. Consequently,

$$v(t, t') = -\frac{eE_0}{m_e\omega_0} [\sin(\omega_0 t) - \sin(\omega_0 t')] \quad (2.20)$$

and,

$$x(t, t') = \frac{eE_0}{m_e\omega_0^2} [\cos(\omega_0 t) - \cos(\omega_0 t') + \omega_0(t - t') \sin(\omega_0 t')] \quad (2.21)$$

These final expressions provide a general solution for the classical trajectories of an electron for each possible photoionization instant t' . For practical purposes, it is relevant to highlight the connection of these trajectories with the associated return time (or recombination time t_R) of the electron to the parent ion. To do so, we numerically solve the equation $x(t_R, t') = 0$ for $t > t'$. Once the returning time is identified, we can use it to determine the energy of the XUV photon emitted during the recombination step for each trajectory, $\hbar\Omega(t_R, t')$. Denoting $\hbar\Omega_p = I_p$ as the ionization potential of the atom, we can write:

$$\hbar\Omega(t_R, t') = \hbar\Omega_p + \frac{1}{2}m_e v^2(t_R, t') = I_p + \frac{1}{2}U_p [\sin(\omega_0 t_R) - \sin(\omega_0 t')]^2 \quad (2.22)$$

where

$$U_p = \frac{(eE_0)^2}{4m_e\omega_0^2} \quad (2.23)$$

is the ponderomotive energy of the photoelectron, representing the average kinetic energy of the electron in the laser field.

This simple equation (Eq. (2.22)) can be used as the starting point of numerical simulations to evaluate the final kinetic energy of the various recombining trajectories for a generic electromagnetic field.

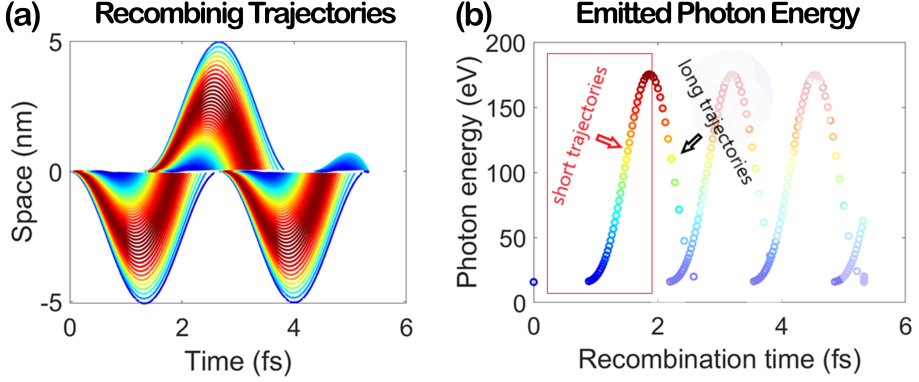


Figure 2.2: Numerical simulation solving the classical equation of motion for the electron in a 100-fs IR (centred at 800 nm) and peak intensity of $8 \times 10^{14} \text{ Wcm}^{-2}$. The analysis is confined to a 6-fs temporal window around the intensity peak. a) Set of the recombining trajectories over laboratory time and their distance from the parent ion. The colour of each trajectory is associated with the kinetic energy of the photoelectron at the instant of recombination, assuming an Argon target. b) Plots the photon energy at the instant of recombination, allowing easy identification of the final kinetic energy of the photoelectron trajectory and the associated photon energy at the instant of recombination.

As depicted in Fig. 2.2, within each half-cycle (spanning 1-2 fs as shown in the figure), two distinct categories of trajectories emerge: *short* and *long* trajectories, with the former predominantly utilized in applications due to their cleaner spatio-temporal properties. This simulation, based on the resolution of the three-step model equations, effectively illuminates several fundamental aspects of HHG: i) the inherent sub-femtosecond character of the recombining electron trajectories, which is consistent with the generation of attosecond pulses, and ii) the cyclical repetition of these pattern in each half-optical cycle, approximately 1.25 fs. Consequently, as expected, Fig. 2.2 points towards the generation of a train of attosecond pulses.

Moreover, as demonstrated analytically in [95, 98] or through numerical consideration, the maximum kinetic energy of the photoelectron can be approximated as $E_{k,max} \approx 3.17U_p$. Consequently, the maximum energy of the XUV photon is determined by the well-known *cut-off law*.

$$\hbar\Omega_c \approx I_p + 3.17U_p \quad (2.24)$$

This result, combined with Eq. (2.2.1), underscores the proportionality between the photon energy and the square of the driving field wavelength, $\hbar\Omega_c \propto \lambda_0^2$. Therefore, an effective strategy for achieving photon energies within the keV range is to employ

longer wavelengths, thereby increasing the electron travel distance in the continuum [29].

The γ -model: attosecond chirp

The fundamental insight at the basis of the γ -model, also evident from the three-step model[95], is the observation that as a consequence of the energy dispersion of the electron trajectories (see Fig. 2.2) different photon energies are emitted at distinct times. This implies that the produced attosecond radiation inherently exhibits an energy (frequency) chirp caused by the dispersion of the recombination trajectories. Specifically, within each half-laser cycle, it is noted that photoelectrons following the short trajectory lead to positively chirped attosecond pulses (i.e., $\frac{d\Omega(t_R)}{dt_R} > 0$), whereas those on the long trajectories result to negatively chirped pulses (i.e., $\frac{d\Omega(t_R)}{dt_R} < 0$). This intrinsic phase contribution to the HHG process is called *dipole phase*.

The goal of the γ -model [98] is simply to obtain quantitative insights into this phase and into the attosecond chirp by linearizing the short (or long) trajectory curve. As depicted in Fig. 2.3 for the short trajectories, the energy dispersion curve of the generated XUV photon energy vs recombination time is linearized around the mid-point of the cutoff region, $\hbar\frac{\Omega_c + \Omega_p}{2}$.

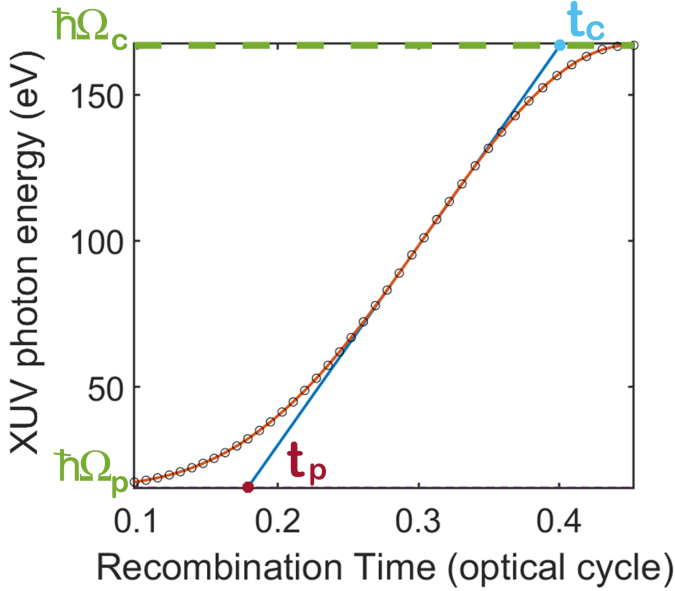


Figure 2.3: Sketch of the linearization procedure used in the γ -model for the electron trajectories. Here reported for a particular numerical simulation (100-fs pulse centred at 800-nm, $8 \times 10^{14} \text{ Wcm}^{-2}$, Argon). The linearization allows for an easy determination of the attosecond chirp of the short-trajectories.

By defining t_p , the linearized return time associated with the XUV frequency,

Ω_p , and t_c , the time at which the cut-off energy crosses the tangent curve, we can invert Eq. (2.22) and obtain a straightforward equation for the recombination time as a function of photon frequency, Ω :

$$t_R(\Omega) \approx t_p + \frac{t_c - t_p}{\Omega_c - \Omega_p} (\Omega - \Omega_p) \quad (2.25)$$

Consequently, the spectral phase $\Phi(\Omega)$ of the emitted attosecond pulses is given by the integral of Eq. (2.25), so that:

$$\Phi(\Omega) = \Phi(\Omega_p) + t_p(\Omega - \Omega_p) + \frac{t_c - t_p}{\Omega_c - \Omega_p} \frac{(\Omega - \Omega_p)^2}{2} \quad (2.26)$$

The quadratic terms of Eq.(2.26) are the source of the attosecond chirp in HHG. It can be easily shown[98], exploiting Eq. (2.24), that:

$$\frac{t_c - t_p}{\Omega_c - \Omega_p} = \frac{2\gamma}{I} \quad (2.27)$$

where $I = \frac{1}{2}\epsilon_0 E_0^2$ represents the local intensity of the laser, and γ is a parameter determined by the chosen laser wavelength. Specifically, for a wavelength of $\lambda = 800$ nm, γ is assigned values of $\gamma_s = 1.03 \times 10^{-18} \text{ s}^2 \text{ W/cm}^2$ for short trajectories and $\gamma_l = -0.874 \times 10^{-18} \text{ s}^2 \text{ W/cm}^2$ for long trajectories.

Therefore, we arrive at the γ -model equation for the dipole phase that serves as a foundation for subsequent discussion and as the starting point to understand the results on the spatio-temporal chromatic aberration of HHG radiation, presented in Section 3.2:

$$\boxed{\Phi_i(\Omega) = \alpha I + t_p(\Omega - \Omega_p) + \frac{\gamma}{I}(\Omega - \Omega_p)^2,} \quad (2.28)$$

where α is a intensity-independent constant equal to $\alpha_s \approx 0$, for the short trajectories and $\alpha_l = \alpha_{fs} \lambda^3 / (2\pi m_e c^3)$ for the long trajectories [98] (with α_{fs} the fine structure constant).

2.2.1.1 Relativistic correction to γ -model

One can think to further expand the presented model and discussion by solving the equation of motion for a free electron propagating in the continuum as a relativistic particle subjected to both the electric and magnetic field [103, 104, 105].

A new and simple way to solve numerically this problem is here proposed.

In special relativity, the momentum of the particle is given by $\mathbf{p} = \zeta m \mathbf{v}$, where $\zeta = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$, and c is the speed of light in vacuum.

Using Newton's equation formalism, the force acting on a relativistic particle is given by:

$$\mathbf{F} = \frac{d}{dt}(\zeta m \mathbf{v}) = \frac{d}{dt}\zeta m \mathbf{v} + \zeta m \frac{d}{dt}\mathbf{v} \quad (2.29)$$

Following this formulation, it can be shown that:

$$\frac{d}{dt}\zeta = \frac{\zeta^3}{c^2} \mathbf{v} \cdot \frac{d}{dt}\mathbf{v} \quad (2.30)$$

Hence, we can rewrite the force as:

$$\mathbf{F} = m\zeta \frac{d}{dt}\mathbf{v} + m \frac{\zeta^3}{c^2} (\mathbf{v} \cdot \frac{d}{dt}\mathbf{v}) \mathbf{v} \quad (2.31)$$

By evaluating the scalar product from both sides of Eq. (2.31), we obtain:

$$\mathbf{F} \cdot \mathbf{v} = m\zeta \frac{d}{dt}\mathbf{v} \cdot \mathbf{v} + m \frac{\zeta^3}{c^2} v^2 \frac{d}{dt}\mathbf{v} \cdot \mathbf{v} = m\zeta^3 \frac{d}{dt}\mathbf{v} \cdot \mathbf{v} \left(\frac{1}{\zeta^2} + \frac{v^2}{c^2} \right) = m\zeta^3 \frac{d}{dt}\mathbf{v} \cdot \mathbf{v} \quad (2.32)$$

where $\frac{1}{\zeta^2} + \frac{v^2}{c^2} = 1$.

We can exploit this result to modify Eq. (2.31) as:

$$m\zeta \dot{\mathbf{v}} = \mathbf{F} - \left(\frac{1}{c^2} \mathbf{F} \cdot \mathbf{v} \right) \mathbf{v} \quad (2.33)$$

In a strong field regime, we can disregard the impact of the motion of the electron on the electromagnetic field. Therefore, to describe light-matter interaction in this classical framework, can use the Lorentz force. Thus, following Eq. (2.33), the system of equations for the motion of the relativistic electron in a time-varying electromagnetic field assumes the following form:

$$\begin{cases} m\zeta(t)\dot{v}_x(t) = -eE_x(t) + ev_z(t)B_y(t) + \frac{1}{c^2}eE_x(t)v_x^2(t) \\ m\zeta(t)\dot{v}_z(t) = -ev_x(t)B_y(t) + \frac{e}{c^2}E_x(t)v_x(t)v_z(t) \end{cases} \quad (2.34)$$

where $\mathbf{E}$ and $\mathbf{B}$ are the externally applied electric and magnetic fields.

The object presented in Eq. (2.34) is a non-linear system of differential equations, which is not trivial to solve.

Nevertheless, in our regime, the relativistic motion of the particle is expected to be a minor correction from the classical scenario. Therefore, we can exploit the following iterative procedure to find a numerical solution.

Let us call $(v_x^{NR}(t), v_y^{NR}(t))$ the solution obtained (numerically) from the non-relativistic system of equations (Eq. (2.18)), assuming a specific emission time t' .

Then, we can linearize the system as follow:

$$\begin{cases} m\zeta^{NR}\dot{v}_x(t) = -eE_x(t) + ev_z(t)B_y(t) + \frac{1}{c^2}eE_x(t)v_x(t)v_x^{NR} \\ m\zeta^{NR}\dot{v}_z(t) = -ev_x(t)B_y(t) + \frac{e}{c^2}E_x(t)v_x^{NR}v_z(t) \end{cases} \quad (2.35)$$

where ζ^{NR} is the relativistic factor calculated with the non-relativistic solution. This procedure is now repeated by updating v_x^{NR}, ζ^{NR} with the newfound solution v_x^i, ζ^i . It can be shown, that up to $v \approx 0.1c$ a couple of iterations is already sufficient to have a negligible iteration error ($\epsilon_i = v_x^i - v_x^{i-1}$).

The newly derived equation (Eq. (2.35)) can be effectively used as the starting point for numerical simulation with the aim of enhancing the γ -model. However, a comprehensive discussion on this topic is beyond the scope of this dissertation. Yet, it could be shown, as expected, that the impact of this correction on the HHG trajectories and key parameters (e.g. cut-off or attosecond chirp) is minor, $\approx 1\%$ for driving field wavelength $\approx 2\mu m$ at moderate intensity ($8 \times 10^{14} W/cm^2$).

2.2.2 TDSE and SFA in HHG

While the three-step model (γ -model) provides significant insights into the HHG process, it can only describe the continuum electron trajectories. As such, this model does not explain the core mechanisms underpinning the ionization and recombination phases. Furthermore, being a classical model, it fails to elucidate why all potential photoelectron trajectories collectively and simultaneously contribute to the formation of the attosecond pulse train. To highlight this point and the insignificance of the question "when does the photoemission event occur?" a quantum mechanical approach is essential. Also, aspects such as precise characterization of the temporal properties of the attosecond radiation, conversion efficiency, and other important aspects of the HHG mechanism remain unexplored within a ballistic model.

The goal of this next part is to provide a comprehensive understanding of microscopic HHG, delving into its quantum mechanical nature. In essence, once the strong field ionization step is properly described in the proper light-matter interaction framework, HHG is conceptualized as the outcome of an interference between the part of the wavepacket propagating into the continuum (all possible quantum trajectories) and the wavefunction bounded to the atom. This coherent superposition of states gives rise to an oscillating dipole, thereby emitting high-order harmonic radiation.

2.2.2.1 Atom in electromagnetic field: S-matrix solution

Let us consider an electron feeling both a hydrogen-like Coulomb potential, $\Phi \propto +1/r$, from its associated ion and an external electromagnetic laser field, within the dipole approximation.

As extensively detailed in Appendix A, the first step to solve ab-initio this problem is partitioning the Schrödinger equation (Eq. (2.12)) in two terms¹:

$$\hat{H} = \hat{H}_0 + \hat{H}_I(t) \quad (2.36)$$

where $\hat{H}_0 = -\frac{1}{2}\nabla^2 - \Phi$ is the unperturbed Hamiltonian, and $\hat{H}_I^{(l)} = \hat{\mathbf{r}} \cdot \mathbf{E}(t)$ is the interaction Hamiltonian, in the length gauge (l).

It can be proved, through the use of Dyson's equations (Appendix A.2), that another exact solution of Eq. (2.2) (as an alternative to Eq. (2.12)) is:

$$\begin{aligned} |\psi(t)\rangle = & -i \int_{t_0}^t dt' e^{-i \int_{t'}^t \hat{H}(t'') dt''} \hat{H}_I(t') e^{-i \int_{t_0}^{t'} \hat{H}_0 dt''} |\psi(t_0)\rangle + \\ & + e^{-i \int_{t_0}^t \hat{H}_0 dt''} |\psi(t_0)\rangle \end{aligned} \quad (2.37)$$

¹a different approach is the, so-called, Lewenstein model, based on the first quantum HHG-model proposed in 1994 [21].

This precise solution to the equation showcases something truly fascinating and noteworthy. As illustrated in Chapter I, Fig. (1.2), this solution to Schrödinger equations, Eq. (2.37), can now be viewed as a *superposition of quantum paths*². Each path is uniquely identified by an interaction time t' with the external field. In essence, every quantum path consists of an initial phase of evolution without the electromagnetic field, governed by $\hat{H}_0$; a distinct "kick" from the field, $\hat{H}_I(t')$, at a specific time t' , which uniquely identifies the path and redistribute the energy of the system; followed by a final evolution influenced by both the field and the Coulomb potential, represented by $\hat{H}$. While Eq. (2.37) might be complex to work with directly, it can serve as a starting point for numerical calculations [6], more in-depth discussions [106], or various approximations [7].

To describe photo-ionization, one could project Eq. (2.37) onto a specific continuum state $|\xi\rangle$. Consequently, $c_\xi^2(t) = |\langle \xi | \psi \rangle|^2$ represents the probability amplitude of finding the electron in a continuum eigenstate at a given time t .

c_ξ is typically referred to as scatter-matrix amplitude, or S-matrix amplitude.

$$c_\xi(t) = -i \int_{t_0}^t dt' \langle \xi | e^{-i \int_{t'}^t \hat{H}(t'') dt''} \hat{H}_I(t') e^{-i \int_{t_0}^{t'} \hat{H}_0 dt''} | \psi(t_0) \rangle + \langle \xi | e^{-i \int_{t_0}^t \hat{H}_0 dt''} | \psi(t_0) \rangle \quad (2.38)$$

The latter term in Eq. (2.38) accounts for the quantum path where the atomic wave function remains unaffected by the external field. Assuming the initial state coincides with one of the unperturbed Hamiltonian eigenstates, we can express it as:

$$\langle \xi | e^{-i \int_{t_0}^t \hat{H}_0 dt''} | \psi_0(t_0) \rangle = e^{-i E_0(t-t_0)} \langle \xi | \psi_0(t_0) \rangle$$

In the framework of photoionization, this term is often overlooked. However, if the final continuum state is not orthogonal to the bound states, it is, in principle, important to consider it.

The first term of Eq. (2.38) is, instead, particularly noteworthy, as it is directly influenced by the external field. It represents the probability that an initial state, $|\psi(t_0)\rangle$, due to the field influence, transitions to a continuum state $|\xi\rangle$, essentially quantifying the probability of transitioning into the continuum. Hence, this term is referred to as the time-reversed transition amplitude (or T-matrix amplitude), denoted as a_ξ .

$$a_\xi(t) = -i \int_{t_0}^t dt' \langle \xi | e^{-i \int_{t'}^t \hat{H}(t'') dt''} \hat{H}_I(t') e^{-i \int_{t_0}^{t'} \hat{H}_0 dt''} | \psi(t_0) \rangle \quad (2.39)$$

Eq. (2.39) is a fundamental result in strong-field physics. Additionally, it is also the starting point of one of the most used approximations in Attosecond Physics: *Strong Field Approximation* (SFA)[107, 108], presented below.

²A' la Feynman

2.2.2.2 Strong Field Approximation (SFA)

Let us simplify the exact solution given in Eq. (2.39) to derive the commonly used strong field approximation formula [21, 107].

A key strength of the SFA is its lack of reliance on assumptions regarding the interaction intensity relative to the binding potential, nor does it require precise knowledge about the field(s) wavelength, a necessity, instead, in perturbation theory. This provides considerable versatility and broad applicability [7], as long as the dipole approximation is valid [103]. Indeed, by employing SFA theory, we can extract insights for modelling processes such as HHG [6, 108].

The key concept underlying SFA is the *omission of the Coulomb interaction* after the interaction (kick) step. In other words, we assume that after ionization, the freed electron does not feel the Coulomb potential from the atom. Consequently, we can rewrite the T-Matrix evolution as follows:

$$a_{\xi}^{(SFA)} = -i \int_{t_0}^t dt' \langle \xi | e^{-i \int_{t'}^t \hat{H}_F(t'') dt''} \hat{H}_I(t') e^{-i \int_{t_0}^{t'} \hat{H}_0 dt''} | \psi(t_0) \rangle \quad (2.40)$$

where, in principle, $H_F^{(l)} = \frac{1}{2} \hat{\mathbf{p}}^2 + \hat{\mathbf{r}} \cdot \mathbf{E}(t)$.

Now, an important choice has to be made. Although, as stated at the beginning, we are working with the length gauge Hamiltonian, $H_F^{(l)}$, the *free-field Hamiltonian* has an equivalent form in the velocity gauge, $H_F^{(v)}$, expressed as:

$$H_F^{(v)} = \frac{1}{2} (\hat{\mathbf{p}} + \mathbf{A}(t))^2 \quad (2.41)$$

The gauge invariance of physical observables and of the final results might suggest the feasibility of proceeding with either the *length gauge* or the *velocity gauge*. However, this approach in SFA can lead to inconsistencies, resulting in a theory that appears to be gauge-dependent, as highlighted in the literature [7, 106, 109].

In the following, I will derive the SFA amplitude in the length gauge. This derivation initially necessitates familiarity with a specific set of solutions using the free-Hamiltonian in the velocity gauge, $H_F^{(v)}$, known as Volkov states (refer to Appendix A.3), followed by the application of suitable gauge transformations to go back to the length gauge, as detailed in Appendix A.1. As various authors have noted in recent years [7, 110], the length gauge results is the correct one that produces results closer to TDSE.

The first step involves selecting an appropriate final state, ξ in Eq. (2.38), where to project the wavefunction time evolution, $|\psi(t)\rangle$ and evaluate photoionization. A straightforward choice is to adopt the complete set of plane waves with momentum

$\mathbf{p}$, represented by $e^{i\mathbf{p}\cdot\mathbf{r}}$. The corresponding SFA amplitude is then given by:

$$a_{\mathbf{p}}^{(SFA)}(t) = -i \int_{t_0}^t dt' \langle \mathbf{p} | e^{-i \int_{t'}^t \hat{H}_F(t'') dt''} \hat{H}_I(t') e^{-i \int_{t_0}^{t'} \hat{H}_0 dt''} | \psi(t_0) \rangle \quad (2.42)$$

It is important to note, however, that while the momentum operator is always defined as $\hat{\mathbf{p}} = -i\hat{\nabla}$, its interpretation is gauge-dependent, as elaborated in Appendix A.1. Specifically, in the velocity gauge, the momentum aligns with the "drift momentum", $\mathbf{P}_{drift}$, a conserved quantity.

$$\hat{\mathbf{p}}^{(v)}(t) := \hat{\pi}(t) - \mathbf{A}^{(v)}(t) = \hat{\pi}(t) - \mathbf{A}^{(v)}(t) = \mathbf{P}_{drift} \quad (2.43)$$

here, $\hat{\pi}(t)$ denotes the velocity operator, and $\mathbf{A}^{(v)}$, the vector potential, which is equal to the transversal component of the external field, $\mathbf{A}^{(v)}(t) = \mathbf{A}(t) = -\partial_t \mathbf{E}(t)$.

Conversely, in the length gauge, where $\mathbf{A}^{(l)} = 0$, the momentum is equal to the instantaneous velocity, and it oscillates in time guided by the field:

$$\hat{\mathbf{p}}^{(l)}(t) = \hat{\pi}(t) \quad (2.44)$$

In the velocity gauge, as detailed in Appendix A.3, finding the solution of the Schrödinger equation with just the free-field Hamiltonian using the propagator formalism is straightforward (see Appendix A.3. Eq. (79)); as a result, we can write:

$$\langle \mathbf{p}^{(v)}(t) | e^{-i \int_{t'}^t \frac{1}{2} (\hat{\mathbf{p}} + \mathbf{A}(t''))^2 dt''} = \langle \mathbf{p}^{(v)}(t') | e^{-i \int_{t'}^t \frac{1}{2} (\mathbf{P}_{drift} + \mathbf{A}(t''))^2 dt''} = \langle \Psi^{(v)}(t') | \quad (2.45)$$

where $\mathbf{p}^{(v)}(t') = \mathbf{p}^{(v)}(t) = \mathbf{P}_{drift}$ is the eigenstate associated to $|\mathbf{p}^{(v)}\rangle$, in the velocity gauge³. From this result, we can define the semi-classical action $S_{\mathbf{p}}(t, t')$ as:

$$S_{\mathbf{p}}(t, t') = \int_{t'}^t \frac{1}{2} (\mathbf{P}_{drift} + \mathbf{A}(t''))^2 dt'' \quad (2.46)$$

As mentioned, our goal is to derive an SFA probability $a_{\mathbf{p}}^{(SFA)}(t)$ within the length gauge (l); therefore, a proper transformation rule between gauges must be applied, see Eq. (2.15).

$$\begin{aligned} a_{\mathbf{p}}^{(l)}(t) &= -i \int_{t_0}^t dt' \langle \Psi^{(l)}(t') | \hat{H}_I(t')^{(l)} e^{-i \int_{t_0}^{t'} \hat{H}_0 dt''} | \psi(t_0) \rangle = \\ &= -i \int_{t_0}^t dt' \langle \Psi^{(v)}(t') | e^{-i \hat{\mathbf{r}} \cdot \mathbf{A}(t')} \hat{\mathbf{r}} \cdot \mathbf{E}(t) e^{-i \int_{t_0}^{t'} \hat{H}_0 dt''} | \psi(t_0) \rangle \end{aligned} \quad (2.47)$$

³We note how the evaluation of $\langle \mathbf{p}^{(v)}(t) | e^{-i \int_{t'}^t \frac{1}{2} (\hat{\mathbf{p}} + \mathbf{A}(t''))^2 dt''}$ propagates backward in time the wavefunction to $\langle \mathbf{p}^{(v)}(t') |$, see Appendix A.3.

Finally, we substitute in Eq. (2.47) the result obtained in Eq. (2.45),

$$a_{\mathbf{p}}^{(l)}(t) = -i \int_{t_0}^t dt' \langle \mathbf{p}^{(v)}(t) | e^{-i \int_{t'}^t \frac{1}{2} (\mathbf{P}_{drift} + \mathbf{A}(t''))^2 dt''} e^{-i \hat{\mathbf{r}} \cdot \mathbf{A}(t')} \hat{\mathbf{r}} \cdot \mathbf{E}(t) e^{-i \int_{t_0}^{t'} \hat{H}_0 dt''} | \psi(t_0) \rangle \quad (2.48)$$

The next step is to clean the notation and transform the momentum from the velocity gauge to the length gauge, exploiting the following relations:

$$\mathbf{P}_{drift} = \mathbf{P} = \mathbf{p}(t) - \mathbf{A}(t) \quad (2.49)$$

$$\langle \mathbf{p}^{(v)}(t) | = \langle \mathbf{p}^{(l)}(t) | e^{-i \hat{\mathbf{r}} \cdot \mathbf{A}^{(v)}(t)} = \langle \mathbf{p} | e^{-i \hat{\mathbf{r}} \cdot \mathbf{A}(t)} \quad (2.50)$$

Assuming the interaction begins at $t_0 = -\infty$ in an eigenstate of the unperturbed Hamiltonian with energy $E_0 = -I_P$ (where I_P represents the ionization potential), the probability of transition from the bound state to a continuum level with momentum $\mathbf{p}$ at time t can be expressed as:

$$a_{\mathbf{p}}(t) = -i \int_{-\infty}^t dt' \langle \mathbf{p} | e^{-i \hat{\mathbf{r}} \cdot (\mathbf{A}(t') - \mathbf{A}(t))} \hat{\mathbf{r}} \cdot \mathbf{E}(t) | 0 \rangle e^{-i S_{\mathbf{p}}(t, t')} e^{+i I_P t'} \quad (2.51)$$

where the semiclassical action $S_{\mathbf{p}}(t, t')$ is equivalently equal to:

$$S_{\mathbf{p}}(t, t') = \int_{t'}^t \frac{1}{2} (\mathbf{p}(t) - \mathbf{A}(t) + \mathbf{A}(t''))^2 dt'' \quad (2.52)$$

We observe that, if the integral in Eq. (2.51) is evaluated at $t = +\infty$, when the interaction with the electromagnetic field is over, $\mathbf{p}(+\infty) = \mathbf{P}_{drift}$.

The last step is to evaluate the expectation value of the element within bracket in Eq. (2.51). By exploiting the completeness of the position eigenstates $|\mathbf{r}\rangle$, we write:

$$\langle \mathbf{p} | e^{-i \hat{\mathbf{r}} \cdot (\mathbf{A}(t') - \mathbf{A}(t))} \hat{\mathbf{r}} \cdot \mathbf{E}(t) | 0 \rangle = \int_{\mathcal{R}^3} d\mathbf{r} \langle \mathbf{p} | \mathbf{r} \rangle \langle \mathbf{r} | 0 \rangle \hat{\mathbf{r}} \cdot \mathbf{E}(t) e^{-i \mathbf{r} \cdot (\mathbf{A}(t') - \mathbf{A}(t))} \quad (2.53)$$

where,

$$\langle \mathbf{r} | 0 \rangle = \psi_0(\mathbf{r}) \quad (2.54)$$

$$\langle \mathbf{p} | \mathbf{r} \rangle e^{-i \mathbf{r} \cdot (\mathbf{A}(t') - \mathbf{A}(t))} = \frac{1}{2\pi^3} e^{-i \mathbf{p} \cdot \mathbf{r}} e^{-i \mathbf{r} \cdot (\mathbf{A}(t') - \mathbf{A}(t))} = \langle \mathbf{p}(t) - \mathbf{A}(t) + \mathbf{A}(t') | \mathbf{r} \rangle \quad (2.55)$$

hence, the projection of the solution to Eq. (2.2) (in the length gauge) into the continuum eigenstates of momentum is :

$$\langle \mathbf{p} | \psi(t) \rangle \approx a_{\mathbf{p}}(t) = -i \int_{-\infty}^t \mathbf{E}(t') \cdot d[\mathbf{p}(t) - \mathbf{A}(t) + \mathbf{A}(t')] e^{+i(I_P t' - S_{\mathbf{p}}(t, t'))} dt'$$

(2.56)

where $d[\mathbf{p}(t) - \mathbf{A}(t) + \mathbf{A}(t')] = \langle \mathbf{p}(t) - \mathbf{A}(t) + \mathbf{A}(t') | \mathbf{r} | 0 \rangle$ is the "dynamical" dipole expectation element between the bound state and a continuum level.

2.2.2.3 Emission of higher-order harmonics

The previous discussion highlighted how to describe photoionization in quantum mechanics as a superposition of various quantum paths, each with its specific interaction time. This means that both the ionization step and the electron subsequent movement in the continuum, using the three-step model terminology, can be accurately described using either the TDSE result (Eq. (2.39)) or the SFA approach (Eq. (2.51)). Next, we will focus on the recombination step and the associated production of high-order harmonics.

TDSE HHG

As presented in Chapter 3.3, a full-TDSE description of HHG is a consolidated approach used to produce accurate predictions of the spatio-temporal properties of HHG from single and/or multiple emitters[20, 111]. Here, we present a derivation consistent with the Dyson equation formalism presented in the previous section. Thanks to Eq. (2.37), we can describe the full-time evolution of the wavefunction as:

$$|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle = -i \int_{t_0}^t dt' \hat{U}(t, t') \hat{H}_I(t') \hat{U}_0(t', t_0) |\psi(t_0)\rangle + \hat{U}_0(t, t_0) |\psi(t_0)\rangle \quad (2.57)$$

where, in analogy with Appendix A.2, and,

$$\hat{U}(t, t_0) = e^{-i \int_{t_0}^t \hat{H}(t'') dt''} \quad (2.58)$$

$$\hat{U}_0(t, t_0) = e^{-i \int_{t_0}^t \hat{H}_0 dt''} \quad (2.59)$$

The emission of light from a time-varying wavefunction is enclosed within the dipole element. Therefore, by utilizing Eq.(2.6) and the propagator property outlined in Appendix A (see Equation (80)), we can express this relationship as follows:

$$\mathbf{d}(t) = -\langle \psi(t) | \hat{\mathbf{r}} | \psi(t) \rangle = -\langle \psi(t_0) | \hat{U}(t_0, t) | \hat{\mathbf{r}} | \hat{U}(t, t_0) | \psi(t_0) \rangle \quad (2.60)$$

Hence, assuming that at $t = t_0$ we are in the usual eigenstate of $\hat{H}_0$, so that $|\psi_0(t)\rangle = \hat{U}_0(t, t_0) |\psi_0(t_0)\rangle$.

$$\begin{aligned} \mathbf{d}(t) = & -\langle 0 | \hat{\mathbf{r}} | 0 \rangle + i \int_{t_0}^t dt' \langle \psi_0(t) | \hat{\mathbf{r}} \hat{U}(t, t') \hat{H}_I(t') | \psi_0(t') \rangle - \\ & - i \int_{t_0}^t dt' \langle \psi_0(t') | \hat{H}_I(t') \hat{U}(t', t) \hat{\mathbf{r}} | \psi_0(t) \rangle - \\ & - \int_{t_0}^t dt' \int_{t_0}^t dt'' \langle \psi_0(t') | \hat{H}_I(t') \hat{U}(t', t) \hat{\mathbf{r}} \hat{U}(t, t'') \hat{H}_I(t'') | \psi_0(t'') \rangle \end{aligned} \quad (2.61)$$

The first term is typically zero in a spherically symmetric potential, the latter belong to continuum-continuum interaction, while the second and the third are complex conjugates of the other. Therefore,

$$\mathbf{d}(t) = +i \langle \psi_0(t) | \hat{\mathbf{r}} \int_{t_0}^t dt' \hat{U}(t, t') \hat{H}_I(t') | \psi_0(t') \rangle + c.c. \quad (2.62)$$

Equation (2.62) reveals an interesting aspect: to generate radiation from an atom with a strong-field laser, it is necessary to consider the dipole matrix element between the bound state (depicted in the left term) and the continuum trajectories of the photoelectron (illustrated in the right term). This consideration aligns precisely with the argument presented at the beginning of this Chapter.

This finding forms the foundation for subsequent calculations that use the TDSE framework to determine the complete HHG spectrum and attosecond pulse generation as a response of an atom to an intense electromagnetic field [112, 113].

SFA HHG

In our final effort, we focus on deriving the dipole spectrum within the strong-field approximation, a widely used approach for more straightforward and less computationally demanding HHG calculations [21, 114]. By adopting this approximation in Eq.(2.62),

$$\hat{U}(t, t') = e^{-i \int_{t'}^t \hat{H}(t'') dt''} \approx e^{-i \int_{t'}^t \hat{H}_F(t'') dt''} = \hat{U}_F(t, t') \quad (2.63)$$

we effectively transition into the classical SFA framework. Under the assumptions of the dipole approximation and operating in the length gauge, Equation (2.62) can then be transformed accordingly.

$$\mathbf{d}_{SFA}(t) = +i \langle \psi_0(t) | \hat{\mathbf{r}} \int_{-\infty}^t dt' \hat{U}_F^{(l)}(t, t') \hat{H}_I^{(l)}(t') | \psi_0(t') \rangle \quad (2.64)$$

where, for simplicity, we dropped the complex conjugate (c.c.).

At this point, we can exploit the completeness of the Volkov states to write:

$$\mathbf{d}_{SFA}(t) = +i \langle \psi_0(t) | \hat{\mathbf{r}} \int_{-\infty}^t dt' \hat{U}_F^{(l)}(t, t') \int_{\mathcal{R}^3} d\mathbf{P} |\mathbf{P} + \mathbf{A}(t')\rangle \langle \mathbf{P} + \mathbf{A}(t') | \hat{\mathbf{r}} \cdot \mathbf{E}(t') | \psi_0(t') \rangle \quad (2.65)$$

where $\mathbf{P} = \mathbf{p}(t) - \mathbf{A}(t)$, is the drift momentum, selected as a complete space on which run the integration.

Exploiting the results achieved in Eq.(2.45):

$$\hat{U}_F^{(l)}(t, t') |\mathbf{P} + \mathbf{A}(t')\rangle = e^{-iS_p(t, t')} |\mathbf{P} + \mathbf{A}(t)\rangle$$

and combining it with Eq. (2.56) we finally write:

$$\mathbf{d}_{SFA}(t) = +i \int_{\mathcal{R}^3} d\mathbf{P} \int_{-\infty}^t dt' \mathbf{d}^*(\mathbf{P} + \mathbf{A}(t)) e^{-i(S_p(t,t') - I_P t')} \mathbf{E}(t') \cdot \mathbf{d}(\mathbf{P} + \mathbf{A}(t')) \quad (2.66)$$

which coincides with what is derived in [6].

It is fascinating to observe that from Equation (2.66), the well-known three steps of the three-step model in HHG become apparent. The first step involves tunnel ionization at time t' , represented by a combination of the dipole element and the electric field strength $\mathbf{E}(t') \cdot \mathbf{d}(\mathbf{P} + \mathbf{A}(t'))$. In the second step, there is an evolution in the continuum, which is governed by the semi-classical action $S_p(t, t')$. This action is responsible for accounting for the dispersion of the continuum trajectories. Finally, the third step is the recombination, occurring at time t and expressed through the "reversed" dipole element $\mathbf{d}^*(\mathbf{P} + \mathbf{A}(t))$.

To complete the picture, all possible trajectories characterized by distinct ionization times and momenta are integrated, culminating in the full-time evolution of the dipole. This integration encompasses the diverse pathways the electron can undertake, from ionization to recombination.

To further emphasise the link between this quantum mechanical result and the ballistic perspective offered by the classical three-step model, we observe that the integral is directed by a temporally fluctuating complex exponential. This fact permits simplifying the equation by using the saddle-point approximation [21]. While it is not our objective to delve into the model emerging from this additional simplification [114], we note the important implications of applying the saddle point (or stationary-phase) condition:

$$\nabla_{\mathbf{P}} S_p(t, t') = 0 \quad (2.67)$$

By doing so, we are effectively handling an equation of motion:

$$\nabla_{\mathbf{P}} S_p(t, t') = \nabla_{\mathbf{P}} \int_{t'}^t dt'' \frac{1}{2} (\mathbf{P} + \mathbf{A}(t''))^2 = \int_{t'}^t dt'' (\mathbf{P} + \mathbf{A}(t'')) \quad (2.68)$$

In atomic units (a.u.), the term $(\mathbf{P} + \mathbf{A}(t''))$ is equal to the electron velocity $\pi(t'')$. Thus, we have:

$$\nabla_{\mathbf{P}} S_p(t, t') = \int_{t'}^t dt'' \pi(t'') = \mathbf{x}(t) - \mathbf{x}(t') = 0 \quad (2.69)$$

The most significant contributions to solving Eq. (2.66) come from stationary points, which occur when the expectation value of the wavepacket position at time t' , the moment of ionization, coincide with its position at the recombination time, t .

This condition mirrors the central hypothesis of classical electron trajectory analysis

in the three-step model. In other terms, the three-step model finds direct support in its assumptions from this quantum mechanical perspective.

2.3 Macroscopic aspect of HHG

In contrast to cases where the atomic and macroscopic responses of a medium are (almost) identical, such as in two-color interaction metrology [115], the macroscopic contribution in high harmonic generation is essential for optimizing and advancing attosecond technologies [97, 116].

The generation and propagation of electromagnetic fields in an extended medium are governed by the wave equation, introduced at the beginning of this chapter:

$$\left[\nabla^2 - \frac{1}{c^2} \partial_t^2 \right] \mathbf{E} = \mu_0 \partial_t^2 (\mathbf{P}^{\mathcal{L}} + \mathbf{P}^{\mathcal{NL}}) \quad (2.70)$$

where $\mathbf{P}^{\mathcal{L}}$ represents the linear polarization, and $\mathbf{P}^{\mathcal{NL}}$ denotes the non-linear polarization, also serving as the source of high-order radiation [117].

As discussed and presented in section 3.3, a comprehensive approach for describing macroscopic HHG requires considering all linear and non-linear effects on the driving field and subsequently using this modified field to calculate the local high-order response microscopically, applying either the TDSE or the SFA result. Each local response contributes to defining the linear and non-linear polarization of the medium, which in turn allows the calculation of the generation and propagation of HHG radiation.

While reporting the technical details of this approach is beyond the scope of this dissertation, the following section provides simplified models to facilitate understanding of Chapter 3.

2.3.1 Phase-matching in HHG

Assuming a linearly polarized driving field and sticking to the slowly-varying envelope and paraxial approximations, while disregarding any off-axis contributions, it can be demonstrated that for a driving field of frequency ω_0 , its multiple harmonics E_q , at frequency $\Omega = q\omega_0$, obey the equation:

$$(2ik_{q,0}\partial_z - k_q^2)E_q = -\mu_0\omega_q^2 P_q^{\mathcal{NL}} e^{-i\Delta k_q z} \quad (2.71)$$

Here, z represents the propagation axis, and $P_q^{\mathcal{NL}}$ is the non-linear polarization component in the Fourier transform at frequency Ω , given as $P_q^{\mathcal{NL}} = \rho d_q$. The term d_q denotes the local microscopic dipole component oscillating at Ω , and ρ is

the medium density. The wave-vector for the q -th harmonic, k_q , is defined as:

$$k_q = n_q k_{q,0} = n_q \frac{\Omega}{c}$$

In this expression, n_q is the complex refractive index, with its imaginary part indicating absorption and the real part representing dispersion. Lastly, Δk_q is the wave vector mismatch between the generated harmonics, qk_0 , and the polarization of the medium induced by the fundamental field, k_q .

$$\Delta k_q = qk_0 - k_q \quad (2.72)$$

When absorption (and dispersion) are negligible, i.e., $n_q = 1$, and assuming a minimal variation of the dipole and density across the gain medium of length L_{med} , Eq. (2.71) can be simplified as:

$$|E_q|^2 \approx |d_q|^2 \rho^2 L_{med}^2 \text{sinc}^2\left(\frac{\Delta k_q L_{med}}{2\pi}\right) \quad (2.73)$$

Equation (2.73) underscores a fundamental aspect of HHG: the harmonic signal can be expressed as a product of a microscopic single atom response and a macroscopic function:

$$|E_q|^2 = |d_q|^2 S_q(\Delta k_q, L_{med})$$

While boosting the microscopic response is possible to some extent [118], the main technological focus in HHG optimisation is to act on the macroscopic term, $S_q(\Delta k_q, L_{med})$, which, as discussed in this section, plays a dramatic role on the harmonics signal yield.

Following Eq. (2.73), we can define the *coherence length*, for the harmonics q as, $L_c^{(q)} = \pi/\Delta k_q$. The ratio between the coherence and medium lengths ($\frac{L_{med}}{L_c}$) allows a direct estimation of the degree of phase-matched generation, where for simplicity, from now on, we omit the dependence over q .

In the scenario of perfect phase-matching (PM), all atoms in the medium emit in phase $\Delta k_q = 0$, $L_c/L_{med} \gg 1$; hence, the intensity of the generated harmonic field grows quadratically with the medium length L_{med}^2 , as demonstrated in Fig. 2.4a). This condition represents the ideal situation where the contributions from all atoms in the medium constructively interfere. In contrast, in cases of imperfect PM ($\Delta k_q \neq 0$), the atoms in the medium do not emit in phase. Consequently, due to periodic dephasing and rephasing between the generated field and the medium-induced polarization, modulations in the intensity of the emitted harmonic field can be observed, which ultimately limits the total harmonics yield.

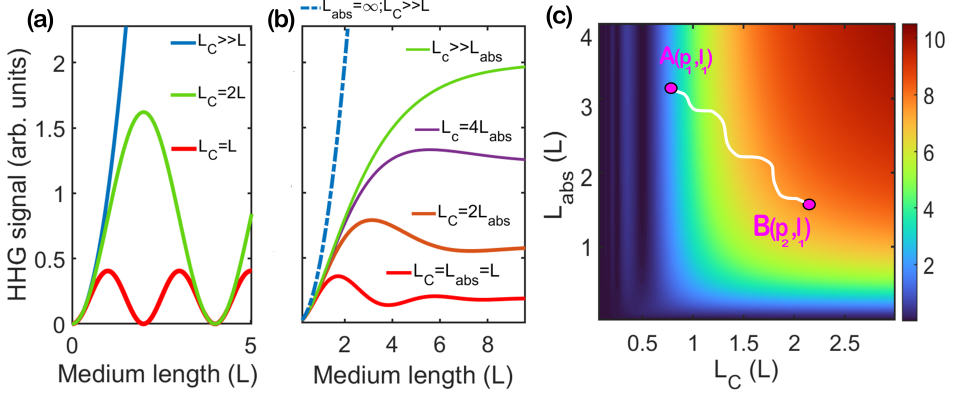


Figure 2.4: a) Representation of Eq. (2.73) for different values of coherence length as a function of medium length, expressed in arbitrary length units L . b) Representation of Eq. (2.74) for different absorption and coherence length. c) 2D-representation of the phase space of coherence length and absorption length fixing the generating medium length at $L_{med} = L$ of Eq. (2.74) for different absorption and coherence lengths. A and B represent two points in the phase space of accessible parameters by changing the gas-medium pressure from p_1 to p_2 , keeping fixed the laser parameters (I_1).

Harmonics absorption effects can also be integrated into this model. In this scenario, the imaginary part of the refractive index accounts for the re-absorption of HHG radiation within the medium. Modifying equation (2.73) to include these effects yields a new phase-matching model [119]:

$$I_q \propto |d_q|^2 e^{-\frac{L_{med}}{2L_{abs}}} \frac{\cosh\left(\frac{L_{med}}{2L_{abs}}\right) - \cos\left(\frac{\pi L_{med}}{L_c}\right)}{\frac{\pi^2}{L_c^2} + \frac{1}{4L_{abs}^2}} \quad (2.74)$$

where, $L_{abs} = \frac{1}{\rho\sigma_{abs}}$ denotes the absorption length, and σ_{abs} is the absorption cross-section at frequency $q\omega_0$, typically obtained from tabulated data [120].

As depicted in Fig. 2.4b), in the presence of a finite absorption length, indefinite quadratic growth of the harmonic signal is not possible, even with infinite coherence lengths. Thus, an equilibrium condition is eventually reached between the generated and reabsorbed signal. As shown for the different solid curves of Fig. 2.4b), shorter coherence lengths will shift this equilibrium point to shorter medium lengths, thus reducing the maximum yield of the harmonic signal.

As highlighted in [119], a rule of thumb for achieving good HHG conversion efficiency (CE), i.e. high harmonic signal for a fixed input energy of the driving laser field, is:

$$\begin{aligned} L_{med} &> 3L_{abs} \\ L_c &> 5L_{abs} \end{aligned}$$

which coincide in working closer to the top-right corner of the solid green-curve condition of Fig 2.4b), where $L_{abs} = L$, $L_{med} = 8L$ and $L_c = 10L_{abs}$.

For a specific medium length and laser conditions (peak intensity, focus position in relation to the medium,...), varying the gas pressure (denoted as p) is the most straightforward strategy to changing PM conditions. Modifying p alters the number of emitters involved in HHG and subsequently changes the values of L_c and L_{abs} . Given that these parameters intrinsically depend on the pressure, this adjustment can potentially enhance the overall harmonic yield. Therefore, as shown in Fig. 2.4c), a practical PM model should offer guidance on selecting the optimal gas pressure to enhance harmonic emission (i.e., moving in the parameter space describing phase-matching and absorption from condition A to B). Additionally, considering that the medium length can also be varied, a comprehensive model for engineering HHG should re-map the total harmonic yield from the (L_{abs}, L_c) space, as derived from Eq. (2.74) (see Fig. 2.4c)), into a more "user-friendly" HHG phase-space, such as (p, L_{med}) .

2.3.2 Hyperbole model for efficient generation

In 2022, a model was proposed to delineate the favourable phase matching conditions as a function of pressure and medium length in HHG. This model, as outlined in [102], starts by decomposing the phase mismatch vector for the harmonic q into four distinct contributions:

$$\Delta k_{(q)} = \Delta k_{at} + \Delta k_{\epsilon} + \Delta k_{foc} + \Delta k_i, \quad (2.75)$$

where Δk_{at} results from the dispersion in the neutral medium, Δk_{ϵ} from the dispersion due to the free electrons created by tunnel ionization, Δk_{foc} accounts for phase variations due to the laser focusing into the medium, and Δk_i is the dipole phase, which is dependent on the microscopic single atom response, varying with the trajectory (short or long).

While the first three components, Δk_{at} , Δk_{ϵ} , and Δk_{foc} , have been extensively discussed in previous works [121, 122], one of the novelties of this model lies in the use of the dipole phase, Φ_i , as derived in the γ -model (presented in Section 2.2) to express Δk_i . Specifically, the model uses the following equation:

$$\Delta k_i = \frac{\partial \Phi_i}{\partial I} \frac{\partial I}{\partial z}, \quad (2.76)$$

This equation underscores the importance of Δk_i in scenarios where macroscopic variations in laser intensity, especially along the propagation axis, need to be considered as potential de-phasing factors. This is particularly relevant for HHG schemes that rely on strongly focused laser pulses.

As discussed in [102], the approximately linear dependence of both the refractive index and the plasma refractive index on the medium density allows for the definitions $\Delta \kappa_{at} = \Delta k_{at}/\rho$ and $\Delta \kappa_{\epsilon} = \Delta k_{\epsilon}/(\eta\rho)$, where η is the ionized fraction, typically

few-percent. By isolating the density from the total wave vector mismatch under the assumption of perfect phase matching ($\Delta k = 0$), one can derive specific conditions for an optimal phase matching density:

$$\rho_{\text{match}} = \frac{\Delta k_{\text{foc}} + \Delta k_i}{\Delta \kappa_{\text{at}} + \eta \Delta \kappa_{\epsilon}}, \quad (2.77)$$

This equation shows that, for a given ionization degree ⁴, η , ideal phase matching (PM) is attainable by suitably choosing the density of the neutral medium. However, the equation tends towards divergence as the ionization degree increases and the denominator approaches zero, indicating the existence of a critical ionization degree beyond which perfect PM on the axis becomes unfeasible.

Merging these insights with the absorption-limited model for HHG outlined in Eq.(2.74), it has been demonstrated[102, 116] that the optimal phase matching pressure can be written as:

$$p_{\text{match}} L \propto 3k_B T \frac{f_i(z)}{\sigma_{\text{abs}}}, \quad (2.78)$$

where $f_i(z)$ encapsulates the geometrical conditions for the possibility of generation outside the focus, in focus $f_i(z) = 1$.

Equation (2.78) delineates a hyperbolic relationship fundamental to achieving efficient phase matching. This formulation directly addresses the challenge of identifying the most appropriate conditions of pressure and medium length for optimal phase matching. The answer provided by the model elucidates that infinite pressure and length combinations can effectively drive phase matching.

As expected, this model remains largely invariant under scaling of the focusing conditions or pulse durations and adheres to the invariant scaling laws identified by [123].

As shown in Fig. 2.5, from the hyperbolic model and pressure-induced phase-matching curves, two distinct phase-matching regimes emerge, associated with a horizontal, i.e. low-pressure p L long-medium, and vertical branches, high-pressure p L short-medium, of the hyperbola:

In the horizontal branch, characterized by a low ionization degree ($\Delta k_{\epsilon} \approx 0$), phase-matching predominantly occurs near when $\Delta k_{\text{at}} + \Delta k_{\text{foc}} + \Delta k_i = 0$. The pressure dependence of Δk_{at} confines phase-matching to a limited pressure range. In this low-pressure regime, the absorption length is extended, necessitating a longer medium for enhanced conversion efficiency. This range can become exceedingly constrained for higher harmonic orders due to the linear relationship between the wave vector mismatch and the harmonic order, $\Delta k_q \propto q$, particularly for pressures $p \neq p_{\text{match}}$.

⁴this term could be exactly calculated by means of TDSE-based or SFA-based numerical codes devoted to quantifying the photoionized electron population.

Conversely, in the vertical branch, where the ionization degree is elevated, phase-matching requires significantly high pressures. Consequently, the absorption length is reduced, demanding the use of a shorter medium. In this scenario, the contributions of the dipole and focusing to the wave vector mismatch are relatively minor compared to the pressure-dependent atomic and free electron contributions. Phase-matching is achieved when $\Delta k_{at} + \Delta k_e \approx 0$, and it tends to become nearly independent of pressure.

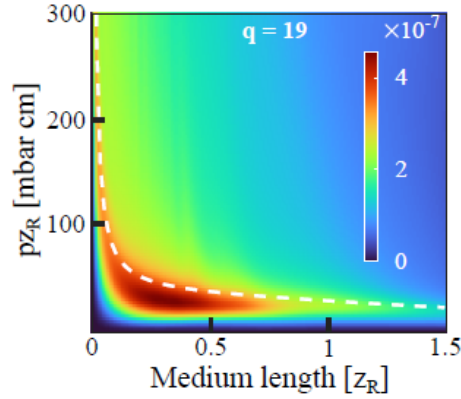


Figure 2.5: SFA-based simulated conversion efficiency as a function of argon gas length and pressure, driving wavelength centred at 800 nm, pulse duration 20 fs, laser intensity $1 \times 10^{14} \text{ W/cm}^2$. The dashed lines represent the phase-matching hyperbole equation portraying the vertical and horizontal branches. Re-printed from [124].

Chapter 3

Optimizing Efficiency and Spatio-Temporal Control of Attosecond Pulse Generation

In Chapter 2, the essential characteristics of HHG were explored, ranging from the atomic-level response to intense electromagnetic fields, manifesting as oscillating dipoles, to the practical use and scalability of the generated radiation by examining the macroscopic response of an extended medium under conditions of phase matching.

In this chapter, I will present interesting findings from my PhD research, exploring critical aspects in harnessing the spatio-temporal properties of HHG-sources technologies and in controlling the generation of isolated attosecond pulses.

In section 3.1, based on [124], we examine an experiment that validates the new theoretical model for optimizing HHG conditions introduced in section 2.3. The central inquiry here is: *Does it exist a general strategy or an optimal setup for boosting HHG efficiency?*

In section 3.2, based on [101], we delve into another crucial attribute of HHG: spatial coherence. HHG provides laser-like XUV radiation (or soft-Xray), valuable not only for ultrafast spectroscopy but also for nano-metrology. The primary focus of this section is on understanding the interplay between spatial aberrations of the field driving HHG and their impacts on the XUV beam distortion. The question here is: *Can we control spatial aberration of the generated XUV radiation by fine-tuning the properties of the driving laser field?*

Section 3.3, based on [SIGCsubmitted], tackles one last crucial feature of HHG: its capability of generating isolated attosecond pulses (IAPs). The question here: *can we*

use extended media to generate IAPs?

3.1 HHG efficiency: measuring the phase-matching hyperbole

As explained in the previous chapter, the generation of high-order harmonics radiation requires the constructive interplay of microscopic and macroscopic effects within the generation volume. On the microscopic level, the single-atom response can be enhanced, for example, by employing short laser pulses [125, 126], which makes the atomic target experience higher intensity before significant ionization. Additionally, tuning the laser wavelength [127] and selecting the appropriate atomic gases [128] can optimize HHG efficiency in the desired photon energy range. Moreover, employing multicolour schemes [118, 129] often increases conversion efficiency (CE) despite necessitating more complex optical setups. From a macroscopic standpoint, the classical wave equation that describes HHG in gases (see Eq. (2.71), chapter 2) is invariant under scaling transformation [97, 130].

Consequently, for a specific CE condition, a common approach to boost the energy of the generated harmonic pulse involves driving the process with high-energy laser pulses. For scaling reasons, this requires a loose focusing geometry, and long, low-density gas target [131]. On the other hand, the need for high-repetition-rate experiments (MHz-level) pushed the research to develop tight-focusing geometries, exploiting high-pressure short-medium schemes [132, 133].

Due to the wide range of geometries explored and the complexity of optimizing HHG, which typically requires the optimization of a wide range of parameters (both microscopic and macroscopic), systematic CE studies for HHG are challenging and, thus, infrequent.

In the context of macroscopic phase-matching optimization, the two most crucial parameters are generation medium length (L_{gen}) and atomic density, or, more commonly, gas pressure, (p). It must be noted, however, that short/long medium or high/low pressure should always be referred to their scale-invariant parameters L_{gen}/z_R and $p z_R$, respectively.

In Chapter 2 (section 2.3), a recent theoretical work [102] was detailed, presenting a novel analytic model supported by numerical simulations. As examined, the model shows that the maximum CE for HHG is achieved when the gas pressure and medium length follow a hyperbolic relationship (see Equation (2.78) of Chapter 2).

The positioning of the gas medium in relation to the laser focus [134], together with the peak intensity of the driving field, influences the absolute CE. However, notably, this model allows us to disregard this complexity as for any given generation length, the inversely proportional relationship (i.e., the hyperbolic trend) with gas pressure remains independent of the intensity and, partially, of the position [102].

In the following section, based on our findings published in [124], the first experimental validation of this phase-matching hyperbola model [102] is reported. These

results are largely independent of the focusing geometry and, to a significant extent, of the pulse duration and laser intensity used in the experiment; therefore, they provide a versatile, practical framework to discuss HHG optimization.

3.1.1 Experimental setups

To test the universality of the model, the experiments were performed on two different HHG beamlines, the GHHG Sylos Long Beamline at the ELI-ALPS facility[135] and the Intense XUV Beamline at the Lund Laser Center[131, 136], which allow exploring a wide range of gas medium lengths. The setups, sketched in Fig. 3.1, are based on a loose focusing geometry to maximize the volume of interaction in the gas and drive the generation process with multi-mJ laser pulses.

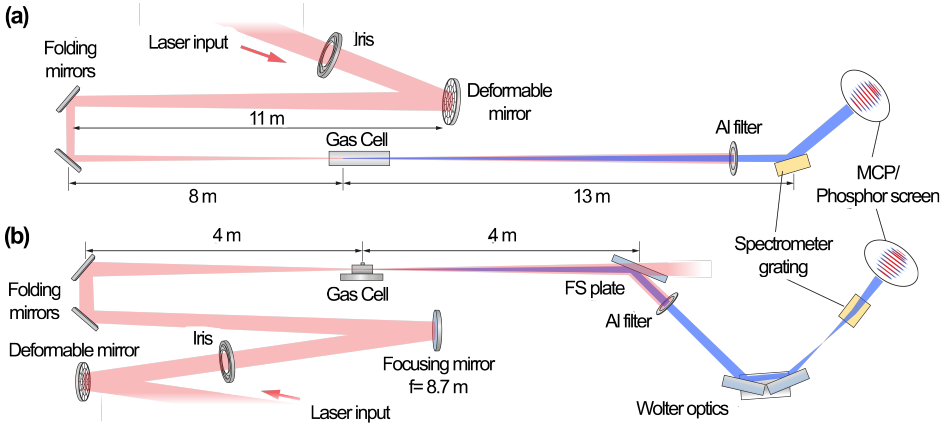


Figure 3.1: Scheme of the a) GHHG Sylos Long Beamline of ELI-ALPS b) High- Intensity Attosecond Beamline at the Lund Laser Center. Re-adapted from [124].

GHHG Sylos long beamline

The Sylos GHHG Long Beamline, as shown in Fig. 3.1a), is designed for extremely loose focusing geometry, capable of accommodating focal lengths up to 55 m, while offering extensive flexibility in XUV generation parameters. During the experiments, a laser pulse with 23 mJ energy, 12 fs duration, and a 10 Hz repetition rate is utilized. The central wavelength of the laser is 825 nm. The beam is focused through a deformable mirror (DM) into a gas cell of variable length, filled with argon gas. A focal length of 19 m is employed, resulting in a spot size of approximately 600 μm in diameter (full-width at half-maximum). The generated XUV radiation then passes through a 200 nm-thick Al filter and is analyzed by an XUV spectrometer. The cell's length can be continuously adjusted from 32.5 cm to 72.5 cm. The measured Rayleigh length is approximately $z_R = 40$ cm, indicating that the gas cell length can vary from $0.81z_R$

to $1.81z_R$. In these setups, the gas pressure is measured directly within the cell. Additionally, four shorter cell lengths were also experimented with, including lengths of 2.5 cm ($0.06z_R$), 4 cm ($0.1z_R$), 8 cm ($0.2z_R$), and 16 cm ($0.4z_R$).

Intense XUV beamline at the Lund Laser Centre

The Intense XUV Beamline in Lund operates via a multi-terawatt Ti:Sapphire laser system. This system generates laser pulses with a 40 fs duration, an 800 nm central wavelength, and a 50 mJ pulse energy at a 10 Hz repetition rate. As illustrated in Fig. 3.1b), the laser pulses are focused into a pulsed argon gas cell using a combination of a deformable mirror (DM) and an 8 m focal length focusing mirror.

As detailed in section 3.2, the DM facilitates wavefront correction and control over the laser focus position within the gas medium. A motorized iris is employed to optimize high harmonic generation (HHG). The XUV radiation is then separated from the remaining IR radiation by reflecting at a 10 degrees grazing incidence on a fused silica (FS) plate, followed by spectral filtering through a 200 nm aluminum foil. Subsequently, the XUV beam is focused via a Wolter-like assembly of two toroidal mirrors (Thales SESO), designed for imaging the generation position with minimal spatial aberrations [137]. Post-focusing, the radiation propagates further and is analyzed by a flat-field spectrometer.

In the experiments [124], the rayleigh length is maintained at approximately $z_R = 30$ cm for three distinct gas cell lengths: 1 cm, 6 cm, and 11 cm, corresponding to $0.03 z_R$, $0.2 z_R$, and $0.37 z_R$, respectively. The gas density within the cell is estimated ex-situ using an interferometric setup. This setup measures the shift in interference fringes as a function of the gas valve opening voltage for a specified opening duration [138].

3.1.2 Results

As discussed, to ensure that the results are independent of any specific focusing geometry, we report in the measurement the quantity $p z_R$ in the units of *mbar cm*. Additionally, the length of the medium is quantified in terms of z_R .

Our experimental procedure involved recording the spectral intensity of the different harmonic orders, ranging from the 19th to the 29th harmonic in each setup. The measurements are repeated for various cell lengths, and for each cell geometry, we methodically scanned the entire range of possible pressure values.

As depicted in Fig. 3.2, we observed that the highest harmonic yield, in the figure reported for the sub-set of harmonics 21,23 and 25, is consistently achieved along the predicted hyperbolic model.

As noted, a unique aspect of the phase-matching model[102] is its independence from the focusing geometry and, particularly, from the laser intensity. To experimentally

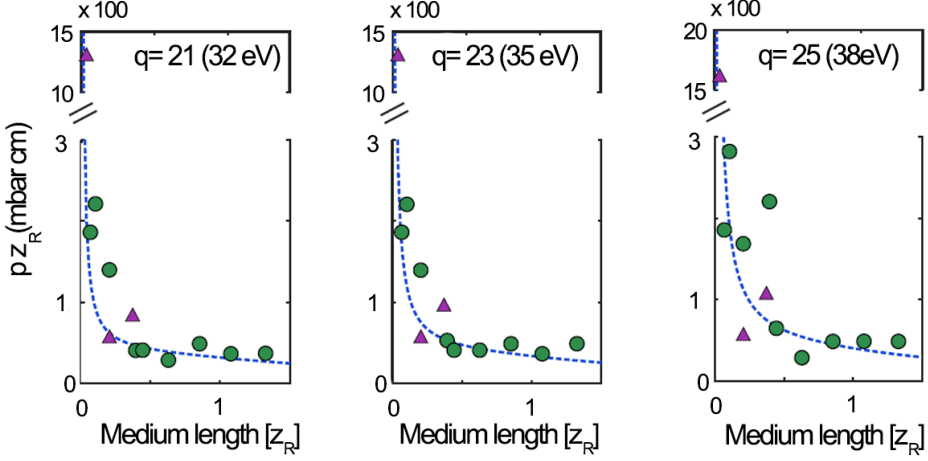


Figure 3.2: Peak harmonic yield conditions for orders 21st – 25th generated in argon gas. Dataset from GHHG Sylos Long beamline (green circles) and Intense XUV Beamline (purple triangles). Re-adapted from [124].

prove it, we performed a series of measurements at varying driving pulse energies: 8 mJ (represented by circles), 10 mJ (squares), and 12 mJ (diamonds). The estimated intensities for these energies fall within the range of 1×10^{14} to 3×10^{14} W/cm². Throughout these measurements, all other experimental conditions were maintained constant. As depicted in Fig. 3.3a), the data from all three energy settings fit the expected hyperbolic trend, illustrated by the blue dashed line.

Another crucial insight from the hyperbole model is the distinct properties of phase-matching regimes across the two branches, leading to diverse spatial profiles for the generated harmonics. In particular, the vertical branch contributes more off-axis emissions than the horizontal branch. Fig. 3.3b) displays far-field spatial profiles for the 23rd harmonic order at two different gas medium lengths: $0.06 z_R$ (vertical branch) and $1.33 z_R$ (horizontal branch). The top figures in this diagram represent simulations, while the bottom ones show experimental data. The simulations were conducted with a laser intensity of 1.9×10^{14} W/cm², emulating experimental conditions. The experimental spatial profiles were acquired from the spectrometer camera after integrating along the spectral axis for each harmonic order. The profiles, both from simulations and experiments, represent the maximum harmonic yield at the corresponding pressures for each medium length. A qualitative match between the simulated and experimental results is evident. In both scenarios, spatial profiles generated on the vertical branch exhibit more irregularities and prominent off-axis contributions. Conversely, harmonics produced on the horizontal branch display a more confined, smoother spatial profile, which is beneficial for applications that require high-quality spatial properties and/or high intensity upon refocusing.

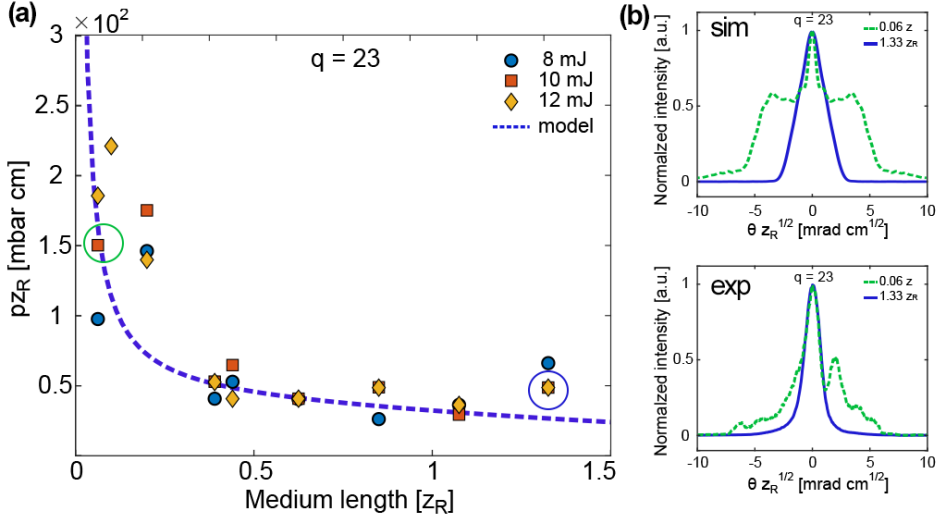


Figure 3.3: a) Maximum yield of harmonic 23rd at three distinct driving pulse energy values: 8 mJ (circles), 10 mJ (squares) and 12 mJ (diamonds). The Blue dashed line indicates the hyperbolic model. b) Simulated, upper panel and measured, lower panel, normalized harmonic intensity ($q = 23$) along the spectrometer spatial axis for a gas medium length of $0.06 z_R$ (dashed green line) and $1.33 z_R$ (solid blue line). The here displayed have been acquired at the GHHG Sylos Long beamline). Re-adapted from [124].

3.1.3 Conclusions: how to optimize HHG

In this study [124], we successfully demonstrated that the optimal phase matching region aligns closely with the predictions made by the hyperbola model [102]. This model helps in identifying two distinct regimes of phase matching: a vertical branch, for medium lengths shorter than the Rayleigh length of the focused driving field, and a horizontal branch, applicable to longer medium lengths.

The vertical branch is characterized by transient phase-matching, where the spatial profiles of the generated radiation tend to show significant off-axis contributions. Moreover, in this regime, laser intensity fluctuations substantially impact the harmonic yield. On the other hand, the horizontal branch, which represents absorption-limited phase-matching occurring over an extended duration, produces radiation that is well-collimated and shows relatively less sensitivity to variations in laser intensity. Given these attributes, the horizontal branch appears to be more favourable for applications requiring superior spatial profiles, potentially leading to higher refocused XUV intensities. However, the simulations in [102] have shown relatively higher conversion efficiencies on the vertical branch for higher harmonic orders.

To conclude, the choice of the most suitable generation regime is highly dependent on the specific experimental setup and intended application. The phase-matching model

we have experimentally validated offers a valuable framework for designing high-flux XUV sources tailored to specific research needs and applications.

3.2 Spatial properties: control of chromatic aberration in HHG

High-order harmonic generation has been a key technique for creating the shortest events humans can harness. An aspect not yet explored in this thesis is the high spatial coherence of HHG, which is inherited directly from the driving IR laser. This characteristic grants high-order harmonics radiation the unique quality of being a laser-like beam, tunable from 80 nm (XUV) down to just a few nanometers (soft-x-ray). Therefore, achieving a high degree of control over the spatial quality of the HHG radiation is crucial. This is not only significant for spectroscopic applications that require high field strength, such as table-top XUV-pump-XUV-probe experiments [89, 139], but also for applications where precise control, shaping, and focusing of the XUV beam spot-size on small structures are essential. Examples include coherent diffraction imaging [140], nano-scale metrology [141], and ptychography [142].

As discussed, the conditions under which HHG is generated, including the driving laser wavelength, intensity profile and wavefront, or the gas medium properties and the position of the generation medium relative to the laser focus, are critical. These factors affect not only the photon flux (or CE) of the generated HHG but also the spatial and focusing characteristics of the XUV radiation [143]. In essence, different harmonics can exhibit varying divergence properties, leading to pronounced chromatic aberrations after refocusing the full HHG spectrum on target. This, in turn, results in spatiotemporal coupling of the attosecond radiation [99, 100].

The presence of significantly distorted XUV wavefronts can give rise to deformed far-field spatial profiles, exemplified by the cross-like patterns shown in Figure 3.4. These distortions impose severe limitations on using XUV profiles in applications demanding high spatial-quality beams. Other studies have noted similar far-field profiles without directly addressing their origin [144, 145].

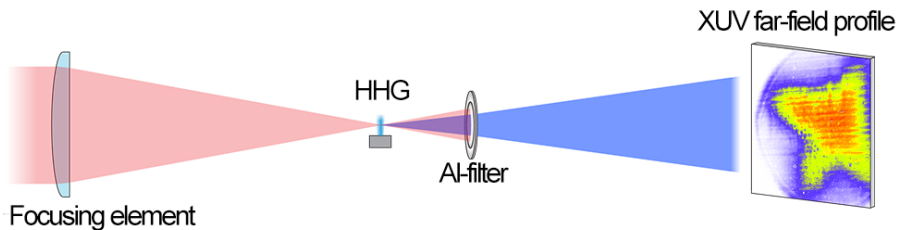


Figure 3.4: Sketch of the generation of an aberrated XUV-beam. An intense IR field is focused into a gas target, giving rise to HHG. Once the driving field is filtered out, the spectrally integrated XUV far-field can exhibit significant distortion, often characterized by a distinct cross-like pattern. This occurs even when the driving fields appear free of aberrations. The concept is re-adapted from [101].

In our research published in [101], we conducted both theoretical and experimental investigations into the HHG process, driven by a non-ideal, slightly astigmatic IR field. By integrating simulations with experimental results, we emphasise the influence of a realistic driving field on the wavefront properties of the resulting XUV beam, as well as its implications for the intensity of the refocused XUV beam. Our study reveals that careful control over the driving field wavefront is critical to mitigate the aberrations in the XUV field. Our model identifies the optimal parameter space for generating high-quality XUV beams, regardless of the specific focusing geometry. Consequently, the outcomes of this study provide general guidelines for different experimental schemes.

We experimentally observe that even minor degrees of astigmatism in the driving field can lead to cross-like patterns in the harmonics. These patterns emerge from the superposition of individual harmonics, each exhibiting spatial profiles elongated in distinct directions. By employing a deformable mirror to correct these aberrations, our work demonstrates that precise adjustments to the driving wavefront are vital for ensuring the optimal spatial quality of the harmonics.

3.2.1 A simple model for HHG aberration

Before entering into the details of the results, we first delve into the model that guided our experimental investigation.

Let us consider a driving laser field exhibiting astigmatism. The laser field is characterized by distinct focal positions along two perpendicular axes and potentially varying beam waists for each focus. Such an astigmatic Gaussian beam can be conceptualized as a product of two Gaussian beams [146], with axes x, y aligned with the principal semi-axes of the beam's profile. The spatial phase, ϕ , and intensity profile, I , of an astigmatic beam propagating along the z -axis, can be expressed as:

$$\phi(x, y, z) = \frac{kx^2}{2R_x(z)} + \frac{ky^2}{2R_y(z)} \quad (3.1)$$

$$I(x, y, z) = I_0 \frac{w_{0x}w_{0y}}{w_x(z)w_y(z)} \exp\left(-\frac{2x^2}{w_x^2(z)} - \frac{2y^2}{w_y^2(z)}\right) \quad (3.2)$$

where k denotes the wave number, and I_0 represents the peak intensity achievable without astigmatism. Here, we concentrate on the radial phase dependence, omitting the Gouy phase.

The radius of curvature $R_x(z)$ and beam radius $w_x(z)$ along the x -axis are defined by:

$$R_x(z) = z - z_{0x} + \frac{z_{Rx}^2}{z - z_{0x}}, \quad w_x(z) = w_{0x} \sqrt{1 + \frac{(z - z_{0x})^2}{z_{Rx}^2}}, \quad (3.3)$$

and similarly for R_y and w_y .

In these expressions, z_{Rx} (z_{Ry}) is the Rayleigh length and z_{0x} (z_{0y}) is the position of the focus along the x (y) axis in the z direction. The astigmatic difference, indicated as $\Delta z = z_{0y} - z_{0x}$, is the distance between the two foci, and the average Rayleigh length is given by $z_R = (z_{Rx} + z_{Ry})/2$.

Fig.3.5 illustrates the evolution of the beam radii (a) for an astigmatic driving field with $\Delta z = z_R$ and $w_{0x}/w_{0y} = 1.15/0.9$, along with the variation of the on-axis intensity (b). The origin ($z = 0$) is set at the midpoint between the two foci at $z = \pm \Delta z/2$. The vertical axes in Fig.3.5 are normalized to the average driving field beam waist, $w_0 = (w_{0x} + w_{0y})/2$.

As outlined in Chapter 2, the three-step model is employed as the starting point to provide an analytical representation of the dipole phase, referred to as the γ -model[98], denoted as $\Phi_i(\Omega)$, where $i = [s, l]$ indicates the trajectory (short or long). This model is expressed as:

$$\Phi_i(\Omega) = \alpha_i I + t_{pi}(\Omega - \Omega_p) + \frac{\gamma_i}{I}(\Omega - \Omega_p)^2, \quad (3.4)$$

where $\hbar\Omega_p$ is the ionization energy of the atom, I denotes the local laser intensity, and α_i and t_{pi} are constants that can be derived from the model (see section 2.1).

In the subsequent discussion, we focus primarily on the short trajectories, which generally constitute the major contribution to the harmonic yield. The dipole phase impacts the spatial characteristics of the harmonics via its intensity dependence, suggesting that only the final term in Eq. (3.4) should be considered.

Assuming a homogeneously distributed, infinitely thin generation medium, we neglect the influence of macroscopic phase matching. This assumption is justified in our experiment, as the medium length is over 100 times shorter than the Rayleigh length of the driving laser focus, validating a thin medium approximation. While the macroscopic response can also affect the spatial properties of the harmonics[102], an exploration of such effects falls outside the aims of this discussion.

Wavefront of the HHG radiation

In the scenario under consideration, the XUV radiation generated by an IR beam at the generation plane, denoted as z_{gen} , can be simply seen as a spatial superposition of individual atomic responses. Each response is driven by a distinct local electric field value, $E(x, y, z_{\text{gen}})$.

Following the approach outlined in [99], we can express the phase of the q -th harmonic field emitted by short trajectories, ϕ_q , as:

$$\phi_q(x, y, z_{\text{gen}}) = q\phi(x, y, z_{\text{gen}}) + \frac{\gamma_s}{I(x, y, z_{\text{gen}})}(q\omega - \Omega_p)^2, \quad (3.5)$$

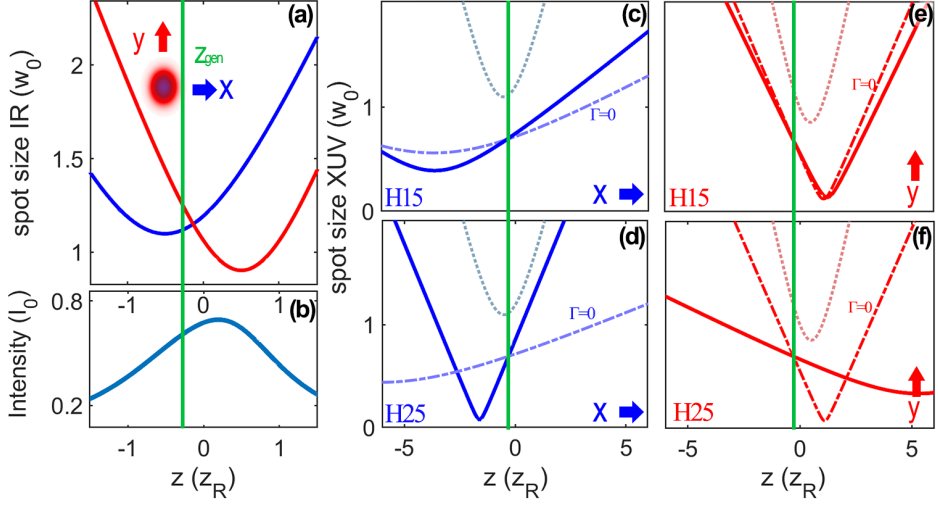


Figure 3.5: a) Varying beam radii for an astigmatic driving field along x (indicated by the blue solid line) and y (red solid line), plotted against the coordinate z normalized to the average Rayleigh length, z_R . The generation plane, z_{gen} , is highlighted by a solid green vertical line. b) Graph showing the on-axis intensity variation of the astigmatic driving field relative to z , scaled to the unit I_0 . c), d) Illustrate the changes in beam radii along x (blue) for the 15th and 25th harmonics, respectively, under the assumption of astigmatic Gaussian harmonic beams, excluding higher-order terms. The dashed blue line represents the beam propagation without the dipole phase ($\Gamma = 0$), while the thinner dotted blue line marks the positions of the driving field x focus from panel a). e) and f) Similar to panels c) and d), but for the y -direction. Re-adapted from [101].

where $q\phi$ represents the phase transferred from the infrared field and $\omega = \Omega/q$ is the laser frequency.

Additionally, we assume that the harmonic intensity, I_q , varies following a power law of the driving field intensity[102, 147, 148]:

$$I_q(x, y, z_{\text{gen}}) = [I(x, y, z_{\text{gen}})]^p, \quad (3.6)$$

with $p \approx 2.6$ as suggested by [102].

The next step involves substituting ϕ and I in Eq.(3.5) with their expressions for an astigmatic beam, Eqs.(3.1) and (3.2), performing a Taylor expansion of the intensity around $x = y = 0$, and keeping only the terms proportional to x^2 and y^2 . This gives an HHG phase up to the second order in x and y :

$$\phi_q^{(2)}(x, y, z_{\text{gen}}) = \frac{qkx^2}{2R_{qx}(z_{\text{gen}})} + \frac{qky^2}{2R_{qy}(z_{\text{gen}})}, \quad (3.7)$$

with

$$\frac{1}{R_{qx}(z_{\text{gen}})} = \frac{1}{R_x(z_{\text{gen}})} + \frac{4\Gamma c}{q\omega w_x^2(z_{\text{gen}})}, \quad \Gamma = \frac{\gamma_s(q\omega - \Omega_p)^2 w_x(z_{\text{gen}})w_y(z_{\text{gen}})}{I_0 w_{x0}w_{y0}}. \quad (3.8)$$

and similarly for $R_{qy}(z_{\text{gen}})$.

Knowing R_{qx} , R_{qy} , as well as the radii $w_{qx}(z_{\text{gen}}) = w_x(z_{\text{gen}})/\sqrt{p}$ and $w_{qy}(z_{\text{gen}}) = w_y(z_{\text{gen}})/\sqrt{p}$, from Eq.(3.6), in the generation plane allows for a purely analytical description of the generated harmonic beams simply as astigmatic Gaussian beams.

The calculated variations of the beam radii are illustrated in Fig. 3.5 for the 15th (c,e) and 25th (d,f) harmonics generated in argon along the x (c,d) and y (e,f) axes, respectively. The dashed lines represent the straightforward phase transfer from the driving field, corresponding to $\Gamma = 0$, while the solid lines include the dipole phase contribution to the radii of curvature. This underscores the significant role of the dipole phase in influencing the curvature transfer to the harmonics.

Given that the focus of the x -axis driving field is positioned before the generation plane, the harmonics emerge as diverging beams with virtual foci along the x -direction, as depicted in Figs.3.5 (c,d). In this scenario, the dipole phase influence increases the divergence for the higher-order harmonics, attributable to the q -dependence of Γ . Conversely, the focus of the y -axis driving field is situated significantly beyond the generation plane, leading to the harmonics being generated as converging beams with actual foci along the y -axis, as shown in Figs.3.5 (e,f). Here, the contribution of the dipole phase acts in opposition to the straightforward phase transfer, causing a reduction in convergence for higher-order harmonics. Consequently, this also leads to a diminished divergence after passing through the real focus.

Our model can be enhanced by incorporating higher-order terms from the Taylor expansion of the XUV radiation's dipole phase. Consequently, Eq. (3.7) is extended to:

$$\phi_q^{(2N)}(x, y, z_{\text{gen}}) = \phi_q^{(2)}(x, y, z_{\text{gen}}) + \Gamma \sum_{n=2}^N \frac{1}{n!} \left(\frac{2x^2}{w_x^2} + \frac{2y^2}{w_y^2} \right)^n. \quad (3.9)$$

The incorporation of these higher-order terms, for $2 \leq n \leq N$, results in the introduction of more complex spatial aberrations, which are particularly relevant for individual harmonics. The effects of these aberrations, while noteworthy and detailed in [101], fall outside the aims of the present discussion.

3.2.2 Results

The experiments were conducted at the High-Intensity Attosecond Beamline at the Lund Laser Center, previously outlined and illustrated in Fig. 3.1. The beamline features a deformable mirror fitted with 32 piezoelectric actuators. The DM plays a key role in reshaping the pulse wavefront by adjusting its surface and in altering the generation position by changing its curvature. A dielectric focusing mirror then directs the beam into the argon gas used for generation. A leak in the final mirror before the gas cell helps to image the driving beam focus.

Figure 3.6 displays the IR and XUV intensity profiles at specific generation positions without any correction from the DM. To enhance clarity, the images are rotated to align the x and y axes horizontally and vertically, respectively. The IR beam focus shows slight astigmatism, with distinct foci observed along the x and y axes, as demonstrated in Fig. 3.6 a) and b). The Rayleigh lengths are calculated as $z_{R,x} = 22.3$ cm and $z_{R,y} = 17.5$ cm, with a separation distance between the foci of 16.8 cm.

The corresponding XUV far-field patterns are depicted in Fig. 3.6c). The images display a circular cutoff due to passage through an aperture and a linear boundary from the camera chip's edge. These measured profiles reveal significant spatial distortions, transitioning from vertical to horizontal orientations and exhibiting cross-like designs at certain intermediate-generation sites.

Fig. 3.6d) show the results of the simulations that incorporate the full model, including the higher-order terms as per Eq. (3.9), with $N = 4$. These simulations are tailored to replicate the experimental condition, particularly utilizing the fitted IR beam radii as shown by the solid lines in Fig. 3.6a).

Although the simulations align broadly with the experimental findings, certain quantitative discrepancies are noted. These differences are anticipated, considering the model's basis on ideal Gaussian beams, which only approximate the actual intensity distribution of the driving laser. Additionally, the model does not account for more complex aberrations, like coma or trefoil. Despite these limitations, the good qualitative agreement allows for discussing the physical origin of the observed far-field patterns, as will be further discussed.

Physical origin of XUV aberration

Figure 3.7 presents the XUV far-field profiles for a subset of the generation positions shown in Fig. 3.6. To simplify the discussion as much as possible, we based the simulations on the pure-gaussian model presented in the section, excluding the higher-order contributions. We show harmonics 15 (a) and 25 (b) as well as the sum of all harmonics from 11 to 29 (c), taking into account their relative spectral weights, characterized experimentally. A figure including the individual far-field profiles of all harmonics is included in the SI of [101].

For harmonic 15, the profile changes from vertically elongated to horizontal when the generation position is moved after the focus. For higher harmonic orders, the same change from vertical to horizontal takes place, but the transition occurs at earlier generation positions (as demonstrated in the SI[101]). For harmonic 25, the profile is horizontal at all generation positions.

The patterns shown in Fig. 3.7 align with the previous analysis of harmonic divergence, particularly harmonics 15 and 25, as discussed in Fig. 3.5. The shifting of the generation position from -5.4 cm to 5.4 cm alternates between the focal points in

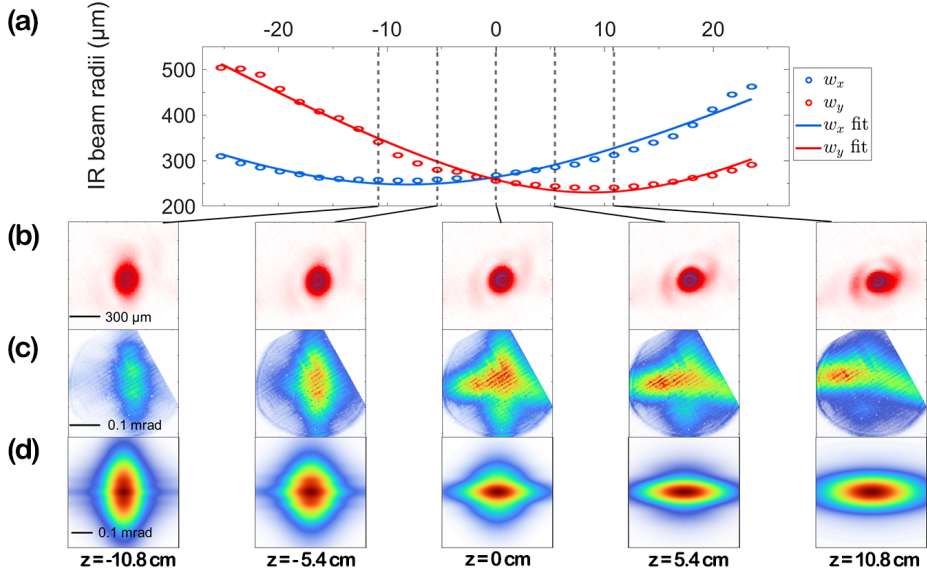


Figure 3.6: a) IR beam radii along the x (blue) and y (red) directions, with open circles denoting experimental data and solid lines showing Gaussian beam fits; b) Captured images of the experimental IR focus at various positions along the z axis. c) Experimental XUV far-field patterns produced at these generation points; d) Simulations of the same XUV far-field profiles, incorporating higher-order terms, utilizing as input of the simulation the Gaussian fits from a). Re-adapted from [101]

the x and y directions, resulting in the IR wavefront always contributing a diverging effect in the x direction and a converging effect in the y direction.

At $z_{\text{gen}} = -5.4$ cm, if we neglect the dipole phase effect on the XUV wavefront curvature, the XUV wavefront would appear relatively flat in the x direction while converging in the y direction. This would produce a more significant far-field divergence in the y direction, leading to a vertically extended far-field pattern. When the dipole phase is considered, harmonic 15 maintains this pattern due to its minimal dipole contribution. However, for harmonic 25, with a more substantial dipole influence, the divergence intensifies in the x direction and reduces in the y direction, resulting in a horizontally stretched far-field pattern.

Conversely, at $z_{\text{gen}} = 5.4$ cm, without the dipole phase influence, the XUV wavefront would diverge in the x direction and be nearly flat in the y direction, resulting in a larger far-field divergence in the x direction and a horizontally elongated profile. This effect persists across all harmonics with the inclusion of the dipole phase, as it amplifies divergence along both the x and y directions.

Upon comparing these observations with the results inclusive of higher-order terms in Fig. 3.6d), it is evident that the model excluding higher-order terms can interpret the cross-like far-field patterns as a composite of individual harmonics, each displaying either horizontal or vertical elongation. However, as shown in Fig. 3.6d), the incorporation of higher-order terms introduces additional complexities, partic-

ularly when the XUV wavefront is nearly flat; thus worsening profile distortions as elaborated in [101].

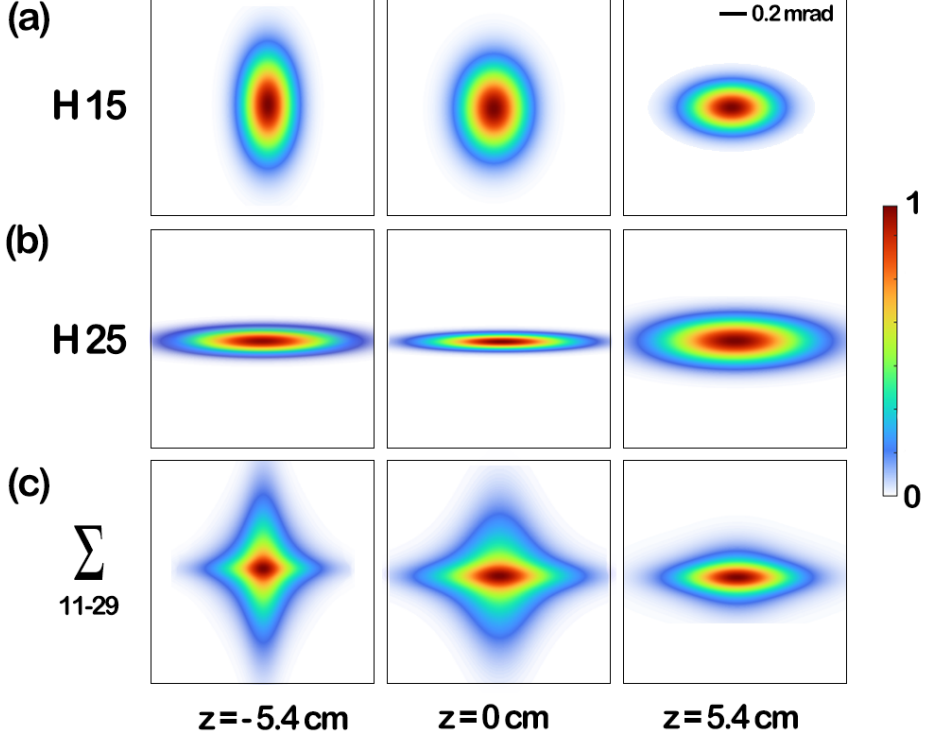


Figure 3.7: Simulated XUV far-field patterns for harmonic orders 15 (a) and 25 (b), together with the sum of the profiles from harmonic 11 to 25 (c). The columns display the simulation of different harmonics at identical generation sites, similar to Fig. 3.6. These simulations were conducted without considering higher-order contributions. Re-adapted from [101]

3.2.3 Analysis of chromatic aberration for different IR-astigmatism

As illustrated in Fig. 3.5 (c-f) and previously discussed, each harmonic possesses distinct beam waist sizes and positions for the x and y foci. Consequently, the divergence of the q th harmonic in the x -direction, denoted as $\theta_{qx} = \lim_{z \rightarrow \infty} (w_{qx}(z)/z)$, and similarly θ_{qy} in the y -direction, undergoes substantial changes by changing the generation position and the driving field aberrations, thereby affecting the final characteristics of the XUV-beam. Although the experimental data presented were specific to a particular astigmatism scenario of the driving field, in this last part, we focus on a broader analysis of how XUV properties change as a function of the driving field astigmatism.

In a typical experimental setting, the far-field profile of the harmonics serves as the most indicator of the XUV beam quality. However, for practical applications, the primary concern often lies in the quality of the refocused XUV pulses, which is closely related to the observed aberrations. To quantitatively assess this aspect in experimental scenarios, we introduce an eccentricity parameter, Θ_{qxy} , for the q th harmonic, defined as follows:

$$\Theta_{qxy} = \frac{\theta_{qy} - \theta_{qx}}{\theta_{qy} + \theta_{qx}}, \quad (3.10)$$

This parameter, Θ_{qxy} , is typically minimized in magnitude during experiments to achieve a circularly symmetric XUV beam profile.

In Fig. 3.8, the eccentricity parameter, Θ_{qxy} , is displayed for harmonic orders 15 and 25. This parameter is plotted against the astigmatism of the driving field, expressed via the astigmatic difference Δz in z_R units, and the difference in beam waist radii $\Delta w = w_{0x} - w_{0y}$ in w_0 units. The analytical model, excluding higher-order contributions, is used to generate these plots, considering a single generation plane at $z_{\text{gen}} = -0.2z_R$ and a peak intensity of $I_0 = 2 \times 10^{14} \text{ W/cm}^2$, approximating the conditions of our previous experiments.

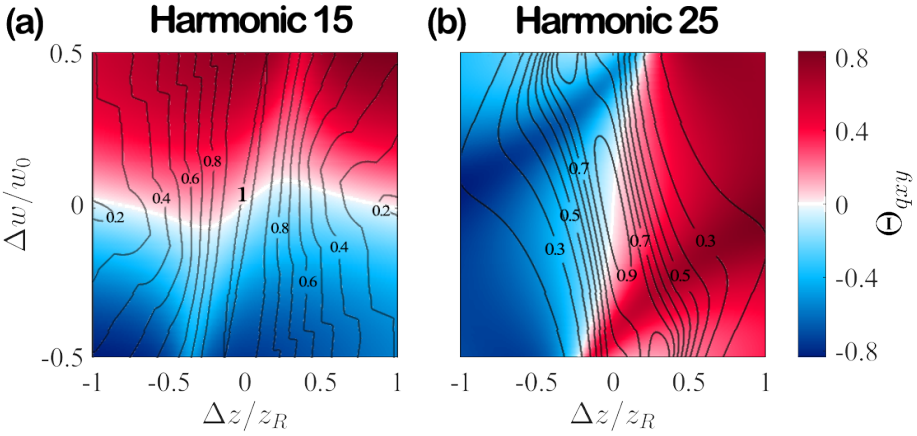


Figure 3.8: Changes in the eccentricity parameter, Θ_{qxy} , for harmonic orders 15 (a) and 25 (b), plotted against the driving field astigmatism ($\Delta z/z_R$) and the normalized difference in beam waist radii ($\Delta w/w_0$). The Strehl ratio is highlighted by the black contour lines.

In scenarios where Θ_{qxy} is positive (indicated in red areas), the far-field harmonic profile appears vertically elongated. Conversely, when Θ_{qxy} is negative (shown in blue areas), it results in a horizontal elongation. For both harmonic 15 and 25, there are zones where Θ_{qxy} approaches zero (white areas), suggesting a circular symmetry in the far field, even though both the driving field and the harmonics exhibit astigmatism.

The 15th harmonic is primarily influenced by changes in the relative beam waist radii of the driving field, while the 25th harmonic is more sensitive to the driving field astigmatism.

This phenomenon, where the harmonic beam far-field eccentricity is null despite intrinsic astigmatism, can be attributed to a balance between the astigmatic distance and the differences in beam waist radii along x and y of the driving field, as proved experimentally in [101]. This balance, influenced by the intensity-dependent dipole phase, yields equivalent far-field divergences along both x and y axes. Nonetheless, the presence of astigmatism in the harmonics may affect their efficacy in experiments where refocusing is typical. The black contour lines in Fig. 3.8, panels (a) and (b), illustrate the variation in the Strehl ratio of a single harmonic, relative to astigmatism and beam waist radius differences of the driving field. Here, the Strehl ratio compares the on-axis peak intensity of the astigmatic harmonic beam to that of a stigmatic harmonic beam generated by a non-astigmatic driving field with $\Delta z = \Delta w = 0$. Such a reduced peak intensity in the refocused XUV beam can be disadvantageous in experiments requiring high XUV intensities[139].

Although the Strehl ratio for an individual harmonic diminishes as one moves away from the center point ($\Delta z = \Delta w = 0$), it is notable that substantial Strehl ratios can be sustained even with considerable differences in beam waist radii, provided there is a slight adjustment in the astigmatism of the driving field. In such cases, the harmonic beam nearly approaches stigmatic characteristics but exhibits varying degrees of divergence along the x and y axes. This results in an elliptical focal spot, which, despite the high Strehl ratio, may not be ideal for specific uses like nano-imaging and metrology [141].

Furthermore, when combining multiple harmonics to create attosecond pulses, the variation in astigmatism across different harmonic orders can lead to sub-optimal spatio-temporal superposition. This, in turn, can significantly affect the temporal characteristics of the pulses [100].

3.2.4 Conclusion: how to control XUV aberrations

This study underscores that for optimal focusability of XUV pulses via HHG, it is imperative to use a non-aberrated, stigmatic driving field. Our experiment exemplifies this principle by utilizing a deformable mirror to rectify any aberrations in the driving field. Figure 3.9a) displays how the beam waists of the corrected IR beam vary along the z propagation axis for both x and y axes. The full beam near its focus is depicted in Fig.3.9b), while Fig.3.9c) illustrates the XUV far-field profiles at corresponding generation positions.

With a stigmatic driving field, the XUV far-field profiles remain symmetric and exhibit minimal dependence on the generation position, contrasting with the results seen in Fig.3.6. Although the IR spatial profiles are comparable in Fig.3.9b) and 3.6b),

the quality of the XUV profiles improves substantially upon correction of the driving field minor aberrations. This indicates that even slight astigmatism in the IR can lead to significant distortions in the XUV far-field profiles. Correcting the aberrations in the driving field can hence visibly enhance the quality of the XUV beam.

In conclusion, to generate high-quality XUV beams that achieve the highest peak

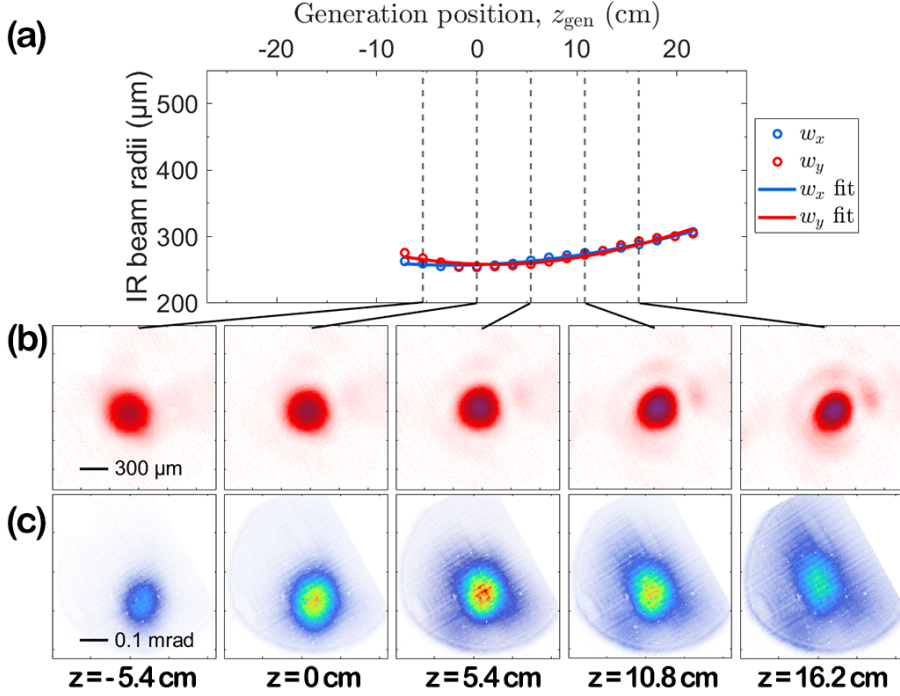


Figure 3.9: a) Experimental IR beam waists in the x (blue) and y (red) directions for an aberration-corrected beam, using the DM; b) Experimental IR focus map at different positions along the z -axis. (c) XUV far-field profiles obtained at the corresponding z -positions.

intensities and smallest focal spots, it is essential to employ aberration-free driving fields. This conclusion remains applicable across various generation positions, driving field intensities, and central wavelengths. Notably, as demonstrated in Eq. (3.8), the XUV aberration patterns, which rely on $\Gamma \propto q^2/I$, will shift towards higher photon energies (or higher harmonic orders, q) as the intensity increases; hence the validity of our results can be extended in spectral regions of high-technological interest (e.g. 10-nm wavelength).

3.3 Temporal properties: engineering isolated attosecond pulse technology

The need for isolated attosecond pulses (IAP)

In addition to enhancing its efficiency (refer to section 3.1) and tailoring its spatial characteristics (refer to section 3.2), HHG can be used to produce exceedingly short pulses of XUV/soft-Xray light [18, 149]. As explained in Chapter 2, this radiation typically manifests as a train of attosecond pulses, each separated by half the optical cycle of the driving field.

However, for numerous applications, the generation and manipulation of isolated attosecond pulses (IAPs) are imperative to precisely track electronic motion in atoms, molecules, and solids with high-temporal resolution [12, 13, 14, 52]. Over the past decade, the significant progress in table-top IAP sources has depended either on using extremely brief driving pulses [150, 151] or employing specialized gating techniques [25, 26, 152]. For example, polarization gating [153, 154] is based on time-dependent polarization shaping of the driving radiation. In contrast, color gating [155] uses a secondary color to disrupt the symmetry of the electric field. The double optical gating method [156] integrates both polarization and color gating strategies. Another prevalent approach is ionization gating [157, 158], which employs a time-restricted window for HHG phase matching [159].

Currently, the leading method for generating IAPs involves using short-medium gas cells at high pressures. However, high-pressure setups often pose challenges in controlling the gas profile and exhibit limited flexibility, especially when increasing the energy of the driving pulse is required. Conversely, longer medium systems operating at low pressure can achieve comparable, if not superior, conversion efficiencies to static cells and pulsed valves [160], and they generally offer improved spatio-temporal properties of the produced XUV radiation [102, 124].

Furthermore, existing studies [161] have highlighted the effectiveness of concluding HHG with a sharp pressure gradient, which facilitates phase matching and minimizes re-absorption, thereby boosting HHG efficiency. However, the feasibility of generating isolated attosecond pulses (IAPs) in an extended gas medium with a controlled gas profile remains an unexplored area. Additionally, to model this scenario accurately, advanced simulation tools are necessary for interpreting experimental data. These tools must handle the complex nonlinear spatio-temporal dynamics of the driving radiation as it focuses through the gas medium, as well as the generation, propagation, and phase matching of the harmonics. Due to the inherent complexity of these processes, the mechanisms leading to IAP generation in extended gas media have not been extensively studied.

In the following discussion, based on our work [SIGCsub], I report on an experi-

mental demonstration of efficient IAP generation in a semi-infinite gas cell (SIGC) in the extreme-ultraviolet region.

By controlling the gas density profile and pressure, the re-absorption of lower-order harmonics and the optimal phase matching temporal window are optimized. This dual control enables a smooth transition from trains of attosecond pulses to the generation of isolated attosecond pulses (IAPs), while preserving the overall flux.

Then, we have successfully produced and characterized IAPs of 180 as within the 20 to 45 eV spectral range. To delve deeper into the physics of the underlying processes, a novel simulation tool for HHG was developed. This method uniquely combines the nonlinear propagation of the driving field with macroscopic HHG (3D-TDSE). Our simulation demonstrates that the nonlinear spatio-temporal transformation of the driving field, observed experimentally as a white filament, serves as a self-regulating mechanism that enhances phase-matching conditions, thereby facilitating the efficient generation of IAPs.

3.3.1 Experimental setup

Our experimental setup features a 25-fs, 800-nm, 1-kHz, CEP-stabilized (< 300 mrad) Ti:Sa laser system (Legend DUO HE+, Coherent). These laser pulses are directed into a 3-m-long stretchable hollow core fiber with a $450\text{-}\mu\text{m}$ inner diameter (Polymicro TSP450670), filled with 1.8 bar of helium in a differential gradient configuration [16, 90]. At the fiber output, the spectrally broadened IR pulse undergoes post-compression using chirped mirrors (Ultrafast Innovations PC1332), resulting in a sub-4-fs pulse with an energy of 2 mJ. The laser is then sent into a delay-stabilized interferometer designed for pump-probe experiments. After a 70/30 beamsplitter and several reflections, $420\text{ }\mu\text{J}$ of pulse energy are focused ($f = 75\text{ cm}$) for HHG in the SIGC apparatus [162, 163, 164, 165].

The SIGC consists of three main chambers, as shown in Fig. 3.10a). In the first one, the IR pulse interacts with a noble gas (Argon) and generates high-order harmonics in the XUV (20-45 eV). The pressure in this section is uniformly distributed and can be adjusted up to 10 mbar. The gas-filled region extends into the second chamber through a mechanically adjustable element, allowing for length variation between 370 mm and 400 mm. Following this, as depicted in Fig. 1b), a plate with a drilled hole of $200\text{-}\mu\text{m}$ diameter and 7-mm length connects the first chamber to the second, where a roughing pump stabilizes the pressure at 0.01 mbar. In our configuration, the SIGC length is set to 380 mm, with the IR focus positioned 5 mm before the exit hole. A second plate with a $500\text{-}\mu\text{m}$ hole separates the second chamber from the final one, where the pressure is maintained at 10^{-6} mbar using a turbo pump with an effective speed of 80 liters per second. At increasing pressures in the first chamber, a distinct white filament spanning several centimeters was observed to gradually form. Consequently, as illustrated in Fig. 3.10c), an exhaustive analysis of

the IR spectrum post-generation was conducted at various pressures using a standard spectrometer (AvaSpecULS4096).

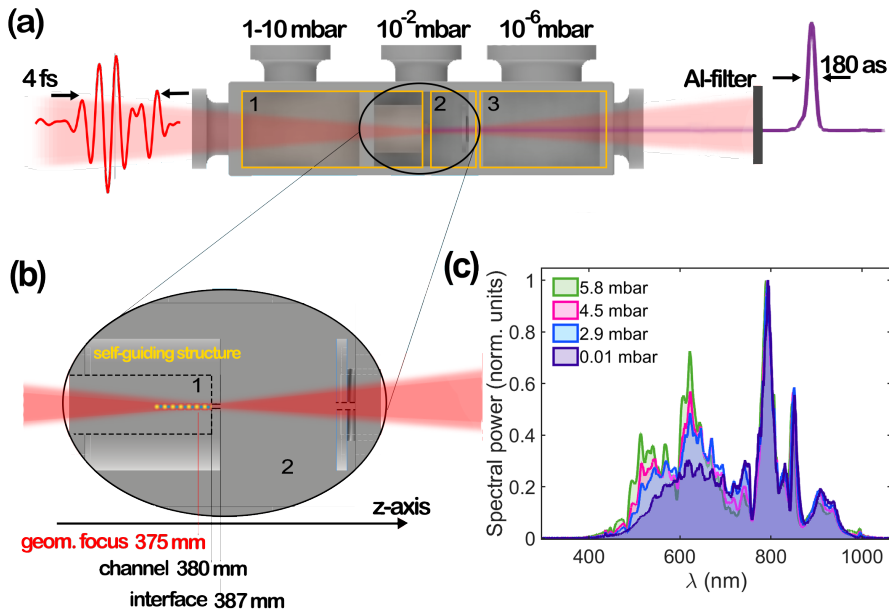


Figure 3.10: a) Illustration of the SIGC setup: The IR driving field, measured with the streaking technique, reaches its focus after 375 mm from the entrance window, 5 mm before the exit channel of the cell at 380 mm. The first chamber (1) is filled with Argon gas, kept at constant pressure, which is adjustable from less than 1 mbar to up to 10 mbar. An intermediate vacuum chamber (2), kept at 0.01 mbar using a roughing pump, separates (1) from a high-vacuum area (3) maintained at 10⁻⁶ mbar by a turbo-pump. The XUV pulses produced (180 as) are analyzed through a streaking measurement. b) Detail of the junction between chambers (1) and (2). A 7-mm channel connects the first chamber to the intermediate one (2). Notably, around the geometric focus at $z = 375$ mm, as highlighted in the diagram, a distinct white filament becomes visible when the pressure exceeds 2 mbar. c) Displays the spectra of the IR driving field measured at the SIGC output under various pressure settings, as detailed in the legend. Re-adapted from [SIGCsubmitted]

Afterwards, the resultant XUV radiation is filtered through a 150-nm Al filter, eliminating any residual IR driving field and harmonics below 20 eV. This XUV radiation is initially focused via a gold toroidal mirror into a time-of-flight spectrometer (TOF, Kaesdorf ETF₁₅) for conducting streaking measurements, as described in [166]. Following this, the radiation is captured by a gold-coated grating (Hitachi 600 lines/mm), spectrally separated, and then directed towards a microchannel plate (MCP). This setup facilitates the measurement of the radiation spectrum, which is visualized on a phosphor screen and recorded by a camera.

3.3.2 Experimental results

Fig. 3.11a) showcases the HHG spectra by changing the gas pressure inside the SIGC. For each pressure level, the carrier-envelope phase (CEP) of the IR driving pulses was fine-tuned to maximize continuous XUV spectrum generation (above ≈ 35 eV). The findings reveal that effective phase-matching of high-order harmonics occurs within a limited pressure range of 3 to 7 mbar. Remarkably, the harmonic spectrum demonstrated stability against minor shifts (approximately ± 5 mm) in the longitudinal position of the 200- μ m exit pinhole.

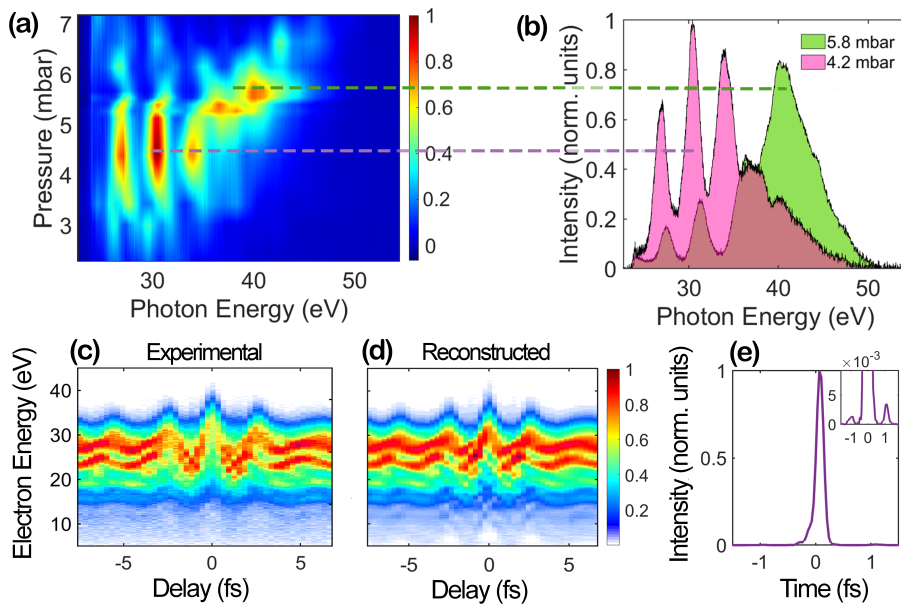


Figure 3.11: a) Variation in the XUV pulse spectrum as a function of gas pressure. The spectrum transitions to a more continuous form around 5.5 mbar. b) Comparative spectra at two different pressures: 4.2 mbar (pink curve) and 5.8 mbar (green curve). c) Experimental streaking trace obtained at a pressure of 5.8 mbar, IR peak intensity used $I_{peak} = 5 \times 10^{12}$ W/cm². d) Reconstructed streaking spectrogram using the ePIE algorithm. e) Reconstructed XUV intensity profile depicting a distinct isolated attosecond pulse (IAP) with a duration of 180 as. The inset illustrates minor (< 1%) IAP satellites, aligning with the modulation patterns seen in both the streaking trace of (c) and the green spectrum in (b). Re-adapted from [SIGCsubmitted]

As the pressure increases, a marked transition in the XUV spectrum is observed, shifting from a modulated profile (illustrated by the pink curve in Fig. 3.11b) at 4.2 mbar) to a more quasi-continuous form (represented by the green curve in Fig. 3.11b) at 5.8 mbar). This shift is followed by a significant decrease in lower-order harmonics and a boost in higher-order ones near the cutoff energy. Crucially, this transition from a discrete to a more continuous spectrum with rising pressure is achieved without any substantial loss in overall harmonic flux. This feature is particularly advantageous compared to other gating techniques, like polarization gating, where a continuous

spectrum often results in reduced XUV flux.

Then, we examined the temporal characteristics of the XUV pulses produced at a pressure of 5.8 mbar, using the Frequency-Resolved Optical Gating for Complete Reconstruction of Attosecond Bursts (FROG CRAB), commonly referred to as streaking technique [115, 167, 168]. As detailed in Chapter 2, a part of the IR beam, distinct from the one used in the generation process, is delayed relative to the XUV pulse and focused in the time-of-flight (TOF) spectrometer with an Argon target. This interaction created a streaking spectrogram, displayed in Fig. 3.11c). To verify the existence of an IAP, we conducted a numerical reconstruction of the trace using the extended ptychographic iterative engine (ePIE) [169]. The reconstructed trace, shown in Fig. 3.11d), allowed the retrieval of both the IR field and the XUV pulse intensity. As seen in Fig. 3.11e), the configuration around 6 mbar indeed supports the generation of an IAP, with a FWHM intensity duration of 180 as. Additionally, we observed less than 1% intensity satellites of the IAP, accounting for the minor modulations in both the photoelectron and XUV spectra. Nonetheless, for most spectroscopic applications requiring IAPs, these minor temporal structures are generally inconsequential.

3.3.3 Simulations and Discussion

Numerical method: 3D-TDSE, Phase matching and non-linear propagation of the driving field

In our joint study detailed in [SIGCsub], the group of Prof. Carlos Hernández-García and Prof. Julio San Román (Universidad de Salamanca) has developed an advanced numerical method that integrates, for the first time, nonlinear IR propagation with macroscopic HHG. On the microscopic scale, this method employs the three-dimensional time-dependent Schrödinger equation (3D-TDSE), focusing on the electron in the outermost valence orbital, in line with the widely adopted single-active electron approximation. Macroscopically, the model considers both the propagation of harmonics and their phase-matching to the detector, taking into account the contributions from a vast number of atoms (trillions) as outlined in [113]. Various approaches have been devised for macroscopic HHG, including the use of the 3D-TDSE [111, 121, 170, 171, 172, 173], and the strong field approximation [114, 174], which, however, is not suitable for scenarios involving few-cycle drivers [175].

The generated harmonics are then propagated to a far-field detector. The IR driving field for each emitting atom is calculated using a comprehensive 3D nonlinear pulse propagation model. This model takes into account various experimental parameters, including gas dispersion, plasma absorption, and realistic gas profiles.

While there have been separate simulations addressing the nonlinear propagation of the driving field and HHG, such as those accounting for soft X-ray generation in a waveguide [29], our method, to the best of our knowledge, is unique as it is the first to couple nonlinear few-cycle IR propagation with macroscopic HHG using the

3D-TDSE at the single-atom level.

In our simulations tailored for a few-cycle driving pulse, we utilized the 3D-TDSE in Argon while applying the single-active electron approximation. The harmonics generated from this process were then propagated to a far-field detector using an electromagnetic field propagator. The phase-matching in our model was achieved by coherently summing up the contributions from each emitter along the gas cell, as described in [113]. To determine the IR driving field at each emitter location, we used a comprehensive 3D nonlinear pulse propagation code [176], which incorporates experimental parameters to simulate IR propagation throughout the entire volume of the SIGC. The simulations accounted for the complete dispersion of the gas, such as the Kerr effect, self-steepening, photoionization, and plasma absorption. We also employed a realistic gas profile distribution calculated using computational fluid dynamics tools (COMSOL) for better accuracy. This profile was included in the harmonic radiation propagation as they pass through the 200- μm -diameter, 7-mm-long channel connecting the first two chambers of the SIGC, with the assumption of constant gas pressure in the HHG generation volume.

To realistically model the nonlinear propagation in the SIGC and the HHG process, we performed experimental characterizations of the driving field radiation. The IR pulse used for HHG was temporally analyzed using the D-scan technique [177]. We also conducted a streaking measurement on a part of the beam directed into the interaction chamber, yielding similar results. Spatial characterization was achieved by measuring the caustic of a small beam segment post-focusing in air. The gathered data from these temporal and spatial characterizations—consisting of 4 fs pulses, a beam waist of $w_0 = 77 \mu\text{m}$, and a Rayleigh length of $z_R = 2.5 \text{ cm}$ —served as inputs for our nonlinear propagation simulations.

Simulation results

In Fig. 3.12, we present the outcomes of our simulated generation of IAPs in the semi-infinite gas cell. As discussed, we utilize the propagated IR electric field within the SIGC as input for macroscopic HHG computations, employing 3D-TDSE and subsequent propagation of the harmonics. This approach enables us to determine the spatially averaged HHG emission spectrum at the far-field detector. This is achieved by integrating the emission along the azimuthal coordinate and up to a divergence angle of 1.5 mrad, capturing the majority of the XUV radiation. Additionally, we simulated the passage of radiation through a 150-nm thick aluminum filter, accounting for both material absorption and dispersion. A response function was also applied to emulate the XUV camera used in the experiments, effectively creating a high-pass filter starting from approximately 23 eV.

As shown in Fig. 3.12a), our calculated harmonic spectra exhibit trends consistent with experimental observations, in spite of minor discrepancies in the phase-matching

pressure range and the purity of the isolated attosecond pulse.

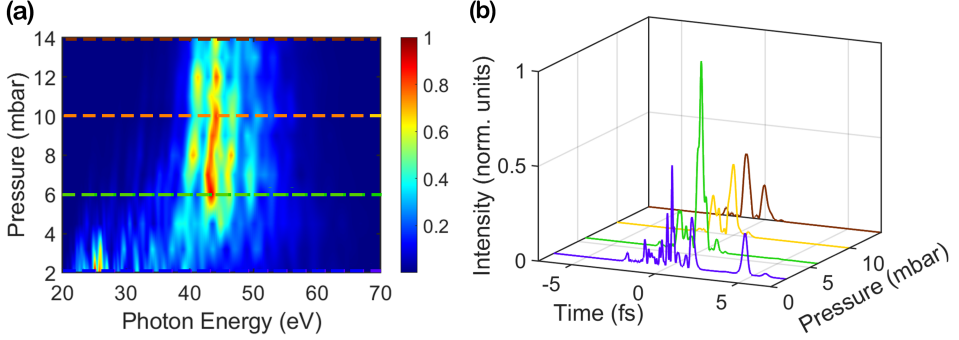


Figure 3.12: a) Results of the XUV spectrum simulations as a function of the gas pressure. b) On-axis IAP obtained at pressure values of 2 mbar (blue), 6 mbar (green), 10 mbar (orange), and 14 mbar (dark red) after performing the Fourier transform of a sub-set of the HHG spectra indicated by dotted lines in (a).

Notably, as gas pressure is increased, the HHG spectrum shifts to higher energies and displays reduced modulation, which is facilitative for IAP generation. This trend is further corroborated by the Fourier transform of the on-axis spectra depicted in Fig. 3.12b). Increasing the pressure leads to a less modulated temporal profile of the XUV radiation, achieving the most clean temporal structure at 6 mbar. The simulations also reflect the experimental trend of declining generation efficiency with increasing pressure. Both experimental and theoretical results, as depicted in Figs. 3.11 and 3.12, identify two key aspects in our HHG spectrum that facilitate IAP generation: i) the emergence of a continuous spectral cutoff and ii) the re-absorption of lower-order harmonic components.

We now turn our focus to understanding the origins of these spectral characteristics.

Discussion

To clarify the physics behind the IAP generation mechanism, we examined the non-linear propagation effects of the driving pulse. As a preliminary step in validating our simulations, we analyzed the experimental IR spectra obtained at the output of the SIGC under various pressure conditions. The experimental findings, depicted in Fig. 1.1c), display a pronounced blue-shift in the spectrum, a phenomenon attributed to ionization-induced self-phase modulation. This effect has been previously identified as a key factor in boosting generation efficiency in recent studies [89, 178].

In Fig. 3.13a), we present our simulation results showing the IR spectra after non-linear propagation through the SIGC at different Argon pressures. These simulations closely mirror the experimental observations of the blue-shifted spectrum (Fig. 1.1c)). Additionally, Fig. 3.13b) illustrates the consequent transformation of the IR driving

pulse at the SIGC output, highlighting the influence of pressure variation on the pulse reshaping process.

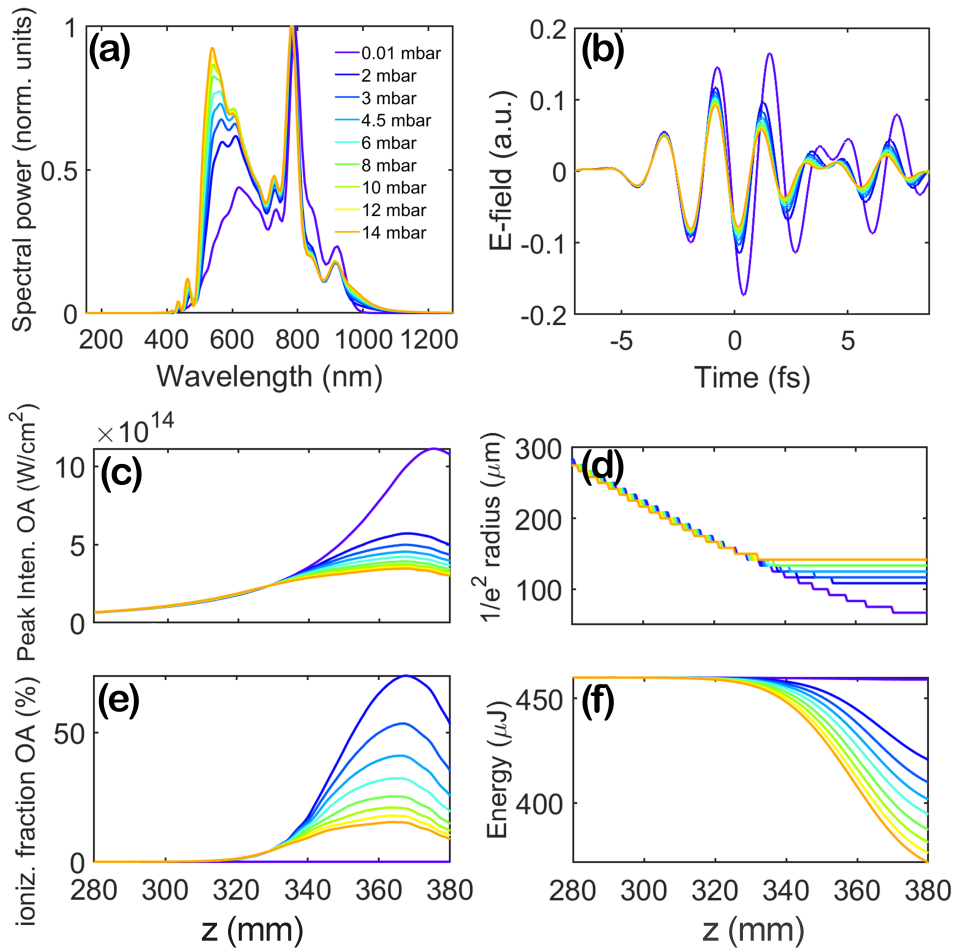


Figure 3.13: a) IR spectra and b) associated on-axis electric field at the SIGC output exploiting the nonlinear propagation code as a function of the gas pressure in the first chamber (the experimentally characterized IR is taken as input). Panels c) to f) exhibit the simulated nonlinear transformation of the driving pulse as it traverses along the z-axis in the latter section of the cell, near the geometrical focus. Specifically, c) shows the peak intensity on the axis, d) details the beam radius, e) illustrates the on-axis percentage of ionized particles, and f) depicts the pulse energy. Re-adapted from [SIGCsubmitted]

Following this empirical validation, we proceed to numerically analyse the nonlinear alteration of the driving field as it progresses along the z-axis within the cell. This investigation deepens our understanding of the spatio-temporal transformation of the IR driving radiation throughout the cell under varying pressure conditions. We examine the evolution of several elements, including the on-axis peak intensity (as shown

in Fig. 3.13c)), the beam radius (Fig. 3.13d)), the extent of ionized species (Fig. 3.13e)), and the pulse energy (Fig. 3.13f)), across different pressure settings. Notably, with an increase in the gas pressure inside the SIGC, there is a clear stagnation of the beam size (illustrated in Fig. 3.13d)), suggesting filament formation, and a decrease in pulse energy (seen in Fig. 3.13f)), attributed to plasma defocusing and losses due to ionization and plasma absorption. These factors collectively cause a reduction in the peak intensity (Fig. 3.13c)) of the driving field, compared to its linear propagation in a vacuum.

This decrease in peak intensity, resulting from plasma defocusing and absorption, appears to function as a self-regulatory mechanism, which recent studies have indicated aids in efficient harmonic generation[178, 179]. It is important to note that the harmonic cutoff energy, corresponding to the diminished intensity, aligns well with the classical cutoff law, diverging from the significantly higher value expected from the peak intensity of a beam focused in a vacuum. This regulatory mechanism also leads to a self-sustained driving field structure, experimentally observed as a white filament, maintaining consistent intensity and phase along its propagation direction in the latter part of the SIGC, crucial for HHG due to reduced harmonic reabsorption.

Moreover, this self-regulatory mechanism is pivotal in harmonic phase-matching. Despite the extended generation medium, the nonlinear progression of the driving pulse minimizes the impact of intensity and phase discrepancies on harmonic phase mismatch, thus allowing geometric and intrinsic factors (i.e. dipole phase) to be disregarded. In our SIGC setup, the phase mismatch, Δk_q (see Eq. (2.75)), primarily arises from free electrons and neutral atoms near the laser focus. This scenario is reminiscent of conditions encountered in capillaries[29, 180, 181], or in high-pressure, short-medium setups [102, 124]. Since these two contributors to Δk_q have opposite signs and vary with the ionization level along the driving pulse, ideal phase matching ($\Delta k_q = 0$) occurs only during a finite temporal window [158, 159]. If this window narrows to just a single laser half-cycle, isolation of a single attosecond pulse is possible, leading to continuous features in the XUV spectrum. Under such conditions, the phase mismatch of the q -th-order harmonic along the propagation axis (z) can be approximated by [158]:

$$\Delta k_q(z, t) \sim p \cdot q \left\{ (1 - \eta(z, t)) \cdot \delta n_q \cdot \frac{2\pi}{\lambda_L} - \eta(z, t) \cdot N_{\text{atm}} \cdot r_e \cdot \lambda_L \right\} \quad (3.11)$$

where p represents the gas pressure, $\eta(z, t)$ indicates the instantaneous ionization fraction, and $\delta n_q = n(\lambda_L) - n(\lambda_q) \sim n(\lambda_L) - 1$ denotes the difference in the index of refraction at the fundamental and harmonic wavelengths at a pressure of 1 atm. The term N_{atm} is the total number density of atoms at 1 atm, r_e symbolizes the classical electron radius, and λ_L refers to the central wavelength of the driving laser (assumed here to be $\lambda_L = 700$ nm, approximately the center of the spectra shown in Fig. 3.13a)).

The duration Δt of the temporal phase-matching window can then be estimated from the inverse of the time derivative of the phase mismatch: $1/\Delta t \propto (\partial \Delta k_q / \partial t) \cdot L$, where L is the length of the medium [159]. Notably, under these considerations, the nonlinear propagation of the driving pulse changes how pressure affects harmonic phase-matching. Firstly, the ideal phase-matching condition ($\Delta k_q = 0$, as seen in Eq. (3.11)), is independent of pressure, and secondly, the temporal phase-matching window narrows as pressure increases. It is also important to mention that the enhancement in harmonic efficiency with increased pressure is constrained not just by the temporal phase-matching window but also by reabsorption effects [119].

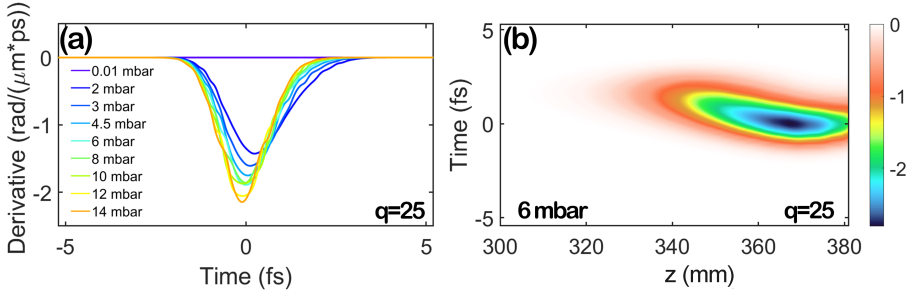


Figure 3.14: a) Time-derivative of the numerical phase mismatch calculated using Eq.(3.11) for the 25th harmonic at the cell output ($z = 380$ mm). b) 2D-representation of the phase mismatch time-derivative for harmonic 25th at 6 mbar as a function of the propagation axis, showing that the isolation of an attosecond pulse takes place in the last 30 mm. Re-adapted from [SIGCsubmitted]

To elucidate the impact of the phase-matching window within the SIGC setup, we present in Fig. 3.14 an analytical calculation of its time derivative for the 25th order harmonic (≈ 44 eV) at the exit of the cell, for various pressures used in this study. This analysis is simplified by considering only the on-axis temporal variation of the ionization rate $\eta(z, t)$, derived from 3D nonlinear propagation simulations. The analysis corroborates that the temporal phase-matching window diminishes with increasing gas pressure, coinciding with the emergence of a continuous cut-off and the isolation of an IAP. At higher pressures (exceeding 6 mbar), the phase-matching window contracts further, eventually becoming too brief for the HHG recombination step to occur within the phase-matched interval. This leads to a marked reduction in the XUV signal at these higher pressures, as observed in Fig. 3.11a).

Further insights from our numerical analysis concern the actual phase-matching length within the SIGC. Figure 3.14b) highlights that efficient HHG predominantly occurs in the cell final 3 cm ($350 < z < 380$ mm), which approximately aligns with the Rayleigh range of the driving field in a vacuum. However, as indicated in Fig. 3.13d), nonlinear spatial reshaping causes an increase in the effective Rayleigh range within the medium, extending up to 10 cm at elevated gas pressures. Thus,

by adjusting the pressure in our SIGC setup, we can explore different ratios between the Rayleigh range and the generating medium length, enabling exploration of various phase-matching regimes as detailed in [102]. It is noteworthy that the narrowest phase-matching window (phase-matching peak) is found at approximately 13 mm before the cell exit (8 mm before the geometrical laser focus) at $z = 368$ mm, aligning well with previous studies on optimal phase matching in SIGC setups [182].

Another critical aspect of our SIGC configuration that facilitates IAP generation is the reabsorption of lower-order harmonics, as shown in Figs. 3.11 and 3.12. To understand the mechanism behind the low-order harmonic reabsorption process, we thoroughly investigated the gas distribution in our generation geometry using COMSOL. The SIGC design includes a 7-mm channel linking the few-mbar pressure region to an evacuated region at 10^{-2} mbar. Under the assumption that generation in this intermediary region is minimal, we can estimate the total transmissivity $T(\epsilon)$ across this channel for different photon energies using Eq. (3.12).

$$T(\epsilon) = \exp\left(-\frac{L}{L_{\text{abs}}(\epsilon)}\right); \quad L_{\text{abs}}(\epsilon) = \int_0^{7 \text{ mm}} \frac{dz}{\rho(z)\sigma_{\text{abs}}(\epsilon)} \quad (3.12)$$

where $\rho(z)$ represents the atomic areal density of the medium varying with z , and $\sigma_{\text{abs}}(\epsilon)$ denotes the absorption cross-section of Argon [120]. Fig. 3.15a) illustrates how the spectral profile of transmissivity aligns precisely with the re-absorption characteristics observed in our experimental XUV spectrum. As the gas pressure increases, harmonics with energies below 35 eV are substantially re-absorbed. Conversely, higher energy levels remain largely unaffected, thanks to the specific absorption cross-section of Argon, leading to nearly complete (100%) transmissivity for these frequencies..

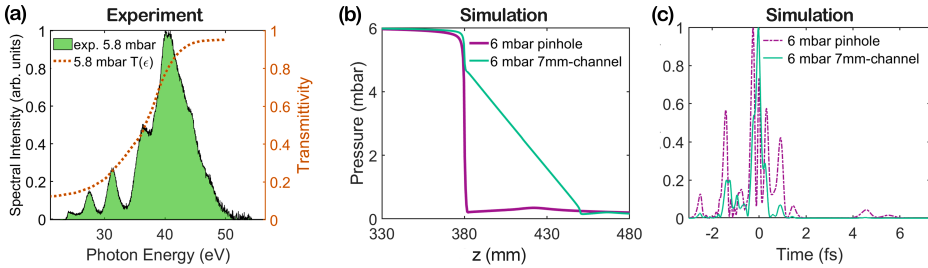


Figure 3.15: a) Experimental (green area) spectrum obtained at 6 mbar of pressure. The dotted orange line indicates the calculated z -integrated transmissivity in the 7-mm channel of the SIGC. b) Comparison between the gas distribution of a 7-mm channel and a geometry with a pinhole, i.e., immediate connection to vacuum. c) Numerical results of XUV temporal profile in the two configurations of panel (b). Re-adapted from [SIGCsubmitted]

The simplicity of controlling the gas profile through a channel is a notable advantage of low-pressure generation geometries like the SIGC. By allowing the gas to flow through a channel spanning a few mm, we create a linear pressure gradient, as depicted by the blue curve in Fig. 6(b). This channel acts as an effective high-pass filter,

selectively transmitting specific spectral regions. It is crucial to note that within this channel, where harmonic generation is minimal, the exact shape of the gas profile is insignificant, as the critical factor for absorption is the total accumulated effect of the gas along the channel.

In contrast, achieving such control in shorter gas cells operating under higher pressures is considerably more complex. Particularly at high pressures, sharp pressure gradients are often recommended to minimize re-absorption across the entire spectrum and ensure efficient phase matching [161]. This necessity often leads to a compromise between creating a sharp gradient and effectively filtering the spectrum.

To underscore the significance of this channel, we conducted additional HHG simulations assuming a sharp cutoff in the gas profile (illustrated by the red curve in Fig. 3.15b)), simulating a scenario akin to a pinhole opening directly into a vacuum chamber. As demonstrated in Fig. 3.15c), the temporal quality of the XUV radiation generated under these conditions is significantly inferior compared to that achieved with a linear gradient, where, as previously shown, a single attosecond pulse can be isolated (blue curve in Fig. 3.15c)). We determined that the optimal length for maintaining over 90% transmittivity in the 40 eV range, while also effectively filtering out lower-order harmonics, ranges between 1 cm and 1.25 cm. Naturally, the length of the channel should be adjusted according to its diameter. A comprehensive exploration of this aspect, however, is beyond the scope of this study.

3.3.4 Conclusion: SIGC, a flexible solution for IAP generation in the XUV spectral region

In our study [SIGCsub], we have successfully demonstrated both experimentally and theoretically the capability of a semi-infinite gas cell to efficiently generate isolated attosecond pulses in the extreme ultraviolet spectrum.

A crucial finding is the key role of the nonlinear propagation effects of the driving field in establishing favourable phase-matching conditions. We have shown that IAPs can be achieved simply by increasing the generation pressure, while simultaneously maintaining a high level of XUV flux. This outcome is the result of a delicate balance between efficient time-gated phase matching and the controlled reabsorption of lower-order harmonics.

To delve deeper into the underlying physics of efficient IAP generation in a SIGC setup, we developed and validated a novel simulation method. This method uniquely combines the nonlinear spatio-temporal reshaping of an intense few-cycle driving pulse with macroscopic high harmonic generation (HHG). This includes comprehensive 3D time-dependent Schrödinger equation (TDSE) calculations and the propagation of harmonics to a far-field detector.

Our simulations highlight that the spatio-temporal reshaping of the driving field, which manifests experimentally as a white filament, leads to a stagnation in beam size.

This dynamic induces a phase-matching condition in our SIGC that is akin to what is observed in capillaries or short-medium configurations. With increasing gas pressure, the temporal window for phase matching becomes increasingly narrow, facilitating the efficient generation of IAPs.

Importantly, our findings reveal that the generation in a SIGC occurs primarily in the final few centimeters of its 38 cm length. This characteristic imparts an intrinsic adaptability to various loose-focusing geometries. Unlike traditional gas cell geometries or capillaries, where scaling up the pulse energy necessitates alterations to the cell length or capillary dimensions, the SIGC coherence length of generation is not limited by any physical constraints.

Therefore, adjusting the laser pulse parameters and focusing optics automatically adapts the SIGC phase-matching region, with only minimal adjustments needed for gas pressure. This flexibility, coupled with the SIGC inherent simplicity and tunability of pressure and generation position, sets the SIGC as a highly versatile tool, which could be used in any setup requiring IAP technology, such as XUV-XUV pump-probe or NIR/VIS/UV pump-XUV probe experiments.

Chapter 4

Initiating and measuring few-fs Electron Transfer in Donor-Acceptor Molecules: Nitroanlines

In Chapter 1, we underscored the significance of measuring charge transfer (CT) processes, sometimes referred to also as electron transfer (ET), with extreme temporal precision. This capability not only deepens our fundamental comprehension of the physics at the core of these processes but also may provide key insights into tailoring the chemical and structural attributes of molecules to modulate or enhance CT. Capturing the ultrafast dynamics of electronic and nuclear wavefunctions is crucial for understanding and potentially influencing the evolution of CT. We conclude that new experiments with few-femtosecond resolution coupled with novel theoretical methodologies are imperative to decipher the ultrafast physics of CT.

This chapter, based on the work [Nitroanlinesubmitted?], describe one of these experiments aimed at clarifying the initial stages of CT following immediate ionization by an isolated attosecond pulse in a prototypical donor-acceptor system: Nitroaniline.

4.1 Nitroaniline a prototypical donor- π -acceptor systems

Although significant progress has been made in understanding charge transfer in donor-acceptor systems, many of the aspects of early-stage dynamics in photoinduced CT processes remain unclear. This is particularly true in scenarios where there is a strong interplay between the electronic and nuclear motion in medium-size and large molecules. A notable knowledge gap, as depicted in Fig. 4.1, is the lack of detailed temporal information on the initial phases of CT, typically represented by a sequence of Lewis diagrams[183]. This arises mainly due to the inadequacy of current methods to compute ultrafast processes in many-body quantum systems combined with the scarcity of experiments providing sufficient time resolution in polyatomic systems.

In the upcoming discussion, based on [Nitroanilinesubmitted], we report on an experimental and theoretical investigation into the initial stages of charge transfer processes initiated by prompt ionization in prototypical donor- π -acceptor molecules, specifically nitroanilines. The real-time imaging of this process combines an attosecond extreme ultraviolet (XUV) pump with a few-fs near-infrared-probe (NIR) spectroscopy and integrates these observations with advanced many-body quantum chemistry calculations.

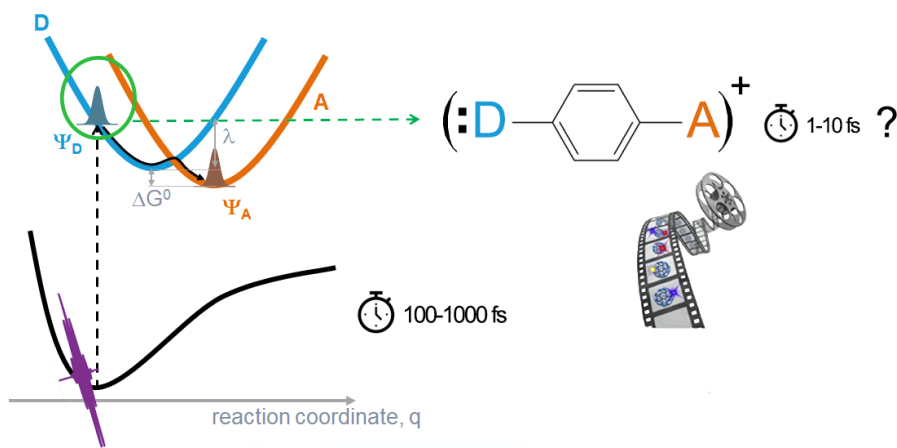


Figure 4.1: Sketch of a charge transfer system in a prototypical donor-acceptor system after the interaction with an isolated attosecond pulse. While the complete charge transfer can take from 100 fs to 1 ps, the first electronic motion dynamics can occur in the first few fs. This motivates the investigation of the early-stage photophysics of charge transfer.

Our study focused on para-nitroaniline (p-NA, CAS Number: 100-01-6), meta-nitroaniline (m-NA, CAS Number: 99-09-2), and N,N-Dimethyl-4-nitroaniline (nd-NA, CAS Number: 100-23-2), all sourced from Sigma-Aldrich. These samples, with their chemical structures illustrated in Fig. 4.2. These molecules are prototypical donor- π -acceptor system and are marked by a pronounced molecular dipole. In these com-

pounds, the electron density is drawn towards the nitro group (NO_2), which acts as the acceptor. This results in a positive partial charge near the donor group, which is the amino group NH_2 in p-NA and m-NA, and $\text{N}(\text{CH}_3)_2$ in nd-NA. Comparing p-NA and m-NA allows for the exploration of the inductive effects of the donor and acceptor groups on ultrafast dynamics. This is evident as the molecular dipole magnitude decreases from 15 Debye in p-NA to 6 Debye in m-NA, as indicated by CBS-QB3 calculations. In nd-NA, the inclusion of methyl groups (CH_3) not only alters the molecule polarity and charge separation between its positive and negative sides [184] but also enhances the electron supply from the donor group due to the positive inductive effect of the methyl groups.

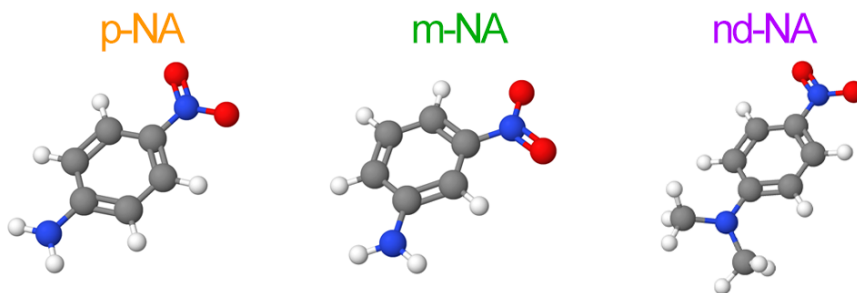


Figure 4.2: Molecular structures of para-nitroaniline (p-NA), meta-nitroaniline (m-NA) and N,N-dimethyl-4-nitroaniline (nd-NA). Re-adapted from [Nitroanilinesubmitted]

As detailed in the next sections, we present both experimental findings and comprehensive numerical simulations that highlight a sub-10-femtosecond CT process in the three ionized nitroaniline species. This rapid CT is driven by an ultrafast planarization of the molecular structure. Subsequently, a more gradual dispersion of the nuclear wave packet within the excited electronic states of the molecular cation starts to play a crucial role in the observed dynamics. Our approach allowed us to unveil the intertwined nature of the CT process that unfolds in few-femtoseconds.

4.2 Experimental methodologies and results

The experiments conducted to unravel the early-stage photophysics of charge transfer (CT) in nitroaniline incorporated two phases. Firstly, a time-resolved study was carried out using an attosecond pump-probe setup. This allowed for the measurement of the temporal aspects of the CT dynamics. Secondly, an energy-resolved campaign was conducted at the Elettra synchrotron facility in Trieste. The necessity for such a dual approach derives from the difficulty in fully interpreting attosecond spectroscopy measurements, which offer extreme-temporal resolution at the cost of an intrinsic complexity.

As emphasized in Chapter 1, in attosecond spectroscopy, choosing the appropriate pump and probe pulses, along with identifying the most revealing physical observable, is crucial for obtaining meaningful information about the ultrafast processes of interest.

As detailed later, our ultrafast measurement strategy involved using an XUV isolated attosecond pulse as the pump and an intense few-cycle NIR pulse as the probe. The initial attosecond pulse photo-ionizes the molecules, populating several electronic states (of the cation, removal of one electron or the education, removal of two electrons) and initiates coupled electron-nuclear dynamics. The interaction with the subsequent NIR pulse, due to its high intensity, can further ionize or excite the molecule, altering its possible fragmentation pathways from the one obtained with the attosecond pulse only, as sketched in the general pump-probe scheme of Fig. 1.4. Therefore, our physical observable is the change in the population of positive ion fragments (fragmentation pathways), created after the interaction with the pulse, as a function of the delay between the pump and the probe events.

In contrast, the synchrotron measurements, while lacking temporal resolution, provide valuable insights into the activation energy of the various fragmentation channels, hence helping in the interpretation. This energy-resolved information is complementary to the time-resolved data obtained from the attosecond measurements.

4.2.1 Time resolved measurement: XUV-IR pump-probe

The molecular samples are ionized using isolated sub-200-attosecond pulses produced in krypton. These pulses had photon energies ranging from 20 to 50 eV, as shown in Fig. 4.3c). The dynamics of the resulting cations were subsequently probed using 4-femtosecond VIS-NIR pulses, Fig. 4.3b), featuring a central photon energy of 1.77 eV and a peak intensity of 5×10^{12} W/cm². This intensity is already sufficient to promote the cations to the molecular dications through multiphoton absorption. The parent ions and their fragments, generated by the interaction with both the pump and probe pulses, were then captured and analyzed using a linear time-of-flight mass spectrometer (TOFMS).

Experimental Setup

The laser system used in our experiments, capable of delivering mJ-level few-cycle VIS-NIR pulses, is the same as the one detailed in Section 3.3.1. In our pump-probe setup, shown in Fig. 4.3a), the visible/near-infrared (VIS/NIR) beam was split into two replicas using a beamsplitter with 20% reflectivity. The beam portion that passed through the beamsplitter was directed into a 3-mm-thick cell filled with krypton at a static pressure using a mirror with a 0.75 m focal length. This cell produced extreme

ultraviolet (XUV) radiation via high-order harmonic generation (HHG)¹. IAPs were generated through ionization gating. A 150-nm-thick aluminum filter was employed to remove the fundamental radiation and lower-order harmonics. The duration of the XUV pulses (190 ± 20 as) was determined using the Frequency Resolved Optical Gating for Complete Reconstruction of Attosecond Bursts (FROG-CRAB) technique [166]. The residual VIS/NIR beam was then recombined collinearly with the XUV beam using a mirror featuring a central aperture.

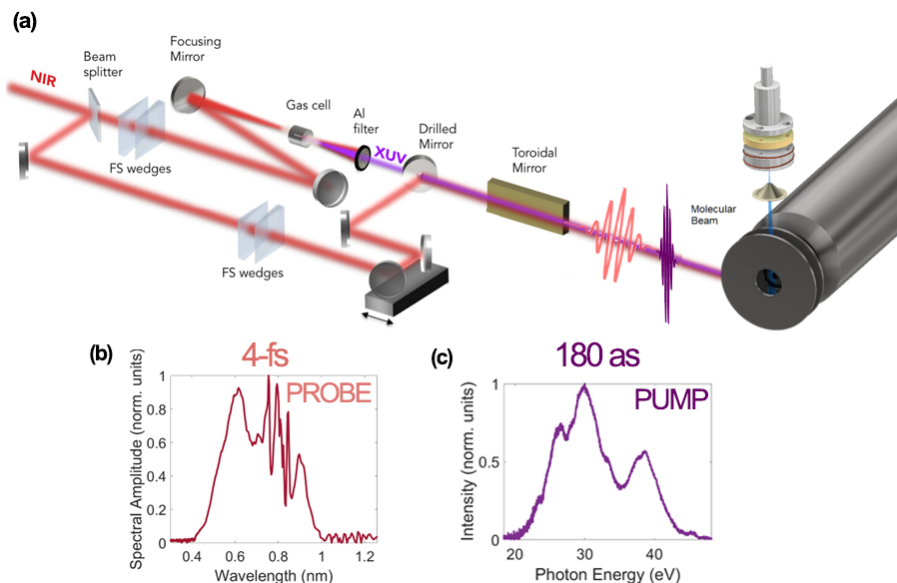


Figure 4.3: a) Sketch of the experimental setup for the pump-probe measurements. b) Power spectrum of the 4-fs-NIR pulse used in the experiment. c) Power spectrum of the 180 as IAP, used in the experiment.

The timing between the pump and probe pulses in our setup was finely adjusted using a piezoelectric translation stage, allowing for attosecond-level temporal resolution. To ensure long-term stability, the interferometer was actively stabilized using a frequency-stabilized He-Ne laser, achieving a temporal stability below 70 attoseconds (rms). Both the pump and probe beams were focused onto the molecular target using a gold-coated toroidal mirror. This focal point was strategically placed at the center of a time-of-flight (TOF) spectrometer (Kaesdorf ETF₁₅ Combined Electron TOF). A notable feature of this TOF spectrometer is its dual functionality, allowing for the switch between ion and electron detection modes. This flexibility enabled us to conduct attosecond streaking measurements prior to each new set of pump-probe experiments,

¹This experimental setup was utilized prior to the installation of the SIGC apparatus discussed in section 3.3. Repeating the experiment with the SIGC nearly a year later yielded comparable results in terms of pump-probe signal and the purity of the isolated attosecond pulse.

facilitating in situ temporal characterization of both pump and probe pulses. The spectrum of the attosecond pulses was captured using a high-resolution flat-field soft x-ray spectrometer comprising a grating, a phosphor screen, and a charge-coupled device (CCD) camera.

The three samples under examination, p-NA, m-NA and nd-NA are stable at room temperature and were used as received, without further purification. They are typically in a powdered form under standard ambient temperature and pressure conditions. For vaporization in a vacuum environment, an effusive oven source was used. The powder was placed into a hollow screw, which was then inserted into the oven, shown in Fig. 4.3. A heating cable was applied to raise the temperature to between 90°C and 110°C, well below the melting points of the samples, ensuring effective sublimation. Argon gas was employed as a carrier to convey the molecules to the interaction region, concurrently reducing their internal kinetic energy prior to interaction.

Photofragmentation and pump-probe signals

Figure 4.4 panels a)-c) present the mass spectra obtained from the ionization of p-NA, m-NA, and nd-NA using only the attosecond pulses. All three molecules exhibit similar dissociation patterns. An exhaustive analysis of every fragmentation channel is beyond the scope of this study, but the fragments that demonstrate ultrafast dynamics are highlighted in color. It was noted that ionization with solely the NIR pulses mainly resulted in the formation of parent ions within the mass spectra.

Specifically, at the mass-to-charge ratio $m/q = 30$, which is indicative of the nitrosonium (NO^+) ion, the mass spectrum displays a distinct profile with a central peak flanked by two shoulders, as marked in the right panels of Fig. 4.4. As we will discuss in the context of energy-resolved measurements, these shoulders are formed by kinetic NO^+ ions that are ejected in a highly repulsive dicationic process known as Coulomb explosion (CbE), moving towards or away from the detector.

With the introduction of a delayed NIR pulse, we tracked changes in the photofragmentation yield, normalizing it to the pump-only (XUV-only) signal. We collected each data point in the pump-probe delay with a 10-second integration time. This pump-probe delay scan was repeated six times, reversing the delay axis with each iteration to counteract any potential long-term drifts. We applied a baseline subtraction algorithm to each dataset, followed by mass-to-charge calibration. Focusing on specific regions of interest along the m/q axis, we then calculated the relative ion yield, $Y(\tau)$, for the various charged fragments using the equation provided here:

$$Y(\tau) = \frac{y_{pu+pr}(\tau) - y_{pu}}{y_{pu}} \quad (4.1)$$

where $y_{pu+pr}(\tau)$ and y_{pu} denote the integrated mass spectra within a specific m/q range surrounding the peak of a given ionic fragment, measured with and without

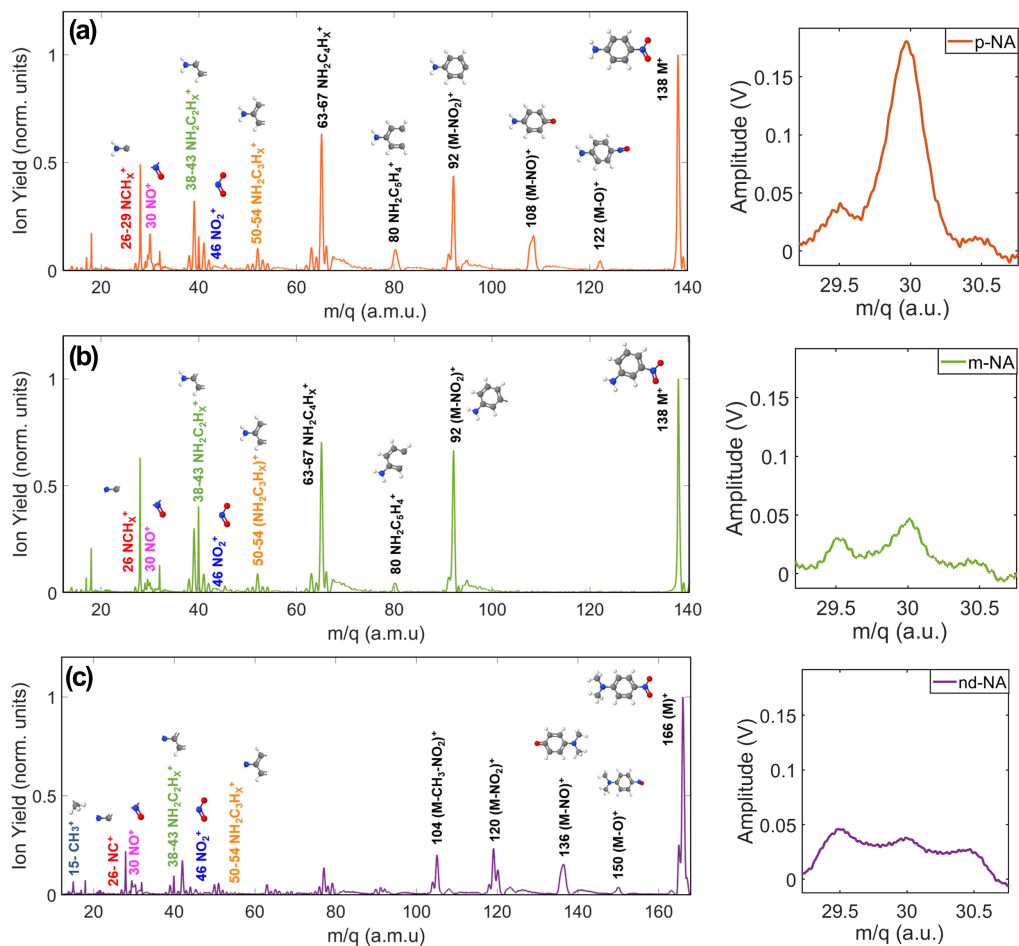


Figure 4.4: (a) p-NA; (b) m-NA; (c) nd-NA. Here, M^+ stands for the parent ion. Fragments showing ultrafast dynamics are colour-highlighted. On the right side of each figure, an insert showing the mass-spectrum detail around $m/q = 30$, identified as NO^+

the presence of the probe pulse, respectively. Due to the multiphoton nature of its interaction, the NIR probe pulse alone may generate certain photofragments. For each molecule studied, we collected two separate datasets: one with a 3-fs delay step between the pump and probe pulses covering a range from -40 fs to 200 fs, and another with a 1-fs delay step covering from -20 fs to 60 fs.

Focusing on the range of signals detected in the experimental pump-probe traces, our attention is particularly drawn to the behavior at $m/q = 30$. Figures 4.5a) and b) demonstrate that only the side shoulders of the mass peak undergo temporal changes, in contrast to the central peak, which remains static across different pump-probe delays, indicating distinct origins for these features. Detailed later, we attribute the dynamics observed in the side peaks to a time-dependent change in the population

of the molecular dication. In contrast, the central peak is likely due to a separate dissociation process at the cation level, which is minimally impacted by the NIR probe pulses.

The change in NO^+ yield, determined by integrating the mass spectra within a 0.25-wide mass-to-charge window centered on the highest point of the shoulder at the lowest m/q , is presented in Fig. 4.5c) over a 50-fs timescale and extended to 200 fs in Fig. 4.5d). The data exhibit a rise time of $\tau_1 = 9.3 \pm 1.4$ fs and an exponential decay with a time constant of $\tau_2 = 22.4 \pm 1.2$ fs. The fitting curves corresponding to these dynamics are depicted with orange lines in Figs. 4.5c) and 4.5d). An analogous trend is observed for the NO_2^+ fragment within mass-to-charge windows centered around $m/q = 45.5$ and $m/q = 46.5$, as depicted in 4.7. The rapid dynamics of the NO^+ and NO_2^+ fragments in m-NA and nd-NA are consistent with this pattern, as illustrated in Fig. 4.5d) and summarized in Table 4.1.

Each experimental data was fitted by the convolution of a Gaussian pulse (4-fs FWHM) with the following function:

$$F(t) = A(1 - e^{-\frac{t-t_0}{\tau_1}})e^{-\frac{t-t_0}{\tau_2}} H(t - t_0) \quad (4.2)$$

Here, t is the pump-probe delay axis of the scan (τ), positive when the NIR probe pulse comes after the attosecond pump pulse. An arbitrary coefficient A is included for generality. τ_1 is a rising time, which considers the formation time of a particular fragment, whereas τ_2 is a relaxation time. t_0 is common for all ionic fragments and defines the zero of the pump-probe delay axis; $H(t)$ is the Heaviside function. The use of a 4-fs Gaussian pulse as an instrument response function is an overestimation of the actual temporal resolution of the pump-probe measurements due to the multiphoton processes involved in the interaction of the VIS/NIR pulses with the molecular samples.

The t_0 was identified by fitting the time-resolved yield of Ar^{2+} ions (carrier gas) generated through a dual ionization process involving XUV and NIR photons, with the latter exhibiting an intensity surpassing $5 \times 10^{12} \text{ W/cm}^2$. The fit for the temporal yield of Ar^{2+} is represented by the blue line in 4.6. Additionally, the temporal profile of the fragment NO^+ yield from p-NA is depicted in the same figure (illustrated with an orange dashed line), along with its fitting curve (indicated by the dot-dashed orange line), highlighting the observable finite rise time in the NO^+ case.

A temporal evolution was also observed in other charged fragments. It is worth mentioning that the yield of production of the fragments CN^+ ($m/q = 26$), C_2N^+ ($m/q = 38$) and C_3^+ ($m/q = 50$), has a rise time comparable to that measured for NO^+ and NO_2^+ fragments ($\tau_1 \approx 10$ fs) and a subsequent much longer relaxation lifetime (see Table 4.1).

Before discussing the nature of these two ultrafast processes observed, i) the rapid

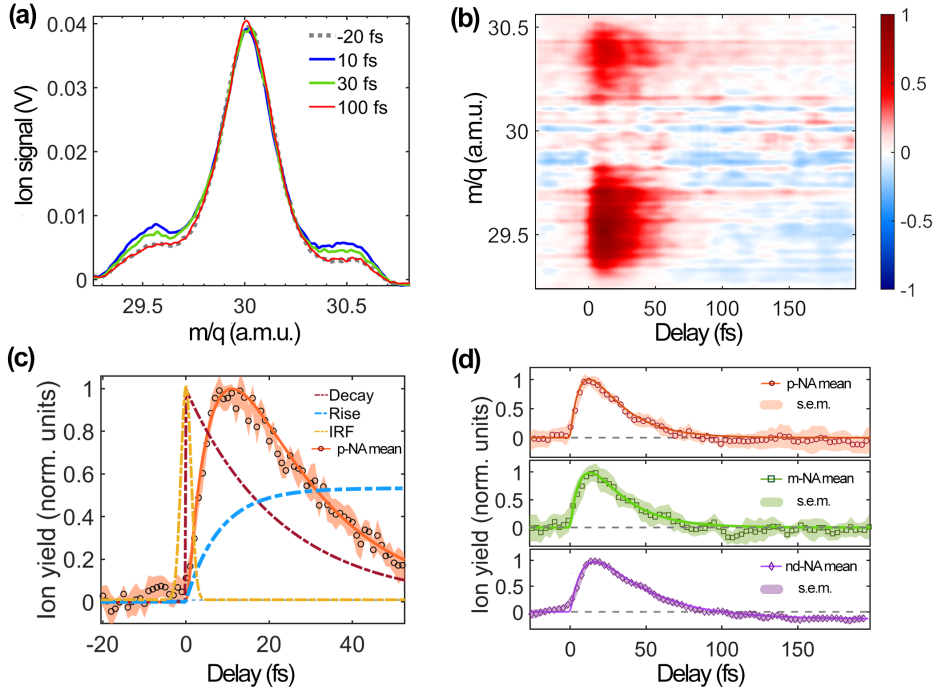


Figure 4.5: Experimental mass/charge (m/q) spectra around the NO⁺ fragment (m/q=30) for different time delays between pump and probe pulses in the case of p-NA. b, Normalized differential mass/charge spectra around m/q=30 for p-NA vs. pump-probe time delay obtained by performing the difference between the spectra acquired with and without the probe pulse. c, NO⁺ yield in the case of p-NA obtained by integrating the mass spectra in a 0.25-wide mass-to-charge window centred around m/q = 29.5. The shaded area indicates the standard deviation over 6 acquisitions. The orange line is a fitting curve with an exponential rise time of 9.3 fs and an exponential relaxation time of 22.4 fs; the light-blue dashed line is the impulsive response function (IRF). d, NO⁺ yield in the case of p-NA (orange, same as c), m-NA (green) and nd-NA (purple) obtained by integrating the mass spectra in a 0.25-wide mass-to-charge window centred around m/q = 29.5. Here, s.e.m. stands for the standard error of the mean.

Table 4.1: Table reporting the results of the fitting procedure for each fragment of the three species showing a time-dependent behaviour.

m/q	p-NA		m-NA		nd-NA	
	τ_1 (fs)	τ_2 (fs)	τ_1 (fs)	τ_2 (fs)	τ_1 (fs)	τ_2 (fs)
26	11.3 ± 4.5	> 200	12.3 ± 6.1	43.5 ± 11.1	7.5 ± 1.9	53.4 ± 11.1
30	9.3 ± 1.4	22.4 ± 1.2	8.4 ± 2.4	21.5 ± 1.6	8.3 ± 1.5	31.4 ± 1.3
38	9.5 ± 3.2	63.1 ± 21	12.5 ± 4.3	38.6 ± 4.2	8.1 ± 1.1	43.6 ± 4.8
46	9.4 ± 1.6	23.1 ± 1.4	8.7 ± 2.1	21.2 ± 1.7	8.5 ± 1.5	33.2 ± 1.5
50	10.3 ± 4.2	> 200	12.1 ± 8.2	61.4 ± 20.3	8.5 ± 1.3	54.3 ± 12.2

rise and ii) the slower decay), it is critical to validate the interpretation of the selected physical observable. In this case, a variation in the fragmentation population of NO⁺ is linked to an increase in the dication population, which subsequently always breaks due to a highly repulsive process, Coulomb Explosion. To corroborate this as-

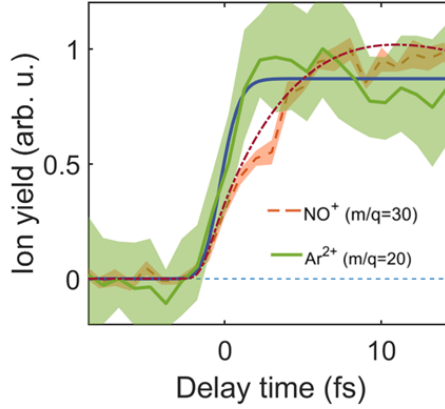


Figure 4.6: Normalized ion yield of Ar^{2+} ($m/q = 20$, green line) and of NO^+ (orange dashed line) in the case of p-NA. The shaded areas extend over twice the s.e.m. calculated over different measurements. The blue solid line and the dot-dashed orange line are the fitting curves.

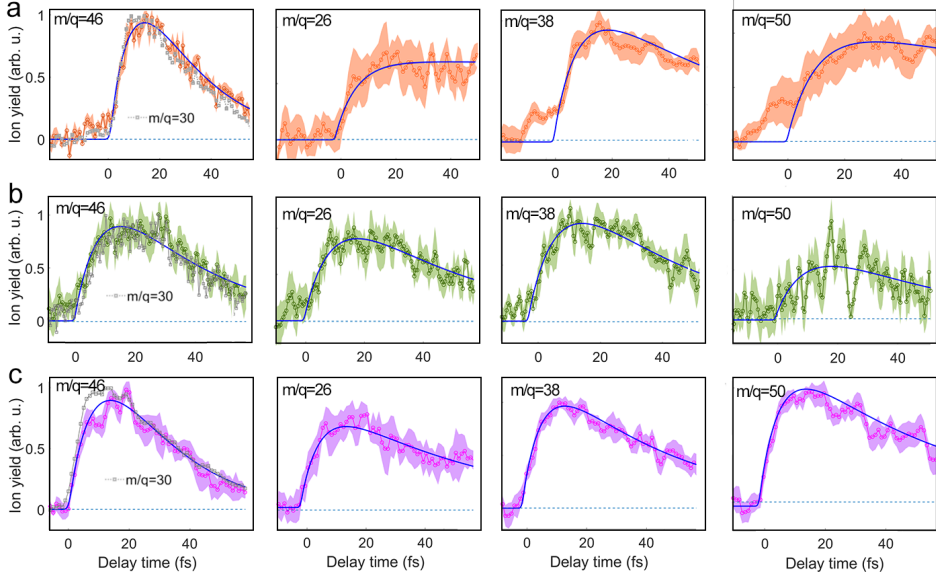


Figure 4.7: Normalized yields of fragments NO_2^+ (at a mass-to-charge ratio, m/q , of 46, with data points derived from integrating the mass spectra within a 0.25-wide window centered at $m/q = 45.5$), CN^+ ($m/q = 26$), C_2N^+ ($m/q = 38$), and C_3N^+ ($m/q = 50$) plotted against the pump-probe delay for p-NA (panel a), m-NA (panel b), and nd-NA (panel c). Additionally, the normalized yield of the NO^+ fragment ($m/q = 30$) is depicted using grey squares in the first column for comparison. The solid blue lines represent the fitting curves for each data set, while the shaded regions correspond to an area spanning twice the standard error of the mean (s.e.m.), which is calculated across different experimental runs.

sociation, we need energy-resolved measurements to determine the energy threshold needed to initiate specific fragmentation pathways.

4.2.2 Energy resolved measurements at synchrotron: PEPICO

Photoemission studies were carried out at the Gas Phase Photoemission (GAPH) beamline [185] at the Elettra synchrotron radiation facility in Trieste, Italy, using nearly monochromatic synchrotron radiation with adjustable central energy. We utilized photon energies of 60 eV for a comprehensive overview of the valence electron states and 37 eV to replicate the central frequency of the attosecond pulses employed in pump-probe experiments. The molecular sample was vaporized using an oven source. The setup at the experimental station includes a hemispherical electron analyzer, which determines the kinetic energy distribution of photoelectrons, thereby providing insights into the binding energy (BE) of molecular valence states, and a Wiley-McLaren time-of-flight (TOF) mass spectrometer, which are positioned opposite each other at the magic angle (approximately 55°) relative to the radiation's polarization axis.

The electron and ion spectrometers were used either independently for photoelectron spectroscopy and photoion mass spectrometry or in tandem for photoelectron-photoion coincidence (PEPICO) experiments. PEPICO experiments enable the simultaneous detection of photoelectrons and photoions from the same photoionization event, facilitating coincident measurement. Despite the added complexity in the experimental setup, data capture, and processing, the method is advantageous due to the enriched data it provides. Specifically, this technique allows for the concurrent measurement of the energy of the emitted electron and its corresponding ion, originating from the same ionization occurrence.

PEPICO spectra were collected at a fixed photon energy of 60 eV with an analyzer pass energy of 30 eV. The electron kinetic energy was scanned over a binding energy range of 8–32 eV in 2.7 eV increments to ensure adequate overlap between successive acquisition windows. PEPICO allows the detection of both photoelectrons and photoions from a single photoionization event in coincidence, offering a direct view of the different decay pathways and their binding energy dependence. The 3D plot in Fig. S2 illustrates the yield of electron-ion coincidences for selected ion m/q values as a function of BE. Integrating along the m/q axis produces the photoelectron spectrum (depicted by the red line in Fig. 4.8a), while integration across the BE axis results in the ion mass spectrum (shown by the blue line in Fig. 4.8a).

Figure 4.8b) shows a zoom of the PEPICO data around $m/q = 30$ (corresponding to NO^+) for the three studied molecules. A considerable broadening of the mass spectra was measured for BEs above ≈ 22 eV, which corresponds to the calculated threshold for dication formation: this is the indisputable signature of the dissociation of an unstable dication following Coulomb explosion.

For BEs in the range 15–22 eV, the mass spectra are characterized by a sharp peak, whose relative amplitude with respect to the broadened structure at higher BEs de-

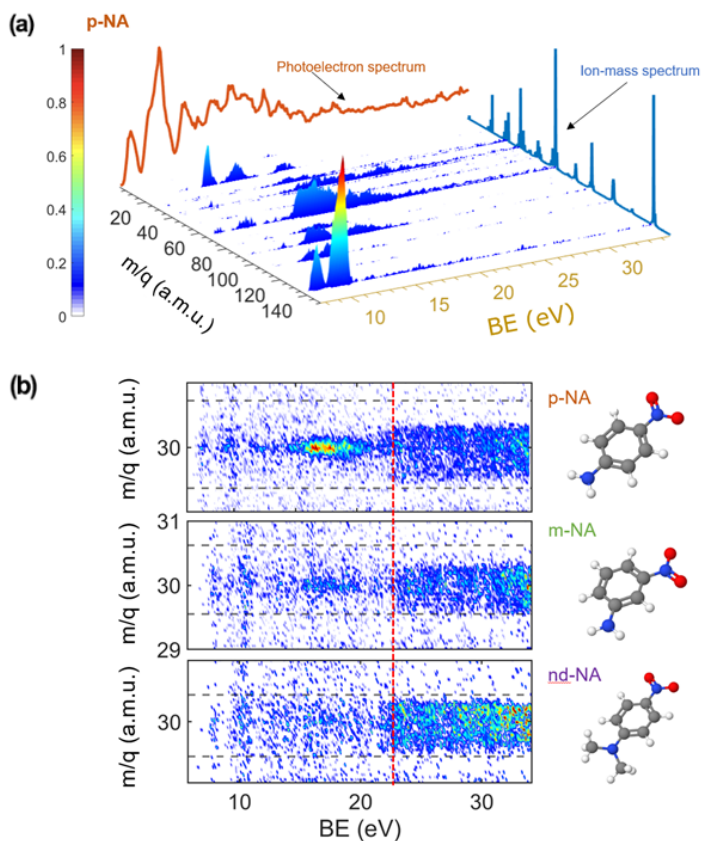


Figure 4.8: a) 3D plot of the PEPICO matrix for p-NA. The x-axis represents the binding energy (BE), the y-axis the mass-to-charge ratio (m/q) and the z-axis the number of events collected at the detector normalized to the maximum number of events. The solid orange line is the photoelectron spectrum, while the blue solid line is the ion mass spectrum. b) Zoom of PEPICO measurements around $m/q=30$ (NO^+) for the three investigated molecules, whose chemical structures are reported in the right column. The red dashed line shows the dication appearance energy

depends on the particular molecules. This peak is pronounced in the case of p-NA and is less marked in the case of m-NA and nd-NA. This is in agreement with the mass spectra measured with the attosecond beamline shown in after XUV excitation??.

A similar behaviour was observed for the cation NO_2^+ ($m/q = 46$), thus reinforcing the conclusion that the formation of this fragment is also driven by Coulomb explosion (CbE) of an unstable dication.

This is consistent with the observation that the measured temporal evolution of the NO_2^+ yield is very similar to that of the NO^+ cation (as shown in Fig. 4.6). Coulomb explosion and photo fragmentation pathways This comprehensive energy-resolved investigation enables us to confirm our pump-probe dynamics interpretation confidently.

The attosecond pulses utilized in the time-resolved experiments are capable of excit-

ing states within both the cation and dication of the molecule, thereby opening up multiple fragmentation routes even in the absence of interaction with the NIR probe pulses. Specifically, the fragments NO^+ (as well as NO_2^+) arise from two distinct mechanisms: the statistical fragmentation of the monocation or the dissociation of the unstable dication. This is illustrated in the upper panel of Fig. 4.9. The statistical fragmentation of the monocation is responsible for the central peak observed in the mass spectrum near $m/q = 30$. In contrast, the dissociation of the unstable dication, propelled by the Coulomb explosion, is what generates the side shoulders observable at $m/q \approx 29.5$ and $m/q \approx 30.5$.

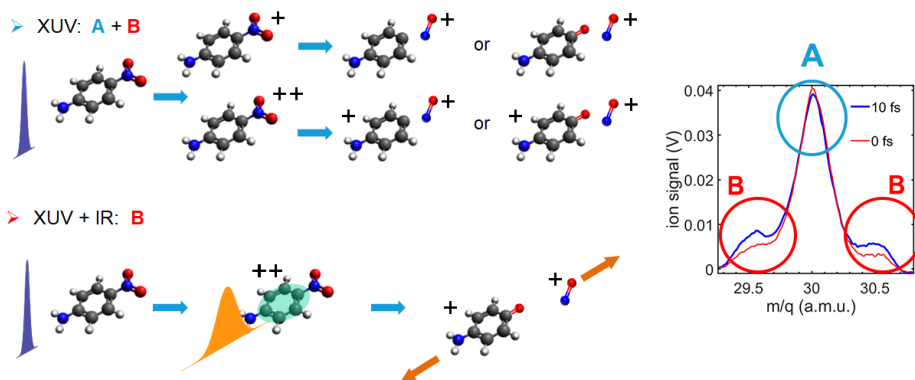


Figure 4.9: Formation pathways of the fragment NO^+ : Upper panel, fragmentation pathways initiated by the XUV pulses. The attosecond pump pulses can generate both cationic states, which may fragment into NO^+ ions, as well as dicationic states which undergo fragmentation by CbE, resulting in the formation of high-kinetic-energy NO^+ fragments. Lower panel, the XUV pulse generates a superposition of cationic states, while the subsequent VIS/NIR probe pulse removes a second electron from the molecule. The probe pulses enhance the pathways leading to CbE and NO^+ formation, confined to the lateral shoulders of the mass spectra at $m/q \approx 29.5$ and $m/q \approx 30.5$.

The distinct generation mechanisms of these fragments explain their differing temporal behaviours once the VIS/NIR probe pulses intervene. The probe pulses can excite the cations through multiphoton absorption to form molecular dications, which then fragment via Coulomb explosion. As schematically represented in the lower panel of Fig. 4.9, the probe pulses increase the number of pathways that lead to CbE and the formation of NO^+ , which is restricted to the lateral shoulders of the mass spectrum. The observed rapid dynamics are, therefore, indicative of the time-varying transition probabilities from the cationic to the dicationic states, as the wavepacket evolves over the potential energy surface of the cation excited state, see 4.10 c). In contrast, the central peak of the mass spectrum, which is associated with NO^+ generated by the statistical fragmentation due to XUV pulses alone, remains unaffected by the probe pulses and exhibits no temporal change.

4.3 Simulation results: ultrafast dynamics in photo-ionized nitroanilines

To unravel the complex electron and nuclear dynamics within the initial few femtoseconds, a thorough theoretical study is essential for interpreting the ultrafast timings observed in our experiments. These calculations were conducted by our colleagues at Universidad Autónoma de Madrid in the group of Prof. Fernando Martin.

Given the broad bandwidth of the attosecond pulse used for ionization (≈ 20 eV), multiple electronic states become accessible in the molecular cation formed. The photoelectron spectra (PES), captured using 60 eV synchrotron radiation, indicate that the primary contributions to the PES for all three molecular cations emanate predominantly from the lowest electronic states (*DX*), see Fig. 4.10a) and b). Our multireference CASSCF theoretical calculations [186] validate this by confirming that the most significant Dyson norms correlate with monocation states up to 4 eV above the ionization threshold, predominantly characterized by a 1-hole (1-h) configuration. This is supported by the close agreement between our measured and calculated spectra, with the latter derived from actual ionization probabilities or Dyson norms (as detailed in the Supplementary of [Nitroanilinesubmitted]).

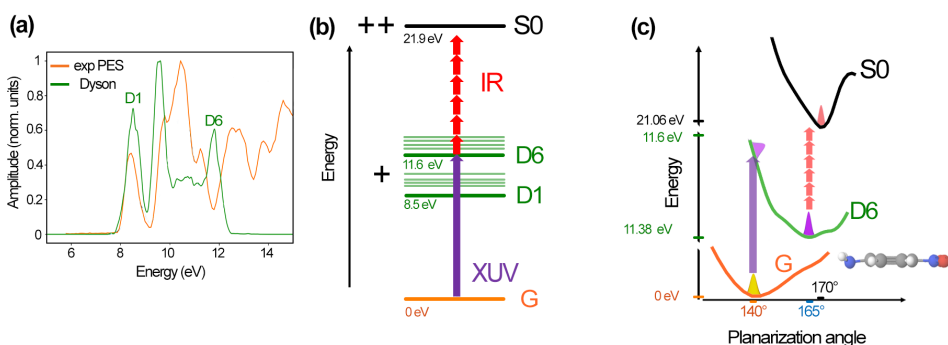


Figure 4.10: a) Comparison of experimental PES, recorded at the synchrotron, and calculated Dyson norm of the different doublet state of the cation (*DX*). b) Scheme of the different energy levels at the cation (green) and the ground state of the dication (singlet) S0 (black). In our experiment, the XUV populates the different cation levels, and subsequent IR promotes the wavepacket from the cation to the dication, via multi-photon absorption. c) Calculated potential energy curves vs. the planarization angle of the amino group with respect to the benzene ring of the ground state, G, of the neutral p-NA molecule, the excited state D6 of the cation and the ground state S0 of the dication. After an initial localization into a minimum of potential in D6, the wavepacket spreads over several degrees of freedom.

4.3.1 Ultrafast rise time and charge transfer

A key finding from the simulations is the ultrafast planarization of the amino group (NH_2) with the benzene ring in the cation immediately after photoionization, regardless of the cation initial electronic state, including the ground state. Figure 4.11 illustrates the time evolution of the root-mean square (rms) deviation of the trajectories relative to the planar geometry in p-NA, signifying a local energy minimum. The rms indicate the proximity of molecular structures to this planar minimum; lower values suggest closer alignment. The nuclear wave packet is seen to converge towards a planar molecular geometry within approximately 7 fs post-photoionization. Fig. 4.10a) gives an idea of the physical reason behind planarization mechanism, after direct ionization from the XUV-attosecond pulse the molecular wavepacket tends to move toward the minimum of D6, which minimizes the planarization angle.

We then analyzed the temporal changes in electron density across different regions of the dynamic molecular cation using the electronic localization function (ELF) theory, as detailed in the Supplementary Information of [Nitroanilinesubmitted]. Figure 4.10b), displays these results. In the first ≈ 10 fs, the most significant electron density variations are observed around the NH_2 group and the adjacent C-N bond, indicating substantial CT from the NH_2 lone pair towards the C-N bond, marked by a color shift from orange to green around NH_2 . This coincides with the NH_2 group planarization (sp^2 -hybridization), which subsequently reverts to a pyramidal structure (sp^3 -hybridization) (in the opposite direction) over the next 10 fs, reversing the CT process.

Figure 4.10c) quantifies this charge (electron) transfer, showing the evolution of net charges derived from integrating the electron density over these regions. The CT reaches nearly a full atomic unit of charge and aligns with the NH_2 group's planarization. Similar ultrafast behaviours were also observed for m-NA and nd-NA (as presented in Supplementary of [Nitroanilinesubmitted]), reinforcing our theoretical interpretation. Notably, this electron transfer initiated by prompt ionization occurs within the same timeframe as the initial rise in the yield of NO^+ and NO_2^+ fragment production.

The analysis of nuclear kinetic energy and the cation-dication Dyson norms, as presented in Fig. 4.11d), corroborates that the initial rise in the yields of NO^+ and NO_2^+ is indeed indicative of the NH_2 group concerted planarization and electron transfer. It is evident that within the first ≈ 10 fs, the nuclear kinetic energy increases, thereby facilitating Coulomb explosion post-probe step and the resultant generation of NO^+ and NO_2^+ fragments. Concurrently, the nuclear wave packet accelerates toward the energy minimum associated with the planar structure, becoming increasingly localized. This localization of the wave packet makes ionization by the VIS-NIR probe pulse more effective, as reflected in the corresponding rise of the cation-dication

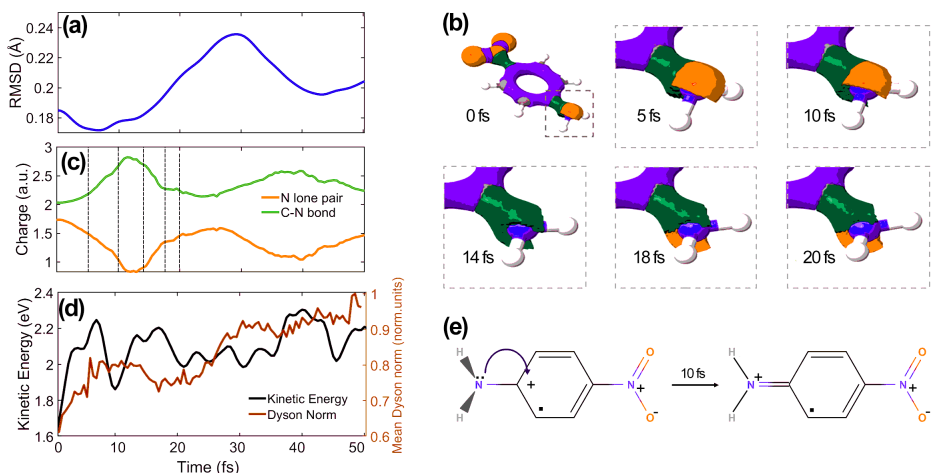


Figure 4.11: a) Calculated temporal evolution of the average Root Mean Square Deviation (RMSD) of all the trajectories initialized in electronic state D6 of p-NA with respect to the planar minimum geometry. The lower the values of the RMSD the closer to the planar geometry. b) Snapshots of the evolution of the electronic density. The colours indicate the basins where the density is assigned. In the NH₂ region, red indicates the lone pair of the N, while green indicates the C-N bond. c) Temporal evolution of the average charge in the ELF basins for the lone pair of N in the NH₂ group (orange) and the C-N bond connecting it to the ring (green). d) Temporal evolution of the average kinetic energy of the nuclear wave packet. (black curve) and the average Dyson norm corresponding to the orbital that results from the projection of the ground state of the mono-cation onto the ground state of the di-cation (red curve). e) Lewis structures representing the charge transfer from the lone pair of N to the C-N bond.

Dyson norm during the same timeframe. Therefore, it is the combination of increased nuclear wave packet localization and nuclear kinetic energy that enhances ionization of the cation by the probe pulse, leading to subsequent CbE and the more efficient production of NO⁺ and NO₂⁺ fragments.

Further supporting this interpretation is the observation that the production yield of various charged fragments related to the C-N bond, which is the initial region where CT occurs, shows an ultrafast increase with a ≈ 10 fs time constant. This suggests that heightened localization and kinetic energy also enhance the likelihood of cation excitation across certain fragmentation barriers. These fragments (CN⁺, C₂N⁺, and C₃N⁺), linked to the transition from lower excited states to higher cationic excited states, exhibit an exponential decay with a time constant ($\tau_2 > 60$ fs, see Table 4.1) significantly longer than the decay time for fragments originating from dication generation and CbE. Thus, we can conclude that the CT from the donor group to the ring, as per the conventional model depicted in 4.11e), occurs in just about ≈ 10 fs. This aligns with the accepted view that the NH₂ group's N atom shifts from sp³ (pyramidal) to sp² (planar) hybridization in the same time span. Our findings assign a ≈ 10 fs duration to this key process in donor-acceptor systems.

It is important to note that the simulation durations in our analysis are too brief to witness CT extending to more distant sites on the phenyl ring or the NO₂ ac-

ceptor group. Contrary to NH_2 , geometrical changes necessary to alter electronic configurations in NO_2 require a longer time due to the significantly greater mass of the oxygen atoms (as detailed in the SI of [Nitroanilinesubmitted]). Hence, the charge transferred to the C-N bond is limited to oscillating between this bond and NH_2 within the calculated short timeframe. This charge oscillation is not discernible in the experiments, given the sub-30-fs attenuation of the fragments resulting from CbE.

4.3.2 Ultrafast relaxation time and inefficient probing of the IR

To clarify the cause of this observed damping, Fig. 4.12a) presents the time-dependent energy gap between the excited cationic states, initially populated by the attosecond pump pulses, and the ground state of the molecular dication formed post-interaction with the NIR probe pulses, as calculated across all nuclear trajectories. It is noticeable that for trajectories originating in the lowest excited states, D1 and D2, the energy required to transition to the molecular dication state remains relatively constant over time. However, for trajectories commencing from higher excited states, the energy difference relative to the education ground state progressively increases, particularly after about 25 fs. This trend indicates a growing energetic barrier for these trajectories to reach the dication ground state as time advances.

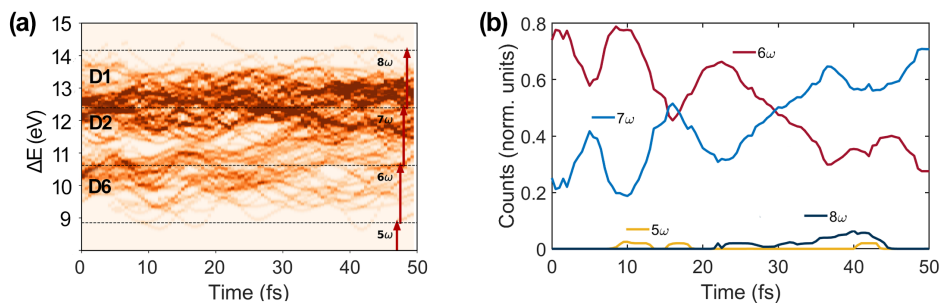


Figure 4.12: a) Temporal evolution of the energy difference between the D1, D2 and D6 states of the cation and ground state of the dication for all of the p-NA trajectories. The dashed horizontal black lines mark energy gaps for absorption of an IR photon (represented by a red arrow). b) Normalized number of trajectories requiring 5, 6, 7 and 8 IR photons to reach the ground state S0 of the dication in p-NA, for the trajectories initiated in the highest electronic states (D6).

This observation pertains to the higher excited states of the cation with significant Dyson norms: specifically, state D6 in p-NA, state D8 in m-NA, and state D5 in nd-NA. Consequently, the number of NIR photons required to ionize the molecular cation increases with time, as illustrated in Fig. 4.12a), where the energies needed to ionize the molecular cation by absorption on n NIR photons at any time are shown. From this figure, we can estimate the number of trajectories which require absorption of a particular number of NIR photons to reach the dication. Fig. 4.12b) displays the

normalized count of trajectories that require 5, 6, 7, or 8 NIR photons to reach the dication ground state So, focusing on the trajectories starting from the cationic state D6 of p-NA.

As shown in Figs. 4.13a)-c), the temporal pattern of trajectories needing the absorption of 6 VIS-NIR photons to reach So mirrors the relaxation dynamics of the NO⁺ yield in all three molecules. A decline in the number of such trajectories corresponds to a diminished probability of double ionization by the combined pump and probe pulses, consequently reducing the production of the dication-related fragments.

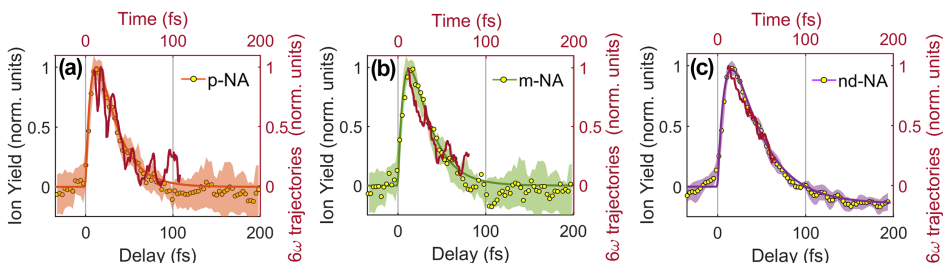


Figure 4.13: c, d, e, Normalized number of trajectories requiring the absorption of 6 VIS-NIR photons to reach So (dark red line) compared with the measured yields (circles and shaded area) for p-NA, m-NA and nd-NA, respectively. To guide the eye, the fits to the experimental spectra are also indicated by thin continuous lines.

This interpretation aligns with the experimental and numerical findings for both m-NA and nd-NA. Intriguingly, the ultrafast CT process remains unchanged by either the inductive effect or methylation. In the case of methylation, this resilience is likely due to the methyl groups being closer to the planar structure, offsetting the increased mass of the donor group. It's also notable that the observed decay time for nd-NA ($\tau_2 = 31.4 \pm 1.3$ fs) is longer than in p-NA, indicating a direct influence of methylation on nuclear wavepacket confinement.

4.3.3 Conclusions: early stage process guiding CT in a donor- π -acceptor system

Our research demonstrates that the initial CT step in prototypical nitroanilines, is an electron transfer from the NH₂ lone pair to the adjacent C-N bond (happening in approximately 10 fs) driven by the NH₂ group planarization.

10-fs is also the time required for the nitrogen atoms to switch from sp^3 to sp^2 hybridization, enabling effective electron transfer toward the donor side of the molecule. This early-stage process is fundamental to subsequent ET/CT processes occurring on longer timescales, ultimately culminating in CT to the acceptor nitro group.

We have also elucidated the reasons behind the decay of ionic fragments observed in this and previous XUV pump/NIR probe experiments at extended pump-probe

delays, attributing it to the reduced efficiency of the probing step due to the continual spreading of the nuclear wave packet.

These findings address a crucial question in chemistry regarding the time needed for charge transfer from an electron donor unit to the adjacent carbon atom of the benzene ring and the accompanying structural changes. Thus, our experimental and theoretical insights contribute significantly to a deeper understanding of textbook diagrams and concepts typically employed to qualitatively predict charge migration/charge transfer in organic molecules.

Chapter 5

Summary and Outlook

The advent of attosecond science revolutionized our comprehension of ultrafast phenomena by enabling real-time tracking of electron dynamics within atoms, molecules and solids. Particularly, this groundbreaking progress opened up new avenues for understanding and manipulating ultrafast processes in molecules at the quantum level, crucial for advancements in photochemistry and optoelectronics. The synergy between advancements in simulating quantum phenomena in complex systems and technical developments in attosecond technology has been instrumental in this evolution, setting the stage for cutting-edge applications in materials science and the field of energy conversion.

In this dissertation, I have delved into both domains, enhancing the technological repertoire for generating attosecond pulses through high harmonic generation in gas (as detailed in Chapter 3), and examining the dynamics of ultrafast photo-induced charge transfer mechanisms (discussed in Chapter 4).

In Chapter 3, section 3.1, it is showcased the first successful experimental demonstration of a new theoretical model that provides simple guidance for optimizing gas-based HHG sources. In Section 3.2, we introduced an innovative model for predicting the transfer of astigmatism from the driving field to the generated harmonics. This model, corroborated by experimental findings, serves as a roadmap for producing high-intensity XUV laser beams with minimal aberrations. Utilizing this model, we are now equipped to forecast the creation of chromatically aberrated XUV beams and accordingly implement strategies to correct them, especially by reducing astigmatism in the driving field using wavefront-correction optics. Section 3.3 introduced an innovative technique for generating isolated attosecond pulses (IAP) utilizing, for the first time, a semi-infinite gas cell (SIGC) combined with a strategically engineered gas profile. The results confirmed that thanks to a combination of time-gated phase matching

and harmonic re-absorption, SIGC apparatuses are suitable for IAPs production. This achievement marks a significant step forward in developing more flexible IAP generation methods compatible with medium-to-long focusing geometries, adaptable to a range of experimental setups, including XUV-XUV pump-probe or NIR/VIS/UV pump-XUV probe systems.

The pulses generated with this technology are then used for ultrafast spectroscopic applications, for example, to investigate the ultrafast photophysics of donor-acceptor molecular systems.

Therefore, in Chapter 4, we examined one of the simplest donor-acceptors: nitroanilines. Specifically, we studied the initial charge transfer stages, triggered by an isolated attosecond pulse, and subsequently probed using a few-femtosecond infrared field. Our research revealed a rapid charge transfer mechanism in nitroaniline, occurring in less than 10 femtoseconds, guided by the planarization of the NH_2 group and an ultrafast-hybridization transition from sp^3 to sp^2 orbitals. This early-stage process critically influences the ensuing electron dynamics, thus affecting the overall charge transfer within the molecular system. Supported by advanced quantum mechanics simulations, these experimental observations provide fresh perspectives on the early photophysics of donor-acceptor systems. These insights have far-reaching implications in photovoltaics, molecular optoelectronics, and understanding the intricate interplay between nuclear and electron dynamics beyond traditional adiabatic approximations.

What is next?

This thesis outlines recent advancements in attosecond technology and atto-chemistry. As discussed, HHG stands out as an exceptional tool for both its temporal and spatial characteristics.

Looking ahead, research is currently extending Attochemistry to the soft-X-Ray region (i.e. water window), where attosecond pulses can offer groundbreaking insights into molecule photophysics with atomic specificity. This research aims to elucidate complex organic molecules for optoelectronic applications (such as molecular transistors and molecular nano-wires) and inorganic molecules (like transition metal complexes and ultrafast photocatalysts). Moreover, the refined control of HHG's spatial properties is opening new paths in nanometrology and HHG-ptychography, presenting exciting possibilities for non-invasive imaging of nanostructures. These advancements hold immense potential for broad applications in nanotechnology and the semiconductor industry.

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Appendix A: Quantum Mechanics Transformations and Dyson Equations for SFA

.I On Gauges transformation in quantum mechanics

The inclusion of a scalar potential, denoted as $A_0(\mathbf{r}, t)$, and a vector potential, represented by $\mathbf{A}(\mathbf{r}, t)$, significantly simplifies the approach to describing and solving physical phenomena within the framework of Maxwell's equations and Light-Matter Interaction. The relationships between these potentials and the electric field $\mathbf{E}$, and the magnetic field $\mathbf{B}$, are given by[93]:

$$\begin{aligned}\mathbf{E} &= -\nabla A_0 - \frac{\partial \mathbf{A}}{\partial t} \\ \mathbf{B} &= \nabla \times \mathbf{A}\end{aligned}\tag{1}$$

where ∇ represents the gradient operator.

However, it is important to note that these potentials are not uniquely defined. We can always introduce a gauge function, $\chi^{(\alpha)}$, that transforms the potentials as follows:

$$\begin{aligned}\mathbf{A}^{(\alpha)} &= \mathbf{A}^{(\beta)} + \nabla \chi^{(\alpha)} \\ A_0^{(\alpha)} &= A_0^{(\beta)} - \frac{\partial \chi^{(\alpha)}}{\partial t}\end{aligned}\tag{2}$$

It can be demonstrated that these transformations preserve the form of Eq. (1). As a result, $A_0(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$ are gauge-dependent, whereas the real fields $\mathbf{E}$ and $\mathbf{B}$ are gauge-invariant.

To minimize the redundancy introduced by the gauge function $\chi(\mathbf{r}, t)$, physicists often constrain this freedom by selecting specific gauges[187]. A common approach involves decomposing the vector potential into its longitudinal and transversal components:

$$\mathbf{A} = \mathbf{A}_L + \mathbf{A}_T\tag{3}$$

where $\mathbf{A}_T$ satisfies $\nabla \cdot \mathbf{A}_T = 0$, and $\mathbf{A}_L = 0$, $\nabla \times \mathbf{A}_L = 0$.

Due to fundamental vector identities (e.g., $\nabla \times \nabla \cdot \mathbf{v} = 0$), irrespective of the chosen α -gauge, $\nabla \chi^{(\alpha)}$ is always longitudinal:

$$\mathbf{A}^{(\alpha)} = \mathbf{A}_T + (\nabla \chi^{(\alpha)})_L \quad (4)$$

This distinction is particularly useful when transitioning between different gauges. By setting $\mathbf{A}_L = 0$, we arrive at the so-called Coulomb gauge (or the *velocity gauge* in the context of strong-field matter interaction). In this velocity gauge (v), according to Eq. (1) and since $\nabla \cdot \mathbf{A}_T = 0$:

$$\nabla \cdot \mathbf{E} = -\nabla^2 A_0^{(v)} = \frac{\rho}{\epsilon_0} \quad (5)$$

where we can recognize in the last part the basic electrostatic Poisson's equation.

Hence, within this gauge, the scalar potential $A_0^{(v)}$ coincide with the electrostatic Coulomb potential, $\Phi = 1/\hat{\mathbf{r}}$ in the simple Hydrogen case.

Consequently, the total electric field $\mathbf{E}$ can be written:

$$\mathbf{E} = -\nabla A_0^{(v)} - \partial_t \mathbf{A}^{(v)} = -\nabla \Phi + \mathbf{E}_{\text{ext}} \quad (6)$$

Thus, within this gauge, we can distinguish the electric field contribution from localized charges, $A_0 = \Phi$, from the one generated by external sources (e.g. laser field), which is embedded in the transversal component $-\partial_t \mathbf{A}_T = \mathbf{E}_{\text{ext}}$.

A more general approach is to define a multipolar α -gauge given by:

$$\mathbf{A}^{(\alpha)} = \mathbf{A}_T - \alpha \nabla \int_0^1 d\lambda \mathbf{r} \mathbf{A}_T(\lambda \mathbf{r}), \quad (7)$$

where the gauge function $\chi^{(\alpha)}$ is expressed as:

$$\chi^{(\alpha)} = -\alpha \int_0^1 d\lambda \mathbf{r} \mathbf{A}_T(\lambda \mathbf{r}) \quad (8)$$

This gauge finds its application in more advanced contexts. In the dipole approximation, where $\mathbf{A}(\mathbf{r}, t) \approx \mathbf{A}(0, t)$, it simplifies to:

$$\mathbf{A}^{(\alpha)}(t) = \mathbf{A}_T(t) - \alpha \mathbf{A}_T(t) \quad (9)$$

When $\alpha = 1$, this yields the so-called *length gauge* in the dipole approximation,

$$\mathbf{A}^{(l)}(t) = 0. \quad (10)$$

In semi-classical quantum mechanics, the light-matter interaction Hamiltonian (in atomic units) in a generic α -gauge for a single electron is:

$$\hat{H}^{(\alpha)} = \frac{1}{2}(\hat{\mathbf{p}} + \mathbf{A}^{(\alpha)})^2 - A_0^{(\alpha)} \quad (11)$$

where $\hat{H}^{(\alpha)}$, is the Hamiltonian operator in the α -gauge, and the $\hat{\mathbf{p}}$ momentum operator $\hat{\mathbf{p}} = -i\nabla$, which keep the same form across different gauges, though its expectation value interpretation may vary, as we will discuss later.

In the velocity gauge (v), the Hamiltonian is given by:

$$\boxed{\hat{H}^{(v)} = \frac{1}{2}(\hat{\mathbf{p}} + \mathbf{A}_T)^2 - \Phi} \quad (12)$$

where we have separated the potential contributions from external fields ($\mathbf{A}_T$) and confined charges Φ , e.g. Coulomb field from a proton in a hydrogen-like system.

The situation in the length gauge is slightly more subtle. Given that $\mathbf{A}^{(l)} = 0$, the scalar potential $A_0^{(l)}$ encompasses both the Coulomb contribution and the external field, which is uniquely defined (regardless from the gauge) in terms of $\mathbf{A}_T$. The gauge function $\chi^{(l)}$ and its gradient are equal to:

$$\begin{aligned} \nabla \chi^{(l)} &= -\mathbf{A}_T, \\ \chi^{(l)} &= -\mathbf{r} \cdot \mathbf{A}_T \end{aligned}$$

By exploiting (2), it follows that:

$$A_0^{(l)} = (A_0^{(v)} - \frac{\partial \chi^{(l)}}{\partial t}) = \Phi + \mathbf{r} \cdot \partial_t \mathbf{A}_T = \Phi - \mathbf{r} \cdot \mathbf{E}_{\text{ext}} \quad (13)$$

hence, $A_0^{(l)}$ effectively integrates the influences of both the Coulomb potential and the external electric field.

Consequently, the Hamiltonian in the length gauge (l), within the dipole approximation is given by:

$$\boxed{\hat{H}^{(l)} = \frac{1}{2}(\hat{\mathbf{p}} + \mathbf{A}^{(l)})^2 - A_0^{(l)} = \frac{1}{2}\hat{\mathbf{p}}^2 - \Phi + \mathbf{r} \cdot \mathbf{E}_{\text{ext}}} \quad (14)$$

This derivation presents a straightforward approach, offering a clear path to interchange between gauges without invoking any unusual properties or complex reasoning.

.I.I Gauges and Wavefunction transformation

Due to the gauge-variant nature of the light-matter Hamiltonian, described in the precedent discussion, it is to be expected that the wavefunction will reflect a gauge dependence in the form of a complex phase-term, identified by a generic operator $\lambda(\hat{\mathbf{r}}, \hat{\mathbf{p}})$:

$$|\psi\rangle^{(\beta)} = \hat{U}_{(\alpha,\beta)} |\psi\rangle^{(\alpha)} = e^{i\lambda_{\alpha,\beta}} |\psi\rangle^{(\alpha)} \quad (15)$$

where $\hat{U}_{(\alpha,\beta)}$ has to be unitary transformation:

$$\hat{U}_{(\alpha,\beta)} \hat{U}_{(\alpha,\beta)}^\dagger = \hat{\mathbf{I}} \quad (16)$$

where $\hat{\mathbf{I}}$ is the identity operator.

It is important to note that while the wavefunction is gauge-dependent, the expectation value of a physical observable, $\hat{O}$, must remain invariant across different gauges. Thus, irrespective of the gauge choice, we have:

$$\langle \psi^{(\alpha)} | \hat{O} | \psi^{(\alpha)} \rangle = \langle \psi^{(\beta)} | \hat{O} | \psi^{(\beta)} \rangle. \quad (17)$$

For instance, both the position operator, $\hat{\mathbf{r}}$, and the velocity operator, $\hat{\pi}$, must exhibit gauge invariance. As commonly defined in many textbooks, the velocity operator in any α -gauge is given by:

$$\hat{\pi} = \hat{\mathbf{p}}_{(\alpha)} + \mathbf{A}^{(\alpha)}(\hat{\mathbf{r}}, t). \quad (18)$$

Following Eqs. (17) and (15), we can deduce that:

$$\hat{U}_{(\alpha,\beta)}^\dagger \hat{\mathbf{r}} \hat{U}_{(\alpha,\beta)} = \mathbf{r} \quad (19)$$

and,

$$\hat{U}_{(\alpha,\beta)}^\dagger (\hat{\mathbf{p}}^{(\beta)} + \mathbf{A}^{(\beta)}) \hat{U}_{(\alpha,\beta)} = \hat{\mathbf{p}}^{(\alpha)} + \mathbf{A}^{(\alpha)} \quad (20)$$

From Eq. (19), we deduce that the two operators commute with each other $[\hat{U}_{(\alpha,\beta)}, \hat{\mathbf{r}}] = 0$.

The notation $\hat{\mathbf{p}}^{(\alpha,\beta)}$ signifies that, depending on the specific gauge chosen, the momentum may have different expectation values, even if its definition as an operator remains consistent. This distinction becomes clear when comparing the momentum between the velocity gauge and the length gauge. In the velocity gauge, the momentum $\hat{\mathbf{p}}^{(v)}$ represents a drift momentum, which remains conserved during the interaction:

$$\hat{\mathbf{p}}^{(v)} = \hat{\pi}(t) - \mathbf{A}^{(v)} = \hat{\pi}(t) - \mathbf{A}_T(t). \quad (21)$$

Conversely, in the length gauge, where $\mathbf{A}^{(l)} = 0$, the momentum is given by:

$$\hat{\mathbf{p}}^{(l)} = \hat{\pi}(t) \quad (22)$$

implying that the momentum is equal to the instantaneous velocity of the particle (in a.u.).

Our goal now is to find a form for $\hat{U}_{(\alpha,\beta)}$, to be used when transforming the wavefunction from one gauge to another. Following Eqs. (20) and (4), we can write:

$$\hat{U}_{(\alpha,\beta)}^\dagger (\hat{\mathbf{p}} + \mathbf{A}_T + \nabla\chi_{(\beta)}) \hat{U}_{(\alpha,\beta)} = \hat{\mathbf{p}} + \mathbf{A}_T + \nabla\chi_{(\alpha)} \quad (23)$$

$$\hat{U}_{(\alpha,\beta)}^\dagger \hat{\mathbf{p}} \hat{U}_{(\alpha,\beta)} = -(\nabla\chi_{(\alpha)} - \nabla\chi_{(\beta)}) + \hat{\mathbf{p}} \quad (24)$$

At the same time, owing to the unitary properties of $\hat{U}_{(\alpha,\beta)}$, the following identity holds:

$$\hat{U}_{(\alpha,\beta)}^\dagger \hat{\mathbf{p}} \hat{U} = \hat{U}_{(\alpha,\beta)}^\dagger \hat{\mathbf{p}} \hat{U}_{(\alpha,\beta)} - \hat{U}_{(\alpha,\beta)}^\dagger \hat{U}_{(\alpha,\beta)} \hat{\mathbf{p}} + \hat{\mathbf{p}} = \hat{U}_{(\alpha,\beta)}^\dagger [\hat{\mathbf{p}}, \hat{U}_{(\alpha,\beta)}] + \hat{\mathbf{p}} \quad (25)$$

From basic quantum mechanics, we know:

$$[\hat{\mathbf{p}}, \hat{U}_{(\alpha,\beta)}] = i \frac{\partial}{\partial \mathbf{r}} \hat{U}_{(\alpha,\beta)} \quad (26)$$

Therefore, combining Eqs. (24) and (26), and multiplying both terms with $\hat{U}_{(\alpha,\beta)}$, we deduce:

$$i \frac{\partial}{\partial \mathbf{r}} \hat{U}_{(\alpha,\beta)} = -\hat{U}_{(\alpha,\beta)} (\nabla\chi_{(\alpha)} - \nabla\chi_{(\beta)}) \quad (27)$$

We have thus determined, in a straightforward manner, a very important transformation operator that allows to adapt the wavefunction into a new gauge:

$$\boxed{|\psi\rangle^{(\beta)} = \hat{U}_{(\alpha,\beta)} |\psi\rangle^{(\alpha)} = e^{i(\chi_{(\alpha)} - \chi_{(\beta)})} |\psi\rangle^{(\alpha)}} \quad (28)$$

As detailed in Chapter 2 and in the next section, this result is extremely useful within the framework of strong-field physics.

General Hamiltonian under gauge transformation

To conclude this section, we derive a rather general transformation rule between gauges of the hamiltonian operator from $\hat{H}^{(\alpha)}$ to $\hat{H}^{(\beta)}$, with gauges function(s) $\chi_{\alpha,\beta}(\mathbf{r}, t)$.

Let us consider the Schrödinger equation in the final gauge β , with the proper wavefunction $|\psi\rangle^{(\beta)}$:

$$i\partial_t |\psi\rangle^{(\beta)} = \hat{H}^{(\beta)} |\psi\rangle^{(\beta)} \quad (29)$$

$$i\partial_t (\hat{U}_{(\alpha,\beta)} |\psi\rangle^{(\alpha)}) = \hat{H}^{(\beta)} \hat{U}_{(\alpha,\beta)} |\psi\rangle^{(\alpha)} \quad (30)$$

$$i\partial_t \hat{U}_{(\alpha,\beta)} |\psi\rangle^{(\alpha)} + i\hat{U}_{(\alpha,\beta)} \partial_t |\psi\rangle^{(\alpha)} = \hat{H}^{(\beta)} \hat{U}_{(\alpha,\beta)} |\psi\rangle^{(\alpha)} \quad (31)$$

From these equations, it follows that:

$$(i\partial_t \hat{U}_{(\alpha,\beta)} + \hat{U}_{(\alpha,\beta)} \hat{H}^{(\alpha)}) |\psi\rangle^{(\alpha)} = \hat{H}^{(\beta)} \hat{U}_{(\alpha,\beta)} |\psi\rangle^{(\alpha)} \quad (32)$$

By multiplying both sides by $\hat{U}_{(\alpha,\beta)}^\dagger$ and using the unitary property of the operator, we obtain:

$$\hat{H}^{(\beta)} = \hat{U}_{(\alpha,\beta)} \hat{H}^{(\alpha)} \hat{U}_{(\alpha,\beta)}^\dagger + i\partial_t \hat{U}_{(\alpha,\beta)} \hat{U}_{(\alpha,\beta)}^\dagger \quad (33)$$

In the simple case of velocity to length gauge, it can be shown that we can also correctly transform the Hamiltonians by exploiting Eq. (33).

.2 Propagators and Dyson Series

Propagators

As introduced in Chapter 1, in the modern formulation of quantum mechanics [3] time cannot be measured. Hence, although we cannot define a time operator, we can introduce the concept of *time-evolution operator*. Imagine a state initially defined as $|\psi, t_0\rangle = |\psi(t_0)\rangle$. The time-evolution of this state, resulting in $|\psi, t\rangle = |\psi(t)\rangle$, can be viewed as the application of an operator on the initial state:

$$|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle \quad (34)$$

and, similarly:

$$\langle\psi(t)| = \langle\psi(t_0)| \hat{U}^\dagger(t, t_0) \quad (35)$$

Therefore, the Schrödinger equation for a certain state $|\psi(t)\rangle$,

$$i \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \quad (36)$$

can be reinterpreted in terms of the application of this specific operator (Eq. 34):

$$i \frac{\partial}{\partial t} (\hat{U}(t, t_0) |\psi(t_0)\rangle) = \hat{H} (\hat{U}(t, t_0) |\psi(t_0)\rangle)$$

Given that $|\psi(t_0)\rangle$ is no longer time-dependent, we infer that the two operators (left and right-sides) are identical, i.e. have the same effect on the initial state:

$$i \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H} \hat{U}(t, t_0) \quad (37)$$

Eq. (37) is commonly referred to as the *Schrödinger equation for the time-evolution operator* [6?].

Let us first consider the scenario where $\hat{H}$ is a time-independent Hamiltonian, denoted as $\hat{H} = \hat{H}_0$.

The solution is:

$$\hat{U}(t, t_0) = e^{-i\hat{H}_0(t-t_0)} \quad (38)$$

where the exponential operator must be regarded as:

$$e^{-i\hat{H}_0(t-t_0)} = \sum_n \frac{(-i\hat{H}_0(t-t_0))^n}{n!}$$

Thus,

$$|\psi(t)\rangle = e^{-i\hat{H}_0(t-t_0)} |\psi(t_0)\rangle \quad (39)$$

The validity of this result will be demonstrated later in a more general context, yet we can already observe two key aspects:

Firstly, when $t = t_0$, we have:

$$e^{-\hat{0}} = \hat{\mathcal{I}} \quad (40)$$

This leads us to the identity operator $\hat{\mathcal{I}} |\psi(t_0)\rangle = |\psi(t_0)\rangle$.

Secondly, if the following condition holds (standard eigenvalue equation):

$$\hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle,$$

then it follows that:

$$|\psi(t)\rangle = e^{-iE_n(t-t_0)} |\psi(t_0)\rangle. \quad (41)$$

In essence, if $|\psi\rangle$ is an eigenstate of the time-independent Hamiltonian, we recover the expected time-dependence for an eigenstate¹.

Now, let us extend the result of Eq. (38) to scenarios where $\hat{H}(t)$, the Hamiltonian operator, depends on time. Consequently, the solution to Eq. (37) becomes:

$$\boxed{\hat{U}(t, t_0) = e^{-i \int_{t_0}^t \hat{H}(t') dt'}} \quad (42)$$

For completeness, let us demonstrate that Eq. (42) indeed solves Eq. (37). We start by expanding the time-derivative of the propagator $\hat{U}$:

$$i \frac{\partial \hat{U}}{\partial t} = i \frac{\partial}{\partial t} \left(e^{-i \int_{t_0}^t \hat{H}(t') dt'} \right) = i \frac{\partial}{\partial t} \left(\sum_{n=0}^{\infty} \left(-i \int_{t_0}^t \hat{H}(t') dt' \right)^n \frac{1}{n!} \right) \quad (43)$$

Utilizing the following mathematical property, we note that for $n \neq 0$:

$$\frac{\partial}{\partial x} \left[\int_0^x f(y) dy \right]^n = \frac{\partial}{\partial x} [F(x) - F(0)] = \frac{\partial F(x)}{\partial x} [F(x) - F(0)]^{n-1} n$$

where x, y are parameters, and F is the primitive of f :

$$\frac{\partial F(x)}{\partial x} = f(x) \quad [F(x) - F(0)] = \int_0^x f(y) dy$$

This leads to:

$$\frac{\partial}{\partial x} \left[\int_0^x f(y) dy \right]^n = n f(x) \left(\int_0^x f(y) dy \right)^{n-1} \quad (44)$$

¹Specifically, in the Schrödinger picture.

In scenarios where $n = 0$, the derivative naturally equals zero, posing no issues. By applying this concept to Eq. (43), we arrive at:

$$i \frac{\partial}{\partial t} \hat{U} = i \sum_{n=1}^{+\infty} \frac{(-i)^{n-1}}{n!} n \hat{H}(t) \left[\int_{t_0}^t \hat{H}(t') dt' \right]^{n-1} = \hat{H}(t) \sum_{m=0}^{+\infty} \frac{(-i)^m}{(m)!} \left[\int_{t_0}^t \hat{H}(t') dt' \right]^m.$$

Consequently, the remaining left term, summed over m is equal to $\hat{U}$, hence, we have confirmed that Eq. (2.37) solve Eq. (37).

Notably, through Eq. (42), we have obtained a general exact solution for every non-relativistic quantum mechanical problem. Indeed, given knowledge of the initial state, its evolution is determined by:

$$\boxed{|\psi(t)\rangle = \hat{P} |\psi(t_0)\rangle = e^{-i \int_{t_0}^t \hat{H}(t') dt'} |\psi(t_0)\rangle} \quad (45)$$

where $\hat{P}$ is the full-time propagator.

Despite the elegance of Eq. (45), its practical applicability is limited in most cases, with very few exceptions (see Volkov states).

Dyson Equations

In order to fully describe the time-evolution of $|\psi(t)\rangle$ the operator $\hat{H}(t')$ must be replaced with a function that may depend on both time and space. To accomplish this in the framework of strong-field physics, an interesting approach can be followed[6]. The first step is to reformulate the problem by dividing the Hamiltonian into distinct components:

$$\hat{H} = \hat{H}_0 + \hat{H}_I(t) \quad (46)$$

where now the full Hamiltonian is composed by a time-independent Hamiltonian $\hat{H}_0$ (typically including kinetic energy and Coulomb interaction) and $\hat{H}_I(t)$, the interaction Hamiltonian, which depends on external electromagnetic field, often in the dipole approximation in either the length or the velocity gauge.

Let us reintroduce the time-independent propagator $\hat{U}_0(t, t_0)$ as:

$$i \frac{\partial}{\partial t} \hat{U}_0(t, t_0) = \hat{H}_0 \hat{U}_0(t, t_0) \quad (47)$$

Our aim is to solve Eq.(36) by refining the result of Eq.(45), this approach is based on the so-called Dyson expansion (or Dyson equations).

First Dyson Equation

Starting from Eq. (36), we write:

$$i \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H} \hat{U}(t, t_0) = (\hat{H}_0 + \hat{H}_I(t)) \hat{U}(t, t_0)$$

from which it follows:

$$(i \frac{\partial}{\partial t} - \hat{H}_0) \hat{U}(t, t_0) = \hat{H}_I(t) \hat{U}(t, t_0) \quad (48)$$

To find a more elegant solution for Eq. (48), let us first address the following problem:

$$(i \frac{\partial}{\partial t} - \hat{H}_0) \hat{G}_0(t, t') = \delta(t - t') \quad (49)$$

According to Green's function theory (Green operators, in this case), if we find $\hat{G}_0(t, t')$ that solves Eq. (49), the solution to Eq. (48) can be expressed as [6]:

$$\hat{U} = \hat{U}_0(t, t_0) + \int_{t_0}^t \hat{G}_0(t, t') \hat{H}_I(t') \hat{U}(t', t_0) dt' \quad (50)$$

where the term $\hat{U}_0$ from Eq. (47) has also been included as it solved the homogeneous equation (i.e. without the interaction hamiltonian).

We now seek to intuitively determine the correct form of $\hat{G}_0$ under the causality condition $t > t'$, implying that the perturbation occurs before the final evolution time t .

Defining the operator $\hat{G}_0(\omega, t')$, as used in a different context in Quantum Optics [5], we have:

$$\hat{G}_0(t, t') = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \hat{G}_0(\omega, t') e^{i\omega t} d\omega \quad (51)$$

Then, based on Eq. (49):

$$(i \frac{\partial}{\partial t} - \hat{H}_0) \int \hat{G}_0(\omega, t') e^{i\omega t} d\omega = \delta(t - t') \quad (52)$$

and,

$$\int i \frac{\partial}{\partial t} (\hat{G}_0(\omega, t') e^{i\omega t}) - \hat{H}_0 \hat{G}_0(\omega, t') e^{i\omega t} d\omega = \int (-\omega - \hat{H}_0) \hat{G}_0(\omega, t') e^{i\omega t} d\omega.$$

Upon Fourier transforming the delta function shifted at t' , Eq. (52) becomes:

$$\int (-\omega - \hat{H}_0) \hat{G}_0(\omega, t') e^{i\omega t} d\omega = \int e^{-i\omega t'} e^{i\omega t} d\omega \quad (53)$$

By equating the integrands, we derive:

$$\hat{G}_0(\omega, t') = -\frac{e^{-i\omega t'}}{\omega + \hat{H}_0} \quad (54)$$

Consequently:

$$\hat{G}_0(t, t') = -\frac{1}{2\pi} \int \frac{1}{\omega + \hat{H}_0} e^{i\omega(t-t')} d\omega. \quad (55)$$

Upon applying standard residue calculus to Eq. (55), and considering the physically relevant condition $t > t'$, we arrive at the following expression:

$$\hat{G}_0(t, t') = -ie^{-i\hat{H}_0(t-t')} = -i\hat{U}_0(t, t') \quad (56)$$

This leads us to a significant conclusion:

$$\boxed{\hat{U}(t, t_0) = \hat{U}_0(t, t_0) - i \int_{t_0}^t \hat{U}_0(t, t') \hat{H}_I(t') \hat{U}(t', t_0) dt'} \quad (57)$$

This simple approach allow to derive what is called the *first Dyson equation* [6], simply and straightforwardly.

Second Dyson Equation

Establishing a *second Dyson equation* is less straightforward, as it presents a "time-reversed" perspective[7] compared to Eq. (57). To demonstrate this, consider:

$$\hat{H}_0 = \hat{H} - \hat{H}_I(t)$$

leading to:

$$i \frac{\partial}{\partial t} \hat{U}_0(t, t_0) = \hat{H}_0 \hat{U}(t, t_0) = (\hat{H} - \hat{H}_I) \hat{U}_0(t, t_0)$$

from which we can write:

$$(i \frac{\partial}{\partial t} - \hat{H}) \hat{U}_0(t, t_0) = -\hat{H}_I \hat{U}_0(t, t_0) \quad (58)$$

This equation mirrors Eq. (48), enabling us to formulate:

$$(i \frac{\partial}{\partial t} - \hat{H}(t)) \hat{G}_1(t, t') = \delta(t - t') \quad (59)$$

As before, by employing Green function theory, the solution is expressed as:

$$\hat{U}_0(t, t_0) = \hat{U}(t, t_0) - \int_{t_0}^t \hat{G}_1(t, t') \hat{H}_I(t') \hat{U}_0(t', t_0) dt'$$

or equivalently:

$$\hat{U}(t, t_0) = \hat{U}_0(t, t_0) + \int_{t_0}^t \hat{G}_1(t, t') \hat{H}_I(t') \hat{U}_0(t', t_0) dt' \quad (60)$$

where $\hat{U}$, now, serves as the homogeneous solution for Eq. (59). The solution for Eq. (59) is then:

$$\hat{G}_1(t, t') = -ie^{-i \int t'^t \hat{H}(t'') dt''} = -i\hat{U}(t, t') \quad (61)$$

Thus, the *Second Dyson equation* is derived:

$$\hat{U}(t, t_0) = \hat{U}_0(t, t_0) - i \int_{t_0}^t \hat{U}(t, t') \hat{H}_I(t') \hat{U}_0(t', t_0) dt' \quad (62)$$

Both Eqs. (57) and (62) offers a comprehensive method to describe the time evolution of any quantum state $|\psi\rangle$:

$$|\psi(t)\rangle = \hat{U}_0(t, t_0) |\psi(t_0)\rangle - i \int_{t_0}^t \hat{U}(t, t') \hat{H}_I(t') \hat{U}_0(t', t_0) |\psi(t_0)\rangle dt' \quad (63)$$

This result, which we have taken for granted in Chapters 1 and 2, and has been used as the starting point of strong field approximation, now has a formal justification.

.3 Propagators and Volkov wavepackets

To elucidate the practical use of propagator formalism, we address the free electron propagation problem under the influence of an external electromagnetic field. This scenario is commonly encountered when an electron is freed from its parent ion and propagates in space, as seen in processes like high-order harmonic generation (before recombination) or two-color interaction, both discussed in Chapter 2.

In the velocity gauge, the Hamiltonian for a free particle, $\hat{H}_F^{(v)}$ (denoted as $\hat{H}_F$ henceforth), is expressed as:

$$\hat{H}_F^{(v)} = \frac{1}{2}(\hat{\mathbf{p}} + \mathbf{A}(t))^2 \quad (64)$$

The goal is to find the quantum states that satisfy:

$$\hat{H}_F |\psi\rangle = i \frac{\partial}{\partial t} |\psi\rangle \quad (65)$$

This problem is efficiently solved using the propagator formalism, presented in the previous section. Introducing $\hat{U}_V(t, t_0)$ as the time evolution operator, which evolves an initial state $|\psi(t_0)\rangle$ at time t_0 into $|\psi(t)\rangle$, we have:

$$|\psi(t)\rangle = \hat{U}_V(t, t_0) |\psi(t_0)\rangle. \quad (66)$$

Hence, Eq. (65) can be rewritten as:

$$\hat{H}_F \hat{U}_V(t, t_0) |\psi(t_0)\rangle = i \frac{\partial}{\partial t} \hat{U}_V(t, t_0) |\psi(t_0)\rangle.$$

As discussed, the general solution is given by:

$$\begin{aligned} |\psi(t)\rangle &= e^{-i \int_{t_0}^t \frac{1}{2}(\hat{\mathbf{p}} + \mathbf{A})^2 dt'} |\psi(t_0)\rangle \\ \hat{U}_V &= e^{-i \int_{t_0}^t \frac{1}{2}(\hat{\mathbf{p}} + \mathbf{A})^2 dt'} \end{aligned}$$

We can generalize our solution by using the completeness of momentum space:

$$|\psi(t)\rangle = \int_{\mathcal{R}^3} \langle \mathbf{p} | \psi(t) \rangle | \mathbf{p} \rangle d^3 p, \quad (67)$$

where $\langle \mathbf{p} | \psi(t) \rangle$ is given by:

$$\langle \mathbf{p} | \psi(t) \rangle = \langle \mathbf{p} | e^{-i \int_{t_0}^t \frac{1}{2}(\hat{\mathbf{p}} + \mathbf{A}(t))^2 dt} |\psi(t_0)\rangle. \quad (68)$$

Hence,

$$\langle \mathbf{p} | e^{-i \int_{t_0}^t \frac{1}{2} (\hat{\mathbf{p}} + \mathbf{A}(t'))^2 dt'} = \langle \mathbf{p} | e^{-i \int_{t_0}^t \frac{1}{2} (\mathbf{p} + \mathbf{A}(t'))^2 dt'} \quad (69)$$

where now $\mathbf{p}$ is the eigenstate associated to $|\mathbf{p}\rangle$. From this result, we can define the semi-classical action S as follows:

$$S(t, t_0) = \int_{t_0}^t \frac{1}{2} (\mathbf{p} + \mathbf{A}(t'))^2 dt'. \quad (70)$$

This allows us to formulate a (almost) ready-to-use of the time evolution of a generic initial state $|\psi(t_0)\rangle$, influenced by an external electromagnetic field:

$$|\psi(t)\rangle = \int \langle \mathbf{p} | \psi(t_0) \rangle e^{-iS(t, t_0)} |\mathbf{p}\rangle d^3p. \quad (71)$$

This solution can be viewed as decomposing the initial state into a complete set of momentum eigenstates $|\mathbf{p}\rangle$, each modulated by a time-dependent weight. Alternatively, it can be seen as a decomposition into specific states, known as *Volkov states* [6, 7], each associated with time-independent coefficients:

$$|\Psi_{Volkov}(t)\rangle = e^{-iS(t, t_0)} |\mathbf{p}\rangle \quad (72)$$

hence,

$$|\psi(t)\rangle = \int \langle \mathbf{p} | \psi(t_0) \rangle |\Psi_{Volkov}(t)\rangle d^3p.$$

For practical use, we re-frame everything in the spatial domain (position space) by writing the wavefunction of Volkov states as

$$\Psi_{Volkov}(\mathbf{r}, t) = \langle \mathbf{r} | \Psi_{Volkov}(t) \rangle = \frac{1}{(2\pi)^{\frac{3}{2}}} e^{-iS(t, t_0)} e^{i\mathbf{p} \cdot \mathbf{r}}, \quad (73)$$

where we use the fact that $\langle \mathbf{r} | \mathbf{p} \rangle = (2\pi)^{-\frac{3}{2}} e^{i\mathbf{p} \cdot \mathbf{r}}$.

Thus, the general solution of Eq. (65) is:

$$\psi(\mathbf{r}, t) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int \phi(\mathbf{p}, t_0) e^{-iS(t, t_0)} e^{i\mathbf{p} \cdot \mathbf{r}} d^3p, \quad (74)$$

where $\phi(\mathbf{p}, t_0) = \langle \mathbf{p} | \psi(t_0) \rangle$ represents the initial momentum distribution of the electron at time t_0 .

The derivation could also have been performed in the *length gauge*, or by utilizing Eq. (28), where within the dipole approximation:

$$\chi^{(v)} = 0, \quad (75)$$

$$\chi^{(l)} = -\mathbf{r} \cdot \mathbf{A}_T, \quad (76)$$

yielding to:

$$\begin{aligned}\Psi_{Volkov}^{(v)}(\mathbf{r}, t) &= \frac{1}{(2\pi)^{\frac{3}{2}}} e^{-iS(t, t_0)} e^{i\mathbf{p} \cdot \mathbf{r}} \\ \Psi_{Volkov}^{(l)}(\mathbf{r}, t) &= \frac{1}{(2\pi)^{\frac{3}{2}}} e^{-iS(t, t_0)} e^{i(\mathbf{p} + \mathbf{A}(t)) \cdot \mathbf{r}}\end{aligned}$$

Useful trick with propagators

We note that, given t final instant of time, t_0 initial instant ($t > t_0$), $\hat{H}(t)$, generic time-dependent Hamiltonian, the complex conjugate of:

$$(|\Psi(t)\rangle)^\dagger = (\hat{U}(t, t_0) |\Psi(t_0)\rangle)^\dagger = (e^{-i \int_{t_0}^t \hat{H}(t') dt'})^\dagger |\Psi(t_0)\rangle^\dagger \quad (77)$$

is equal to:

$$\langle \Psi(t) | = \langle \Psi(t_0) | e^{i \int_{t_0}^t \hat{H}(t') dt'} = \langle \Psi(t_0) | \hat{U}^\dagger(t_0, t) \quad (78)$$

where, $\hat{U}^\dagger(t_0, t) = e^{i \int_{t_0}^t \hat{H} dt'} = e^{-i \int_t^{t_0} \hat{H} dt'} = \hat{U}(t, t_0)$ is the time reverse-operator. By exploiting the identity property of the propagator, we can rewrite everything as:

$$\langle \Psi(t_0) | = \langle \Psi(t) | e^{-i \int_{t_0}^t \hat{H}(t') dt'} = \langle \Psi(t) | \hat{U}(t, t_0) \quad (79)$$

or

$$\langle \Psi(t) | = \langle \Psi(t) | e^{-i \int_t^{t_0} \hat{H}(t') dt'} = \langle \Psi(t_0) | \hat{U}(t_0, t) \quad (80)$$

In other words, Eq. (79) and Eq. (80) can be seen as applying the time-forward operator on a certain $\langle \cdot |$ -state that reverse time.

Appedix B: Atomic units

In this dissertation, Atomic Units (a.u.) are predominantly utilized due to their effectiveness in simulations and their natural suitability for evaluating microscopic physical laws. Commonly, the following constants are set to unity in a.u.: the elementary positive charge $e = 1$ a.u., Planck's constant divided by 2π , $\hbar = 1$ a.u., the electron's mass $m_e = 1$ a.u., and the permittivity of free space, $4\pi\epsilon_0 = 1$ a.u. It's crucial to remember that the absence of dimensions in atomic units is a matter of convention, and one must avoid inappropriately mixing different basic units.

As elaborated in [6], at the microscopic level, the four fundamental SI quantities are time $[T]$, length $[L]$, charge $[C]$, and mass $[M]$. A connection between these SI units and atomic units is established to create a clear map between any choice of units. This enables the conversion of an arbitrary physical quantity from a.u. to S.I units and vice versa. The relationships are expressed as:

$$\begin{aligned}\hbar &= [M]^{a_{11}} [L]^{a_{12}} [T]^{a_{13}} [C]^{a_{14}} \\ m_e &= [M]^{a_{21}} [L]^{a_{22}} [T]^{a_{23}} [C]^{a_{24}} \\ e &= [M]^{a_{31}} [L]^{a_{32}} [T]^{a_{33}} [C]^{a_{34}} \\ 4\pi\epsilon_0 &= [M]^{a_{41}} [L]^{a_{42}} [T]^{a_{43}} [C]^{a_{44}}\end{aligned}$$

From basic Physics consideration on the nature of these constants, these relationships are represented by the matrix A :

$$A = \begin{pmatrix} 1 & 2 & -1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & -3 & 2 & 2 \end{pmatrix}$$

To derive the relationship between the four fundamental SI units and atomic units,

we use similar equations:

$$\begin{aligned}
[M] &= \hbar^{b_{11}} m_e^{b_{12}} e^{b_{13}} (4\pi\epsilon_0)^{b_{14}} \\
[L] &= \hbar^{b_{21}} m_e^{b_{22}} e^{b_{23}} (4\pi\epsilon_0)^{b_{24}} \\
[T] &= \hbar^{b_{31}} m_e^{b_{32}} e^{b_{33}} (4\pi\epsilon_0)^{b_{34}} \\
[C] &= \hbar^{b_{41}} m_e^{b_{42}} e^{b_{43}} (4\pi\epsilon_0)^{b_{44}}
\end{aligned}$$

For instance, evaluating time in atomic units using the A matrix, we find:

$$[T] = \hbar^3 m_e^{-1} (4\pi\epsilon_0)^2 e^{-4} \approx 24.189 : as.$$

This process can be applied to other units, leading to the matrix B :

$$B = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 2 & -1 & -2 & 1 \\ 3 & -1 & -4 & 2 \\ 0 & -0 & 1 & 0 \end{pmatrix}$$

A more comprehensive overlook on the units is resumed in the following table.

Name	Atomic units	SI value
action	$\hbar$	$1.054571817 \cdot 10^{-34} \text{ Js}$
charge	e	$1.602176634 \cdot 10^{-19} \text{ C}$
length	a_0	$5.29177210903 \cdot 10^{-11} \text{ m}$
mass	m_e	$9.1093837015 \cdot 10^{-31} \text{ kg}$
energy	$E_h = \frac{m_e e^4}{(4\pi\epsilon_0)^2 \hbar^2}$	$4.35971 \cdot 10^{-18} \text{ J (} 27.21 \text{ eV)}$
electric dipole moment	ea_0	$8.4783536255 \cdot 10^{-30} \text{ Cm}$
electric field	$E_h/(ea_0)$	$5.14220674763 \cdot 10^{11} \text{ Vm}^{-1}$
time	$\hbar/E_h$	$2.4188843265857 \cdot 10^{-17} \text{ s}$
velocity	$a_0 E_h/\hbar$	$2.18769126364 \cdot 10^6 \text{ ms}^{-1}$
peak intensity	$\frac{c\epsilon_0}{2} E_h^2$	$3.511 \cdot 10^{16} \frac{\text{W}}{\text{cm}^2}$