Introduction to attosecond time-delays in photoionization

J. M. Dahlström
Department of Physics, Stockholm University,
AlbaNova University Center, SE-10691 Stockholm, Sweden

A. L’Huillier
Department of Physics, Lund University,
P.O. Box 118, 22100 Lund, Sweden

A. Maquet
UPMC Université Paris 6, UMR 7614,
Laboratoire de Chimie Physique-Matière et Rayonnement,
11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
CNRS, UMR 7614, LCPMR, Paris, France

Abstract

This tutorial presents an introduction to the interaction of light and matter on the attosecond timescale. Our aim is to detail the theoretical description of ultra-short time-delays, and to relate these to the phase of extreme ultraviolet (XUV) light pulses and to the asymptotic phase-shifts of photoelectron wave packets. Special emphasis is laid on time-delay experiments, where attosecond XUV pulses are used to photoionize target atoms at well-defined times, followed by a probing process in real time by a phase-locked, infrared laser field. In this way, the laser field serves as a “clock” to monitor the ionization event, but the observable delays do not correspond directly to the delay associated with single-photon ionization. Instead, a significant part of the observed delay originates from a measurement induced process, which obscures the single-photon ionization dynamics. This artifact is traced back to a phase-shift of the above-threshold ionization transition matrix element, which we call the continuum–continuum phase. It arises due to the laser-stimulated transitions between Coulomb continuum states. As we shall show here, these measurement-induced effects can be separated from the single-photon ionization process, using analytical expressions of universal character, so that eventually the attosecond time-delays in photoionization can be accessed.
1 Introduction

Great advances in experimental physics are being made using attosecond pulses of extreme ultraviolet (XUV) radiation, where it is now possible to initiate, control and probe electron dynamics in atoms and molecules in real time. A natural and perhaps naive question then arises: Is it possible to use attosecond pulses to measure the time it takes for a photoelectron to be ionized? It is well-known from fundamental principles in quantum theory that time is not a direct observable quantity \[1\]. Here, our aim is to discuss what temporal aspects of photoionization can be measured in state-of-the-art experiments based on attosecond XUV pulses and phase-locked infrared (IR) probe fields. This tutorial serves as an introduction to the theoretical description of radiative processes taking place in extremely short time intervals, with durations comparable to the temporal response of outer-shell bound electrons within atoms or molecules. An interesting point is that the theoretical background provides a common framework for XUV pulses that propagate through dispersive media, and for non-relativistic photoelectron wave packets that escape from the atomic potential. We wish to stress the similarities and differences between these two types of wave packets and to discuss the associated light-matter interactions occurring on the attosecond timescale. To this end, we shall derive the way in which small perturbations in the medium affect the propagation of the light pulses and we will detail the present ways of probing photoionization of neutral
species in real time. In doing this, special attention must be given to the case of long-range Coulomb potentials, which are important for describing electron motion in photoionization. The theoretical methods used here span different disciplines ranging from ultra-fast optics and non-linear optics, to scattering theory, atomic physics and strong-field physics.

Outline of Tutorial

The content of this tutorial is divided into seven sections. In Sec. 1 we introduce unfamiliar readers to “attophysics” and we present a short overview of the high-order harmonic generation process which is used to generate attosecond XUV pulses. In Sec. 2 we review the role of the spectral phase for the propagation of XUV wave packets. Here, we use the so-called “group delay” to describe the coherent superposition of monochromatic waves in the time-domain. Similarly, in Sec. 3 we investigate the intrinsic phase of photoelectrons and the corresponding time-delay of electron wave packets with special attention to the long-range Coulomb potential. In Sec. 4 we perform time-dependent perturbation calculations for the creation and propagation of photoelectron wave packets generated by an attosecond XUV pulse. In Sec. 5 we review the influence of the laser-probe field by performing time-dependent perturbation calculations to second order in the interaction with the light fields. In Sec. 6 we discuss the state-of-the-art experimental efforts to measure attosecond time-delays in laser-assisted photoionization. Finally, in Section 7 we present our conclusions and outlook.

1.1 Overview of attosecond physics

This section provides an “ultra-short” overview of the historical development and of the key concepts in attosecond physics. High-order Harmonic Generation (HHG), Attosecond Pulse Trains (APT) and Single Attosecond Pulses (SAP) will be introduced. We refer the unfamiliar reader to Ref. [2, 3, 4, 5] for more comprehensive reviews of attosecond physics.

1.1.1 High-order harmonic generation

The work on attosecond light pulses stems from a process discovered in the late 1980s called HHG [6, 7]. It was found that a broad plateau in the XUV range, containing a comb of almost equally strong, odd harmonics, could be produced by focusing an intense ultra-short IR laser pulse into a target of noble gas. A sketch of a typical HHG experiment is shown in Fig. 1(a), where first an intense IR field interacts with a target of Ar-gas to generate high-order harmonics, then these harmonics propagate to a different chamber where they photoionize Ar-atoms so that photoelectrons are emitted.
Figure 1: A typical HHG experiment: (a) A fraction of the IR laser field is converted to XUV through HHG. The XUV field is then filtered out and used to photoionize the detection gas. (b) A representative photoelectron spectra (full) and XUV photon spectra (dotted) from an HHG experiment using Ar-atoms and Al-filter.

With a Titanium:Sapphire laser system (photon energy of $\hbar \omega = 1.55 \text{ eV}$, corresponding to a near-IR laser wavelength of $\lambda = 800 \text{ nm}$) using chirped-pulse amplification [8], the typical laser intensity used for HHG is $I_L \sim 10^{14} \text{ W/cm}^2$. Harmonic conversion efficiencies as high as $10^{-6}$ and photon energies in the soft x-ray range have been obtained [9, 10, 11, 12, 13, 14]. Neither the broad comb of high-order harmonics, nor their high conversion efficiency can be explained using standard theoretical tools of non-linear optics, where the laser field is treated as a perturbation [15]. In the perturbative formalism, an increase in harmonic order $N$ is always accompanied by a strong reduction in conversion efficiency as is evident from the well-known non-linear conversion formula: $I_N \propto I_N^L$, where $I_L \ll 1$ is the intensity of the laser in a scaled set of variables. As an example, the relevant intensity scale for laser-atom interactions is the so-called atomic unit of intensity: $I_{\text{at}} = 3.5 \times 10^{16} \text{ W/cm}^2$. As mentioned above, optimal conditions to observe HHG processes are obtained with Titanium: Sapphire laser devices operated at $I_L \approx 10^{14} \text{ W/cm}^2$, so that, in scaled units $I_L \leq 10^{-2}$. In direct contrast with such perturbative behaviour, the harmonic comb from HHG may contain many harmonic orders of comparable intensity, $I_N \approx I_N^L \ll I_L$, as seen in Fig. 1(b).
A cut-off law for the maximal photon energy in the HHG plateau was found numerically to be

\[ \hbar \Omega_{\text{max}} \approx I_p + 3U_p, \]  

where \( I_p \) is the ionization potential of the atom, and

\[ U_p = \frac{e^2 E_L^2}{4m\omega^2} = \frac{e^2 \lambda^3 I_L}{8\pi^2 \epsilon_0 c^3 m}, \]  

is the so-called ponderomotive energy of the electron in the laser field [17]. The latter energy is associated with the average oscillatory (quiver) motion of a free electron driven by a single-frequency field. Using Eq. (1) and (2) in the limit \( U_p \gg I_p \), the cut-off increases quadratically for longer laser wavelengths, \( \hbar \Omega_{\text{max}} \propto \lambda^2 \), and linearly with the laser intensity, \( \hbar \Omega_{\text{max}} \propto I_L \). This scaling has been used to increase the harmonic photon energies into the keV regime using laser fields with longer wavelengths (mid-IR wavelengths) [18, 19, 20, 21].

Although HHG spectra from simple systems could be reproduced by numerical simulations based on the resolution of the Time-Dependent Schrödinger Equation (TDSE) [16], a convenient scenario to explain the mechanism of the process is based on the so-called three-step model [22]. The three steps are illustrated in Fig. 2.

\[ F = ma \]

Figure 2: The three-step model for HHG: (a) When the electric field of the laser is large, the electron can (1) tunnel through the Coulomb barrier into the continuum. (b) The electron wave packet will then (2) accelerate on almost classical trajectories in the laser field. Finally, a fraction of the electron wave packet may be driven back to the atom and (3) recombine, emitting a high-order harmonic photon.

A more detailed quantum mechanical theory for HHG was published by Lewenstein and co-workers in 1994 [23], showing that the three-step model could be
derived from the Schrödinger equation using the Strong Field Approximation (SFA). In this way, a more exact cut-off law was derived analytically,

\[ h\Omega_{\text{max}} = 1.3I_p + 3.2U_p, \]  

(3)

corresponding to electrons with quasi-classical (complex) trajectories \[ \Omega \approx \frac{3.1}{2}. \] These trajectories are closely-related to Feynman’s path integral approach to quantum mechanics \[ \Omega \approx \frac{3.1}{2}. \] This semi-classical model explained why the harmonics were of comparable strength, but it also revealed that several semi-classical trajectories contribute to the emission of each harmonic. This finding implied that each harmonic was emitted in two bursts per half-cycle of the laser, thus leading to a complicated temporal structure of the harmonic emission. It has been shown, as reviewed in Ref. \[ \Omega \approx \frac{3.1}{2}. \], that the problem of these multiple emission times can be circumvented experimentally thanks to the phase-matching properties of the macroscopic medium, leading to a “selection” of the emission from the shortest family of electron trajectories.

Also, it was soon understood that such frequency combs of high-order harmonics would correspond to light with pulse durations on the attosecond timescale, i.e. shorter than any light pulses ever produced, under some restrictive conditions regarding their relative phases \[ \Omega \approx \frac{3.1}{2}. \]. The generation of such “attosecond pulses” is a challenging task especially because the experimentalists have to find a way of manipulating the relative phase of the harmonics over the large spectral bandwidth of the comb \[ \Omega \approx \frac{3.1}{2}. \]. Another major challenge was to devise a scheme to measure the duration of the pulses. This was because existing methods used in traditional ultra-fast optics could not be directly applied due to the short wavelength and relatively low intensity of the harmonics.

1.1.2 Attosecond pulses

In 2001, more than a decade after the first HHG process was observed, the first Attosecond Pulse Trains (APT) were characterized using a scheme called RABITT (Resolution of Attosecond Beating By Interfering Two-photon transitions) \[ \Omega \approx \frac{3.1}{2}. \]. As measured in a set of experiments, the attosecond pulse duration was \( \sim 250 \) as \( = 250 \times 10^{-18} \) s, corresponding to \( \sim 1/10 \) of the laser period, and to \( \sim 1/100 \) of the laser pulse duration used for HHG. Two attosecond pulses were produced per oscillation of the laser field, resulting in a train of \( \sim 30 \) pulses in the total APT. A typical fraction of an APT is depicted in Fig. 3.
Figure 3: Attosecond pulse train: The attosecond pulse (shaded grey) duration is a fraction of the fundamental laser period (red dashed curve). The pulse separation is a half laser period and the sign of the attosecond electric field (heavy black curve) changes from pulse to pulse.

Making the IR pulse shorter leads naturally to fewer attosecond pulses. It was soon demonstrated that a Single Attosecond Pulse (SAP) could be generated using a few-cycle IR pulse, \( \sim 5 \) fs [34]. The basic properties of the SAP can be determined using the attosecond-streak camera [35], while more complete characterization requires the use of the sophisticated FROG–CRAB scheme (Frequency Resolved Optical Gating – Complete Reconstruction of Attosecond Bursts) [36]. For such short IR pulses, the Carrier Envelope Phase (CEP) is an important parameter that must be controlled. For instance, the generation of a SAP can be changed into the generation of two attosecond pulses by carefully tuning the CEP of the laser field [37, 38]. One of the most impressive applications of SAP was the “direct measurement of light waves” [39], where the SAP was used to map out the oscillating vector potential of a few-cycle optical laser pulse. Another useful way of controlling the HHG process is called “polarization gating” [40, 41, 42, 43], which relies on the dependence of laser-polarization for the yield of HHG. In simple terms, linear polarization implies that the gate is open because attosecond pulses are being produced, while elliptical polarization suppresses the HHG and closes the gate.

From a more fundamental standpoint, attosecond pulses are interesting because they are shorter than any pulses created by conventional optical lasers. Physically, we understand this because the duration of a light pulse can not be shorter than its own period. Optical lasers, corresponding to visible and IR wavelengths, have a period that is longer than a femtosecond, leading to the so-called femtosecond barrier for ultra-short pulses. The power needed to drive a laser scales strongly with the photon frequency, \( P \propto \omega^5 \), which effectively prevents the conventional laser scheme from going beyond optical wavelengths [19]. More formally, a pulse intensity envelope has a minimal duration proportional to the inverse of the supporting coherent bandwidth,

\[
\tau > \frac{C}{\Delta \omega} \approx \frac{C \lambda^2}{2\pi c \Delta \lambda}, \tag{4}
\]
where $\Delta \omega$ (and $\Delta \lambda \ll \lambda$) is the intensity bandwidth of the light. In the case of a Gaussian pulse, $C = 4 \ln 2$ for the intensity envelope. The minimal pulse duration, called the Fourier-limited pulse duration, occurs when all the spectral components are compressed, \textit{i.e.} when the spectral phase is perfectly linear. The attosecond pulses produced through HHG can overcome the femtosecond barrier not only because they have a much shorter wavelength than optical light, but also because they have a broad coherent bandwidth. It is interesting to compare the bandwidth of the laser used for HHG with the bandwidth of the attosecond pulses being generated. An IR laser pulse used for generation of an APT has a typical duration of 30 fs and a bandwidth of 60 meV; while the corresponding attosecond pulses are 100 as with a bandwidth of 15 eV. During the HHG process the coherent bandwidth is increased by a factor of 250 from laser to high-order harmonics.

Attosecond pulses can be used to ionize atoms and molecules at extremely well-defined times, but how do the resulting photoelectron wave packets and holes behave after the ionization event? How can the attosecond pulses be used to obtain temporal information about physical processes occurring on the atomic timescale? Using attosecond pulses to ionize target atoms or molecules does not by itself provide any high-resolution temporal information! When the photoelectrons are collected in an experiment, we can only determine the value of the momentum (or energy) they have gained in the course of the process, but not \textit{how} or \textit{when} it was acquired. This implies that the temporal ionization events must be synchronized and probed with the help of an external “clock” that “ticks” itself on the attosecond timescale. The typical period of light in the optical regime is on the femtosecond timescale, but one can argue that its variation occurs in the sub-femtosecond regime, which then justifies its common usage as a probe in attosecond photoionization experiments. In this way, it is possible to use a fairly long laser pulse, say tens of femtoseconds, to monitor attosecond photoionization events. Clearly, it is important that the probe-field is \textit{phase-locked} with the attosecond pulses, a requirement which is easily satisfied in HHG experiments by using fractions of the \textit{same} laser pulse for both creating the attosecond pulses and for probing the photoionization process. Using attosecond pulses with phase-locked laser probes, has led to a range of experiments where time-delays between photoelectrons from different configurations and systems have been measured \cite{41, 45, 46}. Then, the natural question that emerges is whether or not such attosecond experiments yield direct access to the delay in photoemission, \textit{i.e.} to the time it takes for an electron to photoionize, or if the observed delays should be interpreted in a different way? Before answering these questions, we briefly review different pump-probe schemes that have been used to experimentally study light–matter interactions in real time.

1.2 Pump–probe schemes for ultra-fast measurements

In this tutorial, we provide a theoretical background for the temporal aspects of photoionization. The attosecond pulse structure is shorter than the response time of any detector or electronic device, but it is possible to obtain temporal
information about attosecond photoionization indirectly by investigating coherent cross-correlation photoelectron spectrograms between the attosecond pulse and a weak IR laser probe. In Fig. 4 we present three different kinds of cross-correlation techniques.

![Pump-probe schemes](image)

Figure 4: Pump-probe schemes: (a) Traditional pump–probe experiment with two pulses separated in time by \( \tau \). (b) Simultaneous pump–probe experiment between a SAP and a few-cycle IR field. (c) Simultaneous pump–probe experiment between an APT and a monochromatic IR field. The narrow purple area represents the attosecond XUV pulse envelope and the broader red area represents the one of the probing laser pulse, while the dotted red lines indicate the corresponding E-field.

### 1.2.1 Traditional pump–probe experiment

A typical pump–probe scheme is illustrated in Fig. 4 (a). First, a pump pulse is used to excite the system at time \( t = 0 \). A part of the quantum mechanical wave function is then pumped from the initial state to an excited wave packet: \( \Psi^{(0)}(0) \rightarrow \Psi^{(1)}(0) \). The system can then evolve in a field free environment until time \( t = \tau \), when the probe pulse interacts with the excited wave packet, thus changing its state: \( \Psi^{(1)}(\tau) \rightarrow \Psi^{(2)}(\tau) \). In experiments, the modification of the wave packet leads to the change of the observable quantities as a function of the delay between the pump and the probe pulses. Temporal information about the field-free propagation of the system, e.g. a molecular vibration, can then be extracted in real time by repeating the experiment systematically for different delays of the probe pulse. In this way, the intermediate steps in chemical reactions, the so-called “transition states”, have been investigated in the framework
of Zewail’s femtochemistry. Clearly, the intuitive interpretation of these experiments is limited by the respective pulse durations. Using few-cycle optical-laser fields to pump and probe the system is adequate to study nuclear motion in molecular systems, typically occurring on the femtosecond timescale. Coherent, attosecond XUV pump–probe experiments, where attosecond pulses are used for both pumping and probing, hold promise of observing the electron dynamics on the attosecond timescale, but they are difficult to implement experimentally due to the low probability for absorbing two photons in the XUV range, where we assume that at least one photon must be absorbed from both the pump and the probe for a meaningful signal. We refer the reader to Ref. [51] (and the references therein) for state-of-the-art experimental efforts on XUV-pump and XUV-probe experiments bordering the attosecond timescale. A different kind of pump-probe experiments has been carried out using a SAP as pump and a few-cycle laser pulse as probe, see for instance Ref. [52], where the Fourier transform of the delay-dependent spectrogram yields quantum beats, but also interference between direct and indirect pathways in the ionization.

1.2.2 Simultaneous pump–probe experiment using SAP: “Streaking”

A more commonly used attosecond pump–probe configuration is illustrated in Fig. 3 (b), where the pump and probe pulses overlap in time. In this situation it is not primarily the field-free system that is of interest, but rather the temporal characterization of the pulses or the evolution of the system in the presence of the two fields. The pump probe is an attosecond XUV pulse, while the probe pulse is a longer (few femtosecond) IR-laser pulse. Strictly speaking, this is a laser-assisted photoionization process, where the system is simultaneously pumped and probed. Sub-femtosecond temporal information can be gained by repeating the experiment at different subcycle delays between the attosecond pump pulse and the laser field oscillation of the probe pulse. Clearly, it is essential that the two pulses are phase-locked and that the delay can be controlled with sub-femtosecond precision.

Under these conditions, the system can absorb energy simultaneously from the two fields i.e. while it absorbs one XUV photon, it is “dressed” by the relatively intense IR probe field. Accordingly, a non-perturbative approach is needed to account for the effect of the probe. A simplified theory for the influence of the probe pulse on the photoelectrons is given by the streak camera formalism [35]. This simplified interpretation of the photoelectron distribution relies on the use of the SFA, which is equivalent to assuming that the photoelectron feels the instantaneous laser field while the Coulomb potential of the ionic core is neglected. According to the SFA, the streaked electron momentum distribution is then shifted as

\[ \vec{p}_f(\tau) = \vec{p}_0 - e\vec{A}(\tau), \]

where \( \vec{p}_0 \) is the unshifted, probe-free momentum; \( e > 0 \) is the elementary charge and \( \vec{A}(\tau) \) is the probe-field vector potential at the time of ionization. This con-
cept of “instantaneous streaking” provides a simple map from time to momen-
tum of the streaked electrons, which is valid assuming that the electron is free
shortly after the ionization event, i.e. that it either escapes from a short-range
binding potential or is ejected with a high velocity. In practice, the electron
is not completely free after the ionization event due to the remaining Coulomb
potential from the ion. Smirnova and co-workers found that the simultaneous
action of the long-range Coulomb potential and the probing laser field can result
in a small shift of the streaking process [53], i.e. an uncertainty on the absolute
delay in the experiment. Until recently [45], these delays were considered too
small to be accessible in streaking experiments.

1.2.3 Instantaneous pump–probe experiment using APT: “RABITT”

In Fig. 4 (c), a train of “identical” attosecond pump pulses are probed with
a monochromatic IR-field. This scheme is often referred to as the RABITT
method [31, 32, 33]. Provided that the probe pulses are weak and that the fields
are repeated periodically for many cycles, this scheme can provide equivalent
information as the streak-camera method described above [Fig. 4 (b)]. We will
discuss this equivalence in more detail in Sec. 5 in terms of photoelectron wave
packets, and we suggest that the interested reader should consult Ref. [54] for
a complete derivation in lowest-order perturbation theory. Higher-order effects
in the probe field have been considered using the “soft-photon approximation”
[55], but the high-level of accuracy that is required for attophysics remains a
challenge to theory, especially so in the non-perturbative regime.

The shared periodicity of the APT and the probe field implies that the pho-
toelectrons will appear on distinct energies corresponding the discrete numbers
of absorbed photons. In Fig. 5 we display a typical experimental photoelectron
spectrogram produced by laser-assisted APT ionizing Ar gas.
The advantages of the periodic time-structure of APT are rather practical: First, it is less demanding experimentally to produce APT and multi-cycle probe-fields, than SAP and few-cycle probe fields. Second, the probe field can be weaker than for streaking, thereby, causing less side-effects on the system, e.g. induced polarization of the core or ionization. Third, the signal is read out on zero-background, i.e. in energetic regions where no initial photoelectrons appear. Finally, a monochromatic probe field simplifies the analysis because it leads to less spectral convolutions in the experimental signal, as we shall discuss further in Sec. 5.

In this setup, there is a phase-difference associated with the instantaneous probing by the laser field, which can be traced back to the phase-shift of the relevant two-photon matrix elements. The probability of the sideband peak modulates as

$$S_{2q} = \alpha + \beta \cos[2\omega\tau - \Delta\phi_{2q} - \Delta\theta_{2q}],$$

where $\Delta\phi_{2q} = (\phi_{2q+1} - \phi_{2q-1})$ is the phase difference between the consecutive harmonics $(2q+1)\omega$ and $(2q-1)\omega$; and $\Delta\theta_{2q}$ is an intrinsic atomic quantity, the so-called “atomic phase”, associated to the difference of the phases of the transition amplitudes associated to the distinct quantum paths leading to the sideband [32, 33]. The former phase is related to the arrival time of the attosecond pulses: $\tau_{\phi} = \Delta\phi_{2q}/(2\omega)$, for frequencies $\Omega \approx 2q\omega$. The atomic phases were

Figure 5: *RABITT method*: (a) Photoelectron spectrogram over photon energy and delay between the APT and the IR field. The offset in the modulation of the sidebands contains information about the attosecond pulses and the ionization process. (b) Schematic energy diagram over the quantum paths leading to the same final energy in sideband (SB) $2q$. The experimental data was gathered for Ref. [56].
studied in detail by Toma and Muller already in 2002, using lowest-order perturbation theory, for photoionization from the $3p$ state in Argon [57]. Further numerical work was performed by Mauritsson, Gaarde and Schafer using single-active electron (SAE) effective potentials for Helium, Neon and Argon [58]. The two latter numerical calculations were made with the intention of making calibration curves for attosecond characterization tools such as RABITT. Our aim in this tutorial is to discuss the origin of this atomic phase in detail. We will identify its fundamental physical components in terms of time-delays and we will relate it to the above-mentioned streaking delays.

2 Attosecond pulses of light

It is well-known that short light pulses can be described as wave packets, i.e. as coherent superpositions of monochromatic light waves [59]. The propagation of such wave packets can then be understood in terms of the phase-shifts of the individual monochromatic waves, which will be discussed in Sec. 2.1. An attosecond XUV pulse can be strongly stretched in time by the propagation through a dispersive medium, but conversely, it is also possible to compress a stretched pulse using a medium with negative (anomalous) dispersion. A useful theoretical tool adapted to describe these phenomena is the so-called Stationary Phase Approximation (SPA), which is introduced in Sec. 2.2 and applied to the propagation of attosecond pulses. As we will show later, it applies equally well to the propagation of photoelectron wave packets.

We start our analysis of attosecond XUV pulses from the Maxwell equations in a dielectric medium [15, 59], and recast the wave equation into a time-independent form by exploiting the orthogonality of the Fourier integral expansions of the time-dependent fields

$$\nabla^2 \tilde{E} + \frac{\omega^2}{c^2} \tilde{E} = -\frac{1}{\epsilon_0} \frac{\omega^2}{c^2} \tilde{P} - \frac{1}{\epsilon_0} \nabla (\nabla \cdot \tilde{P}),$$  \hspace{1cm} (7)

where the electric field is expanded as a superposition of monochromatic waves

$$\tilde{E}(t, \vec{r}) = \frac{1}{2\pi} \int d\omega \tilde{E}(\omega, \vec{r}) e^{-i\omega t},$$  \hspace{1cm} (8)

and the polarization is given by

$$\tilde{P}(t, \vec{r}) = \frac{1}{2\pi} \int d\omega \tilde{P}(\omega, \vec{r}) e^{-i\omega t}.$$  \hspace{1cm} (9)

where the fields in space–frequency are written without a tilde: $\tilde{E}(\omega, \vec{r})$. Finding solutions to Eq. (7) requires knowledge of the polarization terms, $\tilde{P}(\omega, \vec{r})$. The polarization induced by a weak attosecond XUV pulse in an isotropic medium can be approximated by the linear response:

$$\tilde{P}(\omega, \vec{r}) = \epsilon_0 \chi^{(1)}(\omega, \vec{r}) \tilde{E}(\omega, \vec{r}),$$  \hspace{1cm} (10)
where the linear susceptibility, $\chi^{(1)}(\omega, \vec{r})$, may vary in space due to changing density or composition of the medium. Strictly speaking, the medium may exhibit a more complicated evolution in time, e.g. due to ionization of the species constituting the medium or due to non-linear polarization, but we will not consider the latter effects here \cite{15, 60}, due to the fact that the interaction between pulses with moderate intensity in the XUV range and matter are typically perturbative. We mention, however, that such contribution may become important when studying the propagation of intense XUV or X-ray radiation pulses, such as the ones generated by XFEL facilities, with peak intensities well above the atomic unit of intensity, i.e. in the range beyond $10^{16}$ W/cm$^2$.

2.1 Phase propagation of light in the linear regime

In order to describe the propagation of linearly polarized, attosecond light pulses in a medium, we insert the following ansatz: $\hat{\mathbf{E}}(\omega, \vec{r}) \propto \exp\{i\phi(\omega, x)\} \hat{z}$, into Eq. (7) to obtain a differential equation for the phase of monochromatic waves:

$$i \frac{\partial^2 \phi}{\partial x^2} - \left(\frac{\partial \phi}{\partial x}\right)^2 + \frac{\omega^2}{c^2} = -\frac{\omega^2}{c^2} \chi^{(1)}.$$

(11)

For slow variations of the optical properties in material, we assume $|\partial^2 \phi/\partial x^2| \ll |\partial \phi/\partial x|^2$, which leads to a simpler differential equation:

$$\frac{\partial \phi}{\partial x} = \frac{\omega}{c} \sqrt{1 + \chi^{(1)}}.$$

(12)

The phase of the electric field can be directly integrated as

$$\phi(\omega, x) = \frac{\omega}{c} \int_{-\infty}^{x} dx' \sqrt{1 + \chi^{(1)}(x')} \equiv \frac{\omega}{c} \int_{-\infty}^{x} dx' \ n(x'),$$

(13)

where $n(x)$ is the local refractive index of the medium. The asymptotic phase-shift obtained after propagation through the material can be written as

$$\delta(\omega) = \lim_{x \to \infty} \frac{\omega}{c} \int_{-\infty}^{x} dx' \ [n(x') - 1],$$

(14)

which will have a finite value assuming a finite material surrounded by free space, e.g. that $n(x) = 1$ for large enough $|x|$. Thus, a frequency-independent refractive index leads to a linear phase-shift in frequency. This linear phase-shift causes a simple time-delay, $\tau = \delta/\omega$, of the attosecond pulse in Eq. (8),

$$\hat{\mathbf{E}}_{\text{free}}(t - \tau, x) = \frac{1}{2\pi} \int d\omega \ \mathbf{E}_{\text{free}}(\omega, x)e^{-i\omega t} \exp[i\omega \tau],$$

(15)

compared to free-space propagation, corresponding to the undistorted waves $E_{\text{free}}(\omega, x)$. Eq. (15) is a direct application of the well-known shift-theorem.
of Fourier transforms. Furthermore, if the medium is absorbing, the asymptotic phase will be a complex quantity, with its real part leading to the actual phase-shift and its imaginary part leading to an exponential reduction of the amplitude, $\exp[i\delta] = \exp[i\Re(\delta)] \exp[-\Im(\delta)]$.

In order to illustrate the shift of the wave packet, we compute the asymptotic phase acquired by an attosecond pulse passing through a material of length, $L$, with a constant refractive index,

$$\delta = \frac{\omega}{c} [n - 1]L = \frac{2\pi}{\lambda} [n - 1]L \approx \frac{\omega}{2c} \chi^{(1)}L,$$

(16)

where $\lambda = 2\pi c/\omega$ is the wavelength of the light wave in vacuum, and where we assumed that the linear susceptibility is small. The corresponding delay of the pulse is

$$\tau = \frac{[n - 1]L}{c} \approx \frac{\chi^{(1)}L}{2c},$$

(17)

where we find an intuitive linear scaling with both the length on the material and with the change in refractive index. [59].

### 2.1.1 Dispersion and group delays

So far we have assumed that the linear response is independent of the frequency of the light. This is an adequate approximation for narrow-bandwidth laser pulses, but it is not a good approximation for attosecond pulses that have a large spectral bandwidth [60]. In a more realistic model, the material will be dispersive, i.e. the refractive index will be frequency-dependent, $n(\omega, x)$ [61, 62, 63]. After passing such a material, the asymptotic (spectral) phase, $\delta(\omega)$, may exhibit a non-linear frequency dependence, which implies that the wave packet in the time domain,

$$\hat{E}(t, x) = \frac{1}{2\pi} \int d\omega \underbrace{E_{\text{free}}(\omega, x)e^{-i\omega t}}_{\text{Free propagation}} \overbrace{\exp[i\delta(\omega)]}^{\text{Phase function}},$$

(18)

may be shifted and deformed with respect to the free propagation. It is convenient to expand the spectral phase in a Taylor series [59],

$$\delta(\omega) = \delta(\omega_0) + \sum_{n=1}^{\infty} \frac{1}{n!} \frac{\partial^n \delta}{\partial \omega^n} \bigg|_{\omega_0} (\omega - \omega_0)^n,$$

(19)

around the central frequency of the pulse, $\omega_0$. In many practical cases it is sufficient to consider the first few terms in this expansion. Note that we have already seen that the zero-order term determines the overall phase of the pulse, and that the first order term determines the delay of the pulse. In the optical regime, most materials have a positive (normal) dispersion, which means that the refractive index increases as a function of frequency. This implies longer delays for higher frequency pulses passing through the same medium. Close to resonances or close to the ionization threshold of a material, the refractive index
may have a negative (anomalous) dispersion. The Group Delay (GD) is defined as
\[ \tau_{GD}(\omega) = \frac{\partial \delta}{\partial \omega}, \] (20)
and it represents a direct generalization of the shift theorem in Eq. (15), stating that the derivative of the spectral phase at any frequency \( \omega \) corresponds to a delay in the propagation of the components of the wave packet in that spectral region. The GD is a rather abstract concept, but a useful interpretation is that it can be related to the time when the coherent superposition of all wave packets in the neighbourhood of \( \omega \) is constructive. The GD is not equal to the time when the instantaneous temporal frequency, \( \frac{\partial}{\partial t} \arg[\tilde{E}(t)] \), equals \( \omega \) for a wave packet in general. However, we will show in Sec. 2.2 that the GD does equal the time of this instantaneous frequency for wave packets that are stretched in the time domain.

In order to illustrate the GD concept, we now consider an XUV wave packet after travelling through a plasma of length \( L \), where
\[ n_p(\omega) = \sqrt{1 - \left(\frac{\omega_p}{\omega}\right)^2} \approx 1 - \frac{1}{2} \left(\frac{\omega_p}{\omega}\right)^2, \] (21)
is the refractive index of the plasma, \( \omega_p = \sqrt{Ne^2/(\varepsilon_0 m)} \), is the plasma frequency, and \( N \) the concentration of free electrons in the plasma. Using Eq. (16), the asymptotic phase becomes negative
\[ \delta_p(\omega) = \frac{\omega}{c} [n_p(\omega) - 1] L \approx - \frac{1}{2} \frac{\omega_p^2 L}{c \omega}, \] (22)
which implies that the phase-velocity, \( v_{phase} = c/n(\omega, x) \), of the monochromatic field is faster than \( c \) (superluminal), because the local refractive index is smaller than one! The corresponding GD is, however, positive
\[ \tau_{GD} = \frac{\partial \delta_p}{\partial \omega} \approx \frac{1}{2} \frac{\omega_p^2 L}{c \omega^2}, \] (23)
which shows that any light pulse is delayed by the plasma, and that it travels at a speed less than \( c \). These effects prove to be practical for phase-matching of nonlinear processes, where control of the superluminal phase velocity is achieved by simply increasing or decreasing the intensity of the laser field. This is because it indirectly alters the density of the plasma due to a changing ionization rate, which affects in turn the electron density in the plasma.

### 2.1.2 Attosecond pulse trains

Our discussion of delays is very general and it clearly applies to the propagation of both SAP and APT. APT arise naturally from the HHG process when the driving laser field is many periods long. The train contains two identical attosecond pulses per period of the fundamental field, with electric fields having opposite signs. In this context, uncompensated dispersion will lead to a
temporal overlap and interference between consecutive attosecond pulses in the APT, when the individual pulse duration increases beyond a half-period of the fundamental laser field. An ideal APT can be written as a Fourier sum, i.e. as a discrete version of Eq. (8), over all high-order harmonics

\[
\tilde{E}(t) = \sum_q |E_{2q+1}| \exp \left[ i \delta_{2q+1} - i(2q + 1) \omega t \right],
\]

(24)

where \(2q + 1\) labels the odd harmonics that are generated from HHG. We write “ideal” to indicate that the APT in Eq. (24) corresponds to an infinite number of pulses in the time-domain, while an actual APT will have a finite duration comparable to that of the fundamental IR laser pulse [65, 66]. A short APT is likely to exhibit strong pulse-to-pulse variations. The subcycle behaviour of the ideal APT can, however, be understood as an average subcycle pulse structure in a long APT composed of many attosecond pulses.

2.1.3 Compression of attosecond pulses using metallic foils

As a general rule, attosecond pulses are generated with a positive intrinsic chirp from the HHG process [24]. However, they can be compressed in time using thin metallic foils in the setup depicted in Fig. 1 (a) [67, 68, 69]. An example of such XUV pulse compression is shown in Fig. 6, where the experimental data corresponds to propagation through a 400 nm thin Al-foil.
Figure 6: Attosecond pulse compression: (a) Attosecond pulses generated in Ar before (grey curve) and after (black curve) passing through a 400 nm Al-foil. In addition to a delay of the pulse of $\sim 250$ as, the pulse shape changes due to the foil. (b) The uncompressed pulse is 180 as and it is asymmetric with small post pulses. (c) After the foil, the compressed pulse is 160 as and more symmetric. The CEP has been set to be “cos-type” and the IR laser field (dashed curve) is plotted for comparison. Amplitude effects due to the foil are neglected for simplicity.

The Al-foil provides negative dispersion in the low-energy part of the transmission window, while the high-energy part provides positive dispersion. In experiments, this property of Al-foils is used to generate close to Fourier-limited attosecond pulses by compensating for the intrinsic positive chirp of the HHG process by the negative dispersion provided by the low-energy part of the metallic transmission window. Notice the structure of the APT, with two pulses per period of the fundamental laser field. We mention again that the electric field of the two adjacent pulses have opposite phases, i.e. that they are $\pi$-shifted.

2.2 Stationary Phase Approximation

The SPA is an essential theoretical tool in attophysics because it can be used to evaluate integrals with complex valued integrands, such as the ones encountered when computing time-frequency Fourier transforms. It has proven itself especially successful for understanding the HHG process [23, 24], and it remains a useful tool for gaining better understanding of strong field dynamics, see for instance Ref. [70, 71, 72]. In the next subsections: Sec. 2.2.3 and 2.2.4, we will apply the SPA to evaluate XUV wave packets. Further on, in Sec. 4.4, we will apply the SPA to the propagation of electron wave packets ionized by attosecond pulses.

In simple terms, the SPA is related to the well-known integral of a Gaussian [73],

$$\int_{-\infty}^{\infty} d\omega \exp \left[ -\beta \omega^2 \right] = \sqrt{\frac{\pi}{\beta}},$$

which has a finite value provided that $\beta > 0$. As an example, we plot the integrand and integral for $\beta = 1$ in Fig. 7(a) and (b) respectively. The integral value in (b) approaches $\sqrt{\pi} \approx 1.7725$ as expected from Eq. (25).
Figure 7: Gaussian integrands and integrals: (a) A real Gaussian function ($\beta = 1$). (b) The real Gaussian integral equals $\sqrt{\pi} \approx 1.7725$. (c) A complex Gaussian function ($\beta = -i$). Notice the fast complex oscillations for large values of $|\omega|$. (d) The complex Gaussian integral equals $\sqrt{\pi} \exp[i\pi/4]$.

2.2.1 Method of steepest descent

In more detail, the SPA belongs to a class of techniques of wide use to compute integrals with integrands containing the exponential of a complex analytical function, $f(z) = u(x, y) + iv(x, y)$, with $z = x + iy$. It is closely related to the so-called steepest descent method which deals with integrals of the following form [73]:

$$K = \oint_C dz \exp \left[ f(z) \right],$$

(26)

where the contour $C$ is chosen so that the ends of the path do not contribute significantly. In the vicinity of a complex saddle-point $z_0$, where $f'(z_0) = 0$, the complex function can be expanded as

$$f(z) \approx f(z_0) + \frac{1}{2}(z - z_0)^2 f''(z_0).$$

(27)

Inserting the expanded function into the exponential yields the approximate integral

$$K \approx \oint_C dz \exp \left[ f(z_0) + \frac{1}{2}(z - z_0)^2 f''(z_0) \right],$$

(28)
where the zeroth-order, \( f(z_0) \), and the second-order, \( f''(z_0) \), coefficients are complex. In order to evaluate this integral, we parametrize the contour: \( z(\rho) = z_0 + \rho e^{i\varphi} \), with \( \rho \) being a real parameter and \( \varphi \) being the angle at which the contour crosses the saddle-point at \( z_0 \) in the complex plane. After this change of variable we get

\[
K \approx \exp \left[ f(z_0) + i\varphi \right] \times \int_{-\infty}^{\infty} d\rho \exp \left[ \frac{\rho^2}{2} \exp[i2\varphi\beta'(z_0)] \right],
\]

where the integral runs over the real parameter, \( \rho \), but the integrand remains complex. Using Eq. (29), it is, however, simple to choose an angle for the contour so that the exponent becomes negative and real, \( 2\varphi + \arg[f''(z_0)] = \pi \), which turns the integrand into a simple real Gaussian with \( \beta = |f''(z_0)|/2 \) in analogy with Eq. (25). A technical point is that we must have \(-\pi/2 < \varphi < \pi/2\) for the contour to run in the “right” direction, i.e. with the real part of \( z \) increasing, but this is typically the case in physical problems. The final result simplifies to the following beautiful expression

\[
K \approx i \exp \left[ f(z_0) \right] \sqrt{\frac{2\pi}{f''(z_0)}},
\]

which we can interpret as the “height” \( \exp[f(z_0)] \) times the “width” \( \sqrt{2\pi/f''(z_0)} \) of the integrated function close to the saddle-point.

It is now of interest to compare the simple integration of a Gaussian, Eq. (25), with the result of our complex analysis, Eq. (30), and conclude that the integrand in Eq. (25) may be complex. The integral converges provided that \( \Re(\beta) > 0 \), but also in the special case of \( \Re(\beta) = 0 \), provided that \( \Im(\beta) \neq 0 \). In the latter case, the convergence can be understood as being due to rapid complex oscillations for large values of \( |\omega| \) as shown in Fig. 7(c), leading to a finite complex integrated value in Fig. 7(d) of \( \sqrt{\pi} \exp[i\pi/4] \).

### 2.2.2 General equation for SPA

Inspired by the results above, we now consider a typical frequency domain integral of a more general function: \( E(\omega) \exp(if(\omega)) \), where \( E(\omega) \) is a smooth amplitude function and \( f(\omega) \) is a smooth phase function. The phase function may contain several saddle-points, also called “stationary” points. In regions where \( f(\omega) \) is varying fast, we expect the contribution to the integral to be small in analogy with Fig. 7(c) and (d). Conversely, we expect significant contributions from regions close to the stationary frequency, \( \omega_s \), where the first derivative of the phase function vanishes: \( \partial f/\partial \omega|_{\omega_s} \equiv f'(\omega_s) \equiv f'_s = 0 \). Then, using the truncated Taylor expansion in Eq. (27) in the vicinity of the stationary points and replacing the exact integrand by the approximate local Gaussian
function, one gets the final result for the SPA approximation [73]:

\[ \int_{-\infty}^{\infty} d\omega \ E(\omega) \exp[i f(\omega)] \approx \sum_s E_s \sqrt{\frac{2\pi}{f''_s}} \exp[i f_s], \]  

(31)

where \( f_s = f(\omega_s), \) \( f''_s \equiv \partial^2 f/\partial \omega^2 |_{\omega_s} \) and \( E_s \equiv E(\omega_s). \) The sum runs over all the roots of the stationary-phase equation:

\[ \frac{\partial f}{\partial \omega} = 0, \]  

(32)

where the roots \( \omega_s \) are labelled by the index \( s. \) The number of solutions depends on the properties of the phase factor, \( f(\omega). \) In the simplest cases, which we will consider here, there is only one solution. The SPA is derived assuming that the second-order term is dominant as compared to higher-order phase terms, e.g. that \( (\omega - \omega_s)^2 f''_s/2 \gg (\omega - \omega_s)^3 f'''_s/6, \) in the neighbourhood of each saddle point, \( |\omega - \omega_s| < \pi. \) If the second-order phase term happens to be zero, \( f''_s/2 = \beta = 0, \) this would correspond to an artificial divergence in Eq. (31). This divergence is most likely non-physical [and it may happen close to the cut-off in the HHG] and the result would be finite if the third-order phase term in the Taylor expansion of the exponent was used in the integral. Having derived the SPA, Eq. (31), we now need to demonstrate that it can help us to make physical arguments about the propagation of XUV wave packets.

2.2.3 Stretched XUV wave packets

It is well-known from ultra-fast optics that uncompensated dispersion can lead to stretched pulses in the time domain [8]. It is illustrative to use the SPA to calculate the properties of such stretched pulses. Consider an attosecond pulse, as expressed in Eq. (18), at \( x = 0, \) with a rather broad Gaussian envelope,

\[ E(\omega) = E_0 \exp[-g(\omega - \omega_0)^2], \]  

(33)

and with a phase factor \( f(\omega) = -\omega t + \delta(\omega), \) where the spectral phase is

\[ \delta(\omega) \approx \delta_0 + (\omega - \omega_0)\delta'_0 + \frac{1}{2}(\omega - \omega_0)^2\delta''_0, \]  

(34)

with a large quadratic chirp, \( |\delta''_0|/2 \gg g. \) The SPA expressed in Eq. (31) then implies that the magnitude of the amplitude factor will be dominated by the contribution of a local value, \( E_s = E_0 \exp[-g(\omega_s - \omega_0)^2], \) occurring at the stationary frequency, \( \omega_s, \) as determined by solving Eq. (32). This is quite similar to the way in which a delta function operates, selecting a specific value of a function. Here it arises from the small constructive window in the complex integral that occurs around the stationary frequency.

The next task is to find the stationary frequency, \( \omega_s, \) which can be seen as the frequency that makes the dominant contribution to the wave packet in a given point in space-time. The stationary-phase equation, Eq. (32), becomes
first-order: \( f'(\omega) \approx \delta_0' + (\omega - \omega_0) \delta_0'' - t = 0 \), which we use to find the stationary
frequency for a given time, \( t \):

\[
\omega_s(t) = \omega_0 + \frac{1}{\delta_0'} (t - \delta_0').
\] (35)

We can rewrite Eq. (35) to see that, due to the chirp induced from propagation,
any frequency of the pulse, \( \omega = \omega_s(t) \), “arrives” at a unique time, \( t = \delta_0' + |\omega_s - \omega_0| \delta_0'' \approx \delta_s' \), which equals the GD as defined in Eq. (20). Furthermore,
one can show that the stationary frequency equals the instantaneous temporal
frequency of the wave packet:

\[
\omega_s(t) = \frac{\partial}{\partial t} \left[ \arg \{ \tilde{E}(t) \} \right],
\] (36)

which provides a simple link between time and frequency for stretched pulses.
In the derivation above, it is only required that the spectral envelope is “broad”
as compared to the spectral width induced by the quadratic chirp. Any other
broad envelope, \( E(\omega) \), will also work, leading to a mapping of the intensity from
the spectral domain to the temporal domain,

\[
\frac{|\tilde{E}(t)|^2}{\text{Temporal}} \propto \frac{1}{|\delta_0''|} \frac{|E(\omega_s(t))|^2}{\text{Spectral}},
\] (37)

because the stationary frequency increases linearly in time as shown in Eq. (35).
The mapping of the spectral envelope to the temporal envelope is scaled by the
inverse spectral chirp, \( 1/\delta_0'' \), so that an increased spectral chirp leads to a more
stretched pulse in the time domain. At the end of Sec. 4.1 we will see that the
properties of these stretched light pulses are similar to the way in which
non-relativistic electrons are dispersed through propagation in vacuum.

### 2.2.4 Ultra-short Gaussian pulse

Consider again an attosecond pulse, Eq. (31), with a Gaussian envelope, Eq. (33),
but this time the envelope is not “broad” compared to the quadratic spectral
chirp, instead, as in the cases of interest in attoscience, one have XUV pulses
so that \( g \approx |\delta_0''|/2 \). Then, for the SPA to be meaningful, the Gaussian envelope
must be included in the phase factor so that it becomes complex:

\[
f(\omega) = \delta(\omega) - \omega t + ig(\omega - \omega_0)^2.
\] (38)

Using the asymptotic phase to second order, Eq. (34), the stationary-phase
equation, Eq. (32), remains first-order, with complex and time-dependent coefficients

\[
f'(\omega) \approx \delta_0' + \delta_0''(\omega - \omega_0) - t + i2g(\omega - \omega_0) = 0,
\] (39)

with the root:

\[
\omega_s(t) = \omega_0 + \frac{\delta_0'' - i2g}{\delta_0'' + (2g)^2} (t - \delta_0').
\] (40)
We mention that it is common to obtain complex stationary points in the SPA in the case of steep variations of the spectral amplitude.

The real part of $\omega_s$ is identified as the instantaneous frequency, as was done in Sec. 2.2.3 while the imaginary part of $\omega_s$ limits the intensity duration (or probability distribution) of the attosecond pulse in time. At the origin, $x = 0$, the intensity of the attosecond pulse will be large only at a time, $t$, close to the group delay: $t \approx \delta'_0$, where the imaginary part of the stationary frequency vanishes. Inserting $\omega_s(t)$ into the right-hand-side of Eq. (31) yields the result:

$$\tilde{E}(t) = \frac{E_0}{2\pi} \sqrt{\frac{\pi}{\beta}} \exp \left[ i (\delta_0 - \omega_0 t) - \frac{(\delta'_0 - t)^2}{4\beta} \right],$$  \hspace{1cm} (41)

where $\beta = g - i\delta''_0/2$. In this particular case, the result of the SPA is exact because it was applied to a Gaussian pulse, but the method is more general and it can be applied also to other spectral envelopes. This is achieved by replacing the third term in Eq. (38) by the more general expression: $\ln[E(\omega)]/i$.

In the special case of a Fourier-limited pulse, $\delta''_0 = 0$, the real part of the stationary frequency becomes the central frequency of the pulse at all times; while the imaginary term remains time-dependent: $\omega_s(t) = \omega_0 + i(\delta'_0 - t)/2g$. This is closely related to the Fourier-limited pulse shape, which has a constant carrier frequency equal to the central frequency. The imaginary part of the stationary frequency imposes the finite duration of the pulse in time.

Summary of attosecond pulse propagation

In this section, we have reviewed the basic properties of light pulses that propagate through a medium in one dimension. Attosecond XUV light pulses are a special kind of light pulse with a large spectral bandwidth. The larger the bandwidth, the more sensitive the pulses are to the dispersion induced by the medium. Using an appropriate medium, it is possible to correct for spectral chirps and reduce the attosecond pulses to their shortest possible duration. Once the attosecond pulses are adjusted, they can be used to ionize atoms at extremely well-defined times [74]. We now review the properties the properties of non-relativistic photoelectron wave packets.

3 Photoelectron wave packets

Attosecond XUV pulses have been used to initiate photoelectron wave packets at well-defined times, but how does such a wave packet evolve after the ionization event? In this section, we perform an analysis of the evolution of these wave packets and we shed light on the similarities with the propagation of attosecond XUV pulses, Sec. 2. Although our final goal is to describe photoionization as a time-dependent process, we start our study with a theoretical treatment of positive energy photoelectron wave packets in the presence of a static binding potential. More details on the actual attosecond-XUV transition are given
in Sec. 4 while the important features related to laser-probing in long-range Coulomb potentials are given in Sec. 5.

In the absence of an external field, the time-evolution of a non-relativistic photoelectron is described by the time-dependent Schrödinger equation (TDSE) \[ H_0 |\Psi(t)\rangle = [T + V_0] |\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle, \tag{42} \]
where $H_0$ is a time-independent Hamiltonian, and $\Psi = \Psi(t, \vec{r}) = \langle \vec{r} | \Psi(t) \rangle$ is the time-dependent wavefunction. The Hamiltonian consists of two parts: $T = -\frac{\hbar^2}{2m} \nabla^2$ being the kinetic energy operator, and $V_0 = V_0(\vec{r})$ being a time-independent, single-electron potential describing the binding of the electron to the atom. For simplicity, we limit ourselves to systems that can be described by a single electron, namely the SAE approximation. A common approach to solving the TDSE, Eq. (42), is to first find the solutions to the time-independent Schrödinger equation, \[ H_0 \psi_\alpha(\vec{r}) = \epsilon_\alpha \psi_\alpha(\vec{r}), \tag{43} \]
where $\epsilon_\alpha$ is the energy (eigenvalue) of the solution (eigenstate), $\psi_\alpha(\vec{r})$ labelled by a set of quantum numbers $\alpha$. In the following, these time-independent solutions are referred to as states. They form the basis that spans the complete space in which the electron moves.

For a spherical potential, $V(r)$, the states can be written on a spherical basis, $\psi_\alpha(\vec{r}) = R_{n,\lambda}(r) Y_{\lambda,m}(\theta, \phi)$, where $R_{n,\lambda}$ is the radial wavefunction and $Y_{\lambda,m}$ is the spherical harmonic, for quantum numbers: $\alpha = [n, \lambda, m]$, with spin neglected for simplicity. It is possible to reduce the Schrödinger equation into separate radial equations, each corresponding to a specific angular momentum quantum number, $\lambda$. To emphasize the similarities and differences between the one-dimensional propagation of light wave packets [Sec. 2] and electron states, $u_{n,\lambda}(r) = r R_{n,\lambda}(r)$, are used. These effective radial states can be interpreted as the solutions of a one-dimensional Schrödinger equation for $r > 0$ with an effective potential \[ [T + V_r(x) + V_\lambda(x)] u_{n,\lambda}(x) = \epsilon_\alpha u_{n,\lambda}(x), \tag{44} \]
where $T = -\frac{\hbar^2}{2m} \partial_{xx}$ is the radial kinetic energy, $V_r(x) = -\frac{e^2}{4\pi\epsilon_0 x}$ is the radial potential (explicit for hydrogen) and $V_\lambda(x) = \lambda(\lambda + 1)\hbar^2/(2mx^2)$ is the centrifugal potential that depends the angular momentum through $\lambda$. Starting with Eq. (44), the radial variable $r$ is relabelled $x$ to ease the comparison between the propagation of one-dimensional light pulses and of photoelectron wave packets. The boundary condition for all states is $u_{n,\lambda}(0) = 0$, and the states are taken to be real. A photoelectron wave packet, in angular subspace $\lambda$, can then be can be written as an integral–superposition of continuum states, \[ \Psi_\lambda(t, x) = \int_0^\infty d\epsilon a(\epsilon, t) u_{\epsilon,\lambda}(x) \exp\left[-i\epsilon t/\hbar\right], \tag{45} \]
where \( a(\epsilon, t) \) is the complex amplitude for the energy-normalized radial state, \( u_{\epsilon, \lambda}(x) \), at energy \( \epsilon > 0 \).

### 3.1 Phase propagation of photoelectrons

The propagation of a photoelectron wave packet, Eq. (45), is governed by the way in which the phases of the continuum states \( u_{\epsilon, \lambda}(x) \) vary as a function of energy, \( \epsilon \). The Wentzel–Kramers–Brillouin (WKB) approximation is well suited for studying continuum states within a semi-classical framework [75]. The WKB approximation relies on a similar ansatz as in Sec. 2.1 for XUV light. For an effective potential which vanishes at infinity, \( \lim_{x \to \infty} V_0(x) = 0 \), the effective radial wavefunction is taken to be

\[
u_{\epsilon}(x) \propto \Im \{ \exp[\im \phi(\epsilon, x)] \} = \sin[\phi(\epsilon, x)],
\]

where reference to \( \lambda \) is dropped for compactness. Inserting the WKB ansatz into the Schrödinger equation, Eq. (44), leads to a differential equation for the phase of the state,

\[
-\frac{i\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} + \frac{\hbar^2}{2m} \left( \frac{\partial \phi}{\partial x} \right)^2 = \epsilon - V_0(x) \quad \text{(47)}
\]

Further, assuming that the local momentum of the photoelectron varies slowly,

\[
|p(x)/\hbar| \equiv |\partial \phi/\partial x| \gg |\partial^2 \phi/\partial x^2|^{1/2},
\]

the above equation can be simplified,

\[
\frac{\partial \phi}{\partial x} = \frac{1}{\hbar} \sqrt{2m(\epsilon - V_0(x))},
\]

and then integrated,

\[
\phi(\epsilon, x, x_0) = \frac{1}{\hbar} \int_{x_0}^{x} dx' \sqrt{2m(\epsilon - V_0(x'))}
= \frac{1}{\hbar} \int_{x_0}^{x} dx' \ p(x'),
\]

where \( p(x) \) is the local momentum of the electron, and \( x_0 \) is from where the electron “starts”. In applications, the parameter \( x_0 \) is associated to a classical turning point, see below. The local momentum corresponds to the local kinetic energy, which is the total energy minus the local potential energy. The phase of the wavefunction varies faster as the local momentum is increased. Eq. (13) and (49) are now compared to highlight the differences between the propagation of XUV light and photoelectrons. In a medium with negligible dispersion, the phase of light is approximately proportional to the photon momentum, \( \omega/c \), leading to a simple translation of the wave packet in space-time according to the shift theorem, Eq. (15). Similarly, in regions of space where the action of the potential is negligible, \( V_0(x) \ll \epsilon \), the phase of the electron is proportional to the electron momentum, but this corresponds to the square root of the energy and frequency, \( p(x) \propto \sqrt{\epsilon} \), in contrast to the linear frequency dependence of
light. This implies that the electron wave packet will not maintain its shape under propagation. This non-linear phase dependence leads to a broadening effect referred to as “quantum diffusion” and it originates physically from the fact that electrons of different energies travel at different speeds. In the more general case with dispersion, we may rewrite Eq. (49) and define an “electron-susceptibility” \( \chi^{(e)} = -\frac{V_0(x)}{\epsilon} \) in analogy with the linear susceptibility phase of light, \( \chi^{(1)} \). The electron phase is real as long as \( \epsilon > V_0 \), but it will be imaginary if \( \epsilon < V_0 \), which implies that the electron must tunnel through some barrier and that the transmission amplitude will be exponentially damped.

When writing the WKB solution, it is natural to include \( |\partial^2 \phi / \partial x^2| \) to leading order \([75]\). This leads to the well-known form for the WKB state

\[
\psi_{\epsilon, \pm}^{(WKB)}(x) = \frac{1}{\sqrt{p(x)}} \exp \left[ \pm \frac{i}{\hbar} \int_{x_0}^{x} dx' p(x') \right],
\]

where the two complex solutions (±) describe an outgoing and incoming electron, respectively. The probability density, \( \rho(x) = |\psi_{\epsilon, \pm}^{(WKB)}(x)|^2 \propto 1/|p(x)| \), is smaller where the electron moves rapidly. Physically, we understand this because the electron will spend a shorter time in a place when moving with a greater velocity. Alternatively, we can form an energy normalized and real WKB solution,

\[
\psi_{\epsilon, \pm}^{(WKB)}(x) = \sqrt{\frac{2m}{\pi \hbar}} \sin \left[ \frac{1}{\hbar} S_{\epsilon}(x, x_0) \pm \phi_{x_0} \right],
\]

which is valid for \( x > x_0 \), where \( x = x_0 \) is a classical turning point, i.e. it separates a classically forbidden region, \( \epsilon < V_0(x) \) for \( x < x_0 \), and a classically allowed region, \( \epsilon > V_0(x) \) for \( x > x_0 \). The phase of the state is a sum of the semi-classical action,

\[
\frac{1}{\hbar} S_{\epsilon}(x, x_0) = \frac{1}{\hbar} \int_{x_0}^{x} dx' p(x'),
\]

plus the quantum mechanical reflection phase, \( \phi_{x_0} \). Depending on the type of potential and on the energy of the electron, the quantum mechanical reflection at the classical turning point can be regarded as either “hard” or “soft” \([74]\). Photoelectrons in a pure Coulomb potential, with no angular momentum, will suffer a hard reflection at \( x = 0 \), with a reflection phase of \( \phi_{x_0} = 0 \), so that the wavefunction is exactly zero at the reflection point, i.e. \( \psi_{\epsilon, \pm}^{(WKB)}(0) \propto \sin(0) = 0 \). Photoelectrons with angular momentum, \( \lambda > 0 \), will reflect in an effective potential composed of the Coulomb potential and the centrifugal potential at \( V_0(x_0) \equiv V_r(x_0) + V_\lambda(x_0) = \epsilon \). This combined barrier typically leads to reflection points further out from the nucleus, \( x_0 > 0 \), and to softer reflections. A soft reflection implies that the photoelectron wavefunction can extend a bit into the classically forbidden region, \( x < x_0 \). The soft reflection limit, i.e. when the effective potential is slowly varying compared to the wavelength of the electron,
can be calculated using a linear potential so that the wavefunction becomes
an Airy function with a reflection phase of \( \pi/4 \) \cite{75}, but this is typically not
a good approximation for photoelectrons that we consider here. An accurate
determination of the reflection phase, \( \phi_{x_0} \), requires a fully quantum mechanical
theory beyond the WKB approximation and \textit{ab initio} calculations of such phases
present a challenge to theory for large atomic systems or complex molecular
systems.

### 3.2 Quantum diffusion and Wigner delays

As an example, consider the situation illustrated in Fig. \[8\] where an electron
passes through a short-range attractive potential.

![Figure 8: Electrons passing through an attractive potential, \( V_0(x) \). The real
WKB solutions (thin black curves), Eq. (51), are compared to the real free
electron states (thick grey curve) at three different energies: \( \epsilon = 1, 2, 3 \) atomic
units of energy (27.2 eV). The phase of the electron wavefunction varies more
rapidly in the potential, which leads to an accumulated phase difference, \( \delta \),
compared to the free case. (Note that the modulations of the wavefunctions
should be interpreted in the third dimension of the graph, and not as an energy
modulation.)

The electron is classically allowed to pass through the potential, but as it does
so, it will acquire a quantum phase. The asymptotic phase difference, between
an electron wave propagating through a short-range potential, Eq. (49), and
free wave propagation, is defined in analogy with Eq. (14):

\[
\delta(\epsilon) = \frac{1}{\hbar} \lim_{x \to \infty} \int_{-\infty}^{x} dx' \left[ p(x) - p_0 \right],
\]

(53)

where \( p_0 = \sqrt{2m\epsilon} \) is the free (asymptotic) momentum of the electron. The GD
concept, Eq. (20), can also be applied to electron wave packets using Eq. (53):

\[
\tau_\lambda(\epsilon) = \frac{\partial \delta}{\partial \omega} = \hbar \frac{\partial \delta}{\partial \epsilon}.
\]

(54)
The electron GD then results only from the interaction with the potential, since the intrinsic delay due to quantum diffusion has been subtracted. Using the asymptotic phase to calculate the delay of electron wave packets was first done by Eisenbud, Wigner and Smith [77, 78, 79], hence the name Eisenbud–Wigner–Smith delay, (or Wigner delay for short). In the simple scattering example given above, the asymptotic phase shift equals twice the radial phase shift: once for the incoming electron (0 > x) and once for the outgoing electron (0 < x). Regarding photoionization, it can be considered as a half-collision because the electron only moves out of the atom (0 < x). As compared to free propagation, the delay of the wave packet in photoemission is, therefore, the derivative of the radial asymptotic phase-shift.

For a weak potential, |V_0| ≪ ϵ, the local momentum is \( p(x) \approx p_0 [1 - V_0(x)/2\epsilon] \), which leads to an asymptotic phase

\[
\delta(\epsilon) \approx -\frac{1}{\hbar} \sqrt{\frac{m}{2\epsilon}} \int_\infty^{-\infty} dx' V_0(x') \equiv -\frac{1}{\hbar} \sqrt{\frac{m}{2\epsilon}} I_V,
\]

where the potential integral can be written as \( I_V \approx \epsilon_V L_V \), in terms of an effective “height” \( \epsilon_V \) and “range” \( L_V \) of the potential well. As expected, in this lowest-order approach, the phase acquired by the electron increases linearly with both the height and range of the barrier. The Wigner delay is

\[
\tau_\lambda = \sqrt{\frac{m}{8 \epsilon^{3/2}}} \approx \sqrt{\frac{m}{8 \epsilon^{3/2}}} L_V.
\]

It takes a shorter time, \( \tau_\lambda < 0 \), for an electron to pass a weak attractive potential, \( \epsilon_V < 0 \), than through free space. Physically, this is due to the higher local velocity of the electron in the potential valley. The opposite is true for a weak repulsive potential, where the electron is slowed down on the potential hill. Furthermore, the timing of slow electrons is affected more than the timing of fast electrons, due to the longer total time that the slow electrons spend in the potential. In terms of numbers, this simple analysis leads to a delay of 5.9 as per eV and nm of the potential barrier, given an electron with one unit of atomic energy (27.2 eV).

### 3.3 Phases and delays in Coulomb potentials

Photoelectrons created from neutral atoms are submitted to the long-range Coulomb potential of the remaining ion, \( V_C = -C/x \), where the constant is \( C = Ze^2/(4\pi\epsilon_0) \) with \( Z = 1 \) for a singly charged hydrogen ion. In order to study this long-range interaction in detail, we consider the WKB approximation, Eq. (51). Then, the local momentum can be expanded as

\[
p(x) = \sqrt{2m \left[ \epsilon + \frac{C}{x} \right]} \approx p_0 \left[ 1 + \frac{C}{2\epsilon x} \right],
\]

with \( p_0 = \sqrt{2me} \) being the asymptotic momentum in the remote region of space where \( \epsilon \gg |C/x| \). Using Eq. (52) and (57), the total phase of the real WKB
state is asymptotically
\[
\frac{S_\epsilon (x, x_0)}{\hbar} + \phi_{x_0} \approx kx + \frac{C}{2\epsilon} \ln(x) - kx_0 - \frac{C}{2\epsilon} \ln(x_0) + \phi_{x_0}
\]
\[
\approx kx + \ln(2kx) \frac{ka_0}{\Phi_{k, \lambda}(x)} + \eta_{k, \lambda} - \frac{\pi \lambda}{2}
\]  
(58)

where \(k = p_0 / \hbar\) is the wave number; \(a_0\) is the Bohr radius; and \(Z = 1\). Line 1 of Eq. (58) corresponds to the WKB notation with an approximate reference to the reflection point \(x_0\), while line 2 follows standard notation from atomic physics with reference to the absolute scattering phase, \(\eta = \eta_{k, \lambda}\). The real WKB state varies as
\[
uk, \lambda(x) \propto \sin \left[ kx + \ln(2kx) \frac{ka_0}{\Phi_{k, \lambda}(x)} + \eta_{k, \lambda} - \frac{\pi \lambda}{2} \right]
\]  
(59)

for \(x \to \infty\). Interestingly, the phase does not settle into free particle behaviour, instead, the phase diverges logarithmically! What does this space-divergent phase mean for the delay of the photoelectron wave packet? When applying the frequency derivative to the logarithmic term, we find a delay that depends on the spatial position of the wave packet,
\[
\tau_{LR}(k, x) = \frac{\hbar}{\partial \epsilon} \left[ \ln(2kx) \right] \frac{ka_0}{\Phi_{k, \lambda}(x)}
\]
\[
\approx \frac{m}{\hbar a_0 k^3} \left[ 1 - \ln \left( \frac{2\hbar k^2}{m \tau} \right) \right],
\]  
(60)

where we have replaced this spatial-position of the electron, \(x\), by the approximate classical position, \(x_{cl}(\tau) \approx v\tau = \hbar k \tau / m\), with \(\tau = t - t_0\) being the time that has passed since the electron was ionized by the attosecond pulse at \(t = t_0\). Interestingly, \(\tau_{LR}\) also diverges logarithmically as \(\tau\) increases and it cannot be neglected. As a consequence, \(\tau_{LR}\) will completely dominate over any (short-range) Wigner delay, \(\tau_{\lambda} \ll \tau_{LR} \ll \tau\), as \(\tau \to \infty\). This implies that there is no absolute delay of the Coulomb wave packet with respect to free propagation. To define a physical delay between two photoelectron wave packets of different energy is already difficult for free propagation, due to the different velocities of the photoelectrons as discussed with Eq. (54), but it is even more difficult for Coulomb wave packets due to the spatial dependence of the phase. In the special case of two different Coulomb wave packets of the same energy, the logarithmic delays cancel and their relative delay then equals the difference in Wigner delay. In this way, we can talk about the delay of a Coulomb wave packet, but only relative to a Coulomb reference, e.g. the hydrogenic system. To summarize this analysis, for the propagation of photoelectron wave packets, we find that the approximate position is predominately given by the linear, free propagation relation, \(p_0 x - \epsilon \tau = 0\). The logarithmic, long-range phase is of intermediate importance, and it dominates over the absolute, short-range phase. On the other
hand, only the short-range phase contain detailed information about the atomic potential.

As already mentioned, the absolute determination of the short-range asymptotic phase-shift, $\eta$, is a difficult problem, because it depends on the detailed atomic potential, which is modified by electron–electron interactions at short range. In the special case of hydrogen system of nuclear charge $Z$, and for a given wave number, $k$, and angular momentum, $\lambda$, the phase is known analytically \[75\],

$$\eta^{(H)}_{k,\lambda} \equiv \sigma_{k,\lambda} \equiv \arg\{\Gamma[\lambda + 1 - iZ/(ka_0)]\},$$  \hspace{1cm} (61)

with $\Gamma(z) = \int_0^{\infty} dt \ t^{z-1} \exp[-t]$ being the complex Gamma function. This result can be generalized for any spherical atom,

$$\eta_{k,\lambda} \equiv \sigma_{k,\lambda} + \delta_{k,\lambda},$$  \hspace{1cm} (62)

where $\delta_{k,\lambda}$ is the phase difference compared to hydrogen that is induced by the short-range deviation from the pure Coulomb potential. The WKB states are compared with the exact Coulomb states for hydrogen in Fig. 9.

Figure 9: Exact hydrogen wavefunctions (thin black curve) for $\lambda = 0, 1$ and 2, corresponding to s-, p- and d-waves in the continuum at three different energies 5, 15 and 25 eV. The asymptotic approximation (grey thick curve) is shown for comparison. It will be explained further in Sec. 4 and 5, but we mention here that it utilizes the long-range WKB phase matched to the correct asymptotic phase-shift, while the amplitude prefactor is taken to be constant [see Eq. (46)]. (Note that the modulations of the wavefunctions should be interpreted in the third dimension of the graph, and not as an energy modulation.)
The exact analytical states of the hydrogen atom are called the regular Coulomb functions of the first kind \[80, 81\]. The WKB states converge quickly to the exact solution, if the correct scattering phase is known and applied \[76\].

4 Photoionization on the attosecond timescale

In this section, we will discuss, within the framework of lowest-order time-dependent perturbation theory \[82, 83\], the photoionization of atoms in the presence of attosecond XUV pulses (SAP or APT). Photoionization is a fundamental process in light-matter interaction, which has been studied extensively using time-independent methods, in parallel with the implementation of synchrotron radiation sources, see for instance the seminal papers about Cooper minima and photoelectron phase-shifts \[84, 85\]. Here we start by studying photoionization in the time-domain, but as we proceed we shall recover the more traditional, spectral representation for the determination of the phase-shifts of the photoelectron states, from which one can recover relative delays between photoelectron wave packets.

Although attosecond pulses of high-order harmonics have relatively high peak intensities, as compared to conventional sources of XUV radiation, single-photon absorption remains the dominant mechanism for atomic ionization. Then, due to this fluence of XUV or X-ray photons being sufficiently small, the interaction between attosecond pulses and atoms can be approximated using first-order, time-dependent perturbation theory \[82, 83\]. The field-free TDSE, as written in Eq. (42), is satisfied by the time-dependent field-free states of the atom,

\[
|\tilde{\alpha}(t)\rangle \equiv |\tilde{\alpha}\rangle \equiv |\alpha\rangle \exp[-i\omega_\alpha t],
\]

where \(\alpha\) labels the quantum numbers for a given energy, \(\epsilon_\alpha = \hbar \omega_\alpha\). The interaction between the XUV field, \(\tilde{V}_I(z,t)\), and the unperturbed, initial state of the atom, \(|\tilde{i}(t)\rangle\) with energy \(\epsilon_i = \hbar \omega_i\) and a binding energy of \(I_p = |\epsilon_i|\), leads to the creation of a photoelectron wave packet

\[
|\Psi(t)\rangle \approx |\tilde{i}(t)\rangle + \sum_\alpha a^{(1)}_\alpha(t) |\tilde{\alpha}(t)\rangle,
\]

where the first-order complex amplitudes are \[82\]

\[
a^{(1)}_\alpha(t) = \frac{1}{i\hbar} \int_{-\infty}^t dt' \langle \tilde{\alpha}(t')|\tilde{V}_I(z,t')|\tilde{i}(t')\rangle.
\]

In the case of photoionization, the interaction Hamiltonian, \(\tilde{V}_I(z,t) = ez \tilde{E}(t)\), is the dipole-interaction operator for the attosecond XUV field, here given in length gauge for linear polarization along \(\hat{z}\). For the case of short, coherent pulses, \(e.g.\) attosecond pulses, the interaction can be expanded as

\[
\tilde{V}_I(z,t) = ez \frac{1}{2\pi} \int d\Omega' E(\Omega') \exp[-i\Omega' t],
\]
where \( E(\Omega') \) are the electric-field, spectral components of the attosecond pulse. After the interaction is over, when the attosecond pulse has passed, the first-order complex amplitude, or \( S\text{-matrix element} \) (not to be confused by the electron action), is proportional to both the dipole matrix element, \( z_{\alpha i} = \langle \alpha | z | i \rangle \), and to the Fourier transform of the electric field,

\[
S^{(1)}_{\alpha/i} = \lim_{t \to \infty} a^{(1)}(t) = \frac{e}{i\hbar} z_{\alpha i} \int dt \, \dot{E}(t) \exp \left[ i(\omega_{\alpha} - \omega_{i})t \right] = \frac{e}{i\hbar} z_{\alpha i} E(\Omega),
\]

at the energy-conserving frequency, \( \Omega = \omega_{\alpha} - \omega_{i} \), where \(|\alpha\rangle\) is a continuum state under the single-active electron (SAE) approximation. This shows that the Fourier components of the attosecond pulse are continuously mapped on the complex transition amplitude associated to the photoionization process. Most attosecond pulse-characterization schemes take advantage of this mapping from XUV light to photoelectron states, see for instance Ref. [36] and [32, 33] for the attosecond streak camera and the RABITT method respectively, which we will discuss further in Sec. 5.

More generally, in order to determine the outcome of the interaction, e.g. the momentum distribution, the complete photoelectron wave packet can be projected on a momentum state,

\[
S_{\vec{k}/i} = \lim_{t \to \infty} \langle \vec{k} | \Psi(t) \rangle,
\]

of the field-free Hamiltonian with energy, \( \epsilon_{k} = \hbar^{2}k^{2}/(2m) \). The real expectation values, \( |S_{\vec{k}/i}|^{2} \), yield then the corresponding probability density of the momentum states. These momentum states are not plane waves, but they do approach a plane-wave like behaviour in the asymptotic limit, \( r \to \infty \). Their wavefunction, \( \varphi_{\vec{k}}(\vec{r}) = \langle \vec{r} | \vec{k} \rangle \), can be expanded on partial-waves as \([83]\)

\[
\varphi_{\vec{k}}(\vec{r}) = (8\pi)^{3/2} \sum_{L,M} i^{L} e^{-i\eta_{L}(k)} Y_{L,M}^* (\hat{k}) Y_{L,M} (\hat{r}) R_{k,L}(r),
\]

where the inserted scattering phases, \( i^{L} e^{-i\eta_{L}(k)} \), are designed to form an \textit{unified phase front}, of all partial waves \((L, M)\), in the forward direction, \( \hat{k} \). For electrons ejected from a neutral system, outgoing waves have the following generic form (as we will discuss further in Sec. 4.3)

\[
u^{(out)}_{k,L}(r) \propto \exp \left\{ i \left[ kr + \frac{\ln(2kr)}{ka_{0}} + \eta_{L}(k) - \frac{\pi L}{2} \right] \right\},
\]

where the asymptotic phases clearly cancel with the phase factors in Eq. \([69]\) for each partial wave. However, there remains a logarithmic term due to the \textit{long-range} Coulomb potential, as derived in Sec. 3.3 which shows that the
asymptotic behaviour of the momentum state is not exactly that of a simple plane wave. Furthermore, it is only the phase difference between the partial waves that is physical, so that the total phase of the state can be set arbitrarily. In this way, the spectral intensity distribution of attosecond XUV pulses can be determined using electron spectrometers, such as time-of-flight (TOF) or velocity-map imaging (VMI), to count the number of photoelectrons reaching the detector, and then correcting for the dipole matrix element, i.e. for the “quantum efficiency” \[86, 87, 88\], as shown in Fig. 1. We stress, however, that in either case, information about the temporal structure of the XUV light pulse is not accessible because the phase of the complex amplitude is not measured.

4.1 Snapshots of photoelectron wave packet

By considering a simple “flat-top” (\(\cap\)) XUV attosecond pulse, we can observe “snap-shots” of how the photoelectron wave packet builds up with time. The flat-top attosecond pulse is of a given duration, \(\tau_I\), and it has a central frequency of \(\hbar\Omega > I_p\). Fig. 10 illustrates the evolution of the complex amplitudes and the corresponding reconstructed photoelectron wave packets, \(\lvert \Psi^{(1)}(t) \rvert\), for increasing interaction durations, \(\tau_I\).
Figure 10: Complex amplitudes (left) and “snapshots” of the corresponding photoelectron wave packets (right) after photoionization of increasing pulse duration, $\tau_I$: (a,b) 120, (c,d) 240, (e,f) 480 and (g,h) 2400 as. (a,c,e,g) The probability distribution over energy (black line) becomes narrower as $\tau_I$ increases. (b,d,f,h) In space, this corresponds to an expanding electron wave packet. The size of the photoelectron wave packet is well estimated by the classical distance $x = v_c \tau_I$ (black circle). This is a one-dimensional model calculation where the continuum states are plane waves and the dipole transition matrix element is approximated as constant. The carrier frequency of the light is $\hbar \Omega = 41$ eV and the binding energy is $I_p = 13.6$ eV, resulting in a central energy, $\epsilon_c = \hbar \Omega - I_p = 27.1$ eV = 1 atomic unit, of the photoelectron. The photoelectron wave packet is complex; the real and imaginary parts being shown in red and blue, respectively.

From standard time-dependent perturbation theory, we know that the total transition probability of a perturbative excitation increases linearly with time, $P = \int d\epsilon |a_\alpha(t)|^2 \propto \tau_I$, as long as the depletion of the initial state can be neglected. The photoelectron wave packet, in Fig. 10, behaves indeed as expected since it extends linearly in space as a function of the interaction time, $\tau_I$. The spatial extent of the wave packet is approximately $x = v_c \tau_I$, where $v_c = \sqrt{2\epsilon_c/m}$ is the classical velocity of the photoelectron after ionization and $\tau_I$ is the duration of the interaction. Inside this “classical” extent of the wave packet, the probability density is roughly constant.

Because the electron is ionized at a “well-defined time”, namely during the brief interaction with the attosecond pulse, the uncertainty principle dictates that its energy content must be very broad. This can also be verified in Fig. 10 (g,e,c,a) for progressively shorter interactions. It may be of interest to know how long the photoelectron wave packet remains “localized” in time and space. At time $\tau$ after the ionization, the electron wave packet will have spread in space to an extent of $\Delta r$, which can be estimated from a classical ensemble of velocities,

$$\Delta r = (v_{max} - v_{min}) \tau \approx \frac{\Delta \epsilon}{mv_c} \tau \quad (71)$$

where $v_{min}$, $v_c$ and $v_{max}$ are the minimal, central and maximal velocity, corresponding to an energy width of $\Delta \epsilon$ at a central energy of $\epsilon_c = mv_c^2/2$. Furthermore, the temporal extent can be estimated as

$$\Delta t \approx \frac{\Delta r}{v_c} \approx \frac{\Delta \epsilon}{2\epsilon_c} \tau. \quad (72)$$

Interestingly, from this simple analysis, we find that the photoelectron wave packet will extend its duration linearly in $\tau$. For photoelectrons ionized by attosecond pulses, with a large bandwidth $\Delta \epsilon \approx \epsilon_c$, this implies that the temporal extent of the electron wave packet is approximately equal to its time of propagation, $\Delta t \approx \tau$. In other words, we should not consider these photoelectron wave packets as attosecond quantities. We will return to the propagation of photoelectrons in Sec. 4.4 for a more detailed analysis, but first we must consider the actual photoionization process in more detail.


4.2 Exponential turn-on of ionization

In the previous subsection, we considered a “flat-top” XUV pulse shape, but envelopes with such sharp features represent a rather poor idealization of the often smoothly varying physical pulses. Rather than turning on the ionizing field instantaneously, as was done above, the electric field can be smoothly increased from minus infinity using a “slow” exponential turn-on [82]. Even though this represents an infinitely long interaction, we will show that it is extremely important for a deep theoretical understanding of photoionization phenomena also on the attosecond timescale. The electric field is written \( \tilde{E}(t) = iE \exp[-i\Omega t + \beta t] \), including an attenuation factor, \( \beta > 0 \), that reduces the field strength as \( t \to -\infty \). The attenuation factor ensures that the probability for the emission of a photoelectron is zero at remote negative times. Inserting the attenuated field into Eq. (65) yields

\[
a^{(1)}_{\alpha}(t) = \lim_{\beta \to 0^+} e^{i\pi(\Delta \omega_{\alpha})} \left( \frac{1}{\beta + i\Delta \omega_{\alpha}} \right) e^{i\Delta \omega_{\alpha}t + \beta t}
\]

(73)

with \( \Delta \omega_{\alpha} = \omega_{\alpha} - \omega_i - \Omega \), and where the limit corresponds to the “well-known theorem from complex function theory” [89]. The notation used requires some explanation: We write \( \delta \) for the Dirac delta function, and \( \wp \) is written to indicate that the discontinuity of \( 1/\Delta \omega_{\alpha} \) has been removed, so that when integrated the result is Cauchy’s principal value. We mention that this limiting form can be recovered by multiplying the denominator of Eq. (73) by its complex conjugate and then identifying the limits of the delta function, \( \beta/(\beta^2 + \Delta \omega_{\alpha}^2) \to \pi\delta(\Delta \omega_{\alpha}) \); and the principal value, \( \Delta \omega_{\alpha}/(\beta^2 + \Delta \omega_{\alpha}^2) \to \wp(1/\Delta \omega_{\alpha}) \).

Similarly, we can model a slow turn-off using \( \tilde{E}(t) = iE \exp[-i\Omega t - \beta t] \) for \( t > 0 \) as \( t \to \infty \), giving the same result as in Eq. (73), but with the opposite sign of the principal value part. Combining the slow turn-on and the slow turn-off, therefore, leads to symmetric cancellation of the principal value contribution. The resulting complex amplitude, corresponding to an interaction with a field of central frequency \( \Omega \) for times going from minus infinity to plus infinity, shows that energy must be conserved,

\[
S_{\alpha/i}^{(1)} = e\pi(\epsilon_{\alpha} - \epsilon_i - \hbar \Omega),
\]

(74)

and that only an energy-conserving state, with \( \epsilon_{\kappa} \equiv \hbar^2 \kappa^2/(2m) = \hbar \Omega + \epsilon_i \), will be populated. This result corresponds to a Fourier transform of a continuously oscillating electric field, Eq. (67). We stress that it is valid as \( t \to \infty \), which we interpret as the electric field being turned off.

The interesting aspect of the exponential turn-on model, Eq. (73), is that it allows us to reconstruct a photoelectron wave packet at any finite time, \( t \), while...
the ionization is ongoing and the electric field is on,

\[ |\tilde{\Psi}(t)\rangle = \sum_{\alpha} a^{(1)}_{\alpha}(t) |\tilde{\alpha}(t)\rangle \]

where the total phase of the wave packet is evolving at a common angular frequency, \(\omega_\kappa\), corresponding to energy conservation. In Eq. \((75)\), the time, \(t\), is finite. This implies that all states can be populated, also those that do not conserve energy. In fact, the time-independent part of the wave packet consists of two terms: the first one is associated to the energy-conserving states, while the second term is a non-trivial principal-value superposition of non-energy-conserving states. The latter states are out of phase by \(\pm \pi/2\) compared to the energy-conserving contribution depending on whether the energy denominator is positive or negative. This total phase displacement of \(\pi\) can be understood in analogy with a classical pendulum, which is set in motion by an external oscillating force either in an over-driven or under-driven mode. Here, because we are dealing with quantum mechanics, we need to sum over all possible “pendulums” corresponding to the continuum states above and below the resonance located at \(\epsilon_\kappa\).

More explicitly, the energy-conserving transition goes from the initial, partial-wave state, \(|i\rangle \equiv |n_i, \ell_i, m_i\rangle\), to a superposition of energy-conserving, partial-waves states, \(|\alpha\rangle = |\kappa, \lambda_c, \mu_c\rangle\), where the summation over \(c\) implies that \(\lambda_c = \ell_i \pm 1\) and \(\mu_c = m_i\) for linearly polarized light. Similarly, the non-energy-conserving states can be written explicitly as partial-wave states, \(|\alpha\rangle = |\kappa', \lambda', \mu\rangle\), where \(\alpha\) runs over both the bound and continuous states, but \(\kappa' \neq \kappa\).

### 4.3 Asymptotic form of the photoelectron wave packet

It is not easy to directly infer the form of the first-order wave packet from Eq. \((75)\), but we expect that it should be an outgoing wave. To see this, we first note that the energy-conserving part is real and that the principal-value part is imaginary, at \(t = 0\). Next, we consider the asymptotic form of the radial wavefunction for a photoelectron state with \(\epsilon = \epsilon_\alpha = \epsilon_{\kappa'}\), corresponding to quantum numbers \(\alpha = [\kappa', \lambda, \mu]\),

\[ \langle \tilde{r}|\alpha\rangle \equiv \frac{1}{p} u_{\kappa',\lambda}(r)Y_{\lambda,\mu}(\hat{r}) \]

where we have separated the radial part from the angular part. In the asymptotic limit, we may substitute for the approximate form of the radial part, as
derived in Eq. (59),

\[
\langle \vec{r}|\alpha \rangle \approx N_{\kappa'} \frac{1}{r} \sin \left[ \kappa' r + \frac{\ln(2\kappa' r)}{\kappa' a_0} + \eta_{\kappa',\lambda} \frac{\lambda \pi}{2} \right] Y_{\lambda,\mu}(\hat{r}),
\]

where \( \Phi_{\kappa',\lambda}(r) \) is the radial-dependent and \( \lambda \)-dependent phase-shift, and where

the coefficient for energy re-normalization is

\[
N_{\kappa'} = \left[ \frac{2m}{\pi^2 \hbar^2 \epsilon_\alpha} \right]^{1/4} = \sqrt{\frac{2m}{\pi \hbar^2 \kappa'}}.
\]

The asymptotic part of the bound states can be neglected, because they decay exponentially with the distance from the nucleus and can not affect the outgoing photoelectron. This allows us to aggregate the sum over the bound state spectrum with the contribution of the continuous spectrum in a single integral from minus infinity to plus infinity. In this way, the smoothed “bound part” is still exponentially damped and it will not contribute, but the integral is easier to handle.

The principal-value part of the wave packet, Eq. (75), is evaluated by rewriting the sine-function in Eq. (77) as outgoing and incoming waves, \( u^{(\text{out/in})}_{\kappa',\lambda}(r) \sim \exp\left[ \pm i\kappa' r \right] \). It is then possible to integrate analytically for the principal-value using Cauchy’s integral theorem, as sketched in Fig. 11.

Figure 11: Integration paths in the complex plane for obtaining the principal value \( P = I_1 + I_2 \) of outgoing waves: \( \exp[i\sqrt{2\epsilon r}]/(\epsilon - \epsilon_\alpha) \). The outer integration path vanishes, \( I_0 \rightarrow 0 \), as the electron enters the asymptotic region, \( r \rightarrow \infty \). The semicircle over the pole \( I_{1/2} \) becomes \( -i\pi \) times the corresponding residue as the arc is reduced. Using Cauchy’s integral theorem, we write: \( I_0 + I_1 + I_{1/2} + I_2 = 0 \), which implies that the principal value is: \( P \approx -I_{1/2} = i\pi \exp[i\sqrt{2\epsilon_\alpha r}] \). A similar calculation can be made for the incoming waves, but here the integration paths go into the negative imaginary axis which results in an additional minus sign. For simplicity, we have here omitted the phase-shifts, \( \Phi_{\kappa',\lambda}(r) \) and the amplitude prefactors, since they present no further complication. Atomic units were used for compactness.

The result from this calculation is that the imaginary part of the wave packet
takes a cos-like form at the energy-conserving wave number, \( \kappa \), so that

\[
\langle \vec{r} | \varphi \sum_\alpha \frac{z_{\alpha i}}{\epsilon_\alpha - \epsilon_\kappa} | \alpha \rangle \approx \pi \sum_c z_{ci} N_\kappa \cos \left[ \kappa r + \Phi_{\kappa,\lambda}^{(c)}(r) \right] Y_{\lambda,\mu}^{(c)}(\hat{r}),
\]  

(78)

where the sum over \( c \) is needed if the wave packet populates multiple angular channels (with short-hand notation: \( Y_{\lambda,\mu}^{(c)} \), so that \( [\lambda, \mu] = [\lambda_c, \mu_c] \)). Inserting these asymptotic expressions into Eq. (75), we find that the photoelectron wave packet is, indeed, a sum of outgoing Coulomb waves for each angular channel \( c \)

\[
\tilde{\Psi}^{(1)}(t, \vec{r}) \approx \pi eE \sum_c z_{ci} N_\kappa \exp \left[ i \left( \kappa r + \Phi_{\kappa,\lambda}^{(c)}(r) - \omega_\kappa t \right) \right] Y_{\lambda,\mu}^{(c)}(\hat{r}),
\]  

(79)

where the result of the long-range Coulomb interaction and of the short-range interactions are contained in \( \Phi_{\kappa,\lambda}^{(c)}(r) \) for the wave number, \( \kappa \), corresponding to energy conservation. This intuitive form of the first-order wave packet is valid asymptotically, as can be identified in Fig. 12, where we have numerically calculated a representative first-order wave packet for hydrogen.

![Figure 12](image-url)  

Figure 12: First-order radial wave packet (perturbed wavefunction) calculated numerically for Hydrogen at a kinetic energy of 40 eV. The real (red) and imaginary (blue) part oscillate as an outgoing wave, as expected from the asymptotic approximation.
Our result for the asymptotic form of the wave packet, Eq. (79), is quite general and it can be applied to many atomic systems by choosing an appropriate phase, $\Phi_{\kappa,\lambda}(r)$, with different asymptotic phase-shifts, $\eta_{\kappa,\lambda}$, but also ionic charges, $Z$. Close to the core, the imaginary part of the wave packet will go to zero (it will not diverge like the irregular solution [75]). The polarization of the bound states is clearly visible in Fig. [12] as a “bump” in the imaginary part. Using the asymptotic approximation, we neglect this short-range feature, which turns out to be an excellent approximation for laser-assisted photoionization, as we shall discuss in Sec. 5. The asymptotic form of the wave packet [90] can be also expressed in terms of the Coulomb Green’s function [91, 92]. In the special case of an hydrogenic system, exact calculations can be performed by using compact representations of the Coulomb Greens function [93, 94]. Furthermore, the wave packet can be related to the so-called perturbed wavefunction, which satisfies a corresponding inhomogeneous, time-independent differential equation [53, 57]. In this sense, the wave packet that we have derived using time-dependent perturbation theory is a time-independent quantity, which plays a key role also in time-independent perturbative methods!

4.4 Generalization of first-order photoelectron wave packets

With the help of an integration performed in the complex energy-plane, we have just shown that a monochromatic ionizing XUV field, with frequency $\Omega$, leads to an outgoing photoelectron wave packet: $|\tilde{\Psi}^{(1)}(t; \Omega)\rangle = |\Psi^{(1)}(\Omega)\rangle \exp[-i\omega(\Omega)t]$, which oscillates at the characteristic frequency of energy conservation, $\omega(\Omega) = \omega_i + \Omega$, but with no other time-dependence. Likewise, the effective wave number of the wave packet varies with the photon energy so that the phase of the wave packet (in angular channel $\lambda$) is:

$$\arg \left[ (\hat{n}^{(1)}(t; \Omega) \right] \propto \phi_{\Omega} + \kappa(\Omega)r + \Phi_{\kappa(\Omega),\lambda}(r) - \omega(\Omega)t, \quad (80)$$

where $\phi_{\Omega}$ is the phase of the XUV field, and $\kappa(\Omega)$ is the wave number upon absorption of one such photon with frequency $\Omega$. Any attosecond XUV pulse can be written as a linear superposition of monochromatic waves, and the corresponding photoelectron wave packets can be written in terms of their time-independent (spectral) components,

$$|\tilde{\Psi}^{(1)}(t)\rangle = \frac{1}{2\pi} \int d\Omega \left| \tilde{\Psi}^{(1)}(t; \Omega) \right\rangle$$

$$= \frac{1}{2\pi} \int d\Omega \left| \Psi^{(1)}(\Omega) \right\rangle \exp[-i\omega(\Omega)t], \quad (81)$$

where $\tilde{\Psi}^{(1)}(0; \Omega) \equiv \Psi^{(1)}(\Omega)$. Note that the superposition presented here is different from the one in Eq. (45), because the latter includes a superposition of
both ingoing and outgoing waves, while Eq. (81) only contains outgoing waves. This is due to the fact that we have already imposed a time-boundary condition, namely that the laser field was not on at $t \rightarrow -\infty$. As a consequence, Eq. (81) describes the physical process at all times and for any pulse shape, without the need for time-dependent complex amplitudes to describe the population of the states, as would be required with Eq. (45). The wave packet properties of this superposition can be analysed using the SPA, Eq. (31), because, in the limit of time going to infinity, the oscillations of the phase factor will be fast compared to all pre-factors [79]. The SPA is applied as

$$\tilde{\Psi}^{(1)}(r, t) = \frac{1}{2\pi} \int d\Omega \ a(\Omega) \ \exp[i f(\Omega; r, t)]$$

$$\approx \frac{1}{2\pi} a(\Omega_s) \ \sqrt{\frac{i\pi}{f''(\Omega_s)}} \ \exp[i f(\Omega_s)],$$

where $f(\Omega; r, t) \equiv f(\Omega)$ is the phase function; and $a(\Omega)$ is a pre-factor, which is a slowly varying function of $\Omega$. It contains both the spectral envelope function of the attosecond pulse and the dipole matrix element. As given in Eq. (80), the phase factor for the wave packet (in angular channel $\lambda$) is

$$f(\Omega; r, t) = \phi_\Omega + \kappa(\Omega) r + \Phi_{\kappa(\Omega), \lambda}(r) - \omega(\Omega)t,$$

where $\kappa$ and $\omega$ are determined by energy conservation from an initial bound state after absorbing one photon from the $\Omega$-field. The stationary phase equation, Eq. (32), yields the XUV frequencies, $\Omega_s$, that give the dominant contribution to the electron wave packet at a given space–time position, $(r, t)$ [95]. Using Eq. (83), the solution to the stationary-phase equation gives the time when an electron with wave number $\kappa$ arrives at $r$

$$\frac{\partial f}{\partial \Omega} = \frac{\partial \phi_\Omega}{\tau_{GD}} + \frac{\partial \kappa}{\tau_{free}} + \frac{\partial \Phi_{\kappa(\Omega), \lambda}(r)}{\tau_\lambda + \tau_{LR}(r)} - \frac{\partial \omega}{\partial \Omega} = 0,$$

where we have identified the group delay of the attosecond pulse, $\tau_{GD}(\Omega)$; a free-particle trajectory $\tau_{free} = \nu_c r$; the short-range Wigner delay, $\tau_\lambda$; the long-range Coulomb delay, $\tau_{LR}(r)$; and the actual time itself, $t \gg \tau_{GD}$. This implies that the electron with wave vector $\kappa$ will arrive at $r$ at

$$t = \tau_{GD} + \tau_{free} + \tau_{LR} + \tau_\lambda,$$

which clearly depends on when the appropriate frequency ionized the atom, $\tau_{GD}$; and the time it takes for the electron to propagate to the detector, $\tau_{free} + \tau_{LR} + \tau_\lambda$. If the electron followed a free-particle trajectory the delay would be $\tau_{free}$, but due to the Coulomb interaction the electron is delayed by an additional amount $\tau_{LR}(r) + \tau_\lambda$, corresponding to the long-range and short range corrections to the timing of the trajectory.
The “delay” from the long-range interaction is difficult to interpret, as we already discussed in Sec. 3.3 but we may note that it has a negative sign asymptotically

\[
\tau_{LR}(r) = \frac{\hbar}{\epsilon 2\kappa} \left\{ 1 - \ln(2\kappa r) \right\} \approx -\frac{\hbar}{2\kappa \epsilon} \ln(2\kappa r),
\]  
(86)

which implies that the electron arrives faster than if it was propagating freely! The physical reason is that, as we discussed in relation to Eq. (56), attractive potentials lead to a greater local velocity of the electrons. Also the short-range interaction may have a negative delay, which classically can be interpreted as the electron being somewhat advanced, i.e. starting at a small radial distance,

\[a_{ef} = -\tau_\Lambda/v_c > 0,\]
outside the origin. In the case of the Coulomb potential, the Wigner delays are, however, positive, and such simple arguments do not apply. In the asymptotic limit these corrections are very small compared to the free travel time and can be neglected. This implies that the dominant contribution to the electron wave packet at a given point in space–time \((r, t)\), arises from the part of the wave packet that fulfills the simple relation: \(v_c t \approx r\). We then obtain that the probability density of the photoelectron in an integrated angular channel is

\[\rho(t, r) = |\Psi^{(1)}(r, t)|^2 \sim |a_\kappa|^2 \frac{m}{\hbar},\]
(87)

where \(a_\kappa\) is the complex amplitude of the state with wave number \(\kappa\) and the time-dependence can be understood as a radial quantum diffusion of the wave packet, in good agreement with the simple classical analysis presented above in Eq. (72). This mapping of complex amplitudes into space and time is the basic principle of the TOF detection scheme, which is used in many attosecond experiments. In Fig. 13 we sketch the rough dynamics of photoionization.

(a) \(\rho(x, t)\)  
(t = 0)  
\(x = 0\)  
\(t \to \infty\)  
(b) \(|a_k|^2\)  
\(k_0\)  
\(k\)  
\(x \approx v_0 t\)  
\(x = 0\)  
\(v_0 t\)  
\(k_0\)  
\(k\)  

Fast e\(^{-}\)  
Slow e\(^{-}\)  
TOF  
Propagation  

41
Figure 13: Photoionization in time and space: (a) Initially, at the ionization event $t = 0$, the wave packet is located at the atom. As the electron leaves the atom, the slow part of the wave packet is stretched far away from the fast part due to quantum diffusion. (b) The momentum distribution, $|a_k|^2$, of the wave packet is naturally accessible using a time of flight (TOF) detector, where the probability distribution of fast electrons are detected first, and the slow electrons arrive later. To make this example more interesting, the attosecond pulse has a “cat” encoded in its momentum distribution, this “cat” eventually appears in the space–time distribution. (A more conservative momentum distribution would correspond to the odd harmonics of HHG.)

The photoelectron momentum-to-space mapping, described above, is similar to the frequency-to-time mapping for super-chirped light pulses, which was discussed in Sec. 2.2.3. For photoelectrons, the mapping occurs automatically after long enough times, and there is no need for a dispersive material. Classically, the electron mapping is obvious since electrons in a classical distribution are moving at different speeds. If we know that they all started at a distinct point in space–time, then we know that the fast electrons will reach the detector (at $\vec{r}$) first.

In the case of an APT consisting of high-order harmonics, the photoelectrons from the highest harmonic will arrive first, followed by an empty region and then the next highest harmonic, and so on. The fact that they were ionized at several short instances apart, namely at each peak of the APT, can not be observed directly in TOF spectrometer due to the strong quantum diffusion taking place in the flight tube. In some sense, the signature of the APT or SAP is seen already in the energy and momentum distributions because the electrons do arrive in bursts for each harmonic or in a continuous bunch [96], but in order to access the detailed attosecond time scale, one has to probe the photoelectron wave-packets with a coherent IR laser field. Next, we shall describe different implementations of this concept.

5 Theory of XUV photoionization in the presence of an IR field

As shown in the preceding sections, attosecond delays in photoionization can be deduced from the energy dependence of the phases of the transition amplitudes associated with the process. In the experiments reported so far, an auxiliary IR laser field is used as a “clock” to measure the delays. Then the analysis is somewhat more complicated by the presence of this additional dressing field. Indeed, in the presence of an IR laser field, the photoelectron released upon absorption of one XUV photon can absorb and emit IR photons, thereby changing its energy. Provided that the IR field is weak, the energy of the electron will change as the result of the exchange of only one IR photon at most, so that the overall process amounts to a two-photon transition. In this section, we give a theoretical background relevant to treat this class of laser-assisted photoion-
ization, with special emphasis on the contribution from stimulated continuum–continuum transitions using second-order time-dependent perturbation theory \[^{[82]}\]. These transitions are associated to the so-called Above-Threshold Ionization (ATI) processes, because the electron is already free when it exchanges the second photon.

The time-dependent dipole interaction with the fields, linearly polarized along the \(z\)-axis, is written as \(\hat{V}(z,t) = \hat{V}_{I}(z,t) + \hat{V}_{II}(z,t)\), where we have separated the dipole interaction with the XUV field, \(\hat{V}_{I}(z,t)\) in Eq. \((66)\), from the subsequent dipole interaction with the laser field,

\[
\hat{V}_{II}(z,t) = \int d\Omega \, e^{-i\Omega_{II}t}/2\pi. \tag{88}
\]

With this notation, it is implied that \(\Omega \approx \Omega_{I} > I_p \gg \Omega_{II} \approx \omega\), where the former and latter frequencies correspond to the central frequency of the XUV and laser field, respectively. We may include a broad bandwidth, \(\Delta\Omega_{I}\) and \(\Delta\Omega_{II}\), on both fields, provided that the bandwidths do not overlap. The second-order complex amplitude for the time-ordered interaction with \(\hat{V}_{I}(t)\) and \(\hat{V}_{II}(t)\) is:

\[
a^{(2)}_{f}(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} dt' \sum_{\alpha} \langle \tilde{f}(t') | V_{II}(z,t') | \tilde{\alpha}(t') \rangle a^{(1)}_{\alpha}(t')
\]

\[
\equiv \frac{1}{i\hbar} \int_{-\infty}^{t} dt' \langle \tilde{f}(t') | V_{II}(z,t') | \tilde{\Psi}^{(1)}(t') \rangle, \tag{89}\]

where we have identified the first-order wave packet from Eq. \((81)\). It is of interest to compare the second-order complex amplitude, Eq. \((89)\), with the first-order one, as given in Eq. \((65)\). In the latter, the electron makes a transition from the initial bound state into the field-free continuum, creating a first-order wave packet, \(|\tilde{\Psi}^{(1)}(t)\rangle\). In the second order amplitude, this first-order wave packet can be seen as the initial state for the second interaction, and the transition towards the final state will occur towards a different continuum state. We can write the second-order wave packet formally as

\[
|\tilde{\Psi}^{(2)}(t)\rangle \equiv \sum_{\alpha} a^{(2)}_{\alpha}(t) |\tilde{\alpha}(t)\rangle, \tag{90}\]

in analogy with Eq. \((64)\) and our task is now to determine the second-order complex amplitudes. After the interactions are over, the S-matrix for the two-photon process, \(S^{(2)}_{f/i} = \lim_{t \to \infty} a^{(2)}_{f}(t)\), can be rewritten as:

\[
S^{(2)}_{f/i} = \frac{e}{\hbar} \int_{-\infty}^{\infty} dt \, \exp\left[i(w_f - \Omega_{II} - \omega_c(\Omega_I))t\right], \tag{91}\]

43
where we have expanded the time-dependent quantities as Fourier integrals over frequency, using Eq. (81) and (66), and where we have changed the order of integration so that all time-dependence is trapped in a simple inner integral. This time-integral is identified as a delta function that enforces energy-conservation of the two-photon process, and it is now used to eliminate the spectral integral over $\Omega_{II}$ so that the final result becomes:

$$S_{f/i}^{(2)} = \frac{e}{i\hbar} \frac{1}{2\pi} \int d\Omega_I \langle f|z|\Psi^{(1)}(\Omega_I) \rangle \ E_{II}(\Omega_{II}),$$

(92)

where $\Omega_{II} = \omega_f - \omega_i - \Omega_I$. This corresponds to the well-known S-matrix for two-photons, here derived assuming a general bandwidth on both fields.

The two-photon S-matrix, Eq. (92), has an intuitive time-independent interpretation: The integral over $\Omega_I$ can be seen as an integral over all the different quantum paths that can lead to the final state $|f\rangle$. In order to reach this specific final state, the photon energies of the XUV and IR fields must satisfy a global energy conservation requirement. If both interactions have a broad bandwidth then there is also a broad range of photon-pairs available. This results in a “blurring” effect that arises from the convoluted quantum paths. If one of the fields, say the probe, is quasi-monochromatic: $\Omega_{II} = \pm \omega$, which implies that $\Delta\Omega_{II} \ll |\omega|$, the effects of this convolution are negligible. Specializing to the dominant contributions associated to the transitions taking place when an XUV photon is absorbed first, only two distinct quantum paths are possible:

$$S_{f/i}^{(a)} = \frac{e}{i\hbar} E^{(a)} \langle f|z|\Psi^{(1)}(\Omega_c) \rangle$$

$$S_{f/i}^{(e)} = \frac{e}{i\hbar} E^{(e)} \langle f|z|\Psi^{(1)}(\Omega_>) \rangle,$$

(93)

where $E^{(a)} = E_{II}(\omega)$ and $E^{(e)} = E_{II}(-\omega) = E^{*}_{II}(\omega)$, corresponding to absorption (a) and emission (e) of a laser photon from the fields as depicted in Fig. 14. Note that the intermediate XUV photon energy is different in the two paths to ensure global energy conservation.
Figure 14: Photon-diagrams for laser-assisted photoionization: Single XUV-photon absorption contributes with a direct path (d) to the final state. The dominant two-photon processes involve the absorption or emission of a laser photon indicated by paths (a) and (e). Higher-order processes involve the exchange of more laser photons.

Here, the photoelectron undergoes ATI transitions that require a precise representation of the continuum states, which makes ab-initio computations a formidable task for multi-electron atoms or molecules. However, as we shall show next, it is feasible to derive a convenient approximation method designed to evaluate the phase-shift induced by the continuum–continuum transition stage of the process. An accurate determination of these phases are, in fact, essential to interpret correctly the delays as measured in recent attosecond time-delay experiments.

5.1 Asymptotic approximation for ATI transition amplitudes

In order to obtain an estimate for the phase of the two-photon matrix element, we will rely on an approximation, which utilizes the asymptotic forms of the final state and the first-order wave packet [46, 54]. Both these wave functions are of continuum character, with positive energies, and their phase-shifts can be derived from their asymptotic behaviour in the limit of a large radial distance, \( r \). Atomic units are used in this section for compactness: \( \hbar = m = e = 1/(4\pi\epsilon_0) = 1 \). Specializing to the case of a hydrogenic system with nuclear charge \( Z \), the approximate form of the two-photon matrix element for a given photon-pair, \( (\Omega, \omega) \), becomes

\[
S^{(2)}_{k/i} \approx i\pi(8\pi)^{3/2}E_\omega E_\Omega \langle R_{K,\lambda}|r|\rangle_{n,i,\ell,i} \\
\times \sum_{L,M} (-i)^L e^{i\eta_{k,L}(k)} Y_{L,M}(\hat{k}) \times \sum_{\lambda,\mu} \langle Y_{L,M}|Y_{1,0}|\rangle_{\lambda,\mu} \langle Y_{1,0}|Y_{\mu,0}|\rangle_{\lambda,\mu} \times N_k N_{\kappa} \int_0^{\infty} dr \sin[kr + \Phi_{k,L}(r)] \, r \exp\{i(\kappa r + \Phi_{k,L}(r))\},
\]

where we have performed a partial-wave expansion with the final state having an asymptotic momentum, \( \hat{k} \), using Eq. (69); and where we have replaced the exact form of the radial wave functions by their asymptotic forms. The radial functions are written with the short-hand notation for the Coulomb phase-shift,

\[
\Phi_{k,L}(r) = \frac{Z \ln(2kr)}{k} + \eta_{k,L} - \frac{\pi L}{2},
\]

as defined in Eq. (58), where \( \eta_{k,L} = \sigma_{k,L} + \delta_{k,L} \). Here \( \sigma_{k,L} = \text{arg}\{\Gamma[L+1-iZ/k]\} \) is the pure Coulomb phase with \( \Gamma[z] \) being the complex gamma function; and \( \delta_{k,L} \) is a phase-shift due to an additional short-range interaction. The wave numbers of the first-order wave packet, \( \kappa \), and of the final state, \( \hat{k} \), satisfy
energy conservation after one XUV photon: $\epsilon_\kappa = \epsilon_i + \Omega$, and after the exchange of one IR photon: $\epsilon_k = \epsilon_\kappa \pm \omega$, respectively. Following Ref. [54], we evaluate the radial integral and obtain:

$$S_{\vec{k}/i} \approx -\frac{\pi}{2} (8\pi)^{3/2} E_\omega E_\Omega N_k N_\kappa$$

$$\times \frac{(2\kappa)^{Z/\kappa} \Gamma[2 + iZ(1/\kappa - 1/k)]}{(2k)^{Z/k} (\kappa - k)^{Z(1/\kappa - 1/k)}}$$

$$\times \frac{1}{|k - \kappa|^2} \exp \left[ -\frac{\pi Z}{2} \left( \frac{1}{\kappa} - \frac{1}{k} \right) \right]$$

$$\times \sum_{L = \ell_i, \ell_i \pm 2} Y_{L,m_i}(\hat{k}) \sum_{\lambda = \ell_i \pm 1} \langle Y_{L,m_i}|Y_{1,0}|Y_{\lambda,m_i}\rangle$$

$$\times \langle Y_{\lambda,m_i}|Y_{1,0}|Y_{\ell_i,m_i}\rangle \langle R_{n,\lambda}|r|R_{n,\ell_i}\rangle i^{-\lambda} e^{i\eta(\kappa)}.$$  (96)

Reading this equation from below, the XUV dipole transition from the initial state, $|i\rangle = |n_i, \ell_i, m_i\rangle$, to the intermediate state, $|\vec{k}\rangle$, is found on line five. The fourth line contains the trivial angular part of the second dipole transition from $|\vec{k}\rangle$ to $|\vec{\kappa}\rangle$, while the radial part of this continuum–continuum transition is divided into two factors on line two and three. On the third line, the pre-exponential factor: $1/|k - \kappa|^2$, is characteristic for free-free transitions [89]. If the IR frequency is relatively small as compared to the kinetic energy of the photoelectron, namely in the soft-photon limit, we have $\kappa \approx k - \omega/k$, so that $1/|k - \kappa|^2 \approx k^2/\omega^2$, which makes clear that the transition amplitude increases for high electron momenta, as well as in the soft-photon limit, $\omega \to 0$.

Because we consider transitions between Coulomb states, the transition amplitude contains also a real exponential that depends on the nuclear charge, $Z$, together with $\kappa$ and $k$. More interestingly, the second line is complex and it depends on the same three quantities, thus, introducing a new phase-shift into the matrix element. Note that these correction factors are universal since they depend neither on the angular momentum nor on the short-range atomic interactions. Finally, the first line contains some pre-factors, such as the electric field amplitudes and normalization constants of the wavefunctions associated to the relevant electronic states.

To address the question of the phase of the two-photon matrix element, one notices that besides a trivial contribution from the spherical harmonic in the final state, $Y_{L,m_i}(\hat{k})$, it contains only phase-shifts that are governed by the angular momentum $\lambda$ of the intermediate state, i.e. a state that can be reached via single-photon ionization. More precisely, for a given transition channel (characterized by the angular momenta of the intermediate and final state: $\ell_i \to \lambda \to L$), the phase of the matrix element reduces to:

$$\arg[S_{\vec{k}/i}^{(L,\lambda,m_i)}] = \pi + \arg[Y_{L,m_i}(\hat{k})] + \phi_\Omega + \phi_\omega$$

$$- \frac{\pi \lambda}{2} + \eta_\lambda(\kappa) + \phi_{cc}(k, \kappa),$$  (97)

where $\phi_\Omega$ and $\phi_\omega$ are the phases of the XUV field, $\Omega$, and of the IR laser, $\omega$, respectively.
respectively, and where the \textit{continuum–continuum phase} can be approximated by

\[
\phi^{(P)}_{cc}(k, \kappa) \equiv \arg \left\{ \frac{(2\kappa)^{iZ/\kappa}}{(2k)^{iZ/k}} \Gamma \left[ iZ(1/\kappa - 1/k) \right] \right\} , \tag{98}
\]

corresponding to the argument of line \textit{2} in Eq. (96). The superscript, \((P)\), indicates that this result is obtained when using long-range \textit{phases} of the type in Eq. (95). The continuum–continuum phases for absorption and stimulated emission of one IR laser photon are shown in Fig. 15.

![Figure 15: Continuum–continuum phases: ATI phase-shifts for absorption (a) of one 800 nm laser photon; and for stimulated emission (e) of one laser photon, in a Coulomb potential with \( Z = 1 \). The asymptotic approximation (P) provides the correct qualitative behaviour, while the long-range amplitude corrections (P+A and P+A’) lead to quantitative agreement, at high enough energy, with the exact calculations in hydrogen (+ and \( \times \)). We stress that the final state scattering phase, \( \eta_L(k) \), cancels out and that it enters neither in Eq. (96) nor in Eq. (97).]

5.1.1 \textit{Long-range amplitude corrections}

So far, we have established that the “long-range phases”, \( i.e. \) the logarithmic divergence of the Coulomb phases in Eq. (95), is important for the phase of ATI transitions in an ionic potential of charge \( Z \). In order to improve our asymptotic approximation, we must include also long-range amplitude-variations. We do this by returning the normalization constants \( N_k \) and \( N_\kappa \) back inside the
radial integral in Eq. (94), and write them as functions $N_k(r)$ and $N_\kappa(r)$ for the radial amplitude variations \[54\]. In analogy with the local momentum from WKB theory, as stated in Eq. (50), these effects can then be approximated by expanding the normalization factors, so that

$$N_k(r)N_\kappa(r) \equiv \sqrt{\frac{2}{\pi p_k(r)}} \sqrt{\frac{2}{\pi p_\kappa(r)}} \approx \sqrt{\frac{4}{\pi^2 k_\kappa}} \left[ 1 - \frac{1}{2} \left( \frac{1}{k^2} + \frac{1}{\kappa^2} \right) \frac{Z}{r} \right]$$

(99)

to first-order in the Coulomb potential. It is also possible to recover a similar asymptotic form of the Coulomb functions by using the iterative formulas in Ref. \[80\], i.e. without the need for a semi-classical approximation. Including this correction term, the continuum–continuum phase becomes:

$$\phi_{cc}^{(P+A)}(k, \kappa) \equiv \arg \left\{ \left( \frac{(2\kappa)^{i\frac{Z}{\kappa}}}{(2k)^{i\frac{Z}{k}}} \frac{\Gamma[2 + iZ(1/\kappa - 1/k)]}{(\kappa - k)^{iZ(1/\kappa - 1/k)}} + \gamma(k, \kappa) \right) \right\}$$

(100)

where the additional term is

$$\gamma(k, \kappa) = iZ \frac{(k - \kappa)(k^2 + \kappa^2)}{2k^2 \kappa^2} \Gamma[1 + iZ(1/\kappa - 1/k)]$$

(101)

with Eq. (100) corresponding to the long-range phase and amplitude data (P+A) in Fig. 15. We note that this amplitude correction leads to an excellent agreement with the exact calculation at high energies. The Taylor expansion in Eq. (99) is, however, problematic because the Coulomb potential will dominate over the kinetic energy close to the core, $Z/r > \epsilon_k$ as $r \to 0$, which implies that the expansion is invalid for $r < Z/\epsilon_k$. This leads to an artificial divergence of the electron wavefunction close to the core, which is physically unreasonable because the wavefunction should vanish at $r = 0$.

Because an accurate analytical expression for the continuum–continuum phase can be a valuable tool in the analysis of experimental data, we may try to avoid the region close to the core, by an ad-hoc mathematical trick, namely by changing the starting point of the radial integral. Indeed, the result presented as (P+A’) in Fig. 15 is slightly better, where the gamma function in Eq. (101) was replaced by an incomplete gamma function represented by an integral with an imaginary starting point, $r_0 = iZ(1/k^2 + 1/\kappa^2)/4$. (We note that this “regularization procedure” is slightly more systematic than the procedure presented in Ref. \[54\], but the best matching point was found by trial-and-error.) Strictly speaking, at very low kinetic energy, typically below 10 eV, the asymptotic approximation starts to break down. Physically, this is due to an increasing influence of the Coulomb potential for slow electrons. Mathematically, this is expected since the asymptotic expressions for Coulomb function have $kr$ as arguments, which implies that a small $k$ will lead to a “good” asymptotic wavefunction only at a large distance $r$ from the core \[50\].
5.2 Extracting time-delay information from laser-assisted photoionization signals

Having established the asymptotic approximation for the complex amplitudes of ATI processes, we now turn to the probability for the emission of a photoelectron with energy $\epsilon_k = \epsilon_i + \Omega$, as depicted in Fig. 14. The probability is given by the square of the sum of the amplitudes:

$$P_k \approx |S_d + S_a + S_e|^2$$

$$= |S_d|^2 + |S_a|^2 + |S_e|^2 + 2R\{S_d^*S_a + S_a^*S_e\}.$$ \hspace{1cm} \text{(102)}

where $d, a$ and $e$ label the paths associated to the lowest-order processes: (d), (a) and (e) in Fig. 14. The total probability depends on the relative phase of all individual quantum paths and the maximal probability for photoemission occurs when all paths are in phase, $\text{arg}[S_d] = \text{arg}[S_a] = \text{arg}[S_e]$. In experiments, the phase of the two-photon amplitudes labelled (a) and (e) can be controlled by changing the sub-cycle delay, $\tau$, between the probe field and the attosecond pulses. More precisely, one controls the relative phase of the IR field, $\phi_{\pm \omega} \equiv \pm \omega \tau$ in Eq. (97), with respect to the group delay of the XUV pulse. The probe-phase dependence is $S_a \propto E_\omega \propto \exp[i\omega \tau]$ and $S_e \propto E_\omega^* \propto \exp[-i\omega \tau]$. This implies that the cross-terms in Eq. (102) vary differently as a function of $\tau$: (d)-(a) and (d)-(e) are modulated with periodicity $\omega \tau$ associated to the exchange of only one IR photon [97]; while the cross-term (a)-(e) is modulated with periodicity $2\omega \tau$ due to the two IR photons involved [32, 33].

The latter transitions are directly involved in the RABITT scheme, since path (d) does not contribute. This is because only odd XUV harmonics are used to photoionize the atom, as was indicated in Fig. 5, so that the signal from cross-term (a)-(e) occurs at zero-background. Let us emphasize that in the case of a SAP of XUV radiation, the delay-dependent modulation of the photoionization signal at the central energy $\Omega_0$, will also be given by the cross-term (a)-(e) alone, because the other two cross-terms cancel with each other [54]. All the cross-terms in Eq. (102) together form the on-set of streaking, i.e. a small constructive or destructive interference at the high or low momentum respectively, so that the average momentum of the photoelectron is deflected by different amounts depending on $\tau$. Provided that the soft-photon approximation is valid, the displacement of this entire structure for a laser-assisted SAP is exactly equal to that of APT [54]. Therefore, the maximal probability for photoemission occurs when the amplitudes associated to paths (a) and (e) are in phase, $\text{arg}[S_a] = \text{arg}[S_e]$, which is equivalent to

$$\phi_{\Omega_>} + \omega \tau + \eta_\lambda(\kappa_<) + \phi_{cc}(k, \kappa_<) =$$

$$\phi_{\Omega_<} - \omega \tau + \eta_\lambda(\kappa_>)+ \phi_{cc}(k, \kappa_<)$$ \hspace{1cm} \text{(103)}

where we have used the explicit phases of the relevant two-photon matrix elements in Eq. (97), assuming one dominant intermediate angular channel, with
angular momentum $\lambda$; and momenta $\kappa_<$ and $\kappa_>$ corresponding to absorption of photon $\Omega_<$ and $\Omega_>$, respectively. The solution to Eq. (103) is:

$$\tau = \frac{\tau_{GD}}{2\omega} + \frac{\eta_\lambda(\kappa_>) - \eta_\lambda(\kappa_<)}{2\omega} \frac{\phi_{\kappa_>(k, \kappa_>) - \phi_{\kappa_<(k, \kappa_<)}}{\tau_\lambda} + \frac{2\omega}{\tau_{\kappa_>}},$$  

(104)

where we observe that the probe-delay, $\tau$, that maximizes the yield is a sum of three delays:

- $\tau_{GD}$: the group delay of the XUV field is when the attosecond pulse arrived on target, i.e. when the fields $\Omega_<$ and $\Omega_>$ added constructively at the atom.

- $\tau_\lambda$: the Wigner delay is the “delay” in single-photon ionization, i.e. an asymptotic temporal-shift of the photoelectron wave packet. Strictly speaking, this delay is interesting, i.e. giving information on the electron dynamics, only in difference with a Coulomb reference, e.g. hydrogen with $\eta_\lambda^H(\kappa) \equiv \sigma_\lambda(\kappa) = \arg \{ \Gamma[1 + \lambda - i/\kappa] \}$. In this way, we may say that the photoelectron is delayed by $\tau_\lambda - \tau_\lambda^H$, as compared to hydrogen.

- $\tau_{cc}$: the continuum–continuum delay, i.e. a measurement-induced delay due the electron being probed by an IR laser field in a long-range potential with a Coulomb tail of charge $Z$. This delay can be traced back to the phase-shifts of the ATI matrix elements.

We stress that the delays presented in Eq. (104) are calculated from the finite-difference approximations to the actual derivatives, $\tau_{GD} = \partial \phi_{\Omega_<}/\partial \Omega$ and $\tau_\lambda = \partial \eta_\lambda/\partial \Omega$. For these approximations to be valid, we must require that the spectral phases vary slowly, e.g. that $|\Delta \phi_{\Omega_<}| \equiv |\phi_{\Omega_>} - \phi_{\Omega_<}| \ll 2\pi$, corresponding to a small phase variation over two laser photons, $\Delta \Omega = 2\omega$. Using the framework presented in Sec. 2.1.1, one can easily show that these slowly varying phases imply that the frequency components of the attosecond pulse must be confined to within a fraction of the laser period. In this sense, “slow reactions”, e.g. resonances, which induce a dramatic phase jump in the spectral domain are difficult to study using the conventional RABITT scheme. In the case of streaking, the delays arise also as finite-difference approximations to the actual delays, but here the smallest energy difference is instead one laser photon, $\Delta \Omega = \omega$. The atomic delays, $\tau_\theta = \tau_\lambda + \tau_{cc}$, are shown in Fig. [6] corresponding to the case of hydrogen, with $\tau_\lambda$ for a few different values of the angular momentum, $\lambda$. 

50
In this way, it is possible to “measure” the group delay of the attosecond pulse provided that the atomic delay: \( \tau_\theta = \tau_\lambda + \tau_{cc} \), can be calculated accurately and that it is subtracted from the experimental data. The first observation of attosecond pulse structures in 2001 was made in this way by subtracting the influence of the “atomic phase” as calculated by means of complex two-photon matrix elements [31]. We stress that the exact temporal structure of the attosecond pulse is not measured directly, neither with the RABITT nor with the attosecond streak-camera technique, but that the influence of the atomic potential tends to decrease at high kinetic energy. The question of the precise determination of these “atomic delays” (also called “streaking delays”) and of their importance in RABITT and streaking measurements has motivated a large number of theoretical studies, see Ref. [98, 99, 100, 101, 102, 103, 104, 105, 106]. Much of this recent work has focused on the attosecond streak-camera technique, where typically non-perturbative approaches are employed to account for high-order photon processes with the probe field. In the next subsection, we will also comment on the influence of such an intense probe field with a view-point from perturbation theory using the asymptotic approximation.

Alternatively, the Wigner-like delay, \( \tau_\lambda \), can be determined if \( \tau_{GD} \) is known from independent measurements and if \( \tau_{cc} \) can be calculated [46, 54]. However, since the precise characterization of the attosecond pulse requires the previ-
uous knowledge of \( \tau_{\lambda} \), it would seem that we have run into an uncomfortable circular argument. Instead, if the “same” attosecond pulse is used to photoionize simultaneously different atomic states, information about the differences in atomic delays, \( \tau_{\theta} = \tau_{\lambda} + \tau_{cc} \), can be obtained directly in the experiment, without any need to know the temporal structure of the attosecond pulse \[45, 46\].

Then, by simply subtracting the universal \( \tau_{cc} \) as given by Eq. (104), the \( \tau_{\lambda} \)-difference between the two photoelectrons is obtained. A similar separation of the time-delays as shown in Eq. (104) was reported by the group of Burgdörfer for streaking of SAP by solving numerically the TDSE \[104, 105\]. Interestingly, they also showed that \( \tau_{cc} \) [there called: “the Coulomb-laser coupling”] could be calculated from a classical ensemble of electrons interacting simultaneously with both the laser field and the Coulomb potential. Prior to these successful demonstrations of the separability of the two contributions, the influence of the short-range scattering phase-shifts was shown by Yakovlev and coworkers \[99\] and the importance of the long-range Coulomb tail was discussed by Zhang and Thumm \[102\].

5.3 Towards higher probe intensities

So far the discussion has been conducted within a perturbative framework, by retaining the lowest-order contributions from the IR probe field. A natural task is then to investigate the consequences of an increased probe-field intensity. Numerical evaluations of the TDSE show that a strong probe field will alter the temporal information \[58\]. A modest increase of the probe intensity will, however, not alter the observed delay. This stability of the delay at low-intensity probe fields was first pointed out by Zhang and Thumm \[100\] within the Eikonal-Volkov Approximation \[53\] by considering a weak probe field.

Using perturbation theory for the interaction with the probe field makes it difficult to draw conclusions about the strong-probe field interaction, but it is possible to apply the asymptotic approximation, Eq. (94), also for processes involving additional probe photons. In Fig. 14 the complex amplitudes involving two probe photons are labelled: (d\textsubscript{ae}), (d\textsubscript{ea}), (aa) and (ee). Here, (d\textsubscript{ae}) and (d\textsubscript{ea}) can be regarded as corrections to the direct path (d), because they exchange two probe photons so that the total energy is unchanged. Any such “probe-photon loops”, indicated by grey rings in Fig. 14 involve two continuum–continuum transitions: \( k \rightarrow \kappa \rightarrow k \). Therefore, they acquire two continuum–continuum phases: \( \phi_{cc}(k, \kappa) \) and \( \phi_{cc}(\kappa, k) = -\phi_{cc}(k, \kappa) \), which compensate each other. For instance, the phase of (d\textsubscript{ae}) and (d\textsubscript{ea}) is equal to that of the direct path (d) [except for trivial perturbation expansion coefficients]. The two other paths (aa) and (ee) yield a new probability modulations at \( 4\omega\tau \), due to the four photons involved in the (aa)-(ee) cross-term, and they will not disturb the lower-order modulations. One can show that the modulation shift of the (aa)-(ee) cross-term will be approximately equal to that of the (a)-(e) cross-term, so that no fundamentally new information is obtained at this higher-modulation rate, as reported in the experimental work by Swoboda and co-workers \[107\]. In this way, including additional probe-photon loops, one can argue for the validity
of Eq. (104), also when higher-order contributions become important, at least while the probe-interactions remain in the perturbative regime and the bound states are not too much dressed.

In the following section, we will review the state-of-the-art experimental efforts to measure these delays in laser-assisted photoionization. As we will see, there are so-far few experimental results to compare with the theoretical predictions, and in addition, these experimental data points are located in highly complex regions, \textit{e.g.} close to pseudo-resonances in Neon \cite{106} and correlation-induced Cooper minima in Argon \cite{108}, where the SAE approximation is likely to break down.

6 Experimental observations of attosecond delays in photoemission

The approximations for laser-assisted photoionization described in Sec. 5 hold very well for atomic systems, where the photoelectron can be described within the SAE approximation. In fact, the accuracy of the asymptotic approximation was first bench-marked by comparison with exact calculations in hydrogen carried out by R. Täib \cite{46, 54}. The experimental work on photoionization time-delays, on the other hand, is carried out on many-electron systems, most often noble gas atoms such as Neon and Argon. The question then arises to which degree the SAE approximation is valid for these systems, and especially so when the photoelectron is released, not from the outer-most orbital, but from “inside” the core. Screening effects due to electron correlation can be accounted for using many-body perturbation theory (MBPT), such as the random-phase approximation (RPA), or more elaborate methods \cite{101, 105, 106, 108}, but we have not considered such corrections here. We predict, however, that in the coming years, the interpretation of attosecond experiments will offer a new testing ground for many-body calculations. Future experiments will provide interesting opportunities to test various theoretical methods, such as MBPT, for light-induced electron-electron interactions in connection to measurements of phases and delays in complex atomic and molecular systems. At this point, we report that a satisfactory agreement between theory and experiment has not yet been reached, and that more experiments are needed in “simple” energy regions, where perhaps more straight-forward analysis would apply. In the following, we will proceed with a brief overview of the current experimental efforts. We will place special emphasis on the time-delay measurements and phase measurements using APT, where we have taken active part, but we will also discuss the experiments using SAP. We stress that both approaches aim at measuring the so-called atomic delays \cite{31}, and that the one-photon Wigner delay can be accessed only after subtracting the continuum-continuum delay as computed by either the quantum mechanical or classical approaches \cite{103, 104}. 

53
6.1 Atomic-delay measurements using APT

A delay of 110 as between the 3p and 3s states in Argon has been measured experimentally by Klünker and co-workers using an APT with a photon energy of $\sim 35$ eV [46]. Theoretically, this delay is identified as a difference of atomic phases between two orbitals. These concepts in laser-assisted photoionization dates back to the first measurements of attosecond pulses in 2001 using RABITT [31, 33], but the “atomic delays”, by themselves, had never been accessible experimentally before due to the simultaneously unknown GD of the attosecond pulses. A breakthrough in measuring these atomic delays was possible due to the new way that the experiment was performed, where two RABITT scans were recorded simultaneously from two different initial orbitals. Interestingly, in this setup, the unknown temporal structure of the attosecond pulses can be subtracted without ever knowing their exact shape, as can be understood by considering Eq. [104]. While the experiments is distinctly different, the method was inspired by the previous delay-measurements using SAP [44, 45]. A schematic illustration of the experiment is shown in Fig. [17].

![Schematic illustration of the experiment](image-url)
Figure 17: Delay experiment for the 3s and 3p states in Ar using APT: The APT is composed of three odd harmonics, \(2q + 1\), that ionize (pump) electrons from either initial state, 3s or 3p, into the continuum. After absorbing a harmonic photon, the photoelectron can either absorb or emit a laser probe photon in order to reach an even number sideband (SB) state, labelled by \(2q\). The SB probability oscillates with the delay APT-IR delay, \(\tau\), due to interference between the two quantum paths. Information about the attosecond timing is found in the relative modulation offset between the same sideband numbers from different initial states [46].

In this work, the high-order harmonic comb was first passed through a thin Chrome foil acting as a band-pass to separate four odd harmonics (21-27). In this way, only three sidebands, SB: 22, 24, 26, were produced when ionizing argon atoms from either orbital. This limiting of the harmonic comb was made to prevent different sidebands from different orbitals to overlap in photoelectron kinetic energy. The analysis of the experiment [46] was first carried out within the SAE approximation using Hartree-Fock phase-shifts from the literature [55], an adequate theoretical method for photoelectrons from the outer orbital, 3p. On the other hand, photoelectrons from the inner orbital, 3s, couple strongly with the outer orbital, and the corresponding single-photon phase-shifts are greatly altered. This important effect was identified by Kheifets by including RPA effects in the absorption of a single XUV-photon. Interestingly, these photoelectrons exhibit a correlation-induced minimum in the one-photon ionization step, i.e. a complex kind of Cooper minimum [84], with a corresponding peak of several hundreds of attoseconds in the atomic delay [108]. This is, indeed, a challenging spectral region, where several quantum paths can interfere, and the results become difficult to interpret theoretically.

The signal can also be strongly altered by atomic resonances. In the spectral domain, an APT corresponds to harmonics that can be “aimed” towards specific energy regions of interest. The frequency of the harmonics from the HHG process can be tuned naturally by changing the fundamental (driving) laser pulse frequency, \(\omega + \delta\omega\), so that the high-order harmonic frequencies increase or decrease by \(\delta\Omega = (2q + 1)\delta\omega\). Swoboda et al. found that the phase of the modulation of the lowest-lying sideband in Helium depended critically on the frequency of the harmonics [109]. In Fig. 18, an illustration of the principle of the experiment is shown.
The observed modulation-shifts were attributed to a phase effect occurring over the intermediate bound state, 1s3p1P1, which was “on resonance” with a below-threshold harmonic, 15\hbar\omega < I_p^{(He)}. The modulation-shift was then compared to the corresponding case in Argon, where the harmonic instead directly creates a photoelectron, 15\hbar\omega > I_p^{(Ar)}, and where the bound-states do not contribute considerably. By tuning the harmonic over the sharp resonance, an abrupt \pi-shift is expected. The experimental \pi-shift is, however, “smoothed” due to the finite duration of the laser probe field and of the APT (∼30 fs), which is much shorter than that of the long-lived bound state. In order to fully resolve the abrupt rise of the delay due to pure atomic effects, one needs harmonics that are more narrow in frequency than the atomic resonance, i.e. an APT which is longer that the lifetime of the state. Similar phase-shifts have also been found and analysed at short-lived complex continuum resonances in Nitrogen molecules [110, 111]. In this case, the life-times are more comparable to the duration of the APT, implying that observed modulation-shifts contain some information of about the lifetime of the resonances.
6.2 Atomic-delay measurements using SAP

It was for a long time believed that the so-called “attosecond streak-camera”\cite{35}, provided a direct link between the time-domain and the energy-domain, as often illustrated by measuring the oscillations of few-cycle optical light pulses\cite{39}. This standpoint needed to be revised after an experiment by Schultze and co-workers, where it was stated that “the zero of time in atomic chronoscopy is currently tainted with an error of up to several tens of attoseconds”\cite{45}, due to a measured time-delay of $\sim 20$ as between the streaked photoelectrons from the $2p$ and $2s$ shells in Neon at an XUV photon energy of 100 eV. The key to obtaining this intriguing experimental result was to collect simultaneously two streaked photoelectron spectrograms from two different initial atomic states, thus accessing the difference in streaking delay between the two processes. Interestingly, by measuring this difference in timing, the unknown GD of the attosecond pump pulse cancels out, because it is the same in both processes, as can be identified using Eq. (104). The experimental results motivated a great deal of further theoretical work, where it was concluded that the long-range Coulomb tail is responsible for a considerable part of the observed delay in streaking\cite{100,102,104}. In addition to this long-range effect, the laser-induced polarization of the atom can lead to a shift of the streaking delay if the probe field is too strong\cite{53,98}. Extensive theoretical work including many multi-electron effects have so far only accounted for a fraction of the experimental time-zero shift\cite{101,106}. The theory of the attosecond streak-camera has been refined to account for the long-range Coulomb tail by matching the asymptotic wavefunction to the appropriate scattering phase\cite{103}, but these modifications are controversial as they go against Eq. (104), as is also stressed in Ref.\cite{105}. More experimental results from other systems than Neon, are required to compare with these new theoretical models.

In conclusion, the attosecond pump–probe schemes using a SAP or APT, Fig. 4 (b) and (c) respectively, can be used to obtain information about the probe field-dressed system, and not directly the probe-free system. To explore properties of the unprobed system using experimental data where the probe is present, a theoretically reliable way of accounting for the probe must be found\cite{46,104}. By decreasing the intensity of the probe field, the streaking modulation is reduced and one arrives in a regime where standard perturbation theory is applicable\cite{54}. This presents a large advantage for quantitative theoretical work, since it can be based on well-established MBPT.

6.3 Other attosecond time-delay experiments

Finally, in this subsection we briefly discuss other attosecond delay experiments that are not directly related to single-photon ionization by an XUV field. This important class of attosecond experiments are conducted in the HHG cell directly, and they are sometimes referred to as self-probing systems, see Ref.\cite{112} for a recent tutorial on self-probing of molecules with HHG. In these experiments, the electron wave packet in the continuum is thought of as a probe for
the entire system, holding promise of simultaneous temporal and spatial resolution of molecular dynamics [50]. In this subsection, we will restrict ourselves to one of the simplest self-probing systems, namely, atoms undergoing HHG in two-colour laser fields consisting of a strong fundamental, $\omega$, and a much weaker, parallel second harmonic, $2\omega$. An interesting aspect of this two-colour setup, is that the presence of the second harmonic breaks the inversion symmetry of the HHG process, which leads to the production of odd and even harmonics [113, 114, 115]. A phase-difference (or time-delay) in the intensity modulation of different even harmonics was observed as a function of the delay between the $\omega$ and $2\omega$ fields. Early experimental and theoretical work suggested that the phase of this modulation could be used to characterize the emission times of attosecond pulses [21, 56, 116]. Experimentally, it was eventually found that the phase behaved in an unexpected way close to the harmonic cut-off [117], which, after some more detailed calculations [72], lead to a new interpretation of the observed delays with, instead, a connection to the Keldysh tunnelling parameter [118].

The delay in tunnelling ionization has been studied by the group of Keller using angular streaking, often referred to as the “attoclock” [119, 120, 121]. In this setup, a close-to-circularly polarized femtosecond laser field is used to tunnel-ionize electrons. Subcycle resolution is obtained by studying angular displacements of the final momentum of the photoelectrons. Using this angular streaking method a vanishing tunnelling delay has been confirmed. We need to stress the differences between the two kinds of streaking: The conventional form of streaking requires a SAP and a femtosecond probing laser field with linear polarization, while the angular streaking requires only a single femtosecond pulse with a tailored polarization. In regular streaking, temporal information about laser-assisted, single-XUV-photon ionization is gained; while in the case of angular streaking, the temporal aspects of strong-field (multi-photon) tunnelling is studied. The theoretical work presented in Ref. [121] highlights the difficulties and prospects of self-probing systems involving electron continuum probes initiated through strong-field tunnelling.

7 Conclusions and outlook

Attosecond science is attracting a great deal of attention because it promises accurate control and probing of electron processes in atomic and molecular systems in real time. In this tutorial, we have presented a detailed theoretical analysis of photoionization of neutral atoms by attosecond XUV pulses and coherent XUV high-order harmonics. We have found that, indeed, attosecond pulses can be used to initiate photoionization at well-defined times, but to probe such an ultra-fast event requires careful considerations about the quantum mechanical interactions between the photoelectron and the remaining ion. Ultimately, it is commonly believed, that the probing process will be carried out using a second attosecond pulse, but such experiments are demanding due to the need for two-photon processes in the XUV range. We refer the reader to Ref. [51] for
a state-of-the-art experimental scheme using XUV for both pumping and for probing the processes on a time-scale bordering the attosecond domain.

At the present time, the temporal aspects of photoionization are more often probed by a phase-locked, IR-laser field. This has the advantage of a much stronger interaction with the photoelectron, in fact, here the interaction can be so strong that many such laser photons are absorbed. This situation is called “streaking” because it can shift the photoelectron momentum distribution to higher or lower values depending on the subcycle delay between the attosecond pulses and the probe field. This highly non-linear process is difficult to handle with high-fidelity in theory, and this is the main reason why we have considered instead the interaction with a moderate probe field, which may induce exchange of a single IR-laser probe photon at most.

Such moderate probe fields are the standard choice in the temporal probing of APT using the RABITT scheme. We have demonstrated [54] that this interferometric interpretation is valid also for SAP in the on-set of streaking. Using this “photon-picture”, we have identified the phases of the lowest-order quantum paths and we have shown that the same temporal information about the photoionization process is gained with either pulse structure, SAP or APT.

Placing an interpretation on the “delay” in laser-assisted photoionization, is not as straight-forward as indicated by the early streak-camera formalism [36]. This is because the strong-field approximation is not a reliable approximation for laser-assisted photoionization. Instead, it turns out that the long-range interaction between the photoelectron and the remaining ion leads to a shift of the time-delays [100], which often dominates over the one-photon, Wigner-like delays of the photoelectron [99]. Using time-dependent perturbation theory, we have shown that these “measurement artifacts” can be separated from the Wigner-like delays, as written explicitly in Eq. (104), in the case of both APT [46] and SAP [104]. Furthermore, we have shown that these temporal artifacts can be traced back to phase-shifts in ATI transition-matrix elements between continuum states, hence the name “continuum–continuum phases” [54]. We have here presented both correction curves and analytical expressions for the purpose of correcting for such artifacts in the quest for the true delay in single-photon ionization.

In this tutorial, we have limited ourselves to the SAE approximation, with a single photoelectron in a static atomic potential. While this approach is certainly valid for hydrogenic systems [54], it is likely to break down in many-electron atoms, when electron–hole interactions are strong and when the electron relaxation plays an important role for the dynamics. Here, accurate calculations that include multi-electron screening effects of the ion are required. Although a few full-scale simulations have been made including many-electron dynamics [101, 106], a conclusive agreement between experiment and theory is yet to be presented. This calls for both more experimental data and detailed theoretical work, and then a careful comparison of the two. In this way, the time-delay experiments provide an important testing ground for more exact analysis and interpretations in attosecond physics and strong-field physics. Only when understanding these detailed ultra-fast phenomena, will “attophysics” truely provide
a route to accurate control and probing of electron processes in atomic and molecular systems in real time.

Acknowledgements:

This research was supported by the Marie Curie program ATTOFEL (ITN), the European Research Council (ALMA), the Joint Research Programme ALADIN of Laserlab-Europe II, the Swedish Foundation for Strategic Research, the Swedish Research Council, the Knut and Alice Wallenberg Foundation, the French ANR-09-BLAN-0031-01 ATTO-WAVE program, COST Action CM0702 (CUSPFEL). Parts of the computations have been performed at IDRIS, and part of the work was carried out at the NORDITA workshop: “Studying Quantum Mechanics in the Time Domain”, in Stockholm. I (J.M.D.) would like to thank University Lecturer Johan Mauritsson for guidance and discussions during my PhD-studies in Lund and for his comments on the manuscript; CNRS Research Director Richard Taïeb for performing the exact computations on hydrogen in Fig. 15 and for this comments on the manuscript; Diego Guénot for stimulating discussions and for help with preparing Fig. 1 and also Dr. K. Klünder, Dr. M. Gisselbrecht and the attophysics-group in Lund. I thank Dr. T. Carette for proof-reading the manuscript and I thank Professor Eva Lindroth for discussions about electron-correlation effects.

References

[1] See for instance: W. Pauli. General Principles of Quantum Mechanics, Springer, Berlin p. 63 (1980) or J. J. Sakurai. Modern Quantum Mechanics. Addison-Wesley Publishing Co. p. 68 (1994).

[2] **P. Agostini and L. F. DiMauro. The physics of attosecond light pulses. Rep. Prog. Phys 67, 813 (2004).

[3] *P. B. Corkum and F. Krausz. Attosecond Science. Nature Physics 3, 381 – 387 (2007).

[4] *M. F. Kling and M. J. J. Vrakking Attosecond Electron Dynamics doi: 10.1146/annurev.physchem.59.032607.093532

[5] ***Ferenc Krausz and Misha Ivanov. Attosecond physics. Rev. Mod. Phys. 81, 163–234 (2009).

[6] A. McPherson, G. Gibson, H. Jara, U. Johann, T. S. Luk, I. A. McIntyre, K. Boyer and C. K. Rhodes. Studies of multiphoton production of vacuum-ultraviolet radiation in the rare gases. J. Opt. Soc. Am. B 4, 595 (1987).

[7] M. Ferray, A. L’Huillier, X. F. Li, G. Mainfray and C. Manus. Multiple-harmonic conversion of 1064 nm radiation in rare gases. J. Phys. B 21, L31 (1988).
[8] D. Strickland and G. Mourou. Compression of amplified chirped optical pulses. Opt. Commun. 56, 219 (1985).

[9] Z. Chang, A. Rundquist, H. Wang, M. M. Murnane and H. C. Kapteyn. Generation of Coherent Soft X Rays at 2.7 nm Using High Harmonics. Phys. Rev. Lett. 79, 2967 (1997).

[10] Ch. Spielmann, N. H. Burnett, S. Sartania, R. Koppitsch, M. Schnürl, C. Kan, M. Lenzner, P. Wobrauschek and F. Krausz. Generation of Coherent X-rays in the Water Window Using 5-Femtosecond Laser Pulses. Science 278, 661 (1997).

[11] M. Schnürl, Z. Cheng, M. Hentschel, F. Krausz, T. Wilhein, D. Hambach, G. Schmahl, M. Drescher, Y. Lim and U. Heinzmann. Few-cycle-driven XUV laser harmonics: generation and focusing. Appl. Phys. B 70, S227 (2000).

[12] A. Paul, R. A. Bartels, R. Tobey, H. Green, S. Weiman, I. P. Christov, M. M. Murnane, H. C. Kapteyn and S. Backus. Quasi-phase-matched generation of coherent extreme-ultraviolet light. Nature 421, 51 (2003).

[13] E. A. Gibson, A. Paul, N. Wagner, R. Tobey, D. Gaudiosi, S. Backus, I. P. Christov, A. Aquila, E. M. Gullikson, D. T. Attwood, M. M. Murnane and H. C. Kapteyn. Coherent Soft X-ray Generation in the Water Window with Quasi-Phase Matching. Science 302, 95 (2003).

[14] E. Seres, J. Seres, F. Krausz and C. Spielmann. Generation of Coherent Soft-X-Ray Radiation Extending Far Beyond the Titanium L Edge. Phys. Rev. Lett. 92, 163002 (2004).

[15] R. W. Boyd. Nonlinear Optics. Academic Press (2003).

[16] J. L. Krause, K. J. Schafer and K. C. Kulander. High-order harmonic generation from atoms and ions in the high intensity regime. Phys. Rev. Lett. 68, 3535 (1992).

[17] **P. H. Bucksbaum, R. R. Freeman, M. Bashkansky and T. J. McIlrath. Role of the ponderomotive potential in above-threshold ionization. J. Opt. Soc. Am. B 4, 760 (1987).

[18] J. Tate, T. Auguste, H. G. Muller, P. Salieres, P. Agostini and L. F. DiMauro. Scaling of Wave-Packet Dynamics in an Intense Midinfrared Field. Phys. Rev. Lett. 98, 013901 (2007).

[19] H. Kapteyn, O. Cohen, I. Christov and M. Murnane. Harnessing Attosecond Science in the Quest for Coherent X-rays. Science 317, 775–778 (2007).

[20] T. Popmintchev, M. C. Chen, O. Cohen, M. E. Grisham, J. J. Rocca, M. Murnane and H. C. Kapteyn. Extended phase matching of high harmonics driven by mid-infrared light. Opt. Lett. 33, 2128–2130 (2008).
[21] G. Doumy, J. Wheeler, C. Roedig, R. Chirla, P. Agostini and L. F. DiMauro. Attosecond Synchronization of High-Order Harmonics from Midinfrared Drivers. Phys. Rev. Lett. 102, 093002 (2009).

[22] **P. B. Corkum. Plasma perspective on strong-field multiphoton ionization. Phys. Rev. Lett. 71, 1994 (1993).

[23] *M. Lewenstein, Ph. Balcou, M.Yu. Ivanov, A. L’Huillier and P. B. Corkum. Theory of high-order harmonic generation by low-frequency laser fields. Phys. Rev. A 49, 2117 (1994).

[24] **M. Lewenstein, P. Salières and A. L’Huillier. Phase of the atomic polarization in high-order harmonic generation. Phys. Rev. A 52, 4747 (1995).

[25] P. Salières, B. Carré, L. Le Déroff, F. Grasbon, G. G. Paulus, H. Walther, R. Kopold, W. Becker, D. B. Milošević, A. Sanpera and M. Lewenstein. Feynman’s Path-Integral Approach for Intense-Laser-Atom Interactions. Science 292, 902 (2001).

[26] R. P. Feynman. Space-Time Approach to Non-Relativistic Quantum Mechanics. Rev. Mod. Phys. 20, 367–387 (1948).

[27] **M. B. Gaarde, J. L. Tate and K. J. Schafer. Macroscopic aspects of attosecond pulse generation. J. Phys. B 41, 132001 (2008).

[28] G. Farkas and C. Tóth. Proposal for attosecond light pulse generation using laser induced multiple-harmonic conversion processes in rare gases. Phys. Lett. A 168, 447 (1992).

[29] S. E. Harris, J. J. Macklin and T. W. Hänsch. Atomic scale temporal structure inherent to high-order harmonic generation. Opt. Commun. 100, 487 (1993).

[30] Ph. Antoine, A. L’Huillier and M. Lewenstein. Attosecond Pulse Trains Using High-Order Harmonics. Phys. Rev. Lett. 77, 1234 (1996).

[31] ***P. M. Paul, E. S. Toma, P. Breger, G. Mullot, F. Augé, Ph. Balcou, H. G. Muller and P. Agostini. Observation of a train of attosecond pulses from high harmonic generation. Science 292, 1689 (2001).

[32] *V. Véniard, R. Taïeb and A. Maquet. Phase dependence of (N+1)-color (N>1) ir-uv photoionization of atoms with higher harmonics. Phys. Rev. A 54, 721 (1996).

[33] ***H. G. Muller. Reconstruction of attosecond harmonic beating by interference of two-photon transitions Appl. Phys. B 74, S17 (2002).

[34] *M. Hentschel, R. Kienberger, Ch. Spielmann, G. A. Reider, N. Milosevic, T. Brabec, P. Corkum, U. Heinzmannß, M. Drescher and F. Krausz. Attosecond metrology. Nature 414, 509 (2001).
[35] **J. Itatani, F. Quéré, G. L. Yudin, M. Yu Ivanov, F. Krausz and P. B. Corkum. *Attosecond Streak Camera*. Phys. Rev. Lett. 88, 173903 (2002).

[36] *Y. Mairesse and F. Quéré. Frequency-resolved optical gating for complete reconstruction of attosecond bursts. Phys. Rev. A 71, 011401(R) (2005).

[37] ***A. Baltuška, Th. Udem, M. Uiberacker, M. Hentschel, E. Goulielmakis, Ch. Gohle, R. Holzwarth, V. S. Yakovlev, A. Scrinzi, T. W. Hänsch and F. Krausz. *Attosecond control of electronic processes by intense light fields*. Nature 421, 611 (2003).

[38] *E. Goulielmakis, M. Schultze, M. Hofstetter, V. S. Yakovlev, J. Gagnon, M. Uiberacker, A. L. Aquila, E. M. Gullikson, D. T. Attwood, R. Kienberger, F. Krausz and U. Kleineberg. *Single-Cycle Nonlinear Optics*. Science 320, 1614 (2008).

[39] **E. Goulielmakis, M. Uiberacker, R. Kienberger, A. Baltuska, V. Yakovlev, A. Scrinzi, T. Westerwalbesloh, U. Kleineberg, U. Heinzmann, M. Drescher and F. Krausz *Direct Measurement of Light Waves*. Science 305, 1267 (2004)

[40] I. J. Sola, E. Mével, L. Elouga, E. Constant, V. Strelkov, L. Poletto, P. Villloresi, E. Benedetti, J.-P. Caumes, S. Stagira, C. Vozzi, G. Sansone and M. Nisoli. *Controlling attosecond electron dynamics by phase-stabilized polarization gating*. Nature Phys. 2, 319 (2006).

[41] I. J. Sola, A. Zaïr, R. López-Martens, P. Johnsson, K. Varjú, E. Cormier, J. Mauritssson, A. L’Huillier, V. Strelkov, E. Mével and E. Constant. *Temporal and spectral studies of high-order harmonics generated by polarization-modulated infrared fields*. Phys. Rev. A 74, 013810 (2006).

[42] Zenghu Chang. *Controlling attosecond pulse generation with a double optical gating*. Phys. Rev. A 76, 051403 (2007).

[43] *H. Mashiko, S. Gilbertson, C. Li, S. D. Khan, M. M. Shakya, E. Moon and Z. Chang. Double optical gating of high-order harmonic generation with carrier-envelope phase stabilized lasers*. Phys. Rev. Lett. 100, 103906 (2008).

[44] ***A. L. Cavalieri, N. Müller, Th. Uphues, V. S. Yakovlev, A. Baltuška, B. Horvath, B. Schmidt, L. Blümel, R. Holzwarth, S. Hendel, M. Drescher, U. Kleineberg, P. M. Echenique, R. Kienberger, F. Krausz and U. Heinzmann. *Attosecond spectroscopy in condensed matter*. Nature 449, 1029 (2007).

[45] ***M. Schultze, M. Fie, N. Karpowicz, J. Gagnon, M. Korbman, M. Hofstetter, S. Nepp, A. L. Cavalieri, Y. Komninos, Th. Mercouris, C. A. Nicolaides, R. Pazourlec, S. Nagele, J. Feist, J. Burgdörfer, A. M. Azzeer, R. Ernstof-fer, R. Kienberger, U. Kleineberg, E. Goulielmakis, F. Krausz and V. S. Yakovlev. *Delay in Photoemission*. Science 328, 1658–1662 (2010).
[46] K. Klünder, J. M. Dahlström, M. Gisselbrecht, T. Fordell, M. Swoboda, D. Guénot, P. Johnsson, J. Caillat, J. Mauritsson, A. Maquet, R. Taïeb, and A. L’Huillier Probing Single-Photon Ionization on the Attosecond Time Scale Phys. Rev. Lett. 106, 143002 (2011)

[47] S. Pedersen, J. L. Herek and A. H. Zewail The Validity of the Diradical Hypothesis: Direct Femtosecond Studies of the Transition-State Structures Science 266 (1994) 1359-1364.

[48] A. H. Zewail The Birth of Molecules Scientific American Dec. 1990 p 40-46.

[49] A. H. Zewail and R. B. Bernstein Real-Time Laser Femtochemistry: Viewing the Transition from Reagents to Products Chemical and Engineering News, 66, 45, 24-43 (1988)

[50] H. J. Worner, J. B. Bertrand, D. V. Kartashov, P. B. Corkum and D. M. Villeneuve, Following a chemical reaction using high-harmonic spectroscopy Nature 466, 604 (2010)

[51] P. Tzallas, E. Skantzakis, L. A. A. Nikolopoulos, G. D. Tsakiris and D. Charalambidis Extreme-ultraviolet pump-probe studies of one-femtosecond-scale electron dynamics Doi: 10.1038/NPHYS2033 (2011)

[52] J. Mauritsson, T. Remetter, M. Swoboda, K. Klünder, A. L’Huillier, K. J. Schafer, O. Ghafur, F. Kelkensberg, W. Siu, P. Johnsson, M. J. J. Vrakking, I. Znakovskaya, T. Uphues, S. Zherebtsov, M. F. Kling, F. Lépine, E. Benedetti, F. Ferrari, G. Sansone and M. Nisoli, Attosecond Electron Spectroscopy Using a Novel Interferometric Pump-Probe Technique Phys. Rev. Lett. 105, 053001 (2010)

[53] O. Smirnova, M. Spanner and M. Y. Ivanov Coulomb and polarization effects in laser-assisted XUV ionization J. Phys. B 39 S323 (2006).

[54] J. M. Dahlström, D. Guénot, K. Klünder, M. Gisselbrecht, J. Mauritsson, A. L’Huillier, A. Maquet and R. Taïeb Theory of attosecond delays in laser-assisted photoionization Chem. Phys. (2012), doi:10.1016/j.chemphys.2012.01.017

[55] A. Maquet and R. Taïeb. Two-colour IR + XUV spectroscopies: the ‘soft-photon approximation’. J. Mod. Opt. 54, 1847–1857 (2007).

[56] J. M. Dahlström, T. Fordell, E. Mansten, T. Ruchon, M. Swoboda, K. Klünder, M. Gisselbrecht, A. L’Huillier, and J. Mauritsson Atomic and Macroscopic Measurements of Attosecond Pulse Trains Phys. Rev. A 80, 033836 (2009)

[57] E. S. Toma and H. G. Muller. Calculation of matrix elements for mixed extreme-ultraviolet-infrared two-photon above-threshold ionization of argon. J. Phys. B 35, 3435 (2002).
[58] J. Mauritsson, M. B. Gaarde and K. J. Schafer. Accessing properties of electron wave packets generated by attosecond pulse trains through time-dependent calculations. Phys. Rev. A 72, 013401 (2005).

[59] O. Svelto. Principles of Lasers. Plenum Press, New York (1998).

[60] A. L’Huillier, X. F. Li and L. A. Lompré. Propagation effects in high-order harmonic generation in rare gases. JOSA B 7, 527–536 (1990).

[61] A. Dalgarno and A. E. Kingston. The Refractive Indices and Verdet Constants of the Inert Gases. Proceedings of the Royal Society of London Series A-Mathematical and Physical Sciences 259, 424 (1960).

[62] B.L. Henke, J.C. Davis, E.M. Gullikson and R.C.C. Perera. A Preliminary Report on X-Ray Photoabsorption Coefficients and Atomic Scattering Factors for 92 Elements in the 10-10,000 eV Region. Lawrence Berkeley National Laboratory (1988).

[63] E. M. Gullikson B. L. Henke and J. C. Davis. X-ray interactions: photoabsorption, scattering, transmission, and reflection at E=50-30000 eV, Z=1-92,. Atomic Data and Nuclear Data Tables 54(no.2), 181–342 (1993).

[64] C. Kittel. Introduction to Solid State Theory. John Wiley and Sons (1996).

[65] K. Varjú, Y. Mairesse, B. Carre, M. B. Gaarde, P. Johnsson, S. Kazamias, R. Lopez-Martens, J. Mauritsson, K. J. Schafer, Ph. Balcou, A. L’Huillier and P. Salières. Frequency chirp of harmonic and attosecond pulses. J. Mod. Opt. 52, 379 (2005).

[66] K. Varjú, Y. Mairesse, P. Agostini, P. Breger, B. Carré, L. J. Frasinski, E. Gustafsson, P. Johnsson, J. Mauritsson, H. Merdji, P. Monchicourt, A. L’Huillier and P. Salières. Reconstruction of Attosecond Pulse Trains Using an Adiabatic Phase Expansion. Phys. Rev. Lett. 95, 243901 (2005).

[67] O. E. Martinez, J. P. Gordon and R. L. Fork. Negative group-velocity dispersion using refraction. J. Opt. Soc. Am. B 1, 1003 (1984).

[68] R. López-Martens, K. Varjú, P. Johnsson, J. Mauritsson, Y. Mairesse, P. Salières, M. B. Gaarde, K. J. Schafer, A. Persson, S. Svanberg, C.-G. Wahlström and A. L’Huillier. Amplitude and phase control of attosecond light pulses. Phys. Rev. Lett. 94, 033001 (2005).

[69] E. Gustafsson, T. Ruchon, M. Swoboda, R. López Martens, Ph. Balcou and A. L’Huillier. Broadband attosecond pulse shaping. Optics Letters 32, 1353–1355 (2007).

[70] M. Y. Ivanov, M. Spanner and O. Smirnova. Anatomy of strong field ionization. Journal of Modern Optics 52, 165–184 (2005).
[71] C. C. Chirilă and I. Dreissigacker and E. V. van der Zwan and M. Lein. *Emission times in high-order harmonic generation* Phys. Rev. A 81 033412 (2010)

[72] J. M. Dahlström, A. L’Huillier and J. Mauritsson *Quantum Mechanical Approach to Probing the Birth of Attosecond Pulses using a Two-Color Field* J. Phys. B 44, 095602 (2011)

[73] H. J. Weber and G. B. Arfken. *Essential Mathematical Methods for Physicists*. Elsevier Academic Press (2004).

[74] J. Mauritsson, P. Johnsson, E. Mansten, M. Swoboda, T. Ruchon, A. L’Huillier and K. J. Schafer. *Coherent Electron Scattering Captured by an Attosecond Quantum Stroboscope*. Phys. Rev. Lett. 100, 073003 (2008).

[75] H. Friedrich. *Theoretical atomic physics*. Springer (1994).

[76] J. Trost and H. Friedrich *WKB and exact wave functions for inverse power-law potentials* Phys. Lett. A 228 (1997) 127-133

[77] E. P. Wigner. *Lower Limit for the Energy Derivative of the Scattering Phase Shift*. Phys. Rev. 98, 145–147 (1955).

[78] F. T. Smith. *Lifetime Matrix in Collision Theory*. Phys. Rev. 118, 349–356 (1960).

[79] C. A. A. de Carvalho and H. M. Nussenzveig. *Time delay*. Physics Reports 364, 83 – 174 (2002).

[80] M. Abramowitz and I. A. Stegun *Handbook of Mathematical Functions With Formulas, Graphs, and Mathematical Tables* National Bureau of Standards, Applied Mathematics Series 55.

[81] E. W. Weisstein. *MathWorld*, [http://mathworld.wolfram.com/](http://mathworld.wolfram.com/)

[82] J. J. Sakurai. *Modern Quantum Mechanics*. Addison-Wesley Publishing Co. (1994).

[83] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Nonrelativistic Theory* 3rd edition, Pergamon Press, Oxford (1977); §136.

[84] J. W. Cooper. *Photoionization from Outer Atomic Subshells. A Model Study*. Phys. Rev. 128, 681 (1962).

[85] D. J. Kennedy and S. T. Manson. *Photoionization of the Noble Gases: Cross Sections and Angular Distributions*. Phys. Rev. A 5, 227 (1972).

[86] P. Kruit and F. H. Read. *Magnetic field paralleliser for 2π electron-spectrometer and electron-image magnifier*. J. Phys. E 16, 313 (1983).
[87] A. T. J. B. Eppink and D. H. Parker. *Velocity map imaging of ions and electrons using electrostatic lenses: Application in photoelectron and photofragment ion imaging of molecular oxygen*. Rev. Sci. Instr. 68, 3477 (1997).

[88] M. J. J. Vrakking. *An iterative procedure for the inversion of two-dimensional ion/photoelectron imaging experiments*. Rev. Sci. Instr. 72, 4084 (2001).

[89] *R. D. Mattuck, A Guide to Feynman Diagrams in the Many-Body Problem* 2nd edition, Dover Publications, inc., New York (1992)

[90] *M. Aymar and M. Crance, Theory of two- and three photon ionisation of helium atoms* J. Phys. B 13, 2527 (1980)

[91] B. A. Zon, N. L. Manakov, and L. P. Rapoport, *Sov. Phys. Doklady* 14 904 (1970).

[92] M. Edwards, X. Tang and R. Shakeshaft, *Multiphoton absorption by alkali-metal atoms above the ionization threshold. II. Further results on Cs and Rb ionization* Phys. Rev. A 35, 3758 (1987).

[93] A. Maquet. *Use of the Coulomb Green’s function in atomic calculations*. Phys. Rev. A 15, 1088–1108 (1977).

[94] A. Maquet, V. Véniard and T. A. Marian, *The Coulomb Green’s function and multiphoton calculations*. J. Phys. B 31, 3743 (1998).

[95] *M. Wollenhaupt, A. Assion, D. Liese, Ch. Sarpe-Tudoran, T. Baumert, S. Zamith, M. A. Bouchene, B. Girard, A. Flettner, U. Weichmann and G. Gerber. Interferences of Ultrashort Free Electron Wave Packets*. Phys. Rev. Lett. 89, 173001 (2002).

[96] E. Mansten, J. M. Dahlström, J. Mauritsson, T. Ruchon, A. L’Huillier, J. Tate, M. B. Gaarde, P. Eckle, A. Guandalini, M. Holler, F. Schapper, L. Gallmann, and U. Keller *Spectral Signature of Short Attosecond Pulse Trains* Phys. Rev. Lett. 102, 083002 (2009)

[97] *M. Chini, S. Gilbertson, S. D. Khan, and Z. Chang Characterizing ultra-broadband attosecond lasers* Optics Express 18, 13006 (2010)

[98] J. C. Baggesen and L. B. Madsen *Erratum: Polarization Effects in Attosecond Photoelectron Spectroscopy* Phys. Rev. Lett. 104, 209903 (2010)

[99] **V. S. Yakovlev, J. Gagnon, N. Karpowicz and F. Krausz. Attosecond Streaking Enables the Measurement of Quantum Phase*. Phys. Rev. Lett. 105, 073001 (2010).

[100] ***C. H. Zhang and U. Thumm *Electron-ion interaction effects in attosecond time-resolved photoelectron spectra* Phys. Rev. A 82, 043405 (2010).
[101] **A. Kheifets and I. Ivanov Delay in Atomic Photoionization Phys. Rev. Lett. 105, 233002 (2010)

[102] *C. H. Zhang and U. Thumm Streaking and Wigner time delays in photoemission from atoms and surfaces Phys. Rev. A 84, 033401 (2011).

[103] O. Smirnova and M. Y. Ivanov How accurate is the attosecond streak-camera? Phys. Rev. Lett. 107, 213605 (2011)

[104] ***S. Nagele, R. Pazourek, J. Feist, K. Doblhoff-Dier, C. Lemell, K. Tókési and J Burgdörfer Time-resolved photoemission by attosecond streaking: extraction of time information J. Phys. B 44, 081001 (2011).

[105] *S. Nagele, R. Pazourek, J. Feist and Joachim Burgdörfer Time shifts in photoemission from a fully correlated two-electron model system Phys. Rev. A 85, 033401 (2012)

[106] **L. R. Moore, M. A. Lysaght, J. S. Parker, H. W van der Hart and K. T. Taylor Time delay between photoemission from the 2p and 2s subshells of neon Phys. Rev. A 84, 061404 (2011)

[107] M. Swoboda, J. M. Dahlström, T. Ruchon, P. Johnsson, J. Mauritsson, A. L’Huillier and K. J Schafer Intensity dependence of laser-assisted attosecond photoionization spectra Laser Physics 19, 1591 (2009)

[108] D. Guénot, K. Klünder, C. L. Arnold, D. Kroon, J. M. Dahlström, M. Miranda, T. Fordell, M. Gisselbrecht, P. Johnsson, J. Mauritsson, E. Lindroth, A. Maquet, R. Taïeb, A. L’Huillier and A. S. Kheifets Photoemission time-delay measurements and calculations close to the 3s ionization minimum in Ar [arXiv:1204.4009v1 [physics.atom-ph], Accepted for Phys. Rev. A (2012)

[109] ***M. Swoboda, T. Fordell, K. Klünder, J. M. Dahlström, M. Miranda, C. Buth, K. J. Schafer, J. Mauritsson, A. L’Huillier and M. Gisselbrecht Phase Measurement of Resonant Two-Photon Ionization in Helium Phys. Rev. Lett. 104, 103003 (2010)

[110] *S. Haessler, B. Fabre, J. Hignet, J. Caillat, T. Ruchon, P. Breger, B. Carré, E. Constant, A. Maquet, E. Mével, P. Salières, R. Taïeb, and Y. Mairesse Phase-resolved attosecond near-threshold photoionization of molecular nitrogen Phys. Rev. A 80, 011404(R) (2009)

[111] *J. Caillat, A. Maquet, S. Haessler, B. Fabre, T. Ruchon, P. Salières, Y. Mairesse, and R. Taïeb Attosecond Resolved Electron Release in Two-Color Near-Threshold Photoionization of N2 Phys. Rev. Lett. 106, 093002 (2011)

[112] **S. Haessler, J. Caillat, P. Salières Self-probing of molecules with high harmonic generation J. Phys. B 44, 203001 (2011)

68
[113] *J. Mauritsson, P. Johnsson, E. Gustafsson, A. L’Huillier, K. J. Schafer and M. B. Gaarde. Attosecond Pulse Trains Generated Using Two Color Laser Fields. Phys. Rev. Lett. 97, 013001 (2006).

[114] M. V. Frolov, N. L. Manakov, A. A. Silaev and N. V. Vvedenskii. Analytic description of high-order harmonic generation by atoms in a two-color laser field. Phys. Rev. A 81, 063407 (2010).

[115] D. Shafir, Y. Mairesse, H. J. Worner, K. Rupnik, D. M. Villeneuve, P. B. Corkum and N. Dudovich. Probing the symmetry of atomic wavefunctions from the point of view of strong field-driven electrons, New J. Phys. 12, 073032 (2010)

[116] N. Dudovich, O. Smirnova, J. Levesque, Y. Mairesse, M. Yu. Ivanov, D. M. Villeneuve and P. B. Corkum. Measuring and controlling the birth of attosecond XUV pulses. Nature Phys. 2, 781 (2006).

[117] X. He, J. M. Dahlström, R. Rakowski, C. M. Heyl, A. Persson, J. Mauritsson, and A. L’Huillier Interference Effects in Two-Color High-Order Harmonic Generation Phys. Rev. A 82, 033410 (2010)

[118] L. V. Keldysh. Ionization in the Field of a Strong Electromagnetic Wave. Sov. Phys. JETP 20, 1307 (1965).

[119] P. Eckle, A. N. Pfeiffer, C. Cirelli, A. Staudte, R. Dörner, H. G. Muller, M. Büttiker and U. Keller. Attosecond Ionization and Tunneling Delay Time Measurements in Helium. Science 322, 1525–1529 (2008).

[120] P. Eckle, M. Smolarski, P. Schlup, J. Biegert, A. Staudte, M. Schoffler, H. G. Muller, R. Dorner AND U. Keller Attosecond angular streaking Nat. Phys. 4, 565 (2008)

[121] A. N. Pfeiffer, C. Cirelli, M. Smolarski, D. Dimitrovski, M. Abu-samha, L. B. Madsen and U. Keller Attoclock reveals natural coordinates of the laser-induced tunnelling current flow in atoms Nat. Phys. 2125 (2011)