1
Attosecond and XUV Physics: Ultrafast Dynamics and Spectroscopy

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1.1
Introduction

Scientific progress is tied to the observation and modeling of the world. Our ability to observe atomic and molecular matter requires tools beyond our natural senses. Following the development of X-ray techniques, it became possible in the twentieth century in biology and chemistry research to observe static structures, from the macroscopic scale down to the nanoscale and even beyond, with atomic resolution. However, many important material properties are not static, and involve elementary physical processes that occur on ultrafast time scales.

The natural time scale for the motion of atoms in molecules, and therefore for the making and breaking of chemical bonds, is in the femtosecond domain ($1\,\mathrm{fs} = 10^{-15}$ s). The observation of chemical or biological transformations therefore typically requires measurements with femtosecond time resolution. Such observations are only possible with correspondingly short light pulses, which then allow the photo-induced initiation of a process of interest using a short "pump" laser pulse, followed by a stroboscopic observation after a well-defined time delay, using an equally short "probe" pulse. In the last few decades, widely tunable femtosecond laser pulses were developed, allowing the emergence of femtosecond spectroscopy ("femtochemistry") a research field that has meanwhile greatly enriched our understanding of physical, chemical and biological processes. This feat was recognized with the Nobel Prize in Chemistry that was awarded to Ahmed Zewail (Caltech) in 1999 [1].

Photochemical reactions studied by the methods of femtochemistry can commonly be described as making use of the Born–Oppenheimer approximation, where potential energy surfaces describe the energy of all electrons as a function of the atomic coordinates, as well as the resulting forces acting on the atoms. As the atoms move under the influence of these forces, the electrons adiabatically adapt until curve crossings are encountered, where the Born–Oppenheimer approximation breaks down and where the electronic structure may undergo drastic changes on time scales that are however still determined by the atomic motion.

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Purely electronic motion, without involvement of atomic motion, can occur on much faster, attosecond time scales ($1\,\text{as} = 10^{-18}\,\text{s}$), as can be appreciated from the 152 attosecond orbital period of an electron in the Bohr model of atomic hydrogen. Until recently, direct measurements on these time scales were impossible. However, two new ultrafast, extreme ultraviolet (XUV)/X-ray sources, that is, high harmonic generation (HHG) and free-electron lasers (FELs) operating on the basis of self-amplified stimulated emission (SASE), have burst onto the scene in the last decade and are now beginning to provide unprecedented time-resolved access to processes reaching down into the attosecond domain.

It is against this background that the ATTOFEL Initial Training Network was established in 2009 as a training network within the FP7 Marie Curie Program of the European Commission. The acronym ATTOFEL stands for "Ultrafast dynamics using ATTOsecond and XUV Free-Electron Laser sources", expressing ATTOFELs goal of connecting the emerging attosecond and XUV/X-ray FEL scientific communities. ATTOFEL also aims to give scientific training, in the broadest sense, to early stage researchers in this emerging field. The book in front of you is a direct outcome of this training effort and covers material that was presented at an ATTOFEL summer school, organized on the island of Crete in May of 2011, supplemented by a number of additional chapters. In this book, leading scientists in the field of attosecond and XUV/X-ray FEL research provide a comprehensive introduction. The book is intended for new researchers entering the field, while at the same time providing a reference text for researchers that are already active in this research area.

1.2 The Emergence of Attosecond Science

In 2001, two independent research groups around Pierre Agostini at CEA Saclay and Ferenc Krausz at the TU Vienna showed almost simultaneously that attosecond XUV pulses can be created through HHG [2, 3]. These experiments were the result of a decade-long effort aimed towards understanding the dynamics of HHG, and culminating in the realization that HHG might be a viable way to produce attosecond pulses.

In HHG, an intense femtosecond laser, usually a femtosecond Ti:sapphire laser with a central wavelength around 800 nm, is focused on an atomic or molecular gas. As described by Anne L'Huillier in Chapter 10, it was discovered in the late 1980s that XUV radiation can then be produced at laser frequencies that are odd, and in some cases very high multiples of the driver laser frequency (hence the name "high harmonic generation") [4, 5]. The explanation for the process was provided a few years later by Paul Corkum, who proposed a three-step mechanism starting with strong-field ionization of the target gas by the intense femtosecond laser, followed by acceleration of the released electron in the oscillatory electric field of the laser and, finally, a recombination of the accelerated electron with the ionized atom or molecule, where all the laser energy absorbed in order to ionize and accel-

erate the electron is released in the form of an energetic XUV or X-ray photon [6]. One of the early triumphs of the three-step model was its ability to explain the observed high-energy cutoff of HHG spectra given by $E_{\text{cutoff}} \approx \text{IP} + 3.2\,U_{\text{P}}$, where IP is the ionization potential of the target gas and U_{P} the ponderomotive energy, that is, the average kinetic energy of a free electron that is oscillating under the influence of a strong laser field. As Corkum showed using simple classical mechanics applied in the strong field approximation (i.e., neglecting the atomic potential once ionization has taken place, see Chapter 6 by Misha Ivanov), the maximum return energy of an electron that has left a target atom/molecule by tunnel ionization is equal to $3.17\,U_{\text{p}}$, in close agreement with the experimental observations.

The three-step model can also be used to rationalize why HHG leads to the formation of attosecond laser pulses. The initial ionization step is a highly nonlinear process that requires the absorption of a significant number of photons. Therefore, this process strongly favors the maxima of the oscillatory electric field of the laser, in particular at laser intensities where the tunneling picture applies. Consequently, electrons are not continuously being removed from the target atoms/molecules, but are formed in ultrashort bunches that have a duration much smaller than the optical period of the driving laser. The optical period of an 800 nm laser is only 2.7 fs long, and therefore the electron wave packet that is accelerated has a duration that is typically no more than a few hundred attoseconds long. Accordingly, the re-collision of the electron wave packet with its parent ion necessarily leads to attosecond laser pulses [7]. Of course, rationalizing that HHG ought to lead to the formation of attosecond pulses is one thing; to prove that it does is quite another matter, and this was the main accomplishment of the two aforementioned papers published in 2001 [2, 3].

1.2.1
Attosecond Pulse Trains and Isolated Attosecond Pulses

According to the three-step model, the attosecond pulse formation will occur twice during every intense enough cycle of the driving femtosecond laser pulse. In other words, using typical commercially available femtosecond laser pulses with a few tens of femtosecond duration, HHG will have the tendency to form an attosecond pulse train (APT), rather than an isolated attosecond pulse (IAP). This has had several important consequences.

First of all, performing attosecond pump–probe experiments with an APT intuitively seems very problematic. After all, if we use such a train in a pump–probe experiment (where the pump laser initiates the dynamics of interest and the probe laser makes a time-delayed observation of the evolving dynamics), then there is an uncertainty in the time delay between the pump and probe, since we do not know which attosecond pulse in the train has excited or probed the system. In the years since the first demonstration of APTs in HHG [2], attosecond scientists have learned how to deal with this problem, in particular by configuring experiments where the APTs are used in combination with a co-propagating near-infrared (NIR) laser field (typically a replica of the 800 nm femtosecond laser that was used to gen-

erate the APT). Rather than using the pulse envelope of the co-propagating 800 nm laser, the experiments use the optical cycle of this laser as a clock with attosecond time resolution. After all, 12 h on a normal clock correspond to only 2.7 fs on this "attoclock"! Given that the spacing between the attosecond pulses in the APT is exactly half the 800 nm optical period, all attosecond pulses experience the same 800 nm electric field (up to its sign), making time-resolved studies of electron dynamics on sub-fs time scales possible. For example, small time delays between the XUV-induced ionization of different argon atomic orbitals could be characterized in two-color XUV+NIR experiments using an APT [8]. Several examples of these types of experiments are discussed in this book, see, for example, Chapter 13 by Franck Lépine.

Secondly, very extensive efforts have been developed to tailor the HHG process in a manner that rejects all but one of the attosecond pulses that are produced, in order to be able to configure experiments with IAPs. A number of different routes towards the generation of IAPs have been taken [9], and work in this direction continues to this day [10]. The first successful demonstration by the team of Ferenc Krausz used the selection of cutoff harmonics generated in HHG with a very short (7 fs long) 800 nm driver pulse. When the duration of the 800 nm driver pulse is short enough, the highest energies (produced when U_p is highest) will only be produced during a single half-cycle of the driving laser pulse, thereby producing an IAP. In the years since the initial publication, this technique has been perfected, culminating in the reporting of 80 as IAPs in 2008 [11–16]. Alternatively, methods have been developed over the years that have relied on the use of a driving laser pulse with a time-varying polarization [17, 18], use of a two-color laser field [12], use of intensities that very rapidly increase and ionize the medium, leading to transient phase-matching [13], or using combinations of the above. One of the most recent developments has been the "attosecond lighthouse effect" where HHG is performed with a driver pulse with a time-varying wavefront tilt, leading to a situation where IAPs can be extracted from an APT because in the far field they move off in different directions [10, 19].

1.2.2 Characterization of Attosecond Laser Pulses

Somewhat different characterization methods have been developed for APTs and IAPs. A comprehensive overview of these methods is presented by Adam Wyatt in Chapter 3 of this book. The first characterization of APTs used the RABBITT (reconstruction of attosecond harmonic beating by interference of two-photon transitions) method [20], see also Chapter 10 by Anne L'Huillier, and Chapter 11 by Louis DiMauro. Here, a weak co-propagating NIR laser field (typically $\leq 2 \times 10^{11}$ W/cm^2) is used. In the measurement, interferences in two-color XUV+NIR photoelectron sidebands are used to characterize the relative phase of a comb of harmonics, providing a full characterization of the APT when combined with a measurement of the harmonic spectrum.

The characterization of IAPs generally relies on stronger NIR laser fields, and uses the principle of the attosecond streak camera [21]: depending on the delay be-

tween the IAP and a co-propagating, moderately strong (typically 10^{12}–10^{13} W/cm^2) NIR laser field, the photoelectrons resulting from ionization by the IAP will be up- or down-shifted. It has been shown that measuring a complete streaking trace, that is, a complete set of photoelectron spectra as a function of XUV-NIR delay, allows the full characterization of both the IAP [18] and the NIR laser pulse [13]. An example of a streaking measurement may be found in Chapter 12 by Giuseppe Sansone.

1.2.3 Experimental Challenges in Attosecond Science

Although the first experimental demonstration of the formation of an IAP was almost immediately followed by a remarkable demonstration of the use of attosecond techniques to measure the lifetime of highly excited atoms undergoing Auger decay (see [22], discussed in Chapter 12 by Giuseppe Sansone), the first few years after that were largely devoted to improvement of the attosecond pulse production and characterization techniques. To do so was necessary, since the experimental use of attosecond pulses poses a number of major challenges.

Given that attosecond pulses can only be synthesized using wavelengths with an optical period in the attosecond domain, the central wavelength of attosecond pulses is automatically in the XUV/X-ray range, where the development of highly reflective dispersive optics is extremely challenging. Moreover, since XUV radiation is absorbed by all materials, the experiments have to be entirely performed in vacuum. This creates challenges for the separation of the attosecond pulses from the NIR laser that has generated them and for the separation of the attosecond pulses generated via the "short" trajectory from those generated via the "long" trajectory (see Chapter 7 by Olga Smirnova and Misha Ivanov). Moreover, attosecond experiments pose extreme requirements on the stability of optical setups. When one considers that a light pulse travels a distance of 30 nm in 100 as and that in certain types of attosecond setups the "pump" and "probe" lasers travel along separate paths over a distance of several meters, then it becomes clear that active stabilization of optical beam paths is often an absolute necessity to retain the attosecond time resolution. Finally, the attosecond pulses obtained by HHG are typically very weak. The conversion efficiency from NIR to XUV is typically on the order of 10^{-6} in HHG, meaning that millijoule-level 800 nm driver pulses will only lead to nanojoule-level XUV/X-ray pulses. In the approaches used for the generation of IAPs, the efficiency is usually even lower. For this reason, the two color XUV-NIR experiments that were described above were up to now the only attosecond experiments possible. However, this is about to change. In the last few years, significant efforts have been undertaken to increase the pulse energy of attosecond pulses, and – in particular – the pulse energy of IAPs, in attempts to make IAP pump-IAP probe experiments possible [23]. Such experiments are extremely important, since they will allow more facile and reliable tracking of electronic motion over time delays exceeding the NIR optical period. Several laboratories have developed attosecond experiments on the basis of larger scale laser systems delivering 800 nm

pulses with several hundreds of millijoule pulse energy [24, 25]. With these systems IAPs with pulse energies in the 100 nJ range have recently been reported [25], which should be enough for IAP pump-IAP probe experiments. At the same time, as discussed by Uwe Morgner in Chapter 2, novel laser architectures like optical parametric chirped pulse amplification (OPCPA) are being introduced, that deliver 800 nm laser pulses with characteristics (in particular, with pulse durations) that are more favorable for generating IAPs than traditional Ti:sapphire lasers [26]. The first experiment using an IAP both to pump and probe attosecond dynamics has recently been published [27].

1.2.4 Attosecond Science as a Driver for Technological Developments

As can already be understood from the previous paragraph, the development of attosecond science is strongly dependent on developments in, especially, laser technology. Conversely, it may justifiably be stated that many current developments in laser technology are directly motivated by their utility in attosecond science.

At the time that the first attosecond experiments got underway, hollow core fiber compression for the generation of intense few-cycle laser pulses had been shown a few years earlier [28, 29]. Furthermore, the development of frequency combs, allowing the production of pulses with a stable carrier envelope offset (CEO) phase and a reproducible carrier envelope phase (CEP) had just been demonstrated for oscillator lasers producing low power (nanojoule-level) laser pulses [30, 31]. Both of these developments were vital for the development of attosecond science, since both of the methods that were conceived early on for the development of IAPs, that is, selection of cutoff harmonics [3, 32] and polarization gating in order to generate IAPs in the plateau region of high harmonic generation [18], required the availability of high power few-cycle CEP-stable driver pulses for the HHG. A key breakthrough came in 2003, when Baltuska *et al.* published the realization of the first CEP-stable driver laser for HHG, based on chirped pulse amplification (CPA) of the output of a CEP-stable oscillator [12]. This allowed, for the first time, the fully reproducible production of IAPs. Since then, stabilization of the carrier envelope phase has remained a key topic in attosecond science, and therefore this topic is discussed in detail in Chapter 4 by Vincent Crozatier, who furthermore discusses novel CEP stabilization schemes that have been developed in the last few years, which greatly improve the CEP quality [33].

As discussed in Chapter 2 by Uwe Morgner, attosecond science continues to stimulate laser development in a number of important directions. As already stated, the development of IAP pump-IAP probe experiments has motivated the implementation of higher power lasers in attosecond experiments, and a first Terawatt-class CEP-stable CPA Ti:sapphire laser has been reported in the literature [34]. Still, to reach the combination of pulse energies and pulse durations that are desirable for IAP production [26], a shift from Ti:sapphire-based CPA technology to OPCPA appears imminent and is already being actively pursued by a number of laser laboratories around the world. A major advantage of OPCPA is that

the sub-10 fs pulse durations that are a prerequisite for many of the IAP generation schemes can readily be obtained directly from the amplifier, benefitting from the large phase-matching bandwidth in a noncollinear optical parametric amplifier (NOPA). One of the main challenges is the development of suitable picosecond pump lasers for pumping the OPCPA. However, in the last few years a number of ytterbium-based systems have been reported with pulse characteristics that are fully adequate [35, 36], and first OPCPA-based attosecond experiments are likely to be performed very soon.

Another direction for OPCPA that is likely to become very important is the development of high repetition rate amplifier systems. Current Ti:sapphire lasers that are appropriate for use in attosecond science are largely limited to repetition rates $\leq$ 10 kHz, making it extremely challenging to implement detection schemes that rely on coincident detection of multiple particles from a single pump–probe event, such as the electron(s) and ion(s) formed in an ionization event (see Chapter 16 by Artem Rudenko). However, with attosecond experiments addressing increasingly complex systems, the needs for the implementation of such coincident detection schemes has grown substantially in the last few years. Using OPCPA, the development of CEP-stable, high repetition rate, few-cycle drivers that are developed for attosecond science has already been reported and we may anticipate the first pump–probe experiments on attosecond time scales soon [37, 38].

Finally, we would like to draw attention to the development of mid-infrared lasers motivated by attosecond science. As discussed in detail by Louis DiMauro in Chapter 11, the scaling of the photon energy of the attosecond pulses with U_p, allows a dramatic scaling with wavelength, given that $U_p = F_{laser}^2/4\omega_{laser}^2$ (a.u.), where F_{laser} is the peak electric field of the laser and $\omega_{laser} = 2\pi c/\lambda_{laser}$ is the laser frequency. In other words, the ponderomotive energy, and hence the photon energy achievable in HHG, scale quadratically with the laser wavelength. In principle, the efficiency of HHG at longer wavelength scales very unfavorably [39], but this can be overcome to a large extent using appropriate target and phase-matching geometries [40], providing a major impetus for the further development of mid-infrared, OPCPA-based driver lasers for HHG. In fact, the generation of keV X-rays by HHG using a 4 μm driver laser was recently demonstrated [41].

The usefulness of sophisticated, short pulse laser techniques in ultrafast pump–probe experiments is only as good as the characterization of the pulses. To this end, Chapter 3 by Adam Wyatt discusses in detail the wide range of available methods for pulse characterization at both the near-infrared driver wavelengths and in the XUV.

1.3 Applications of Attosecond Laser Pulses

One decade after the first demonstrations of attosecond laser pulses [2, 3], two-color attosecond pump–probe experiments have addressed electron dynamics in atomic [22, 42–45] and molecular physics [46–48], in surface science [49] and in

solid-state physics [50]. In addition, attosecond time scale dynamics has been inferred in a range of strong field laser-induced phenomena [51–54], paving the way to both current and future attosecond experiments.

Along the way, the arsenal of possible observables used in attosecond experiments has been significantly expanded. While many of the experimental implementations of attosecond pump–probe spectroscopy have used photoelectron-based measurements schemes developed for the characterization of attosecond laser pulses (i.e., RABBITT-like detection in the case of APTs and streaking in the case of IAPs), the technique of attosecond chronoscopy, that is, measuring atomic/molecular charge states as a function of delay, has been used for experiments involving multiple ionization, such as experiments where shake-up and/or Auger decay play a role [42, 55]. These experiments are discussed by Giuseppe Sansone in Chapter 12. Another technique that is discussed in this chapter is attosecond transient absorption spectroscopy (ATS), which is rapidly becoming the technique of choice in many attosecond laboratories around the world [43, 56]. In ATS, NIR-induced changes in the XUV transmission through a sample are measured. A major advantage of this method is that the time resolution that can be achieved in the pump–probe experiment and the energy resolution in the absorption measurement are not limited by a Fourier relationship, in other words very high spectral resolution (~ 20 meV) can be combined with very high time resolution (≤ 50 as).

In molecular systems, a main interest is in the attosecond time scale observation and control of intramolecular electronic processes such as charge transfer and charge migration. For this, measurements of charge asymmetries in fragment ion kinetic energy and angular distributions resulting from dissociative ionization have proven to be a useful method, allowing to visualize both coupling of electronic and nuclear degrees of freedom, and correlations in the optical response of multiple electrons [46]. In molecular systems, the development of attosecond experiments has sparked considerable theoretical interest. It has been proposed that attosecond time scale excitation of electronic coherences (e.g., by means of the ultrafast removal of an electron, thereby producing the molecular ion in a coherent superposition of ionic states [57–59]), may lead to migration of the hole in the electron density across the molecular frame, on time scales preceding any nuclear motion, and thereby possibly paving the way for novel control schemes for molecular reactivity [60]. First experiments have recently been performed that may be seen as first steps towards this perspective, which along with an overview of existing results are discussed in detail by Franck Lépine in Chapter 13.

Ionization by an XUV pulse is not the only way that a hole can be produced in the electron density of a molecular wave function. After all, as described by the three-step model, the process of HHG starts with an ionization process itself [6]. In the last few years, the production of multiple electronic states in atomic/molecular strong field ionization [61] in the course of HHG and correspondingly, the creation of rapidly moving holes in the electron density, has been intensively discussed. In fact, working alongside the attosecond science community relying on pump–probe spectroscopy using attosecond pulses, a second "dynamical imaging" research community has developed, where the process of HHG itself is studied in great detail.

Important successes of this work have been tomographic reconstruction of the orbitals that participate in the HHG process [62], the reconstruction of electronic wave packets that exist within HHG from the time that the photoelectron leaves the atom/molecule via tunneling, until the time of the laser-driven electron-ion recombination [63, 64], the extraction of molecular structural information from HHG experiments [65], and the quantitative extraction of the time when an electron exits from the tunneling barrier in a HHG experiment [66]. Against this background Olga Smirnova and Misha Ivanov discuss, in Chapter 7, the quantum-mechanical framework for a theoretical description of HHG, connecting the so-called simple man's model to more sophisticated methods that have been developed in the last few years. In doing so, they also address the role of multiple electrons in the HHG process.

Though not yet studied experimentally in attosecond pump–probe experiments, multielectronic (plasmonic) aspects are of the essence in experiments on nanoparticles and nanostructures that are discussed by Matthias Kling in Chapter 14. Nanoparticles and nanostructures allow both spatial and temporal tailoring of light fields on, respectively, nanometer length scales and (sub)-femtosecond time scales. In combination with the field enhancement effects that are intrinsic to these structures, this offers the promise of important implications in nanotechnology relevant to ultrafast computation and telecommunication. Already, plasmonic effects have been exploited in above threshold ionization (ATI) from nanoparticles [52] and nanoscale metal tips [53], and although very controversially discussed, in HHG from bowtie arrays [67] and three-dimensional metal nanostructures [68]. The possibility to visualize the nanoplasmonic field through streaking of photoelectrons is discussed in the chapter and is an active field of research.

1.4
Ultrafast Science Using XUV/X-ray Free Electron Lasers

As discussed in Section 1.2, one of the main challenges in attosecond science is the relatively low pulse energy, which makes it very challenging to perform attosecond pump-attosecond probe experiments. Moreover, although scaling of HHG techniques to keV photon energies has shown considerable progress in the last few years [41], the photon energies where HHG is used in pump–probe experiments so far tend to remain quite significantly below the energies required for the ionization of core shell electrons. For example, HHG in the "water window" region between the carbon K-edge at 284.2 eV (4.4 nm) and the oxygen K-edge at 543.1 eV (2.3 nm) [69] has been demonstrated, but has not yet been extensively exploited in experiments. These two limitations of HHG, the low pulse energy and the limited tuning range towards high photon energies, are overcome in dramatic fashion by the first SASE XUV/X-ray free-electron lasers (FELs) that have come into operation within the last decade. On these instruments, the interest in the use of XUV/X-ray light is not so much the short optical period that provides access to the generation of attosecond pulses, but the high pulse intensities and high photon

energies, the latter allowing the configuration of diffraction experiments, either using the XUV/X-ray photons directly, or using the XUV/X-ray photons to eject energetic photoelectrons with a short de Broglie wavelength, that can be used to extract structural information [70]. FELs provide unprecedented XUV/X-ray intensities, allowing studies of multiphoton ionization in this wavelength range for the first time.

As we observed in beginning of this introduction, X-ray techniques acquired a great prominence in the twentieth century as a tool for resolving structural information, the main implementation being X-ray diffraction from crystalline materials using synchrotron radiation. The development of XUV/X-ray FELs is driven to a considerable extent by the desire to be able to use X-ray diffraction techniques on systems that cannot be crystallized [71], with the added bonus of time resolution down into the femtosecond domain. Based on this motivation, intensive research efforts have gotten under way around the world to develop X-ray FELs, as well as the science that is made possible by them.

In Hamburg, the Tesla Test Facility (TTF) at DESY became the first operational XUV SASE FEL in 2000. TTF was used for pioneering experiments on Coulomb explosion of rare gas clusters [72], revealing novel ionization mechanisms that had not been observed in NIR-induced Coulomb explosions that had been intensively studied a decade earlier. In 2005, FLASH succeeded TTF as the world's first soft X-ray FEL user facility [73]. At FLASH, the first proof-of-principle experiments on coherent diffractive imaging were performed, showing that the technique can be implemented at FELs, and allowing the imaging of structures with sub-100 nm resolution before irreversible damage of the object under investigation set in [74–76]. Some of the early experiments at FLASH and the conceptual and theoretical framework underlying coherent diffractive imaging are discussed in detail by Willem Boutu in Chapter 17 of this book.

Beside the initial experiments on coherent diffractive imaging, FLASH was used to study the interaction of atoms and molecules with intense XUV light at a fundamental level. As explained in detail by Artem Rudenko in Chapter 15, ionization at high intensity by an XUV/X-ray FEL proceeds according to mechanisms that are radically different from the mechanisms that are at play at NIR wavelengths. For example, the ponderomotive energy, which plays such an important role in the description of NIR laser-induced HHG, is virtually absent at XUV/X-ray wavelengths. Accordingly, ionization processes are best described in a (multi)-photon picture. Besides studies of ionization processes, experiments were also performed at FLASH exploiting the femtosecond time resolution inherent in the source to monitor time-resolved molecular dynamics, and these experiments are discussed as well.

The year 2009 saw the commissioning of the Linac Coherent Light Source (LCLS) in Stanford, the world's first hard X-ray FEL, producing multi-mJ, femtosecond X-ray pulses down to 1.2 Angström (10 keV) [77]. This soon led to major improvements in the resolution that could be achieved in coherent diffractive imaging experiments. First experiments on serial crystallography of nanocrystals were published in 2011, and showed how the accumulation of a large number of single-

shot diffraction patterns enabled retrieval of the structure of Photosystem I with 8 Å spatial resolution [78]. While these initial experiments were performed using a "moderate" photon energy of 1.8 keV, this result has since been improved upon, by using 9.4 keV hard X-ray photons, leading to a spatial resolution of just 2.1 Å [79].

LCLS allowed studies of X-ray laser-induced ionization at unprecedented intensities. These experiments, which are highly relevant for defining the conditions where coherent diffractive imaging experiments are possible, are discussed in detail in Chapter 16 by Linda Young, underscoring the greatly increased importance of inner shell and Auger processes in the ionization at X-ray wavelengths. She also discusses some of the other atomic and molecular physics pursued at LCLS shortly after it came on-line, including efforts to characterize the temporal properties of the LCLS beam.

Since 2011, the SACLA hard X-ray FEL is operational in Japan [80]. Moreover, a number of additional hard X-ray FELs are planned around the world, including the European XFEL in Hamburg that is expected to generate first light in 2015, and the SwissFEL that is expected to come online in 2017. Extending the capabilities of FELs in the soft X-ray range, FERMI@ELETTRA came into operation just before the end of 2010 [81]. A special feature of this FEL is its seeded operation, thereby greatly improving the coherence properties of the source, as well as the synchronization of the FEL with external lasers, which is of crucial importance for pump–probe experiments. Seeding of hard X-ray FELs is also vitally important, and first results were recently obtained at LCLS [82].

Free-electron lasers are clearly "big machines" running at enormous costs and subject to considerable restrictions on the available beam time for individual users. For this reason, efforts to obtain high-energy XUV/X-ray pulses by alternative methods continue to this day. In Chapter 5, Philippe Zeitoun describes ongoing efforts aimed at developing tabletop X-ray lasers to a level where single-shot coherent diffractive imaging becomes possible. He reviews progress that has been achieved in recent years, including the operation of HHG-seeded tabletop X-ray lasers, and describes a roadmap for the development of an approximately 6 mJ, fully coherent X-ray laser, that is, even surpassing what can be achieved at an FEL today.

1.5
The Interplay between Experiment and Theory

The complexity of the atomic and molecular physics that is addressed by the attosecond pump–probe and FEL experiments described above is considerable. Therefore, this book also contains a number of chapters that are devoted to the theoretical methods that are vitally important for understanding the results of experiments that are being performed or that are likely to be performed shortly. The importance of Chapters 6 and 7 by Misha Ivanov and Olga Smirnova, explaining the fundamentals of strong field ionization and the theory underlying high harmonic generation, has already been explained in Sections 1.2 and 1.3. Complementing these chapters, Armin Scrinzi discusses several methods for numerically solving

the time-dependent Schrödinger equation (TDSE) in Chapter 8. He discusses in detail considerations that come into play when one seeks to numerically integrate the TDSE on a grid, as well as the development of a number of methods that deal with multielectron problems by working with a suitable "essential states" basis. An important example is the multiconfiguration time-dependent Hartree–Fock method (MCTDHF), which allows, for example, to assess the role of multielectron effects in HHG.

In view of their increasing importance in many pump–probe experiments, Robert Lucchese and Danielle Dowek discuss in Chapter 9 the formalism for calculating and evaluating photoelectron angular distributions (PADs) in atomic or molecular photoionization. They show how PADs can be completely described in terms of five angular functions, and describe methods that can be used to compute and measure these PADs, including the use of coincident photoelectron-fragment ion detection (leading to molecular frame photoelectron angular distribution (MFPAD), respectively recoil frame photoelectron angular distribution (RFPAD) measurements), and the use of dynamically aligned or oriented molecular samples [83–86]). Using HHG and FEL sources and exploiting the short de Broglie wavelength of high-energy photoelectrons, novel methods for time-resolved femtochemistry may become possible that no longer rely on detailed knowledge of the potential energy surfaces of the molecules under investigation, but that allow the extraction of the time-dependent positions of all atoms through a measurement of holographic interferences [70]. We note that this type of structural information is not exclusively available in XUV-induced photoionization processes, but may also be available when energetic photoelectrons are generated by means of near-infrared or mid-infrared induced strong-field ionization, where first experiments have recently been performed illustrating the possibility of achieving attosecond time resolution [87, 88].

1.6 Conclusion and Outlook

Attosecond and XUV Physics, in the form of ground-breaking experimental work exploiting novel XUV/X-ray sources (both HHG and FELs), and in the form of novel theoretical and numerical methods, provides a new path towards understanding and controlling microscopic light-induced processes, that is, on atomic length scales and on time scales reaching down into the attosecond domain. In this book, mirroring the program of a summer school organized by the ATTOFEL network where the latest progress in this research field was presented, a range of internationally renowned specialists provide a snapshot of the current status of this extremely rapidly developing field. It is our hope that in the next few years, until its contents will be superseded by innovations that currently take place or will take place in laboratories around the world, this book will provide a valuable reference, introducing and inspiring scientists that want to acquaint themselves with this exciting field.

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