

2006 ITAMP WORKSHOP

on X-ray Free-Electron Lasers: Challenges for Theory

FINAL PROGRESS REPORT

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1 Introduction

The development of novel, coherent light sources in the x-ray regime promises to revolutionize how x-rays are used in physics, chemistry, and biology. These novel light sources include both accelerator-based free-electron lasers (soft and, in particular, hard x-rays) and tabletop sources based upon high harmonic generation (XUV and, to some degree, soft x-rays). The revolutionary aspect of the x-ray free-electron lasers (XFELs) is the extremely high peak intensity combined with ultrashort pulse durations.

The flagship project in the United States is the Linac Coherent Light Source (LCLS) [1], which is currently under construction at the Stanford Linear Accelerator Center. The likelihood of new discovery, particularly at inception in 2008, is extremely high. An AMO team of about thirty researchers will get first access to LCLS. Applications of LCLS range from the exploration of x-ray nonlinear effects in matter to the time-resolved structure determination of single molecules. While LCLS will provide much shorter and much more intense x-ray pulses than ever available before, the average x-ray flux will be comparable to that already available at third-generation sources. The European XFEL project [2] will take longer to complete (operation is scheduled to begin in 2014), but will boost the average photon flux by about two orders of magnitude.

Since XFELs will move science into completely uncharted territory, the success of the proposed experiments depends crucially on the support by theory. The purpose of this workshop was to bring experimentalists and theorists together in order to develop a road map for AMO theory related to LCLS and other XFELs in the world. A central goal, to attract theorists that are new to the field, was achieved.

The multidisciplinary nature of this field was reflected in the scientific backgrounds of the workshop participants (AMO physics, accelerator physics, plasma physics, chemical physics, materials science, bio-imaging). It is widely recognized that the insights that may be gained utilizing AMO methods, in particular, lie at the heart of many of the proposed experiments at LCLS and elsewhere. ITAMP was therefore a natural choice to hold this workshop. ITAMP, through a grant from the National Science Foundation, provided financial support, helped with organizational details, and created a stimulating workshop environment. All this contributed significantly to the success of the workshop. On behalf of all workshop participants, we would like to thank ITAMP for making this workshop possible.

In the following, we summarize some of the topics discussed in the workshop.

2 SASE XFELs

The XFELs currently under construction are expected to supply x-ray pulses that are about 10^3 to 10^4 times shorter than the pulses delivered by state-of-the-art synchrotron radiation sources such as the Advanced Photon Source (where a pulse duration of ~ 100 ps is currently the lower limit). Even more impressively, the peak intensity will be 10^9 to 10^{10} times greater, with 10^{12} to 10^{13} x-ray photons per shot. XFELs will, in principle, be broadly tunable x-ray laser sources. For instance, LCLS will cover the photon energy range between 800 eV and 8 keV. (The intensity of the third harmonic, which will push the maximum photon energy to 24 keV, will be about 1 % of the intensity of the fundamental.) The relative spectral line width will be smaller than 10^{-3} .

An FEL is a relativistic electron beam and an electromagnetic wave (the laser light) co-propagating through an oscillating magnetic field. The magnetic field is produced by an approximately 100-m long array of dipole magnets. (This is called an undulator.) A resonance occurs when the electrons slip one optical wavelength λ_r after each undulator period λ_u . λ_r and λ_u are connected via

$$\lambda_r = \frac{\lambda_u}{2\gamma^2}(1 + a^2) .$$

The expression displays the two sources of slippage: 1) the electron speed v is smaller than the speed of light c [$\lambda_u/(2\gamma^2)$, where $\gamma = 1/\sqrt{1 - (v/c)^2}$] and 2) there is slippage due to the wiggling motion through the undulator [the a^2 factor]. The undulator radiation acts back on the electron beam, which causes microbunching (a self-organization effect) through the self-amplified stimulated emission (SASE) process. The resulting coherence length at LCLS will be a few femtoseconds times c . The pulses will be transversely coherent (diffraction limited) and linearly polarized. However, longitudinally they will display a hundred spikes or so in a pulse duration of about 230 fs. Details may be found in the LCLS Design Report [1]. Strategies exist for achieving, with a SASE-XFEL, pulse durations of the order of 1 fs or shorter [3].

The basic physics and operating principles of SASE-FELs were demonstrated at the University of California in Los Angeles [4–6] and later at Argonne National Laboratory [7, 8]. These studies were extended to shorter wavelengths at DESY in Hamburg [9, 10]. It was at DESY, using the Tesla Test Facility FEL operating at a photon energy of around 13 eV, that the enormous potential for interesting science applications of SASE-FELs was demonstrated [11–14]. This stimulated interest from the theory community [15–20].

3 Experiments at FLASH (DESY)

The DESY FEL, now referred to as FLASH, has recently been upgraded and has achieved lasing at 32 nm [21]. The results of some of the first experiments carried out at the new FLASH user facility were presented at this workshop. Four kinds of experiments were discussed.

In the first category, the ionization efficiencies of free argon atoms and argon clusters were compared [22]. The 32-nm radiation pulses were 30 fs long, with a peak intensity of about 2×10^{13} W/cm². Under these conditions, it was observed that ion charge states up to 4+ could be produced in gaseous, cluster-free argon. By contrast, after exposing argon *clusters* to the radiation pulses, no traces of Ar⁴⁺ could be detected. This behavior is fundamentally different from what had been seen at 98 nm [11, 12], where cluster targets produced higher charge states than pure atomic targets did. Photoelectron spectroscopy on Ar clusters at 98 nm revealed thermionic electron emission, which demonstrated that plasma electrons underwent many collisions before leaving the cluster [14]. Using 32-nm radiation, however, the electrons are emitted serially from the clusters and no thermionic electrons could be detected, indicating a fundamentally different photon–matter interaction process [22].

The second category of experiments was based on imaging objects via single-shot XUV diffraction [22, 23]. In diffraction experiments on argon clusters of 32-nm radius, the cluster size could be correctly reconstructed from the scattering image [22]. (About 100 clusters were in the interaction region. It was not a single-molecule experiment.) A combination of the scattering experiments with time-of-flight spectroscopy showed that the cluster ions moved less than 3 Å during exposure to the pulse. Another set of diffraction experiments on microfabricated structures was similarly successful [23]. In each case, the object studied was completely destroyed after its interaction with a FLASH XUV pulse. Nevertheless, the observed diffraction image was apparently sufficiently unperturbed so that the original structure of the object could be determined with a resolution of the order of 10 nm. In the near future, the FLASH photon energy will approach 100 eV. This will make it possible to investigate xenon clusters near the Xe 4*d* giant dipole resonance. An interesting question in this context is the impact of an ionized cluster environment on the Auger decay of an inner-shell hole.

In the third category, pump-probe experiments were performed using the FLASH beam as a pump and as a probe by illuminating spheres atop Si₃N₄ membranes, and reflecting the forward scattered light as well as the FLASH beam back onto the sample [23]. By the time the FLASH beam hits the

sample a second time, the sample has exploded. The measured signal consists of the superposition of the diffraction signals of the undamaged sphere and the exploded sphere. These data allow one to extract quantitative information about the explosion process. These studies are important to benchmark our understanding of the speed of the damage process. The theoretical description of the damage processes so far is rather simplistic, as it relies on tools that were actually developed for hot-dense plasmas. However, in these experiments the material enters the warm-dense matter regime, for which a good theoretical description is still amiss. Substantial further experimental and theoretical work has to be done to improve the understanding of the complex state of matter in this regime.

The fourth kind of experiment was a pump-probe scheme, in which atomic helium was photoionized by a FLASH pulse in the presence of an optical laser field [24]. Because the photoelectron released by the absorption of an XUV photon is not in a free-particle state (the electron still interacts with the parent ion), it can absorb photons from the laser mode or emit photons into the laser mode. This leads to the emergence of so-called sidebands in the kinetic energy spectrum, i.e., in addition to the main band at the difference of the XUV photon energy and the ionization potential, weaker electron energy bands appear that are separated from the main band by integer (positive or negative) multiples of the laser photon energy. This effect, which requires spatial and temporal overlap of XUV and laser beams, may be useful for XFEL experiments because it may allow one to determine the duration of a given XFEL pulse (see also Refs. [25, 26]).

4 X-ray diffraction imaging and sample damage

The first experiments planned at LCLS [27] fall into the following areas:

- Coherent scattering at the nanoscale (XPCS)
- Atomic, Molecular, and Optical Science
- Pump/probe diffraction dynamics
- Pump/probe high-energy-density (HED) science
- Nano-particle and single-molecule (non-periodic) imaging

Among the unique aspects characterizing XFELs are the high peak power, high coherence, and short pulse duration—at a wavelength as short as an Ångström. This makes it possible to explore matter with unprecedented time and space resolution. However, the high peak power, while enabling fundamentally new experiments, poses a challenge. Ways must be found to handle the high radiation intensity. For instance, a biomolecule exposed to an XFEL pulse will become highly ionized and will undergo a Coulomb explosion [28]. Matter will be severely damaged, even with unfocused (1 mm) LCLS pulses.

4.1 The need for theory

Damage considerations are crucial to determine the durability of x-ray optical devices such as mirrors. They are also key to assessing the potential success of the proposed single-molecule single-shot x-ray diffraction experiments [28–32]. If the damage mechanisms are well understood, then one can attempt to correct the measured, pulse-integrated diffraction pattern for the damage. One can add to the molecule of interest a molecular tamper, i.e. a sacrificial layer of, e.g., water molecules, to reduce the atomic motion and delay the Coulomb explosion. But this will not reduce the local electronic (ionization) damage.

Since x-ray diffraction is not sensitive to atomic positions as such, but only to the electron density, any modification of the electron density during the XFEL pulse due to photoionization, Auger decay, shake-off processes, collisional ionization, etc. will be reflected in the apparent molecular geometry. It is therefore an important challenge to determine the relative cross sections for elastic x-ray scattering (leading to signal) and absorption (leading to ionization and Coulomb explosion), at the high x-ray fields necessary for single-molecule imaging using an XFEL. Estimates indicate that 1 mJ pulses, at 10 keV photon energy, nominally 1 fs, focused to 100 nm will be required to get useful diffraction images. (Note that if the measured, pulse-integrated diffraction pattern can be corrected, then it may be possible to work with pulse durations of the order of 10 fs.) This corresponds to a focused intensity of the order of 10^{22} W/cm². This is so high that multiphoton processes are unavoidable. In fact, this might be too high for perturbation theory to be applicable. Multiphoton x-ray scattering and absorption cross sections for the relevant atomic species (carbon and oxygen, among others) are not yet known, but will have to be determined. If the electronic structure of a sample changes substantially during exposure to an XFEL pulse, then how would this affect methods that are currently used to solve the phase problem of the x-ray diffraction pattern [33]? For instance, how would the oversampling method [34,35] have to be modified?

The development of an integrated theoretical/computational modeling capability to simulate the complete time-dependent event when high-intensity ultrafast, short-wavelength radiation interacts with bulk material would be of great benefit to many XFEL application researchers. Such a simulation code would include the processes of photon absorption and scattering, creation and transport of photo, Auger, and secondary (collisionally ionized) electrons, electron–electron interactions, electron–atom and electron–ion interactions, atom and ion motion, and thermal and mechanical effects. Such a model would likely require quantum calculations of photon and electron interactions with atoms, molecules and/or solids (see below) coupled to classical descriptions of electron and atom/ion motion.

In order to develop the modeling capability described above, theoretical calculations of fundamental interactions of photons and electrons with atoms, molecules and condensed matter will be required. There already exist good data on single photon interactions and electron interactions with atoms/ions and many (cold) solid materials. What is needed are specific accurate calculations of additional processes, such as multiphoton interaction processes and electron interaction cross sections with molecules and “warm” solids. Density and ionization effects on Auger processes are also needed.

It is important to achieve a clear elaboration of where quantum theories, particularly for electron processes, are needed and where quasi-classical treatments are sufficient. One example is the treatment of ionization and internal excitation by rate equations. Here one assumes that electron motion can be described by classical trajectories and that excitation/ionization collisions with atoms or ions can be treated via rates determined from mono-energetic cross sections, which are either measured or calculated. It is important to verify (or disprove) this approach. Must the motion of electrons not bound to atoms be treated quantum mechanically or is a classical theory sufficient? Are the atom/ion rates adequate to describe a bulk material?

4.2 Insights gained from cluster studies

At this workshop, electronic effects in inner-shell excited systems were discussed that can, inherently, not be described by reference to isolated atoms. One of these processes is known as Interatomic (or Intermolecular) Coulombic Decay (ICD), first theoretically predicted in connection with inner-valence holes in clusters [36–40]. Recent experiments confirmed the existence of ICD [41–43]. Moreover, ICD has been predicted to occur in clusters as a secondary process following the Auger decay of a core hole [44], as confirmed experimentally in Ref. [45]. In connection with the electronic damage of

a sample, ICD as well as interatomic (intermolecular) Auger decay deserve particular attention since they lead not only to an increased delocalization of the electron density, but also to the separation of the initially localized positive charge between the neighboring atoms or molecules. The relevant open question is whether these processes are fast enough to affect significantly the electron density during an XFEL pulse. Even if they turned out to be slow on a time scale of a few fs, the degradation of bulk materials exposed to the XFEL beam is likely to be enhanced by interatomic electronic decay. The challenge for theorists is to develop accurate and efficient computational approaches for calculating the rates of interatomic decay. These approaches must be applicable to the decay of multiply ionized systems. Once this objective is achieved, it will be possible to use the predicted decay rates in a simulation code (such as the one envisioned above). Another challenge is to identify new decay pathways that are unique to matter–XFEL interaction. One such pathway might be the collective decay of two or more inner-shell vacancies.

Theoretical research on small argon clusters interacting with an intense soft x-ray beam [46] suggests two additional cooperative effects in finite systems. The emission of electrons from a cluster (or macromolecule) leads to a large ionic background charge within the cluster, which, depending on the magnitude of the photon energy relative to the relevant inner-shell ionization thresholds, may eventually suppress additional photon absorption. The second effect is that inner-shell photoionization lowers the potential energy barriers between ions inside the cluster. This causes the valence levels to become delocalized. Estimates in Ref. [46] indicate that as a consequence, the Auger decay rates of inner-shell holes may be reduced. (Note, however, that the one-center picture of Auger decay is not always meaningful [47, 48]. ICD or interatomic Auger decay, which we mentioned above, may dominate.) Due to these two effects, the ionization of a cluster could be suppressed in comparison to a single atom. For x-ray diffraction imaging, the consequences of electron delocalization and suppression of Auger decay might imply a contraction of the diffraction signal toward small angles, i.e., a loss of structural information.

5 Gas-phase studies

The advent of ultrafast x-ray light sources is timely, since, even with the major advances in the capabilities of lasers, we lack a detailed understanding of the mechanisms of the action of radiation at very short times following a broad range of energy depositions in an isolated system. We also lack understanding of the time-dependent energy dissipation from a quantum mechanical point of view. Comprehensive information on the interaction and decay pathways following energy deposition is much needed in gas-phase systems such as atoms, molecules, clusters, and their ions. Time-dependent studies of carefully selected systems and comparison with the results of forefront theoretical methods will provide the basic knowledge of the behavior of matter in the ultrafast and ultra-intense regime accessed by XFELs.

One area of atomic physics that might also benefit from the development of XFELs is the measurement of one-photon-mediated processes that are characterized by a small cross section. The study of nondipole effects on photoelectron angular distributions [49–51] is an example. It should be noted, however, that at LCLS at least, the average photon flux will be comparable to the average photon flux available at third-generation sources such as the Advanced Photon Source.

In the United States, the LCLS AMO team plans to capitalize on the unique attributes of the LCLS, such as the extreme peak power and spatial and good temporal resolution of the photon beam, to investigate complexity in atoms and molecules, multi-charged positive and negative ions, atomic and metallic clusters, and biological molecules. The proposed studies will lead to significant advances in our understanding of the behavior of matter at the fundamental time scales of nuclear motion.

The extreme peak power of the LCLS beam will allow access to highly excited states of matter

due to multiphoton excitation/ionization, such as inner-shell hollow target and multiply-charged targets. These previously inaccessible states will allow detailed investigations of collective tunneling effects, rescattering of ionized electrons with the targets and most certainly new and unexpected phenomena that will reveal themselves, including nonlinear phenomena and high-field dynamics. The spatial and temporal resolution of the LCLS beam will allow us to follow nuclear motions of molecules and clusters in real time using laser/LCLS pump-probe schemes.

Initially, it is planned to investigate the inner-shell photoexcitation of simple targets such as atoms and small molecules. The challenge will then be increased by exploring bigger molecules, clusters and ions with the LCLS beams. They are complex systems whose study is at their infancy, since they could only be preliminarily explored with third-generation light sources. Finally, on a longer time scale, the single shot diffraction capabilities of the LCLS will be used to directly determine structures of size-selected metal and semiconductor clusters.

Focused LCLS x-ray beams are expected to produce multiple core holes in atoms and on different atomic sites of molecules. Instrumentation is being designed to study their decay spectra: ion charge states and fragmentation patterns, photoelectron, Auger-electron, fluorescence, and coincidence spectra. Theoretical calculations on rare gases and small molecules would provide useful benchmarks. Two-photon absorption cross sections for Ne [52,53] and ion charge-state yields from cascade decay of multiple hole states in Ar and Kr [54] have been calculated. Those results should be confirmed by alternative theoretical approaches and extended to derive partial cross sections. One of the challenges for theory is that the decay dynamics need to be treated as well as the photoabsorption step. Will inner-shell photoexcitation and decay processes, particularly near resonances and thresholds, be modified in intense LCLS beams or in pump-probe experiments with optical lasers? Laser-pump/x-ray-probe experiments using third-generation sources have already been carried out at Lawrence Berkeley National Laboratory [55] and at Argonne National Laboratory [56] in order to develop the methodology needed for successful measurements at LCLS.

Radiation pulses generated in the SASE process are chaotic, i.e., the time evolution of the field amplitude and phase during a pulse changes from shot to shot in a random manner [57–59]. Therefore, in order to facilitate the utilization of SASE FELs as superior research tools, a detailed pulse characterization is necessary. A shot-to-shot SASE FEL characterization has been demonstrated at Argonne’s Low-Energy Undulator Test Line [8]. However, currently available techniques for this purpose are restricted to long wavelengths. In the x-ray regime, the development of analogous capabilities is in its infancy.

Currently planned x-ray diagnostics downstream of the LCLS undulator consist mainly of a CCD camera and a spectrometer [60], which serve the purpose of monitoring the performance of the FEL and the alignment of the x-ray beam. Applications of XFELs will typically require more detailed information about the properties of the radiation pulses. There have already been suggestions how to measure the FEL pulse arrival time [61] (for pump-probe experiments) and pulse duration (see above). In order to determine more detailed XFEL pulse properties, gas-phase techniques are ideal: In a gas-phase experiment, XFEL pulses can be analyzed without wasting the x-ray photons. Moreover, a gas target can be continuously replenished.

The chaotic nature of the SASE FEL radiation makes it necessary to adopt either of two different approaches to performing and interpreting measurements using XFELs:

1. Performing experiments on a single shot basis. This would imply that the XFEL electromagnetic field has to be fully characterized for every single shot.
2. The alternative is to tackle the problem from a statistical point of view, i.e., by collecting data from several shots and averaging over them.

The main question to be asked in the latter case is, which statistical information about the radiation is needed to describe a given experiment and which experiment allows one to determine the necessary statistical properties. For an n -photon process, the problem can be reduced to finding the initial field-correlation function of order n . A one-photon single-ionization process via photoabsorption would in principle allow to determine the first-order field correlation function. For completely chaotic radiation, all higher-order correlation functions are determined by the first-order correlation function. The exact properties of XFEL radiation are, of course, not known. By carefully selecting nonlinear x-ray processes, it would become possible, by measuring the ejected photoelectrons, to determine the relevant correlation functions. Preliminary estimates suggest that neon might serve as a suitable diagnostic system. Note that the probability of ejecting a certain number of photoelectrons with specific properties by an n -photon process is a convolution of the n th-order correlation function with atomic transition matrix elements.

- Crucial ingredients are therefore atomic multiphoton transition matrix elements in the x-ray regime. This is clearly an opportunity for atomic theory.
- The inversion problem, i.e., the reconstruction of the n th-order correlation function from experimental data and theoretical matrix elements, must be solved.

6 Spectroscopy and photochemistry: some visions

With XFELs, science enters into new, never-considered, domains of light-matter interaction, something that will require new theory building and simulation technologies right from the start. The role of theory as a prerequisite to outline new experiments, and to disclose their feasibility and informational content, will be stronger than ever before. The photon coherence, in both time and space and at ultra-high intensities, will introduce unprecedented possibilities to study structure and dynamics at atomic dimensions through a multitude of new experiments using inelastic scattering of x-rays, where Raman spectroscopy, nonlinear processes, and pump-probe techniques will be put at the disposal for a multidisciplinary user community. All this requires a concomitant development of theory and modeling. In order to fully exploit these new possibilities, a very challenging effort is thus required to provide theoretical models that can associate the intrinsic properties of the electronic and nuclear wave functions with interferential effects in their spectroscopic signatures. By gaining deeper insight into the dynamics of photoinduced processes on the ultrafast time scale, we can foresee strong and direct impact on different areas in biology, photochemistry, nanotechnology, as well as an extension of general knowledge of the basic mechanisms that might be used for, at the moment, unforeseen applications. We can anticipate new models that range all the way from pure classical models, over semi-classical and quantum models, to full quantum electrodynamics.

6.1 Nonlinear x-ray spectroscopy

First and foremost, the parameters of the new XFEL light sources will bring x-ray physics from the linear to the nonlinear domain. Conventional linear theory of x-ray scattering and spectroscopy needs complete revision in order to deal with the x-ray-matter interaction in the nonlinear region and under conditions of strong damage of the sample. Even more accentuated than in the optical region, the physics of nonlinear absorption of a few coherent x-ray pulses will open new unique opportunities in fundamental science, as well as in applied sciences like bio and nanotechnologies. The intensity of the XFEL will easily saturate x-ray transitions, which is of crucial importance for analyzing the multiphoton x-ray processes like nonlinear absorption, harmonic generation, wave mixing, that become real though the XFEL and which can be used in medical-biological and technological applications. Coherent multi-x-ray photon

absorption will also bring about completely new penetration and confocal properties of x-rays, with "x-ray tweezers" and "x-ray scissors" being two of many application examples.

6.2 Phase-dependent, multidimensional x-ray spectroscopy

The enormous energy of a short x-ray pulse focused in a small spot makes it important to study time-resolved kinetics of highly ionized samples, post-collisional interactions and plasma conditions. Controlling the coherence of electron dynamics by exploiting the coherence of XUV light pulses, offers the twofold advantage of pushing the temporal resolution to the attosecond scale, and of making it possible to excite electronic core levels, thus adding elemental selectivity. The phase of x-rays will serve as a new instrument to explore today's limits of nanotechnology. Multidimensional x-ray spectroscopy [62–65] will become very important in the dynamical studies of electron correlation. In x-ray pump-probe experiments, the application of coherent radiation will allow fundamental processes of light-matter interactions to be studied with extremely high, and up to now inaccessible, degrees of precision and time-resolution.

6.3 Nonlinear response functions

Developing a systematic theoretical framework for the description and computation of nonlinear ultrafast x-ray spectroscopies (both pure x-ray and mixed optical/x-ray techniques) constitutes a major theoretical challenge [66–68]. Nonlinear ultrafast spectroscopy in the visible and the infrared regime has been successfully described using the machinery of nonlinear response functions (NRF), which are expressed as combinations of multitime correlation functions of the dipole operator and which provide the most compact and general formulation of optical signals. Extending this powerful apparatus and associated techniques to the x-ray domain should open up exciting new possibilities for looking at electron–electron correlations and the flow of charges in a wide class of molecular systems and materials. Prior to the introduction of NRF in the sixties, nonlinear optical processes were treated phenomenologically. The NRF provided a firm unified theoretical basis for nonlinear optics. The current status of theoretical understanding of nonlinear x-ray processes is reminiscent of nonlinear optics in the sixties and, similar to the optical regime, the NRF could provide a unifying framework that will help the design of new x-ray techniques. The NRF carry all the relevant material information and offer a compact description of a broad range of nonlinear spectroscopies. A time domain language, based on electronic and vibrational wavepackets focusing on coherence effects, has proven to be extremely useful in femtosecond optical spectroscopy. This language should be extended to provide an intuitive picture for attosecond x-ray techniques.

Coherent nonlinear multidimensional signals, which differ by the temporal sequences of pulses as well as their frequencies and wavevectors, should provide a wealth of information, inaccessible by linear EXAFS and XANES spectroscopies. They could directly probe the interaction between core excitations at different sites, disentangle congested spectral features by projecting the signal on multiple axes, and monitor electron dynamics in real time. Models and theoretical simulation techniques will be required in order to design and interpret these spectra. Developing new pulse sequences and methodologies for the simulation of nonlinear x-ray response in many-electron systems should receive considerable theoretical attention.

6.4 XFEL for photochemistry

A major application of XFEL in the area of photochemistry is to control the reaction dynamics of processes such as proton transfer, electron transfer, solvation, isomerization, dissociation and recombination,

fast non-adiabatic electronic dynamics in vibronically coupled core excited potential surfaces. Time and frequency resolved pump-probe spectroscopy, applying an IR short pulse pump laser and the XFEL radiation as the probe pulse, is presently under intense theoretical investigation as a method for monitoring the photochemical dynamics of polyatomic molecules. These ongoing studies, regarding both basic and applied aspects, give insight in the experimental conditions (intensity, duration, shape, coherence, etc. of the laser and XFEL pulses) that are required for optimally detecting of chemical dynamics of the system.

The coherent mixing of vibrational/electronic states results in a nuclear/electronic wave packet (WP) which evolves with the time and depends on the phase, intensity, and shape of IR/optical field. IR-x-ray-pump probe spectroscopy is a proper tool to study the dynamics of proton transfer in systems with hydrogen bonding networks (for example, liquid water) [69–73]. Thus, the spatial confinement of the WP allows it to be selectively excited to the proton transfer well, thereby offering the possibility to map out the molecular potential along the reaction coordinate. A topic of fundamental interest is the dynamics of the proton transfer in vibronically coupled core-hole states localized on sites. X-ray photoionization of IR driven molecules offers a unique opportunity to study the electronic recoil effect, which is enhanced due to the large size of laser-induced nuclear WP. The WP revival caused by the anharmonicity allows to detect the anharmonical shift through the time resolved measurements.

In all these studies the phase of pump radiation strongly affects the x-ray probe spectra because the WP trajectory is sensitive to this phase. In order to clock photochemical processes, the time and spatial resolution of pump-probe measurements are of great importance. The observation of nuclear motion requires rather high spatial resolution following the localization of the wave packet. The formation of the nuclear WP deserves therefore special attention: the degree of localization (about 0.1-0.5 a.u.) depends strongly on the intensity and the shape of IR pulse. The localization of the WP requires a coherent excitation of many vibrational levels; this makes it necessary to apply IR pulses of about 10^{12} - 10^{14} W/cm². The key to achieve the necessary time resolution is a short duration of the x-ray pulse. The XFEL combined with the slicing technique or with wakefield-induced energy chirps allows the desired region of 10-50 fs to be approached. The IR and XFEL pulses must be synchronized and have matching repetition rates. In all these studies the phase of pump radiation strongly affects the x-ray probe spectra because the WP trajectory is sensitive to this phase.

7 Prospects for nonlinear physics with XFEL sources

7.1 Historical perspective

Forty-five years ago, a new optical radiation source, the laser, ushered in a revolution in atomic and molecular spectroscopy, which to some extent is still going on. Owing to its intensity, coherence and more recently short pulse duration, it became possible to go beyond traditional single-photon transitions, revealing aspects of atomic and molecular structure and dynamics that, until then, could only be speculated about.

It may be useful to recall here a few examples of such nonlinear processes:

- Few-photon transitions between bound states as well as into the continuum, which allowed the study of states with higher angular momentum, ionization from such states, as well as transitions to manifolds of autoionizing states inaccessible from the ground state. One outgrowth of such studies was a technique now known as REMPI (Resonantly Enhanced Multiphoton Ionization), which has become a standard tool of spectroscopy.
- Strongly driven transitions in combination with few-photon schemes, the simplest being double

optical resonance, which among other aspects allowed the study and elucidation of the connection between nonlinear photointeractions and the statistical properties of the radiation source; an issue that does not arise in single-photon transitions under weak excitation.

- Pump-probe or multicolor experiments, in which transitions could be studied and/or manipulated in real time, or the flow of atomic population in, for example, a ladder scheme could be optimized.
- Coherent control in channelling transitions through selected quantum paths, through either the manipulation of pulse shapes or the combination of two judiciously chosen colors whose relative phase could be controlled.
- Strong-field effects under sources of ultrashort duration, down to a few femtoseconds or even sub-femtosecond.

That revolution, however, has been limited to processes accessible to wavelengths not shorter than the UV, which means processes in which practically only valence electrons participate. Even under the strongest sources of infrared radiation, namely ~ 780 nm, for which double or multiple electron ejection can be observed, it is one valence electron, strongly driven into the continuum, that initiates the chain of events which also involve other valence electrons. On the other hand, a long tradition and vast amounts of data and understanding of inner-shell transitions have, and continue to be, accumulated, owing to the continuous progress in the technology of short-wavelength sources such as synchrotrons, especially the third-generation light sources. Yet, it is mostly single-photon transitions that have been accessible thus far. It could then be said that subvalence and inner-shell transitions stand at this point where valence electron transitions stood forty five years ago.

7.2 New opportunities

Upcoming developments, however, such as the FEL-based short-wavelength sources, suggest that we may be at the threshold of a second revolution in the physics of atomic transitions and spectroscopy, paralleling that of the laser, but at much shorter wavelengths corresponding to photon energies reaching below or well below the valence shell. In addition, the FEL-based sources have the advantage of tunability by construction, whereas strong lasers come in two or three wavelengths with hardly any tunability.

Let us consider then possible nonlinear process in that wavelength range, assuming that the necessary intensities will, as expected, be available.

- Two-photon ionization from inner shells. Relevant cross sections could be and in certain cases have been calculated. There is, however, a problem with screening. If, in order to eject one electron from say an L-shell, a photon of energy $h\nu$ is needed, although two photons each of energy $h\nu/2$ have sufficient energy to do the same, it is questionable whether these photons will "see" the L-shell, because of screening by the electrons of the higher shells. It is most likely that instead, one electron from a higher shell, for which the energy $h\nu/2$ is sufficient will be ejected through a single-photon process. This is, in fact, the reason that a very powerful 780-nm laser interacts practically only with valence electrons. And it is only through the ponderomotive energy of a valence electron that nonsequential double or even multiple ionization is initiated, despite the fact that such a laser has an enormous number of photons of total energy sufficient to strip "instantly" several shells. In the very few cases in which a second electron has been ejected directly by few-photon absorption from the shell just below the valence shell of a rare gas, it has occurred under UV radiation ($h\nu \sim 5$ eV) and only after the outer shell has been "opened" by the ejection of one

electron. Needless to add that, the issue of screening being a matter of degree, it poses a question for theory, which most likely will be settled by experiment.

- A process related somewhat to the above would be the "simultaneous" ejection of two electrons from two different shells—say, an L and an M shell—by two photons with the appropriate energy, assuming two such pulses could be available. The idea represents a generalization of two-photon double ionization of helium through XUV photons, presently under both theoretical [74] and experimental [75] investigation. It does, however, involve a much richer set of possibilities and events, as there would be two holes to be filled. If one could, in addition, contemplate some control of the temporal sequence of the two pulses and/or even their duration, a completely new territory of phenomena could be explored.
- An extension of the above, again through two pulses of appropriate frequencies, would be the ejection of an electron from one shell while an electron from a higher shell is driven by the second pulse so as to fill the hole. It would be stimulated hole-filling and possibly Rabi-type driving which would affect, and maybe control, the Auger process that would normally follow the ejection of the first electron. It is unclear what screening would do.
- The excitation of an Auger resonance, in the presence of a second pulse of suitably chosen wavelength and intensity coupling it to another Auger resonance, would provide unique information on the matrix element (not necessarily dipole, depending on wavelengths) connecting the two resonances; a severe and otherwise unavailable test of structure and theory.
- A most exciting prospect would be 3-photon triple ionization of lithium, providing a unique landscape of interacting discrete structures embedded in multiple continua and studied through the selection of pathways involving two or even three different and judiciously chosen wavelengths.

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