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Making Optical Waves, Tracing Electrons in Real-Time: The Onset of the Attosecond Realm

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(*Invited Review*)

Abstract—Tracing the dynamics of electrons inside atoms molecules or solids as they occur in real time resides at the forefront of modern science and technology. Advances in attosecond physics over the last decade and beyond are now enabling this essential experimental capability. Here we discuss some of the key developments in light sciences that made possible attosecond metrology and control of electronic processes inside matter on native time scales. These developments hold the promise for new, fundamental insights into the innerworkings of the microcosm as well as the identification of innovative routes for light-based electronic and photonic devices operating at PHz rates.

1. INTRODUCTION

Some of the most fundamental advances in physics can be linked to the measurement of the electronic properties of matter. The use of light as a tool to probe fine details of the electronic structure has been proven to be one of the key enablers not only in discovering the quantum character of nature — with far reaching implications on the advancement of chemistry, biology and solid state physics —, but also the exploitation of the quantum properties of materials at microscopic and mesoscopic scales, advancing modern technological applications.

Following the development of lasers [1] in the 1960s, the breathtaking pace of advancement of light spectroscopies has today allowed unprecedented levels of precision. Fine detail in determining the energy of electronic levels measured in research laboratories allow understanding of the physical and chemical properties of materials and hold the promise of unveiling the fate our universe by tracing the subtlest variation of cosmological constants [2]. Spectroscopies in extreme spectral ranges such as the x-ray [3] regime are now probing the structure of atoms, molecules and solids with a precision that suffices to unveil fine structural and topological details of complex materials and chemical shifts caused in chemical bonding.

When electronic systems are driven by external perturbations out of equilibrium their dynamic evolution is critically important to understanding these systems but it cannot be accessed by the mere knowledge of their electronic structure. Although the characteristic time scale of this dynamic evolution can be estimated on the basis of pure energetic criteria, e.g., through the Heisenberg principle, such estimations hardly capture the details or the implications of the unfolding dynamics in the microscopic or macroscopic response of matter.

Tracing the dynamic character of physical processes in matter hinges on the capability to manipulate light in the time domain. Instead of continuum illumination, flashes of incoherent light (Figure 1(a)) confined to, and clocked within, microsecond time intervals allowed first insight into the chemistry of photolysis and planted the idea of the pump-probe technique: the first flash of light initiated the chemical

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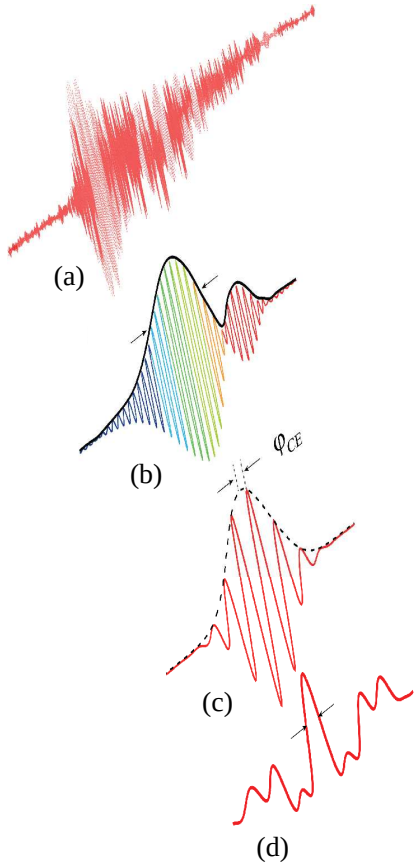

Figure 1. Evolution of light control. (a) Incoherent flashes of light. (b) Femtosecond pulse shaping: control of lights envelope and chirp. (c) Carrier envelope phase control of few-cycle pulses. (d) Direct field control of light waves. Adapted from [4].

reaction whilst the second probed subsequent creation of chemical radicals. The advent of coherent light laser sources and the possibility to confine their energy into pulses of reproducible spectrum and phase extending over picosecond and femtosecond time intervals (Figure 1(b)) brought about a second revolution in the quest for dynamic observation and control of the microcosm. The real-time tracing of processes of fundamental relevance to chemistry and solid state physics such as the rupture and formation of the chemical bond [5] or the distribution of coherence in larger scale molecules and solids are merely few representative examples. Pulse shapers [6] — devices capable of manipulating fine details of the temporal profile of femtosecond laser pulses such as the temporal variation of the frequency and amplitude along the pulse profile — allowed a broad range of advances in controlling the outcome of atomic scale dynamics in gasses [7] solids and condensed phase systems.

Porting this broad range of capabilities into the time scale of electrons — the attosecond time scale — is not simply driven by the desire of exploring nature on even faster time scales. Any material process outside the atomic nucleus is initiated and driven by the electrostatic forces exerted and mediated by electrons. Even in the simplest representative case: the rupture of a chemical bond, it is the force of the electrostatic potential formed by electronic excitation that drives the motion of the nuclei. In pure analogy to excitation of coherences among vibrational levels, the phase along with the amplitude of the excited wavefunction and its precise evolution plays a key role in manipulating the intramolecular forces [8]. Coherent excitation of several electronic states gives rise to attosecond or few-femtosecond evolution of these forces and may provide new routes to control the chemical reactivity [9–12]. But in order for optical pulses to attain the onset and manipulation of electronic coherences in matter they would have to drive the excitation or control of quantum systems ten to hundred times faster than that intuitively implied by their typical femtosecond duration. These possibilities lie beyond the reach

of modern femtosecond techniques and much of the physics on these time scales has remained largely speculative.

Extension to the attosecond realm called for new paradigms [13] on how we conceive and control the interaction of light with matter. In principle, and from a pure time domain perspective, a light field embodies enormously higher resolution than that typically exploited in femtosecond experiments. This resolution is relevant to the time structure of the field waveform itself rather than that of its envelope. In an optical waveform, a half-field cycle embodies a resolution better than 1 femtosecond: the time it takes the electric and magnetic fields to build up and disappears before the onset of a next half-field cycle.

For light field waveforms generated in typical femtosecond lasers two fundamental shortcomings prevented experimental exploration of the above-mentioned paradigm. The first is that consecutive pulses emerging from these sources do not posses mutual field coherence [2]. In other words, the interference of consecutive pulses do not yield a stable interference pattern over extended periods of time. The second is that even though each field crest incorporates attosecond resolution in principle, its action on an electronic system cannot be isolated from that of other half-field-cycles of the same waveform inhibiting attosecond resolution.

Two important advances in the science of light allowed overcoming this essential frontier towards the attosecond realm. The first is the frequency comb technique [14] which permitted attaining mutual coherence between consecutive pulses of a femtosecond source, i.e., generation of light fields with not only identical field envelopes envelopes by also field waveforms from pulse to pulse. The common intensity field envelope (Figure 2(c)) between consecutive pulses in a laser provided an absolute reference to define the phase of each waveform and it is referred to as the Carrier Envelope Phase (CEP). But even for pulses with identical and controllable CEP phase, isolation and exploitation of the action of a single half-cycle of the field on a quantum system required further efforts. The compression of CEP-stabilized intense light waveforms to few-cycle durations (Figure 2(c)) and their use to drive extreme nonlinear processes in atoms provided this advancement.

2. ATTOSECOND STRONG-FIELD PHYSICS IN THE FEW-CYCLE REGIME

It has been long recognized that atoms, molecules or solids exposed to impulsive intense optical fields, comparable in strength with the electronic forces that hold electrons bound in atomic potentials, give rise to highly non-perturbative response [15] which is sensitive to the instantaneous field of the driving waveform. Early experimental work in the study of phenomena such as high harmonic generation [16, 17] or above threshold ionization [18, 19] in atomic and molecular species represents classical examples where extreme nonlinearity is manifested in optically driven microscopic processes.

Explorations in attosecond physics took advantage of this pronounced nonlinearity to demonstrate generation of attosecond pulse trains in the extreme ultraviolet part of the spectrum [21, 22]. It was however, not before few-cycle pulses were employed in the study of strong field phenomena that relevant dynamics were confined to occur in a fraction of a field-cycle, opening the way to the attosecond realm. Although precise CEP stability was absent in these early works [23, 24] additional nonlinearity contributed by the propagation of the intense driver in the strongly ionized medium [25] assisted the isolation of highly energetic ($E > 90\,\mathrm{eV}$) attosecond pulses [24] and their subsequent use in tracing physical processes such as the atomic Auger decay in real-time [26].

The generation of field-reproducible, intense few-cycle pulses [27] and their application in driving strong-field phenomena opened up a plethora of possibilities for attosecond control of electronic processes. First experiments [20] (Figure 2) utilizing these pulses for high harmonic generation in Neon atoms demonstrated field sensitive control of the soft x-ray emission. The precisely controllable CEP of a near-infrared driving waveform could be used to adjust both the ionization yield [28] in each field half-cycle and the classical excursion of the ionized electron in the continuum to generate, upon recombination with the parent ion, single or twin soft x-ray attosecond bursts of radiation near the cutoff of the emitted spectra. This first essential paradigm of attosecond control was followed by equally crisp demonstrations of strong-field controlled electron emission from atoms [29, 30], their double ionization [31], the sub-cycle control and the dissociation in simple molecular species [32]. More recently, this paradigm was further extended to field sensitive control of chemical dynamics in more

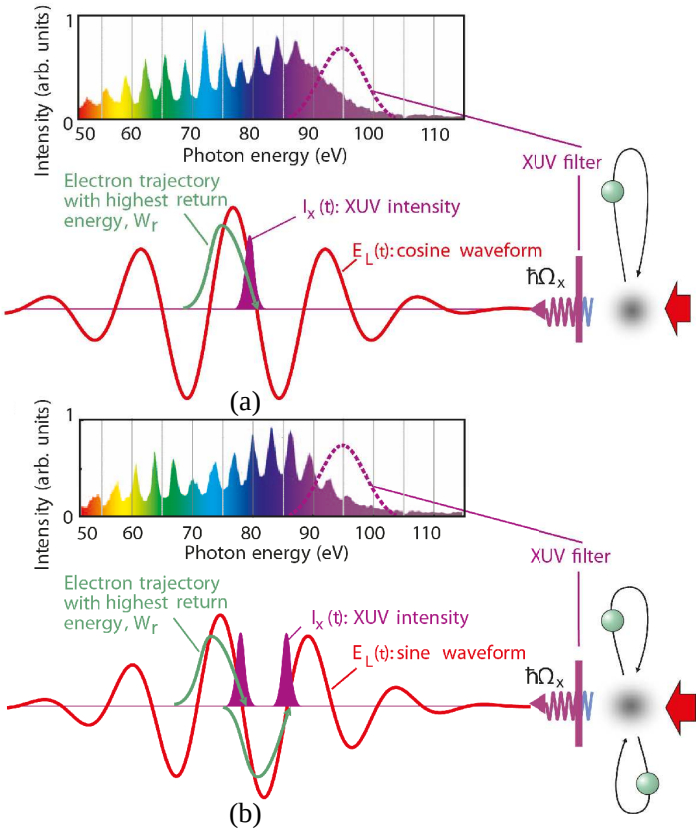

Figure 2. High-order harmonic spectra obtained with a few-cycle near infrared pulse (5 fs) for two phase setting of the CEP phase. Adapted from [20]. The cosine wave gives rise to a smooth spectrum in the cutoff range, suggesting emission in a single burst of potentially sub-fs duration, whereas the appearance of modulation for the sine wave suggests that that the emission is distributed in two bursts half a cycle apart.

complex molecules [33, 34] or towards the sub-cycle manipulation of EUV generation in strongly driven surface plasmas [35] and the photoemission from metal nanotips [36].

Although the above control schemes offered the first direct experimental evidence of attosecond control of electronic processes, considerably more detailed information about the strong field process can be gleaned by probing the temporal structure of the emitted soft x-ray pulses. Conventional femtosecond pulse metrology could, in principle, be exploited to characterize the temporal profile of this emission in schemes such as higher order autocorrelations [37, 38]. However, the rather moderate photon yields of these sources at the soft x-ray regime, along with the limited nonlinear response of matter in these extreme spectral ranges has so far led to diminishing returns.

An essential innovation in the attosecond metrology (Figure 3) of the microcosm came about with the invention of the technique of attosecond streaking. Replacing metal anodes by atoms and the fast rising electric field of a capacitor by that of an optical waveform, attosecond streaking was the first technique ever to port the well-known concept of streak cameras from the picosecond to the attosecond domain. Even though first hinds of the key ideas behind attosecond streaking can be recognized in earlier experiments [23, 24], it was the implementation of the technique by CEP controlled few-cycle pulses that boosted resolution to characterize attosecond electron photoemission with a resolution below 100-as [40]. Further advancement provided access to ever shorter x-ray pulses [41] nearing to the atomic unit of time [42]. The concept of attosecond streaking is summarized in Figure 3. Attosecond streaking does not only decode the temporal structure of the generated x-ray pulse [43]. As long as the latter is considerably shorter than a half-cycle oscillation of the streaking field the roles can be intuitively inversed. The time resolved energetic shift of the photoelectrons can be directly associated to the

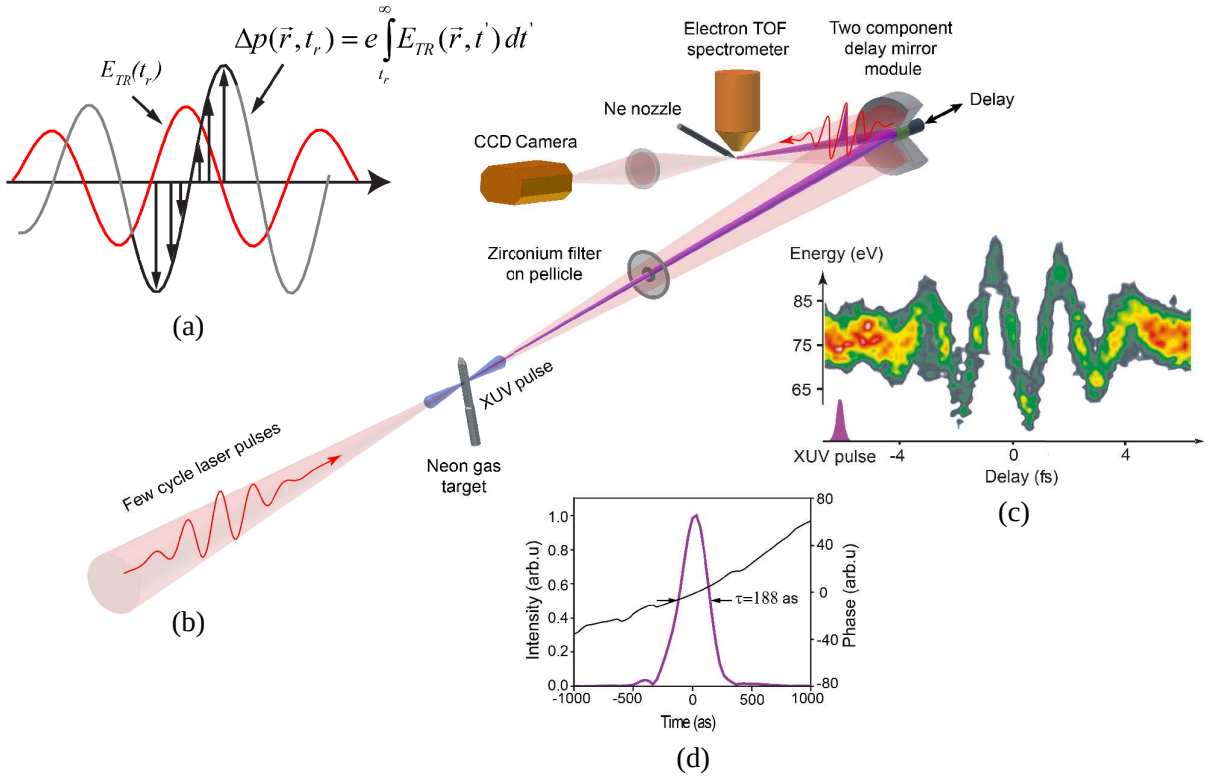

Figure 3. Attosecond streaking technique and its basic elements. (a) Principles of attosecond light sampling based on the attosecond streaking technique. A synthesized light transient $E_{TR}(t)$, along with a synchronized attosecond EUV pulse, is focused into an atomic gas target. The EUV pulse knocks electrons free by photoionization at an instance t_r. The field of light E_{TR} $(t > t_r)$ imparts a momentum change Δpt_r ((black arrows) to the freed electrons, which scales as the instantaneous value of the vector potential A_{TR} (t_r) at the moment of release. The momentum change is recorded by an electron time-of-flight detector, placed along the direction of the linearly polarized $E_{TR}(t)$. (b) Schematic diagram of the experimental setup for sampling synthesized light field transients(see text for details). (c) The first attosecond streaking spectrogram of a few-cycle light wave [39]. (d) Retrieved temporal intensity profile and spectral phase of the EUV pulse.

instantaneous vector potential of the optical waveform [44], based on simple mathematical formalism and therefore allows for a direct and complete reconstruction of its electric field. First implementation of attosecond streaking as an oscilloscope of light waves [39] allowed direct access into the detailed field waveform of a few-cycle pulse. This demonstration brought to an end to century long pursuit towards capturing the most basic feature of a light wave in real time: its field oscillation. In his Nobel speech Braun, (Karl Ferdinand Braun, Nobel 1909), reveals his efforts to capture optical signals by their rectification in the mineral Galena *"...I had repeatedly, though in vain, attempted to obtain direct current from oscillations of light"*. We now understand that such a rectification is not possible by semiconducting devices and much faster techniques are required. But beyond this essential demonstration of light sampling with few-cycle pulses, attosecond light sampling provides a strong foundation for realizing the next enabling technology in attosecond science, the attosecond synthesis of light waves discussed further in this review.

Importantly, EUV triggered attosecond photoemission also carries information about the dynamic response or the electronic topology of the atomic, molecular or solid phase systems. Photoelectrons relased from multiple orbitals in atoms [45] or core shells and valence bands in metals [46] has offered a unique potential to study how electronic structure in atoms or ballistic transportation in solids influences photoemission by revealing attosecond scale time delays in the emission of electrons under ultrafast excitation. These experiments were the first to re-examine a fundamental phenomenon — the

photoelectric effect — under a new dynamic perspective and hold great promise for future applications where timing of photoemission may become important in condensed or gas phase applications.

3. SYNTHESIS OF LIGHT FIELDS: THE NEXT FRONTIER

However important the manipulation of electronic processes with few-cycle intense light fields has turned out to be, for a plethora of quantum systems [47] CEP manipulation of light represents only a single and therefore limited control knob in the quest to dynamically explore and manipulate matter. Extension beyond this limit brings about the necessity of controlling of and confining the optical waveform of intense light pulses within attosecond time intervals and considerably increases the demands for more advanced light technologies permitting sculpting and confinement of ultrafast light waveforms with sub-cycle precision Figure 1(a). Earlier work based on the technique of molecular modulations [48, 49] contributed a notable progresses towards this essential goal. The adjustment of the relative phase or amplitude of quasi-monochromatic modes extending over superoctave spectrally allowed a sub-cycle sculpting of these waveforms but the overall picosecond to nanosecond confinement of these pulses considerably inhibits application in attosecond metrology and control.

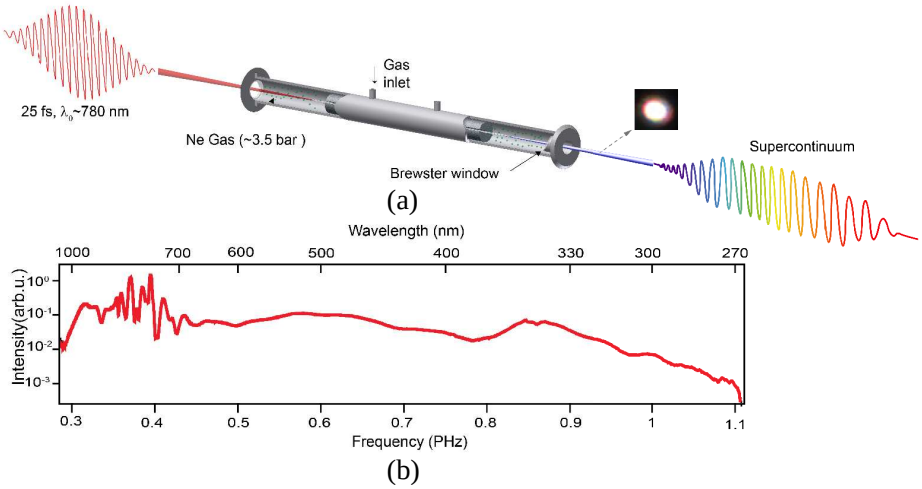

Figure 4. Superoctave light source in the visible and flanking ranges. (a) Supercontinuum generation in a Ne-filled hollow-core fiber pressurized at ∼3.5 bar. (b) The generated supercontinuum spanning over more than two optical octaves (∼0.8 PHz or ∼3.5 eV) with nearly uniform intensity (∼20–30 dB). Adapted from [4].

To enable synthesis of light in the attosecond regime, intense utrawideband pulses of continuum spectra extending over more than an optical octave are required. Hollow-core fiber based nonlinear broadening of femtosecond pulses generated by commercial systems (Figure 4) can provide this essential ingredient [50–52]. Remarkably though a nearly 5-fold increase of the spectral width with respect to that achieved in the inaugural experiments of this technique is essential to achieving superoctave pulses that fulfill the requirements for sub-cycle field synthesis.

The nonlinear propagation of near infrared pulses, typically shorter than ~ 25 fs, in pressurized noble gasses confined into hollow-core waveguides enable this possibility (Figure 4(a)). Earlier and more recent works studying propagation of short pulses in pressurized media underpin the importance of shockwave dynamics [53] along with self-phase modulation of input driver field in achieving this goal.

With intense ($> 300\,\mu$J) pulses extending over nearly two octaves [54] the next essential ingredient (Figure 4(b)) is an efficient methodology to manipulate the field of the generated, intense ultrabroadband pulses. Dispersive mirrors [55, 56] have laid a strong foundation for temporally compressing intense light pulses to near single-cycle durations [47] but this capability is limited to octave bandwidths. Moreover, compression of a predetermined spectral phase leaves little room for precise and dynamic manipulation of the field waveform.

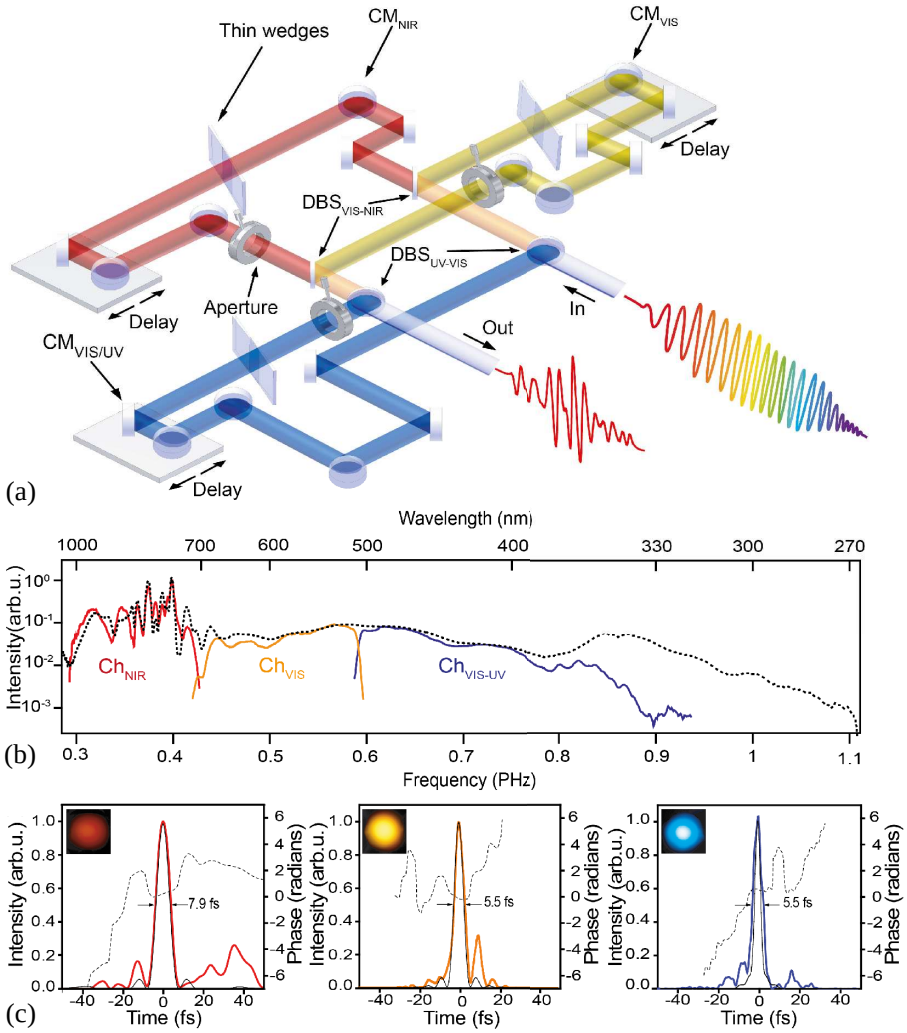

Figure 5. Apparatus for superoctave field synthesis. (a) Schematic representation of a prototypical three-channel light field synthesizer. (b) Spectrum of the coherent radiation at the exit of the hollow-core fiber (dashed line). Spectra exiting the individual channels (not to scale) are shown in red for Ch_{NIR} (700 to 1100 nm), yellow for Ch_{VIS} (500 to 700 nm), and blue for $Ch_{\mathrm{VIS\text{-}UV}}$ (350 to 500 nm). (c) Temporal intensity (solid lines) and phase profiles (dashed curves) of the respective pulses. The thin black lines depict the intensity profiles of the corresponding bandwidth-limited pulses, with durations of $\tau_{Ch(\mathrm{NIR})} = 6.8$ fs, $\tau_{Ch(\mathrm{VIS})} = 5$ fs, and $\tau_{Ch(\mathrm{VIS\text{-}UV})} = 4.5$ fs. Insets show photos of the respective beam profiles taken at the exit of the apparatus. Adapted from [54].

A more sophisticated approach for implementing light field synthesis, taking full advantage of the capabilities of dispersive optics in the optical, near infrared and ultraviolet regime [54] is illustrated in Figure 5. The ultrabroadband pulse emerging from a hollow-core waveguide, is spectrally divided by broadband, low dispersion dichroic beamspliters into several bands, each representing a different part of the electromagnetic spectrum. In a first proof of concept implementation of a synthesizer, three bands representing the near infrared the visible and the near UV part of the spectrum [54] were realized. Dispersive mirrors installed in the path of each band (hereafter: channel) — compress the pulses to nearly Fourier limited durations before they are recombined, by the same type of beamsplitters, at the exit of the apparatus to create a new optical waveform.

Sculpting of the fine details of the generated fields is now possible either by adjustment of the relative phases between pulses in different channels, i.e., through the variation of their mutual delay or by adjustment of their relative amplitudes. Typically, a wide range of waveforms can already be synthesized by the variation of the relative phases among these pulses; equalization of their relative

amplitudes brings about the possibility to increase the effective bandwidth of the waveform in the interest of creating even shorter transient fields.

Whereas the number of subdivisions of a given superoctave bandwidth may appear at a first glance essential it is only the total spectral width that determines the attainable temporal resolution. On the other hand, the inverse spectral bandwidth of individual spectral channels determines the time aperture, i.e., the temporal window over which the synthesizer can sculpt a light waveform with the highest potential resolution [6]. In the first implementation of the light field synthesizer, the time aperture was approximately 5–6 fs and suffices for a wide range of investigations in the attosecond and the few femtosecond regime. Nevertheless, the interferometric nature of the light field synthesizer allows the possibility of exciting a quantum system by a single channels pulse while probing of its dynamic response can realized by a waveform synthesized by pulses in the rest of the channels.

For innovations that bring about new levels of precision in measuring or controlling physical processes, progress can only be rigorously evaluated on the basis of appropriate metrology of these scientific deliverables. Whereas conventional pulse metrology [57, 58] is appropriate to capture the characteristics of the pulses in each of the constituent channels it fails to offer a reliable, instantaneous-field sensitive characterization required for field-controlled superoctave waveforms. On the other hand, attosecond streaking [39] satisfies these requirements and demonstrates how early innovations in attosecond science have laid the ground work for the next steps in this young but rapidly growing scientific field.

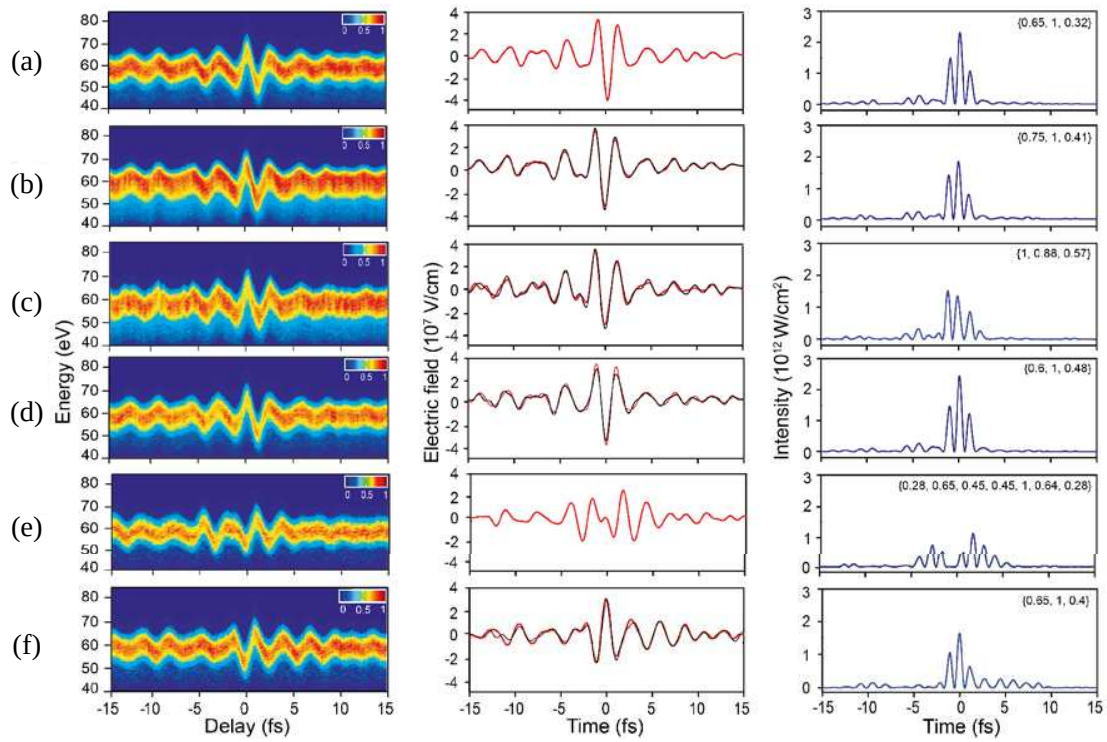

Figure 6. Synthesis of light field transients. (a) to (f) Attosecond streaking spectrograms composed of photoelectron spectra normalized to (left) their integral and (middle) the respective retrieved electric fields and (right) instantaneous intensity. Relative intensities for the most intense field crests normalized to the maximum are given in brackets. From (a) to (c), the delay of $Ch_{\text{VIS-UV}}$ is varied in steps of 200 as ($\sim\frac{\pi}{4}$). Dashed black lines in (b) and (c) show the field transients calculated from the reference waveform of (a). (d) Relative delays and CEPs of the individual channels are adjusted so as to create twin transients with a field minimum in between them. (e) ChNIR is delayed by 1.45 fs ($\sim\pi$), resulting in a high-frequency leading transient followed by a low-frequency tail. The dashed line in (e) shows the field transients calculated from the reference waveform of (d). Transients in (a) to (c), (e), and (f) carry less than one cycle within the FWHM of their temporal intensity profile. (f) τ_{FWHM} $\sim$2.1 fs, incorporating only $\sim$0.88 field cycles at the carrier wavelength of $\lambda_o\sim$710 nm. Adapted from [54].

In analogy to earlier experiments, optical transients generated in the field synthesizer are first used to generate an EUV probe pulse in a first gas jet, which in turn is used to implement attosecond streaking and to sample the field of the optical transient in a second gas jet. Each field waveform synthesized and measured by the apparatus can be used as a reference to determine critical parameters of the constituent pulses in the synthesizer [4, 54]. These include the duration, amplitude, CEP phase and relative phases (or delays) between them. Based on these parameters, a next light waveform can be sculpted on demand. Figure 6 shows a series of streaking spectrograms of pulses synthesized in the apparatus, their reconstructed field (red lines) and instantaneous intensities. The measurements underpin the stunning agreement between predicted (black lines) and measured waveforms (red lines) and establish attosecond synthesis of light fields as the essential tool to manipulate light in ultimate regime.

4. FIRST APPLICATIONS: EXCITING AND TRACING OF ULTRAFAST ELECTRONIC COHERENCES

Time integrated spectroscopy offers detailed information about the structure of neutral and ionized atomic specimens but cannot access how electronic coherences are created or evolve in real time under optical excitation. In a prototypical system, the singly ionized Krypton the energy separation ($\Delta E \sim 0.67$ eV) between the two lowest valence states implies a oscillating period of $\sim$6 fs for the induced coherence. A proof of concept experiment used the sub-cycle transient[54], composed in the field synthesizer, to ionize atoms of krypton and to create a coherent superposition of valence states in the emerging ions [59, 60]. To probe the excited coherence, a synchronous, attosecond EUV pulse was exploited to electronically promote the ionized medium to a common excited state. The temporal evolution of the coherence, more precisely the electron hole dynamics left behind after the excitation of the first electron are encoded on transient absorption spectra depicted in Figure 7. The conspicuous

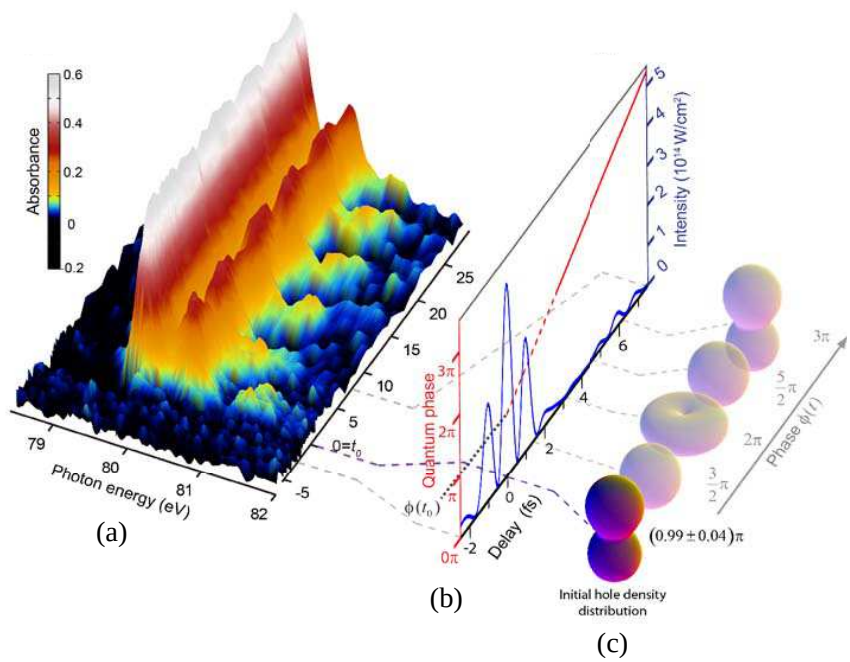

Figure 7. Initial quantum phase and density distribution of a valence electron wavepacket. (a) Attosecond XUV transient absorption spectrogram of Kr atoms field-ionized by a subcycle field transient shown by the blue line in (b). Linear extrapolation of the retrieved quantum phase $\phi(t)$ [shown by the red line in (c)] to time zero as determined through attosecond streaking, allows access to the initial quantum phase $\phi(t_0) = (0.99 \pm 0.04)\pi$ of the valence electron wavepacket. (c) Ensemble-averaged initial hole density distribution in the valence shell at the instant of ionization and its subsequent evolution, as evaluated from (a). Adapted from [54].

modulation of the amplitude of spectral lines (Figure 7(a)) along the pump-probe delay represents a crisp manifestation of the dynamic response of the system following the ultrafast excitation. One can argue, on the basis of pure quantum mechanical considerations, [59] that these amplitude modulations are becoming detectable by the quantum interference of transitions from initial coherent states to a common final state to which the system is promoted by the EUV attosecond pulse, giving rise to the absorption resonances. Equally intuitive is the idea of considering the oscillating electron cloud as an angstrom scale antenna. The orientation of the electron cloud (prolate against oblate orbital shape) enhances or suppresses absorption of the impinging probe electromagnetic wave(Figure 7(c)), depended on weather the antenna is aligned along the polarization (prolate shape) of the EUV field or not (oblate shape). Both the oscillating period ($T = 6.2\,\mathrm{fs}$) and the degree of coherence (85%) of the oscillating electronic wavepacket are obtained via a reconstruction of the trace based on an intuitive model. Interestingly, in comparison to previous experiments by few-cycle pulses, nonlinear excitation of the electronic wavepacket in the same system, the degree of coherence of the induced electronic motion increased by more than 30%. This significant improvement can be attributed to the extreme confinement of the excitation of the electronic wavepacket within the sub-fs width of the single intense half-cycle of the sculpted waveform. Moreover, the precise confinement of the excitation to a time window significantly shorter that the oscillating period of the induced electronic coherence allowed for the first time the determination of the initial phase of the electronic wavepacket, i.e., at the moment of its birth. The value obtained $\phi(t_0) = (0.99 \pm 0.04)\pi$ agreed well with that obtained by state-of-the-art numerical simulations of the interaction.

5. FUTURE PROSPECTS

Merely more than a decade of attosecond science has passed and the field has demonstrated innovation that goes well beyond what was conceivable some fifteen years ago. Recent extension of the key paradigms of few-cycle pulse control to the condensed phase enabled the creation of light induced currents [59, 60] and their precise CEP manipulation in broadband dielectrics bring about new perspectives in electronics and information technologies and the desire to advance their state of the art to the PHz realm. Implementation of these ideas with synthesized fields may further enlarge the range of possibilities. Light field synthesis offers a efficient way for encoding digital (Figure 8(b)) or analog information on the carrier frequency of light waves just as modern electronic sources trivially offer this capability at microwave frequencies. A simple experimental demonstration where the amplitude control of consecutive half-cycles in synthesizer waveform is used to encode a sequence of bits of information is shown in Figure 8(a). Coupling such a waveform to a solid the information can be ported to a plasmon [61] or a current propagating inside an electronic device (Figure 8(b)) or possibly the other way around. Even though such developments are still in their conception, the enormous progress of this new field of science may soon bring such and many more other possibilities a step closer to reality.

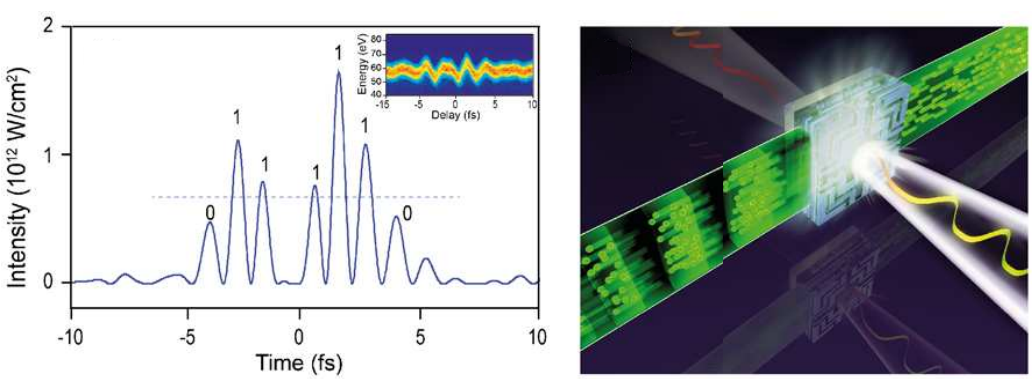

Figure 8. (a) Encoding of digital information at individual half-cycles to transmit and process information on the Pbit/sec scale. (b) Schematic illustration of envisaged control of electronics with these waveforms.

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