Attosecond science

The motion of electrons on the atomic scale has been hidden from direct experimental access until recently. We review the revolution in technology that opened the door to real-time observation and time-domain control of atomic-scale electron dynamics, and address the expected implications of having the tools to monitor electrons with sub-atomic resolution in both space and time.

P. B. CORKUM[1] AND FERENC KRAUSZ[2,3]

[1]National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6
[2]Department für Physik, Ludwig-Maximilians-Universität, Am Coulombwall 1, D-85748 Garching, Germany
[3]Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Strasse 1, D-85748 Garching, Germany

e-mail: paul.corkum@nrc-cnrc.gc.ca; krausz@lmu.de

From 1964, when mode-locking was discovered, until 2001, when the first sub-femtosecond (that is, attosecond) pulses were produced[1,2], laser pulse durations decreased by about three orders of magnitude (Fig. 1). Advances came through constantly refining known concepts of dispersion control and Kerr nonlinearities, aided by improved laser materials. Although a laser scientist from 1965 would have been amazed that pulses of 5 fs (two periods) could be produced[3], he or she would have been very familiar with all of the principles used.

During this time, advancing optical technology repeatedly opened new sub-fields of atomic, molecular and solid-state science, most notably real-time chemistry[4]. It also became possible to do experiments at an unprecedented intensity. In fact, attosecond science arises from research of the early 1990s into intense ultrashort-pulse atomic physics.

There are three important characteristics of the current generation of attosecond technology that imply new directions in science. First, in the nonlinear medium in which they are produced, attosecond optical pulses are always accompanied by an attosecond electron pulse[5]. Thus, the technology of electron physics can be integrated with optical technology. The electron gives attosecond science access to spatial resolution[6,7] determined by electron wavelength (~1 Å), and optics gives electron-collision physics a systematic method for measuring dynamics. Real-time three-dimensional (3D) molecular movies become feasible with sub-angstrom spatial resolution and sub-femtosecond time resolution. Second, attosecond photon or electron pulses are accompanied by a synchronized visible pulse of controlled waveform[8]. Thus, attosecond technology extends conventional ultrafast spectroscopy and strong-field coherent control from the cycle-averaged into the sub-cycle domain of visible light, advancing time-resolved and control techniques from the molecular to the electronic timescale. Furthermore, it is possible to probe atoms or molecules while the strong field is present. Finally, attosecond photon or electron pulses have energies of 10 eV to 1 keV or beyond. Core- level and multi-electron dynamics[9,10] or even nuclear dynamics[11] can be time-resolved.

PRODUCING ATTOSECOND OPTICAL PULSES

The process that leads to attosecond pulses is sketched in Fig. 2a–d[12].

Step 1: Ionization. When induced by a strong (near-)infrared laser field, ionization can be approximated by tunnelling; the electron tunnels through the potential barrier created by the ion charge and the laser electric field (Fig. 2a). Tunnelling determines the ionization probability as a function of time within the wave cycle[13–15]. For 800-nm light (oscillation period $T_{osc} \approx 2.7$ fs), tunnelling is most probable during about 300 attoseconds around each field crest near the pulse peak[10]. Thus, the attosecond timescale arises first during tunnelling. Step 2 will subdivide this 300-attosecond timescale, mapping time-of-birth onto energy.

Step 2: Motion after liberation. A typical electron will gain a kinetic energy of ~50–1,000 eV from the field during its first femtosecond of freedom, representing tens to hundreds of photons. Therefore, classical mechanics roughly accounts for the electron's motion in the direction of the field. Tunnelling launches electrons on classical trajectories. Each instant of ionization is linked to a moment of recollision by a trajectory. The most important trajectory is populated by electrons born at $\sim T_{osc}/20$ following the peak of the electric field. These electrons recollide with maximum kinetic energy about $2/3T_{osc}$ later. The maximum kinetic energy will determine the maximum photon energy in the emitted attosecond photon pulse. It is proportional to the peak electric field E_0^2 and the laser wavelength λ_L^2.

We have tacitly assumed that the electron leaves the 'tunnel' with zero velocity. Quantum mechanics never allows such precision. This assumption is especially inadequate in the direction perpendicular to the laser field. Experiments indicate that for a simple atom the electron expands laterally with a gaussian profile and a typical velocity of ~5 Å fs^{-1} so the wavepacket has a full-width at half-maximum of ~5–10 Å when it recollides. This lateral spread lowers the probability of the electron re-encountering the core. Nevertheless, from a collision-physics point of view, the current density seen by the parent ion is still impressive: with a maximum value of nearly 10^{11} A cm^{-2} (ref. 5) it exceeds the current density delivered by conventional electron sources by several orders of magnitude.

Step 3: Recollision. On re-encountering the core, the electron scatters from its parent ion. Inelastic scattering gives us a chance to validate the semiclassical procedure above, even measuring the equivalent current density. We obtain quantitative agreement for double ionization of helium[16] and H_2 (ref. 5). In addition, the recollision electron may give rise to the emission of an attosecond photon burst (Fig. 2e). On recollision, the free, Ψ_c, and the bound, Ψ_g, components of the (coherent) total wavefunction interfere, producing an oscillating dipole that emits light. During this process, the kinetic energy, amplitude and phase of the recollision electron wavepacket is transferred to the photon pulse through the transition moment. Controlling the shape[17] and the waveform[8]

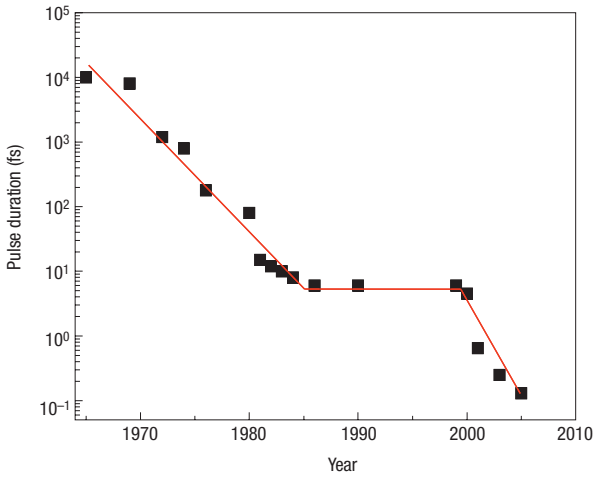

Figure 1 Shorter and shorter. The minimum duration of laser pulses fell continually from the discovery of mode-locking in 1964 until 1986 when 6-fs pulses were generated. Each advance in technology opened new fields of science for measurement. Each advance in science strengthened the motivation for making even shorter laser pulses. However, at 6 fs (three periods of light), a radically different technology was needed. Its development took 15 years. Now attosecond technology is providing radically new tools for science and is yet again opening new fields for real-time measurement. Reprinted in part, with permission from ref. 65.

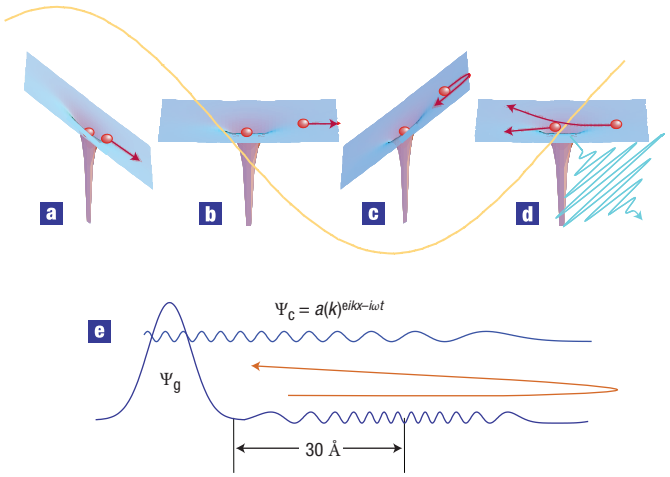

Figure 2 Creating an attosecond pulse. **a–d**, An intense femtosecond near-infrared or visible (henceforth: optical) pulse (shown in yellow) extracts an electron wavepacket from an atom or molecule. For ionization in such a strong field (**a**), Newton's equations of motion give a relatively good description of the response of the electron. Initially, the electron is pulled away from the atom (**a**, **b**), but after the field reverses, the electron is driven back (**c**) where it can 'recollide' during a small fraction of the laser oscillation cycle (**d**). The parent ion sees an attosecond electron pulse. This electron can be used directly, or its kinetic energy, amplitude and phase can be converted to an optical pulse on recollision[12]. **e**, The quantum mechanical perspective. Ionization splits the wavefunction: one portion remains in the original orbital, the other portion becomes a wave packet moving in the continuum. The laser field moves the wavepacket much as described in **a–d**, but when it returns the two portions of the wavefunction overlap. The resulting dynamic interference pattern transfers the kinetic energy, amplitude and phase from the recollision electron to the photon.

of the optical pulse controls the kinetic energy[2], amplitude[17] and phase[18] of the recollision electron and therefore the attosecond pulse[19] that it produces.

In addition to producing attosecond electron and photon pulses, the recollision simultaneously encodes all information on the electron interference. Once the amplitude and phase of the electron interference is encoded in light, powerful optical methods become available to 'electron interferometry'.

Classical trajectory calculations show that filtering a limited band of photon energies near their maximum (cut-off) confines emission to a fraction of a femtosecond[17]. Such a burst emerges at each recollision of sufficient energy. The result is a train of attosecond bursts of extreme ultraviolet (XUV) light spaced by $T_{osc}/2$ (ref. 1).

For many applications, single attosecond pulses (one burst per laser pulse) are preferred. They emerge naturally from atoms driven by a cosine-shaped laser field comprising merely a few oscillation cycles (few-cycle pulse)[3]. Then only the electron pulled back by the central half-wave to its parent ion possesses enough energy to contribute to the filtered high-energy emission (Fig. 3). Turning the cosine waveform of the driving laser field into a sinusoidally shaped one (by simply shifting the carrier wave with respect to the pulse peak[8]) changes attosecond photon emission markedly: instead of a single pulse, two identical bursts are transmitted through the XUV bandpass filter. Controlling the waveform of light[8] has proved critical for controlling electronic motion and photon emission on an attosecond timescale and permitting the reproducible generation of single attosecond pulses[19].

The shortest duration of a single attosecond pulse is limited by the bandwidth within which only the most energetic recollision contributes to the emission. In a 5-fs, 750-nm laser pulse this bandwidth relative the emitted energy is about 10%. At photon energies of ~100 eV this translates into a bandwidth of ~10 eV, allowing pulses of about 250 attoseconds in duration[17]. At a photon energy of 1 keV (ref. 20) a driver laser field with the above properties will lead to single pulse emission over roughly a 100-eV band, which may push the frontiers of attosecond technology near the atomic unit of time, 24 attoseconds. Manipulating the polarization state of the driver pulse[17] enables the relative bandwidth of single pulse emission to be broadened[21,22] by 'switching off' recollision before and after the main event. Together with dispersion control[23], this technique has recently resulted in near-single-cycle 130-attosecond pulses at photon energies below 40 eV (ref. 24). Confining tunnel ionization to a single wave crest at the pulse peak constitutes yet another route to restricting the number of recollisions to one per laser pulse. Superposition of a strong few-cycle near-infrared laser pulse with its (weaker) second harmonic[25,26] is a simple and effective way of achieving this goal.

This attosecond-pulsed XUV radiation emerges coherently from a large number of atomic dipole emitters. The coherence is the result of the atomic dipoles being driven by a (spatially) coherent laser field and the coherent nature of the electronic response of the ionizing atoms discussed above. The pulses are highly collimated, laser-like beams, emitted collinearly with the driving laser pulse. The next section addresses the concepts that allowed full characterization of the attosecond pulses.

MEASUREMENT TECHNOLOGY

Any pulse measurement method must directly or indirectly compare the phase of different Fourier components of a pulse. Autocorrelation, SPIDER and FROG, three extensively used methods to characterize optical pulses[27], use nonlinear optics to shift the frequency of the Fourier components differentially so that neighbouring frequency components can be compared. The electron-optical streak camera — an older ultrafast pulse

measurement[28,29] — follows a different strategy. First a photoelectron replica of the optical pulse is produced and then the electron replica is measured.

Although two-photon ionization of atoms allows autocorrelation of low-frequency attosecond pulses[30,31], at photon energies of 50–100 eV and beyond the streak camera approach[19,32] is the method of choice for measuring attosecond pulses: a photoelectron replica is produced and then measured by deflecting or accelerating it with a rapidly varying optical field.

There are two approaches to producing the photoelectron replica. (1) The recollision electron is a pre-existing replica. It is a replica because its kinetic energy, amplitude and phase are transferred to the attosecond pulse when it recombines with the bound state orbital from which it was released during ionization. (2) A new electron replica can be produced from the attosecond optical pulse by photoionizing an atomic medium. The latter has been applied to measure isolated attosecond pulses[2,19,24] or attosecond trains[1,23].

What makes the photoelectron replica such a powerful idea is that it is so easy for the optical field to add energy to (or remove energy from) ionizing electrons[33]. It is easy conceptually — the exquisite sensitivity of ionizing electrons to laser fields was used (see previous section) to generate attosecond pulses. It is easy experimentally — the replica has a phase-synchronized electric field accompanying it. In fact, a phased strong electric field can be exploited in any attosecond experiment. There is now no fundamental lower limit to the resolution of attosecond measurements[34].

A clear corollary should not be lost on the reader. Because virtually all measurements of attosecond pulses are really measurements of electrons, the recollision electron pulse that stimulates inelastic events can be fully characterized. Equally, the time history of the appearance of any charged fragments that are produced by photoionization or inelastic scattering can be measured. This is a considerable advance for collision physics. Inelastic scattering, including core–hole dynamics and nuclear dynamics[9–11], can be time-resolved. Never before have collision-induced processes seemed systematically accessible for real-time experiments.

STUDYING AND CONTROLLING MOLECULAR STRUCTURE AND DYNAMICS

Molecular structure and dynamics emerge under the influence of interatomic forces that are created by electrons. The laser pulses that produce attosecond pulses are so intense that their time-dependent electric fields are on the scale of the fields that valence electrons experience in molecules and solids. Attosecond technology marries fast times (from the attosecond electron or photon pulse) to strong optical fields that are controllable on the same timescale.

But the technology is even more powerful. The interatomic separation in matter is ~1 Å and the typical structure size of valence electron orbitals is ~1 Å. This almost exactly matches the wavelength of a typical recollision electron (~1–2 Å). Thus attosecond technology is naturally suited to measuring molecular structure. The ability of attosecond and strong-field science in simultaneously controlling and measuring structure and dynamics is unique in science. We now discuss how this can be achieved.

Imagine a 3D molecular movie of a photochemical reaction in which the changing positions of the atoms in the molecule are followed frame by frame. Collision physics has a long tradition of measuring molecular structure[35]. The recollision electron can be used in a similar fashion. That is, the recollision electron wave (Fig. 4a) can diffract (not shown) from its parent ion. This approach to molecular imaging has been named 'laser-induced electron diffraction'[36,37]. Closely related to conventional electron diffraction, it makes use of the spatial coherence of the recollision electron. Measuring the 3D electron momentum of the scattered electron, we gain information required to reconstruct atomic positions within the molecule[38,39].

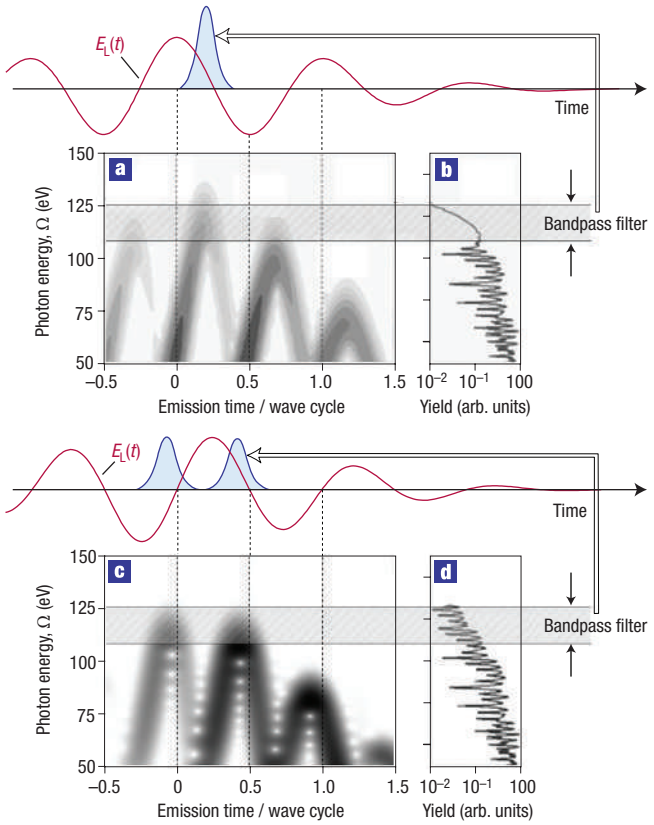

Figure 3 Generation of a single or twin attosecond photon pulse. **a**,**c**, The spectrogram (window Fourier transform) of the atomic high-harmonic emission driven by a few-cycle near-infrared laser pulse (τ_L = 5 fs, λ_L = 750 nm), as accumulated coherently over a macroscopic propagation distance. **b**,**d**, Spectra of the emitted XUV photons. Panels **a** and **b** are calculated for a cosine-shaped driving pulse, panels **c** and **d** are for a sine-shaped driving pulse. Filtering out high-energy emission yields a single (**a**) or double (**c**) sub-femtosecond XUV pulse. Figure courtesy of V. Yakovlev.

Moreover, the recollision electron is coherent in ways that an externally generated electron cannot be — it is produced from a single electron orbital and manipulated with coherent light. These unique properties open the opportunity for electron holography[39]. For example, one part of the laser pulse might produce a reference electron wavepacket (using circularly polarized light) and a second coherent related part of the pulse might produce a wavepacket that re-collides with the ion. The interference pattern between the two is a hologram of the 3D scattering potential. Thus, it seems feasible to fulfil Gabor's[40] original dream of electron holography — frames in a holographic movie.

The unique properties of the recollision electron offer a third opportunity for molecular imaging. Attosecond pulse and high harmonic generation map onto electron interferometry. In optics, interferometry allows us to characterize the interfering waves fully. This should be equally true for electrons. Figure 4a illustrates this mapping. The recolliding electron wavepacket is split from its parent orbital in much the same way that a beam splitter splits a light beam in an optical interferometer. When it returns it interferes with the initial orbital. The figure captures the exact moment at which the recollision electron wavelength matches the structure size of the orbital. Earlier and later the interference will be different. As we have discussed above, attosecond pulses arise from this interference. Therefore, their spectrum encodes the interference[7,41,42]. Clearly the interference

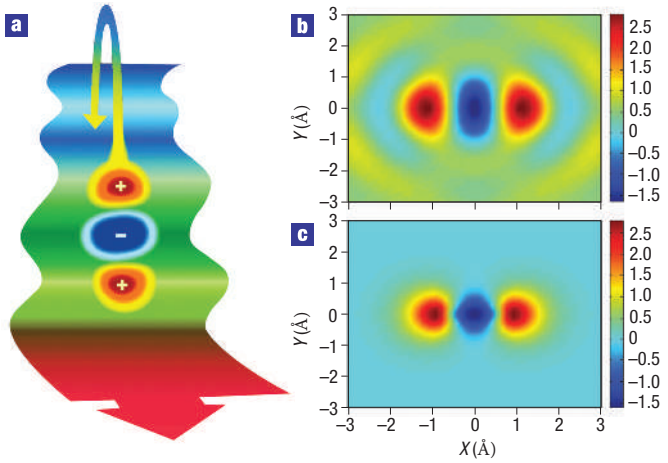

Figure 4 Orbital tomography. **a**, The basic physics of orbital tomography. The recollision electron is shown as a coloured wave that has low frequency at the bottom and high frequency at the top. It emerges from the orbital to be imaged and when it returns it interferes with the orbital. The sketch captures the moment where the recollision electron wavelength matches the orbital size. The interference would be very different earlier (when the wavelength is longer) or later (when it is shorter). It would also be very different for other molecular alignments. All of this information is encoded in the spectrum of the emitted light. **b**,**c**, The measured orbital of N_2 (**b**) can be compared to the calculated image in **c** (ref. 7).

changes as we rotate the molecule. Recording the spectrum as a function of molecular alignment, we obtain a tomographic image of the orbital. This dream has been achieved experimentally. Figure 4b shows the highest occupied molecular orbital of N_2 measured in this way[7]. For reference, the calculated orbital is shown in Fig. 4c.

We have not yet exhausted the opportunities for imaging chemical dynamics. In the last section we emphasized the close connection between attosecond pulse generation and photoionization. If the pre-existing electron replica can be used to measure the 3D structure of orbitals, then the photoelectron replica created from a molecule must contain the same information[43] provided the electron originates from a well-defined orbital. Measuring molecular structure by means of photoionization is closely related to measuring attosecond optical pulses[44]. Finally, all information on the structure of orbitals also resides in the amplitude and phase of the absorption spectrum of an attosecond pulse that passes through an absorbing medium of aligned molecules. Thus, the amplitude and phase of the spectrum of an attosecond pulse provides yet another method for imaging molecules.

In chemical dynamics, the motion of the atoms imposes the natural timescale. Attosecond technology enables the faster dynamics of bound-state electron wavepackets to be measured. Measuring attosecond electron dynamics is almost the same as measuring attosecond photon or electron pulses (see above). In an excited molecule, photoionization will produce multiple electron replicas of the attosecond pulse, one from each state. The interference between these overlapping electron replicas encodes all information on the relative phase of the electronic states. As the wavepacket evolves, the electronic interference of the replicas in the continuum evolves, tracking the motion of the wavepacket[45]. As with measuring attosecond optical pulses, a pre-existing replica is just as good as an attosecond pulse[46] with the corresponding experimental simplification. We now turn to control.

Valence electrons can move across molecules within attoseconds. Control of this motion requires a force that can be varied within attoseconds and strong enough to rival the internal forces acting on the electrons. The electric field of waveform-controlled light provides such a force. Its ability to control the motion of ionizing electrons on a nanometre scale has been demonstrated by the reproducible generation of single and double attosecond photon pulses[19]. The controlled electric force of light was recently shown[47] to be able also to steer the motion of an electron bound to a simple diatomic molecule (D_2^+). The strong infrared laser field drives the electron back and forth between the two nuclei while the nuclei move apart (dissociate) owing to previous excitation. The electron eventually sticks to one of the two nuclei, as they become separated. The waveform of the light pulse controls which one it sticks to.

The experiment conveys important messages. The electron of a chemical bond can be directed in a molecule, leading to control over the reaction products. Steering electrons constitutes the most fundamental way of controlling chemical and biochemical reactions. Light-field-directed reactions hold promise for many surprises. It is just as exciting to envisage implications of a purely electronic nature. When electrons are driven through a molecule, charge is transported. Driven by the field of light, charge can be transferred from one end to the other of even large molecules within attoseconds. Light-field-directed charge in molecules opens the prospect of petahertz-scale electronics.

CAPTURING MULTI-ELECTRON DYNAMICS IN REAL TIME

In atoms and molecules the electrons move in the combined potential of the ion core and all other electrons. Even when the total energy of the system is fixed, these electrons move, interact and exchange places on the attosecond timescale — all electrons entangled with each other. Thus multi-electron dynamics is another natural area for attosecond science. The single-electron approximation is valid when dynamics is slow enough that the other electrons can adjust. Multi-electron dynamics is observable as a result of energetic (electron or ion) collisions or by absorption of an energetic (XUV or X-ray) photon. In both cases one or more electrons can be freed. Before the electrons become free, they interact with each other. These interactions affect both the final momenta and the temporal evolution of emission of the outgoing electrons. Until recently, only measurement of the former provided experimental access to electron–electron interactions. Attosecond technology has spawned ways of measuring the temporal evolution of the outgoing electron wavepackets and hence provides, for the first time, direct time-domain insight into electron–electron interactions.

In conventional collision physics the initial and the final states of the scattered particles are the only accessible experimental observables. Attosecond technology provides access to new variables. First, the collision is accurately timed with respect to the time-dependent field that drives it[12]. That means that it can be timed with respect to a pump pulse, allowing the collision to serve as a probe[48]. All of the power of optical coherent control can be applied to the system to be probed by collision. Second, any charged fragments decay into the phased time-dependent field. That means that they gain a phase-dependent energy which determines their time of birth[49]. This is another application of the optical-field-driven streak camera[19,32] used for attosecond pulse measurement[19]. Third, gating techniques can be imported into collision physics: the time dependence of electrons emerging into the laser field can be fully characterized with the time-varying field. Finally, correlation and entanglement open completely new approaches to measuring collision dynamics — approaches influenced by advances in quantum optics[50,51].

Two experiments on recollision-induced attosecond multi-electron dynamics point the way. In one experiment a pump pulse launches a rotational wavepacket. Catching the wavepacket when

the molecule is aligned parallel or perpendicular to the recollision electron, double ionization dynamics is measured[48]. The experiment shows that electrons are much more likely to leave the molecule within a few hundred attoseconds of each other for parallel than for perpendicular molecules.

The second experiment uses only a single laser pulse, but concentrates on recollision-induced multiple ionization (for example, $Ne \rightarrow Ne^{4+} + 4e$). Only electrons that recollide near the zero crossing of the laser field have enough energy to trigger these very energetic events. Measuring the momentum of the Ne^{4+} fragment, the experiment[52] shows that all four electrons leave the molecule within a few hundred attoseconds, long before the field crests. The measured momentum distribution is consistent with electrons thermalizing in just a few hundred attoseconds[53] — thermodynamics within a single atom.

During any inelastic scattering experiment the electron exchanges its energy with the charged components of the target atom or molecule by means of electric fields. In the case of a few-100-eV electron, the characteristic time of the collision is ~30 attoseconds. Thus, there is a strong affinity between attosecond electron and photon experiments. We now turn to experiments that use attosecond XUV pulses to probe multielectron dynamics.

The XUV photons can, in addition to the valence-band photoelectrons, also liberate electrons from inner shells of atoms, molecules or solids. The inner-shell vacancy decays rapidly through a variety of processes including electron–electron interactions. These interactions eject secondary (Auger) electrons and promote others to excited bound states through a process referred to as shake-up (see Fig. 5). Attosecond technology allows both types of electrons to be probed directly in the time domain. In both cases, dynamics is triggered by an attosecond XUV excitation and measured by the strong, synchronized field of the laser pulse previously used for the generation of the attosecond pulse.

The laser field can modify the momentum (and energy) of the outgoing products of the XUV excitation just as we have described above. Alternatively, the excited bound (shake-up) electrons can be extracted from the atom by means of strong-field-induced bound–free transitions (by tunnelling) also discussed above. In both cases it is the oscillating electric field rather than the pulse envelope that probes the process, ensuring attosecond resolution. We refer to these techniques as attosecond streaking spectroscopy and attosecond tunnelling spectroscopy (Fig. 5).

Attosecond tunnelling spectroscopy recently shed light on how electrons escape from their atomic binding potential under the influence of a strong optical field. They are set free during a time window of less than 400 attoseconds near each field maximum of the ionizing few-cycle laser field[10], just as predicted by the theory of optical field ionization[13–15]. The experiment constitutes real-time observation of light-induced electron tunnelling. The attosecond release of electrons from their bound states enables short-lived transient electronic states of matter to be probed and provides insight into multi-electron interactions (for example, shake up or single and cascaded Auger decay) on the atomic scale.

Attosecond streaking spectroscopy enables direct time-domain observation of the decay of an inner-shell vacancy through Auger relaxation in isolated atoms[9]. Extension of the technique to solids will enable direct experimental access to atomic-scale charge-transport phenomena in solids and surfaces for the first time. The ability to time-resolve attosecond electronic processes in condensed matter will advance a number of fields, all the way from basic science to everyday technologies. This is because a vast number of transient electron phenomena — many of them playing a central role in condensed-matter science and future technologies — evolve on a subfemtosecond-to-few-femtosecond scale. Charge screening, electron–electron scattering, spin–orbit interactions, collective

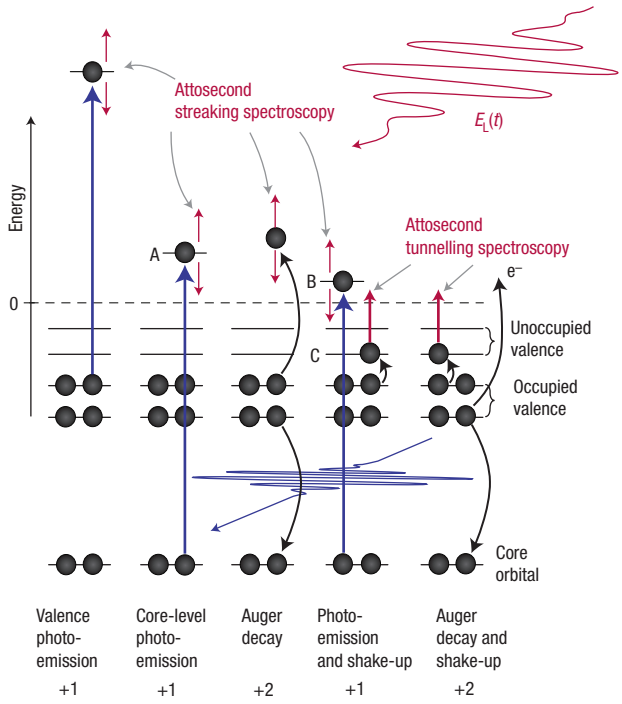

Figure 5 Excitation and relaxation. Electronic excitation and relaxation processes in atoms, molecules and solids, and possible ways of tracing these dynamics in real time. The labels 1+ and 2+ indicate single and double ionization.

(for example, exciton or plasmon) dynamics in metals and semiconductors, charge transfer in host–guest systems or within molecular assemblies constitute merely a few textbook examples. Real-time observation of these phenomena will help explore the limits of current technologies, such as semiconductor electronics, and the potential of new technologies, such as spintronics, plasmonics, molecular electronics, hybrid (dye–semiconductor) photovoltaics, or optical nanostructuring. In this way, attosecond technology may contribute to the advancement of key technologies such as processing and storing information, or ecologically friendly energy production.

CHALLENGES AND PROSPECTS

Proof-of-principle experiments, some of which have been reviewed above, have established experimental attosecond science. To exploit the full potential offered by the new concepts and technologies, the existing tools need to be improved and new tools need to be developed.

Waveform-controlled few-cycle pulses are becoming standard tools of attosecond science laboratories. They allow the controlled and reproducible production of isolated attosecond electron and photon pulses, a prerequisite for future precision attosecond experiments. For future progress, the technology must be further developed. We envisage two main directions, one for advancing measurement, one for advancing control.

(1) Extending controlled few-cycle wave generation into the infrared[54,55] will increase the energy of the recolliding electron and the emitted photon, pushing the frontiers of attosecond collision and photoexcitation studies into the kilo-electronvolt regime. This will enable collisionally excited or photo-excited X-ray atomic transitions to be time-resolved and studied under the influence of strong fields

for the first time. Implications for X-ray laser research are obvious. (2) Shaping the amplitude and frequency of the recolliding electron and emitted photon wavepacket requires shaping of the optical electric field and manipulating its polarization state within the wave cycle. This calls for advancing waveform-controlled light generation to optical waveform synthesis. The prerequisites are coherent light with bandwidth spanning several octaves, say, over the range of 1–10 eV, and selective manipulation of the amplitude, phase and polarization of the individual spectral components. Optical waveform synthesis will be the essential technology for extending the powerful concepts of femtosecond nuclear wavepacket control in molecules to attosecond electron wavepacket control in all forms of matter.

So far, attosecond pulses have been used for triggering or for probing dynamics. Their low flux has prevented them from being applied simultaneously as pump and probe. Scaling waveform-controlled few-cycle light to relativistic intensities holds promise for producing high-intensity attosecond photon pulses in the extreme ultraviolet and soft-X-ray regime that can be simultaneously applied for both purposes. The most promising route to this goal is to expose a solid surface to relativistic-intensity light[56]. The light creates a plasma mirror that oscillates with a velocity approaching that of light. This imposes a relativistic Doppler up-shift of the reflected incident light. If the light pulse contains only several cycles then the reflected blue-shifted photons can be delivered in a single, ultra-intense attosecond ultraviolet[57] or soft-X-ray pulse[58].

These pulses will enable attosecond pump/attosecond probe spectroscopy. New research opportunities include the creation of a localized electron wavepacket in a molecule, or molecular assembly steering it with a synthesized optical wave and then probing the evolution with an attosecond pulse. Real-time observation and control of charge transfer in molecular systems will become feasible for the first time. Molecular electronics[59], bioinformatics and cancer research[60] may benefit from these capabilities.

So far, sub-atomic resolution has been possible in either time or in space. The re-colliding electron, once incorporated in a pump–probe setting, offers both. Here we note that there may be other approaches to capturing the microscopic motion of electrons and atoms with sub-atomic resolution in both space (picometres) and time (attoseconds). They draw on attosecond ångström-wavelength photon and electron pulses. The photon pulses may emerge from future X-ray free electron lasers by manipulating its energy reservoir (a relativistic electron bunch) with a few-cycle optical wave[61]. The electron pulses have been proposed in the form of single-electron pulses from a microwave accelerator, in which phase focusing compresses the duration of the initially multi-femtosecond electron pulse into the attosecond regime[62]. If these tools can be developed, they will advance current 4D imaging techniques drawing on sub-picosecond X-ray[63] or electron[64] pulses into the attosecond–picometre regime, enabling true imaging of virtually any transient structures of matter.

CONCLUSION

Attosecond science is a revolution in technology. It integrates optical and collision science, greatly extending the reach of each. From a collision perspective, collision physics and X-ray science, long dominated by time-integrated measurements, can now resolve time-dependent mechanisms. Theoretically, time-independent scattering theories will need to be supplemented by time-dependent theories to describe attosecond experiments. From an optical perspective, imaging the position of both basic ingredients of matter — nuclei and electrons — with sub-atomic unit resolution simultaneously in space and time in any transient state of matter is within reach. This will have impact well beyond physics, ultimately influencing chemistry, biology and future technologies.

doi:10.1038/nphys620

References

1. Paul, P. M. *et al.* Observation of a train of attosecond pulses from high harmonic generation. *Science* **292,** 1689–1692 (2001).
2. Hentschel, M. *et al.* Attosecond metrology. *Nature* **414,** 509–513 (2001).
3. Brabec, T. & Krausz, F. Intense few cycle light pulses: frontiers of nonlinear optics. *Rev. Mod. Phys.* **72,** 545–591 (2000).
4. Zewail, A. Femtochemistry: atomic-scale dynamics of the chemical bond. *J. Phys. Chem. A* **104,** 5660–5694 (2000).
5. Niikura, H. *et al.* Sub-laser-cycle electron pulses for probing molecular dynamics. *Nature* **417,** 917–922 (2002).
6. Zuo, T., Bandrauk, A. D. & Corkum, P. B. Laser induced electron diffraction: a new tool for probing ultrafast molecular dynamics. *Chem. Phys. Lett.* **259,** 313–320 (1996).
7. Itatani, J. *et al.* Tomographic imaging of molecular orbitals. *Nature* **432,** 867–871 (2004).
8. Baltuska, A. *et al.* Attosecond control of electronic processes by intense light fields. *Nature* **421,** 611–615 (2003).
9. Drescher, M. *et al.* Time-resolved atomic inner-shell spectroscopy. *Nature* **419,** 803–807 (2002).
10. Uiberacker, M. *et al.* Attosecond real-time observation of electron tunnelling in atoms. *Nature* **446,** 627–632 (2007).
11. Milosevic, N., Corkum, P. B. & Brabec, T. How to use lasers for imaging attosecond dynamics of nuclear processes. *Phys. Rev. Lett.* **92,** 013002 (2004).
12. Corkum, P. B. A plasma perspective on strong field multiphoton ionization. *Phys. Rev. Lett.* **71,** 1994–1997 (1993).
13. Keldysh, L. V. Ionization in the field of a strong electromagnetic wave. (Multiphonon absorption processes and ionization probability for atoms and solids in strong electromagnetic field.) *Sov. Phys. JETP* **20,** 1307–1314 (1965).
14. Ammosov, M. V., Delone, N. B. & Krainov, V. P. Tunnel ionization of complex atoms and of atomic ions in an alternating electromagnetic field. *Sov. Phys. JETP* **64,** 1191–1194 (1986).
15. Yudin, G. L. & Ivanov, M. Y. Nonadiabatic tunnel ionization: looking inside a laser cycle. *Phys. Rev. A* **64,** 013409 (2001).
16. Yudin, G. L. & Ivanov, M. Y. Physics of correlated double ionization of atoms in intense laser fields: quasistatic tunneling limit. *Phys. Rev. A* **63,** 033404 (2001).
17. Corkum, P. B., Ivanov, M. Y. & Burnett, N. H. Sub-femtosecond pulses. *Opt. Lett.* **19,** 1870–1872 (1994).
18. Dudovich, N. *et al.* Measuring and controlling the birth of attosecond pulses. *Nature Phys.* **2,** 781–786 (2006).
19. Kienberger, R. *et al.* Atomic transient recorder. *Nature* **427,** 817–821 (2004).
20. Seres, J. *et al.* Source of coherent kiloelectronvolt X-rays. *Nature* **433,** 596 (2005).
21. Chang, Z. Single attosecond pulse and XUV supercontinuum in the high-order harmonic plateau. *Phys. Rev. A* **70,** 043802 (2004).
22. Sola, I. J. *et al.* Controlling attosecond electron dynamics by phase-stabilized polarization gating. *Nature Phys.* **2,** 319–322 (2006).
23. Lopez-Martens, R. *et al.* Amplitude and phase control of attosecond light pulses. *Phys. Rev. Lett.* **94,** 033001 (2005).
24. Sansone, G. *et al.* Isolated single-cycle attosecond pulses. *Science* **314,** 443–446 (2006).
25. Pfeifer, T. *et al.* Heterodyne mixing of laser fields for temporal gating of high-order harmonic generation. *Phys. Rev. Lett.* **97,** 163901 (2006).
26. Oishi, Y., Kaku, M., Suda, A., Kannari, F. & Midorikawa, K. Generation of extreme ultraviolet continuum radiation driven by a sub-10-fs two-color field. *Opt. Exp.* **14,** 7230–7237 (2006).
27. Diels, J.-C. & Rudolph, W. Ultrashort laser pulse phenomena: fundamentals, techniques and applications on a femtosecond time scale. (Academic, Boston, 1996).
28. Bradley, D. J., Liddy, B. & Sleat, W. E. Direct linear measurement of ultrashort light pulses with a picosecond streak camera. *Opt. Commun.* **2,** 391–395 (1971).
29. Schelev, M. Ya., Richardson, M. C. & Alcock, A. J. Image-converter streak camera with picosecond resolution. *Appl. Phys. Lett.* **18,** 354–357 (1971).
30. Tzallas, P. *et al.* Direct observation of attosecond light bunching. *Nature* **426,** 267–271 (2003).
31. Sekikawa, T. *et al.* Nonlinear optics in the extreme ultraviolet. *Nature* **432,** 605–608 (2004).
32. Itatani, J. *et al.* Attosecond streak camera. *Phys. Rev. Lett.* **88,** 173903 (2002).
33. Kienberger, R. *et al.* Steering attosecond electron wave packets with light. *Science* **297,** 1144–1148 (2002).
34. Quéré, F. *et al.* Attosecond spectral shearing interferometry. *Phys. Rev. Lett.* **90,** 073902 (2003).
35. Hargittai, I. & Hargittai, M. (eds) *Stereochemical Applications of Gas-Phase Electron Diffraction.* (VCH, Weinheim, 1988).
36. Zuo, T., Bandrauk, A. D. & Corkum, P. B. Laser induced electron diffraction: A new tool for probing ultrafast molecular dynamics. *Chem. Phys. Lett.* **259,** 313–320 (1996).
37. Lein, M., Marangos, J. P. & Knight, P. L. Electron diffraction in above-threshold ionization of molecules. *Phys. Rev. A* **66,** 051404 (2002).
38. Yurchenko, S. N. *et al.* Laser-induced interference, focusing, and diffraction of rescattering molecular photoelectrons. *Phys. Rev. Lett.* **93,** 223003 (2004).
39. Spanner, M. *et al.* Reading diffraction images in strong field ionization of diatomic molecules. *J. Phys. B* **37,** L243–L250 (2004).
40. Gabor, D. A new microscopic principle. *Nature* **161,** 777–778 (1948).
41. Kanai, T., Minemoto, S. & Sakai, H., Quantum interference during high-order harmonic generation from aligned molecules. *Nature* **435,** 470–474 (2005).
42. Baker, S. *et al.* Probing proton dynamics in molecules on an attosecond time scale. *Science,* **312,** 424–427 (2006).
43. Yudin, G. L. *et al.* Attosecond photoionization of coherently coupled electronic states. *Phys. Rev. A* **72,** 051401 (2005).
44. Remetter, T. *et al.* Attosecond electron wave packet interferometry. *Nature Phys.* **2,** 323–326 (2006).
45. Yudin, G. L., Bandrauk, A. D. & Corkum, P. B. Chirped attosecond photoelectron spectroscopy. *Phys. Rev. Lett.* **96,** 063002 (2006).

46. Niikura, H., Villeneuve, D. M. & Corkum, P. B. Mapping attosecond electron wave packet motion. *Phys. Rev Lett.* **94,** 083003 (2005).
47. Kling, M. *et al.* Control of electron localization in molecular dissociation. *Science* **312,** 246–248 (2006).
48. Zeidler, D. *et al.* Controlling attosecond double ionization dynamics via molecular alignment. *Phys. Rev. Lett.* **95,** 203003 (2005).
49. Weckenbrock, M. *et al.* Electron–electron momentum exchange in strong field double ionization. *Phys. Rev. Lett.* **91,** 123004 (2003).
50. Resch, K. J., Lundeen, J. S. & Steinberg, A. M. Experimental observation of nonclassical effects on single-photon detection rates. *Phys. Rev. A* **63,** 020102 (2000).
51. Niikura, H. *et al.* Probing molecular dynamics with attoscecond resolution using correlated wave packet pairs. *Nature* **421,** 826–829 (2003).
52. Rudenko, A. *et al.* Correlated multielectron dynamics in ultrafast laser pulse interactions with atoms. *Phys. Rev. Lett.* **93,** 253001 (2004).
53. Liu, X. *et al.* Attosecond electron thermalization by laser-driven electron re-collision in atoms. *J. Phys. B.* **39**, L305–L311 (2006).
54. Fuji, T. *et al.* Parametric amplification of few-cycle carrier-envelope phase-stable pulses at 2.1 μm. *Opt. Lett.* **31,** 1103–1105 (2006).
55. Hauri, C. P. *et al.* intense self-compressed, self-phase-stabilized few-cycle pulses at 2 μm from an optical filament. *Opt. Lett.* **32,** 868–870 (2007).
56. Dromey, B. *et al.* High harmonic generation in the relativistic limit. *Nature Phys.* **2,** 456–459 (2006).
57. Naumova, N. M., Nees, J. A., Sokolov, I. V., Hou, B. & Mourou, G. Relativistic generation of isolated attosecond pulses in a λ^3 focal volume. *Phys. Rev. Lett.* **92,** 063902 (2004).
58. Tsakiris, G. D., Eidmann, K., Meyer-ter-Vehn, J. & Krausz, F. Route to intense single attosecond pulses. *New J. Phys.* **8,** 19 (2006).
59. Nitzan, A. & Ratner, M. A. Electron transport in molecular wire junctions. *Science* **300,** 1384–1389 (2003).
60. Distant charge transport. *Proc. Natl Acad. Sci.* **102** (special feature), 3533–3592 (2005).
61. Zholents, A. A. & Fawley, W. M. Proposal for intense attosecond radiation from an X-ray free-electron laser. *Phys. Rev. Lett.* **92,** 224801 (2004).
62. Fill, E., Veisz, L., Apolonski, A. & Krausz, F. Sub-fs electron pulses for ultrafast electron diffraction. *New J. Phys.* **8,** 272 (2006).
63. Pfeifer, T., Spielmann, C. & Gerber, G. Femtosecond X-ray science. *Rep. Prog. Phys.* **69,** 443–505 (2006).
64. Zewail, A. 4D ultrafast electron diffraction, crystallography, and microscopy. *Annu. Rev. Phys. Chem.* **57,** 65–103 (2006).
65. Levesque, J. & Corkum, P. B. Attosecond science and technology. *Can. J. Phys.* **84,** 1–18 (2006).

Acknowledgements

This research was supported by the DFG cluster of excellence Munich Centre for Advanced Photonics – MAP (www.munich-photonics.de).
Correspondence and requests for materials should be addressed to P.B.C. or F.K.

Competing financial interests

The authors declare no competing financial interests.