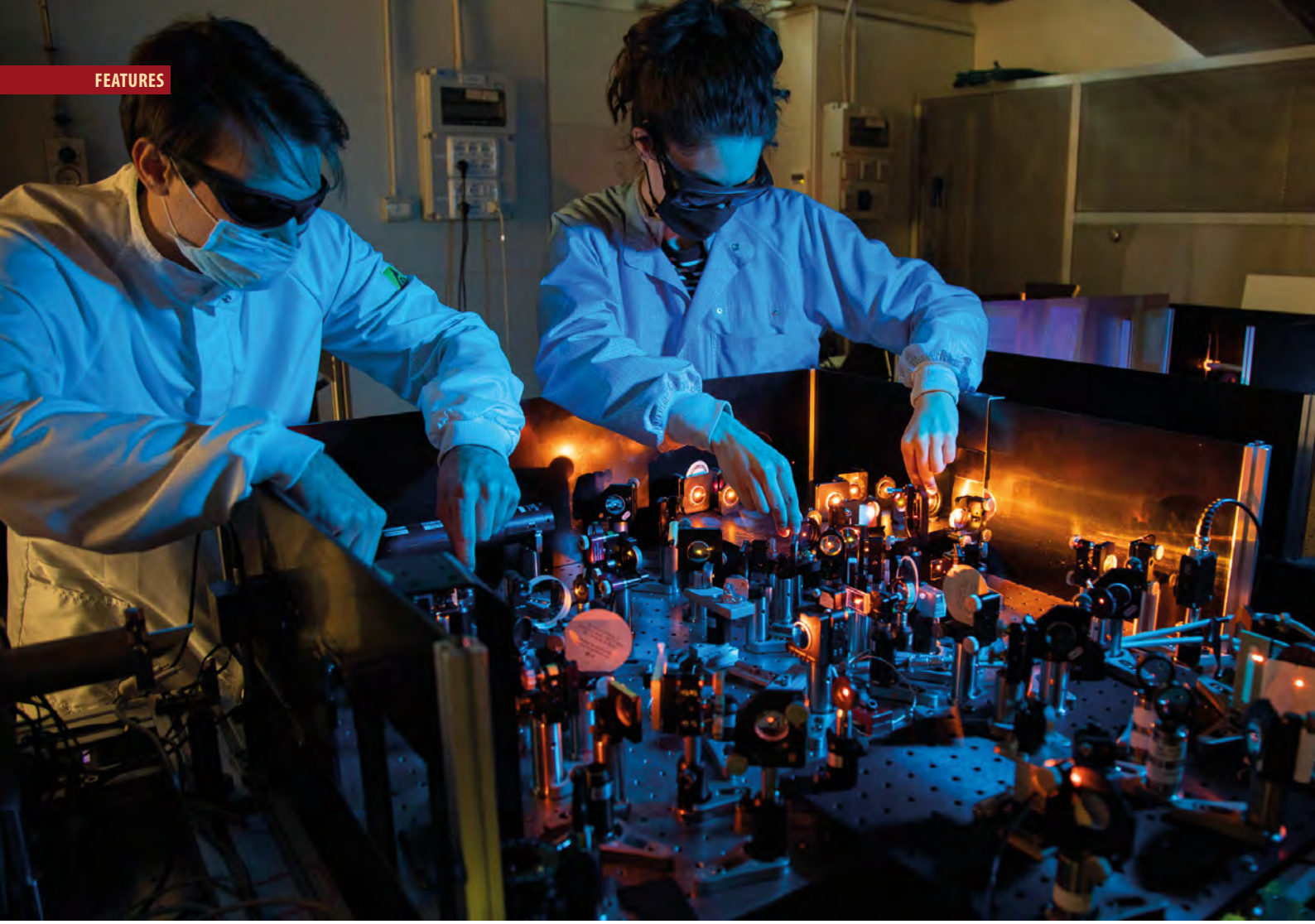

ATTOSECOND SCIENCE
the art of making electron movies

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After 22 years since the first experimental demonstration of attosecond pulses, the attosecond science has become a very active field of research, with prominent applications in atomic, molecular and solid-state physics. Experimental advances, in terms of new sources, devices and techniques, are still required, together with new theoretical tools and approaches, but attosecond physics has firmly established as a mature research field.

▲ Attosecond laboratory at Politecnico di Milano

The Nobel Prize in Physics 2023 was awarded jointly to Pierre Agostini, Ferenc Krausz and Anne L'Huillier "for experimental methods that generate attosecond pulses of light for the study of electron dynamics in matter." Since the first demonstration of sub-femtosecond pulses in 2001, Attosecond Science has demonstrated a great impact on atomic, molecular and solid-state physics. The introduction of new attosecond spectroscopic techniques, together with the development of sophisticated theoretical methods for the interpretation of the experimental outcomes, allowed unravelling and investigating physical processes never observed before [1]. In this Feature article, we look back at the key steps that have led to the most recent and exciting advances in the Attosecond Science.

The ultimate limit to the duration of a light pulse is

the period of the optical cycle of its electric field: it is in fact not possible to create a pulse containing less than one oscillation of the electric field. For this reason, the minimum duration of a pulse in the visible spectral region, *i.e.* with a wavelength between 400 and 700 nm, is necessarily limited to approximately 1-2 fs. To overcome the femtosecond barrier, it is first necessary to produce light in the extreme ultraviolet (XUV). The technique commonly used for producing pulses in this spectral range is called high-order harmonic generation (HHG) and is based on nonlinear effects initiated by short and intense laser pulses focused on noble gases. In short, when a femtosecond laser pulse is focused on a gaseous medium at intensities of the order of 10^{13}-10^{14} W/cm^2, the spectrum of the radiation transmitted by the gas contains components at frequencies multiples of the fundamental one. The spectral amplitude of the harmonics is characterized by a sharp decrease from the third to typically the fifth harmonic, followed by a region, called plateau, first observed by Anne L'Huillier and coworkers [2], where the harmonic intensities remain approximately constant up to a maximum photon energy, hνmax , given by the cutoff law: $h\nu_{max} \approx I_p + 3.17U_p$, where: I_p is the ionization potential of the gas; $U_p \propto I\lambda^2$ is the ponderomotive potential (*i.e.*, the mean kinetic energy of an electron oscillating in the laser field); I and λ are the peak intensity and central wavelength of the driving pulse, respectively. Above this photon energy a sharp decrease in generation efficiency occurs.

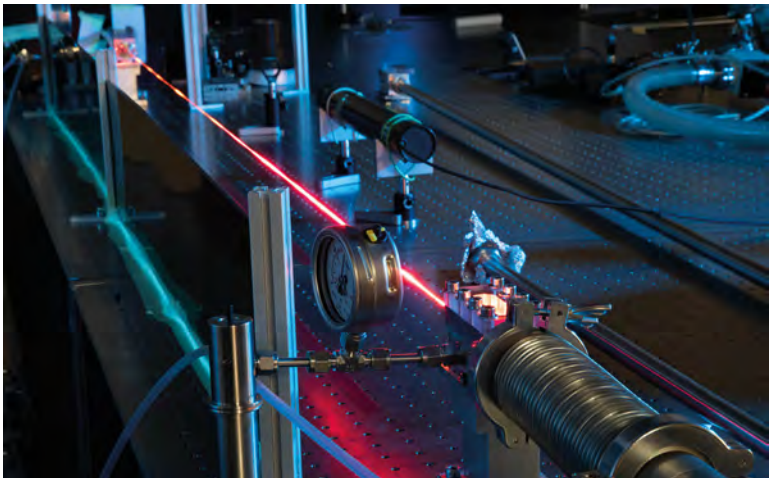
Generation and characterization of attosecond pulses

The first experimental proof of the generation of trains of attosecond pulses was reported by the group of Pierre Agostini in 2001 [3]. A train of 250-as pulses was generated in argon and was measured by using a novel experimental technique: the Reconstruction of Attosecond Beating By Interference of two-photon Transitions (RABBITT). RABBITT was the first example of an attosecond measurement method and it is at the heart of important applications in attosecond metrology and spectroscopy. In the same year, isolated attosecond pulses were reported by the group of Ferenc Krausz, by measuring the cross-correlation between the electric field of a femtosecond infrared (IR) pulse and the attosecond pulse intensity by means of two-colour photoionization [4]. This was the first demonstration of attosecond streaking spectroscopy, subsequently used to study a plethora of physical processes initiated by attosecond pulses in atoms, molecules, nanoparticles and solids [1]. The use of isolated attosecond pulses is particularly important, for example, if one wants to follow the temporal evolution of an ultrafast physical process using pump-probe techniques. The generation of isolated attosecond pulses was driven by the introduction of important technological advances in the field of ultrafast optics. In particular, the invention of the hollow-fiber compression technique [5], which enabled the compression of high-energy laser pulses (a photograph of the hollow-fiber compressor is shown in Fig. 1), and the active stabilization of the carrier-envelope phase of femtosecond pulses.

Attosecond atomic physics

Attosecond pulses were first employed for the investigation of ultrafast electron dynamics in atomic systems, immediately after their experimental demonstration. They were used to measure the lifetime of a core hole in krypton [6]. This pioneering experiment opened the door to time-resolved spectroscopy with sub-femtosecond resolution in a wide range of atomic processes.

One of the most interesting applications of attosecond pulses in atomic physics is the investigation of the electron dynamics initiated by photoionization and, in particular, the measurement of the time it takes for the emitted electron to appear in the continuum. From a quantum mechanical perspective, the delay in photoemission is related to the phase shift experienced by the wavefunction of the emitted photoelectron, induced by the potential of the ionized atom. After the interaction with the potential, the phase of the photoelectron is shifted by a scattering phase, as shown in Fig. 2. The derivative of this phase with respect to the electron kinetic energy can be interpreted as the group delay of the ionized electron wavepacket as it propagates in the atomic potential (Wigner delay) and it is typically on the order of tens of attoseconds, depending on the excitation energy and the ionic core structure. In 2010, by using attosecond streaking spectroscopy with isolated attosecond pulses, Schultze and coworkers measured a delay of ~20 as in the emission of electrons ionized from the 2*p* orbitals of neon atoms with respect to those released from the 2*s* orbital, about a factor of two longer than theory would predict. Using the RABBITT technique with trains of attosecond pulses, the group of Anne L'Huillier reported on a precise measurement of photoemission time • • •



▼ **FIG. 1:** Hollow-fiber setup for the compression of high-energy laser pulses. 25-fs pulses with 6-mJ energy are injected into a 3-m-long stretched fiber filled with neon. The pulses are then compressed down to 4 fs by a set of ultrabroadband chirped mirrors.

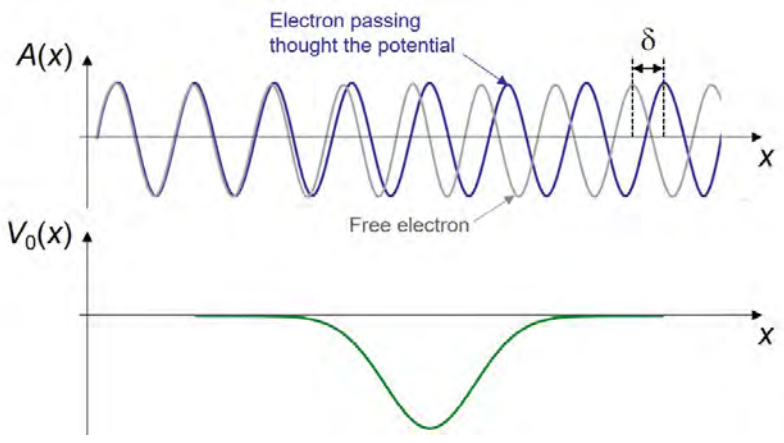
• • • delays in argon and subsequently in neon, which, by spectrally disentangling the direct ionization from ionization with shake-up, turned up to be in excellent agreement with theoretical predictions.

Attosecond molecular physics

The first application of attosecond pulses to molecular physics was reported in 2010, with the measurement of the electron localization dynamics in hydrogen molecules after prompt ionization [7]. The experiment demonstrated the possibility to directly control electron localization inside a molecule on an attosecond timescale by using the electric field of a few-femtosecond IR pulse. A very intriguing result of the experiment was that the motion of the electron in the covalent bond after ionization of the molecule can be controlled by acting on the electron ionized by the attosecond pulse. Localization control therefore relies on entanglement between the electron removed from the molecule by the attosecond pulse and the parent H_2^+ ion. As a matter of fact, the ion/photoelectron entanglement could be rather ubiquitous in attosecond science and it could establish a link with the field of quantum information.

A central topic in any dynamical molecular process is the charge motion. Photo-induced charge transfer in molecules is a ubiquitous fundamental process in Nature. Charge transfer plays an important role in many areas of both natural and synthetic processes, namely in photosynthesis or in photovoltaics and in molecular electronics. What all these processes have in common is that the charge follows the motion of the nuclei, so that the rearrangement is mainly a structural one in nature and the electronic character adapts adiabatically. At the end of the '90s of the last century, some experiments have been done by Weinkauf and Schlag on small peptides in gas phase and they have found a very specific fragmentation of the molecule after ionizing the peptide at a specific point, namely at the aromatic group. These observations could not be explained with traditional rate theories. Instead, a different mechanism has been invoked, the charge migration, occurring on a purely electronic time scale. From numerical simulations, it became clear that the experimental investigation of the *charge migration* process would require the use of attosecond pulses.

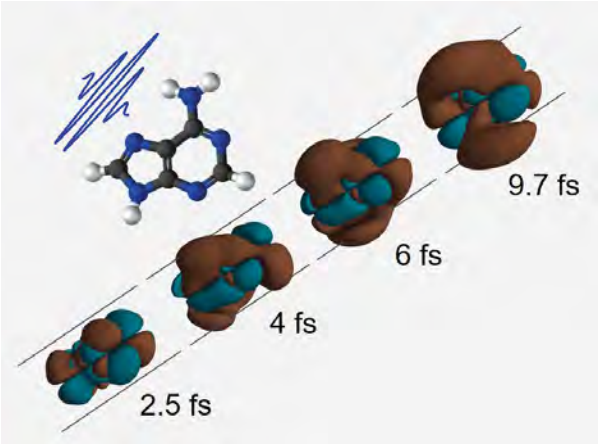
The experimental observation of charge migration driven by coherent superposition of molecular states was first reported in 2014 by the group of Nisoli in the aromatic amino acid phenylalanine [8]. The experimental approach was attosecond-pump/femtosecond-probe scheme in combination with mass spectroscopy. The observable was the temporal variation of the quantum yield of a particular molecular fragment, which was observed to oscillate as a function of the pump-probe delay, with a period of ~4 fs. These oscillations were associated to a charge migration process and were interpreted as the signature of the coherent electron dynamics generated by the attosecond pulse on the remaining molecular cation. In 2015 the group of Wörner reported on the measurement of attosecond charge migration in ionized iodoacetylene [9] and, later, in neutral silane. Charge migration purely driven by electron correlation was measured in 2021 in the nucleic-acid base adenine after ionisation with isolated attosecond pulses [10] (snapshots of the electron density after the attosecond excitation are displayed in Fig. 3), thus demonstrating real-time mapping of many-body effects in ionized molecules: this is the first important step towards a control of the molecular photo-reactivity at the electronic time scale, which is at the heart of attochemistry.



▼ **FIG. 2:** (Upper panel) The blue curve represents a plane wave associated to an electron passing through a short-range attractive potential $V_0(x)$, shown in the lower panel, from left to right. After passage, it acquires an additional phase δ compared to an electron propagating without any interaction with the potential (grey curve).

Towards attochemistry

The objective of attochemistry is the possibility to achieve a complete control of chemical processes by controlling the electron dynamics. A chemical reaction requires bond breaking and bond formation, and the motion of atoms inside or between molecules. These dynamical processes can be properly investigated by femtosecond techniques. Attosecond pulses, possibly in combination with few-femtosecond pulses, offer the possibility to control the ultrafast motion of electrons inside a molecule, and this motion can, in turn, influence the subsequent nuclear dynamics unfolding on a longer timescale. Therefore, the use of attosecond pulses allows one to manipulate a chemical reaction acting directly on electrons, on their natural timescale. In this context, the concept of attosecond charge directed reactivity, which refers to the use of attosecond pulses to control the formation and breaking of chemical bonds by controlling electron dynamics in molecules, is of crucial importance. The challenge is the possibility of generating a coherent superposition of electronic states characterized by a sufficiently long coherence time, to be able to influence the outcome of a photo-induced chemical reaction [19]. Indeed, this is a crucial prerequisite to ensure that the electron dynamics initiated by the attosecond excitation can trigger the desired nuclear dynamics, which evolve over a much longer temporal scale. Furthermore, it is important to design the



▲ **FIG. 3:** Charge migration in adenine (molecular structure shown in the left upper corner) driven by electron correlations generated by attosecond pump pulses. Snapshots of the variation of the electronic density with respect to the density immediately after the attosecond excitation. A significant out-of-plane charge migration is observed.

electron wave packet, namely the relative amplitude and relative phases of the electronic states involved in the coherent superposition, to induce an otherwise impossible chemical reaction or to greatly increase the yield of a possible yet inefficient photochemical process. ■

About the Author

Mauro Nisoli is Full Professor at Politecnico di Milano, where he leads the Attosecond Research Center. His research focus are the following: attosecond science, ultrashort-pulse laser technology, and control and real-time observation of electronic motion in atoms, molecules and solids. He is author of more than 200 research papers in international journals.

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