Extreme Nonlinear Optics: Coherent X Rays from Lasers

Ultrashort laser pulses can generate even shorter bursts of coherent soft x rays. The technology now makes it possible to manipulate atoms on attosecond time scales to create designer wavefunctions.

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Laser technology—the ability to generate intense and coherent light with controllable properties—is one of the most significant enabling achievements of 20th-century science. Because atoms interact through the electromagnetic force, researchers can probe—and in some cases control—the properties and dynamics of atomic, molecular, or condensed matter systems with unprecedented precision simply by applying external, controlled electromagnetic fields.

In recent years, nonlinear-optical techniques that convert one frequency of light to another have played an increasingly pivotal role in that technology—a role second in significance only to that of the laser itself. Optical frequency doubling or parametric amplification, for instance, converts laser light into coherent radiation tunable over the near-IR, visible, and near-UV regions of the spectrum. Recent years have also seen the development of ultrashort-pulse technologies. The uncertainty principle $\Delta E \Delta t \geq \hbar/2$ dictates that a very short pulse of light must have broad spectral bandwidth. However, generating such a short pulse also requires that the colors in that broad spectrum have a well-defined phase relationship with each other; that is, the coherence must span the entire spectrum. More generally, control over broad-spectrum coherence makes it possible to implement the optical analog of an arbitrary waveform generator, a device that can sculpt the shape of a light pulse over time and precisely manipulate atomic or molecular dynamics.

By taking concepts of nonlinear optics and ultrashort pulse generation to an extreme limit, one can generate coherent light at even shorter wavelengths using a process called high-harmonic generation (HHG). This process shifts femtosecond laser light from the near-IR (1–2 eV) to the extreme-UV (tens to hundreds of eV) and soft x-ray (up to a keV) regions of the spectrum. The EUV is a difficult region of the spectrum for nonlinear optics because traditional nonlinear optics because it is intimately linked to the attosecond time domain. Moreover, the physics of the process differs radically from traditional nonlinear optics because it is intimately linked to the attosecond time domain. The quantum dynamics of the atom–field interaction determines the wavelength range, efficiency, coherence properties, and pulse duration of the generated light (see PHYSICS TODAY, April 2003, page 27).

Making coherent soft x rays

In nonlinear optics, passing an intense beam of light through a material alters the beam in a coherent and intensity-dependent way—by converting the light to a different wavelength, for instance. Microscopically, electrons in the material act like driven oscillators that respond to the laser’s electric field. Ordinarily, those electrons remain bound but are driven strongly enough that the potential that binds an electron to its atomic core is no longer a purely parabolic, harmonic-oscillator potential. The motion of the electrons themselves becomes anharmonic, which gives rise to a time-dependent nonlinear polarization. That reradiates electromagnetic waves not only at the driving laser frequency, but also at higher harmonics of the driving laser field.

High-harmonic generation takes this concept to its extreme: The laser’s intensity is increased to the point where the electric field becomes strong enough to ionize an atom (see box 1). Once stripped from the atom, the electron still moves in response to the oscillating field. Oscillating free electrons do not emit harmonics in the nonrelativistic limit; however, the electron can recollide with its parent ion after a fraction of a single optical cycle and recombine with the ionized atom. If that happens, the electron must give up its kinetic energy by emitting an energetic photon.

In the classical picture, the maximum or cutoff photon energy emitted can be calculated by considering the recollision energy of the electron. The maximum energy is given by

$$E_{\text{max}} = I_p + 3.2 U_p,$$

where $I_p$ is the ionization potential of the atom and $U_p$ is the ponderomotive energy of the atom. $U_p = e^2 E^2/4m \omega^2 \approx I \lambda^2$, where $e$ and $m$ are the electron charge and mass, and $E$, $\omega$, $I$, and $\lambda$ are the field’s amplitude, frequency, intensity, and wavelength, respectively. $U_p$ is the average kinetic energy of an electron oscillating in response to light with...
Box 1. Microscopic Physics of High-Order Harmonic Generation

High-harmonic generation is simple to demonstrate—provided one has access to a femtosecond laser. By focusing such a laser to intensities of $10^{13}$ to $10^{16}$ W/cm$^2$ into a gas (as sketched in the top image), the beams that emerge contain not only the original laser frequency, but also a tightly collimated beam of ultraviolet light at much shorter wavelengths. The photon energies, tens to hundreds of electron volts, correspond approximately to odd-order harmonics of the original laser frequency $v$—$(2n+1)\nu$, with $n$ an integer. Both semiclassical and quantum pictures explain the process. In the semiclassical perspective (middle image), the electron is field ionized in a strong laser field, oscillates away from the ion, and then recombines with it, emitting any excess energy as a photon. Small, blue curves depict the evolution of a quantum wavepacket over a classical trajectory.

The bottom sequence of images illustrates the more realistic, fully quantum calculation of the extended wavefunction of an electron as it ionizes in an ultrashort pulse of intensity $3 \times 10^{14}$ W/cm$^2$. This wavefunction was calculated by numerical solution of the two-dimensional Schrödinger equation (in atomic units, where $\hbar$ and the charge and mass of an electron are set equal to 1):

$$i \frac{\partial}{\partial t} \psi(r, t) = \left[-\frac{1}{2} \nabla^2 + V(r) + r \cdot E(z, t)\right] \psi(r, t),$$

where $V(r)$ is the atomic potential, and $E(z, t)$ is the laser field with $z$ the direction of propagation. The time-dependent nonlinear polarization can be calculated from

$$\frac{\partial^2}{\partial t^2} \mathbf{P}(z, t) = N \left\langle \frac{\partial^2}{\partial t^2} \mathbf{d} \right\rangle = N \left\langle \psi (r, t) \left| \frac{-\partial V}{\partial r} + E(z, t) \right| \psi (r, t) \right\rangle,$$

where $N$ is the number density of atoms and $\mathbf{d}$ the dipole moment. As the electron accelerates in response to the laser field, its probability density extends many tens of angstroms away from the ion core. Note that the spatial extent of the wavefunction changes with the time evolution of the laser pulse. Periodic recollisions of the extended, spatially modulated electron wavefunction with the atomic core produce the high-order harmonics, with periodic attosecond bursts occurring during each half cycle of the laser field.

intensity $I$, and $3.2 \, U_{1}$ is the maximum kinetic energy of the electron at recollision. Electrons ionized at different times within the optical cycle recollide with different energies.

Gérard Mainfray and coworkers at the Center of Studies in Saclay, France, and Charles Rhodes's group at the University of Chicago performed the first HHG experiments in the late 1980s, soon after the development of large-scale, intense picosecond and femtosecond lasers. However, broader interest in HHG as a light source was limited because those early experiments observed small numbers of photons generated at a very low repetition rate.

Two developments dramatically changed the picture. First, rapid advances in ultrashort-pulse lasers using titanium-doped sapphire led to instruments that produced high-power pulses with unprecedented duration—20 fs, or less than 10 optical cycles. Originally developed by Peter Moulton at MIT Lincoln Labs in the early 1980s, Ti:sapphire has the broadest bandwidth of any laser material. Moreover, it is durable, with an energy capacity orders of magnitude greater than the laser dyes used in the 1980s. Ti:sapphire increased the average power of ultrafast laser systems from just 10 milliwatts to about 10 watts, while it dramatically reduced pulse duration and shrunk the overall size of the system. Because HHG depends on creating an intensity sufficient to ionize target atoms, the decrease in pulse duration translates into a corresponding increase in conversion efficiency. In 1996, our group developed the technologies necessary to generate such intense 20-fs light pulses and showed how their use in HHG extends the accessible wavelength range and increases the flux. The second advance came from the realization that concepts from conventional nonlinear optics—in particular, matching the phase velocity of the laser fundamental to the phase velocity of the harmonic—could be applied to optimize the conversion efficiency.

Phase matching

Anne L'Huillier from the Center of Studies in Saclay and coworkers realized the effect of such phase matching on the emission characteristics of the high-harmonic light in the early 1990s. Appreciating that such phase matching was actually engineerable took longer. Conventional nonlinear optics generally makes use of the birefringent properties of crystals to eliminate the phase mismatch between the laser and harmonic beams. However, HHG is implemented most often in a gas, to avoid absorption of the light by a solid.

Fortunately, guiding the light inside a gas-filled, hollow-core waveguide can achieve phase matching (see figure 1). In that scheme, the laser beam propagates with a controlled intensity and phase as glancing reflections from the walls guide the light downstream. Because the laser pulse slows down in a neutral gas but speeds up in a waveguide or plasma, the phase delay between the driving laser and the harmonic light can be manipulated.

When the level of ionization is small, phase matching of the laser and harmonic beams can be accomplished by
adjusting the gas pressure so that the waveguide dispersion balances the dispersion due to neutral atoms. That balance effectively adjusts the phase velocity of the fundamental laser beam to match that of the high-harmonic light. Because the harmonic light travels at a phase velocity roughly the speed of light in vacuum due to its high frequency, the bandwidth of that pressure-tuned phase matching is very broad and encompasses many harmonic orders. When phase matched, the harmonic signal initially increases quadratically with interaction length.

Compared with conventional nonlinear optics, phase-matched HHG is still limited in efficiency. First, the frequency conversion occurs in the presence of strong back-ground absorption from the ionization. That absorption limits the conversion efficiency to very small values (around $10^{-1}$–$10^{-2}$) compared with the more than 50% efficiency that can be obtained in frequency doubling. Nevertheless, a waveguide geometry makes it possible to produce fully co-
P Paraphrase of the text:

Optimized structures

Extending phase-matching techniques to soft x-ray energies required new approaches. Based on experience in visible-wavelength nonlinear optics, researchers have long known that when phase matching cannot be achieved, so-called quasi-phase matching (QPM) can efficiently enhance the frequency conversion signal. Rather than completely eliminating the phase slip between the driving laser and the generated signal, QPM periodically corrects it.

But how does one implement such a phase corrective technique when—unlike a nonlinear crystal—an isotropic atomic gas exhibits no sense of orientation? One of us (Christov) realized that because HHG is so highly nonlinear, small changes in the laser intensity can strongly modulate the generation of harmonics. Considering equation 1, a 1% change in intensity of the driving laser, for example, changes the cutoff photon energy by roughly 1%, or 1 eV at 100 eV. Such an intensity modulation is enough to produce an effect akin to periodic poling. Emission from regions where the wave would interfere destructively can then be suppressed and the generated signal continue to increase, but with periodic pauses in generation.

Modulating the driving laser intensity can be accomplished in a simple and practical way in a waveguide, by weakly modulating the diameter of the guide itself (see box 2). The laser intensity is sufficient to generate the cutoff harmonics only in regions where the diameter is small. The required modulation period corresponds to the distance over which the phase mismatch would change by $\pi$. At very high levels of ionization, plasma dispersion complicates the phase mismatch $\Delta k$. In that limit,

$$\Delta k \approx \frac{q_n e^2 \lambda}{4 \pi m e^2},$$

where $\lambda$ is the laser wavelength, $q$ is the harmonic order, and $n_e$ is the electron density. Modulation periods of a
fraction of a millimeter can compensate for substantial ionization levels. To date, our group has extended QPM to photon energies of 300 eV.\textsuperscript{7,8} How far can scientists take this phase-matching technique? It’s unclear whether coherent hard x rays (energies greater than a keV) can be produced, but there is reason for optimism. Currently obtainable photon energies scale linearly with the driving laser intensity. In contrast, the power requirements for x-ray laser systems typically scale as $(\hbar \nu)^a$ for $a$ between 3 and 6. (For more discussion of table-top x-ray lasers, see reference 9.) To exploit that favorable scaling for harmonic generation, it is necessary to generate the harmonics in advanced stages of ionization of a gas, since neutral atoms can survive only a limited intensity. However, recent experiments clearly show that the neutral-atom limit is not a limit for HHG. A waveguide helps to keep the laser light confined at high intensities and limits defocusing that would otherwise occur due to generation of a plasma. Our group recently used this effect to observe emission of very high photon energies from argon ions.\textsuperscript{8}

**Attosecond electron dynamics**

In conventional nonlinear processes, such as second-harmonic generation, the oscillations of the bound electron are closely related to the laser field that drives them. In HHG, though, because the electron wavefunction evolves significantly for a fraction of an optical cycle between ionization and recollision with the core, the atomic emission depends on the history of the driving field over the preceding interval of a few hundred attoseconds. The shape of the driving laser pulse—that is, its amplitude and phase—determines the trajectory of the electron as it oscillates in the laser field, and hence the shape of the electron emission.

**Box 2. Photonics at Short Wavelengths: Quasi-Phase-Matching**

In the ionizing gas used for high-harmonic generation, plasma-induced dispersion causes the laser light to outrun the x-ray light by traveling at a faster phase velocity. A waveguide whose diameter changes periodically can correct the mismatch using a technique called quasi-phase matching (QPM). The high harmonics are generated in the narrow regions of the waveguide where the laser intensity is highest. In between the narrow sections, the phases of laser light and x-ray light can re-align, so that x-ray light always contributes in phase with the existing x-ray beam. The left-hand figure shows a visible microscope picture of a hollow-core modulated waveguide, with periodicity $\Lambda$ of 0.25 mm, inner diameter of 150 $\mu$m, and modulation depth of 10 $\mu$m. The visible reflectance varies with the intensity of the light, so the bright spots illustrate how the modulation physically confines the intensity peaks to periodic regions in the guide. The data on the lower right show that as $\Lambda$ is decreased—to correct for the phase slip more often—the effect is to extend the x rays to a higher energy.\textsuperscript{8} Thus, QPM allows researchers to generate higher harmonics more efficiently at higher laser intensities and ionization levels. Recent experiments from our group\textsuperscript{15} have extended QPM to the carbon K-edge at 284 eV—a wavelength in the “water window” region of the soft x-ray spectrum, a region useful for ultrahigh-resolution microscopy of biological samples.
wavefunction at the time of electron–ion recollision. That wavefunction, in turn, determines the phase of the attosecond burst of x rays emitted at each recollision.

More precisely, when an electron begins to field-ionize from an atom, part of its wavefunction begins to “leak” from the atom—the probability density becomes delocalized well away from the atomic core. As the wavefunction evolves with the electric field of the laser, the wavelength of the electron follows the de Broglie relationship $\lambda = h/p$, where $p$ is the electron’s momentum. Between the time that the electron is field-ionized and the time that it recollides a fraction of an optical cycle later, the electron wavefunction advances in phase by several cycles in a way that is related to both the energy of the electron and the intensity of the light.10 The high-harmonic light is therefore not locked in phase with the driving laser. This property fundamentally distinguishes HHG from other nonlinear optical processes (in which the harmonics originate from bound electrons).

Remarkably, even the ultrashort—but finite—time delay can be controlled to manipulate and optimize HHG in useful ways. Key to such precise control is the use of quantum learning-control algorithms, originally proposed by Herschel Rabitz at Princeton University to optimize and study any quantum system (see PHYSICS TODAY, August 2003, page 43). Coupled with optical pulse shapers, the algorithms can generate optimal laser pulse shapes to control the high-harmonic phase. This extraordinary technology uses optical Fourier-transform techniques to precisely manipulate broad-bandwidth pulses in the frequency domain.

In a learning-control experiment, one formulates a specific target outcome and programs an iterative search to find the optimal pulse shape that creates it. In one of our experiments, for instance, the objective was to selectively enhance a particular harmonic order relative to neighboring orders (see figure 3).11,12 In general, if a simple Gaussian laser pulse drives the HHG in time, the emissions at any given high-harmonic frequency from each of the attosecond-duration recollisions are not necessarily in phase with each other. The time-varying intensity on the rising edge of the pulse causes a cycle-by-cycle change in the intrinsic quantum phase shifts of the harmonics. Those shifts correspond to about one optical cycle at the 27th harmonic order, or a total time variation of about 150 attoseconds. Thus, to optimize the laser pulse is to compensate for that quantum-phase-induced variation by changing the instantaneous frequency and intensity of the driving laser. In this case, the peaks in the electric field of the laser pulse are adjusted to compensate for the 150-attosecond recollision time lag, so the phase of HHG is constant to a precision of about 10–20 attoseconds.

Therefore, pulse shaping creates a unique, spatially modulated electron wavefunction that produces bright emission of a selected harmonic when the electron recollides with the ion. Compensating for the difference in HHG and laser phases for each harmonic order makes a selective optimization process possible. As a particular harmonic becomes optimized, the spectral linewidth of that harmonic narrows, which improves in the temporal coherence of the emitted harmonics.

The physics of the optimization process was “found” using the evolutionary algorithm—the experimental result motivated the development of theoretical models to explain the process. Indeed, Christov, using learning algorithms to optimize the computer simulations, uncovered a deeper understanding in much the same way as experiment would. Thus, the term “learning algorithm” is literally true.

**Present and future**

HHG is a unique light source that delivers femtosecond-to-attosecond pulse durations tunable throughout the UV and soft-x-ray regions of the spectrum—all on a tabletop.
Box 3. Attosecond-Duration Light Pulses

High-harmonic generation consists of a series of bursts—the blue emission spikes pictured at right—twice per optical cycle. As early as 1994, Paul Corkum and Misha Ivanov recognized that HHG might generate closely spaced trains of such attosecond pulses and perhaps even provide the means to obtain isolated pulses. Three years later, our group proposed the most straightforward way to generate an isolated attosecond pulse—by driving the HHG process with a very-short-duration linearly polarized pulse.16 As the figure illustrates, reducing the pulse width of the femtosecond laser also reduces the number of attosecond bursts, until—using a roughly 5 fs pulse, say—the high-energy harmonics are generated during only 3 half cycles of the laser pulse. To isolate a single subfemtosecond burst from that 5-fs pulse, a thin metal film can serve as a filter (the dashed lines) to pass only the highest cutoff energies. Such isolated attosecond pulses would be more useful in experiments designed to resolve dynamics that occur between 1 and 10 fs.

Experimental confirmation of the concept required measuring the time structure of the short wavelength emission. Harm Muller (Institute for Atomic and Molecular Physics in Amsterdam) and Pierre Agostini (Atomic Energy Commission in Saclay, France) introduced techniques that rely on ionization of an atom by the harmonic light in the presence of a strong, visible light pulse.17 When such a pulse occurs, the electron is born in a rapidly oscillating potential; after the pulse leaves, the energy of the ejected electron is modulated by an amount that depends on exactly when within the optical cycle the electron was ionized. This modulation can manifest as either electron energy sidebands or as a continuous energy shift. In 2001, the Muller–Agostini team18 experimentally confirmed the attosecond pulse train, and 3 years later Ferenc Krausz (Max Planck Institute for Quantum Optics in Garching, Germany) and his group19 confirmed the production of a single isolated attosecond burst (see PHYSICS TODAY, October 2004, page 21).

The output beams are coherent, emerge at high repetition rates (1–10 kHz currently, and potentially much higher), and are perfectly synchronized to a laser pulse. Moreover, soft x rays have unique advantages for observing dynamics of atoms, molecules, or materials because the position of the core levels in an atom is sensitive to the local chemical environment. Therefore, by monitoring changes in the chemical bonds between atoms and molecules or surfaces as a function of time delay between a pump and probe pulse, researchers can observe ultrafast, nonequilibrium dynamics. Richard Haight at IBM has used photoelectron spectroscopy to understand excited-state electron dynamics in semiconductors and organic materials. Our group and Steve Leone at the University of California, Berkeley, used the technique to monitor real-time, subpicosecond molecular dissociation, rotation, and charge transfer reactions on catalytic surfaces and in gas-phase reactions. Other applications, including high-density plasma imaging, are also under way.

New applications are also possible. Our group has used high-order harmonics to generate and probe very high-frequency acoustic oscillations in materials and also to implement coherent imaging. Measurements of ultrafast (below 10 fs) Auger-electron decay rates in atoms have been performed by Ferenc Krausz (Max Planck Institute for Quantum Optics in Garching, Germany) and his coworkers. For a discussion of isolating even single attosecond pulses, see box 3. Several new applications will extend work already possible at synchrotron sources, such as high-resolution imaging and metrology, to tabletop setups and femtosecond-to-attosecond time resolution. By extending harmonic generation to ever shorter wavelengths, and by further increasing the efficiency, new science and technology are bound to arise. One can imagine compact x-ray microscopes and new generations of x-ray nanoprobe, for instance, as our ability to control and manipulate nature continues to evolve.

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References
