Molecules in Intense Laser Fields
Femto to Attosecond Dynamics

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Science and technology

The fast show

Extremely short laser pulses can illuminate electrons in motion.

ON THE atomic scale, things move incredibly quickly. Electrons jump between orbits to escape the nucleus altogether in a few hundred attoseconds—a few hundred of a billionth of a second. Indeed, one attosecond is to one second what one second is to the age of the universe. Seeing such accelerations takes wit and ingenuity, but it is possible. Moreover, if such processes could be manipulated—and the early signs are that they can—they would have applications in fields as far apart as computing and medicine.

A report just drafted by America’s National Research Council, “Controlling the Quantum World”, outlines how scientists might manipulate the inner workings of a molecule. A long-term workshop at the Kavli Institute for Theoretical Physics, part of the University of California, Santa Barbara, is also investigating how this might be achieved. And, at a conference held recently at the institute, Detlev Kern of the Max Planck Institute of Quantum Optics in Garching, Germany, and Marc Van Rensburg of the FOM Institute for Atomic and Molecular Physics in Amsterdam described one way that it could be done.

Lasers work by creating a chain reaction in which photons of light prompt the generation of further photons. These photons are emitted in bursts. Shortening each burst sufficiently is what makes attosecond science possible. The researchers employed what they call “high harmonic pulse generation” to create pulses a few hundred attoseconds long. They did this by using a laser that emits short pulses of light to drive a second laser that then emits even shorter pulses. In fact, the pulses are so tight that they come close to the limit imposed by Heisenberg’s famous uncertainty principle, which states that the precision of a true measurement is limited by the precision of a corresponding energy measurement.

Also boys

Dr Krause and Dr Van Rensburg fired their laser at a molecule of deuterium. Deuterium, also known as heavy hydrogen, is a single molecule, consisting of two atomic nuclei and two electrons. The sample under investigation consisted of a deuterium atom, consisting of a nucleus and an electron, and a deuterium ion, consisting of an ion.

Using conventional laser pulses causes atoms to be ejected to the right and left at random. Using ultrafast laser pulses, though, makes the atoms fly off to the right and the ions to the left. The researchers were thus able, in effect, to control on which of the two deuterium atoms the electron resides at the end of their experiment. That is to say, they had separated the atoms from the ions.

Exactly how this works is complicated—not least because all of the atoms are interacting simultaneously with the laser and with each other. But the researchers think that the laser pushes the electron, which initially binds the two atoms together, back and forth between the two atoms until, at some point, the distance between the two gets too large and it is no longer able to jump from one to the other.

The ability to manipulate electrons in this way is important because electronic exchanges is essential to chemical bonding. Ultrashort lasers could thus be used to change the outcome of chemical reactions. Proposals point to possible applications in magnetic information storage devices, which would lead to much more powerful computers. Other possibilities include the development of compact, portable x-ray lasers for medical imaging that needs to be done outside hospital radiology departments, and bright ultrafast x-ray lasers for use within those departments.

The motion of electrons is the fundamental basis of chemistry. Watching the steps in the dance of the electrons will help chemists work out why some atoms are bound to others (or not), why reactions take the route that they do, and how some molecules bend one way and not the other. Brighter x-ray lasers could also be used to reveal the atomic details of chemical catalysis or the way that light energy is absorbed and stored during photosynthesis, according to the National Research Council report. Knowing exactly how to capture sunlight and turn it into chemical energy would be a prize indeed.
Potential energy: \( V_o \cdot \frac{e^2}{\alpha_o} \cdot 1 \) Hartree = 27.2 eV, \hspace{1cm} (1)

Electric field \( E_o \cdot \frac{e}{\alpha_o} \cdot 5 \times 10^9 \) V/cm, \hspace{1cm} (2)

Intensity \( I_0 = \frac{cE_o^2}{8\pi} = 3.5 \times 10^{16} \) W/cm². \hspace{1cm} (3)

Distance \( \sigma_o = 0.0529 \) nm. \hspace{1cm} (4)

Time \( t_o = 24.2 \) as. \hspace{1cm} (5)

### Table I

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Intensity (Watts/cm²)</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano</td>
<td>10⁻⁹</td>
<td>Giga</td>
</tr>
<tr>
<td>Pico</td>
<td>10⁻¹²</td>
<td>Tera</td>
</tr>
<tr>
<td>SERS</td>
<td></td>
<td>Peta</td>
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<tr>
<td>Femto</td>
<td>10⁻¹⁵</td>
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\[ 1 \text{ a.u.} = 24 \times 10^{-18} \]

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Intensity (Watts/cm²)</th>
<th>Year</th>
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<tr>
<td>Atto</td>
<td>10⁻¹⁸</td>
<td>Exa</td>
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<tr>
<td>Zepto</td>
<td>10⁻²¹</td>
<td>Zetta</td>
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<tr>
<td>Yocto</td>
<td>10⁻²⁴</td>
<td>Yotta</td>
</tr>
</tbody>
</table>

representation these radiatively induced distortions creating LIMP's as discussed above lead to bond softening via laser-induced avoided crossing of molecular potentials [26-27]. At such intensities, one needs to consider further ionization and the remaining molecular ion potentials become LIMP's in the presence of intense laser pulses. The molecular ions, bound or dissociative can also undergo Above Threshold Dissociation, ATD, [20], [26-27].
MAXWELL – SCHROEDINGER

\[ \frac{\partial^2 E}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 P}{\partial t^2} \]

\[ P = \text{Medium Polarization} = P(E) \]

\( (1^{\text{st}} \text{ Order} \ P = \alpha E) \)

SCHROEDINGER

\[ i\hbar \frac{\partial |\psi\rangle}{\partial t} = (\hat{H}_0 + \hat{V}(t))|\psi\rangle \]

\[ P = P(E) = n_0 \langle \psi | \hat{\mu}_0 | \psi \rangle \]

\[ |\psi\rangle = \sum_j c_j e^{iE_j t / \hbar} |\Psi_j\rangle \]

\[ V_{ii} = -P \langle e(z,t) \cos(kz - \omega t) \rangle \]
Orientation dependance of ionization: $1s\sigma_u$ initial state

Initial state: $1s\sigma_u$; $R=2$ au; $E_e=-0.668$ au

Laser: $I=10^{14}$ W/cm$^2$; $\omega=0.057$ au (800 nm)
$\cos^2$ envelop; fwhm=3.0 cyc. $\approx 8$ fs

$1s\sigma_u$ is 12 photons $\omega$ below the threshold

Total (non-differential) ionization probability vs the orientation angle $\theta$ in polar coordinates

The electron cloud is OFF the nuclei

Symmetry effects on Enhanced Ionization (EI)

Maximum EI at a critical distance $R_c = 4/I_p$

Monotonic increase of EI to saturation
Symmetry effects on Enhanced Ionization (EI)

Snapshot of $|\Psi(y,z)|^2$ at the end of the laser pulse

Effective potential seen by on-axis ($\sigma$) and off-axis ($\pi$) electrons

On-axis ($\sigma$) electrons

Off-axis ($\pi$) electrons

Field ionization model

\[ A^+ \rightarrow e^- \rightarrow A^+ \]

\( E(t_0) < 0 \)

\[ \Gamma^+ \quad \Gamma^- \]

Localization + Ionization

\( \Gamma^+ > \Gamma^- \)

\( E_+ \approx E(t_0) + E_c(R) \)

\( E_- \approx E(t_0) - E_c(R) \)

\( E(t_1) = 0 \)

\( \Gamma \)

delocalization via Tunnelling

(\( \Gamma, \omega_L \))

\( E(t_2) > 0 \)

\[ \Gamma^+ \quad \Gamma^- \]

Localization + Ionization

\( \Gamma^+ > \Gamma^- \)

\( E_+ \approx E(t_2) + E_c(R) \)

\( E_- \approx E(t_2) - E_c(R) \)


Schroeder, Uiterwaal, Kompa, Las. Phys. 10, 749 (2000). \( \Rightarrow \) 3D

\( R_c = 4 / I_p \)
Coherent Nuclear Interference via Electron Localization in Dissociative Ionization of H$_2^+$ by Intense Short Laser Pulses

by

A.D. Bandrauk, Université de Sherbrooke.
With S. Chelkowski. Experiment:

Fig. 1
Field ionization model

\[ A^+ \rightarrow e^- \rightarrow B^+ \]

- \( E(t_0) < 0 \)
- \( E(t_1) = 0 \)
- \( E_+(t_2) > 0 \)

\[ E_1 + E \cdot R/2 = E_2 - E \cdot R/2 \]

Ionization via delocalization
\( (\Gamma, \omega_L, \varphi) \) \( \Rightarrow \) Phase dependent!

Motivations

Non-Symmetric Molecules: e.g. CO, HeH²⁺, HeH⁺, BeH₂⁺, LiH⁺, HCL, …

- Unequal distribution of the electron cloud between nuclei
- Existence permanent dipole
- Inversion symmetry of the system is broken

How does Ionization and HOHG for the two configurations compares?

Is any configuration more efficient for EI of HOHG? If so Why?
Asymmetry in ionization and excitation

HeH$_2^+$: $w=0.114$ a.u. (400 nm)

Quantum mechanical v.s. Quasi-static approach

\[ R_{\text{crossing}} = \frac{(I_L - I_R) + \sqrt{(I_L - I_R)^2 - 4|F|(Z_L - Z_R)}}{2|F|} \]

- The arrow shows the locations of the level crossings (avoided) as predicted by the above formula.

- \( R_{\text{crossing}} \) decreases with field intensity

\( Z_L = \) electric charge of He\(^{2+} \).

\( Z_R = \) electric charge of H\(^+ \).

\( I_L = Z_L^2/2 = \) ionization potential of He\(^+ \).

\( I_R = Z_R^2/2 = \) ionization potential of H

Nuclear fusion from explosions of femtosecond laser-heated deuterium clusters

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As a form of matter intermediate between molecules and bulk solids, atomic clusters have been much studied. Light-induced processes in clusters can lead to photo-fragmentation and Coulombic fission, producing atom and ion fragments with a few electronvolts (eV) of energy. However, recent studies of the photoionization of atomic clusters are ionized, electrons undergo rapid collisional heating for the short time (< 1 ps) before the cluster disassembles in the laser field. Through various collective and nonlinear processes, the laser rapidly heats the electrons to a non-equilibrium state (with mean CREI ~ Rc ~ 4 – 5 Å

Figure 1: Layout of the deuterium cluster fusion experiment.
Corkum (Legare) – Bandrauk, Nature 417, 917 (2002)
NEW TECHNIQUE: LIED
LASER INDUCED ELECTRON DIFFRACTION

$$H^+_2 \text{ in a } \delta-\text{pulse (attosecond)}$$

$$E(t) = F\delta(t)$$

$$\varphi(\vec{p}) = \phi_{1\sigma^+}(\vec{p} + \vec{F})$$

$$= 2 \cos \left[ (\vec{p} + \vec{F}) \cdot \frac{\vec{R}}{2} \right] \phi_{1s}(\vec{p} + \vec{F})$$

$$\varphi(p) = 2 \cos \left( \frac{p \cdot \vec{R}}{2} \right) \phi_{1s}(\vec{F} + \vec{p})$$

1. \( F \perp R \)

$$\text{max at } p = \frac{2m\pi}{R \cos \theta} \hspace{1cm} \text{min at } p = \frac{(2m+1)\pi}{R \cos \theta}$$

2. \( F \parallel R \)

$$\varphi(p) = 2 \cos \left[ \frac{FR}{2} \left( 1 + \frac{p \cos \theta}{F} \right) \right] \phi_{1s}(\vec{F} + \vec{p})$$

Small \( p \):

$$\begin{cases} 
\text{max} & F \left\{ \frac{2m\pi}{(2m+1)\pi} \right\} \\
\text{min} & 
\end{cases}$$

Large \( p \):

$$F \left( FR + pR \cos \theta \right) \rightarrow \frac{2m\pi}{(2m+1)\pi}$$
H$_2^+$ R=20au, perpen. to 5e14 532nm 1T pulse.
Physics at the attosecond frontier

Yaron Silberberg

Ultrasound laser pulses allow physicists and chemists to watch fast molecular motion as it happens. But many fundamental atomic processes are even faster and require the shortest pulses ever created.

As every photographer knows, a flash of light can stop the action. Just as a fast flash lamp can freeze the image of a bullet in mid-flight, so short laser pulses can be used to probe fast molecular motion. It is no surprise, then, that laser scientists have been pushing for ever-shorter pulses of light in order to follow ever-more rapid processes. The quest has taken us from the first sub-picosecond (1 picosecond is $10^{-12}$ s) pulses, more than a generation ago, to the development of femtosecond optics (1 femtosecond is $10^{-15}$ s). These time periods are hard to imagine, but a femtosecond is to a minute what a minute is to the age of the Universe.

Femtosecond pulses led to femtochemistry, the experimental study of fast chemical reactions and molecular dynamics. Even the fastest molecular vibrations appear completely still when probed with a pulse lasting a few femtoseconds. Now, we are entering the era of attosecond pulses (1 attosecond is $10^{-18}$ s). On page 509 of this issue Hentschel et al. describe the generation and use of pulses lasting 650 attoseconds, in what might be the dawn of attophysics — the study of dynamics on timescales fast enough to follow electronic motion within atoms.

The road from picosecond to femtosecond light pulses has seen laser technology evolve towards lasers that emit light with greater 'spectral' width — that is, covering a wider range of wavelengths. A short pulse results when all the spectral components in the light beam interfere in a way that adds up to a single burst of light. The duration of this pulse is inversely proportional to the spectral width — so a wider spectral

![Diagram of laser pulse generation and focusing.](image)

Figure 1: Generating and using attosecond laser pulses. In their experiment, Hentschel et al.\(^1\) shine an ultrashort visible light pulse on a gas of neon atoms to produce higher frequency `harmonic' radiation (rainbow-coloured pulses) at ultraviolet and X-ray wavelengths. The visible and harmonic pulses pass together through a zirconium filter, which reduces the train of harmonic pulses to a single attosecond pulse (1 attosecond is $10^{-18}$ s). Both the attosecond pulse and the optical beam are focused onto the krypton target where they accomplish the very first attosecond measurement. The authors monitor the attosecond dynamics of photoelectrons emitted by the krypton gas by varying the delay between the attosecond and visible pulses.

1 attosecond = $10^{-18}$ sec = $\frac{3A^0(3 \times 10^{-8}\, cm)}{C(3 \times 10^{10}\, cm S^{-1})}$
Single fs pulse

Fs + asec pulses

$6 \times 10^{13} \text{ W/cm}^2$

20nm
Step 1: get spectrum

$$a(t) = \langle \psi(t) | \hat{z} | \psi(t) \rangle$$

$$a(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} a(t) e^{-i\omega t} dt$$

Step 2: select frequency region between $\omega_1 < \omega < \omega_2$

Step 3: come back to time domain

$$\tilde{a}(t) = \int_{\omega_1}^{\omega_2} a(\omega) e^{i\omega t} d\omega$$

$$\Delta \omega = \omega_2 - \omega_1$$

$$\tau = \frac{1}{\Delta \omega} \rightarrow \text{attosecond}$$
Time profiles of generated pulses

Yedder, LeBris, Chelkowski, Bandrauk, PRA 69, 041802 (2004)
Measuring electron wave packets

1. Attosecond pulses are fast enough to observe electron wave packets.

2. Electron wave packets are resolved through changes to the photo-electron spectrum as a function of pump-probe time delay.

3. The attosecond pulse projects the momentum distribution into the continuum.

Phys Rev A 72, 51401(R) (2005)
Laser Phase Control of High Order Harmonic Generation at Large Internuclear Distances - The H⁺-H₂⁺ system

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Abstract.

Exact (Born-Oppenheimer) 3-D numerical Solutions of the time-dependent Schrödinger equation, are obtained for the linear H⁺-H₂⁺ atom-molecule system separated by large internuclear distances in interaction with ultra-short (two-cycles) intense (I > 10¹⁴ W/cm²) 800 nm laser pulses. High order harmonic generation, HHG (spectra which are larger than 3U⁺ [1]) are calculated and are shown to be related to the nature of electron transfer, whose direction is shown to depend critically on the absolute (carrier) phase of the ultrashort pulse. Constructive and destructive interferences in the HHG spectrum of coherent superpositions of electronic states in the H⁺-H₂⁺ system are interpreted in terms of multiple electron trajectories from a time series analysis. Efficiencies of HHG are considerably enhanced by refocusing of the ionized electron trajectories with the neighboring ion thus probing nonadiabatic response of nonionized electrons.

PACS numbers: 32.80.Rm, 32.80.Fb


Linear H3++
(Unperturbed first three electronic states)
Laser parameters:

ω = 0.057 a.u. (800 nm)
I = 14 * 10**14 W cm²
T = 2 cycles

Harmonic contributions of H₃²⁺ protons for the absolute phase

ϕ = 0

ϕ = π
Analyse at $\phi = 0$

Electric field

Pulse period

Harm_80_H+ ($\phi = 0$)

Harm_80_H+ ($\phi = 0$)

Harmonic Spectra

Z coordinate

Time profile of the 80-th Harmonic for $\phi = 0$
Analyze at $\varphi = \pi$
Density of probability $|\psi(\rho, z, t)|^2$ at $\varphi = \pi$
High Harmonic Generation of The Linear Triatomic H3++

Bandrauk A. D. and Barmaki S.

Diagram:
- H^+ to H_2^+ with distance R = 2 a.u.

Graph:
- Electronic energy vs. internuclear distance R in a.u.
- Energy levels labeled 3σ, 2σ, 1σ.
Initial Coherent state: combination of unperturbed electronic states 2σ and 3σ:

\[ \psi_{in} = \alpha \psi_{2\sigma} + \beta \psi_{3\sigma} \]

\[ \alpha^2 + \beta^2 = 1 \]

Laser Pulse parameters:

\[ W = 0.028 \text{ a.u.} \quad (\lambda = 1628 \text{ a.u.}) \]
\[ E = 0.053 \text{ a.u.} \quad (I = 10^{14} \text{ Wcm}^{-2}) \]
\[ T = 2 \text{ cycles} \]
Results at $R = 4$ a.u.

- Harmonic spectra
- Electric field
- Harmonic order vs. time
- Oscillation period $T_{osc} = 30$ a.u.
Results at $R = 2$ a.u.

Harmonic Spectra

$\varphi = 0$

$H^+$

$H_2^+$

Harmonic Order

$T_{oscill} = 13$ a.u.

Electric field in a.u.

$\varphi = 0$

$H^+$

$H_2^+$

$R = 2$ a.u.
Measuring electron wave packets

1. Attosecond pulses are fast enough to observe electron wave packets.

2. Electron wave packets are resolved through changes to the photo-electron spectrum as a function of pump-probe time delay.

3. The attosecond pulse projects the momentum distribution into the continuum.

Yudin et al, Phys Rev A 72, 51401(R) (2005)

Fig. 2.

Time delay $\tau_0$ (asec)

Normalized asymmetry $a = \frac{P(30)-P(150)}{\{P(30)+P(150)\}}$, $E_{ph} = 150$ eV, $e_x \parallel R$

- $R=8.0$
- $R=5.0$
- $R=12$

- Atomic curve

- $1s+2p$
- $1s+2s$

- $R=5$
- $R=6$
- $R=6.4$
- $R=6.8$
- $R=6.8$
Atom: 1s+2p and $\gamma_1s+\gamma_u*2p$ in H$_2^+$

**no** asymmetry in atomic 1s + 2s and in molecular: $\gamma_1s+\gamma^*2s$, but there asymmetry in $\gamma_{1s+}\gamma_{,*}2s$
Spectral phase measurement of HHG using a coherent state of Alkali metal

Ryuji ITAKURA (JAEA)

Ionization continuum |
\[ |p, l, m > + ^1S (Ion core) \]

High Harmonics @delay \( t_0 \) from IR

\[ E(t) = \int d\omega \sqrt{I(\omega)} \exp \{ -i(\omega t + \phi(\omega)) \} \]

\[ \Psi(t) = a_1\phi_1 \exp \{ i(2\pi E_1 t/\hbar - \phi_1) \} \]
\[ + a_2\phi_2 \exp \{ i(2\pi E_2 t/\hbar - \phi_2) \} \]

Coherent superposition of \( ^2P^o \) spin-orbit states
The vector potentials of the chirped attosecond x-ray pulse and low-frequency laser field:

\[
A(t) = eA_0 e^{-i\Omega t} \left\{ \exp \left[ -\frac{(t-t_1)^2}{2\tau^2(1-i\xi)} \right] + \varsigma \exp \left[ -\frac{(t-t_2)^2}{2\tau^2(1-i\xi)} \right] \right\}
\]

\[
A_L(t) = -(E_0 / \omega_0) \sin(\omega_0 t)
\]

Sudden approximation:

\[
\omega_0 \ll \Omega \quad p \ll Z_{eff}
\]
$H(1s), \ t_1=0$

$\tau_0 = 400$ asec

$\tau = 150$ asec

Laser off

Integral electron spectrum $[\text{A}^2]$ vs. Photoelectron energy [eV]
H(1s) \quad t_1 = \frac{\pi}{2}\omega_0

Photoelectron spectrum \[ A_0^2 \]

\begin{align*}
E_e &= 170 \text{ eV} \\
E_e &= 140 \text{ eV} \\
E_e &= 110 \text{ eV}
\end{align*}
$H^+_2 \quad t_1 = 0$

$\xi = 3, \quad t_2 = \pi/4\omega_0$

$\xi = 4, \quad t_2 = \pi/4\omega_0$

$\xi = 3, \quad t_2 = \pi/2\omega_0$