



Theoretical/Computation approaches towards application of intense laser

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European Union
European Regional
Development Fund



INVESTING IN YOUR FUTURE

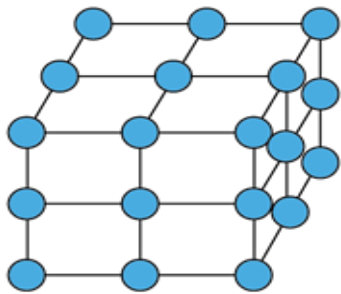
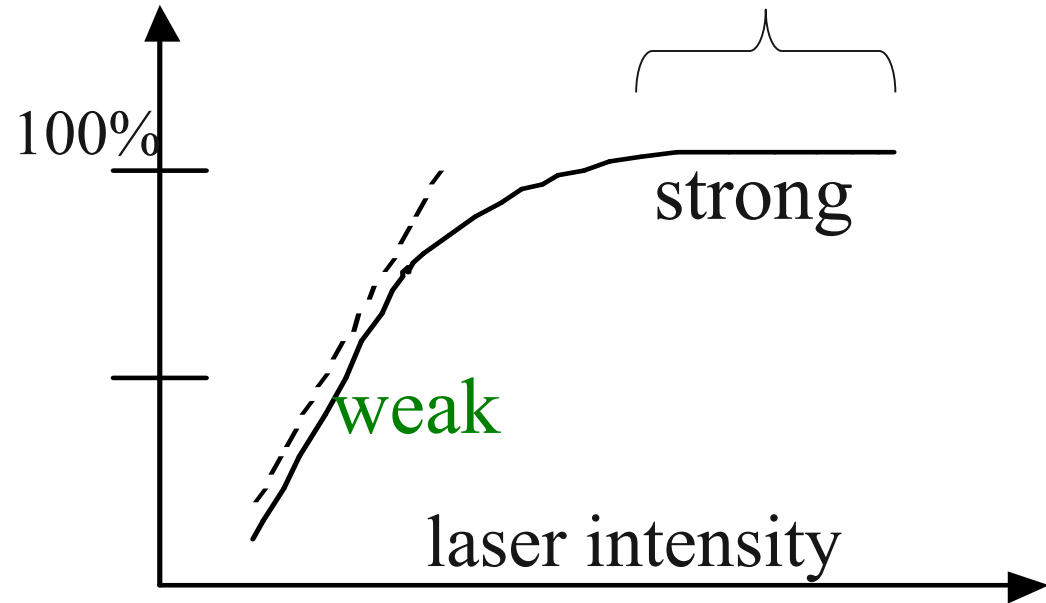
- ❖ Why laser-matter interaction?
- ❖ Two protagonists..... Laser..... And matter.....
- ❖ Tools to address the interaction
- ❖ Numerical simulations
- ❖ Some practical applications
 - ✓ Electronic structures of a material
 - ✓ Probing structure and dynamics
 - ✓ Ultrafast processes in nanostructures

What happens when we shine a material with light

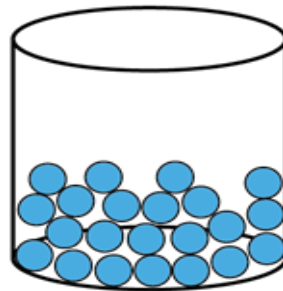


ionization

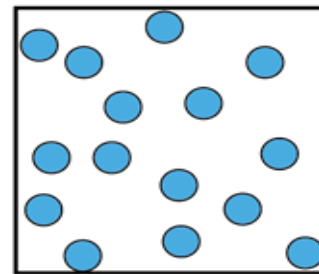
all ionized



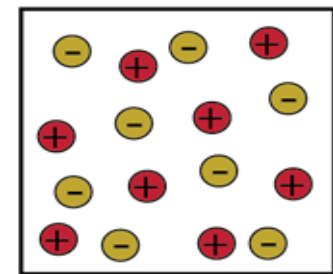
Solid



Liquid



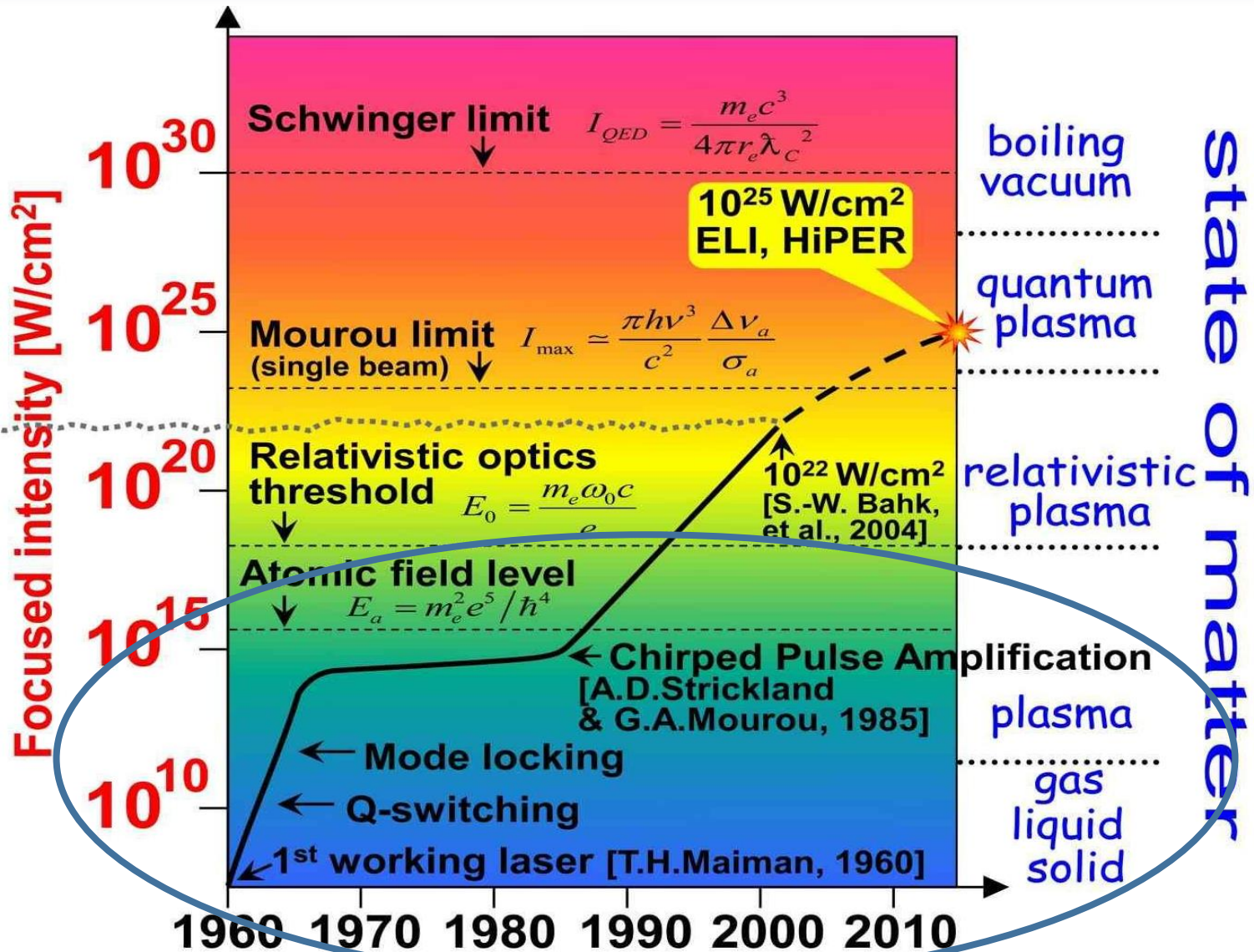
Gas



Plasma

Add Heat

Which regime are we talking about?

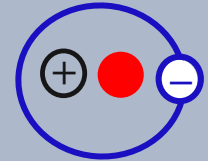


Which regime are we talking about?



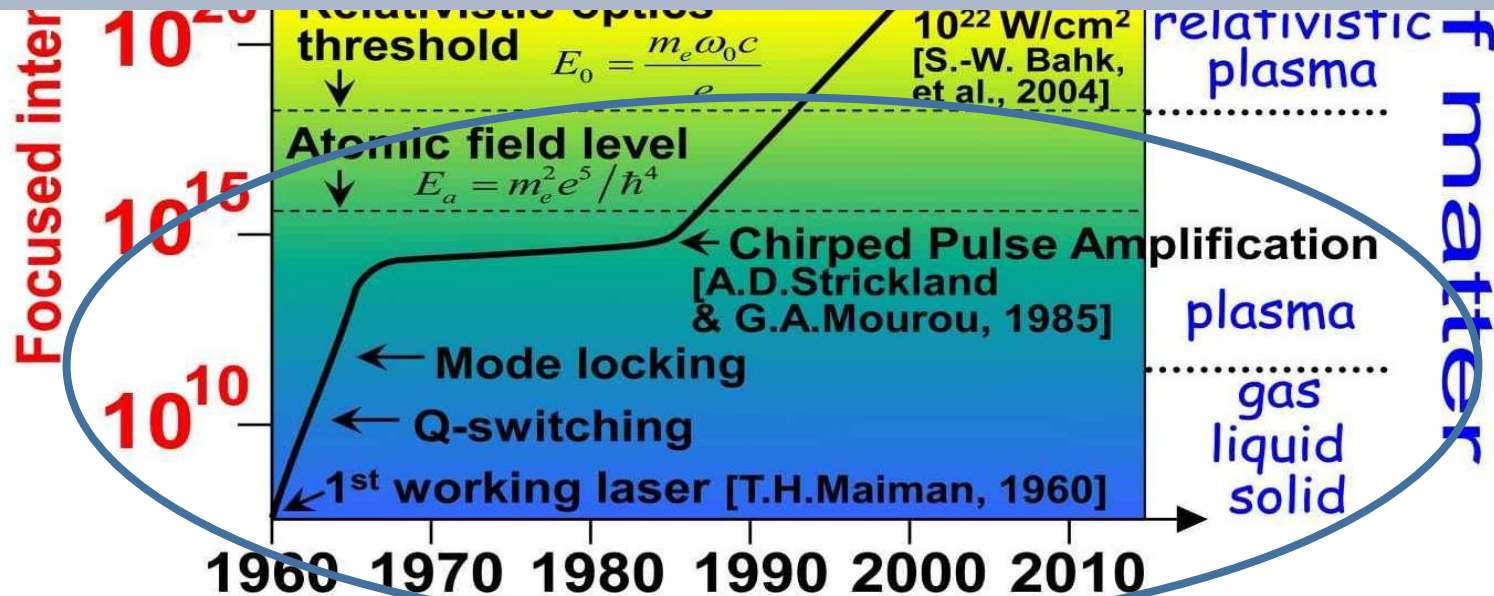
Normally

Increased intensity increases ionization
more chance for electron to pick up energy around nucleus



At super-strong fields

Laser also distorts electron orbits
reduces the chance of interaction with nucleus

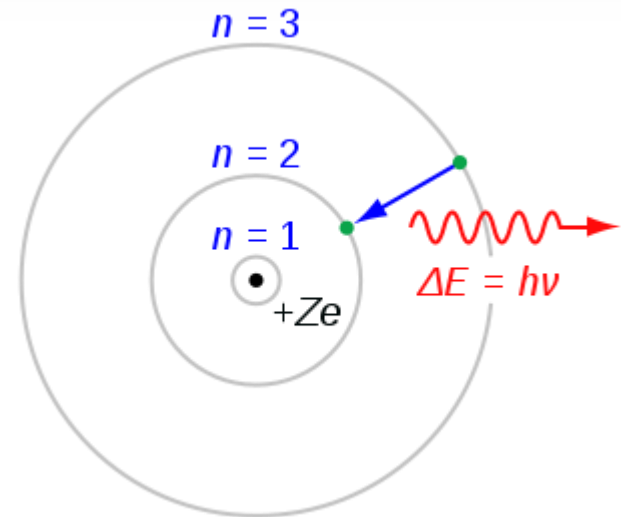


Use LASER to understand and control materials



Periodic Table of the Elements

1 1IA 11A H Hydrogen 1.0079	2 IIA 2A He Helium 4.0026																	18 VIIIA 8A																													
3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.0064	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797																														
11 Na Sodium 22.989769	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.065	17 Cl Chlorine 35.4527	18 Ar Argon 39.948																														
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.9216	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80																														
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9062	44 Ru Ruthenium 101.07	45 Rh Rhodium 103.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8662	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29																														
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [209.9624]	85 At Astatine [209.9871]	86 Rn Radon 222.0176																														
87 Fr Francium [223.0187]	88 Ra Radium [226.0254]	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [265]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [271]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium [284]	114 Fl Flerovium [285]	115 Uup Ununpentium [288]	116 Lv Livermorium [293]	117 Uus Ununseptium [294]	118 Uuo Ununoctium [294]																														
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Period of first Bohr orbit : 150 as

Control and trace the motion of atoms in molecules

⇒ Control chemical reactions

Control & trace electrons inside atoms & molecules

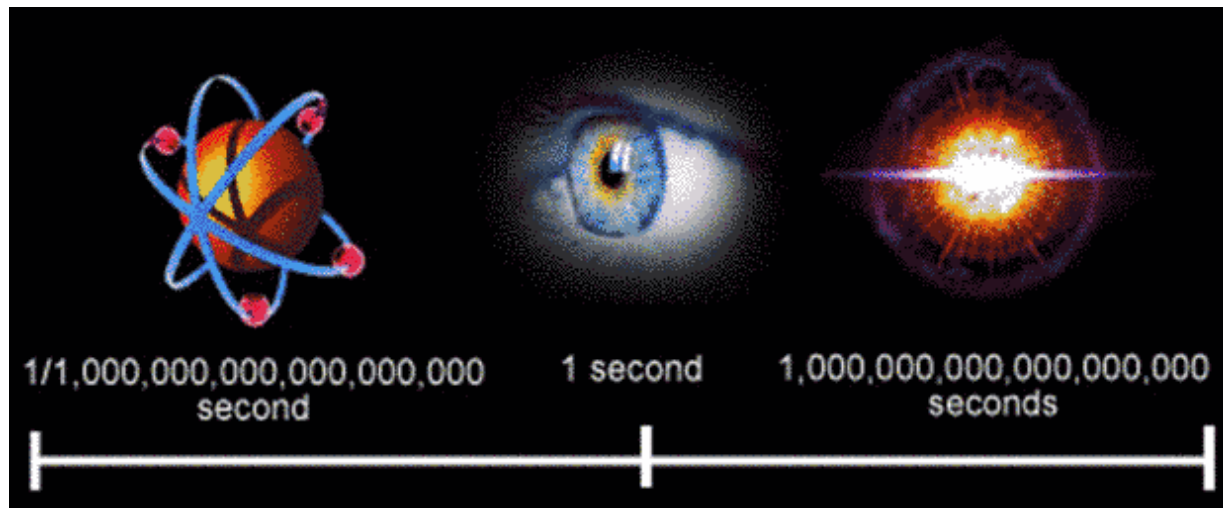
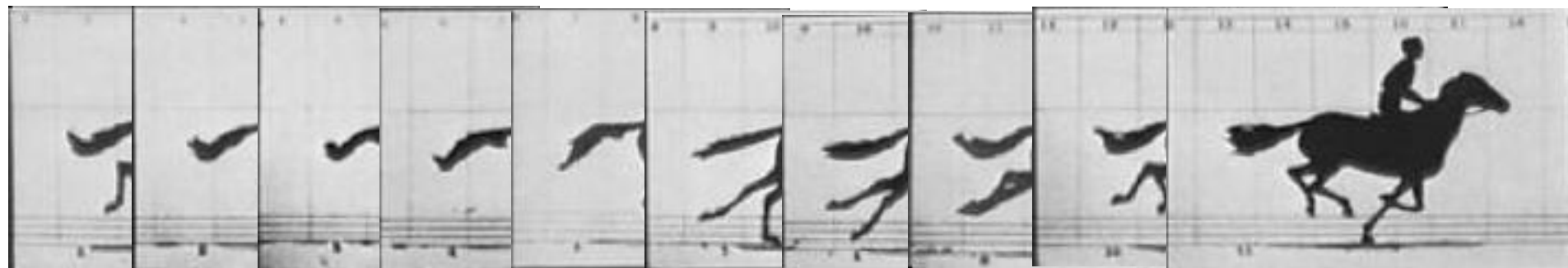
Femto

Atto

Attoscience for dynamical systems



1878- Eadweard Muybridge froze the motion of a horse - a millisecond event.



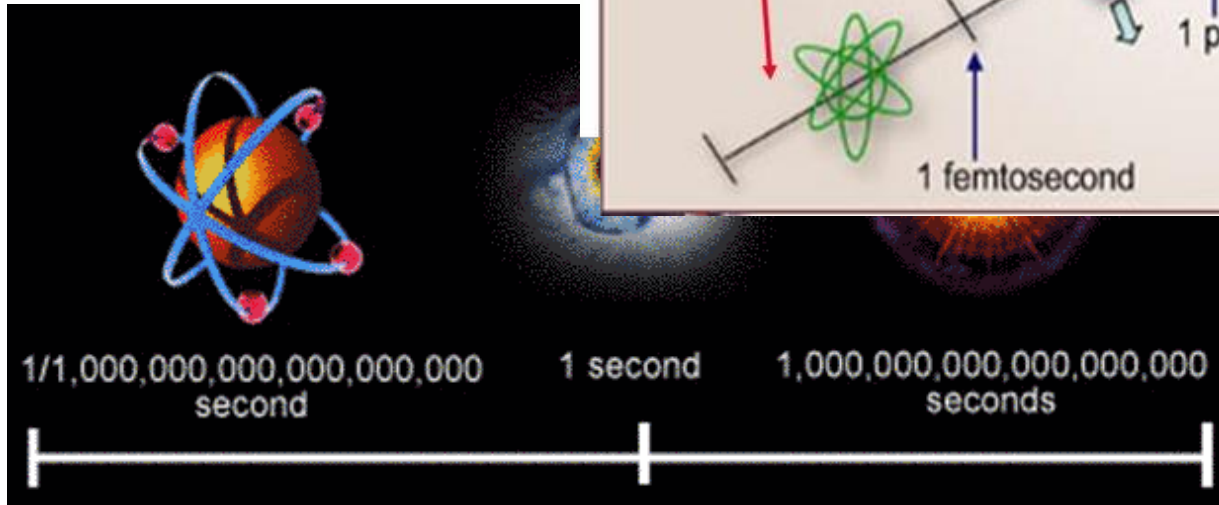
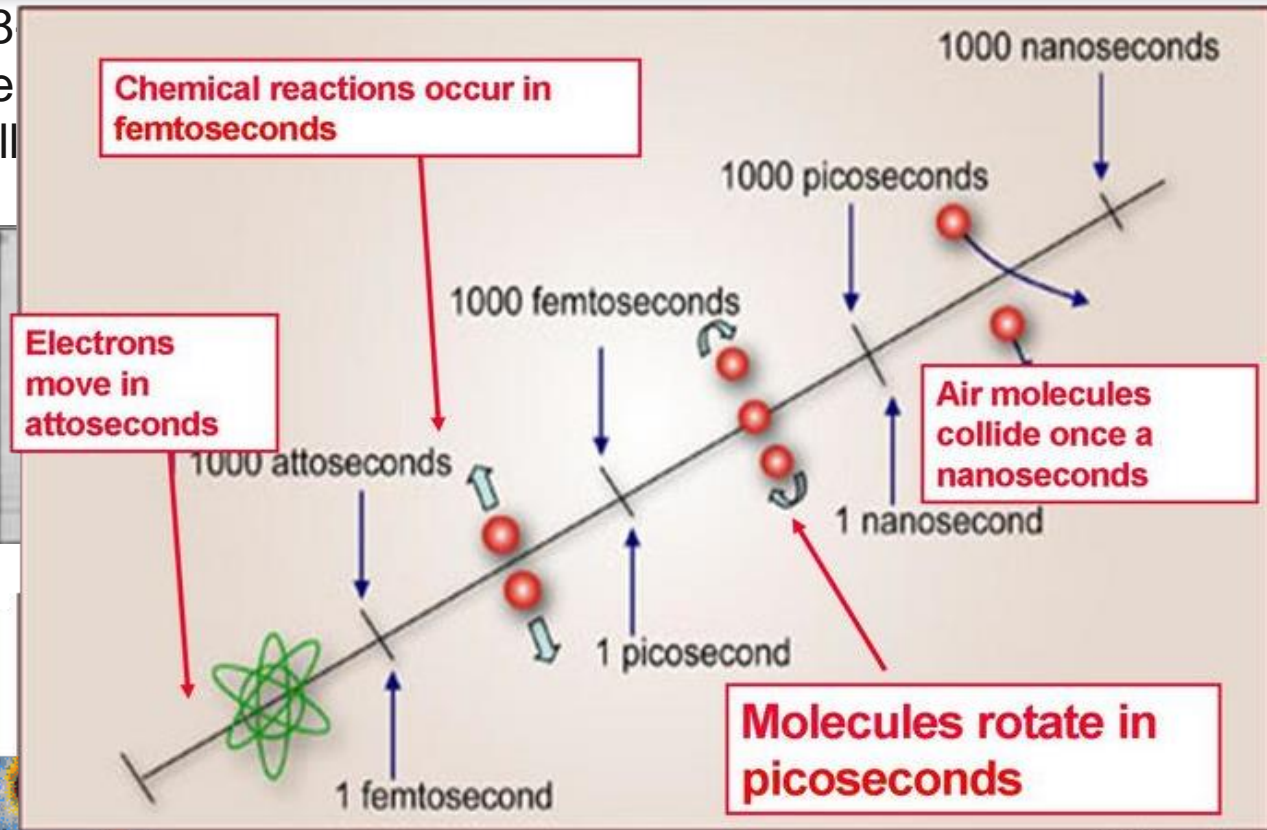
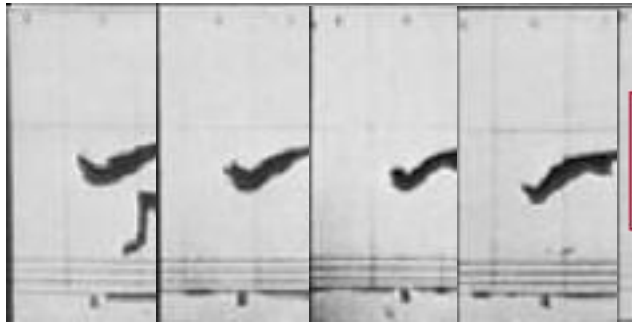
To examine electrons?
we must take “pictures”
at the attosecond level.

1 as : 1/2 second = 1/2 second : the age of the universe.

Attoscience for dynamical systems



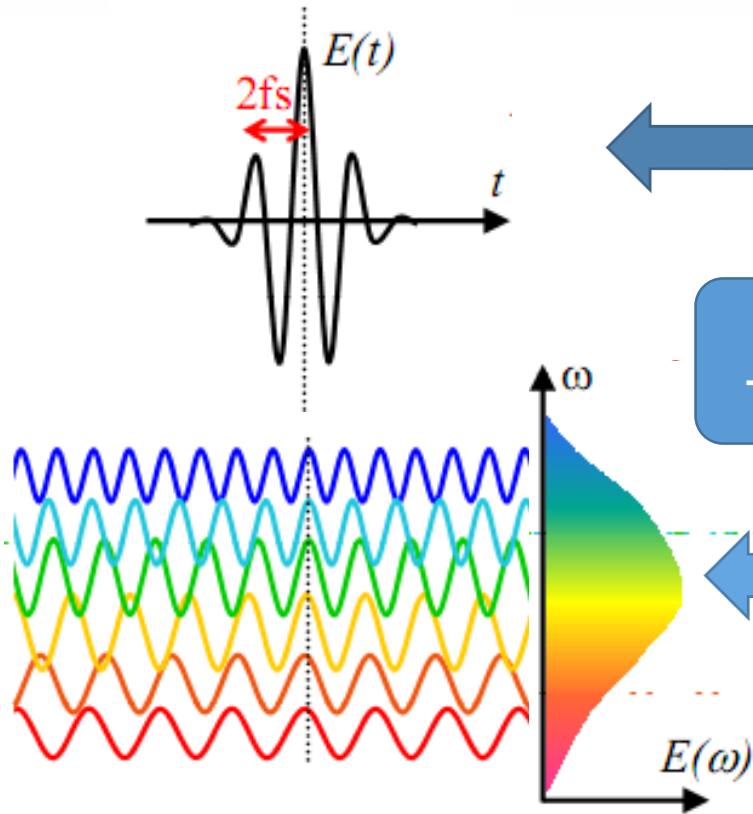
1878
froze
a mill



To examine electrons?
we must take "pictures"
at the attosecond level.

1 as : 1/2 second = 1/2 second : the age of the universe.

Spectral composition of a LASER pulse



Pulse = sum of different spectral components

Fourier decomposition of a signal:

$$F(t) = \sum_{n=0}^{+\infty} a_n \cos(\omega_n t - \varphi_n)$$

LASER Electric field:

$$E(t) = \sum_n E_n(t) = \sum_n a_n \cos(\omega_n t - \varphi_n)$$

More spectral components => **Shorter pulse**

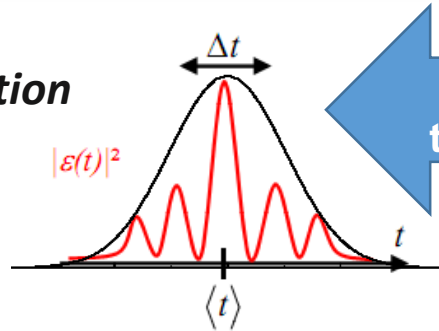
Less number of spectral components/
Spectral components not in phase (« **chirp** »)
=> **Longer pulse**

Single ω => **Monochromatic continuous pulse**

Fourier limit: Pulse duration & its spectral width

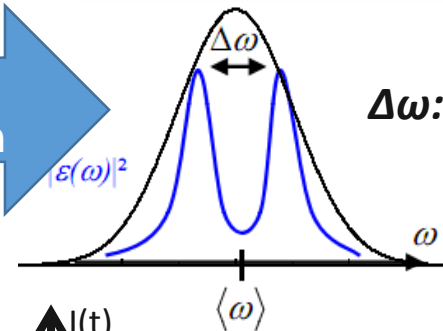


Δt : pulse duration



Fourier transform

$\Delta\omega$: spectral width



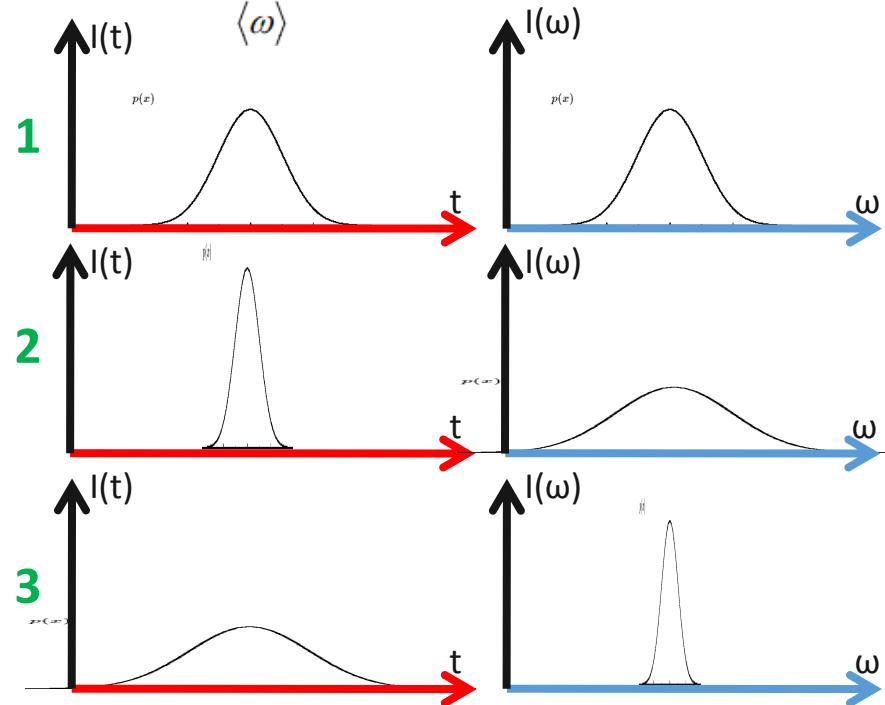
• **Fourier limit: $\Delta\omega \cdot \Delta t \geq \frac{1}{2}$**

• For a perfect Gaussian: $\Delta\omega \cdot \Delta t = \frac{1}{2}$

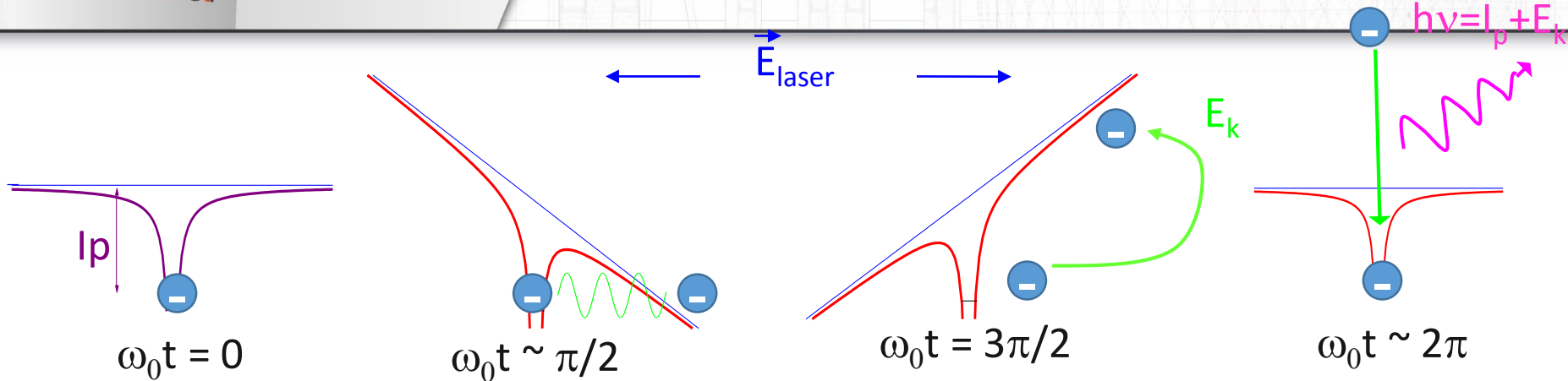
So.... Pulse « limited by Fourier transform »

If the spectral components ω are not in phase, the pulse is lengthened: there is a **chirp**

Shorter pulse -> wider bandwidth + no chirp



Harmonic generation : semi-classical 3-step model



Electron of a gas atom
Fundamental state

- ① Tunnel ionization
- ② Acceleration in the electric LASER field
- ③ Recombination to fundamental state

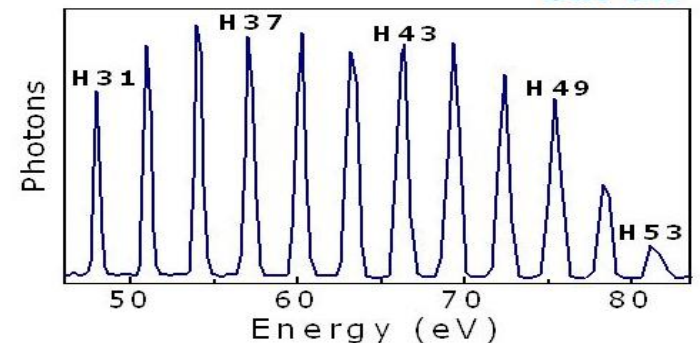
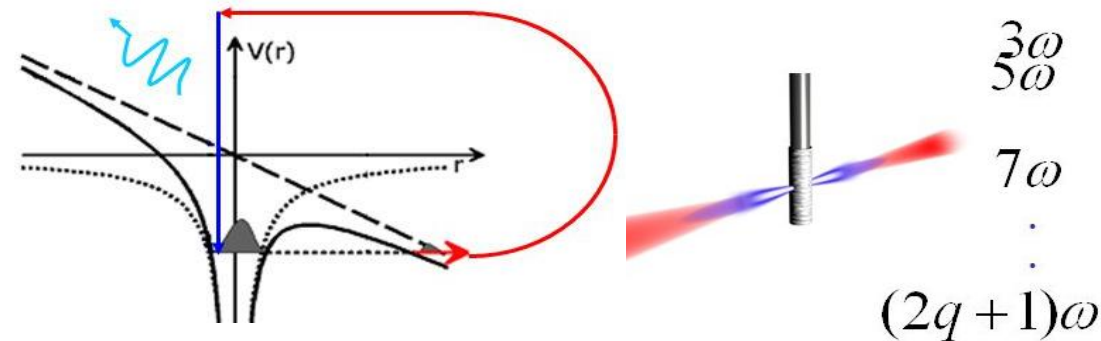
Energy of the emitted photon =
Ionization potential of the gas (I_p) + Kinetic energy won by the electron (E_k)

P.B. Corkum PRL 71, 1994 (1993)

K. Kulander et al. SILAP (1993)

Plateau

Cut-off



Hamiltonian:
$$H = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{\sqrt{x^2 + a^2}} - xV_L(t) - xV_X(t)$$

Strong field

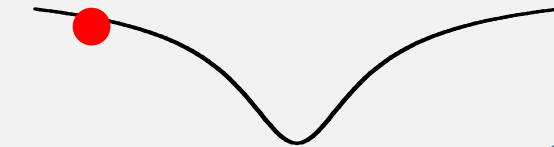
XUV

$$V_L(t) = \varepsilon_L \sin^2\left(\frac{\pi t}{2\tau_L}\right) \sin \omega_L(t - \tau_L)$$

$$V_X(t) = \varepsilon_X \exp\left[-4 \ln 2 \left(\frac{t - t_X}{\tau_X}\right)^2\right] \sin \omega_X(t - t_X)$$

Atomic potential model

$$V(x) = -1/\sqrt{1 + x^2}$$



Soft-core:

Strong laser field:

XUV:

$$a = 1.59 \text{ a.u.}$$

$$\varepsilon_L = 1.5 \times 10^{14} \text{ W/cm}^2$$

$$\varepsilon_X = 10^{11} \text{ W/cm}^2$$

$$\text{Xe } I_p = 12.31 \text{ eV}$$

$$\omega_L = 790 \text{ nm}$$

$$\omega_X = 80 \text{ eV}$$

$$\tau_L = 5 \text{ fs}$$

$$\tau_X = 250 \text{ as}$$

- Calculate bound state electron density

- Ionization occurs in steps with large depletion of the bound states population appearing near the peaks of the strong field.

Effective mass of electrons in crystal, TDSE



Interaction of light with atom

TDSE – simple yet efficient tool to handle dynamics

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x,t)\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad \leftarrow \quad \Psi(x,t) = \psi(x)T(t)$$

LHS involves variation of ψ with t while RHS involves variation of ψ with x . Hence look for a separated solution:

$$\Psi(x,t) = \psi(x) T(t) = e^{i(\pm kx - Et/\hbar)}$$

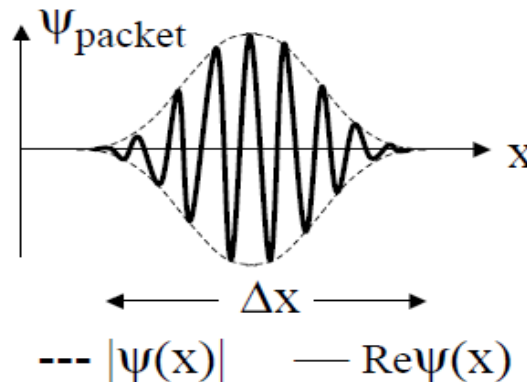
Dynamics of the electron in free space and in the lattice are different.

Effective velocity of the particle
= phase velocity of the wave packet

$$E(k) \sim \frac{\hbar^2 k^2}{2m} + V \sim \frac{\hbar^2 k^2}{2m^*}$$

Free
electron
momentum

Effective
potential in
solid

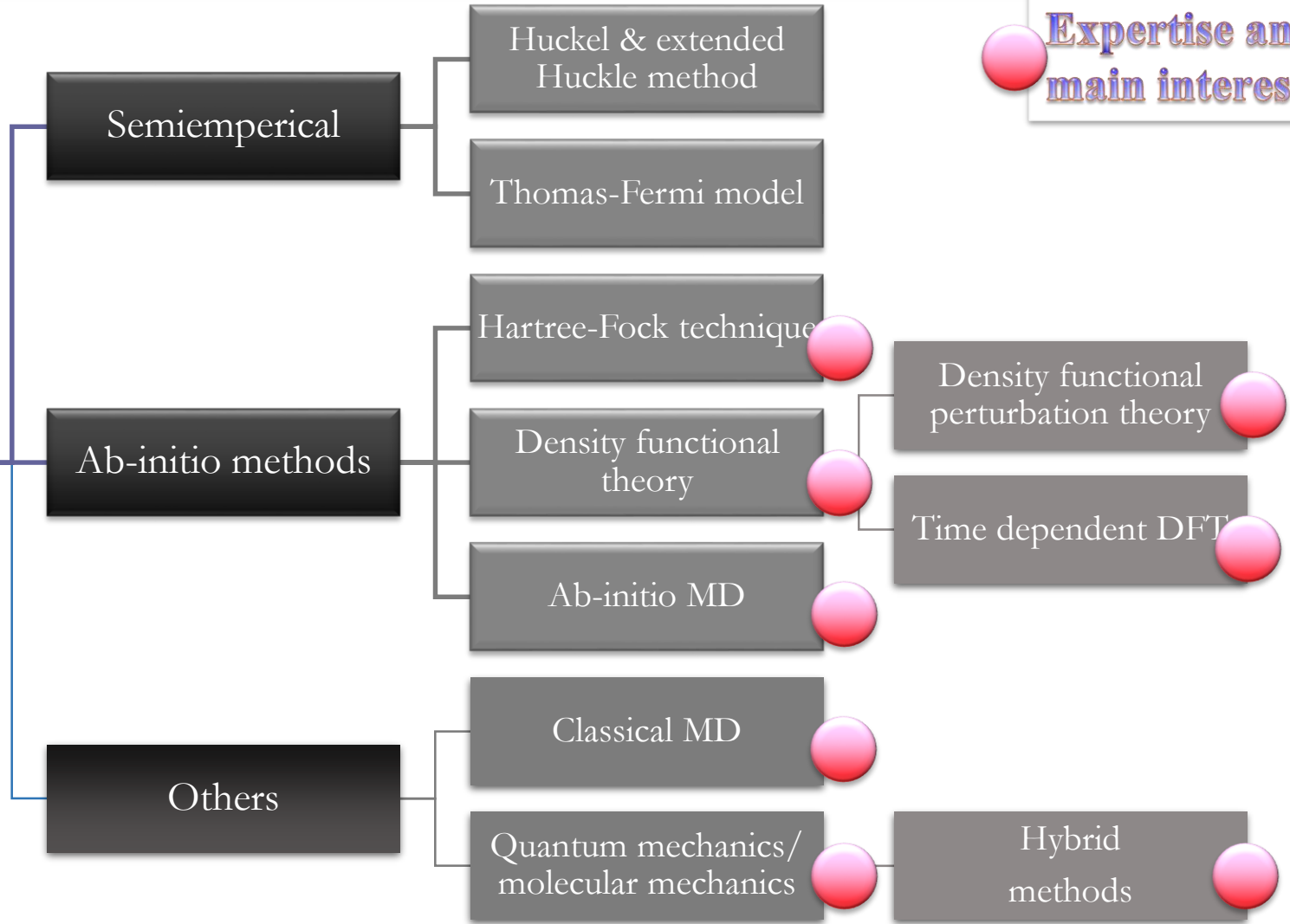


$$F = m^* \cdot \frac{dv_g}{dt}$$

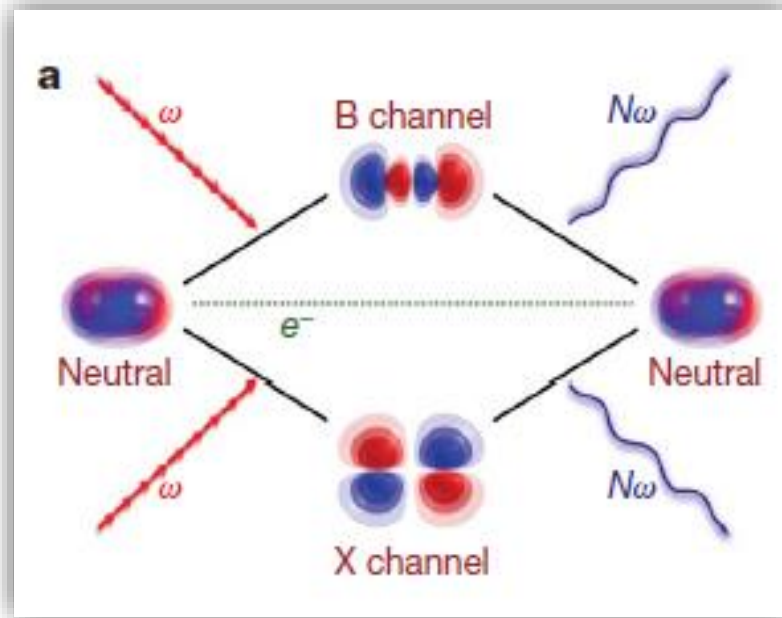
$$m^* = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

**Expertise and
main interest**

**Computational materials
modelling**



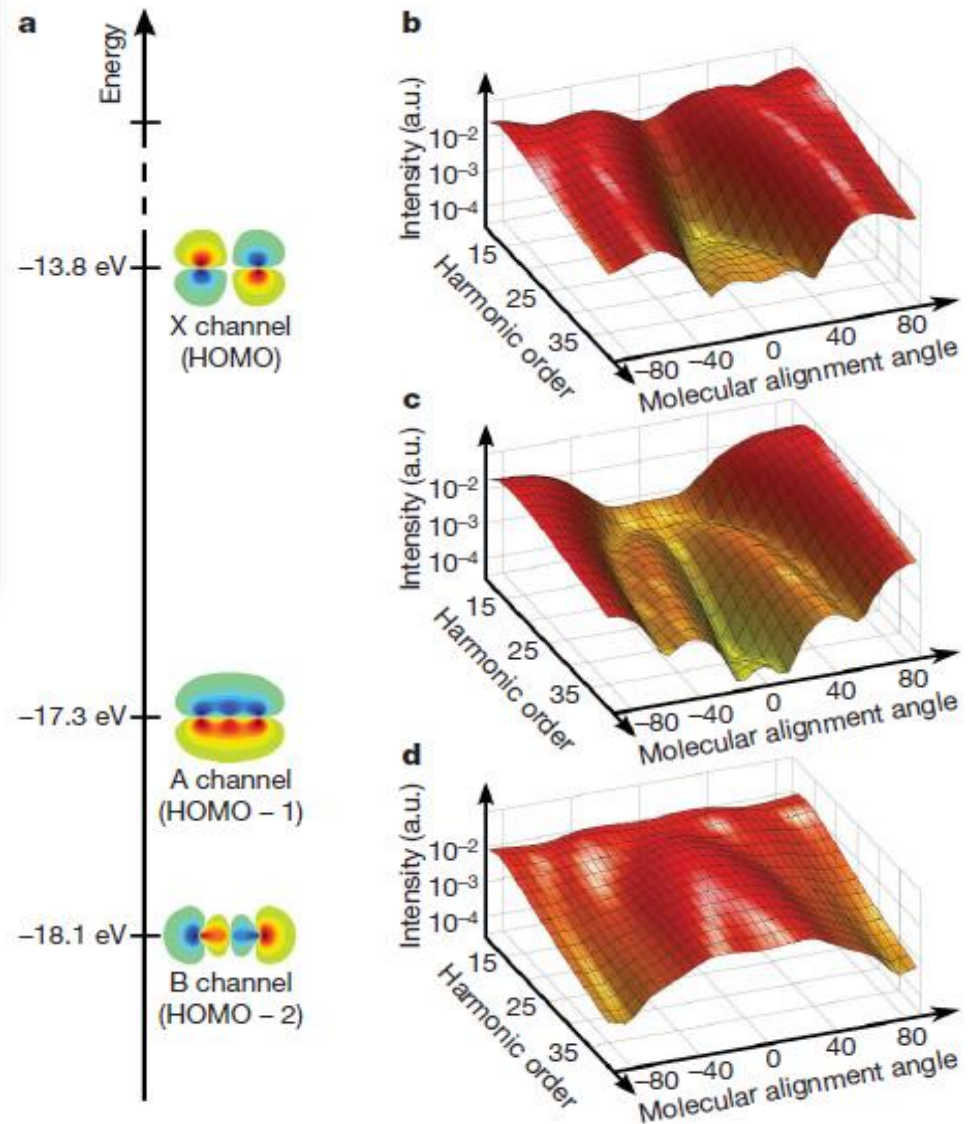
Ab-initio methods for attoscience: High harmonic interferometry & multi-electron dynamics of CO₂



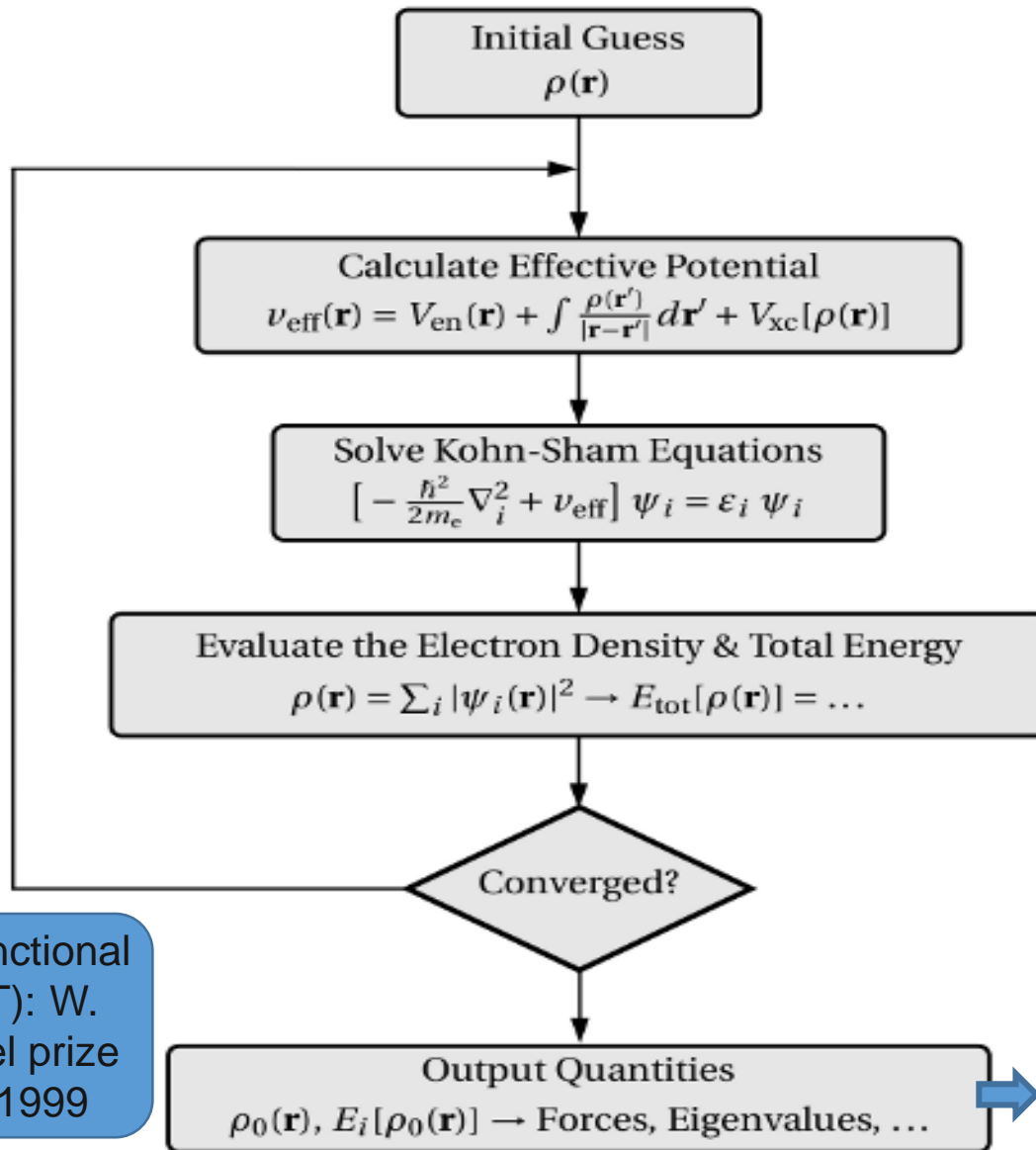
Different molecular orbitals (note their different symmetries) contributing to the harmonic emission

50 Hz Ti:Sa laser, $\tau \sim 30$ fs, 800 nm
 $I \sim 10^{12}$ - 10^{14} Wcm⁻²

O. Smirnova et al, *Nature* (2009).



How ab-initio method works?



- ✓ Quantum espresso (free)
- ✓ Octopus (free)
- ✓ VASP (licensed)
- ✓ Siesta (free)

TDDFT for excited state properties and dynamics.

fundamental variable is the many-body charge density.

➤ Structure, energetics....

➤ Cheap, virtual experiment

Density Functional Theory(DFT): W. Kohn, Nobel prize Chemistry, 1999


Static and time-dependent DFT



Hohenberg and Kohn (1964): $n(\mathbf{r}) \longleftrightarrow V(\mathbf{r})$

DFT : eigen-value problem

All physical observables of a static many-body system are, in principle, functionals of the ground-state density $n(\mathbf{r})$.

 most modern electronic-structure calculations use DFT.

Runge and Gross (1984): $n(\mathbf{r}, t) \longleftrightarrow V(\mathbf{r}, t)$

TDDFT : initial-value problem

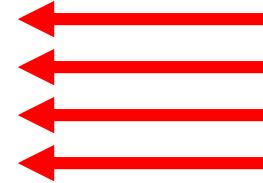
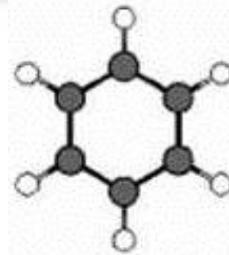
Time-dependent density $n(\mathbf{r}, t)$ determines, in principle, all time-dependent observables.

 TDDFT: universal approach for electron dynamics.

Real-time electron dynamics in materials



Generic situation: Molecule in laser field

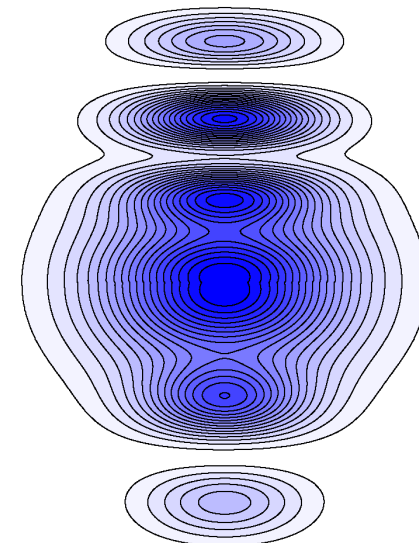
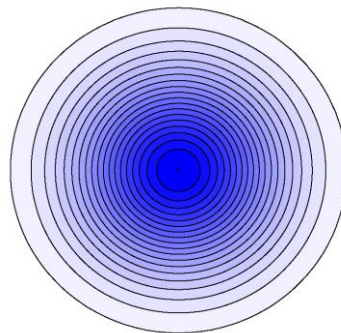
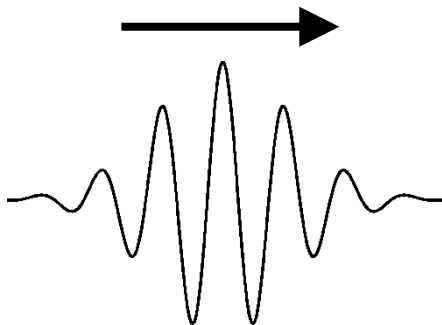


$$\hat{H}(\mathbf{t}) = \hat{T}_e + \hat{W}_{ee} + \sum_{j,\alpha} -\frac{Z_\alpha e^2}{|\mathbf{r}_j - \mathbf{R}_\alpha|} + \vec{E} \cdot \vec{r}_j \cdot \sin \omega t$$

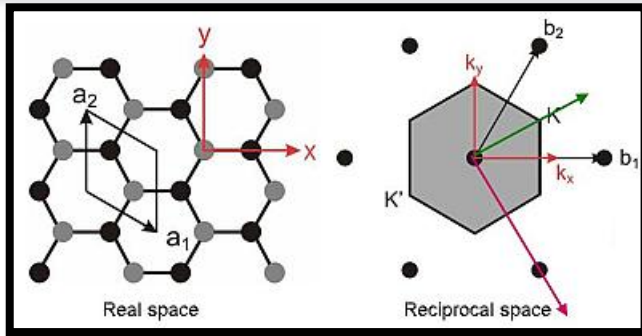
Strong laser ($v_{\text{laser}}(\mathbf{t}) \geq v_{\text{en}}$):

Non-perturbative solution of full TDSE required

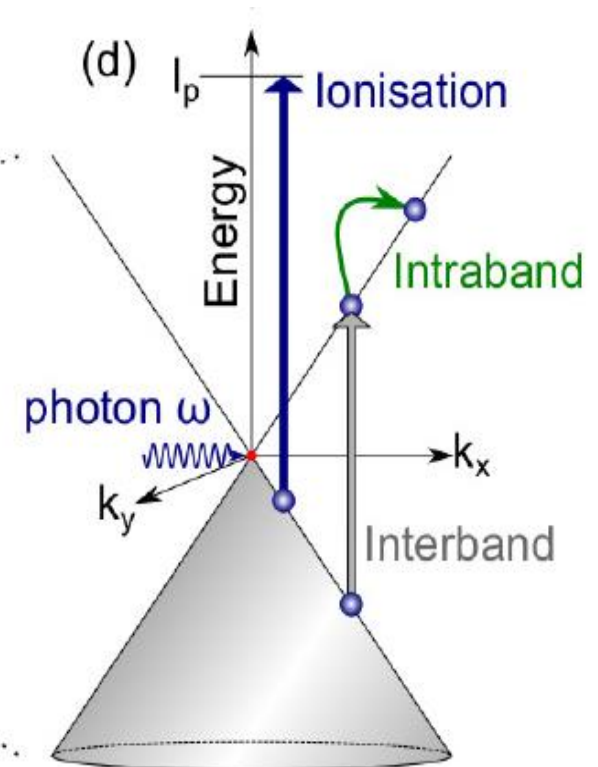
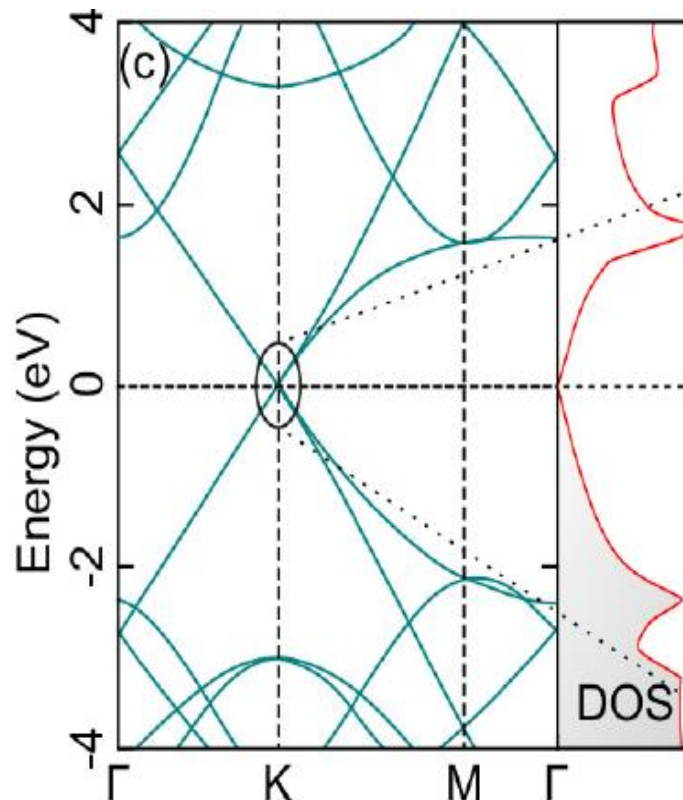
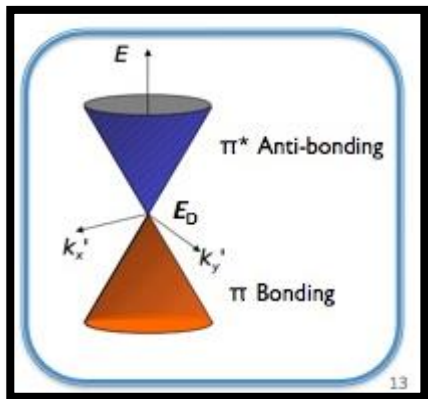
Nonlinear response and ionization of atoms and molecules in strong laser fields



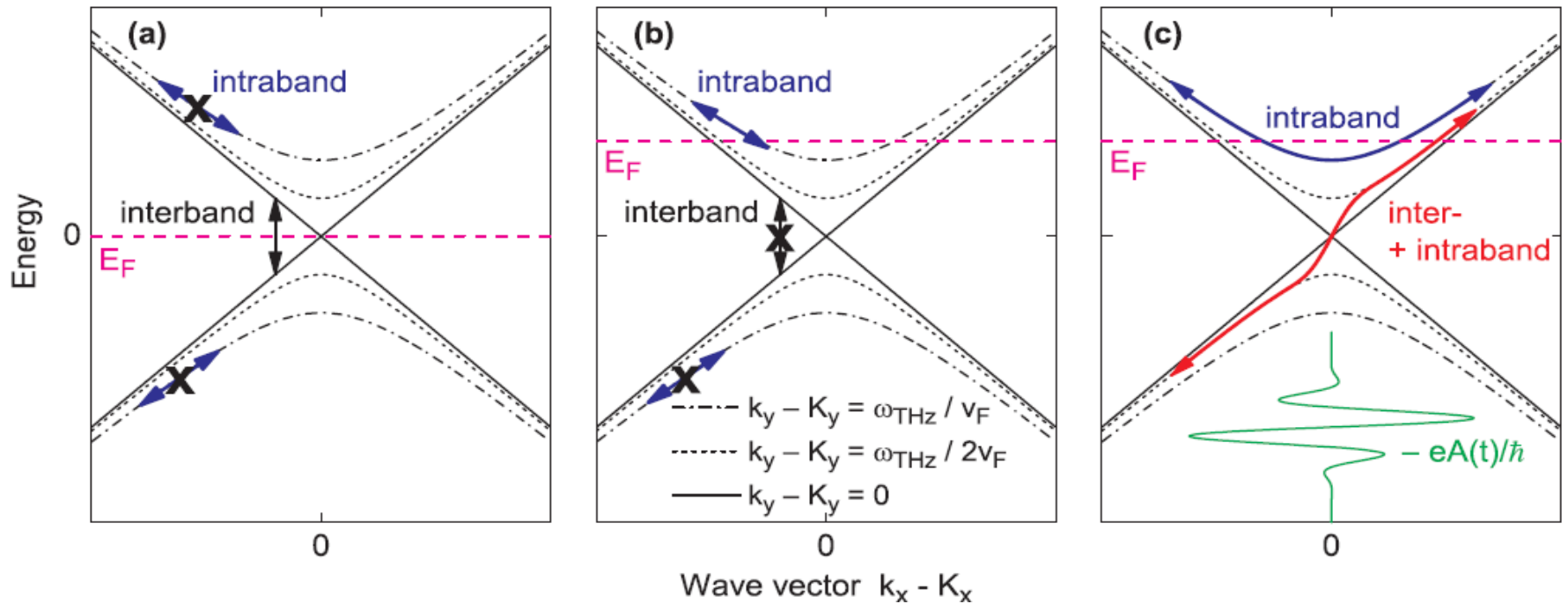
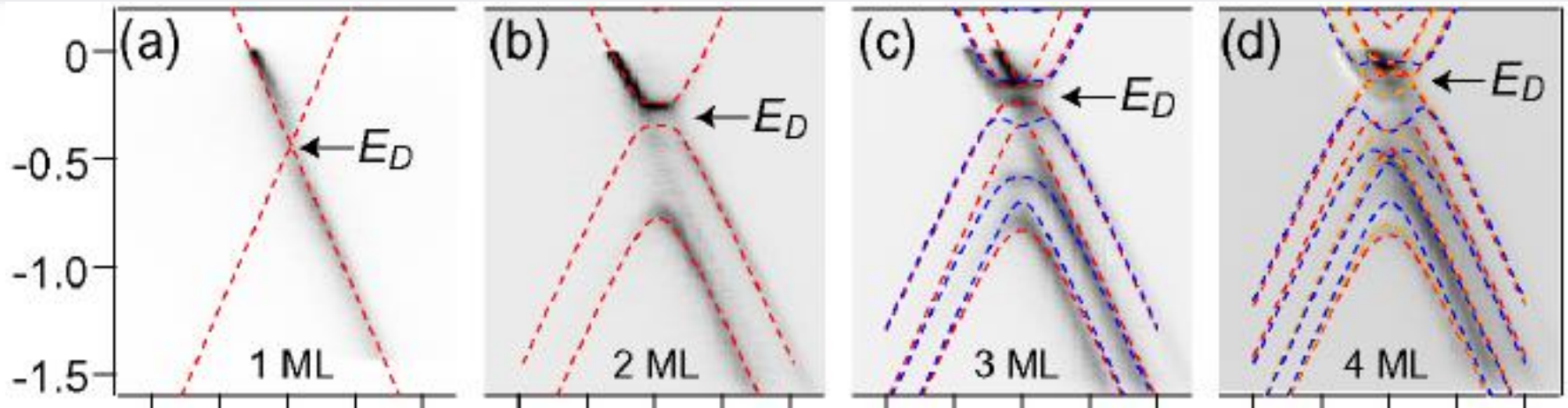
Inter and intra-band transitions in graphene



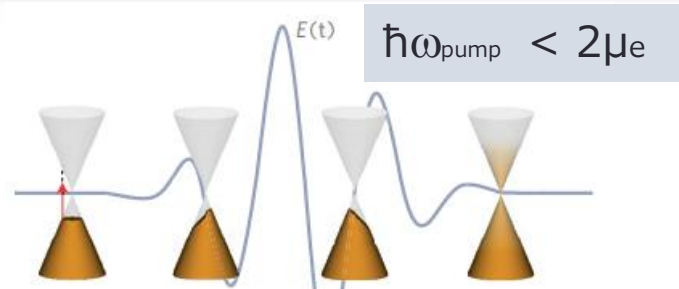
- Massless Dirac Fermion
- Very high mobility, conductivity
- Extreme tunability



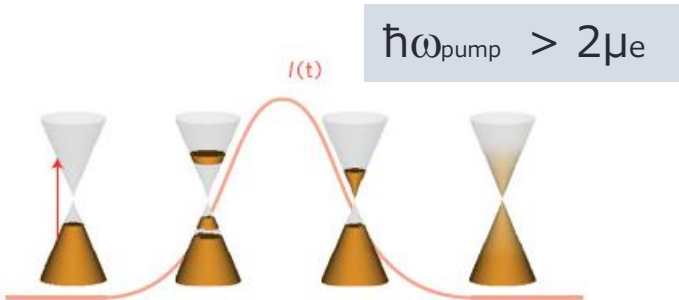
Few layer graphene : shift of Dirac cone



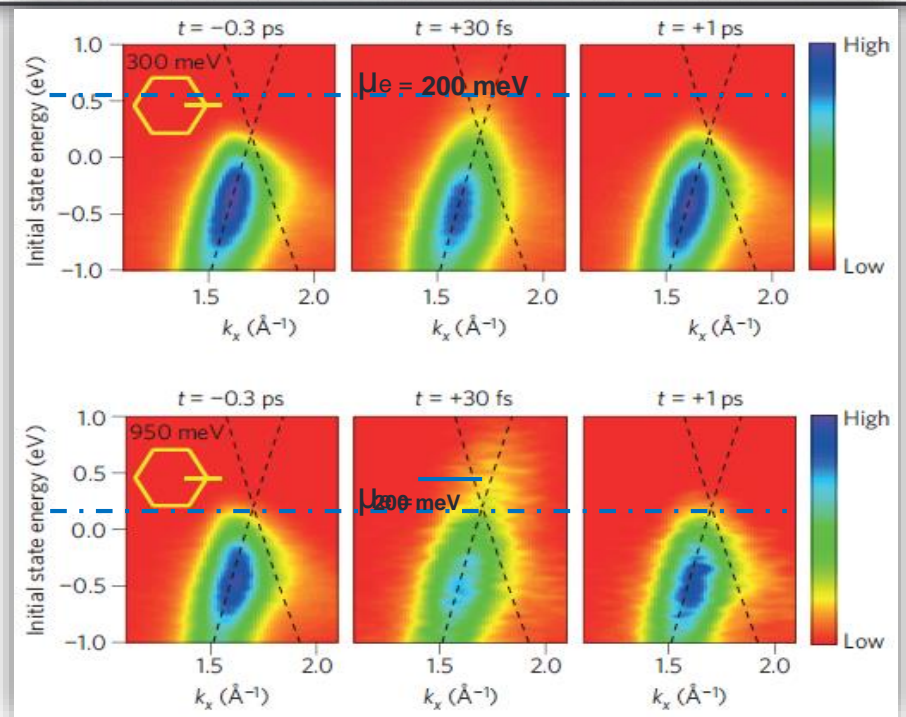
Non-equilibrium Dirac carrier distribution in graphene



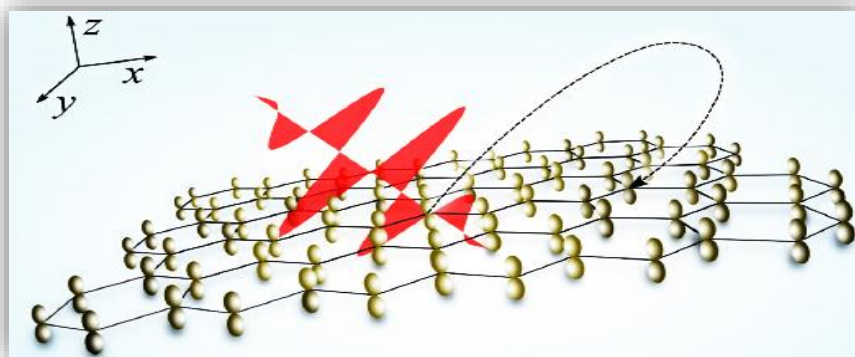
Free carrier absorption in graphene



Direct interband transition => population inversion



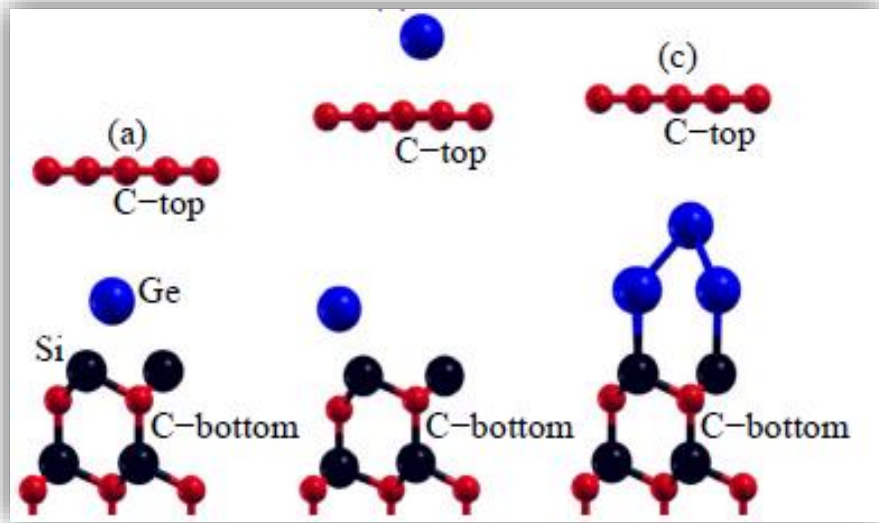
Measured snapshots of the band structure (close to K)



1 kHz Ti:Sa laser, $\tau \sim 30$ fs, 790 nm,
XUV pulse + ARPES
to probe non-eq response of electrons

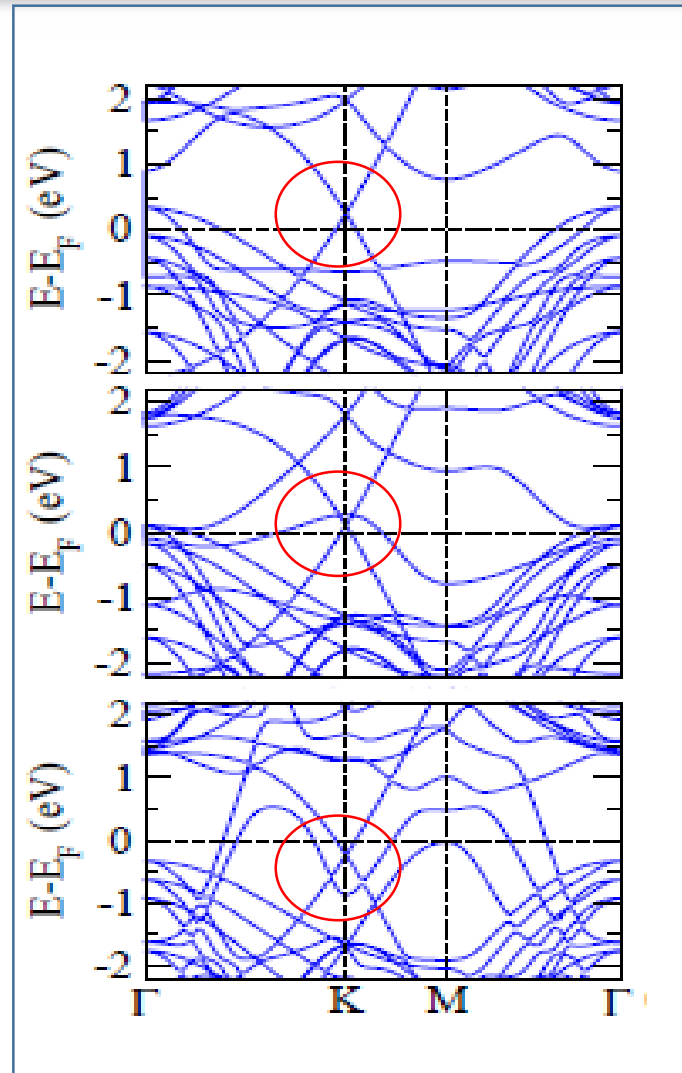
I. Gierz et al, *Nature Mat.* (2013)
Sorngard et al, *Phys. Rev. A* (2013)

Intercalated graphene

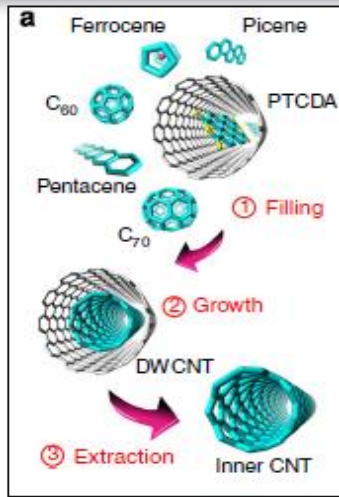


Intercalated graphene on SiC

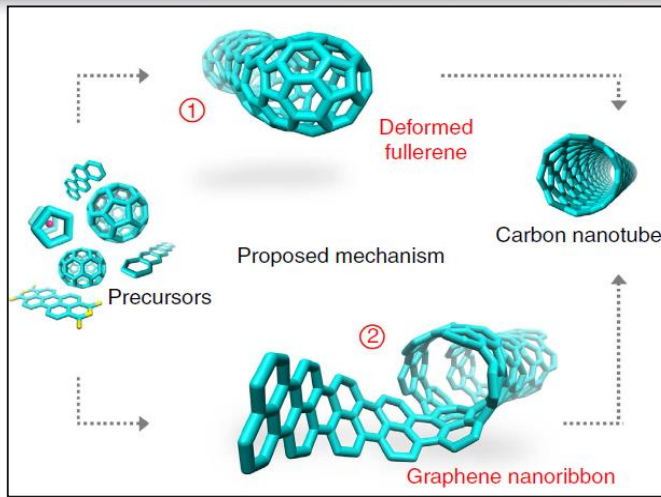
- Variety of intercalant possible
- The Dirac cone of graphene preserved.
- New bands around the Dirac cone, near E_F
- Many new allowed transitions
- Possibility of carrier multiplication



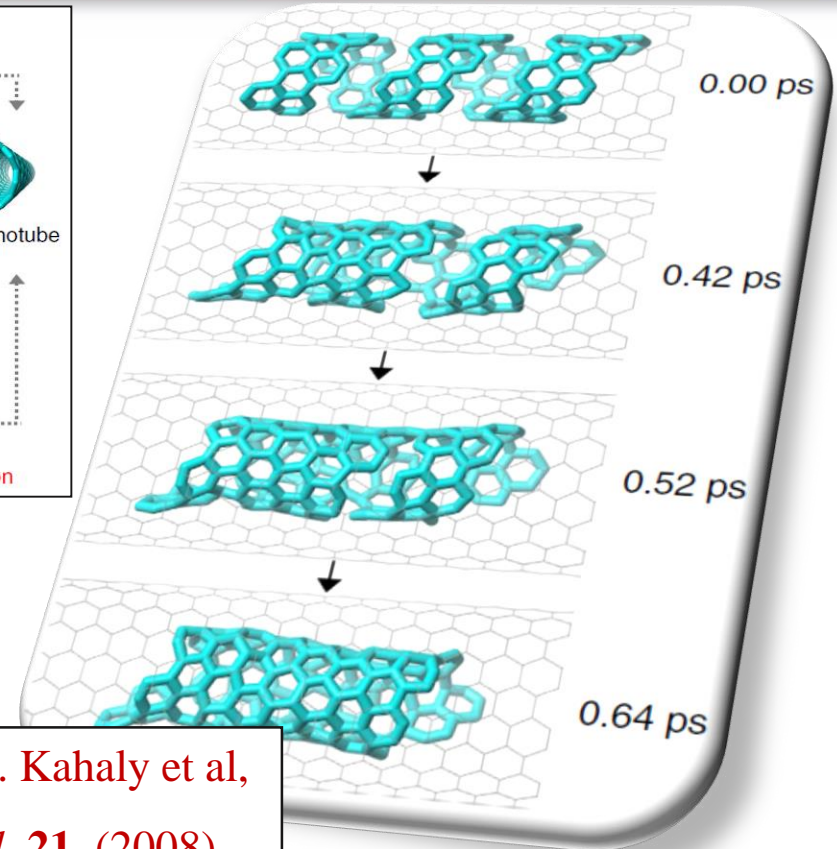
Twisting of graphene ... Defects ... CNT growth



experiment



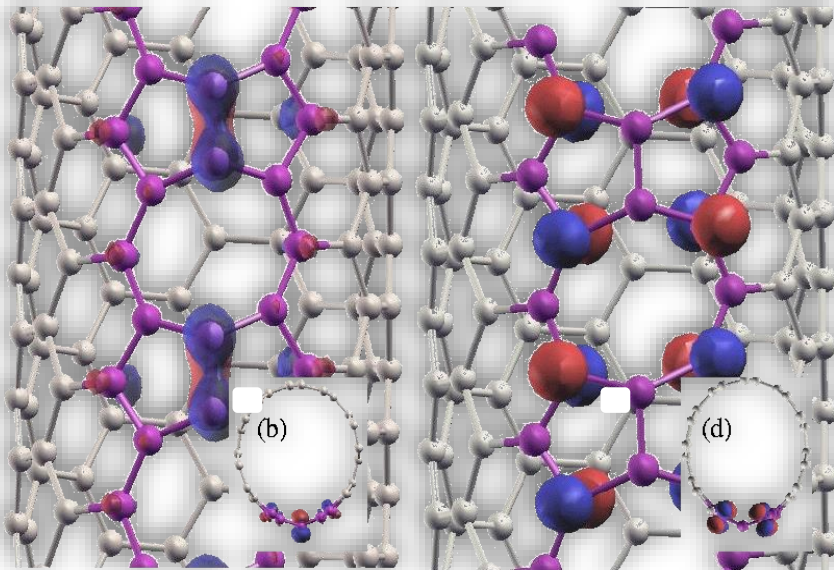
theory



M. U. Kahaly et al,
Small **21**, (2008).

Snapshots of the tube formation process: AIMD simulation

H. Lim et al, *Nature Com.* **4**, (2013).



HOMO: bonding LUMO: anti-bonding

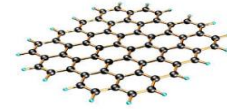
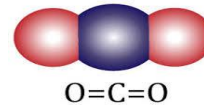
Strong field processes: HHG from TD-DFT



Driver (laser pulse, XUV etc)



Driven system (atoms, molecules, graphene etc)



From static DFT calculation => initial ground state: $\varphi_j(\mathbf{r}, 0)$

TD-DFT

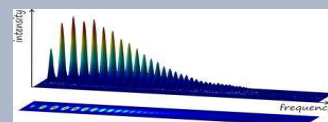
Solve TD KS equations self-consistently => TDKS orbitals:
 $\varphi_j(\mathbf{r}, t) \rightarrow n(\mathbf{r}, t)$

Dipole moment : $d(t) = \int dr \ r n(\mathbf{r}, t)$

Fourier transform

Power spectrum & spectral density : $|d(\omega)|^2$

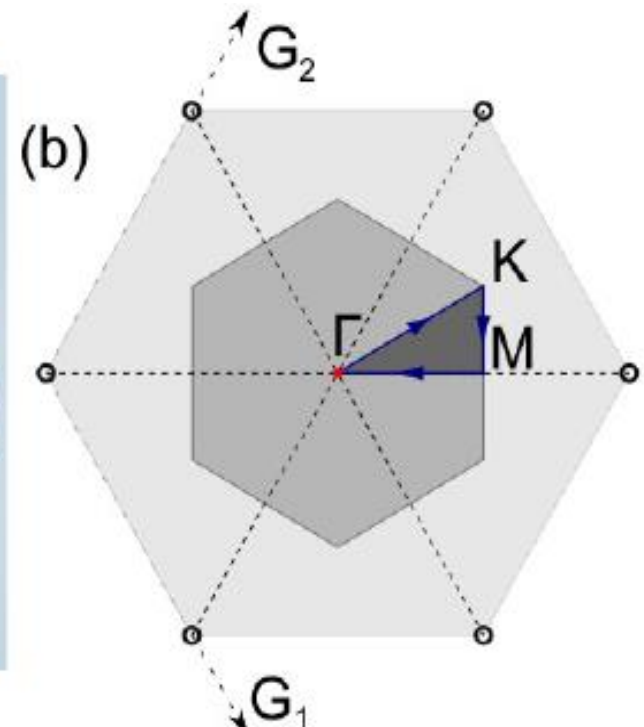
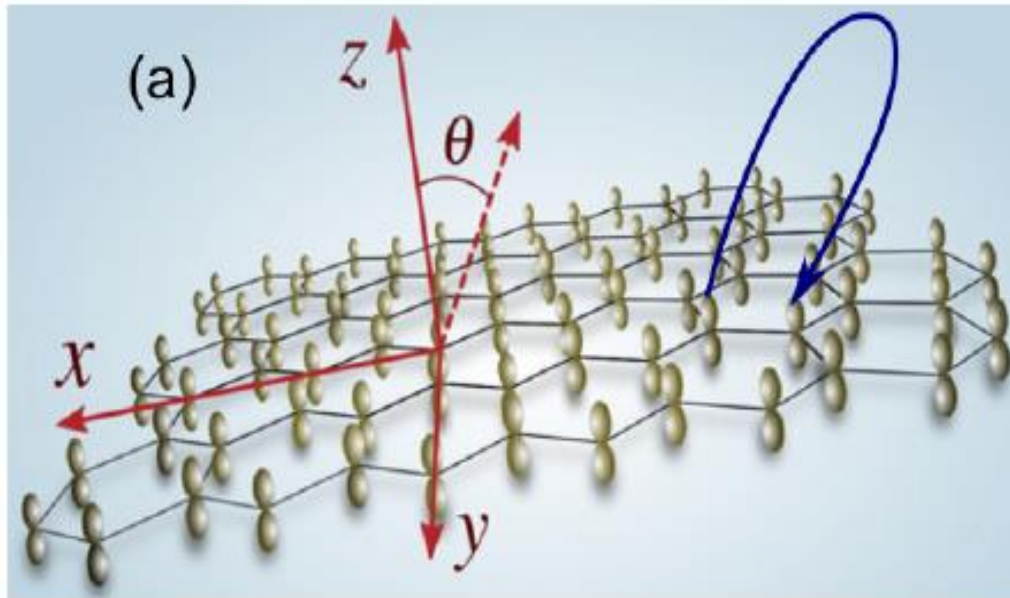
excitation energies,
HHG spectra



Multicentre system (graphene) – extended



- Involves additional multicenter effects because of its in-plane symmetry,
- To take account of the ordered structure of the highest occupied pz-like molecular orbitals



$$\text{ground state wavefunction } \Psi_b(\mathbf{r}) = \langle \mathbf{r} | g \rangle = \frac{1}{\sqrt{N}} \sum_{m=1}^{m=N} \phi(\mathbf{r}_m)$$

$$\phi(\mathbf{r}_m) = z \exp(-\alpha(\mathbf{r} - \mathbf{R}_m)^2)$$

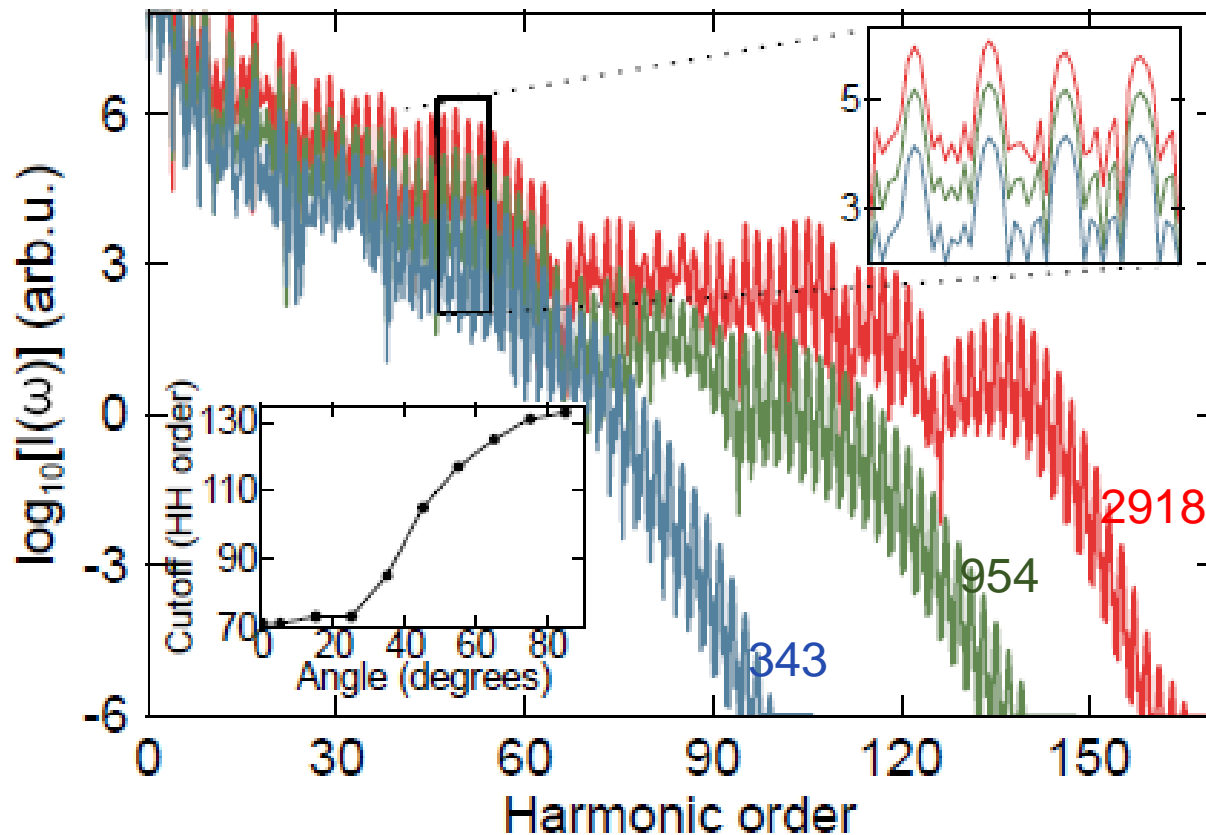
Gaussian type orbitals

HHG power spectrum for circular graphene sheet



$$I(\omega) = \left| \mathbf{n} \cdot \int_{-\infty}^{\infty} dt \mathbf{D}^P(t) \right|^2$$

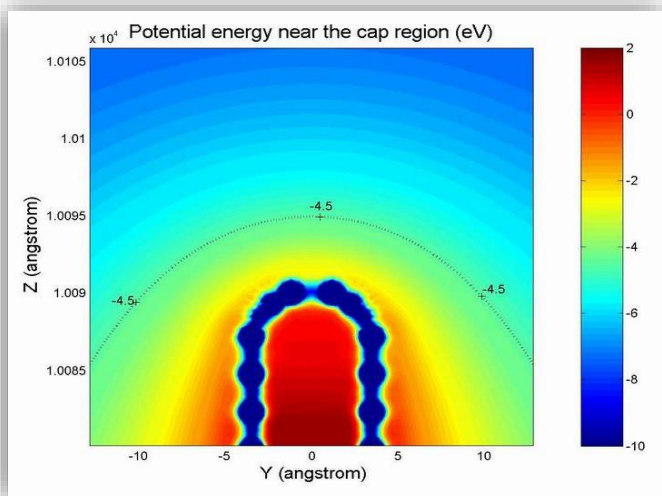
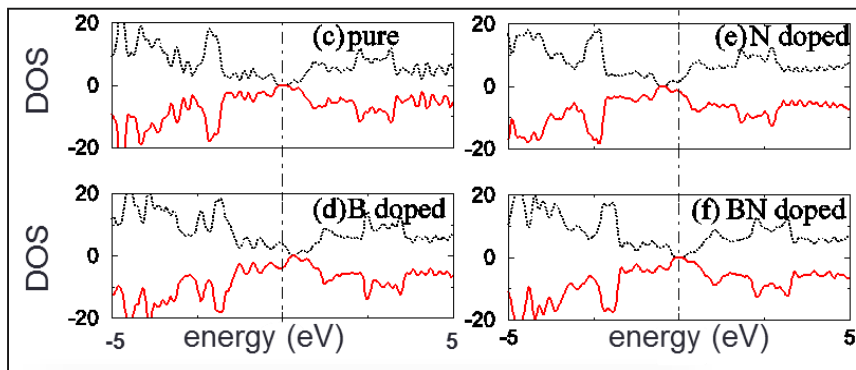
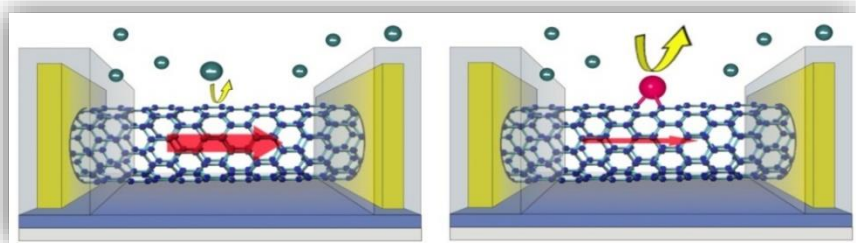
6 cycle, 800 nm laser
Peak intensity = 4.6×10^{14} W/cm²



- ✓ The intensity of the harmonic spectrum reduces with increasing harmonic order.
- ✓ HHG cutoff is sensitive towards the system size.

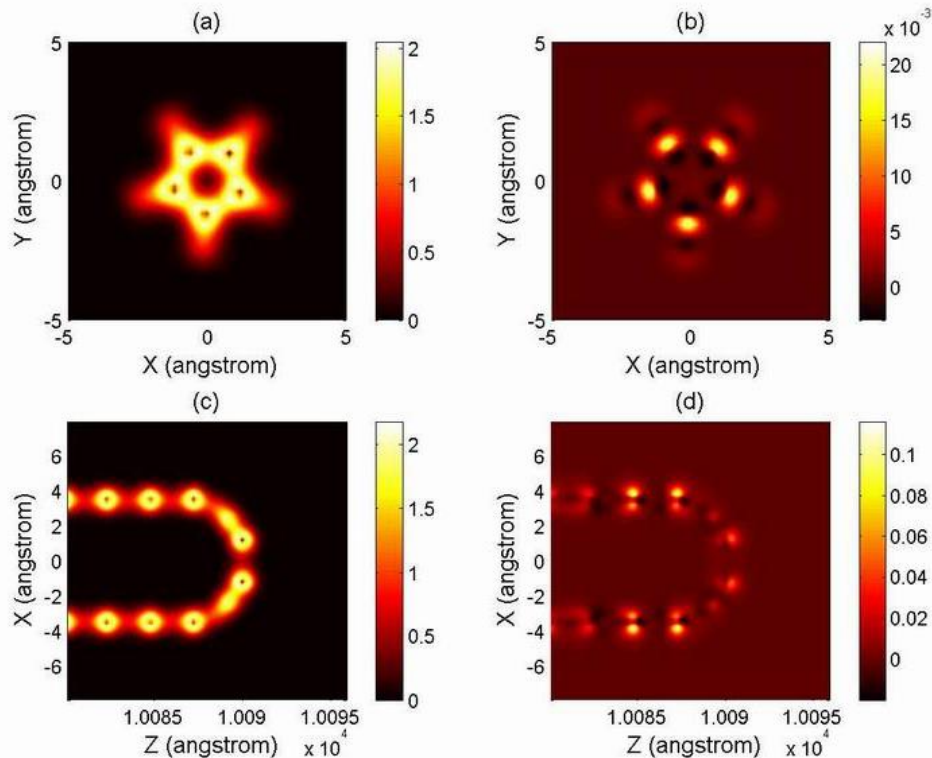
Cut-off harmonic order as a function of polarization angle in case of linearly polarized field : for atoms = 343

Charge modulation & field emission from the tips of CNTs



Experiment

Theory



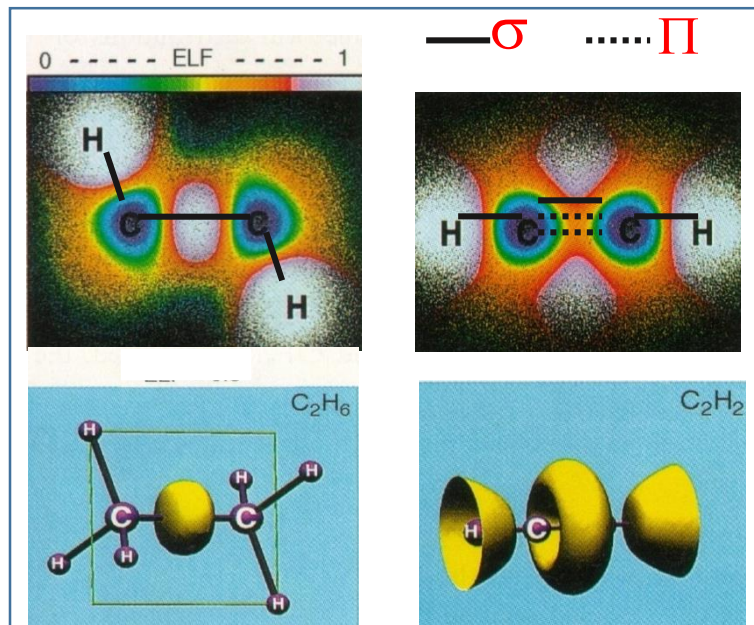
Induced charge distribution ($e/\text{\AA}^3$) of the CNT (a, b) at the tip; (c, d) in a plane bisecting the tube.

Attosecond dynamics in acetylene: from ELF



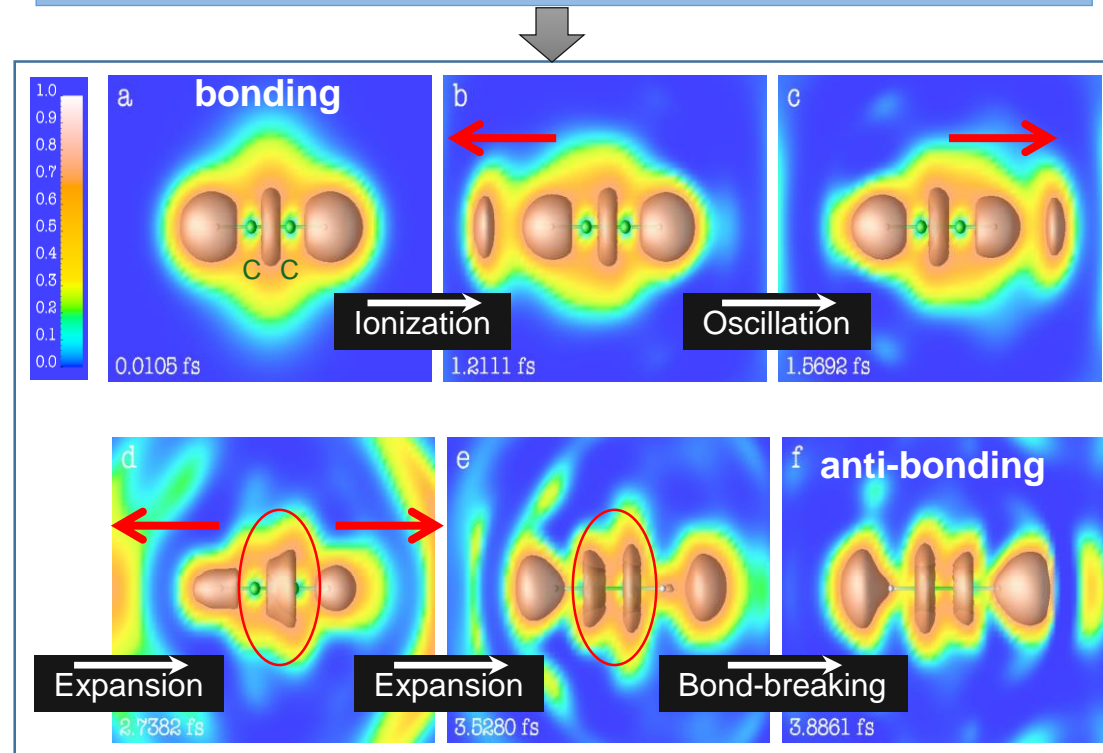
Electron localization function (ELF) : Electron-pair probability

- ❖ Maps localization of electron cloud in a bond in the scale of 0 to 1.
- ❖ ELF=1: perfect localization, =0.5: free electron gas, =0: no electron



Attosecond bond dynamics

Excitation of acetylene; $E \sim 17.15$ eV ($\lambda = 72.3$ nm),
 $\tau \sim 7$ fs, $I \sim 1.2 \times 10^{14}$ Wcm $^{-2}$ (XUV pulse)

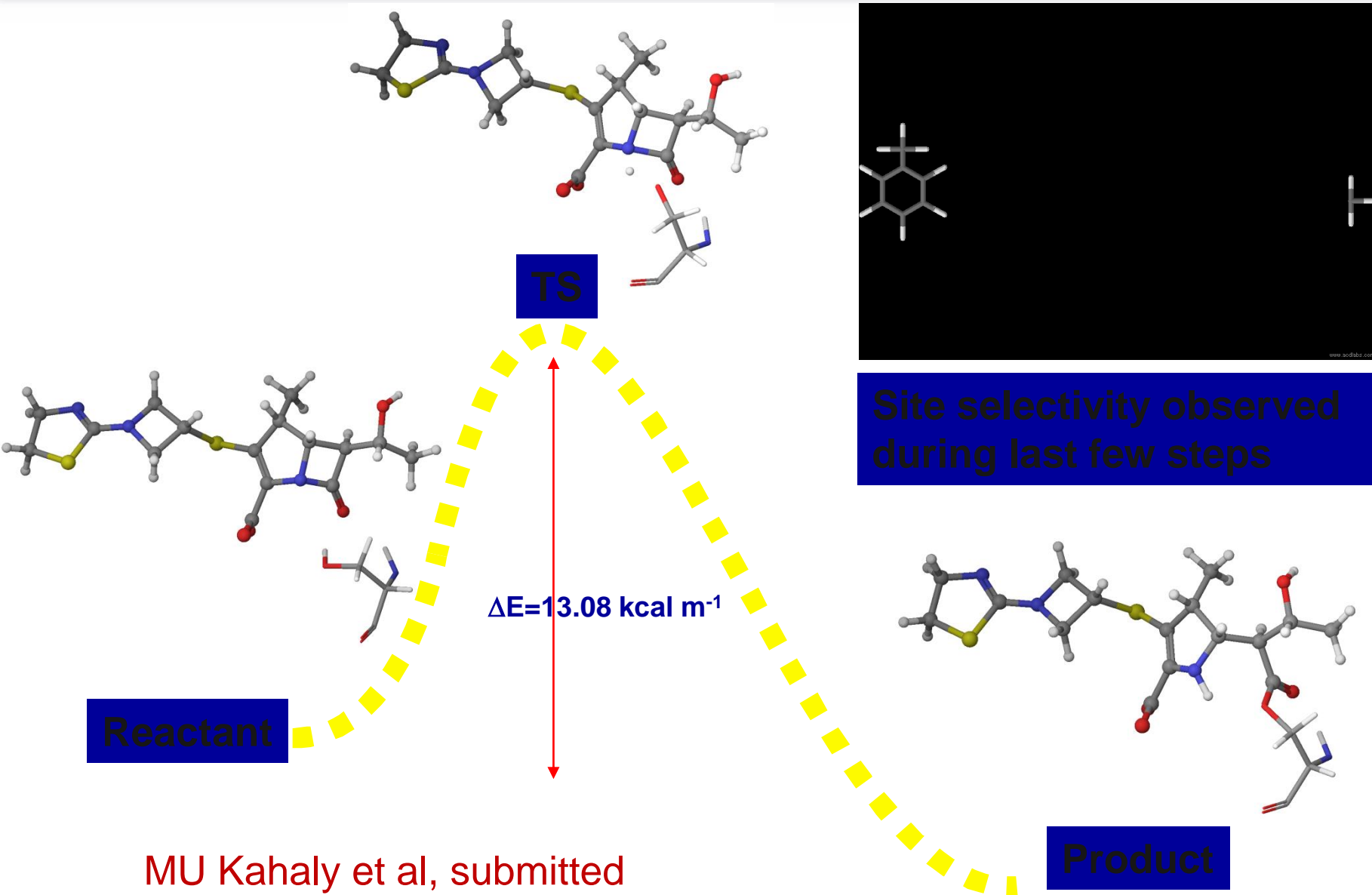


M. U. Kahaly, *J. Phys. Chem. A* **111** (2007)

T. Burnus et al, *Phys. Rev A* **71** (R) (2009)

A. Castro et al, *Phys Stat. Solidi.* **243** (2006)

Acylation of antibiotic: tune the transition barrier



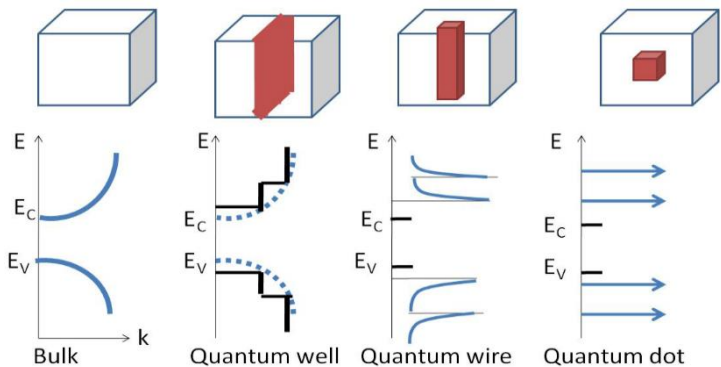
MU Kahaly et al, submitted

Summary

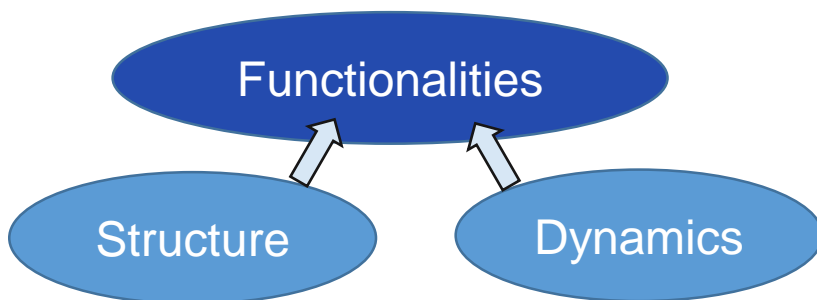
Materials applications: tuned and controlled using laser field



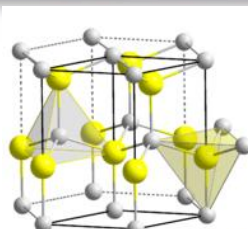
Densities of states



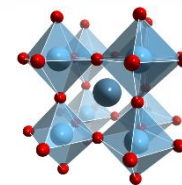
- Reduced dimensions
- Size effects
- DOS : tunable with laser field



3D

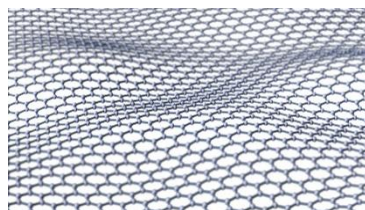


GaN



Perovskites

2D

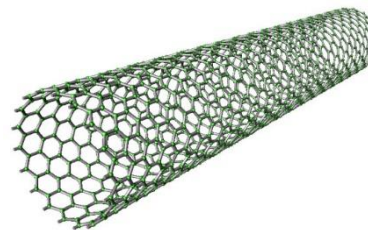


Graphene

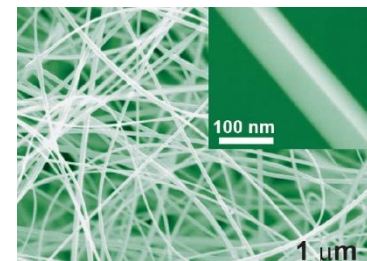


Films and coats

1D

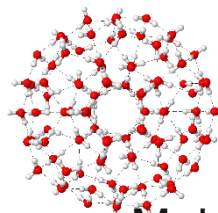


Nanotubes

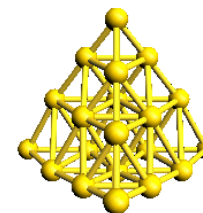
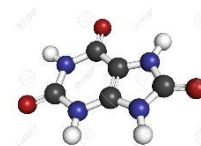


Nanowires

0D

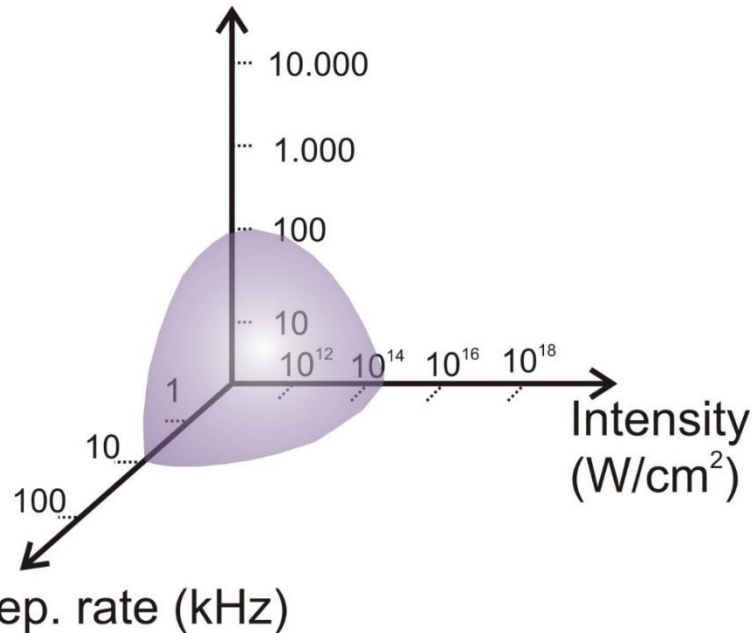


Molecules

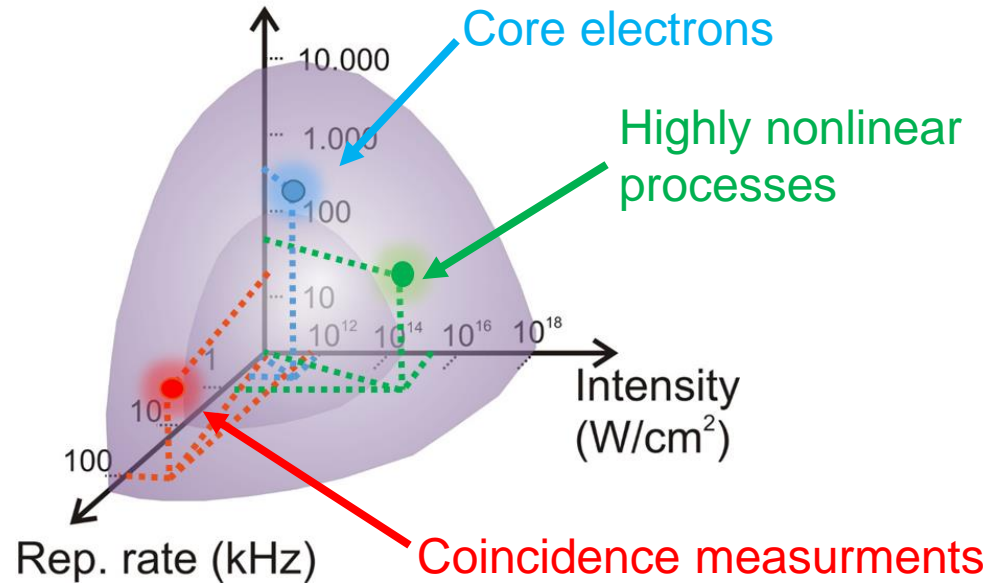


Clusters

Photon energy (eV)



Photon energy (eV)



- 1) Generation of XUV/X-ray femto- and attosecond pulses
 → Attosecond scale of electron dynamics in atoms, molecules, plasmas and solids

ATTOSECOND Beamlines & User Facility

- 2) New direction in attoscience: Advancement of laser science and technology

Acknowledgement



Sai



Kalyani



Jewel (post doc, till 2018)



MAX-PLANCK-GESELLSCHAFT





**THANK YOU
FOR YOUR
ATTENTION!**

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