ELI-ALPS Research Institute
TOWARDS THE SHARP END OF ATTOSCIENCE

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Ultrafast function-property-structure relationship in materials: insights from simulation.

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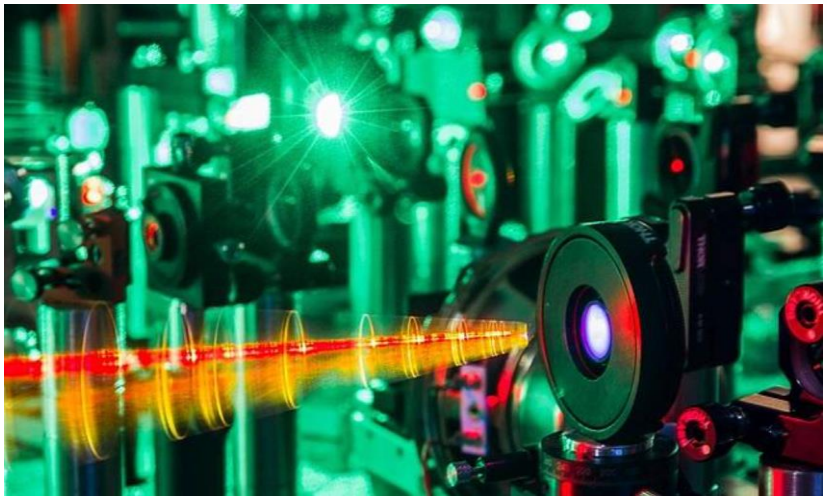
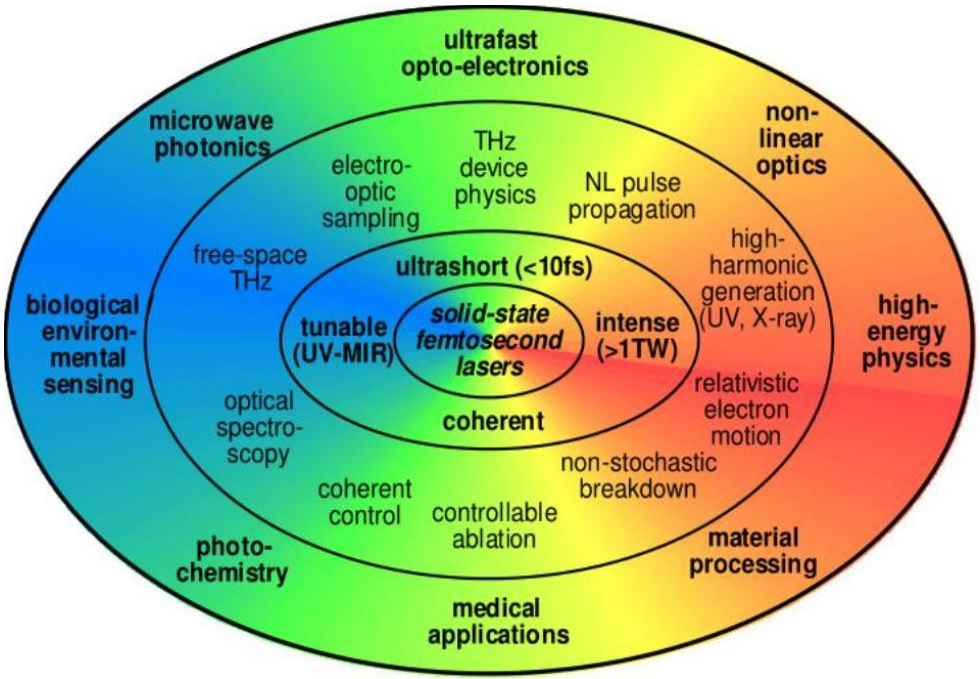
Laser technology:: billion dollars investments ☺



- Advanced experiments on atomic to molecular to solid targets
- Multidisciplinary user applications in imaging, chemistry, photophysics, radiotherapy etc….
- However one experiment == an user campaign.
- Need to understand how the setup works…. To design and device the setup…..
- *Several weeks of operation for smooth service*.

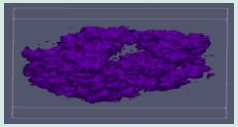


- Remember the cost! ☺
- Much training needed to operate.
- Difficult to get beam-time for experiments.
- Pre-check: which material is best to probe for certain application?.... **Simulations!**

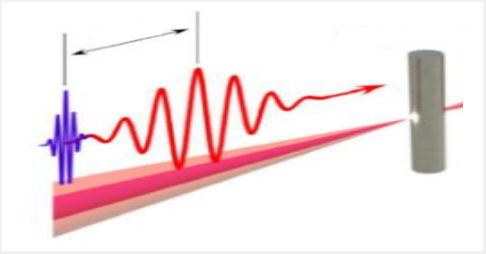
Connecting *macro* to *micro*…..

Sample

- **Material structure**:
  - From experimental data
  - From ab-inito calculations
- **Material properties, parameters**:
  - Structure factor (from literature. or from ab-inito charge density)
  - Electron density, potential
  - …



Material database



Source

Photon:
- Raytracing
- Wavefront (simulated / exp.)

Neutron:
- Raytracing

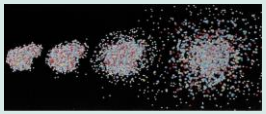
Propagation

- Raytracing
- BPM:
  - FFT
  - Finite Difference
  - Finite Time

Instrument database

Interaction

- TDDFT
- Particle-In-Cell
- Radiation hydrodynamics



Signal detection and processing

- Detector properties, noise…
- Unified data format following FAIR norms

FAIR Database of experiments

https://www.panosc.eu/all-use-cases/

Images:
Neutze, R. et. al., Nature 406, 752–757 (2000).
Ekeberg, T. et al. Physical review letters 114, 098102 (2015).

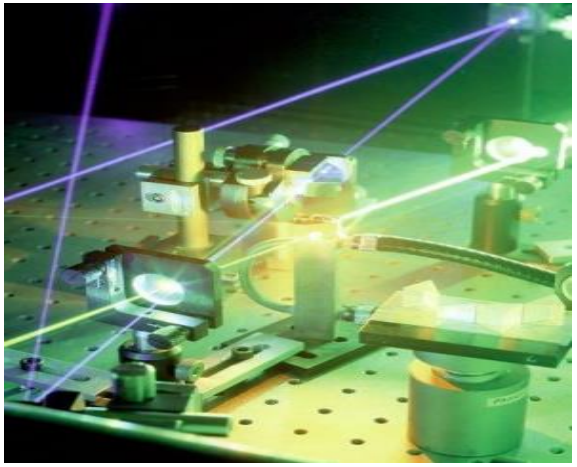
Yoon, C. H. et al. Scientific Reports 6, 24791 (2016).
Fortmann-Grote, C. et al. IUCrJ 4, 560–568 (2017).
Li, J., Lu, J., Chew, A. et al., Nat Commun 11, 2748 (2020).

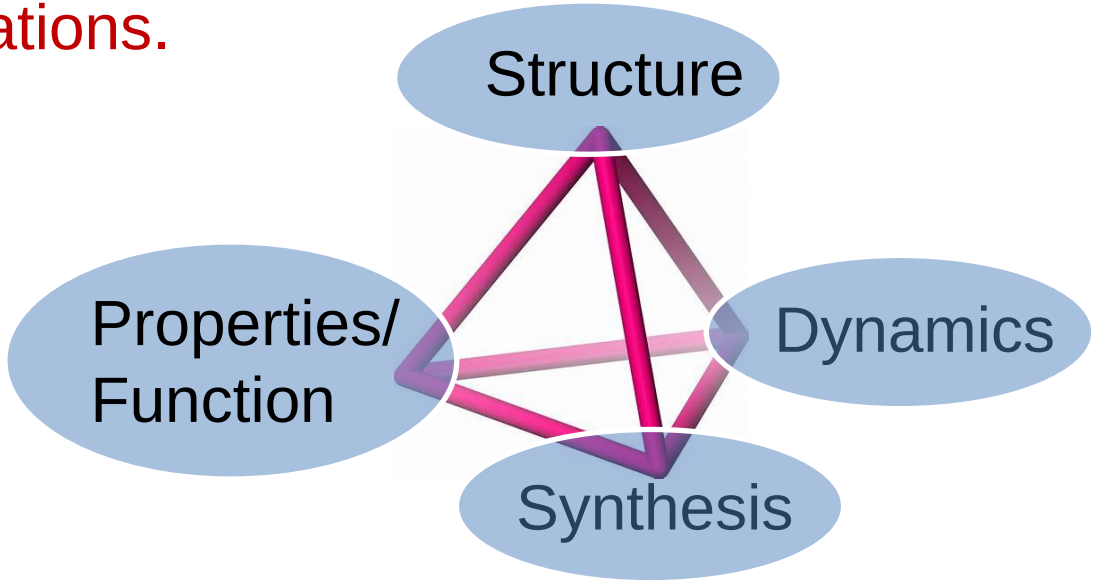
IMPULSE

Outline

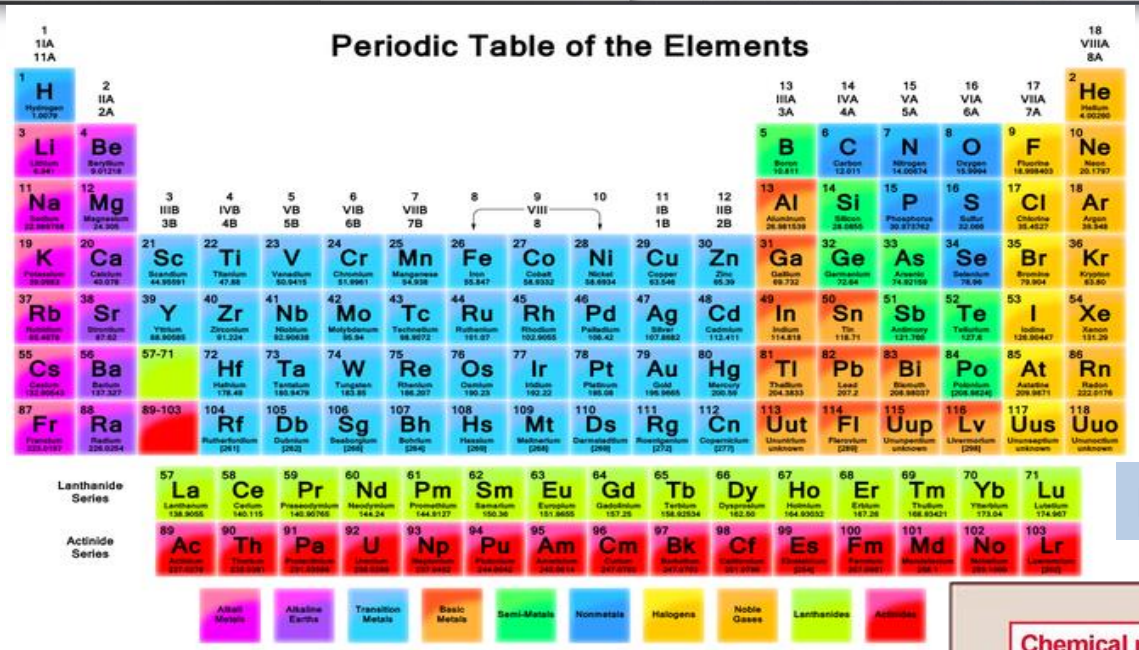
- Material – role of structure, size
- Electronic structures of a material
- How to track structure, ultrafast dynamics?
- How to engineer materials properties?

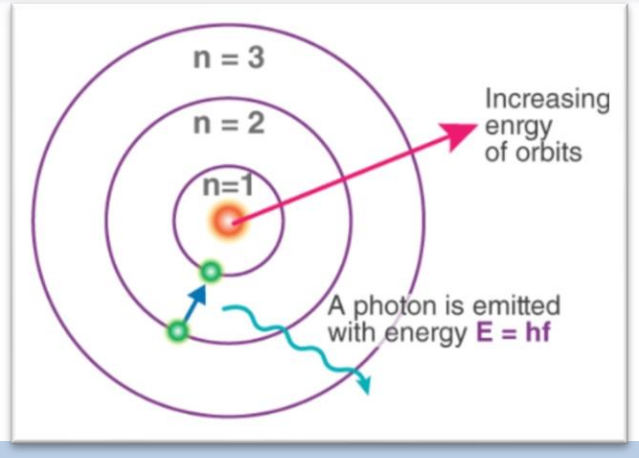
- Probing materials with laser…
- Few examples of applications.



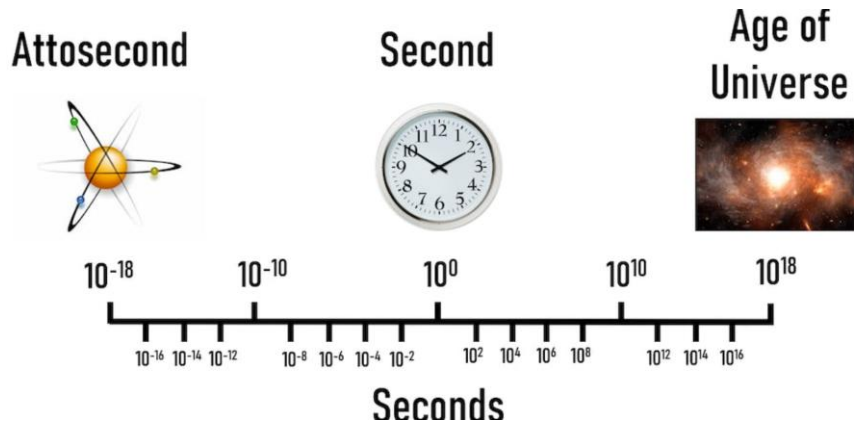


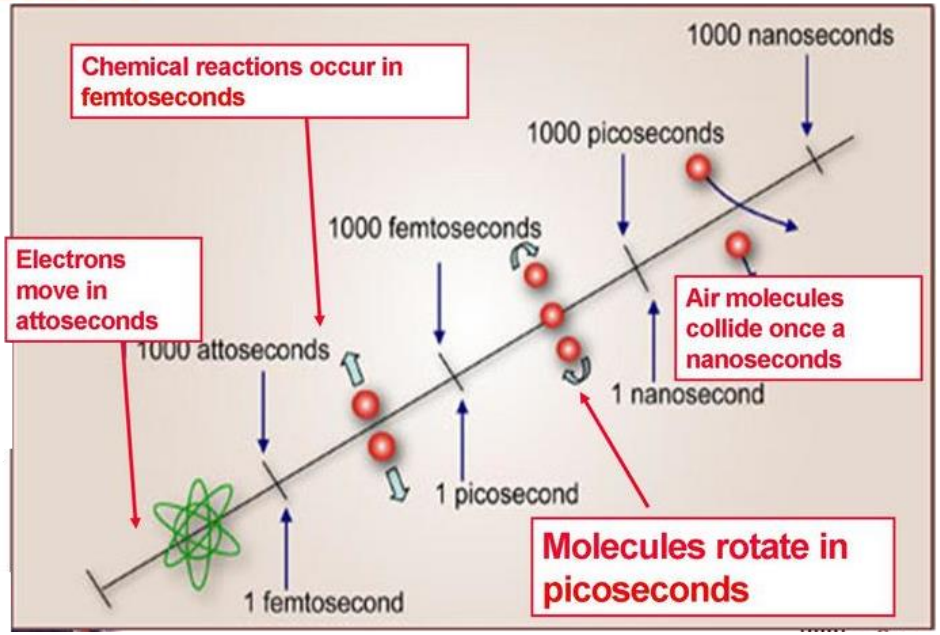
Materials…. And dynamics…..



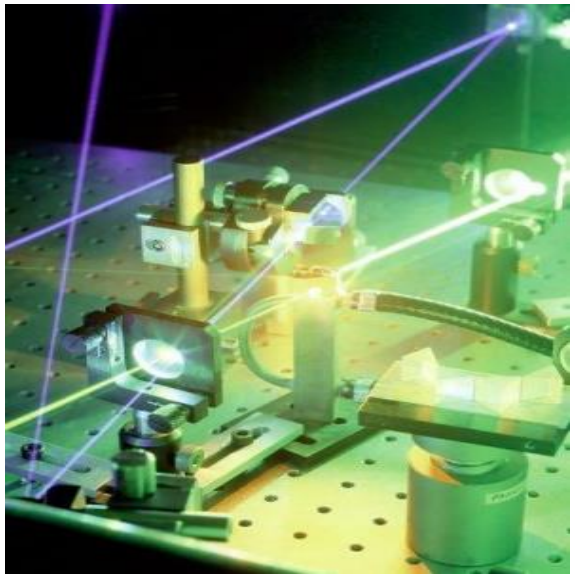


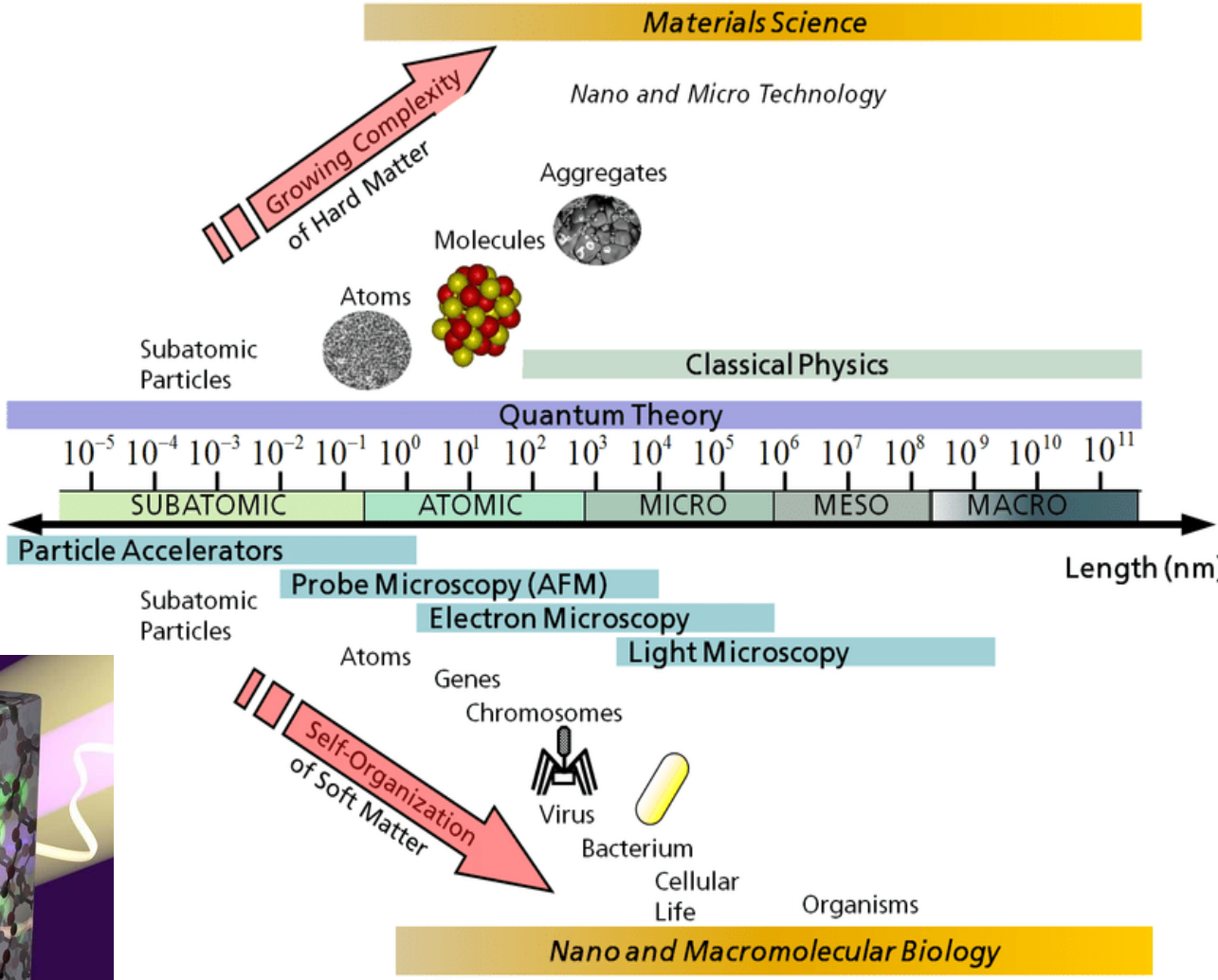
Period of first Bohr orbit : 150.10^{-18}s

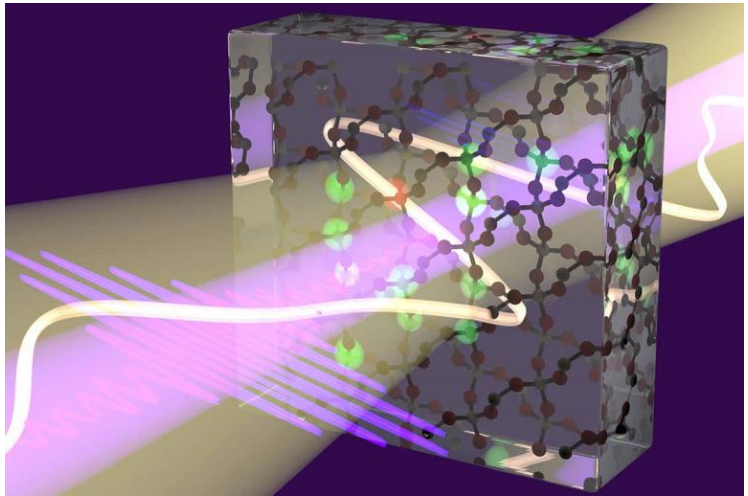




How to probe….. and what to capture?

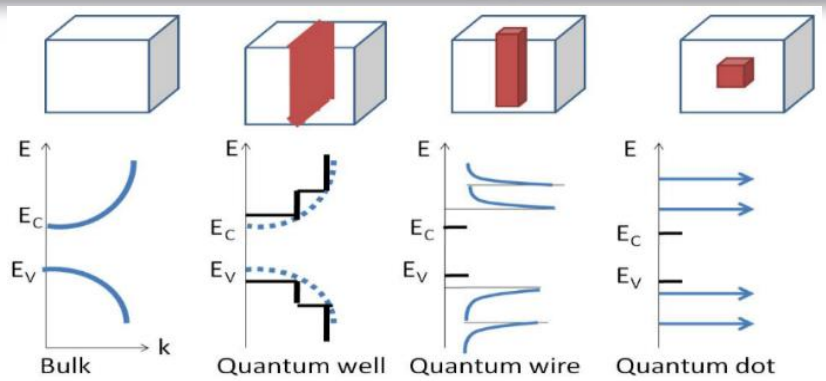




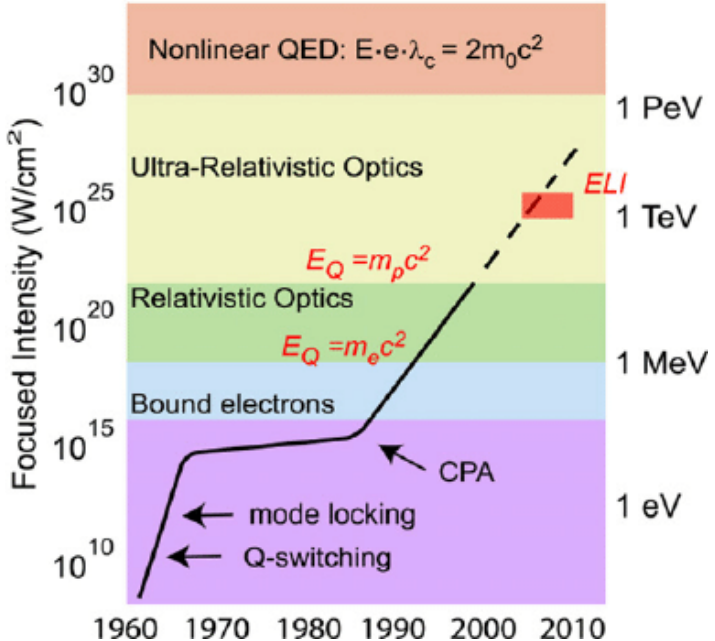


To examine electrons? we must take “pictures” at the ultrafast resolution…

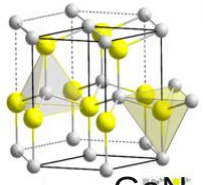
Materials with different dimension…



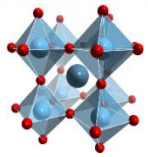
- Reduced dimensions
- Size effects
- DOS : tunable with laser field



3D

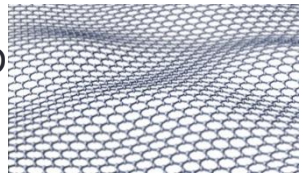


GaN



Perovskites

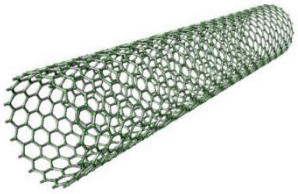
2D



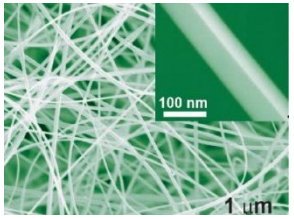
Graphene

Films and coats

1D

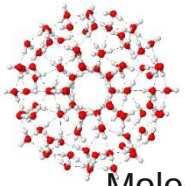


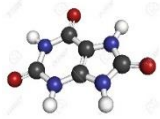
Nanotubes



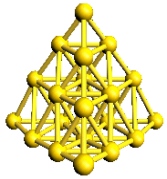
Nanowires

0D





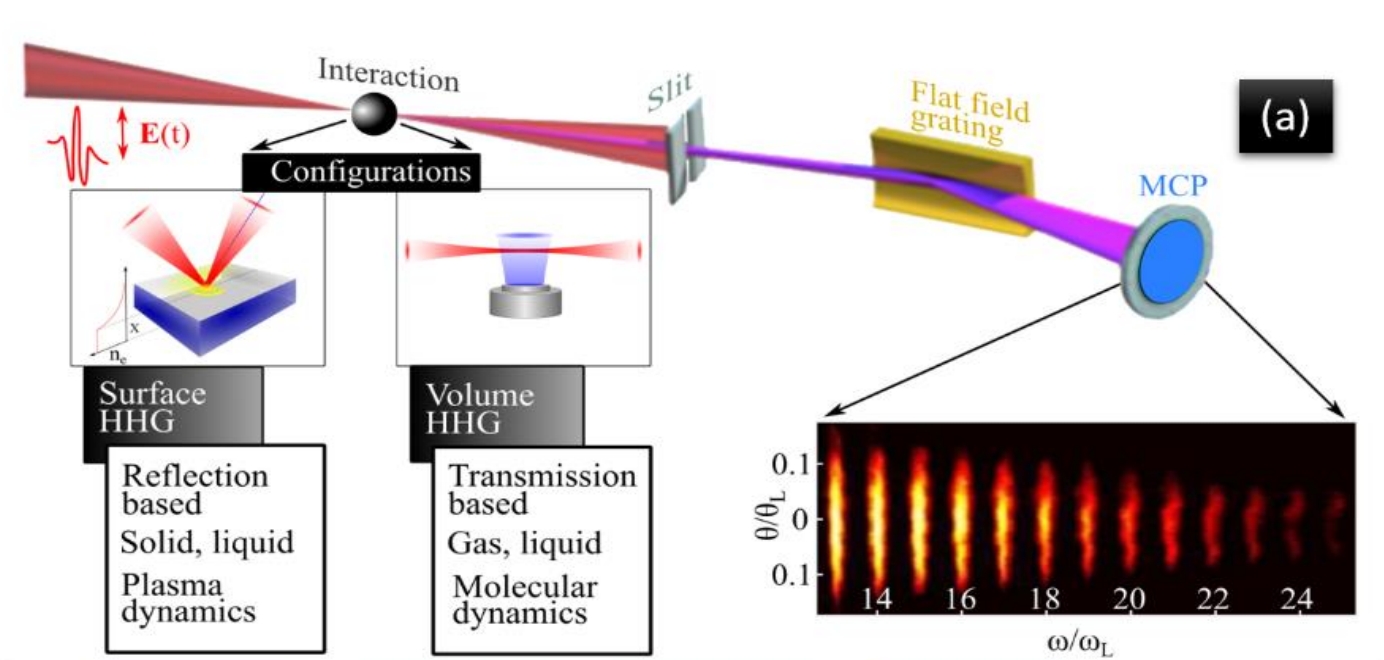
Molecules

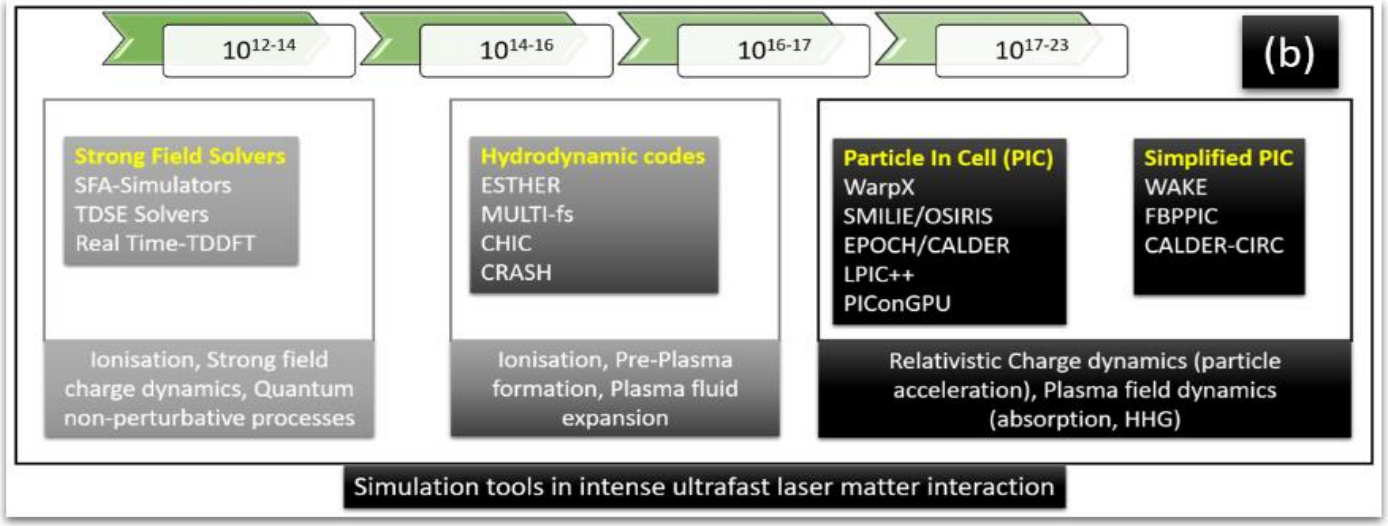


Clusters

- ❖ Control and trace the motion of atoms in molecules Femto
- ❖ Control chemical reactions Control & trace electrons inside atoms & molecules Atto

Simulation tools for different laser-matter interaction

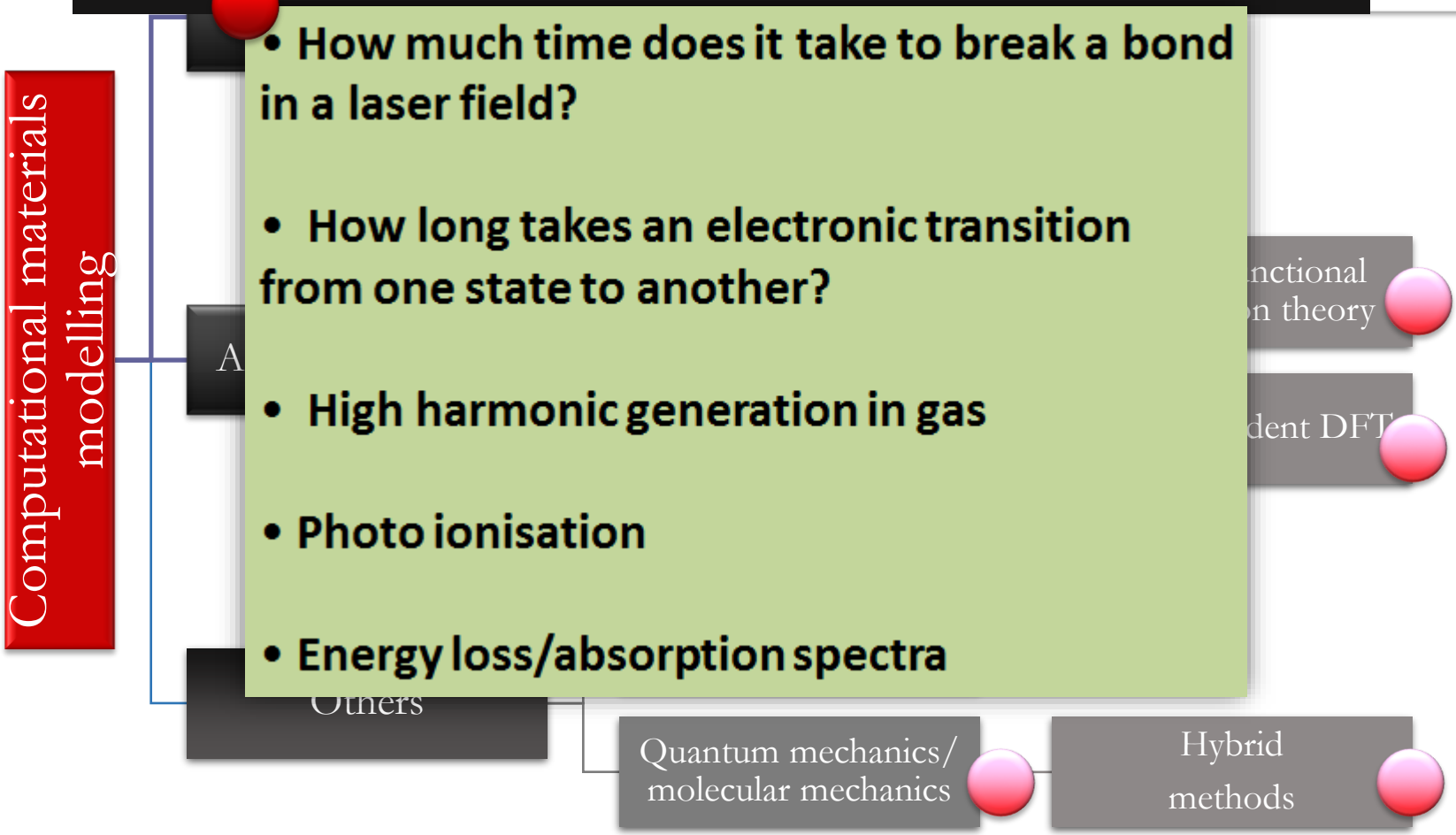




Courtesy:
S. Kahaly

Simulation tools for materials (apart from plasma)

"Time-dependent density functional theory (TDDFT) can be viewed as an exact reformulation of time-dependent quantum mechanics, where the fundamental variable is no longer the many-body wave-function but the density."



First-principles approach

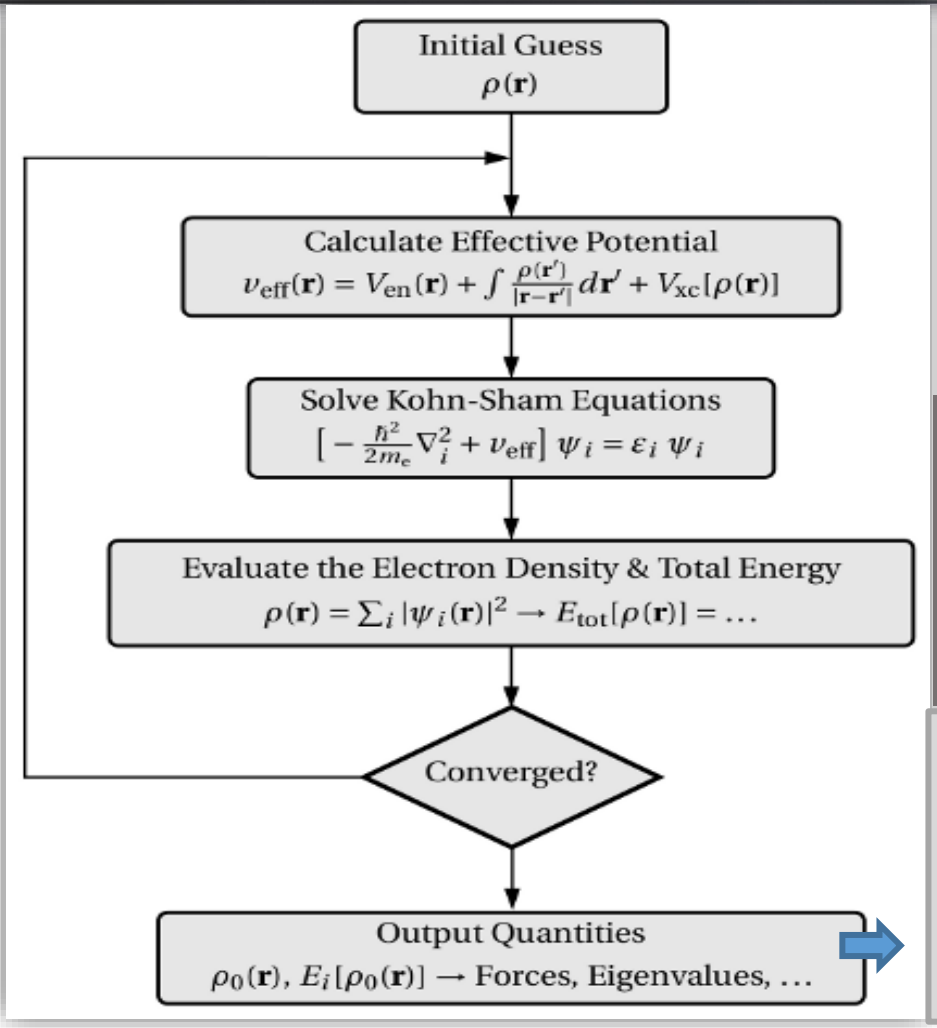
Density Functional Theory(DFT): W. Kohn, Nobel prize Chemistry, 1999

$$n(\mathrm{r}) \Leftrightarrow V(\mathrm{r})$$

DFT

TDDFT

$$n(\mathrm{r},t) \Leftrightarrow V(\mathrm{r},t)$$



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

TDDFT for excited state properties and dynamics.

fundamental variable is the many-body charge density.

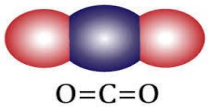
- ➢ Structure, energetics….
- ➢ Cheap, virtual experiment

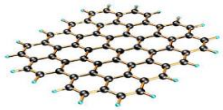
TDDFT : gives time-dependent observables.
An universal approach for electron dynamics.

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:

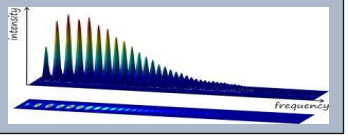
$$\varphi_j(\mathbf{r},t) \rightarrow n(\mathbf{r},t)$$

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

Fourier transform

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

excitation energies, HHG spectra



An atomic case: Ar

External field in the form of a vector potential:

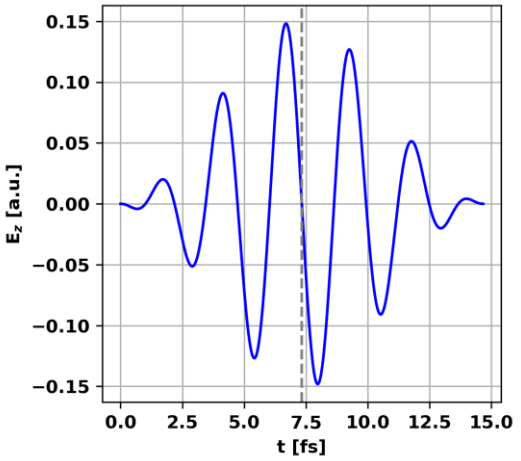
$$A(t) = -E_0 * \frac{c}{\omega} \cos\left(\omega(t - \frac{\tau}{2}) + \phi\right) \sin\left(\frac{\pi t}{\tau}\right)^2,$$

$$E_0 = \sqrt{\frac{I_0}{3.51 * 10^{16}}}, \text{in atomic units,}$$

$$E(t) = -\frac{1}{c}\frac{\partial A(t)}{\partial t}$$

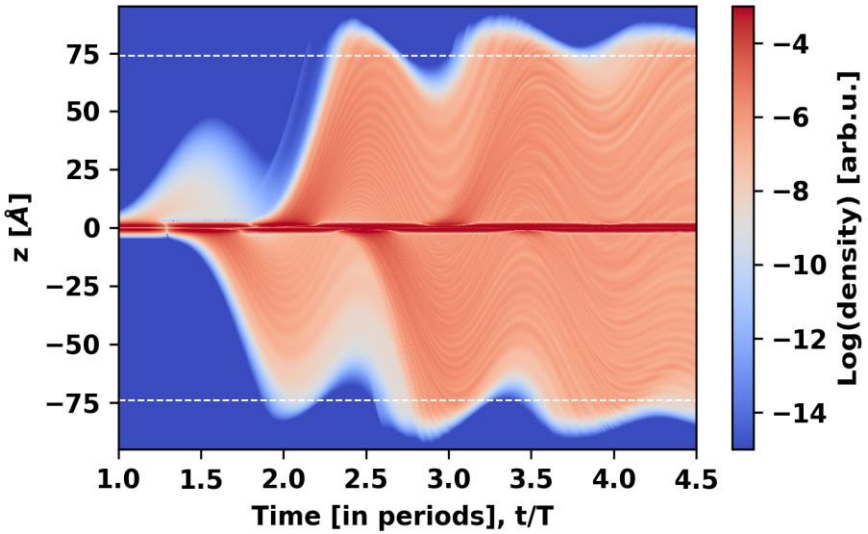
Parameter	Value
Intensity (I_0)	$8*10^{14}$ W/cm^2
wavelength	800 nm
Pulse duration 'τ' in terms of FWHM of intensity 'τ_p'	$\tau=\tau_p\pi/(2\arccos(2^{-1/4}))$; Where τ_p=5.34 fs
Laser polarization direction (along z)	[0,0,1]
CEP (ϕ)	0
Simulation box	Parallelepiped: x:50 bohr, y:50 bohr, z:360 bohr

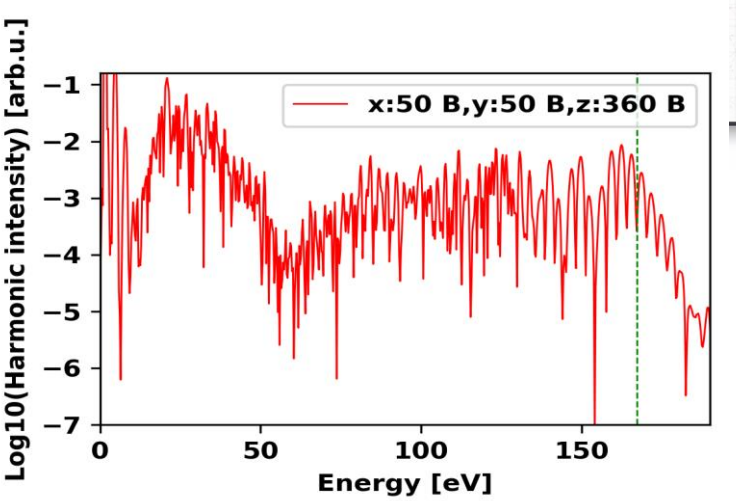
Also in **Hands-on activities**

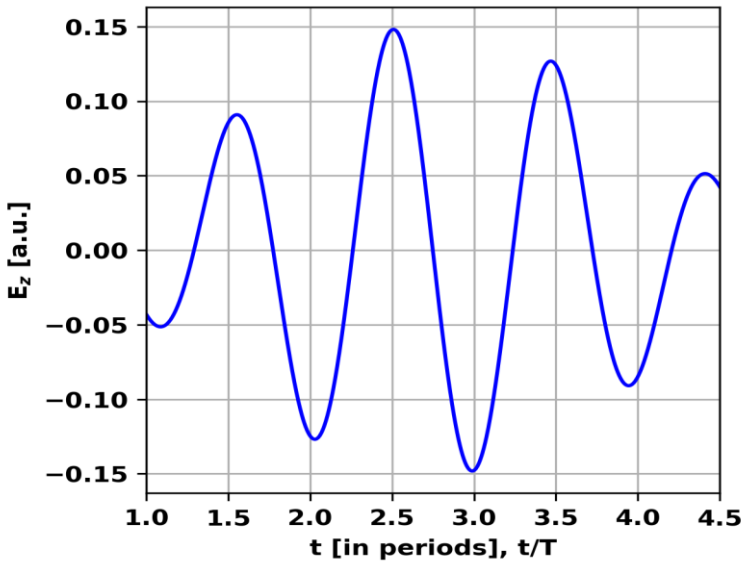


- Electric field
- Pulse duration is represented by dashed vertical line

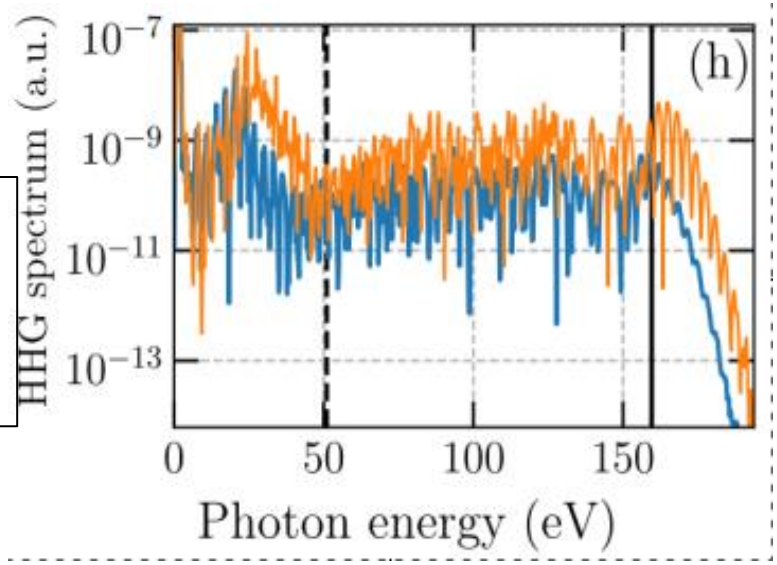
HHG from Ar





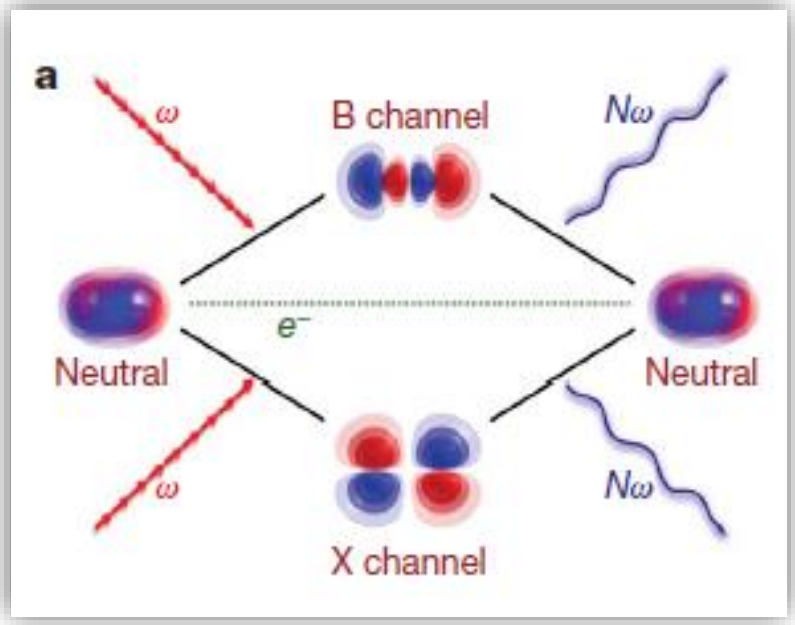


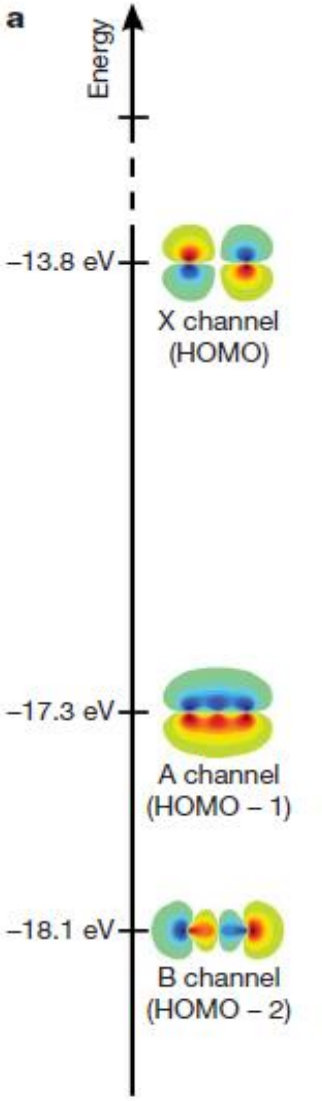
Compare with the orange curve

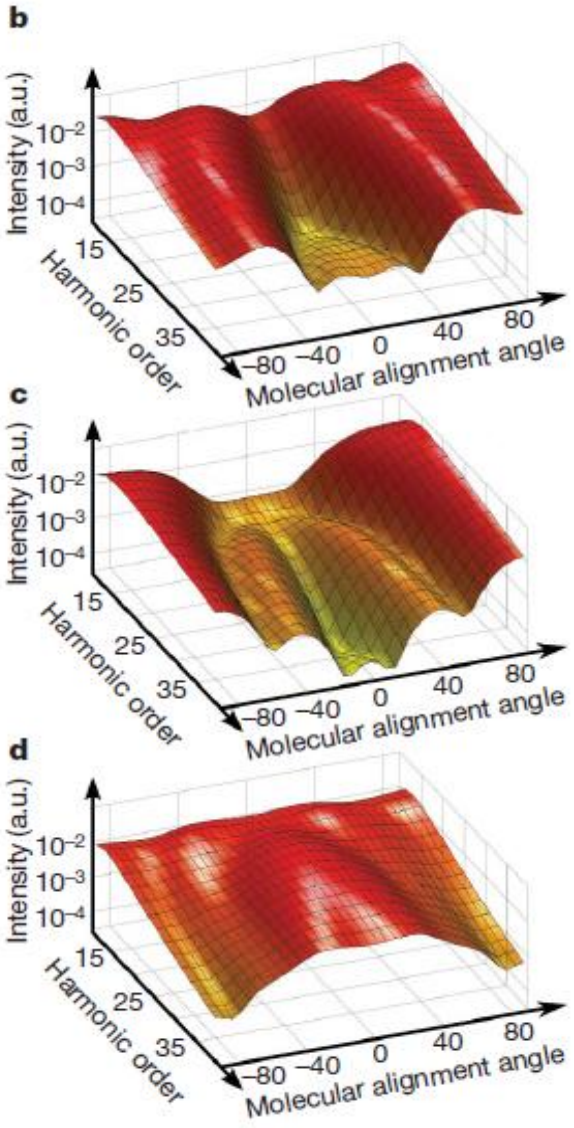


[1] Influence of the polarization of a multielectron atom in a strong laser field on high-order harmonic generation, Romanov et al., PRA, 101, 2020.

Molecule: High harmonic interferrometry & multi-electron dynamics of CO_2





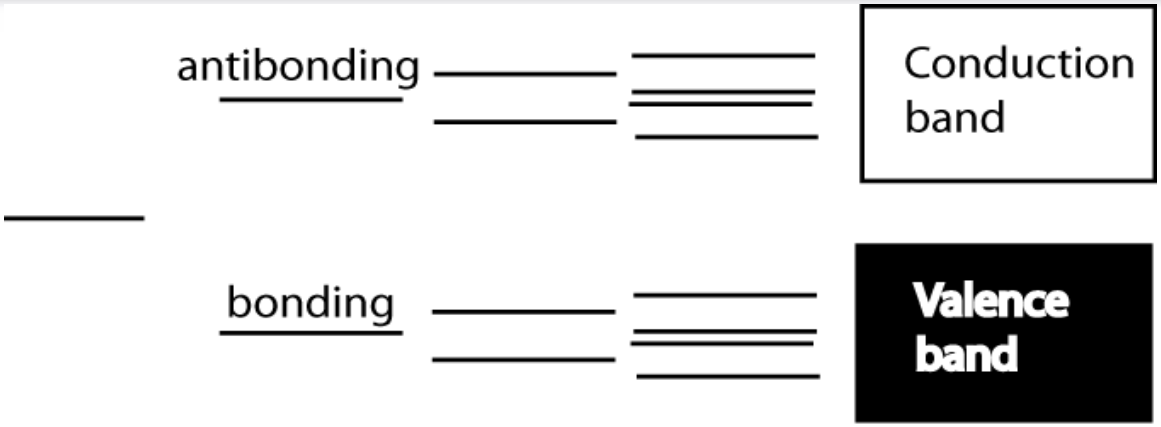


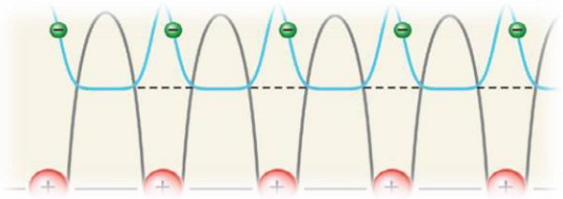
Different molecular orbitals (note their different symmetries) contributing to the harmonic emission

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).

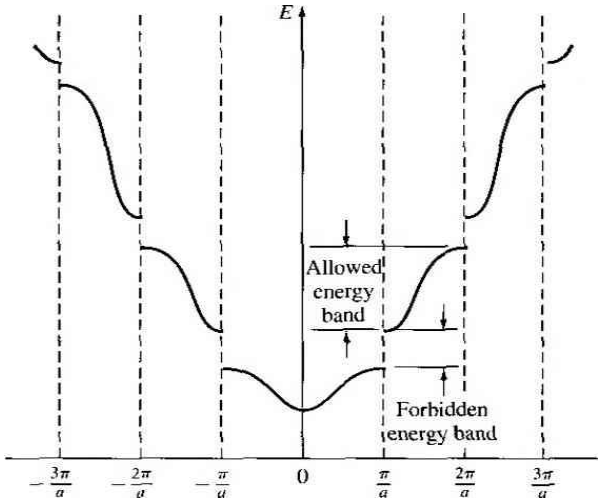
Change of properties as a function of cluster size





$$\Psi_{n,k}(r + R) = e^{ik \cdot R} \Psi_{n,k}(r)$$

$$E_n(k + G) = E_n(k)$$



Periodic solids => bands

Instead of having discrete energies as in the case of free atoms, the available energy states form bands

Band gap = separation of bonding and antibonding states

Electron effective mass in crystal…. Conductivity…

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

Why?

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

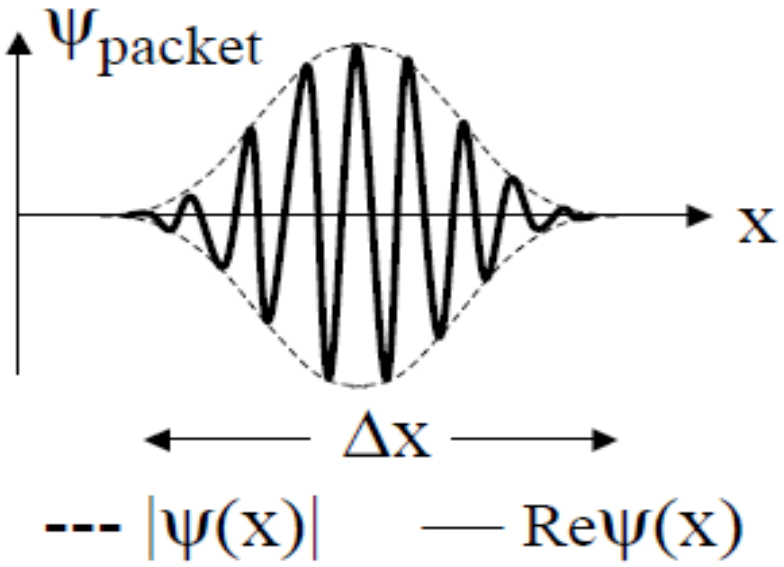
Free electron momentum

Effective potential in solid

Effective velocity of the particle

= phase velocity of the wave packet

$$v_g = \frac{dE}{dp} = \frac{1}{\hbar}\frac{dE}{dk}$$

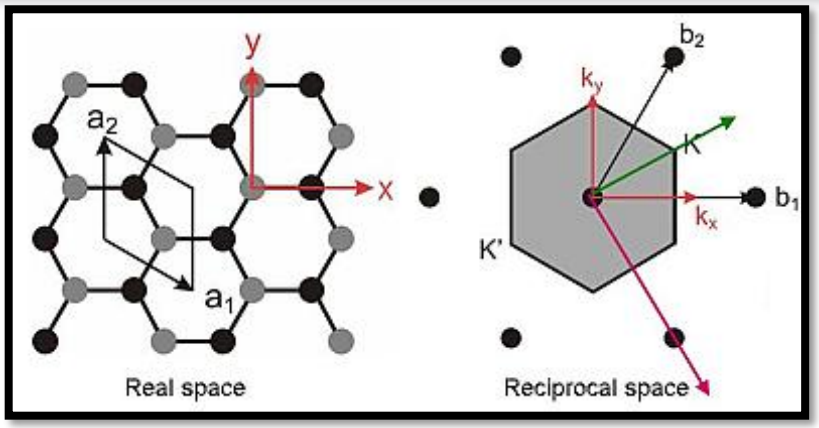


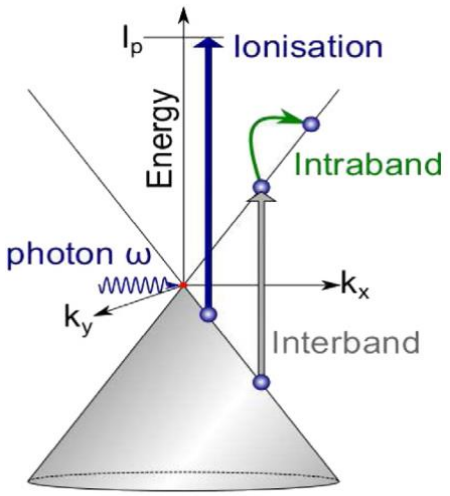
$$F = m* \cdot \frac{dv_g}{dt}$$

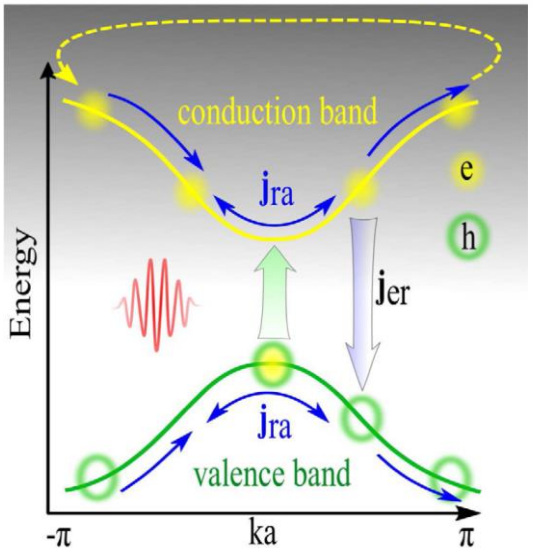
effective mass

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

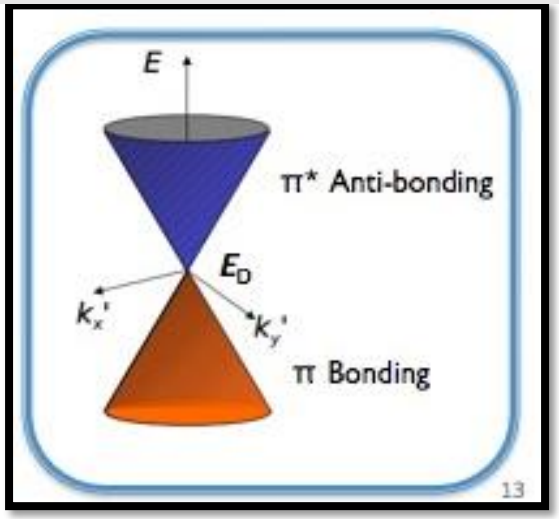
Pristine graphene

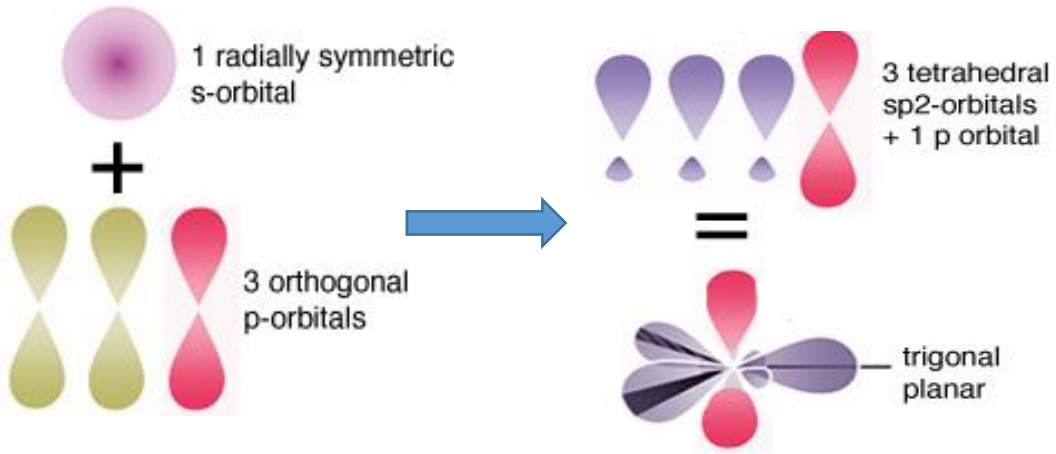






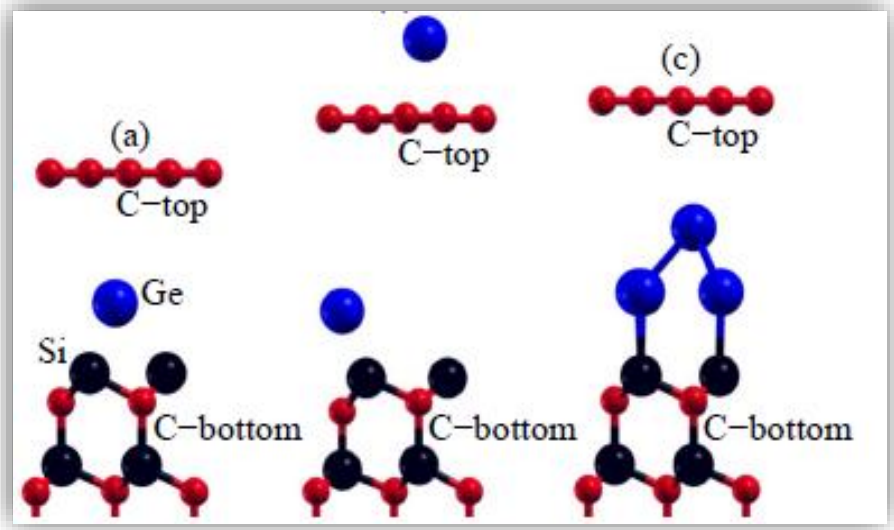
- Massless Dirac Fermion
- Very high mobility, conductivity
- Extreme tunability





MU Kahaly et al, *Chem. Phys. Lett*. **578** (2013), *Eur. Phys. Lett*. **99** (2012)

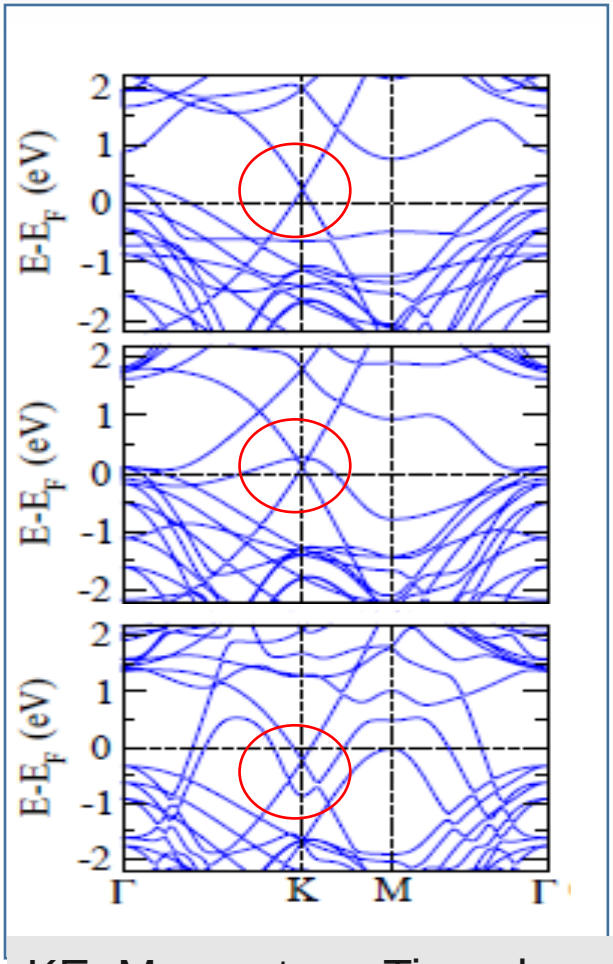
Intercalated graphene



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

MU Kahaly et al, *Eur. Phys. Lett*. **99** (2015)

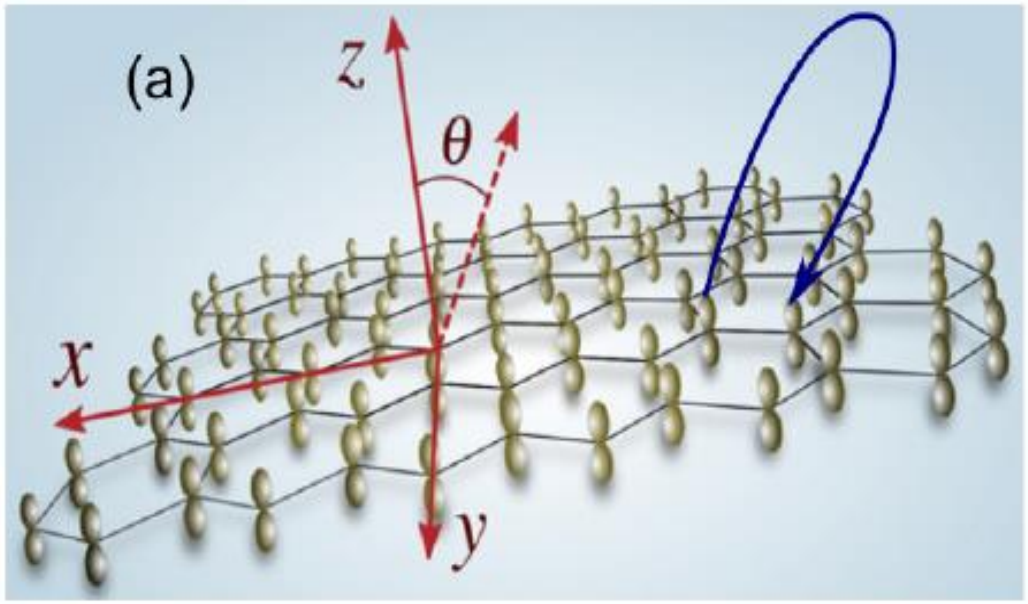


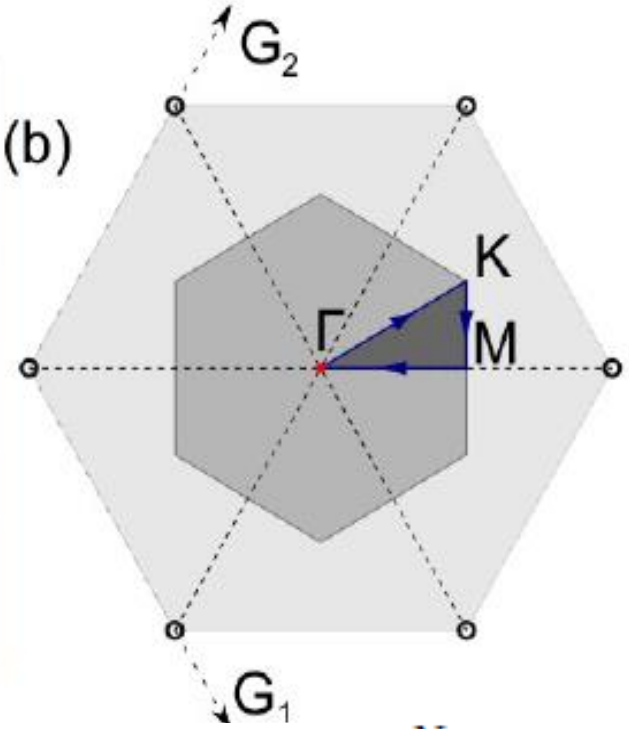
KE, Momentum, Time dependence

2D mapping: Useful for spectroscopy

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





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

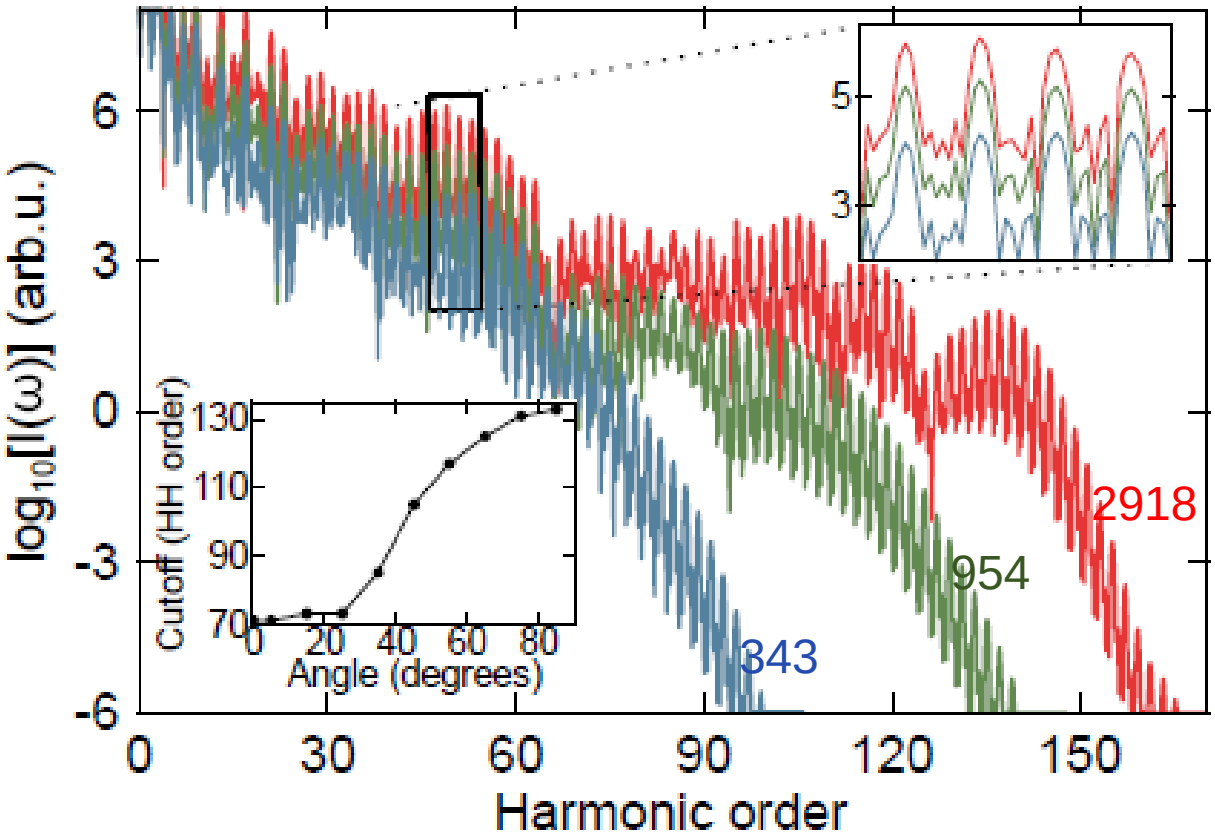
$$\phi(\mathbf{r}_m) = z\exp(-\alpha(\mathbf{r}-\mathbf{R}_m)^2)$$

Gaussian type orbitals

Sorngard et al, J. *Phys. B* (2015)

HHG power spectrum for circular graphene sheet

$$I(\omega) = |\mathbf{n}.\int_{-\infty}^{\infty} \mathrm{d}\, t\mathbf{D}^{\mathbf{P}}(t)|^2$$

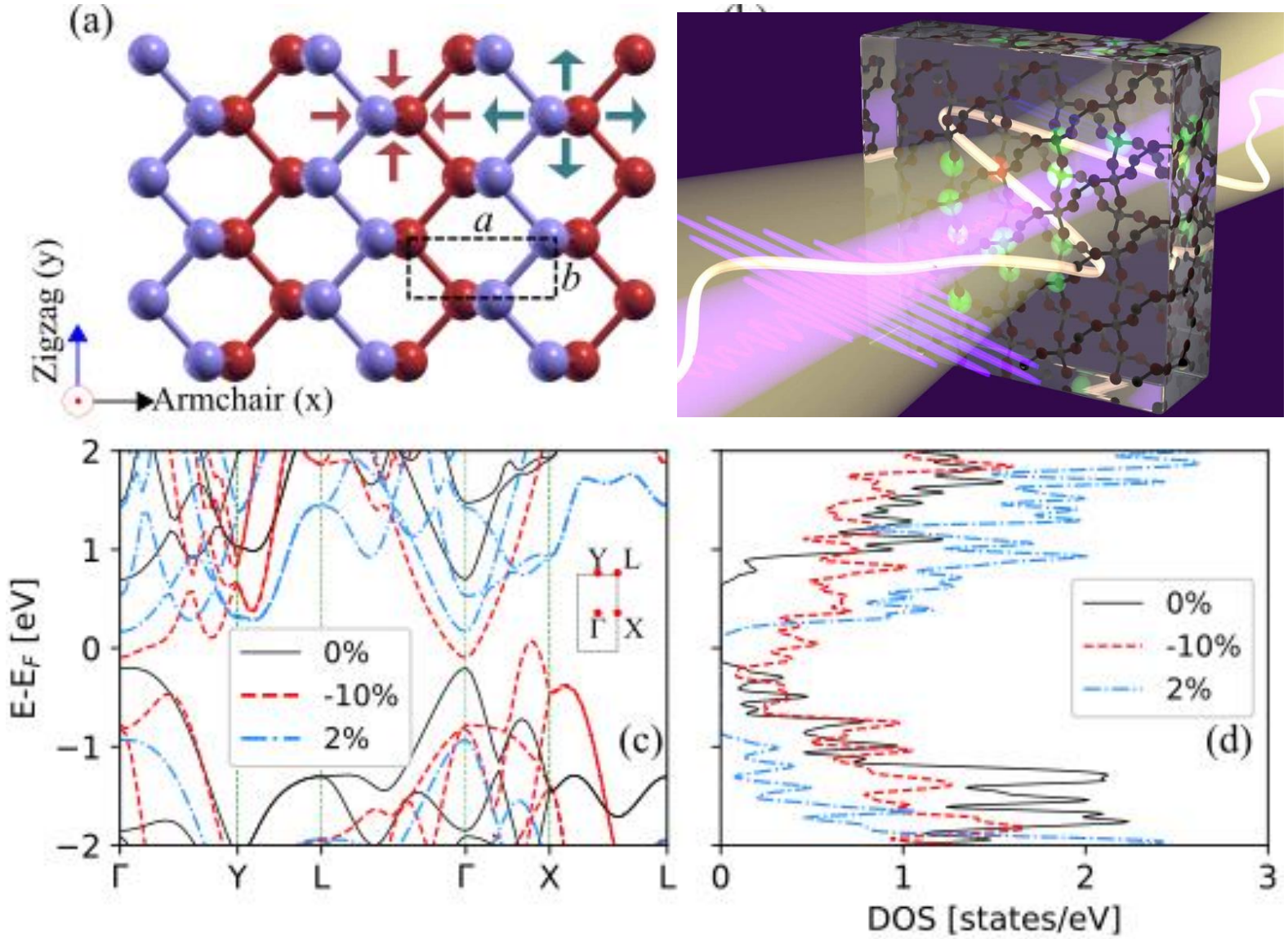


6 cycle, 800 nm laser
Peak intensity= 4.6 X 10^{14} W/cm^2

- ✓ 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

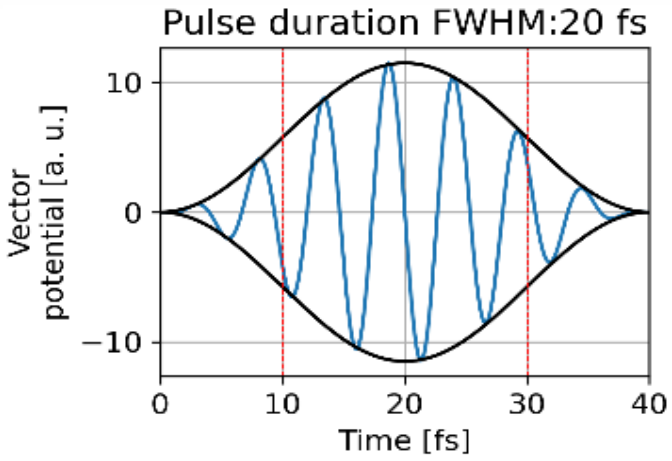
Anisotropic 2D material: phosphorene

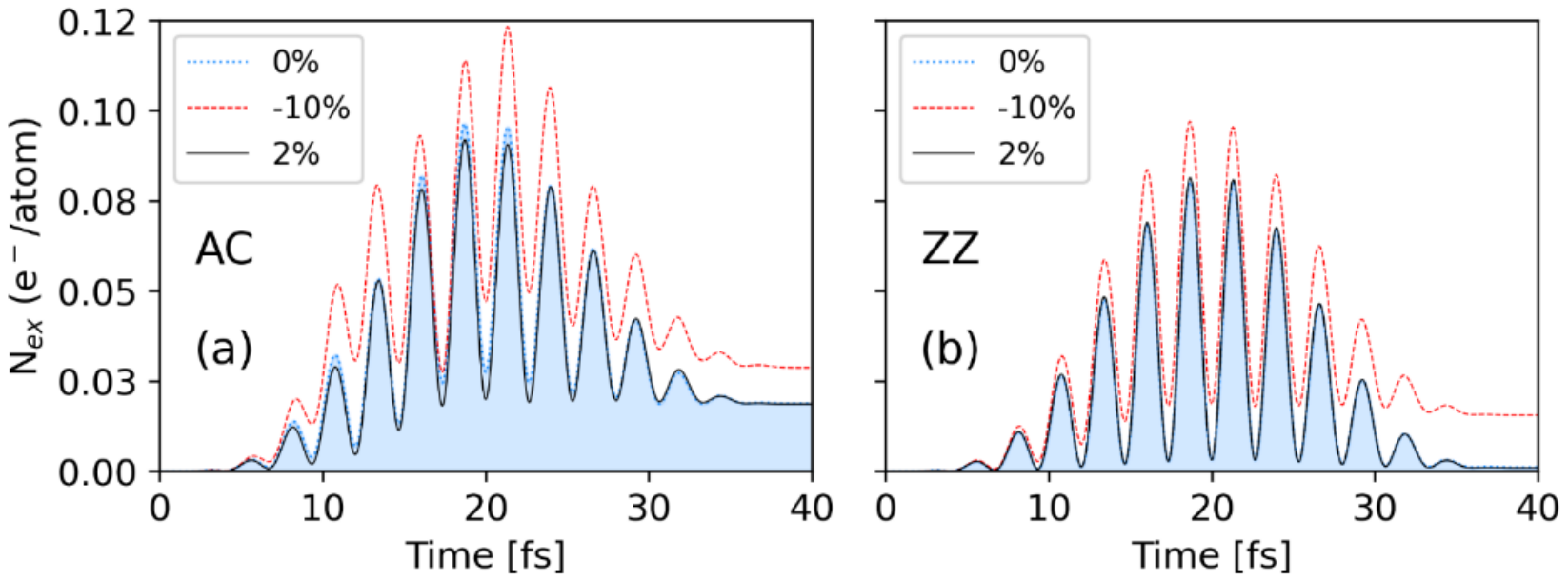


Excited electrons from valence band to conduction band

$$A(t) = -\frac{cE_0}{\omega_0} f(t) cos(\omega_0 t + \phi), \quad E(t) = -\frac{1}{c}\frac{\partial A}{\partial t},$$

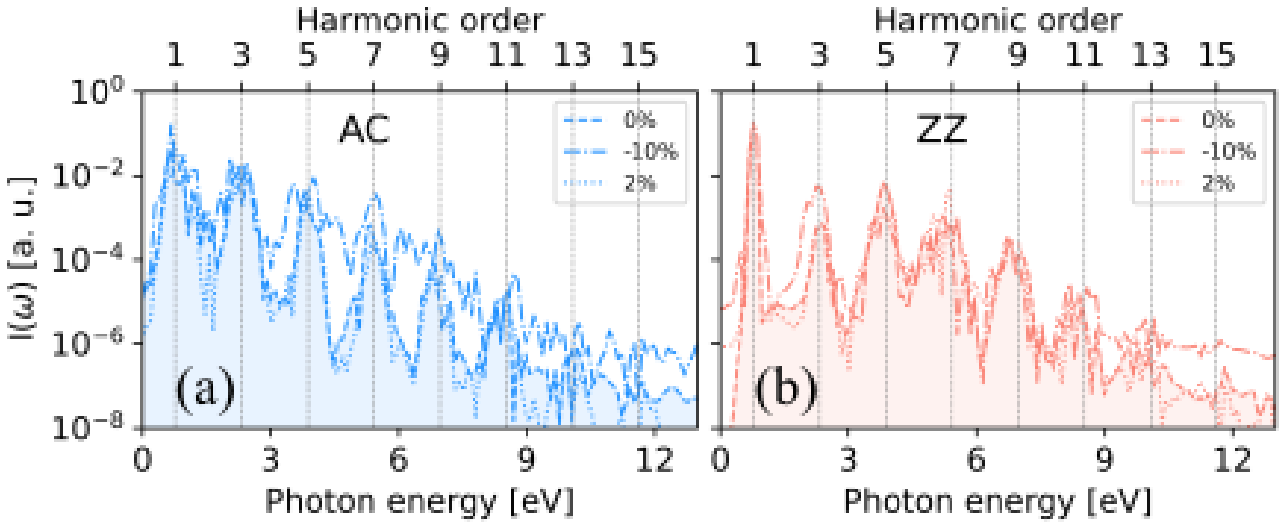
$$N_{ex}(t) = N_e - \frac{1}{N_{\mathbf{k}}} \sum_{i,j}^{occ} \sum_{\mathbf{k}}^{BZ} |\langle \psi_{i,\mathbf{k}}(t) | \psi_{j,\mathbf{k}}^{GS} \rangle|^2,$$

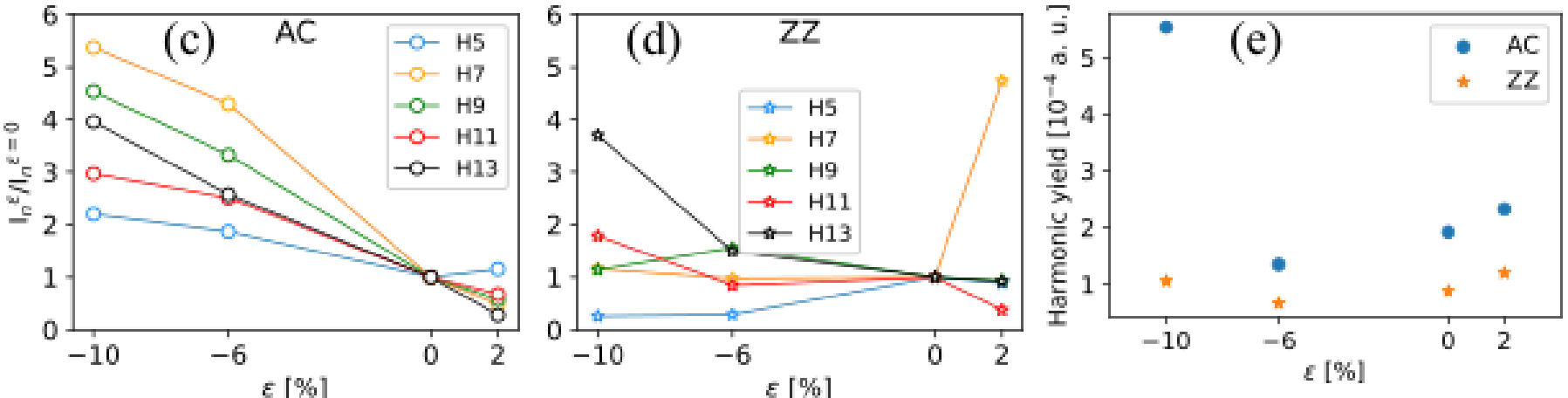




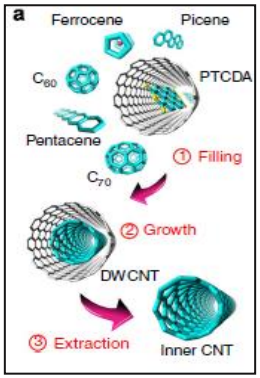
Enhanced HHG : tailored by anisotropy and strain

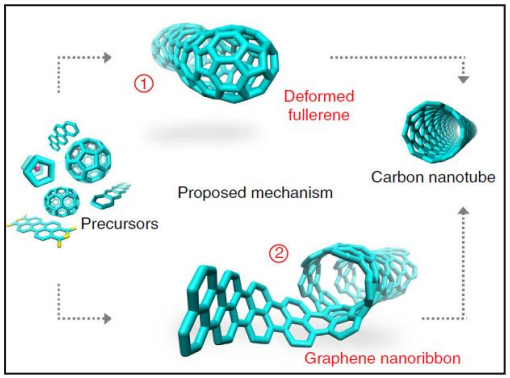
$$I(\omega) = \left| \mathcal{FT}\left(\frac{\partial}{\partial t} \int d^3r \; j(r,t) \right) \right|^2,$$



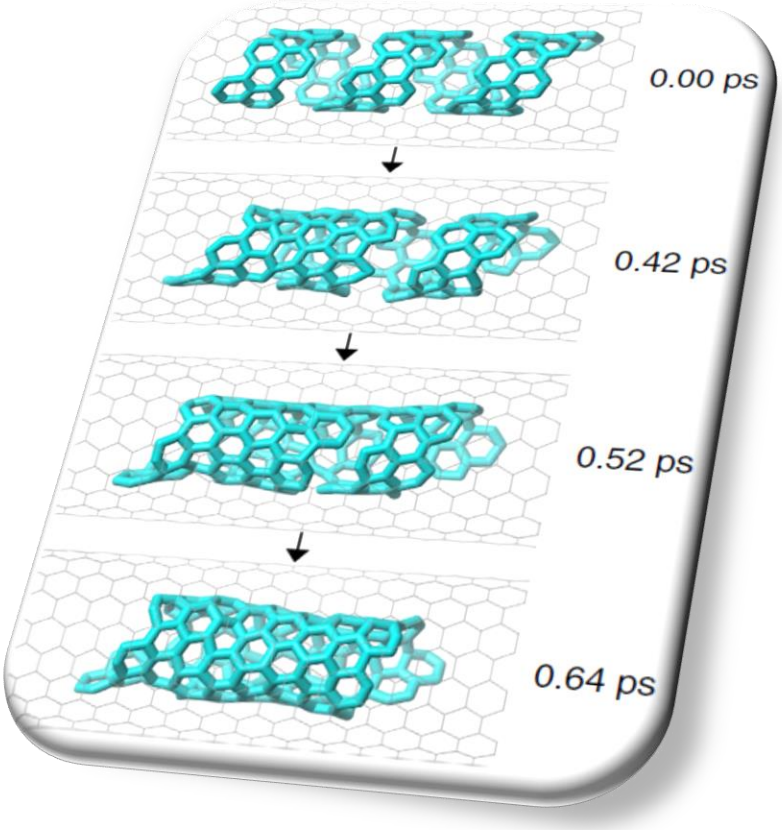


Forming nanostructures…. Defects…. 1D Nantube growth

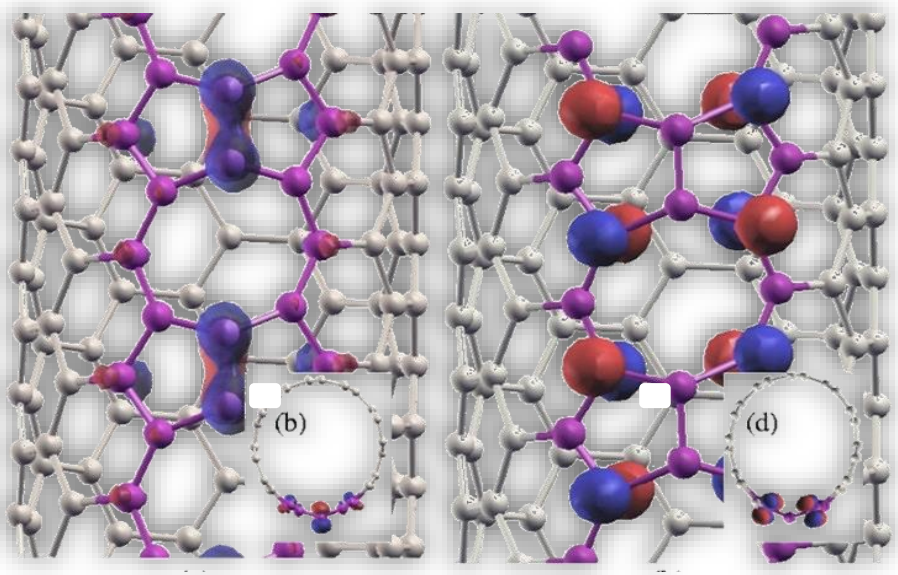




experiment theory



Snapshots of the tube formation process: AIMD simulation

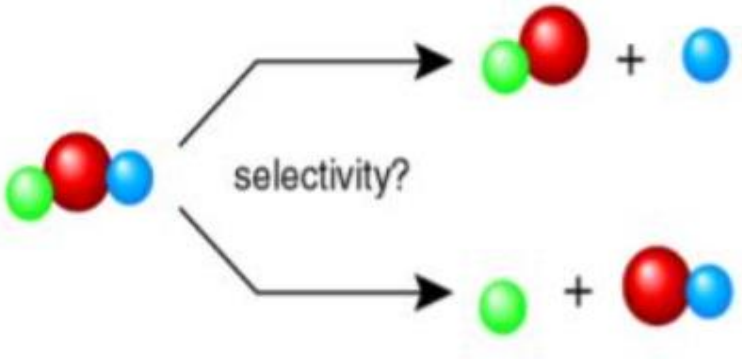


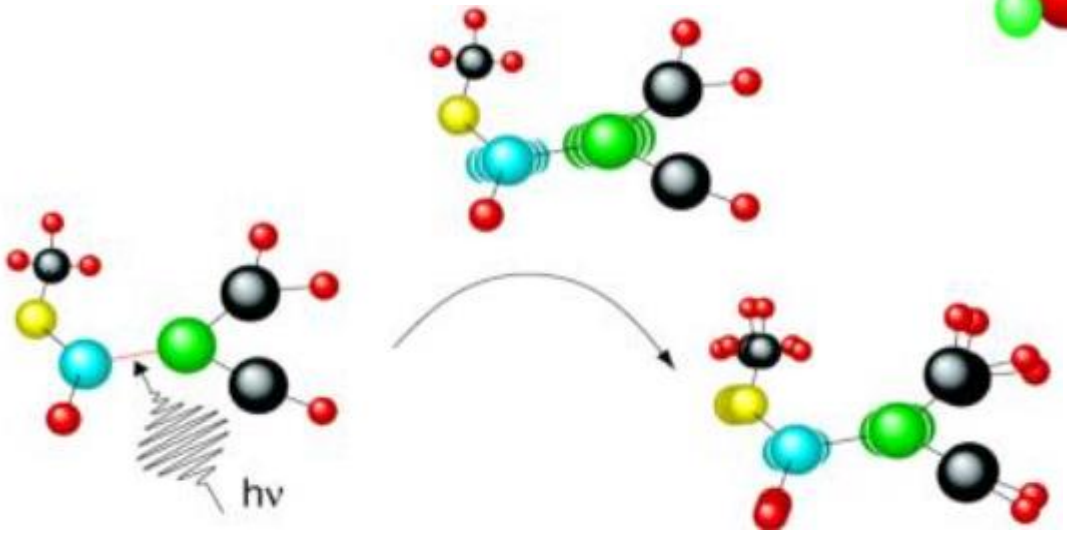
HOMO: bonding LUMO: anti-bonding

From static to time-dependent ➔ Charge density to charge migration

Selective photochemistry with laser

Is it possible to control the chemical reaction pathway (by selective excitation)?....
Chemists' dream! ☺



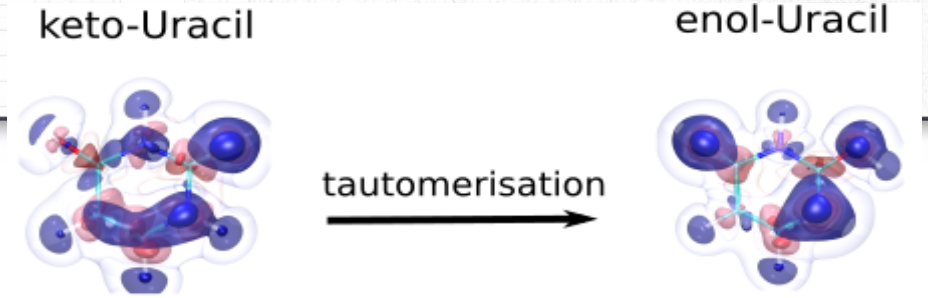


Answer: Almost YES! ☺ The difficulty with using long pulse laser is intramolecular vibrational redistribution (IVR), i.e., exciting one bond, but few fs later, whole molecule vibrates and weakest one break!

However, shaped fs pulse provides *coherent control* !

- Use fs pulse before the IVR occurs
- Shape the pulse to optimize the desired yield.
- Plus, by monitoring and tuning the charge migration dynamics (through molecular symmetries, species etc), desired reaction pathway can be chosen well before the reaction takes place!

Charge migration dynamics: example with a molecule.



Single particle Green's function representation for ionization spectra: Non-Dyson ADC(3)

$$G_{pq}(\omega) = f^{\dagger}(\omega 1 - K - C)^{-1} f$$

within complete set of Intermediate States (ISR), $|\tilde{\Psi}_J^{N-1}\rangle$, n running over excitation classes: 1h, 2h1p; and ionization energies ω

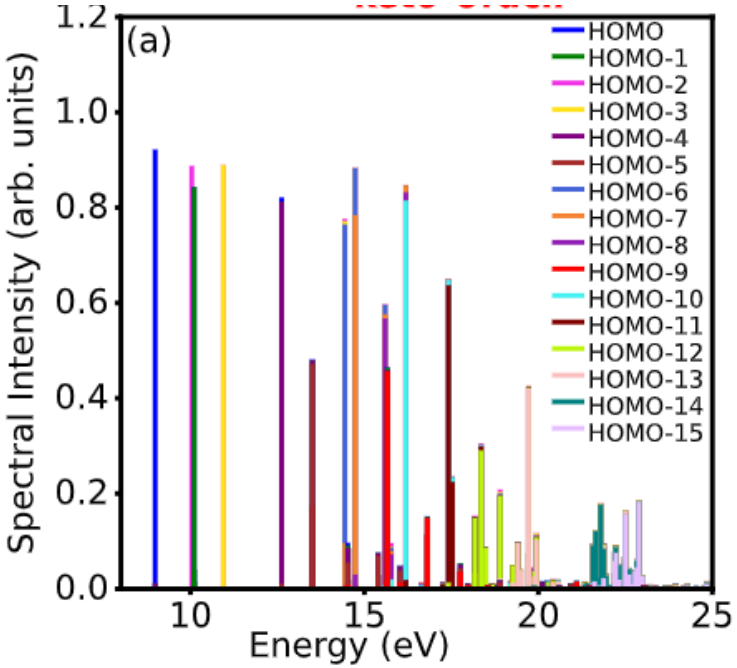
$$(K+C)_{ij} = \langle \tilde{\Psi}_I^{N-1} | E_0^N - H | \tilde{\Psi}_n^{N-1} \rangle$$

effective transition moments

$$f_{1q} = \langle \tilde{\Psi}_I^{N-1} | \hat{a}_q | \Psi_0^N \rangle$$

Cationic states

$$|\tilde{\Psi}_n^{N-1}\rangle \equiv |I\rangle = \sum_j c_j^{(I)} \hat{a}_j |\Psi_0\rangle + \sum_{a,k<l} c_{akl}^{(I)} \hat{a}_a^{\dagger} \hat{a}_k \hat{a}_l |\Psi_0\rangle + \ldots;$$



Intensity

$$x_I = \langle I | \hat{a}_i | \Psi_0 \rangle$$

J. Schirmer, L. S. Cederbaum, and O. Walter, Phys. Rev. A 28, 1237 (1983)
Schirmer, J., AB Trofimov, and G. Stelter. JCP 109.12 (1998): 4734-4744.

Hole density at position $\vec{r}$ and time t

$$Q(\vec{r},t) = \underbrace{\langle\Psi_0|\hat{\rho}|\Psi_0\rangle}_{\rho_0(\vec{r})} - \underbrace{\langle\Phi_i(t)|\,\hat{\rho}\,|\Phi_i(t)\rangle}_{\rho_i(\vec{r},t)}$$

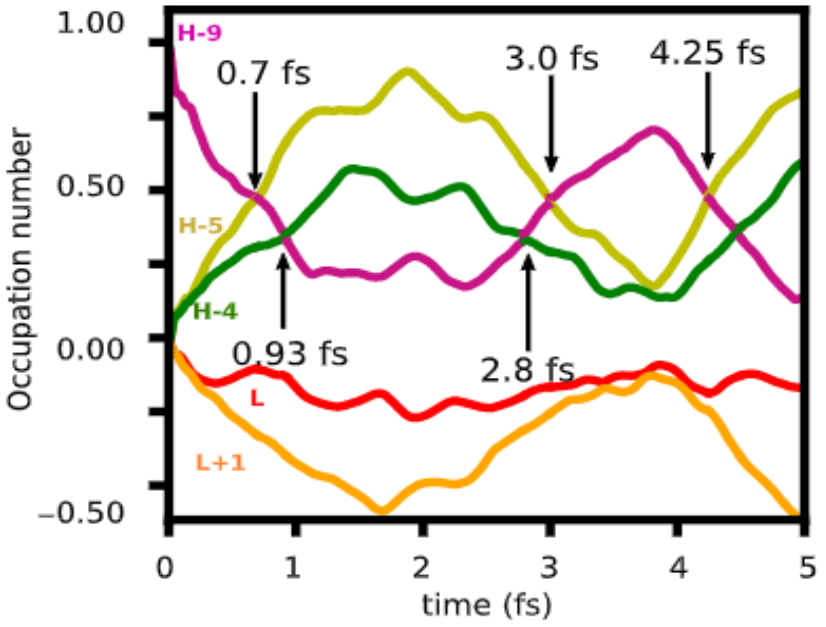
density operator $\hat{\rho}$, HF orbitals $\Phi_p(\vec{r})$
Using resolution of identity within the complete set of ISR basis $|\tilde{\Psi}_M\rangle$

$$\rho_i(\vec{r},t) = \sum_{M,N} \langle\Phi_i(t)|\tilde{\Psi}_M\rangle\, \rho_{M,N}\, \langle\tilde{\Psi}_N|\Phi_i(t)\rangle$$

$\rho_{M,N}$ is the matrix representation of the density operator in the ISR representation and $|\Phi_i(t)\rangle = e^{-i\hat{H}t}|\Phi_i\rangle$ is the propagating multielectron wave packet.
Using the representation of density operator in one-particle basis $\{\phi_p(\vec{r})\}$ and occupation number $\{n_p\}$

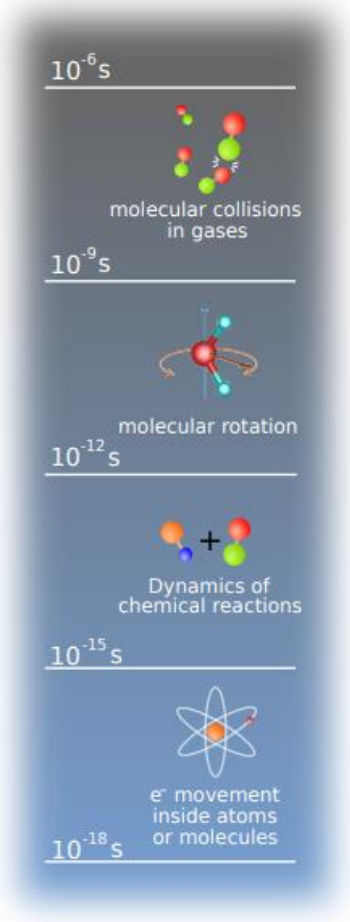
$$N_{pq}(t) = \delta_{pq} n_p - \sum_{M,N} \langle\Phi_i(t)|\tilde{\Psi}_M\rangle\, \langle\tilde{\Psi}_M|\hat{a}_p^\dagger\, \hat{a}_q|\tilde{\Psi}_N\rangle\, \langle\tilde{\Psi}_N|\Phi_i(t)\rangle$$

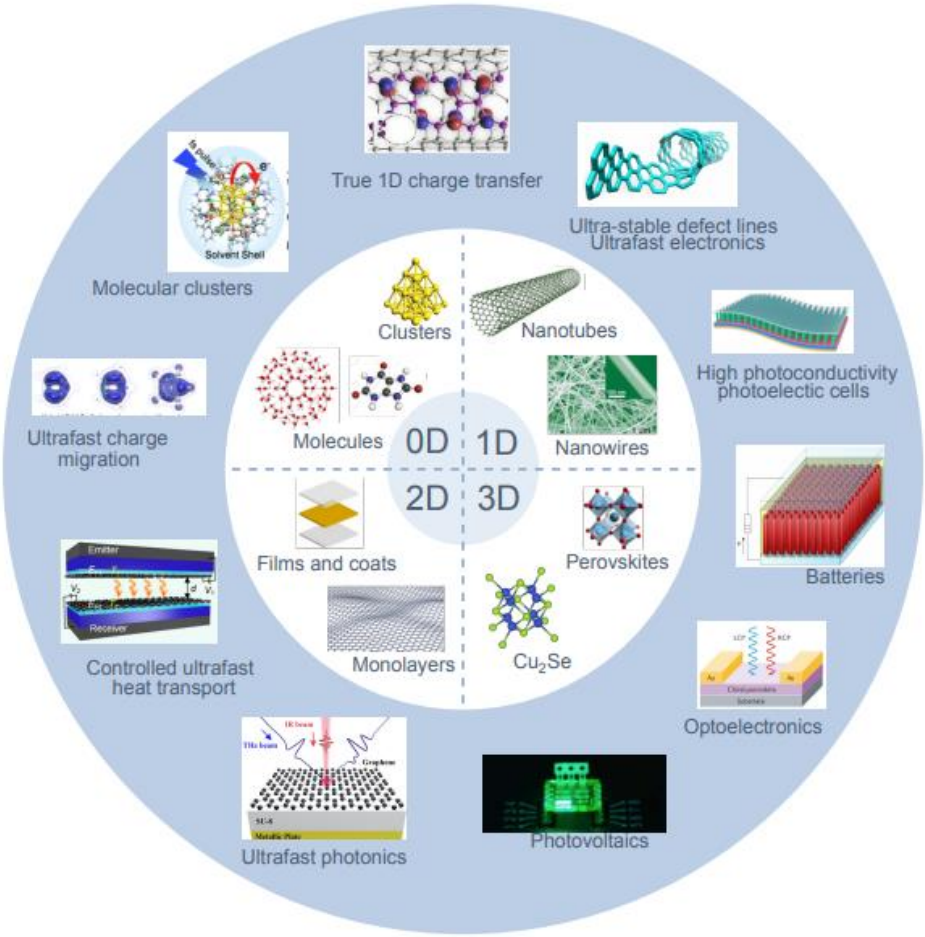
Example:
Hole Density Evolution
On Ionization of keto HOMO-9 Orbital



Al Kuleff et al., J. Chem. Phys. 123 (4) 2005, 044111;
L.S. Cederbaum et al., Chem. Phys. Lett. 307, 3 (1999), pp. 205 –210

Summary:: Ultrafast Materials Science





Semiempirical / analytical

- Time-dependent Schrödinger eq.
- Huckel & extended Huckle method
- Thomas-Fermi method

Ab-inito methods

- Hartree-Fock technique
- Density functional theory
  - *Density functional perturbation theory*
  - *Time-dependent DFT*
- Ab-inito MD

Other methods

- Classical MD
- Quantum / Molecular mechanics
  - *Hybrid methods*

- ✓ Handling Materials…… laser-material interaction
- ✓ Relevant simulations…. Different regimes => different tools
- ✓ Possible applications (amongst many)

Thank you for your kind attention!

- ✓ Internship positions
- ✓ Bachelors/masters project positions

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