Mohammed V university , Faculty of sciences Rabat
Laboratoire de **Matière C**ondensés et
Sciences **I**nterdisciplinaires

Density Functional Theory:

Theoretical concept and application

Pr: ZAARI Halima

8th Biennial African School of Fundamental Physics and Applications (ASP 2024)

Team-work:

- Solar Energy
- Solar Material
- Energy Storage
- Magnetic, Optical and Electronic Materials
- Wind Energy
- Hydrogen and storage
- Energy Efficiency
- Energy Harvesting
- Computational and modeling materials and applications
- 2D-Materials
- Nanostructure and nanomaterials
- Smart Grids
- Complex Systems
- Complex fluid in Microfluidic
- Networks and Traffic
- Laser
- Laser
- Spectroscopy
- Medicinal plant chemistry
- Software engineering
- Quantum cryptography
- Thermal and energy efficiency
- Physics of Surface and interface

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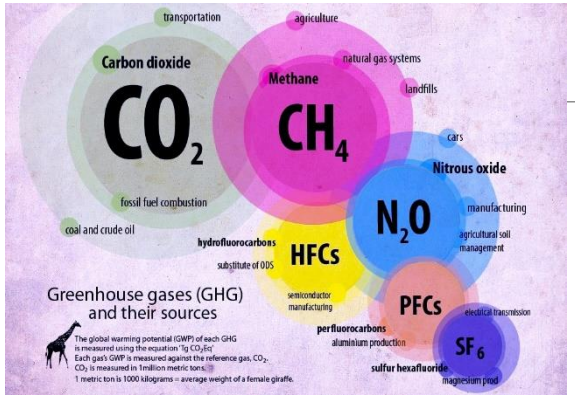
Faculté des Sciences

Density Functional Theory:

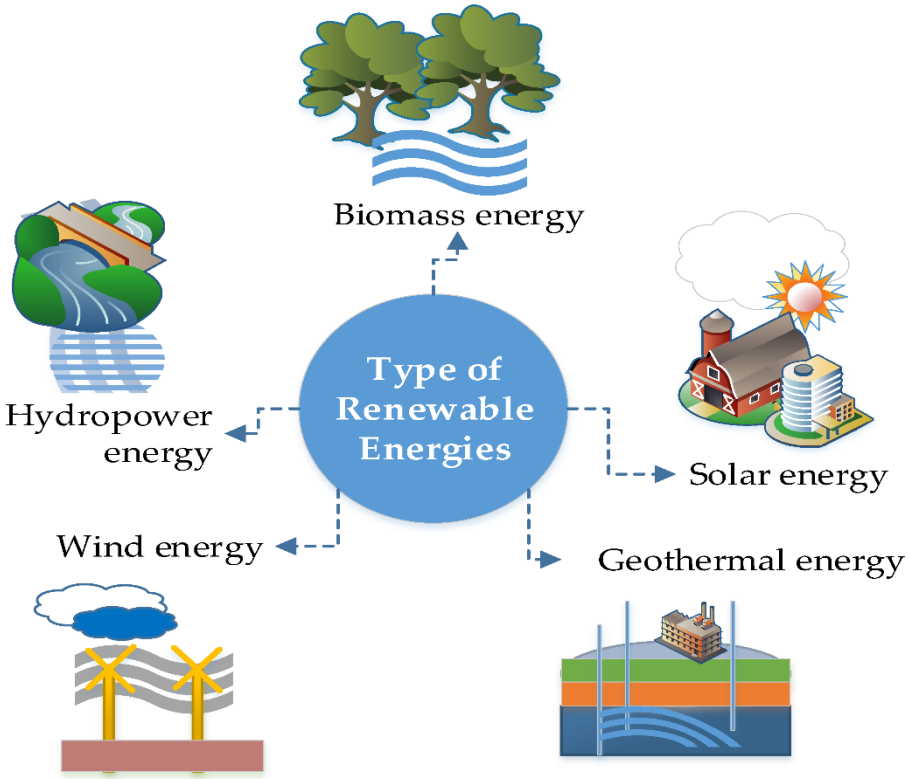
Theoretical concept and application

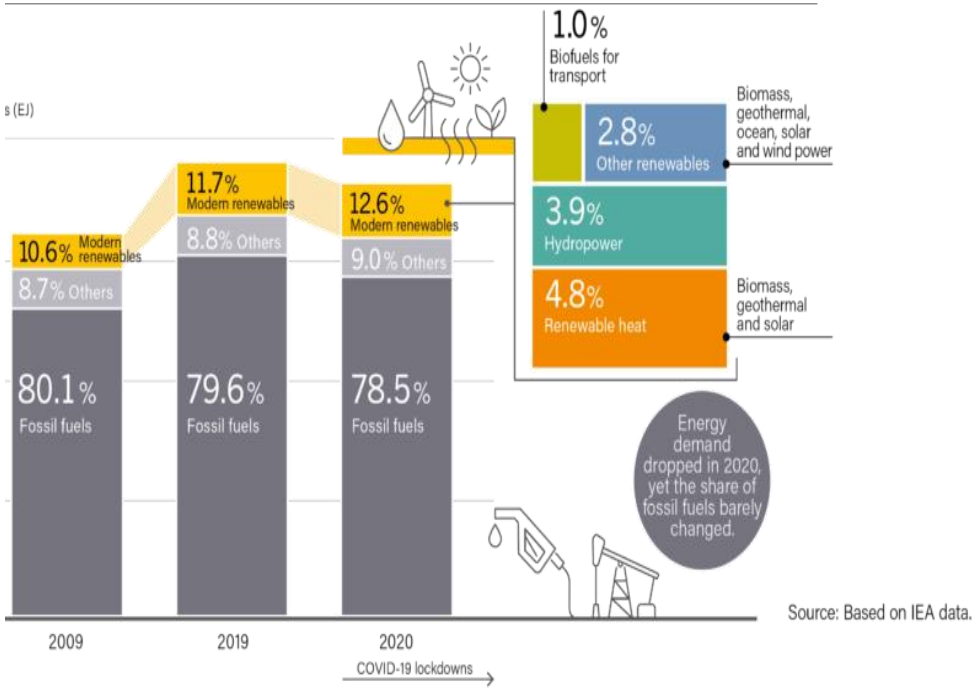
Problems



Role of science in solving these problems??

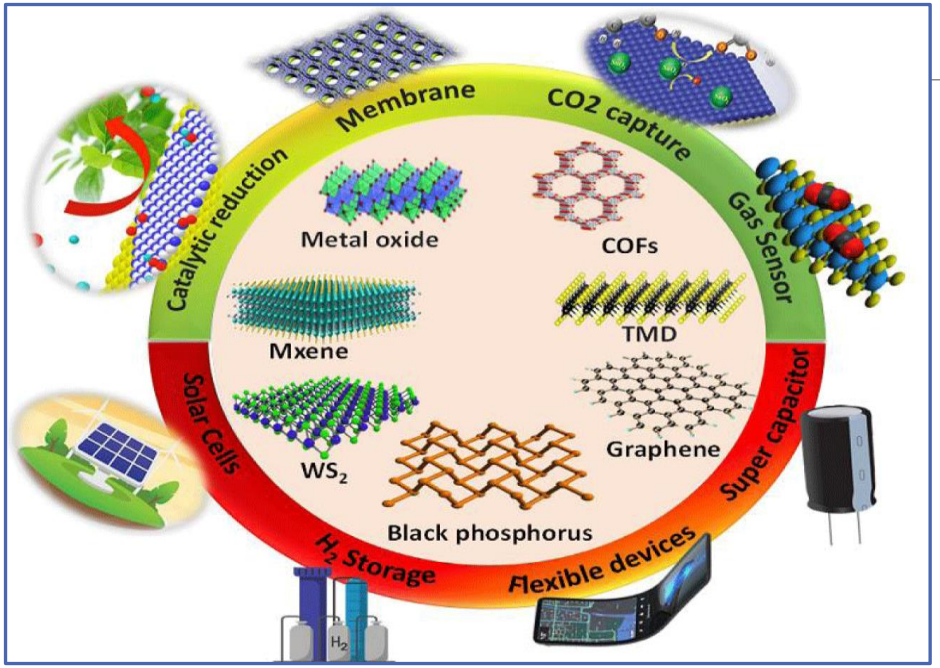
Solution: **Renewable Energy**

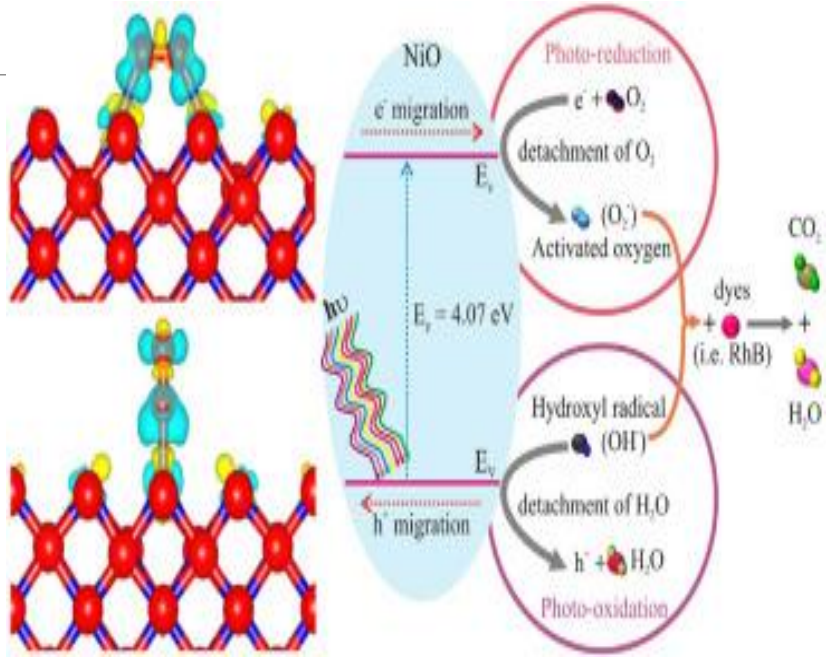




Share of Modern Renewable Energy 2009, 2019 and 2020

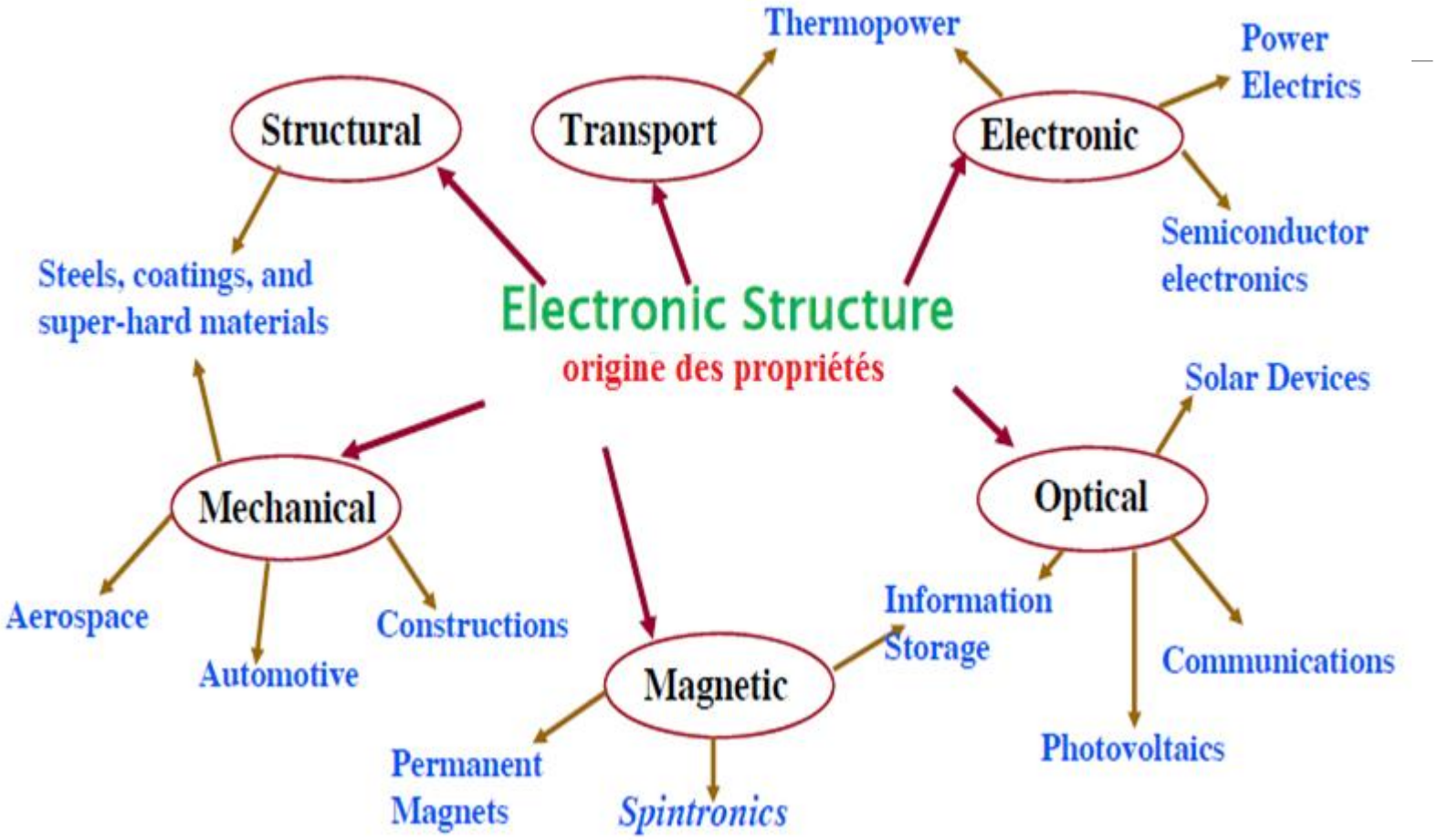
Solution: Materials sciences





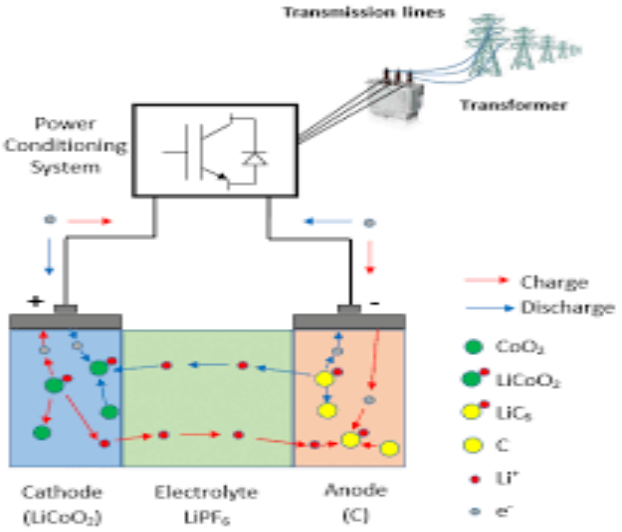
Semi-conductor, insulator, metals Magnetic, or non magnetic…

Solution: Materials sciences

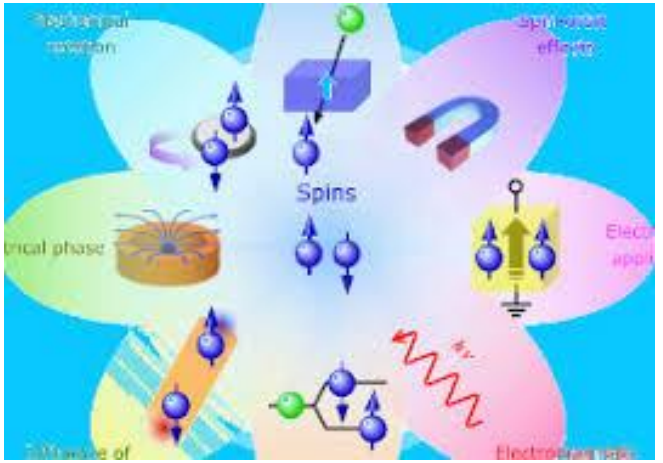


Material sciences : Application

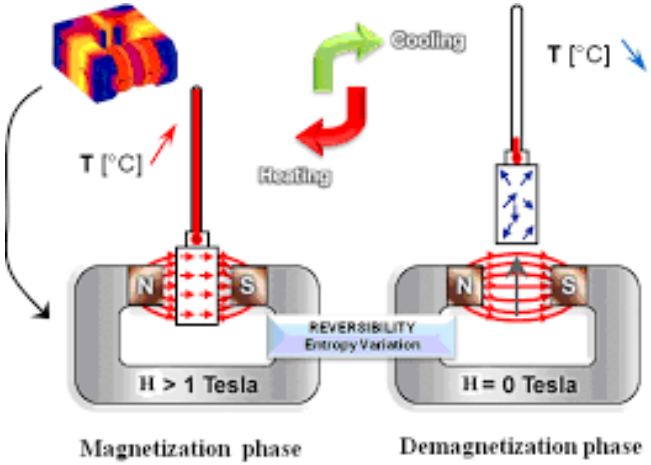
❑ Battery or Energy storage



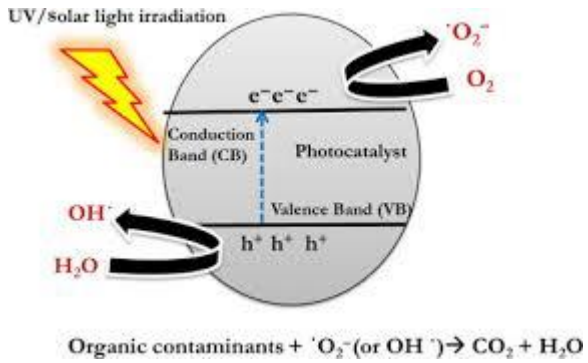
❑ Spintronic



❑ Magnetocaloric Effect

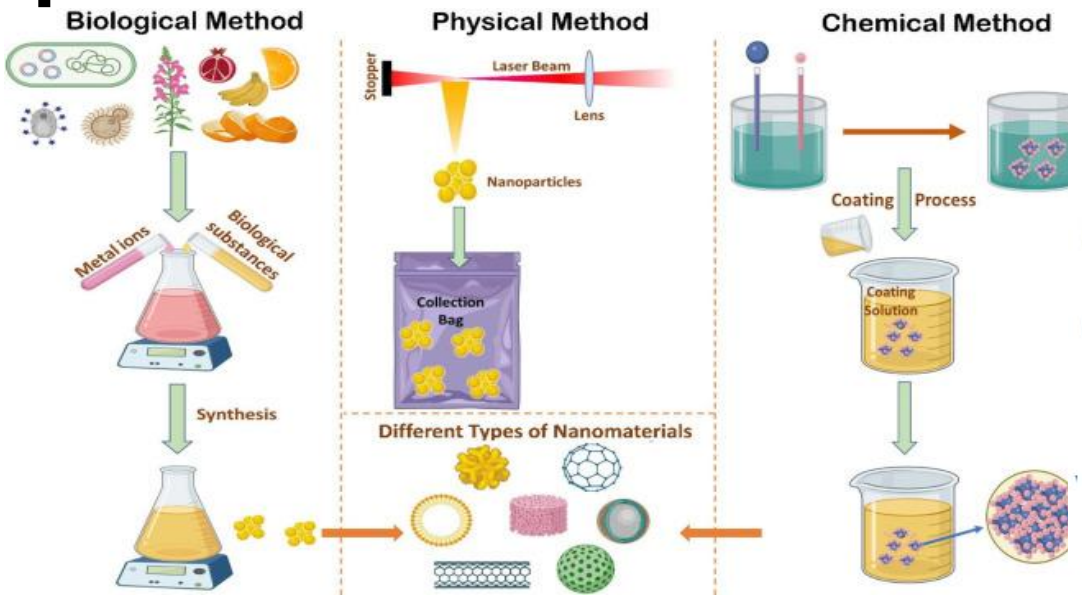


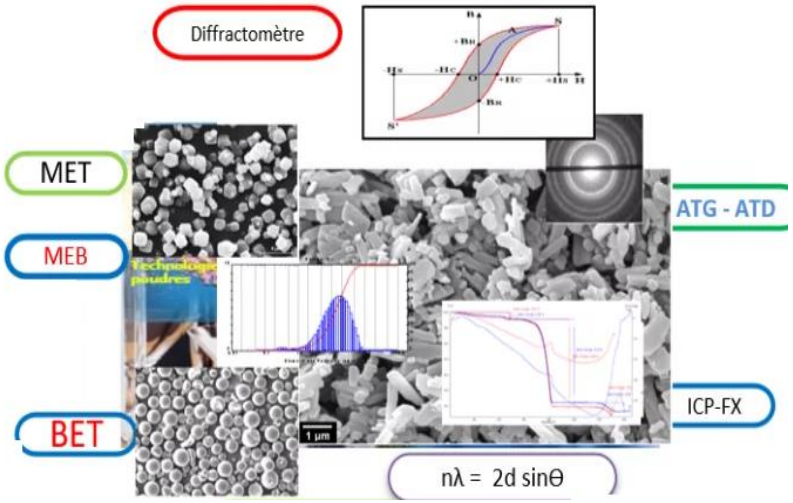
❑ Photocatalysis-Photovoltaic

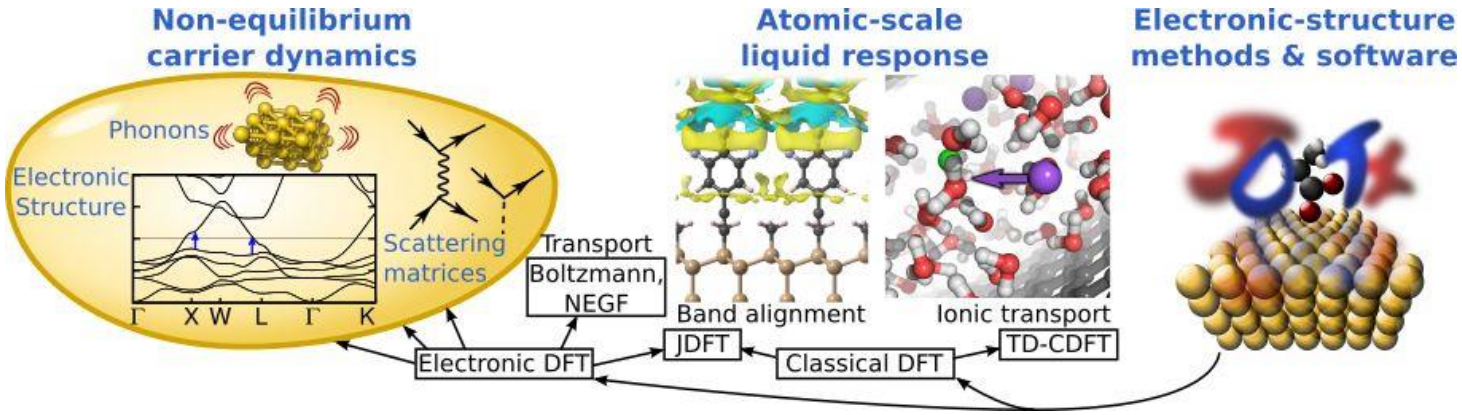


Organic contaminants + $^{\cdot}O_2^-$(or $OH^{\cdot}$) → $CO_2 + H_2O$

Experimental or Theoretical approach



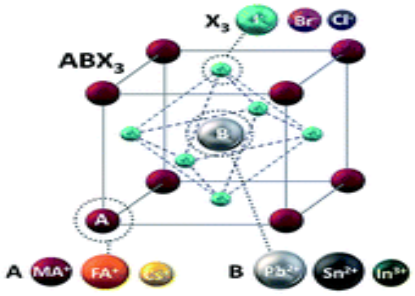




aurabh Shukla, Ramsha Khan, Achlesh Daverey, Synthesis and characterization of magnetic nanoparticles, and their applications in wastewater treatment: A review, Environmental Technology & Innovation, Volume 24, 2021, 101924, ISSN 2352-1864, https://doi.org/10.1016/j.eti.2021.101924.

2. Theoretical approach

How to predict the physical properties without experience??



Background??

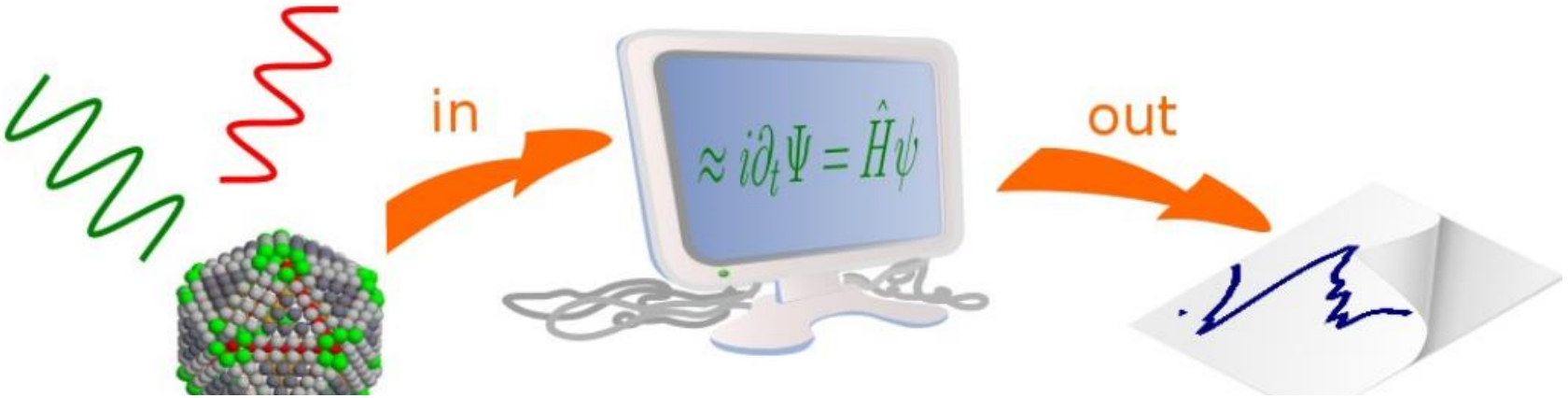
Model?

Simulation, analysis
Input : lattice parameter , atomic positions ...

Physical concept:
Quantum mechanic
Solide state
Schrodinguer equation

Decribe the physical properties:
optical , transport , magnetic …

Density Functional Theory

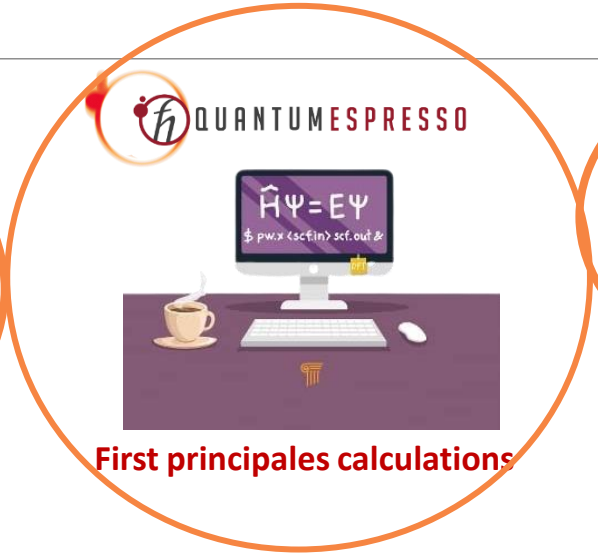


$$\hat{H}\psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) + \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \psi = E\psi$$

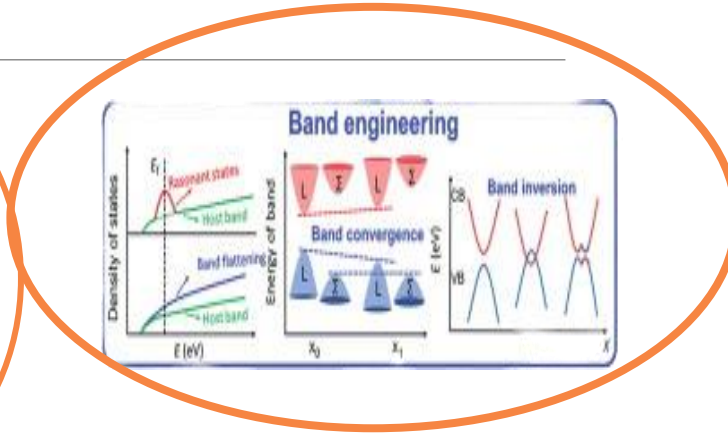
$$\hat{T}_e = \sum_n -\frac{\nabla_n^2}{2}$$

$$\hat{V}_{ee} = \sum_n \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|}$$

Methodology



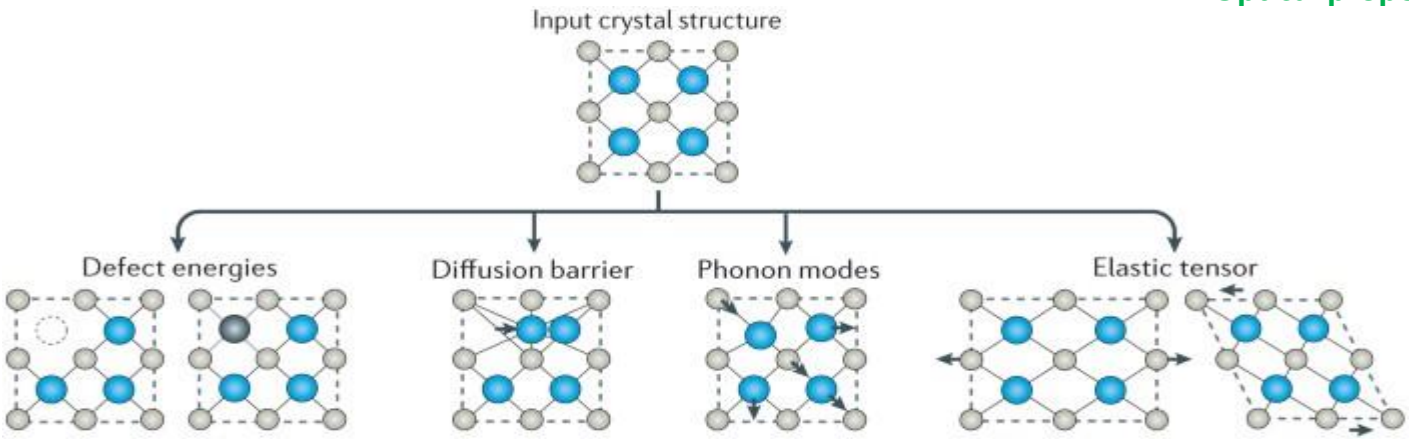
First principales calculations



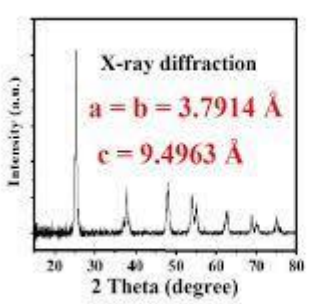
✓ Electronic properties

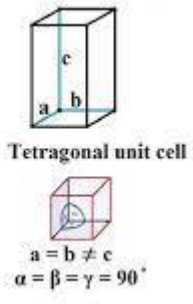
✓ Dynamical properties

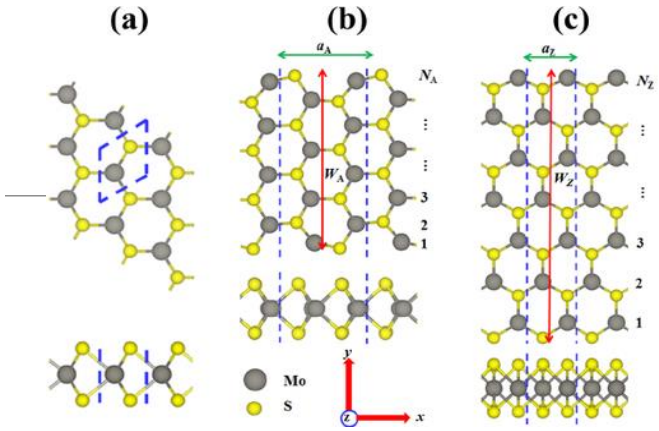
✓ Optical properties

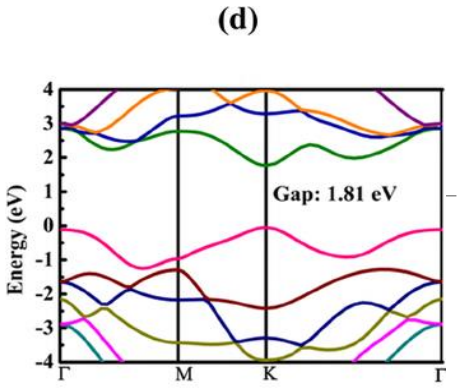


Which parameter we need in DFT?









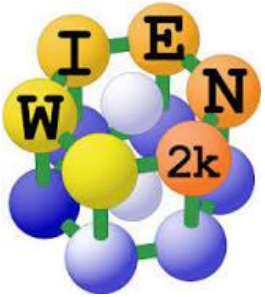
*the choice of Exchange-correlation (XC) functional :LDA or GGA

*wave function (e.g. Gaussian basis functions,

plane wave expansion) and the formalism like pseudopotential or Full potential

$$\rho(r) = \sum_i |\psi_i(r)|^2$$

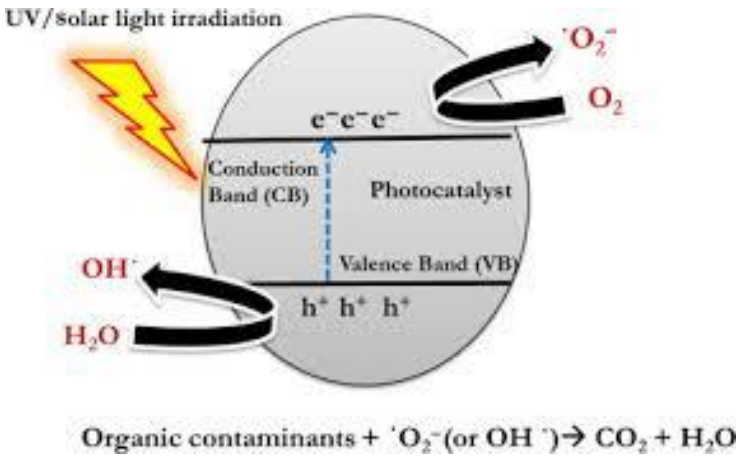
$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$



3. Application:

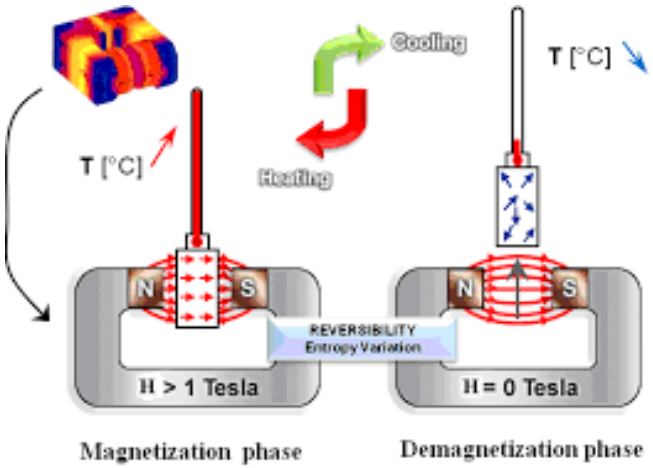
Material sciences : Application

❑ 1. Photovoltaic and photocatalysis



Organic contaminants + $^{\cdot}O_2^-$(or $OH^{\cdot}$) → $CO_2 + H_2O$

2. Magnetocaloric Effect



❑ Photocatalysis-Photovoltaic

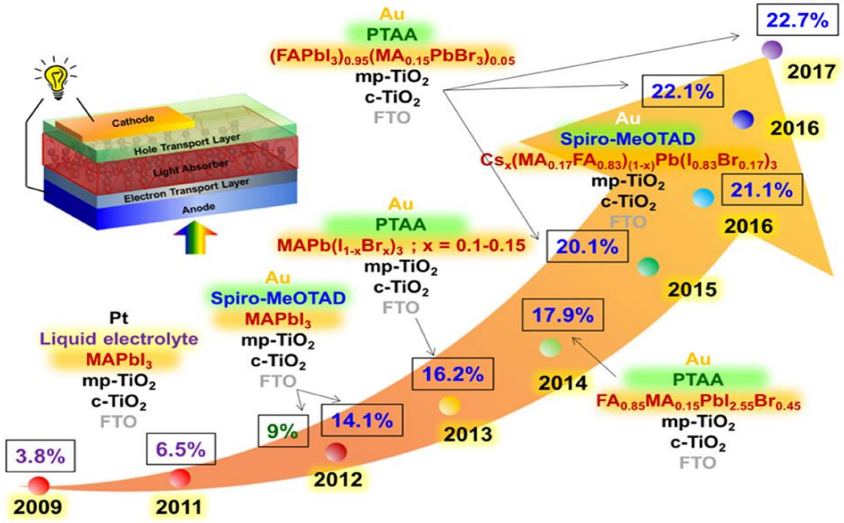
Hybrid perovskite

General formula ABX_3

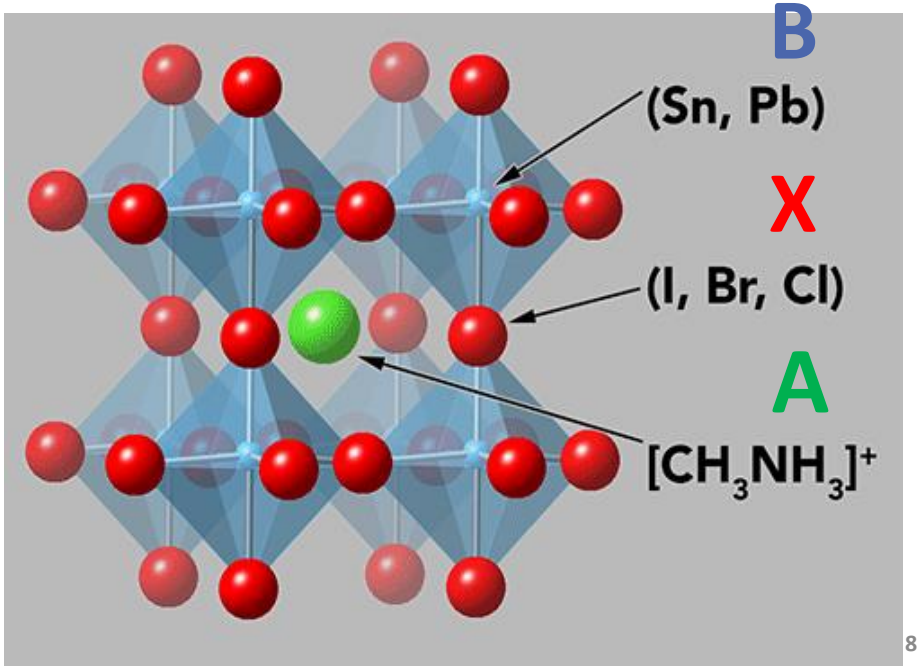
A: Organic cation(MA(CH_3NH_3))

B: Metal (Pb, Sn, Ge)

X: Halide (I, Br, Cl)



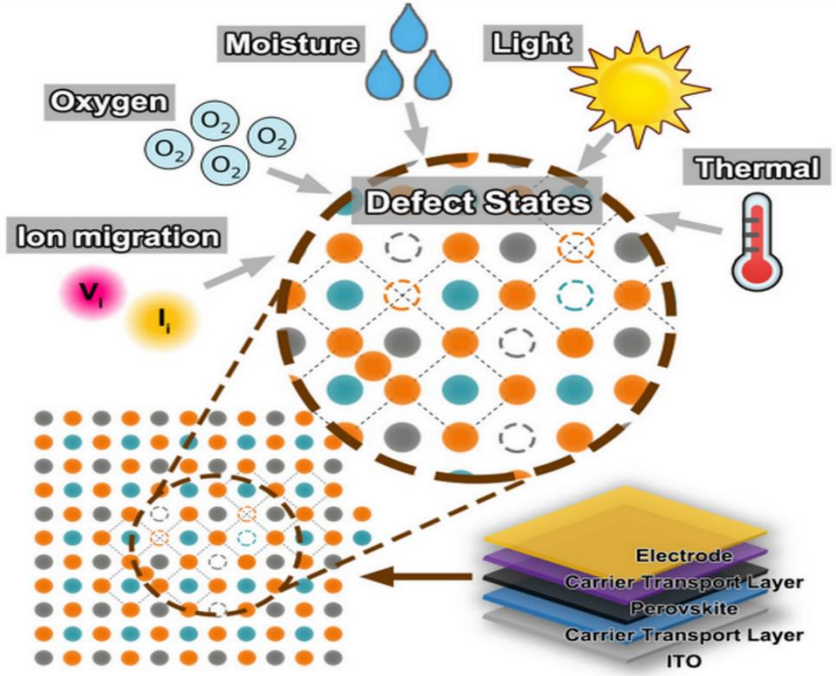
$CH_3NH_3PbI_3$

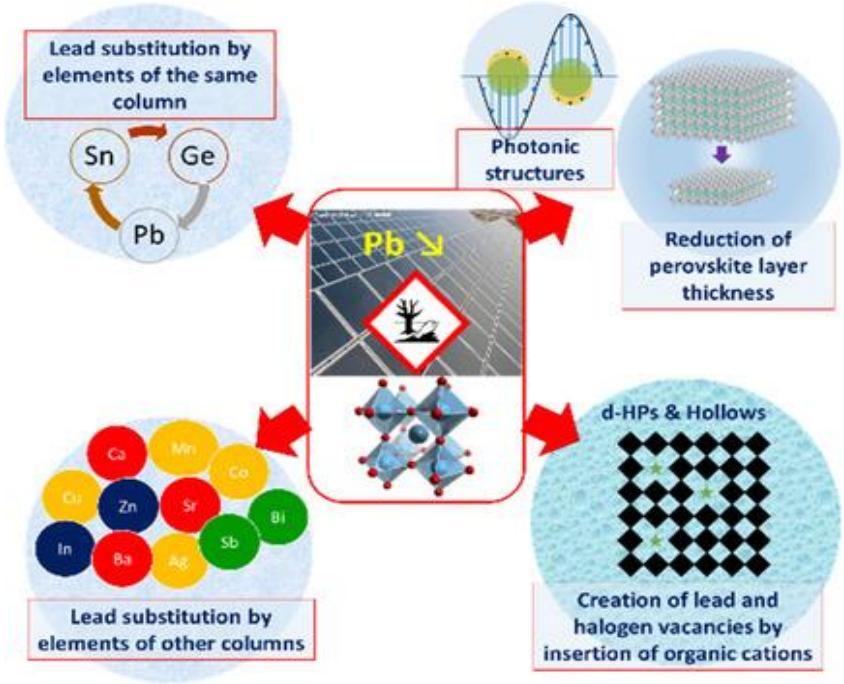


❑ Photocatalysis-Photovoltaic

Potential Problems

- **Stability**
  - ➢ The perovskite is not stable
- **Toxicity**
  - ➢ By eliminating the toxicity we lose in efficiency





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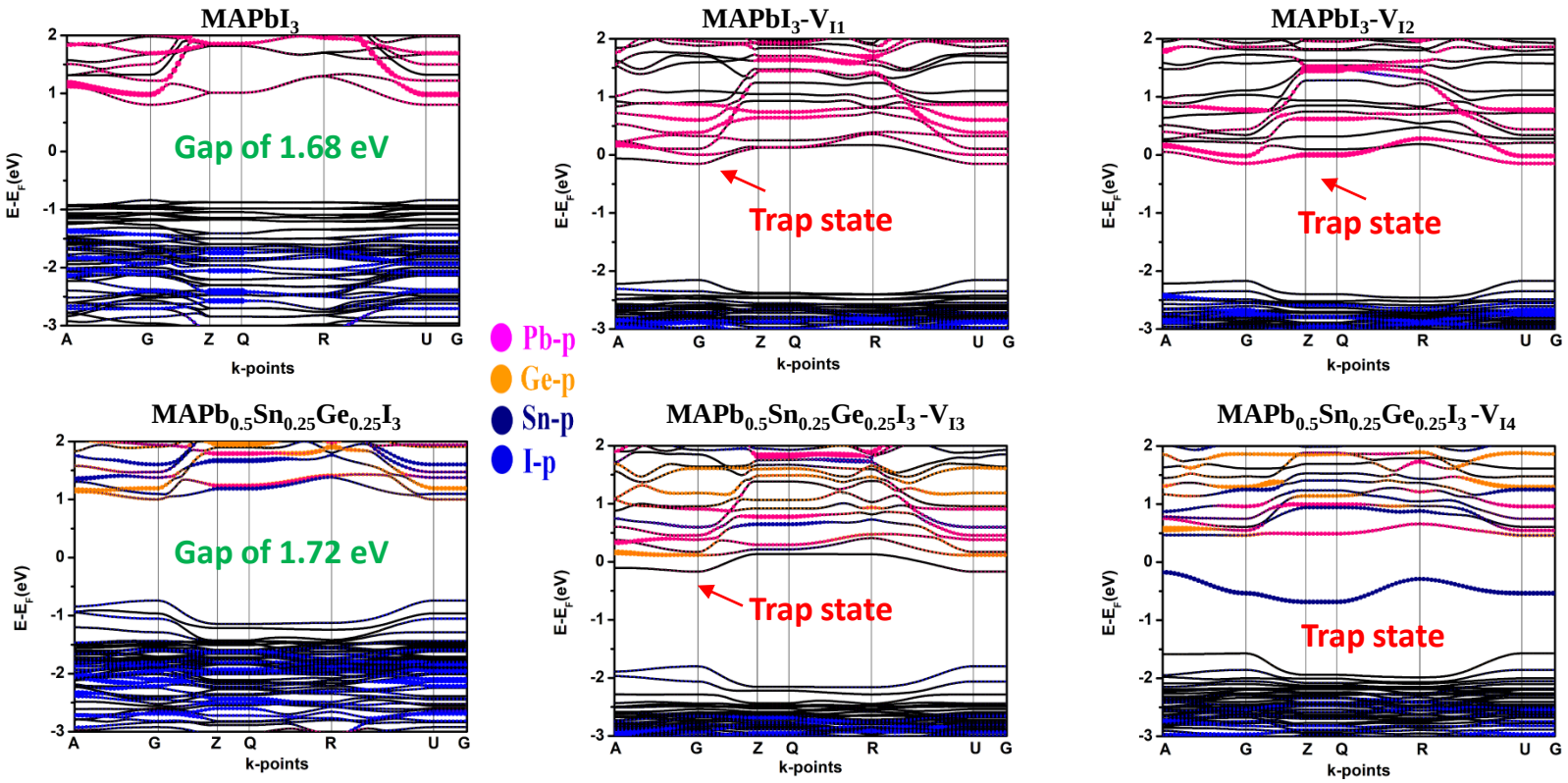
❑ Photocatalysis-Photovoltaic

How can we mitigate the iodine vacant site ?



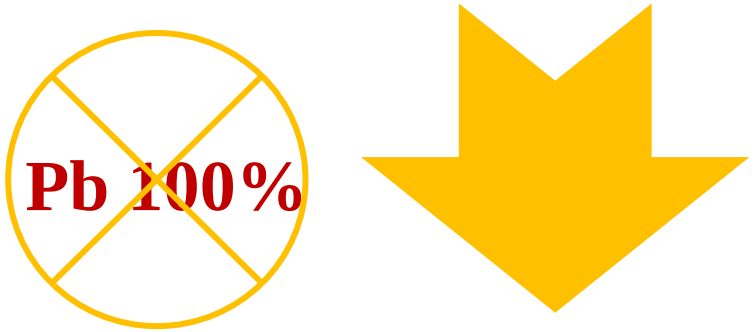
Band structure of $MAPbI_3$ and $MAPb_{0.5}Sn_{0.25}Ge_{0.25}I_3$ in the pure and defective phase

❑ Photocatalysis-Photovoltaic

Interaction of water molecule with the hybride perovskite

	Calculated Adsorption energy (eV)	
Sites	$MAPbI_3$	$MAPb_{0.5}Sn_{0.25}Ge_{0.25}I_3$
CH_3	-0.40	-0.19
NH_3	-0.70	-0.70
I	-0.24	-0.14
Pb	-0.56	-0.54
Ge	----	-0.48
$Pb(V_{I1}$ or $V_{I3})$	-0.54	-0.50
$Pb(V_{I2}$ or $V_{I4})$	-0.49	-0.44

Pb(50%)Sn(25%)Sn(25%)



✓ Enhancement of stability

✓ Reduction of toxicity

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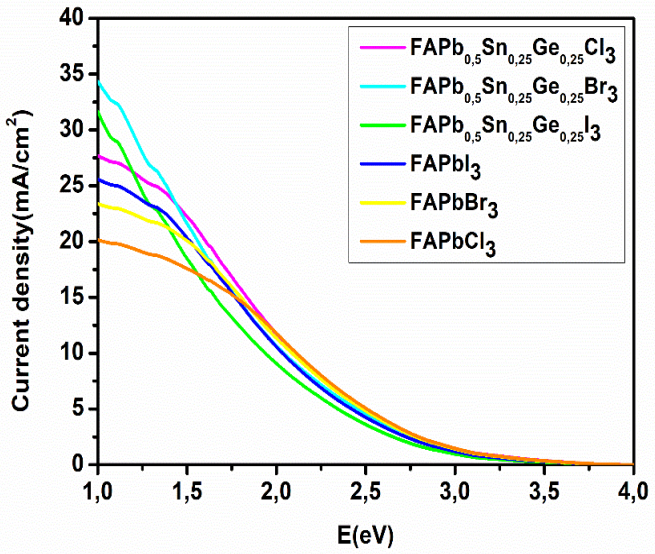
❑ Photocatalysis-Photovoltaic



Short-circuit current density of $FAPbX_3$ and $FAPb_{0.5}Sn_{0.25}Ge_{0.25}X_3$.

Power conversion efficiency

- **Power conversion efficiency:**

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100$$

The calculated bandgap E_g, short-circuit current density J_{sc}, open circuit voltage V_{oc} and power conversion efficiency η of $FAPb_{0.5}Sn_{0.25}Ge_{0.25}X_3$ structures.

Compounds	E_g	V_{oc}		J_{sc}	η %	
		E_{loss}(0.7 eV)	E_{loss}(0.5 eV)		E_{loss}(0.7 eV)	E_{loss}(0.5 eV)
$FAPb_{0.5}Sn_{0.25}Ge_{0.25}I_3$	0.98	0.28	0.48	31.5	6.17	12
$FAPb_{0.5}Sn_{0.25}Ge_{0.25}Br_3$	1.22	0.52	0.72	29	12	17.5
$FAPb_{0.5}Sn_{0.25}Ge_{0.25}Cl_3$	1.7	1	1.2	18	15.8	19.3
$FAPbI_3$	1.5	0.8	1	20.3	14	17.8
$FAPbBr_3$	1.67	0.97	1.17	17.3	14.6	18
$FAPbCl_3$	2.14	1.44	1.64	9.6	12.5	14.3

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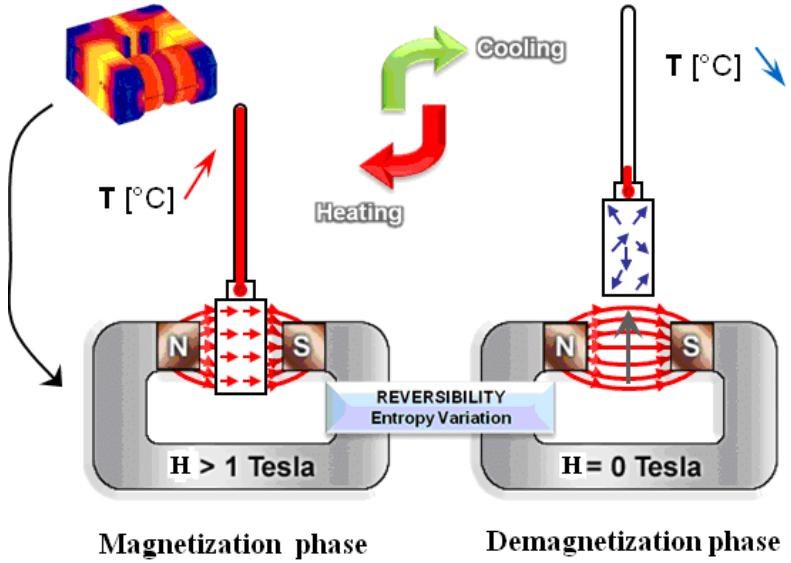
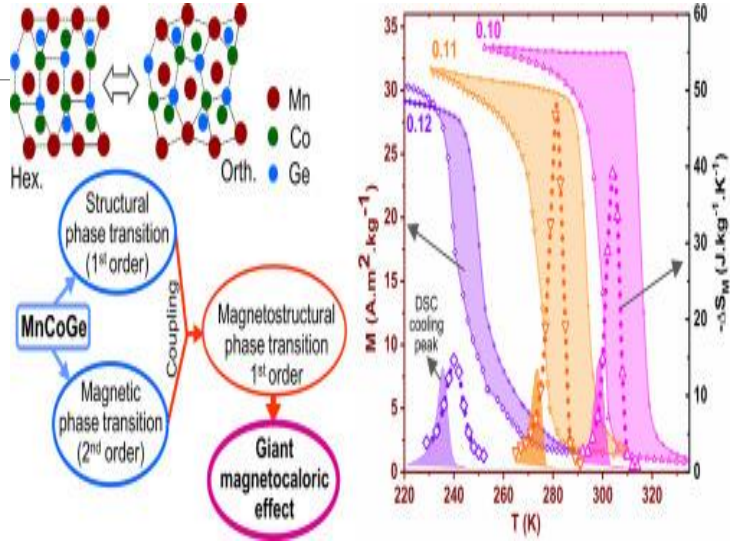
Magnetocaloric effect: multiferoic system





- Criterion:

Large magnetic moment,
Large entropy change
Reduced change in deltaT

$$\Delta S_{mag} = \int_{H_1}^{H_2} \left(\frac{\partial H}{\partial T}\right)_H dH$$

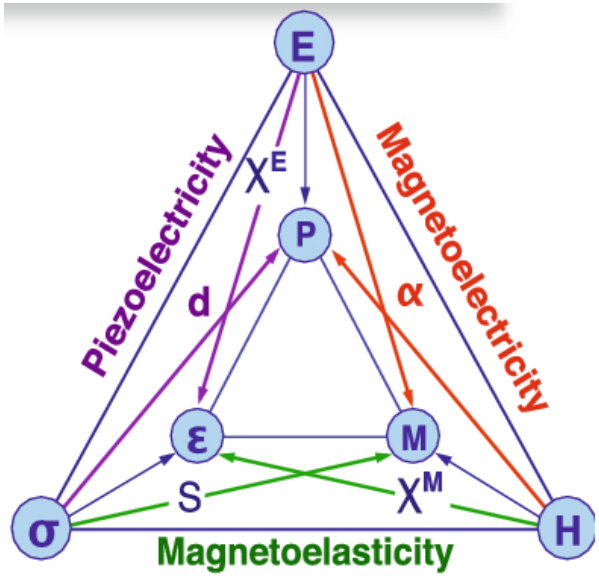
$$\Delta T_{ad} = -T \frac{\Delta S_{mag}}{C_m}$$

$$q = -\int_{T_1}^{T_2} \Delta S_{mag}(T) dT$$

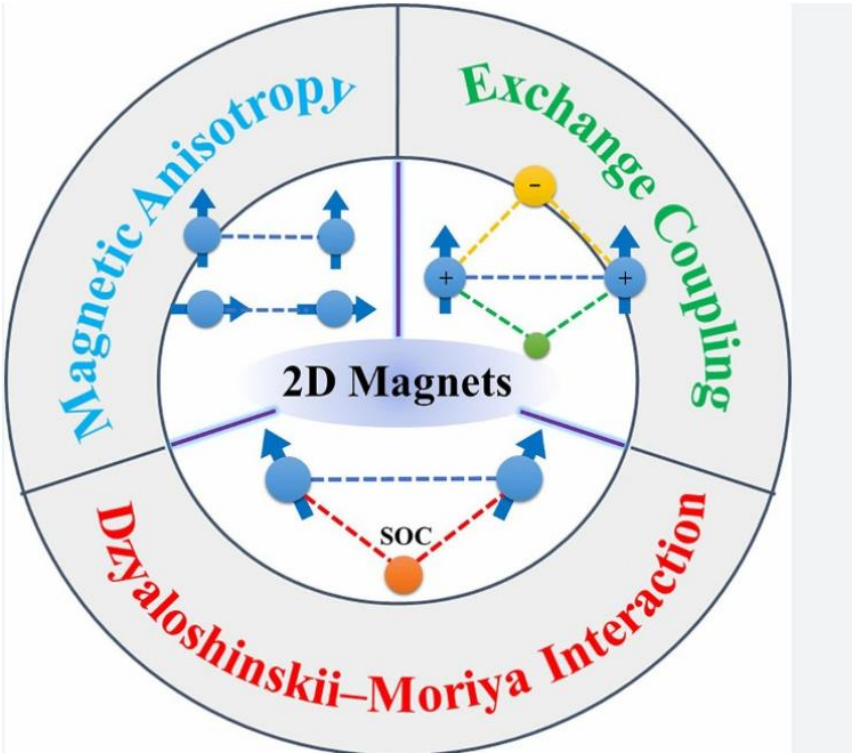
$$\begin{cases} RCP\ (S) = \Delta S_{max} . \delta T_{mi-hauteur} \\ RCP\ (T) = \Delta T_{max} . \delta T_{mi-hauteur} \end{cases}$$

Magnetocaloric effect:

Multiferoic Systems:



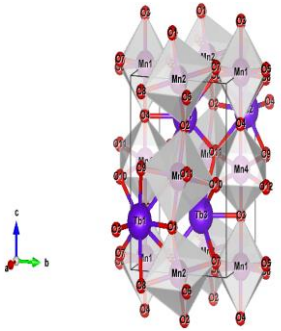
Feibig, *J. Phys. D* **38**, R123 (2005)
Eerenstein, *et al.*, *Nature* **442**, 759 (2006)
Ramesh & Spaldin, *Nature Mater.* **6**, 21 (2006)
Cheong & Mostovoy, *Nature Mater.* **6**, 13 (2006)



Hamiltonian : H=-J.Si.Sj – h….

Magnetocaloric effect: multiferoic system

$TbMnO_3$



AFM — cycloid — Mn ions « sinusoidal — Paramegntic

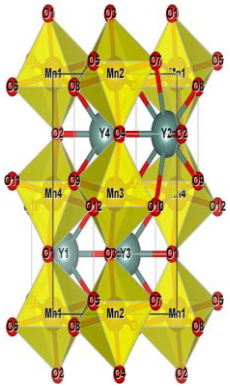
7 — 30 — 40 — T

Ferroeltric — Paraeletric

30 — T électrique

P≈ 700-800 µC/m²

$YMnO_3$



AFM — Mn ions « sinusoidal — Paramagnetic

30 — 40 — T magnétique

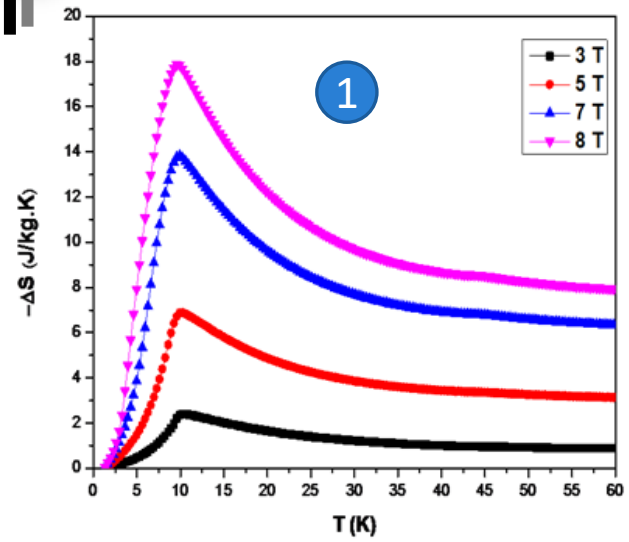
Ferroeltric — Paraeletric

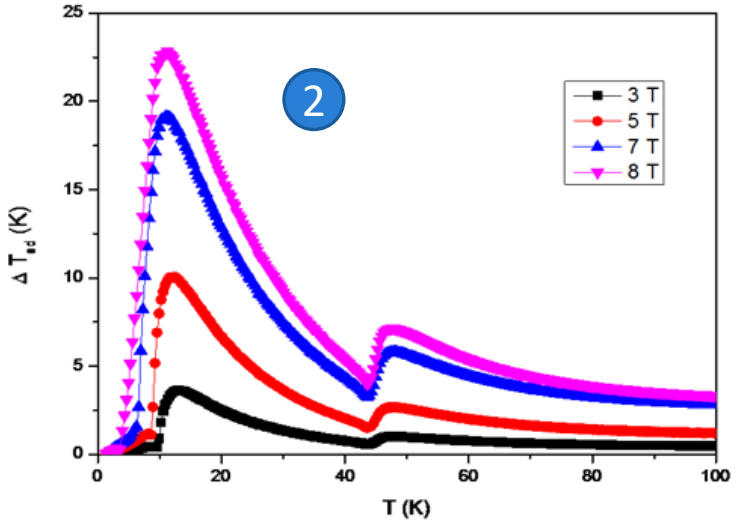
30 — T electric

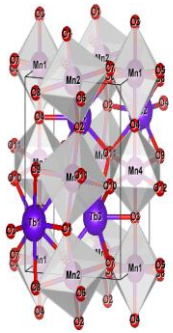
P≈ 250 µC/m²

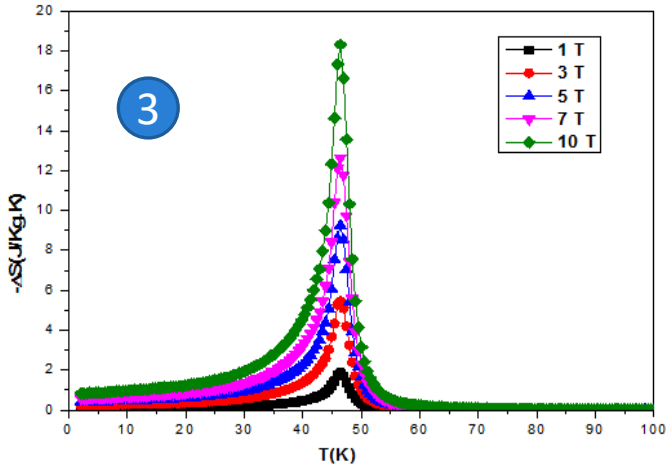
FZ Kassimi, H Zaari, A Benyoussef, A Rachadi, A El Kenz Journal of Superconductivity and Novel Magnetism 35 (9), 2493-2503

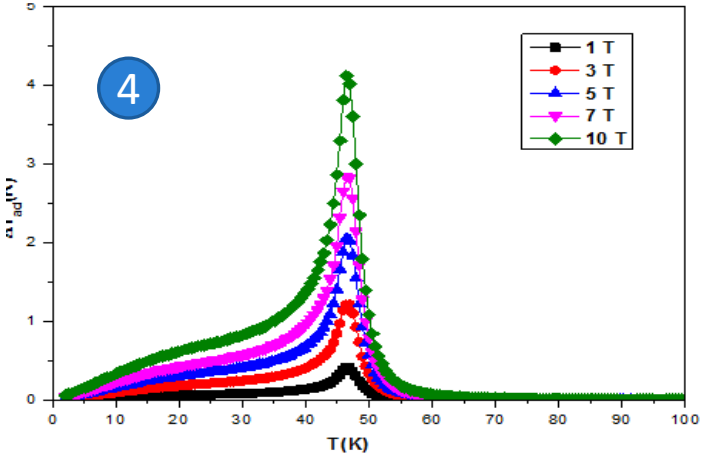
Multiferoic system: Magnetocaloric properties

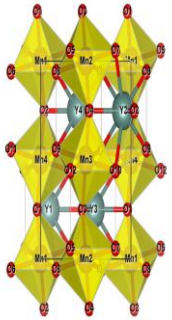








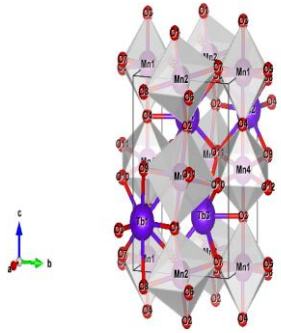




FZ Kassimi, H Zaari, A Benyoussef, A Rachadi, M Balli, A El Kenz Journal of Magnetism and Magnetic Materials 543, 168397

Multiferoic system: Magnetocaloric properties

$TbMnO_3$



Eg=0.56 meV

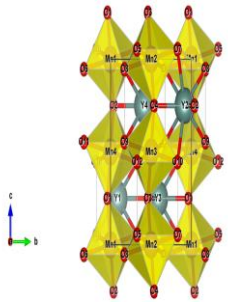
T_N=10 K
T_N=44.6K

H=7T

$-\Delta S$=13.74 J/Kg.K
ΔT_{ad} = 18.75 K
RCP= 420.71 J/Kg

Theoritical result

$YMnO_3$



Eg=0.59 meV

T_N= 46 K

H=7T

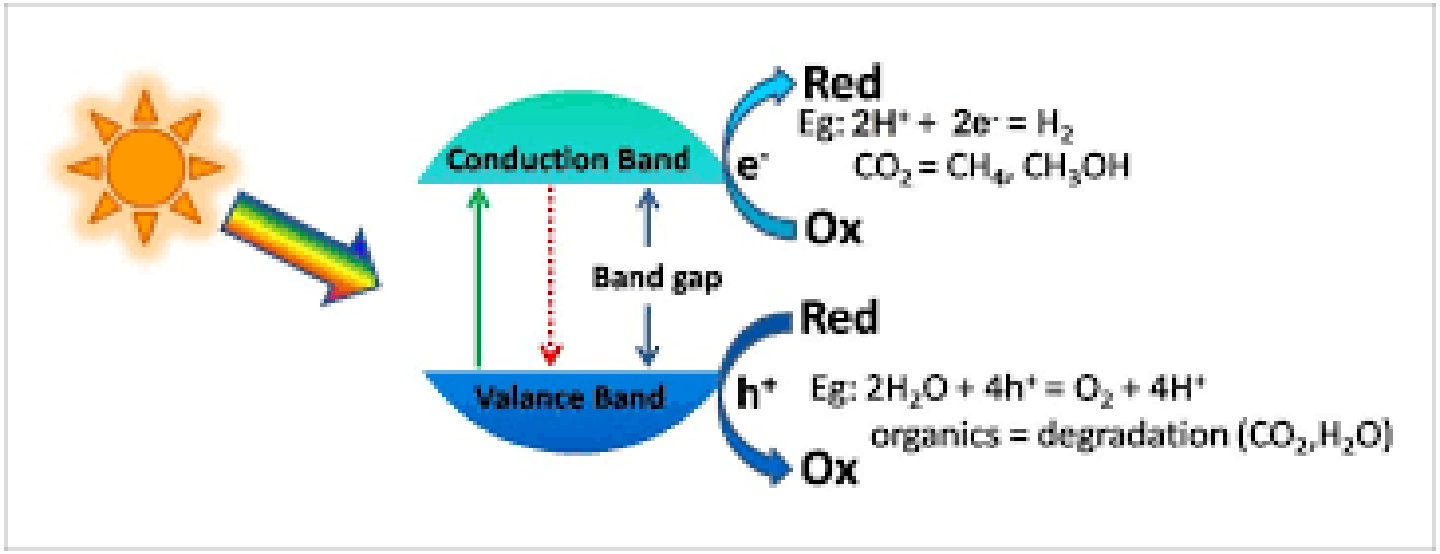
$-\Delta S$=12.64 J/Kg.K
ΔT_{ad} = 2.80 K
RCP= 80 J/Kg

Experimental result

Eg=0.5 meV

TbMnO3	YMnO3
T_1=42 K T_2=27K T_3=7 K	T_1=42 K
$-\Delta S$=18 J/Kg.K RCP= 390.7 J/Kg	-----

Photocatalysis



- Step 1: Absorption of a photon with energy greater than 1.23 eV.
- Step 2: Excitation of electrons and holes and separating them to migrate to the surface.
- Step 3: The adsorbed species (water) are reduced and oxidized by electrons and holes.

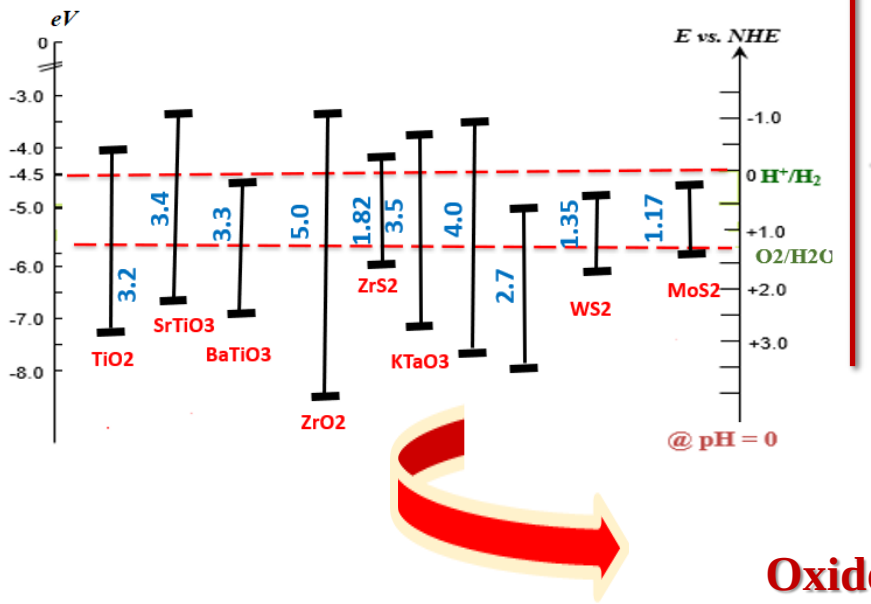
Selection criteria for the choice of catalyst materials

- The valence and conduction band edge were computing by the following equation:

$$E_{CB}^{0} = \chi(S) - E^{0} - \frac{1}{2}E_g \quad (1),$$

$$E_{VB}^{0} = E_{CB}^{0} + E_g \quad (2)$$

How to choose catalyst materials?



Dynamical and chemical stability

Band gap (1,9~ 3,5 eV)

Hign absorption

Efficency

Abondance

Oxide materials

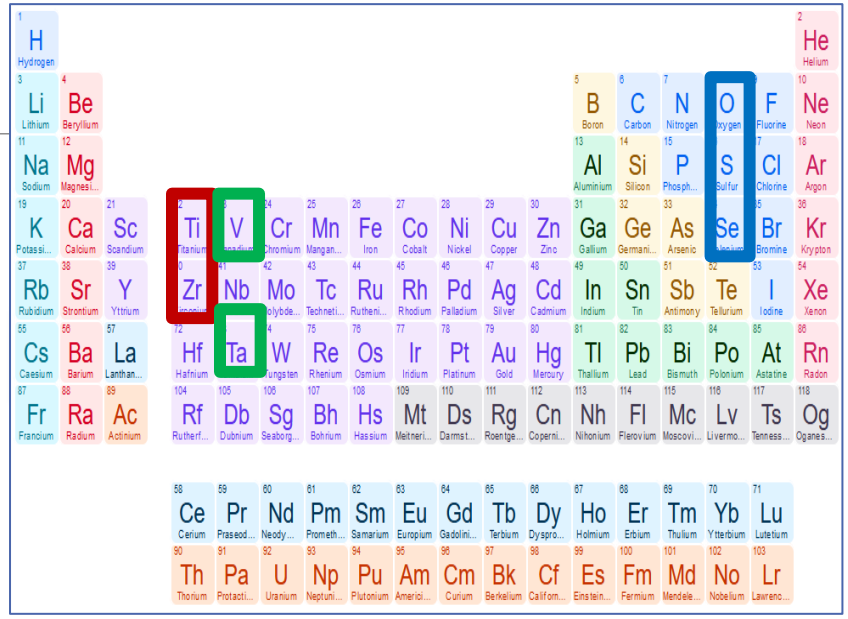
Selection criteria for the choice of catalyst materials

Oxide with large band gap

- **Eg = 3 ~ 3.6 eV**
- **Absorption in UV**

Reduce Eg + **Move to visible range**

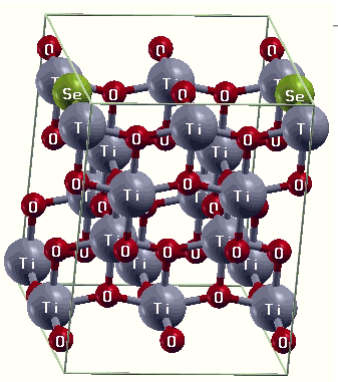
doping



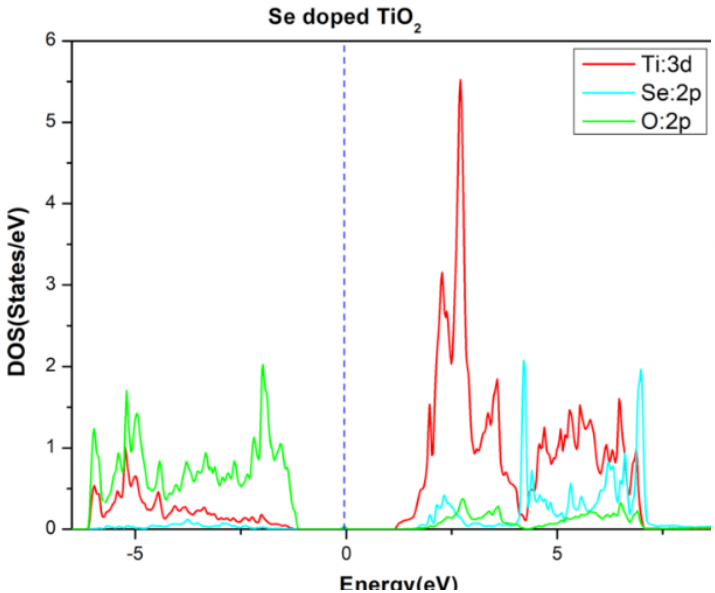
- Study the effect of monodoping and co-doping on stability, electronic, optical and photocatalytic properties.
- Control the bandgap by elements of group IV, V and chalcogens.
- Study the effect of Redox shift and its relationship with pH.

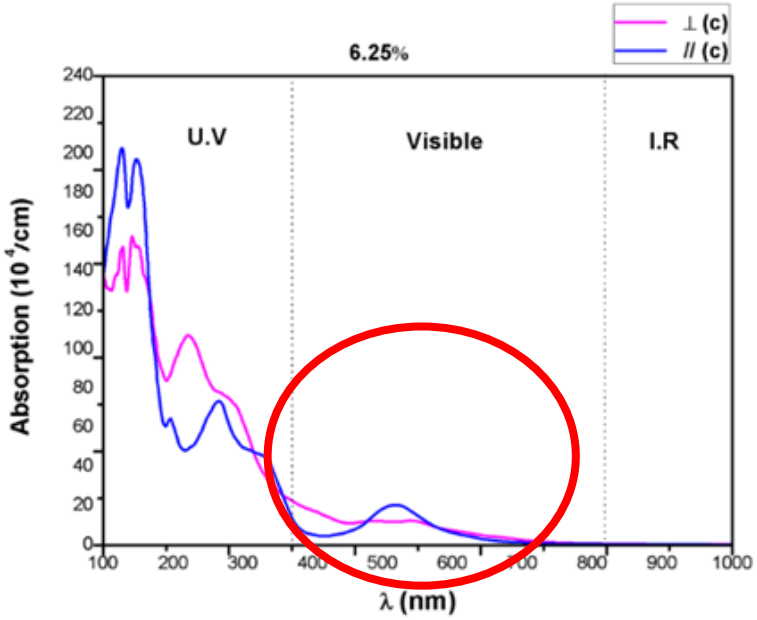
Optical properties and Photocatalysis

TiO2 doped with Se

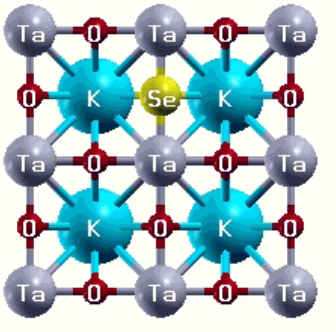


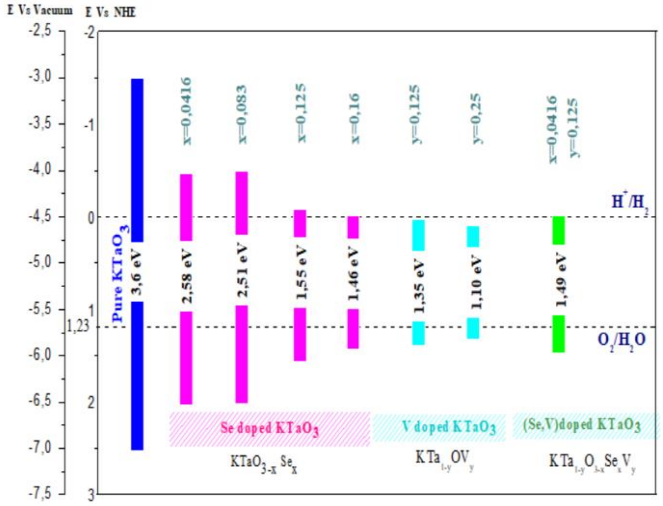
Eg= 1.70 eV

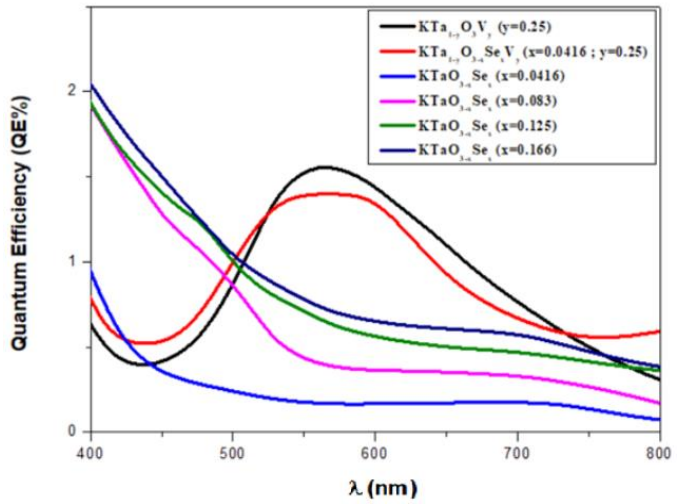




KTaO3 Eg=3eV







*F. Mezzat & al., Effect of metal and non metal doping of TiO_2 on photocatalytic activities: ab initio calculations, Opt. Quant. Electron. 53 (86) (2021).

Density Functionnel Theory :DFT??
More details

Density Functionnel Theory

Schoedinger's Equation

$$\left(-\frac{\hbar}{2m}\nabla^2 + V\right)\Psi(R_i, r_i) = \varepsilon.\Psi(R_i, r_i)$$

Kinetic Energy

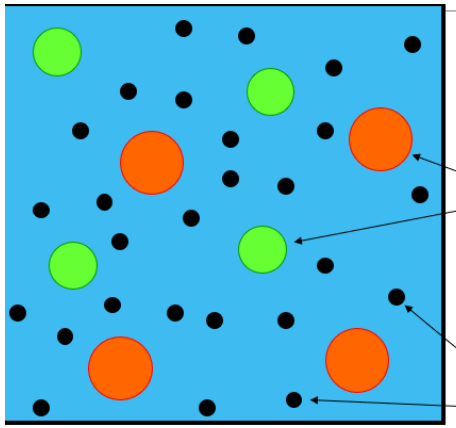
Potential Energy

Coulombic interaction
External Fields

Wave function

Energy levels

Hamiltonian operator



Very Complex many body Problem !!
(Because everything interacts)

First approximations

- Adiabatic (or Born-Openheimer)
  - Electrons are much lighter, and faster
  - Decoupling in the wave function

$$\Psi(R_i, r_i) = \theta(R_i).\phi(r_i)$$

- Nuclei are treated classically
  - They go in the external potential

Density Functionnel Theory

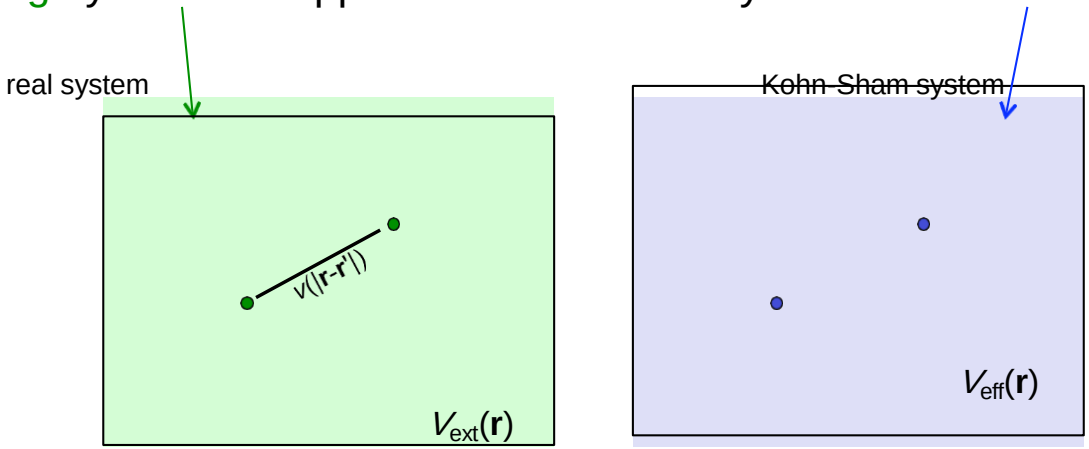
Density-functional theory based on Hohenberg-Kohn theorem (1964):

First statement: one-to-one correspondence $\rho_0 \Leftrightarrow v_{\text{ext}}$

Second statement: variational principle for ground-state energy: $E[\rho_0] \leq E[\rho]$

Kohn-Sham formalism (1965 – 50 year anniversary!):

Interacting system is mapped onto a fictitious system of non-interacting electrons.



$$\rho_0(\mathbf{r}) = \rho_0(\mathbf{r})$$

Density Functionnel Theory

Non interacting electrons: Same Density

=> Back to wave functions, but simpler this time (a lot more though)

(KS1) $$\left(-\frac{\hbar}{2m}\nabla^2 + V_{eff}\right)\varphi_i(r) = \varepsilon_i.\varphi_i(r)$$

(KS2) $$V_{eff}(\mathbf{r}) = V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \mu_{XC}[\rho](\mathbf{r})$$

(KS3) $$\rho(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2$$

N K.S. equations

(ONE particle in a box really)

Exchange correlation potential

Density Functionnel Theory :DFT??

The exchange and correlation energy functional

- **LDA**: The xc energy density of the inhomogeneous system in **r** is locally approximated with that of a homogeneous electron gas with density n(**r**)

$$E_{\mathrm{xc}}^{\mathrm{LDA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r}))$$

- **GGA:** include the dependence on the gradient of the density

$$E_{\mathrm{xc}}^{\mathrm{GGA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r})) = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r})) F_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

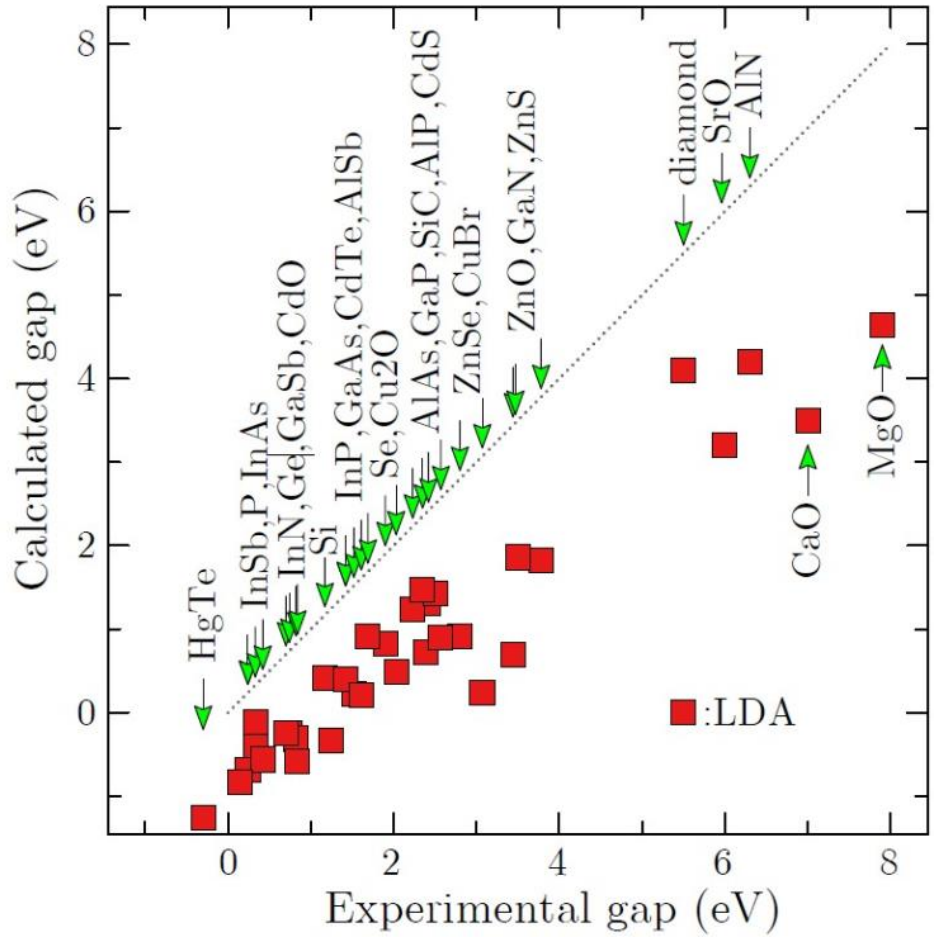
- **Meta-GGA**: include the dependency on the laplacian of the density and kinetic energy density

$$E_{\mathrm{xc}}^{\mathrm{mGGA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau) \qquad \tau = \frac{1}{2} \sum_i |\nabla \psi_i(\mathbf{r})|^2$$

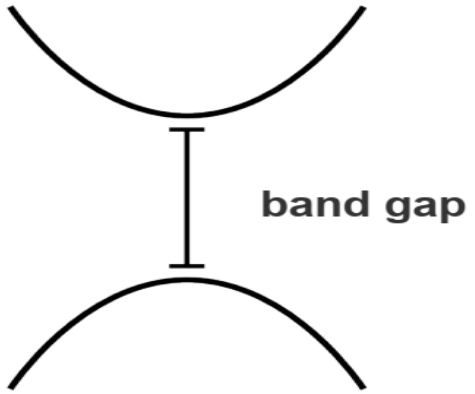
- **Hybrid functionals**: include a fraction of Fock exchange

$$E_{\mathrm{xc}}^{\mathrm{hyb}} = (1 - a_0) E_{\mathrm{x}}^{\mathrm{DFT}} + a_0 E_{\mathrm{x}}^{\mathrm{HF}} + E_{\mathrm{c}}^{\mathrm{DFT}}$$

Failure or success of DFT?



after van Schilfgaarde *et al* PRL **96** 226402 (2008)



Band gap problem!

Solution : corrective approach

DFT

Kohn-Sham Equations

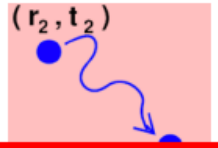
$$H_0(r)\varphi_{KS}(r) + v_{xc}(r)\varphi_{KS}(r) = \varepsilon_{KS}\varphi_{KS}(r)$$

Ground-state properties
KS gaps underestimate
the real QP ones

GW method

$$\varepsilon_i^{QP} \approx \varepsilon_i^{KS} + \langle \varphi_i^{KS} | \Sigma(\varepsilon_{nk}^{KS}) - V_{xc} | \varphi_i^{KS} \rangle$$

Electronic
(transport)
gaps



PES, IPES, ARPES, STS

Quasi-particle
Bandstructures

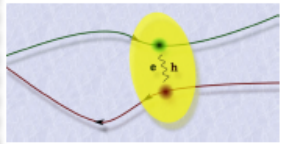
Bethe-Salpeter Equation (BSE)

$$[H_{el} + H_{hole} + H_{el-hole}]A_\lambda = E_\lambda A_\lambda$$

$$Abs(\omega) \propto \sum_\lambda \left| \sum_{vc} A_\lambda^{(vc)} \langle v|D|c \rangle \right|^2 \delta(E_\lambda - \omega)$$

ABSORPTION,
REFLECTIVITY, EELS,..

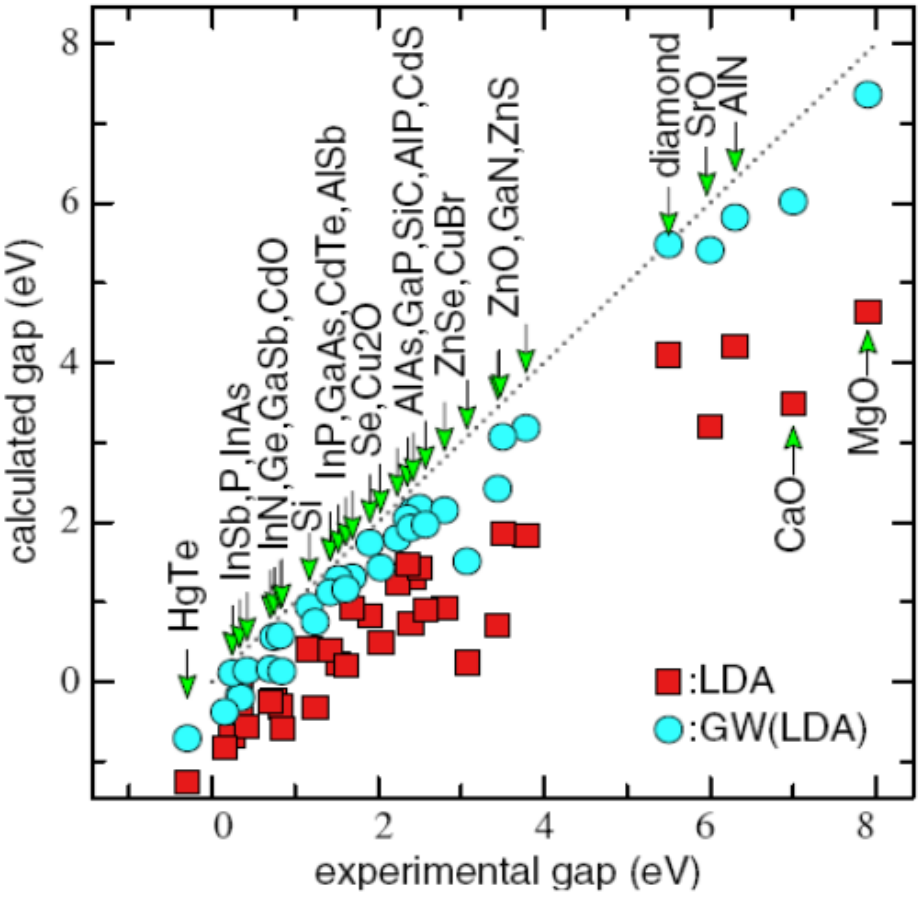
Optical
Gaps,
spectra



A_λ = excitonic eigenfunctions
E_λ = excitonic Eigenvalues

Solution : corrective approach

GW approximation gets good band gap



after van Schilfgaarde *et al* PRL **96** 226402 (2008)

No more a band gap problem !

Density Functionnel Theory :DFT??

Concepts when solving Schrödingers-equation

Treatment of spin

Non-spinpolarized
Spin polarized
(with certain magnetic order)

Form of potential

"Muffin-tin" MT
atomic sphere approximation (ASA)
pseudopotential (PP)
Full potential : FP

Relativistic treatment of the electrons

non relativistic
semi-relativistic
fully-relativistic

exchange and correlation potential

Hartree-Fock (+correlations)
Density functional theory (DFT)
Local density approximation (**LDA**)
Generalized gradient approximation (**GGA**)
Beyond LDA: e.g. **LDA+U**

$$\left[-\frac{1}{2}\nabla^2 + V(r)\right]\varphi_i^k = \varepsilon_i^k \varphi_i^k$$

Schrödinger - equation

non periodic
(cluster)
periodic
(unit cell)

Representation of solid

Basis functions

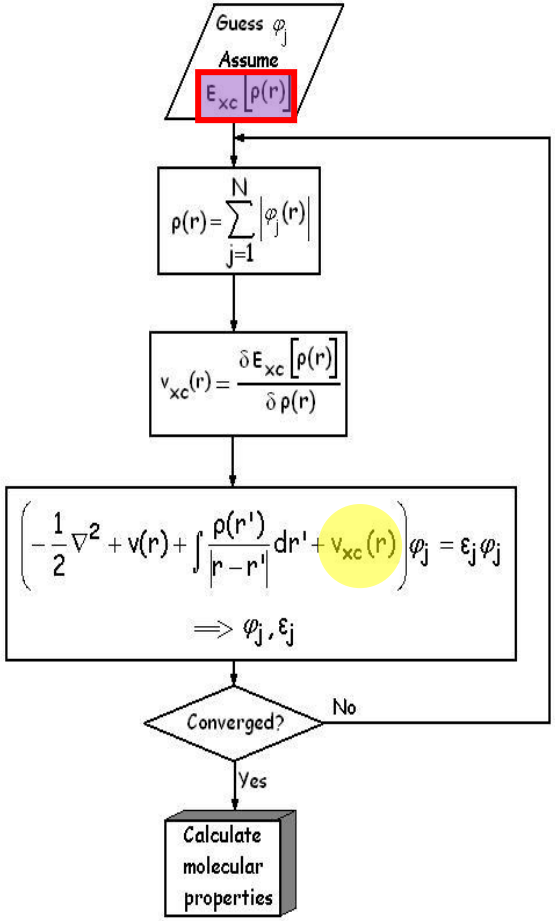
plane waves : PW
augmented plane waves : APW
atomic oribtals. e.g. Slater (STO), Gaussians (GTO), LMTO, numerical basis

WIEN2k: An APW+lo program for calculating the properties of solids.

P. Blaha, K.Schwarz, F. Tran, R. Laskowski, G.K.H. Madsen and L.D. Marks, J. Chem. Phys. 152, 074101 (2020)

Density Functionnel Theory :DFT??

Kohn-Sham Formalism



Kohn-Sham equations

$$\left(-\frac{1}{2}\nabla^2+v(r)+\int\frac{\rho(r')}{|r-r'|}dr'-\sum_i K_i(r)\right)\varphi_j=\varepsilon_j\varphi_j$$

Hartree-Fock equations

W. Kohn, L.J. Sham, *Phys. Rev.* **140**, A 1133 (1965)

Density Functionnel Theory :DFT??

Pseudopotential ⬌ (F)LAPW+lo

Plane-wave pseudopotentials

- Pseudopotentials ...
- ... enable usage of plane-wave basis.
- Basis set mathematically simple!!
  ➔ simple coding,
  ➔ easy to use.
- Basis set complete.

- Pseudization of wave functions.
- Localized states difficult to treat (oxides, *d* states, *f* states).
- No explicit treatment of core states (Frozen-core approximation).

(F)LAPW+lo

Full all-electron potential use

Augmented plane waves.

Complicated basis set!!
➔ complex codes,

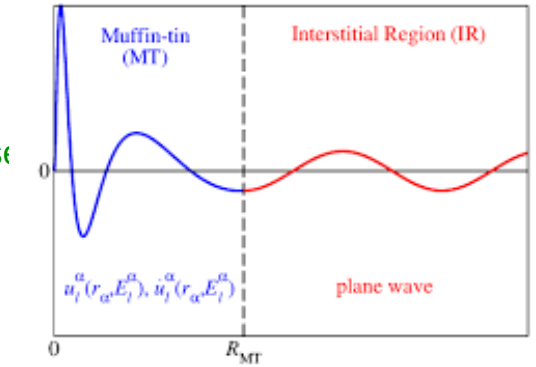
➔ more difficult to use.

Basis can be incomplete or become overcomplete.

- *True* all-electron wave functions.

Localized states efficiently treated (oxides, *d* states, *f* states).

Explicit treatment of core states.



Conclusion

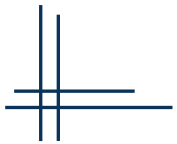
2D /bulk system:
Strucure, lattice parameter
…

Formalism : Full potential
Approximation: GGA, LDA, LDA+U…

Experimental result:

Theoretical results

Comparer les resultas theorique et experimental
Chercher une interpretation physique des resultas



Thank you for your attention

DFT: Summary

The ground state energy depends only on the electronic density (H.K.)

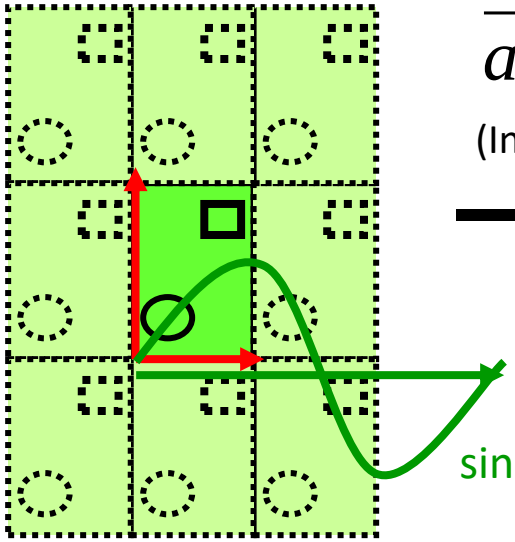
One can formally replace the SE for the system by a set of SE for non-interacting electrons (K.S.)

Everything hard is dumped into E_{xc}

Simplistic approximations of E_{xc} work !

LDA or GGA

Reciprocal space



$$\vec{a}_i \cdot \vec{b}_j = 2\pi.\delta_{ij}$$

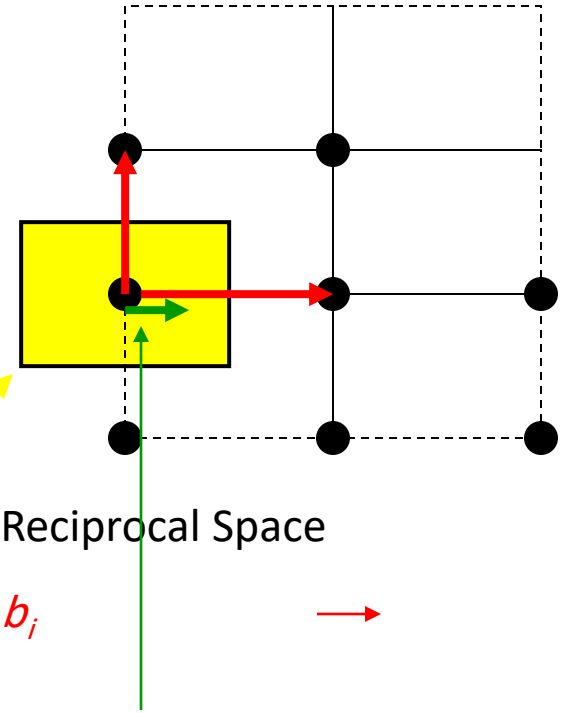
(Inverting effect)

sin(k.r)

Real Space

a_i

Brillouin Zone



Reciprocal Space

b_i

k-vector (or k-point)

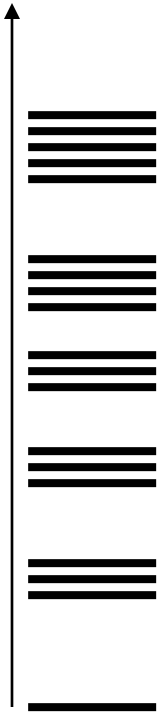
See X-Ray diffraction for instance

Also, Fourier transform and Bloch theorem

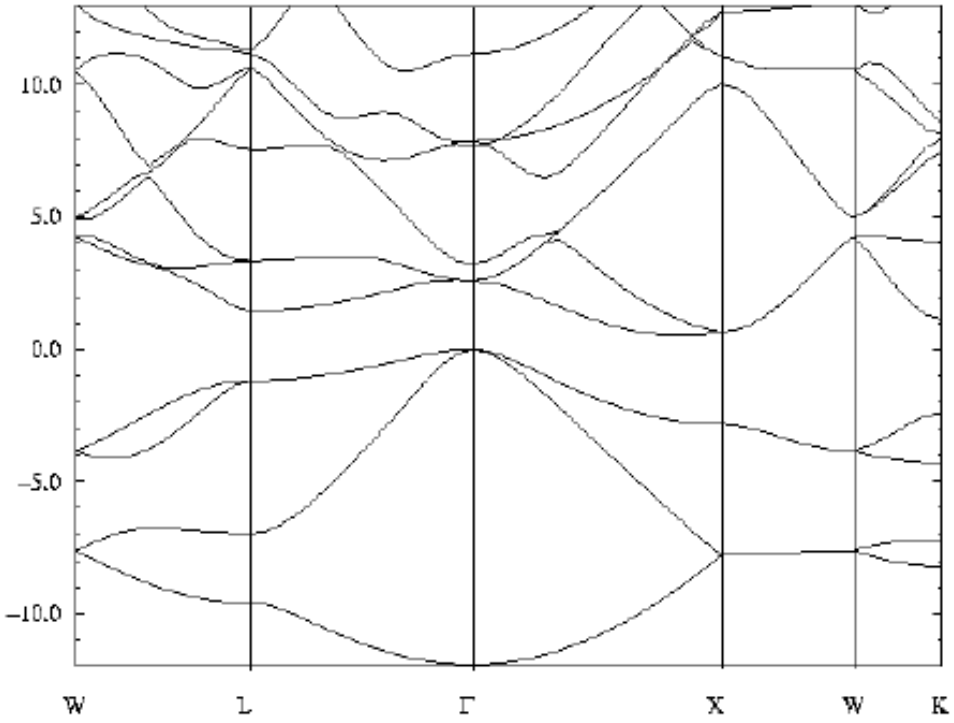
Band structure

E

Energy levels
(eigenvalues of SE)



Molecule



Crystal