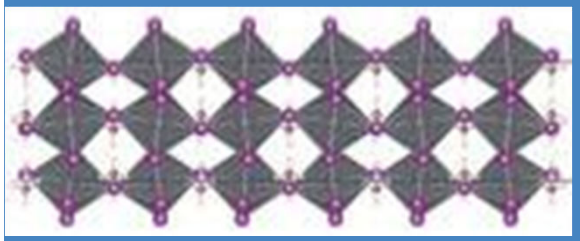
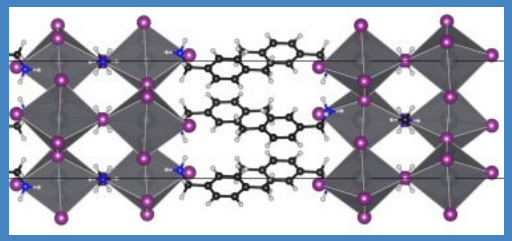
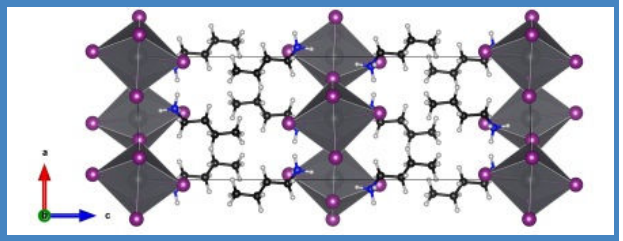
Fonctions Optiques pour les Technologies de l'informatiON

Optoelectronic properties of Halide Perovskite: needs for extremely demanding high performance computing

L. Pedesseau[1], M. Kepenekian[2], B. Traore[1], C. Katan[2], J. Even[1]

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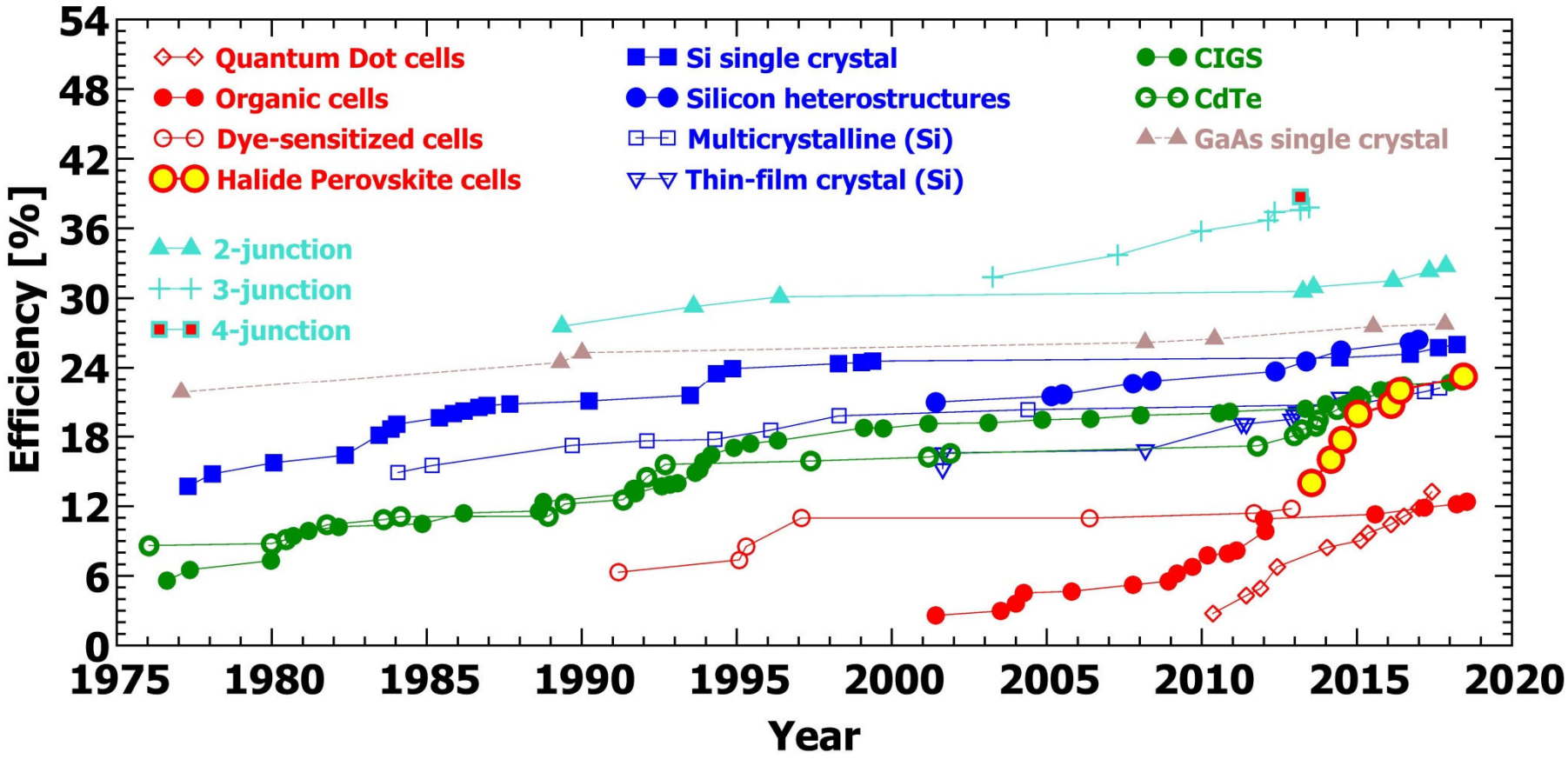
(2) Univ Rennes, ENSCR, CNRS, ISCR - UMR 6226, Rennes F-35000, France

Chercheurs dans les domaines de la Chimie et Physique

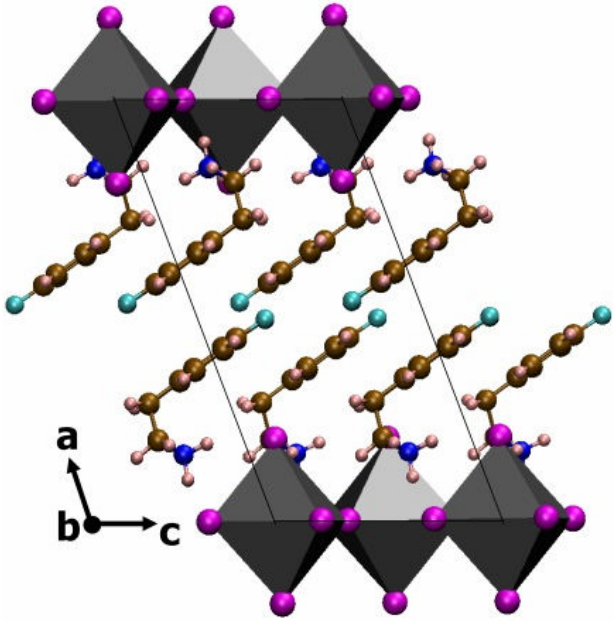
(Workshop CINES) **13th September**

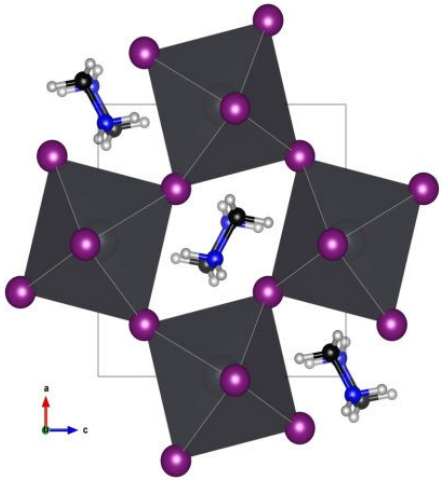
Introduction



Best research-cell efficiencies (NREL) chart (non-concentrator)

Introduction





$$\left(-\frac{\hbar^2}{2m_e}\nabla_j^2 + V_{KS}[n](r) - \epsilon_j\right)\varphi_j(r) = 0$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + V_{xc}(r)$$

$$V_{xc}(r) = \frac{\partial E_{xc}[n](r)}{\partial n(r)}$$

Spin-Orbit coupling

Van der Waals bonding

Band gap problem/Band structure accuracy

limits of current implementations of DFT

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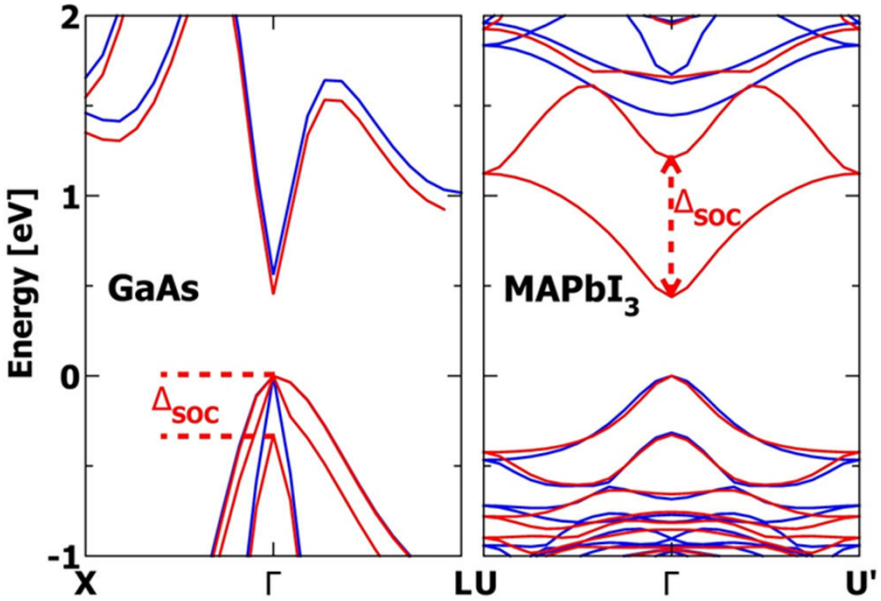
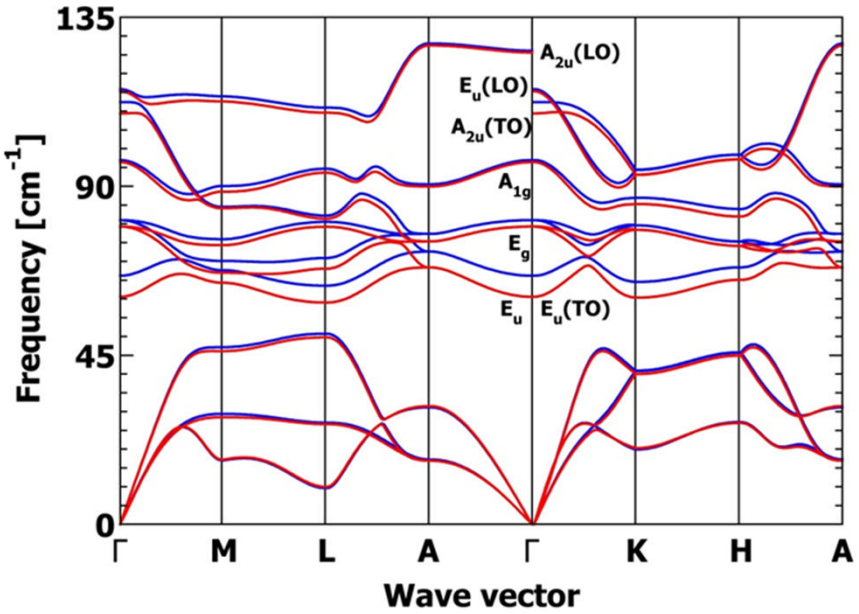
Introduction

Spin-Orbit Coupling (SOC)



Electronic band structures of GaAs (left, SG: F-43m) and $MAPbI_3$ (right, SG: Pnma) materials without (blue) and with (red) SOC. The energy of the valence band maximum is set at zero and the SOC effect is marked in red as Δ_{SOC}.



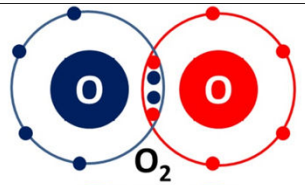
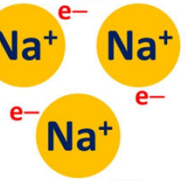
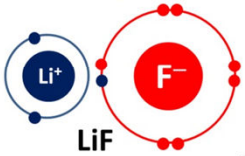
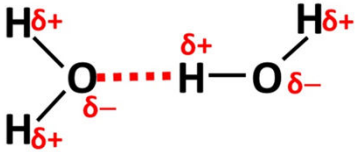
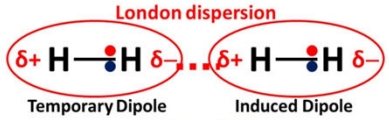
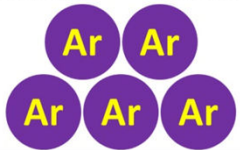
Phonon dispersion of 2H-PbI_2 material without (blue) and with (red) SOC

J Even et al. J. Phys. Chem. Let. 4, 2999, 2013 (left)
@HDR Pedesseau, 2019 (right)

The disadvantage of the SOC is the computational cost about double and the memory is increasing around 5% compared to a LDA/GGA functional.

Van der Waals bonding

Table 1: Comparison of the chemical bond such as covalent, metallic, ionic, hydrogen and van der Waals, schematic illustrations, and DFT methods.

Bond	Order of strength	Example of schematic illustration	DFT method
covalent	few eV		roughly DFT is enough
metallic	*few eV*		*roughly DFT is enough*
ionic	few eV		roughly DFT is enough
hydrogen	*~0.1eV*		*DFT+VDW*
"van der Waals" London dispersion (nonpolar)	~0.01eV		DFT+VDW
"van der Waals"	*~0.01eV*		*DFT+VDW*

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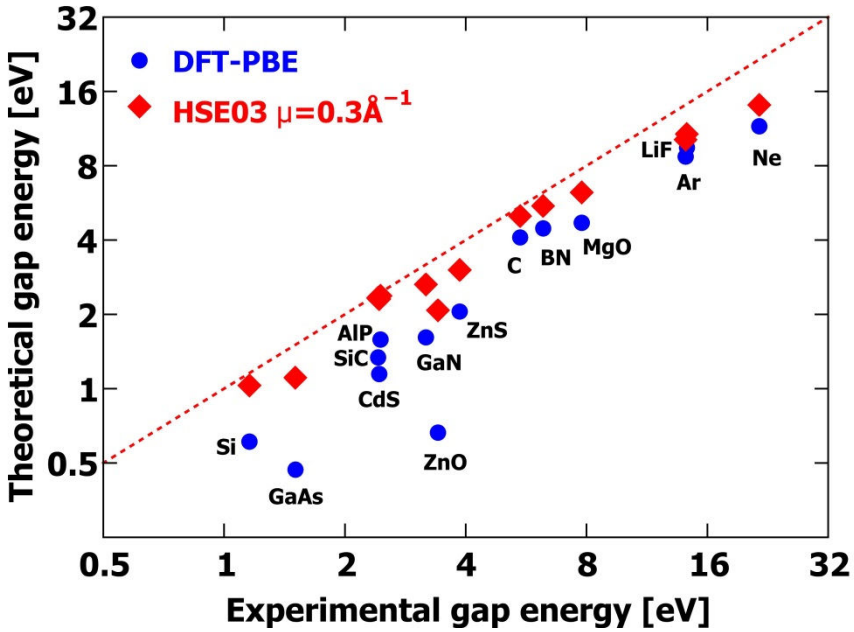
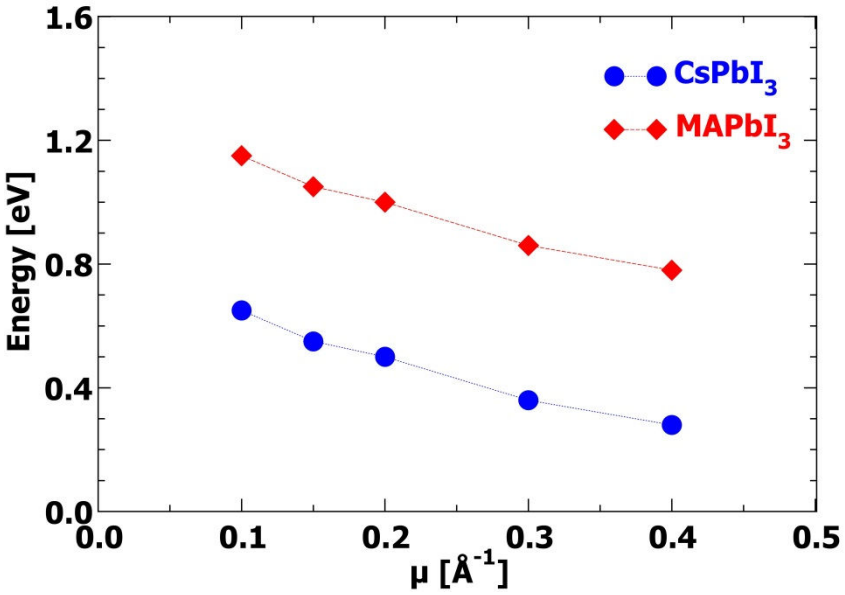
The disadvantage of the van der Waals corrections is the computational cost from 1.5 to 5 compared to a LDA/GGA functional

Introduction

i) Band gap problem/band structure accuracy



Band gaps for the DFT and HSE03[1] functional with μ=0.3Å^{-1}. The latter yields consistently improved band gaps. Source (reference[2])



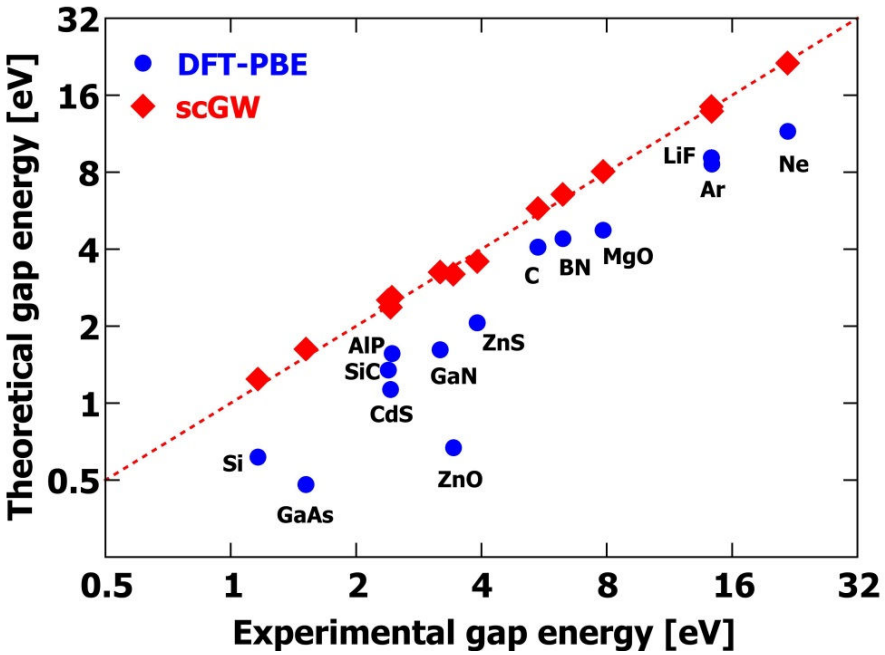
Band gap energies calculated in PBE including SOC effect plus HSE corrections as a function of μ, in Å^{-1}, the range separation parameter for $CsPbI_3$ and $MAPbI_3$ materials

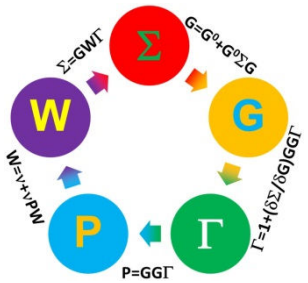
μ=0.2(0.3) is for HSE06(HSE03) respectively.
@HDR Pedesseau, 2019

1 Heyd, J. et al. J. Chem. Phys., 8207, 2003
2 Freysoldt, C. et al. Rev. Mod. Phys. 86, 253, 2014

The disadvantage of the hybrid functional is the computational cost from 10 to 100 and the memory demanding compared to a LDA/GGA functional.

ii) Band gap problem/band structure accuracy





DFT and scGW band gaps with attractive electron-hole interaction (vertex corrections in W). Source (reference[1]).

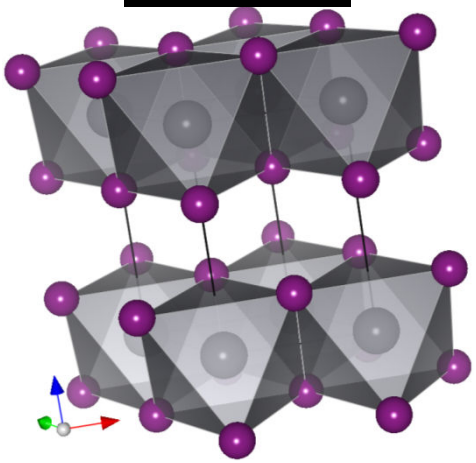
1 M Shishkin, et al. Phys. Rev. Lett. 99, 246403, 2007

In reality, this method is so demanding that it is very challenging to use it for more than 250 occupied and unoccupied bands and a dozen of k points in the Brillouin zone.

The disadvantage of the scGW corrections is the computational cost from 50 to 500 for each step and the memory demanding becomes huge compared to a LDA/GGA functional and even to hybrid functionals.

Introduction

2H-PbI_2

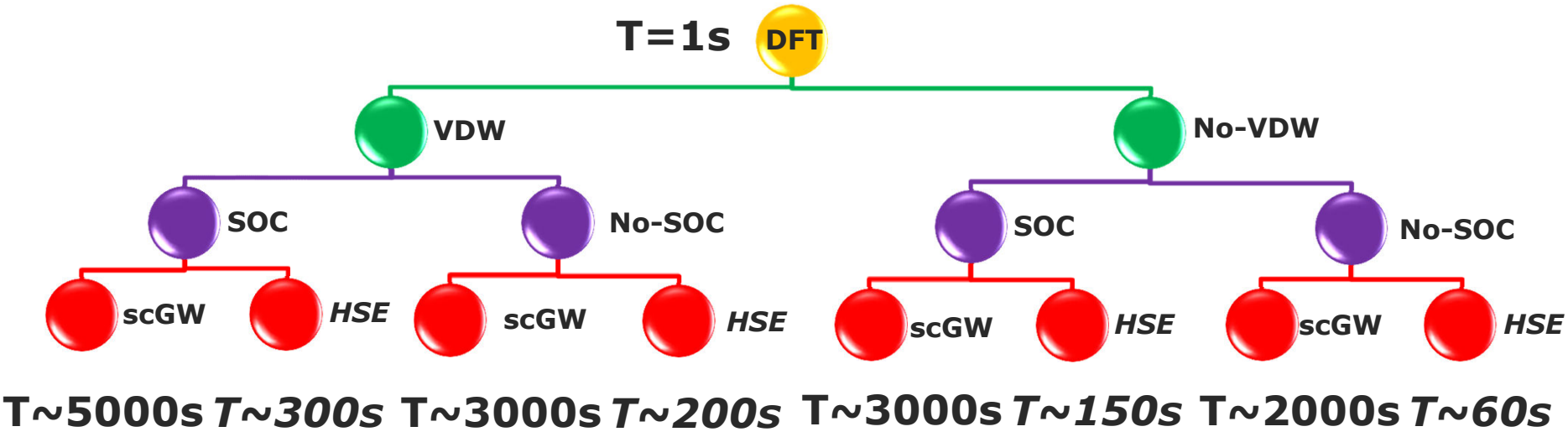


Comparison of the basic parameter of the simulation such as the total number of cpu, the memory, the execution time, and the gap energy for each method* applied to the 2H-PbI_2 material.

DFT	Total cpus	Memory used (Mb)	Time (s)	E^{A}_{gap}(eV)
PBE	144	189.3	12.1	1.74
PBE+SOC	144	198.0	24.4	1.10
PBE+SOC+HSE06	144	373.8	6247.3	1.87
PBE+SOC+sc-GW	456	3418.5	119940.4	2.52 (after 6steps)

* Monkhorst-Pack grid (6x6x4), cut-off energy 500eV. From experimental measurement[1] , the band gap energy E^{A}_{gap} = 2.32eV, at room temperature and 2.55 eV at 4 K.

1 Matuchova, M. et al J. Mater. Sci. Mater. Electron. 20, 289, 2009



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Usual job: VASP on OCCIGEN, CINES

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Total number of cores: TNC

1st PARAMETER, NPAR

NPAR : number of bands which divided NBANDS (adjusted NBANDS).

The ratio has to be in between 6 to 10 to be very efficient!

2nd PARAMETER, KPAR

KPAR : number of k-points which divided the total number of k-points.

In practice, the ratio has to be 2 or 4 to be very efficient!

Total number of cores: TNC=KPAR*NPAR,
Total number of nodes: TNN =TNC/24

UNUSUAL job: VASP on OCCIGEN, CINES

OCCIGEN, 1 node : 128 Go/24cores= **5.3Go per core**

- vasp insufficient virtual memory:

1st : Try to increase NPAR and add KPAR=2 ou 4

2nd : Increase "virtually" the memory per core by using a ratio "a" of the available core

a=2/3 of the available core :
128 Go/16cores= **8.0Go per core**

a=1/2 of the available core :
128 Go/12cores= **10.6Go per core**

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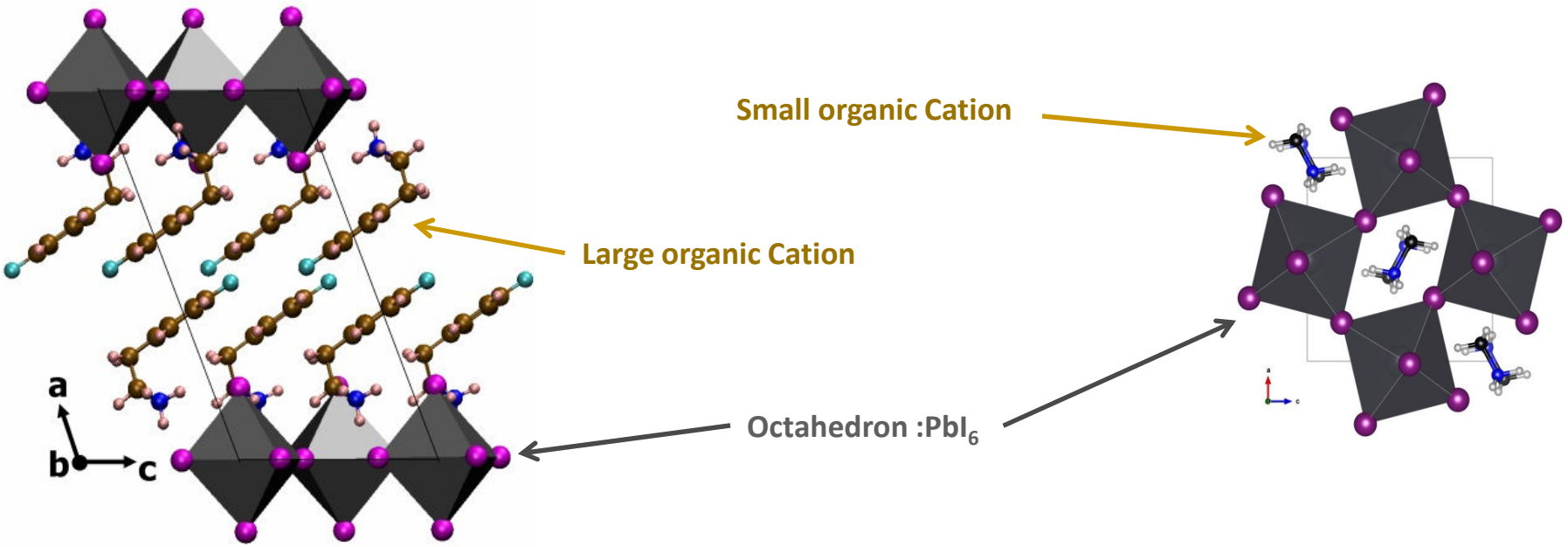
TNC=KPAR*NPAR,

Total number of nodes: TNN =TNC/(24*a)

Introduction

(pseudo) Cubic Hybrid Perovskites

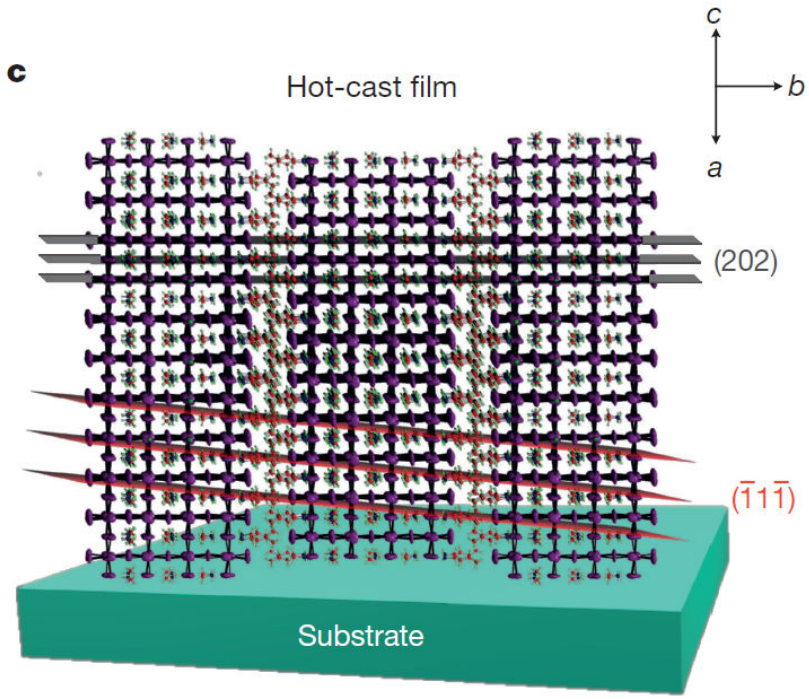


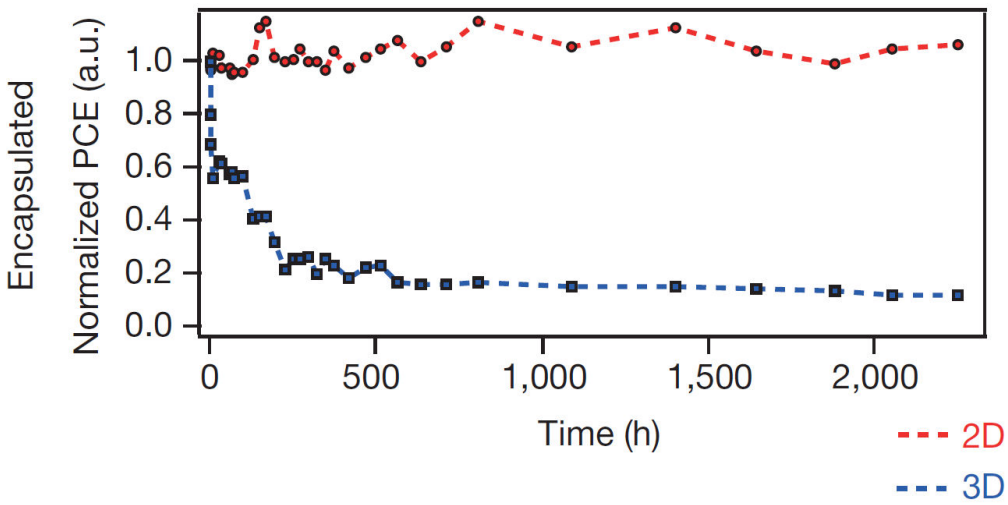
Our approach : adapt solid state physics concepts to hybrid Perovskites

- Optical transitions due to **Bloch states** localized within the inorganic lattice
- **Giant spin-orbit effect** on the conduction band (CB)
- **Strain effect** and loss of inversion symmetry (**Rashba effect**)
- Excitonic effect treated by perturbation : **Wannier exciton**

J Even et al
PRB 86, 205301, 2012
J Even et al
J Phys. Chem. C 118, 11566, 2014

2D Ruddlesden-Popper perovskite solar cells



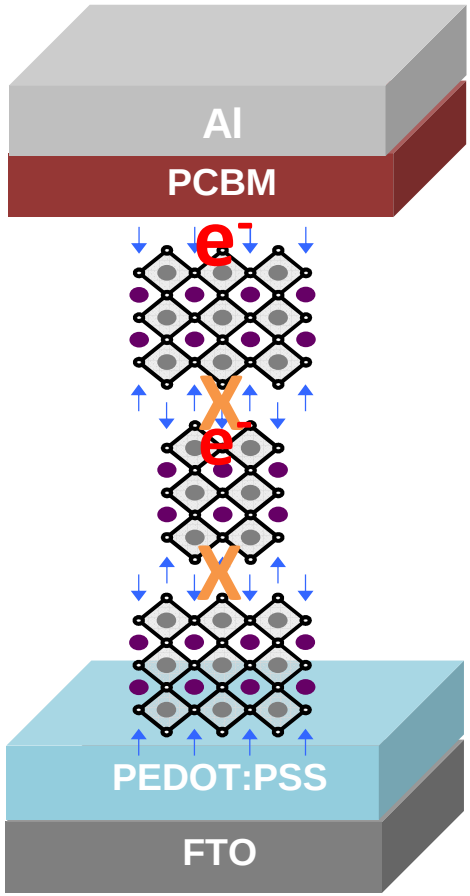


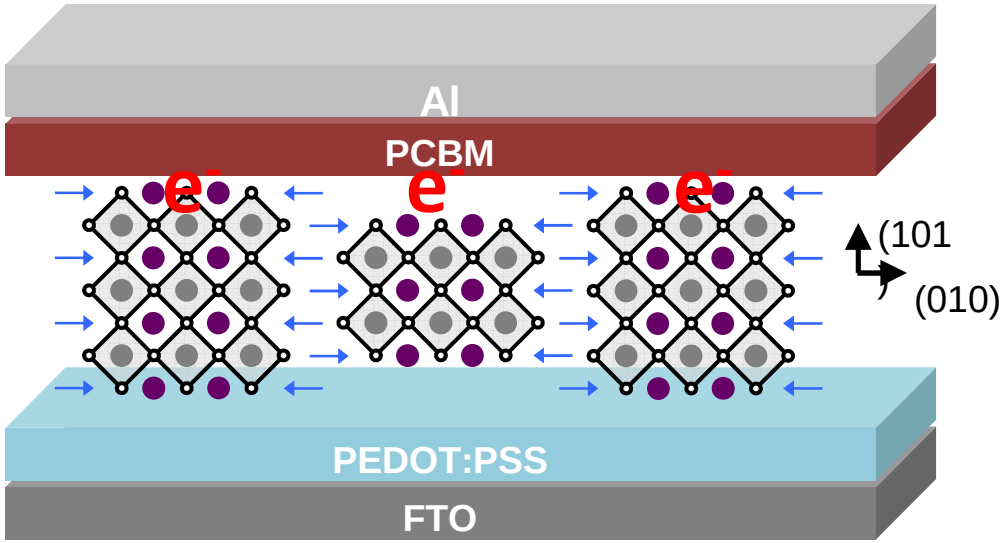
H. Tsai *et al. Nature* (2016)

2D RP perovskite for solar cells

Stability is improved

2D Ruddlesden-Popper perovskite solar cells



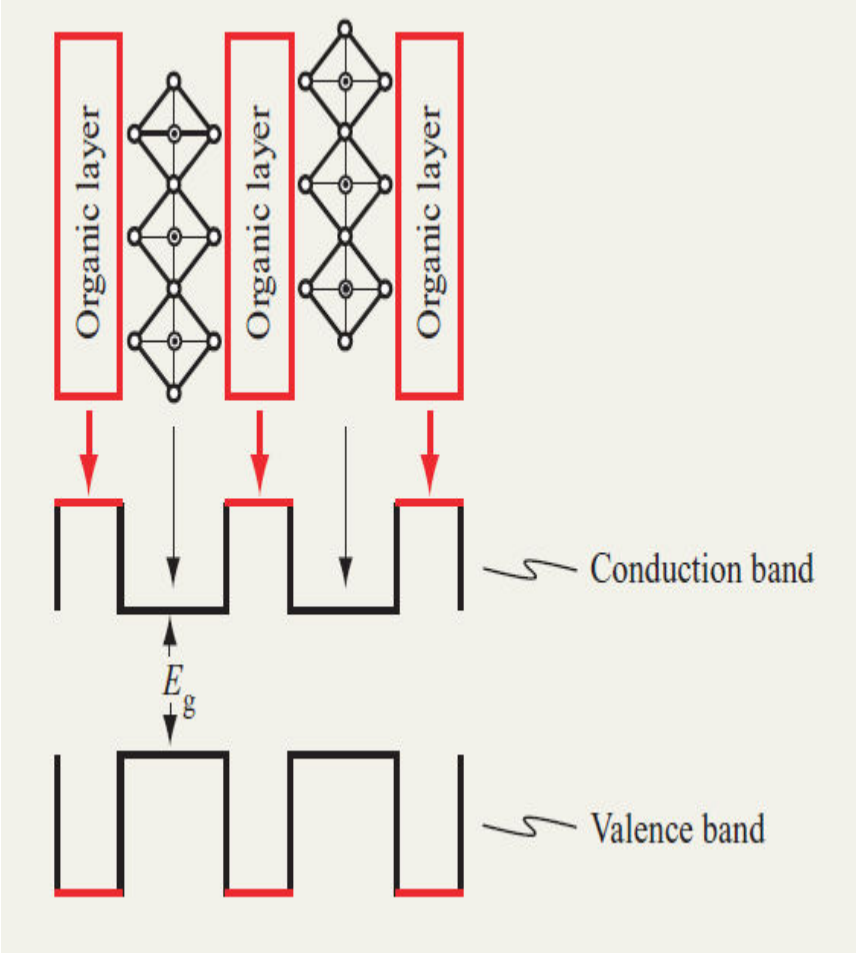


H. Tsai *et al. Nature* (2016)

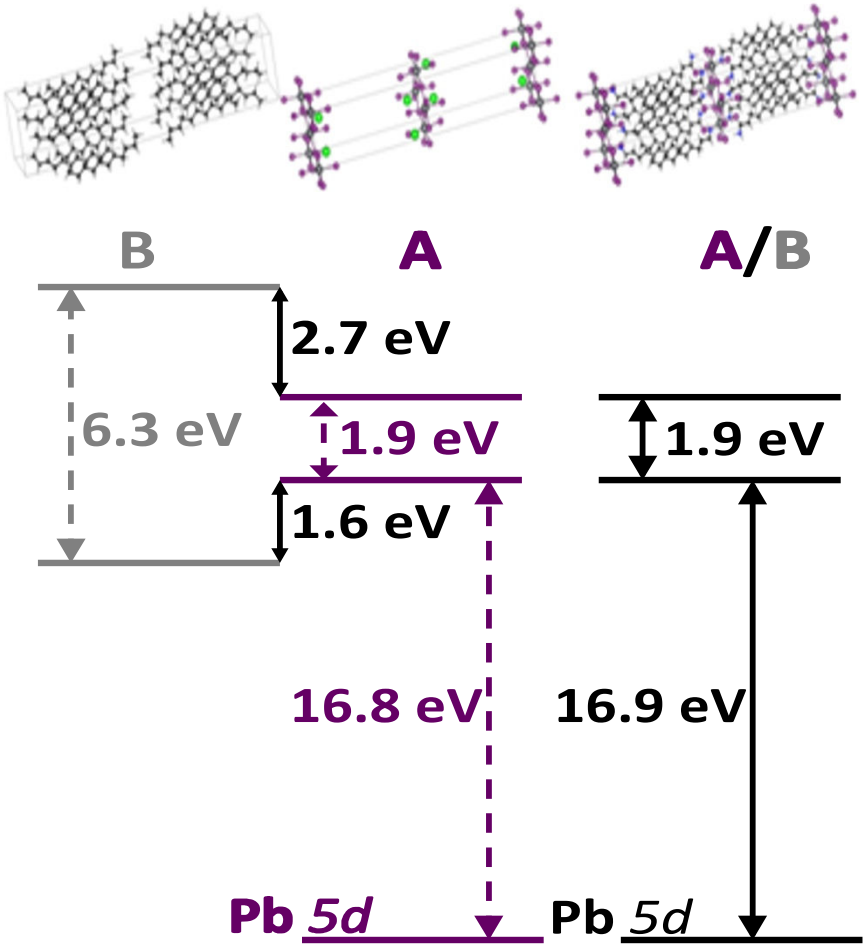
Flipped structure enhances carrier transport → better efficiency

Hybrid Perovskites : 2D / Quantum confinement

Type I confinement potential :
Schematic picture



Type I confinement potential :
quantitative analysis



D. Mitzi et al. IBM J. RES. & DEV. 2001

J. Even et al. Chem. Phys. Chem. 2014

B. Traore et al. ACS Nano 2018

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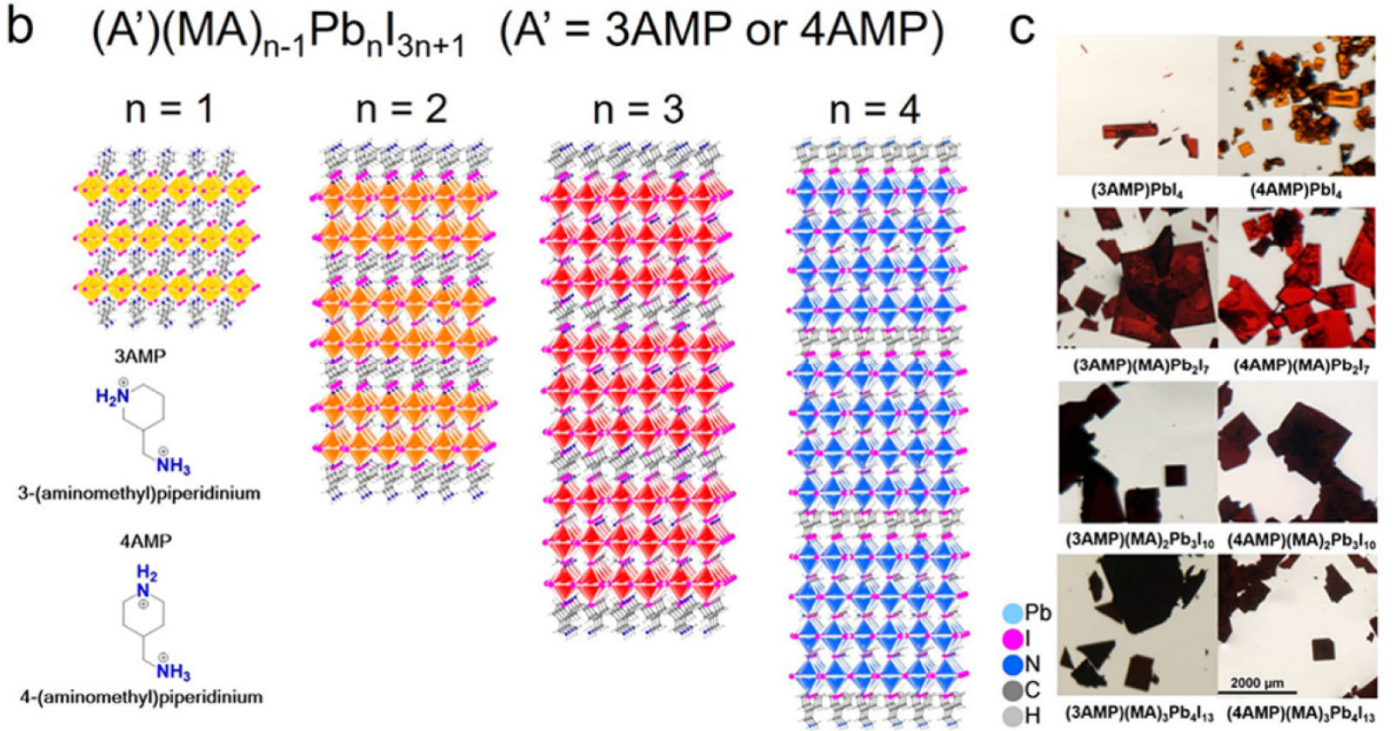
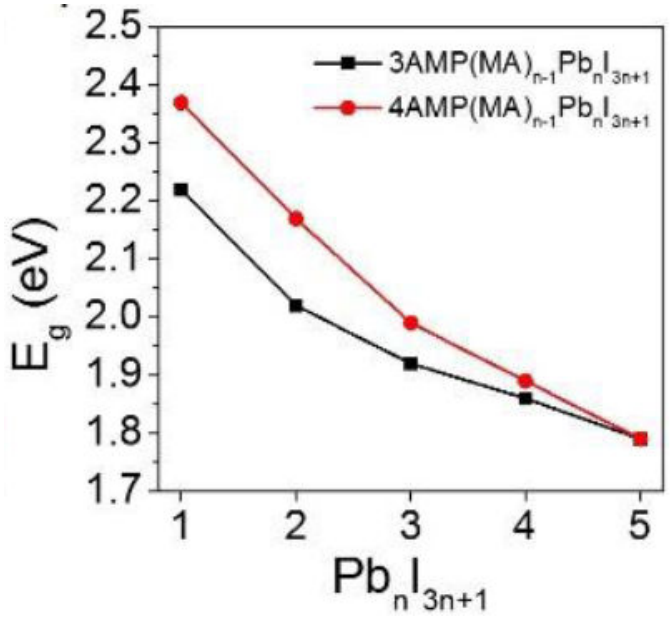
Hybrid Dion–Jacobson 2D Lead Iodide Perovskites

L. Mao et al.
JACS, 2018



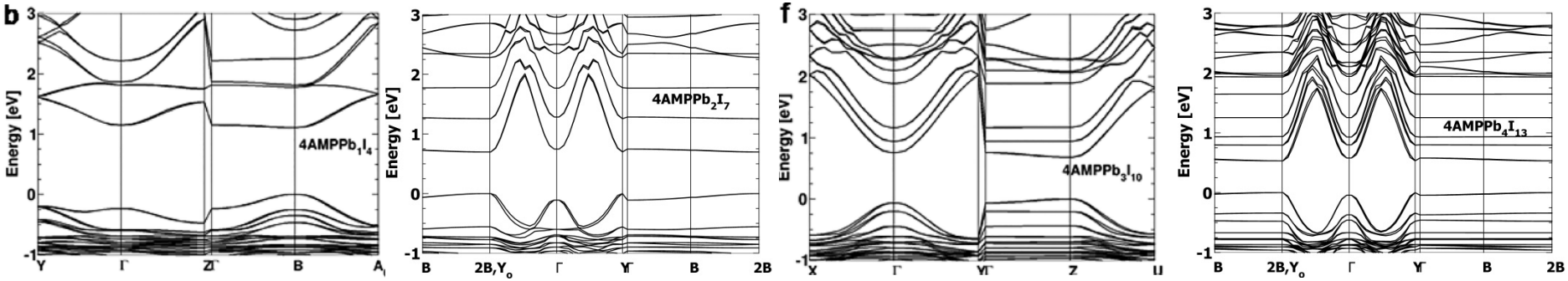
Hybrid Dion–Jacobson 2D Lead Iodide Perovskites



Exp. data

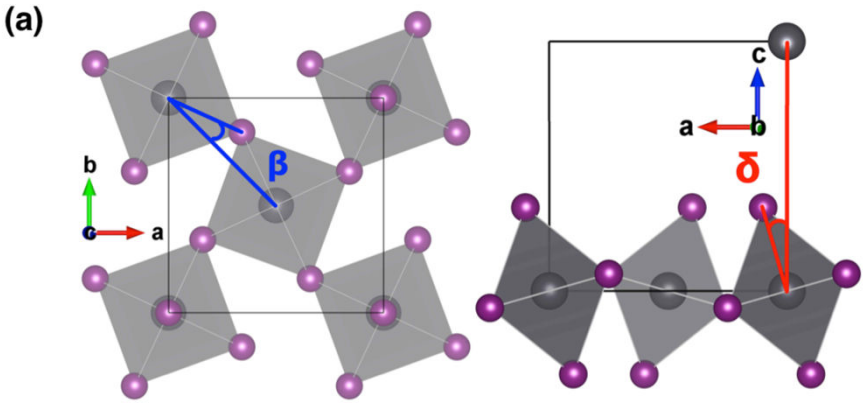
L. Mao et al.
JACS, 2018

Simulation



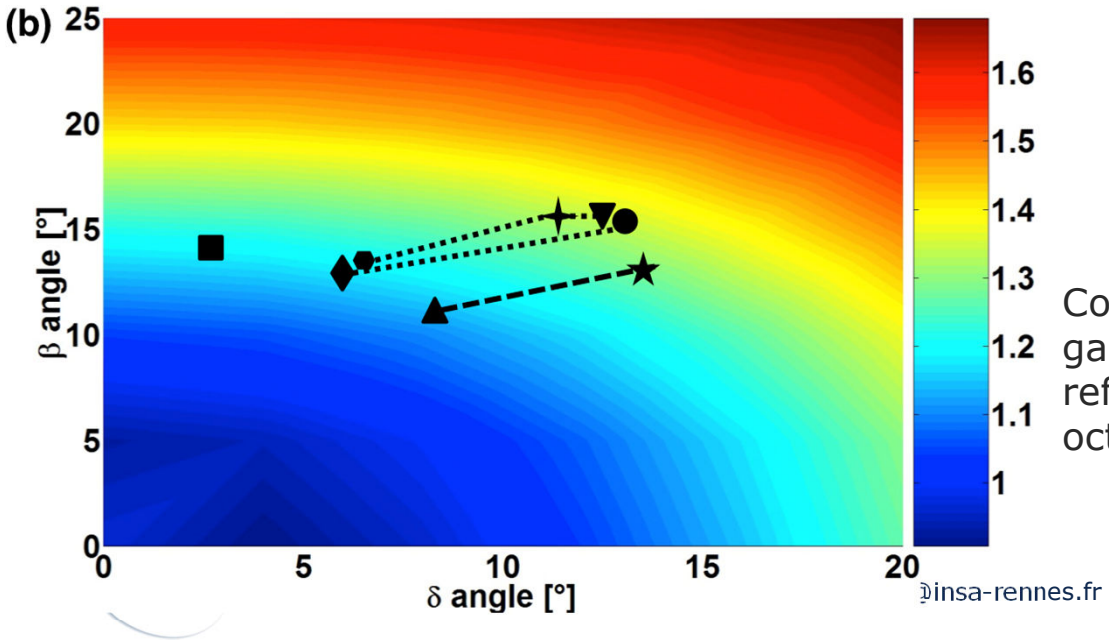
- Band gap energy decreases when N increases

Hybrid Perovskites : 2D and 3D materials



A distorted $(Cs)_2PbI_4$ reference structure with axial d^{ax}_{Pb-I} and equatorial d^{eq}_{Pb-I} distances fixed to 3.18 Å

Schematic representations of the in-plane projection of the M−M−X angle β and the δ angle chosen to characterize the in-plane and out-of-plane octahedral tilting.

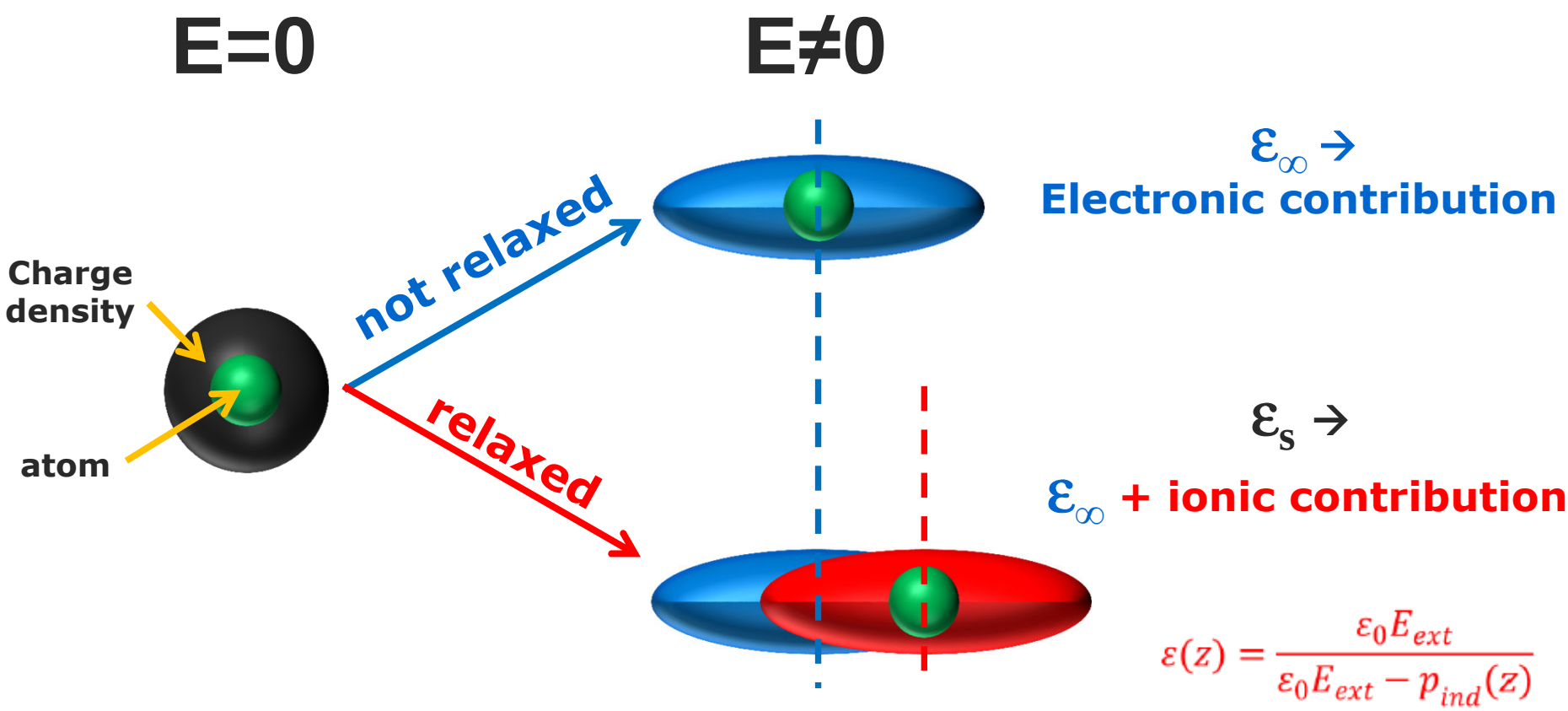


Color map of the computed electronic band gap including SOC for a distorted $(Cs)_2PbI_4$ reference structure as a function of β and δ octahedral tilting angles.

L. Pedesseau et al. ACS Nano, **2016**, 10 (11), pp 9776–9786

Dielectric confinement: from 3D to 2D HOPs

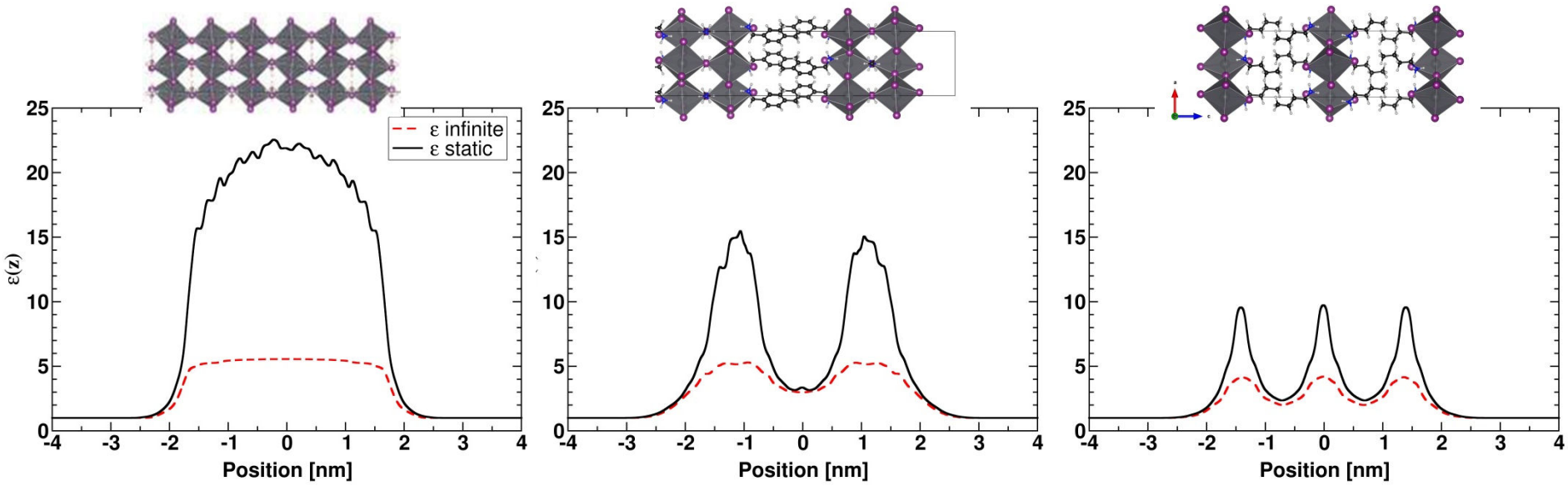
Schematic representation of the charge density response to E



Even et al., *PCCP* 16, 2014
Sapori et al. *Nanoscale*, 8, 2016

ε_s → **Electronic + ionic contribution**

Dielectric confinement: from 3D to 2D HOPs



3D to 2D

ε_{static} → Electronic + ionic contribution

D. Sapori et al. Nanoscale, 2016

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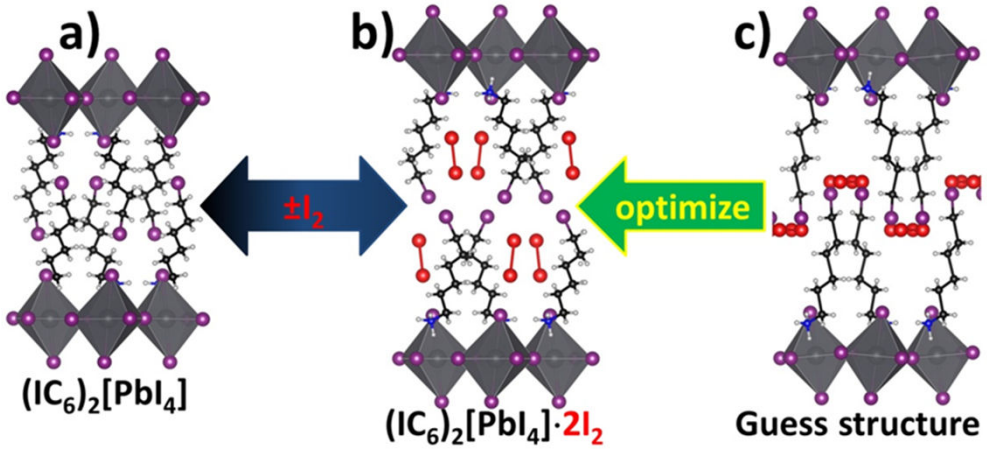
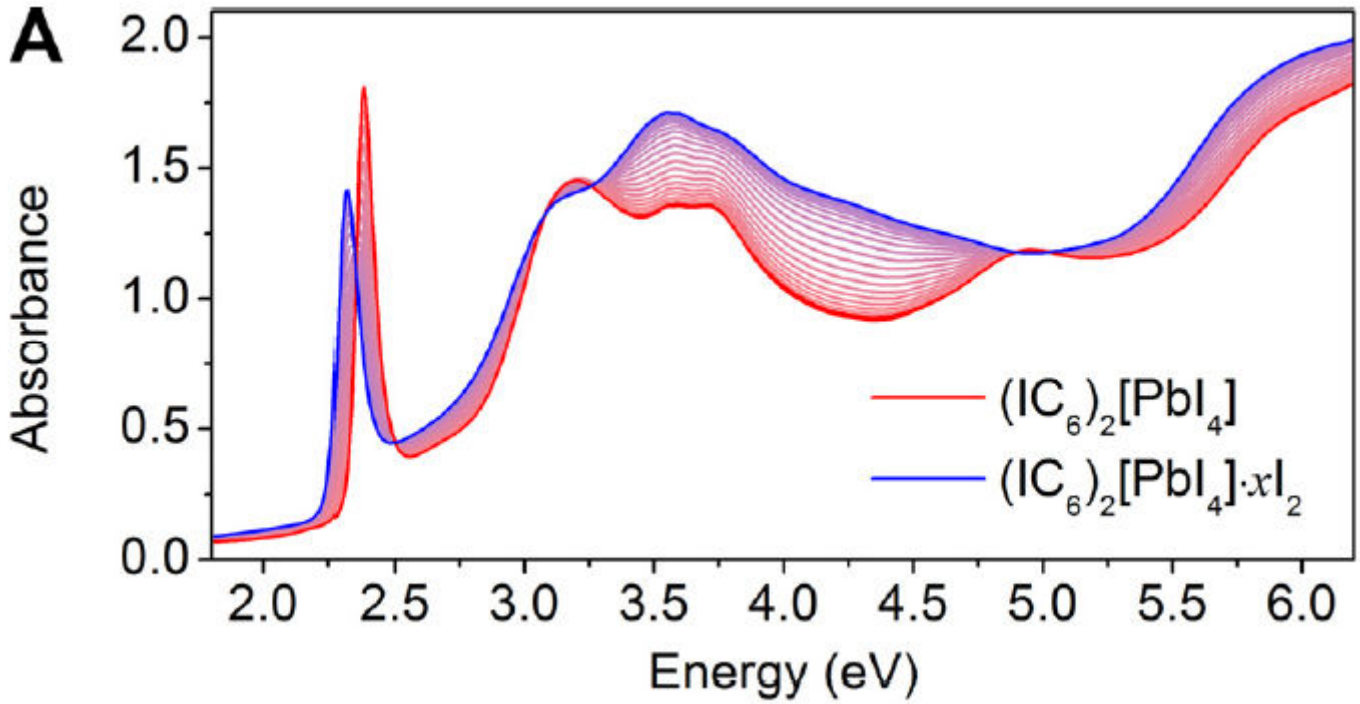
2D Halide Perovskite: intercalation effect of I_2



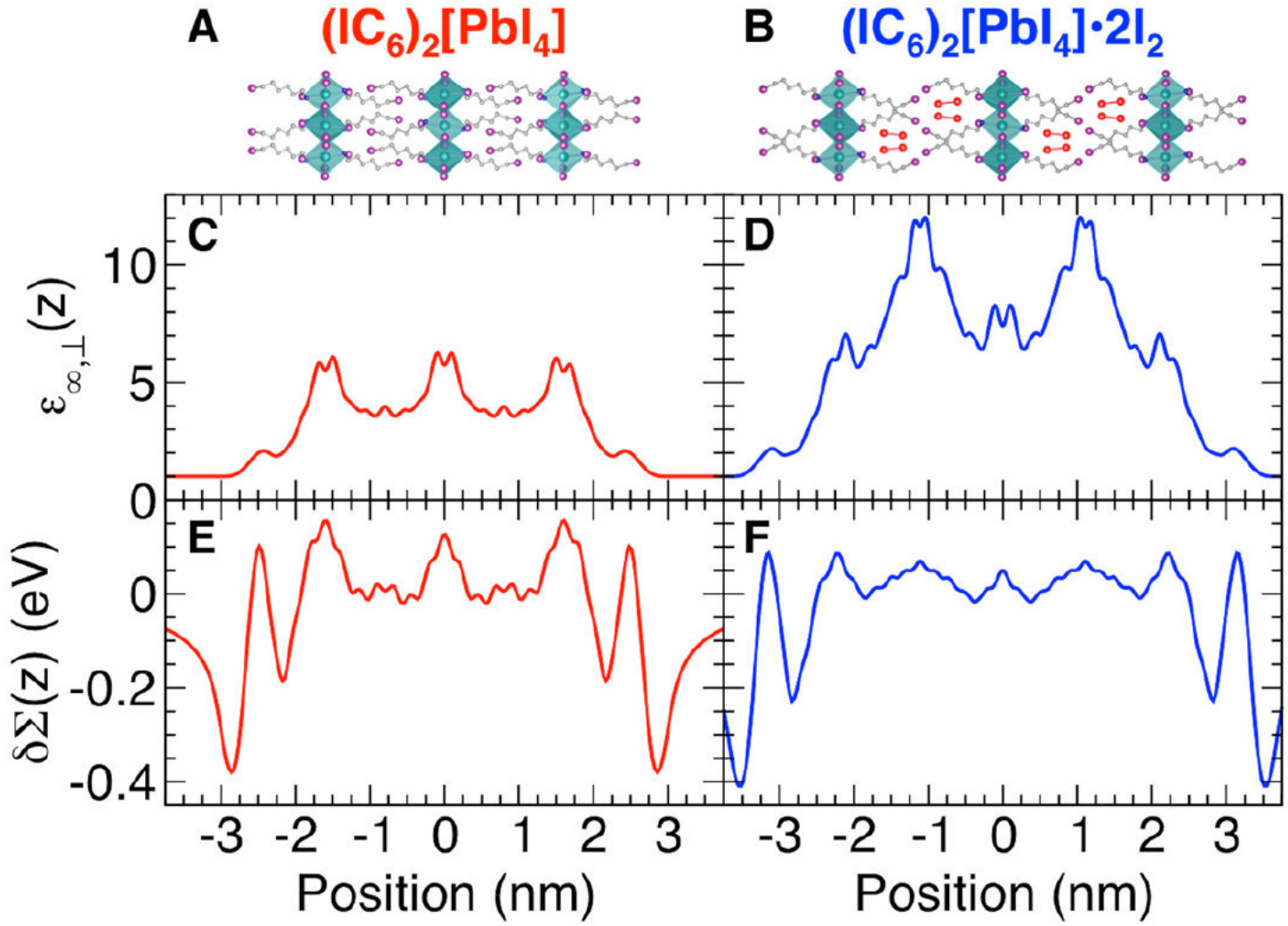
M. Smith et al. Chemical science 8 (3), 1960-1968, 2017



Intercalation of I_2 decreases the Absorbance!

2D HOP: intercalation effect of I_2

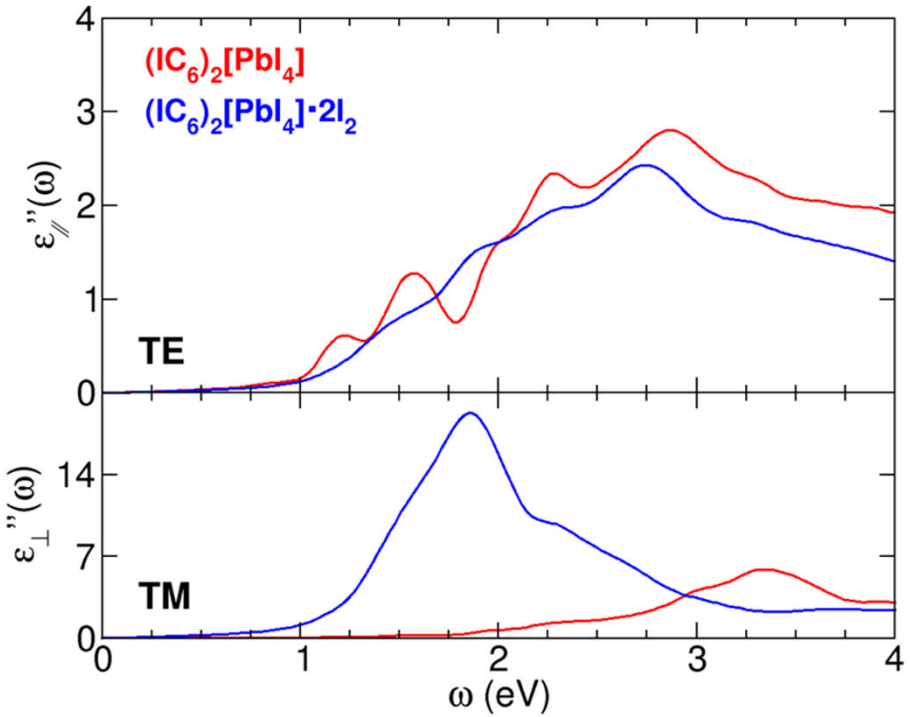
M. Smith et al. Chemical science 8 (3), 1960-1968, 2017

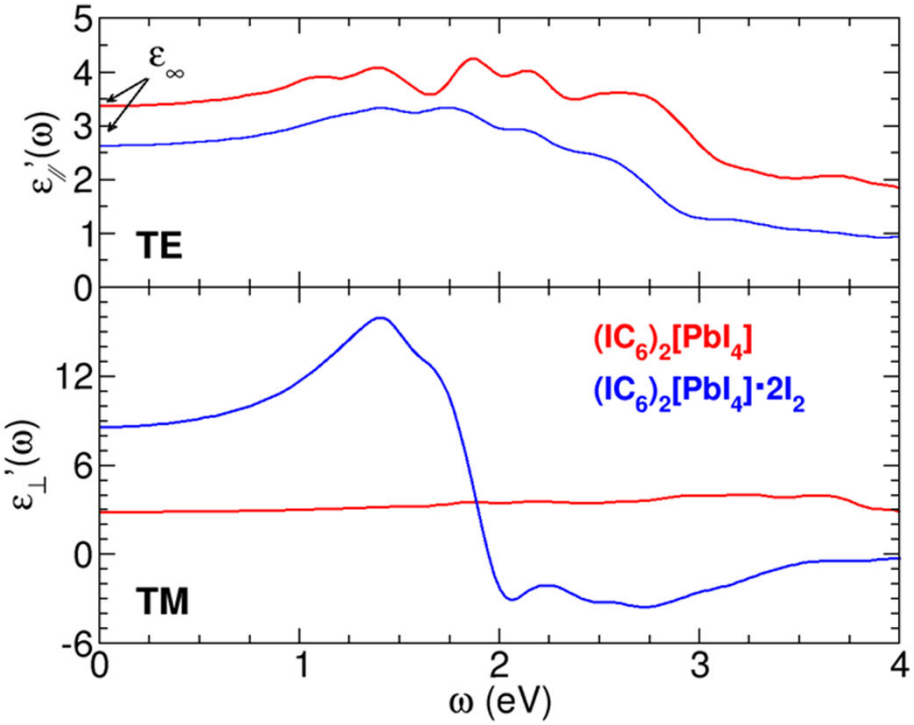


Intercalation of I_2 increases the organic dielectric part

2D HOP: intercalation effect of I_2

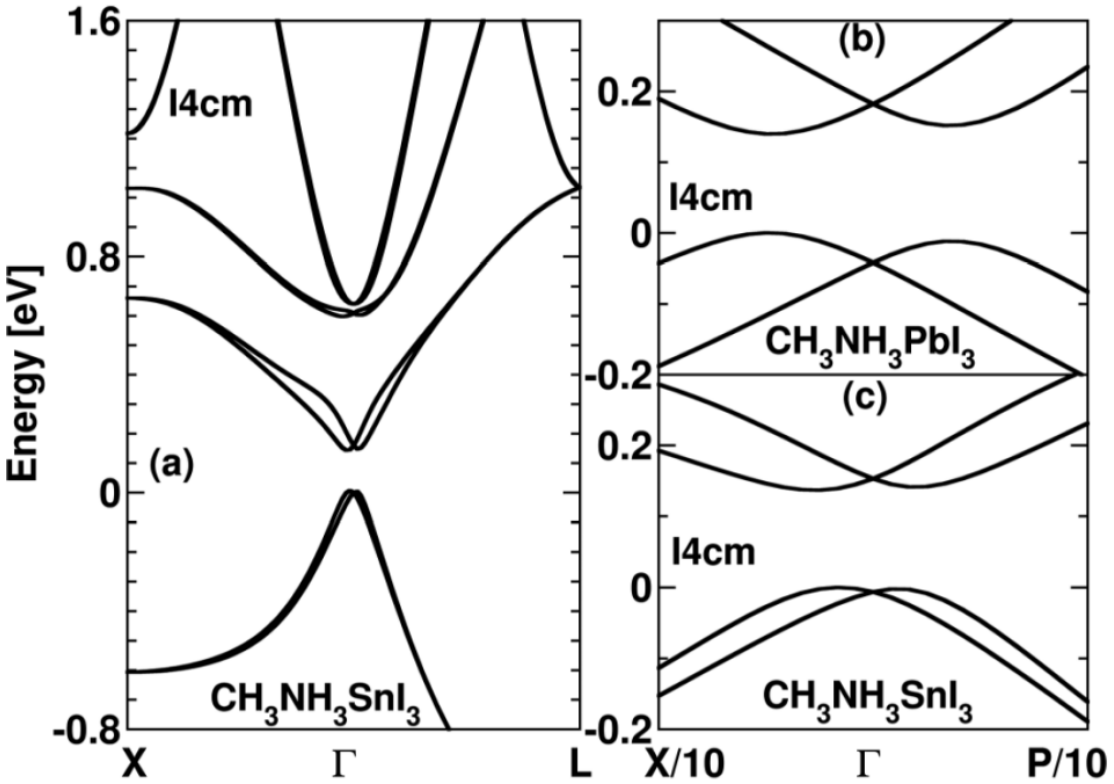
M. Smith et al. Chemical science 8 (3), 1960-1968, 2017





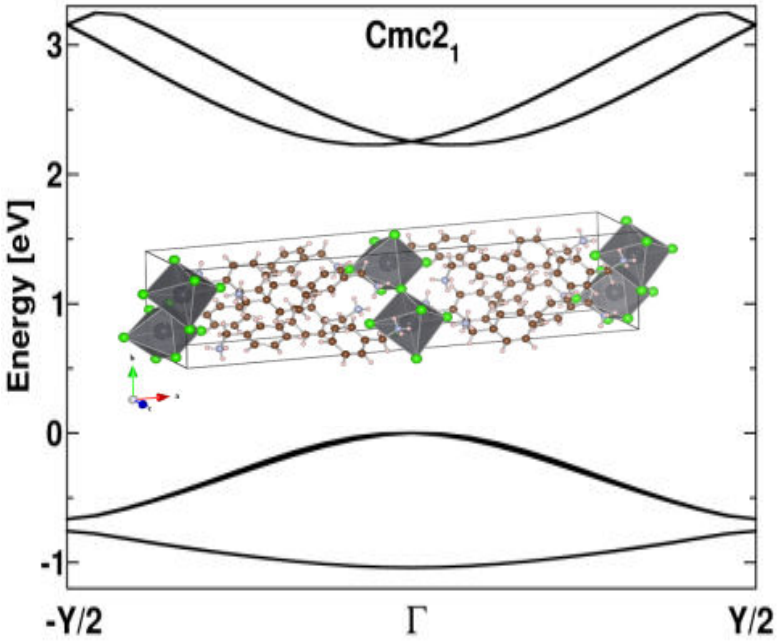
Intercalation of I_2 dramatically modifies the dielectric function orthogonal to the layers.

Hybrid Perovskites for spintronics ?



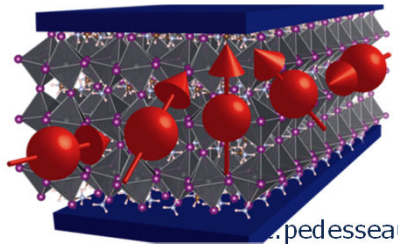
$CH_3NH_3PbI_3$ & $CH_3NH_3SnI_3$

First prediction in :
J. Even et al, *Phys. Status Solidi RRL* 2014



$(C_6H_5CH_2NH_3)_2PbCl_4$

M. Kepenekian *et al.*, *ACS Nano, 9, 11557, 2015*



spin-splitting controlled by an external field

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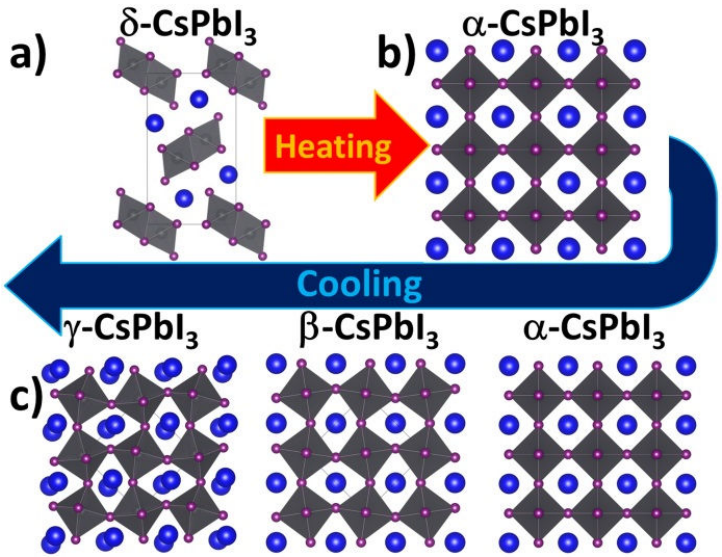
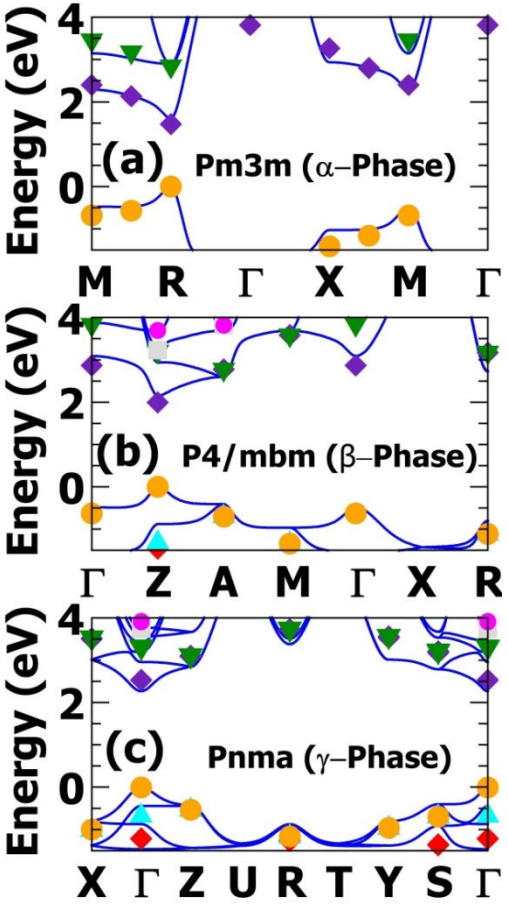
Beyond DFT → Tight-Binding modeling

A Marronnier et al. ACSnano 12, 3477, 2018



i) Cubic phase at high temperature (T > 360°C)

ii) Orthorhombic yellow phase at room temperature, very hard to avoid



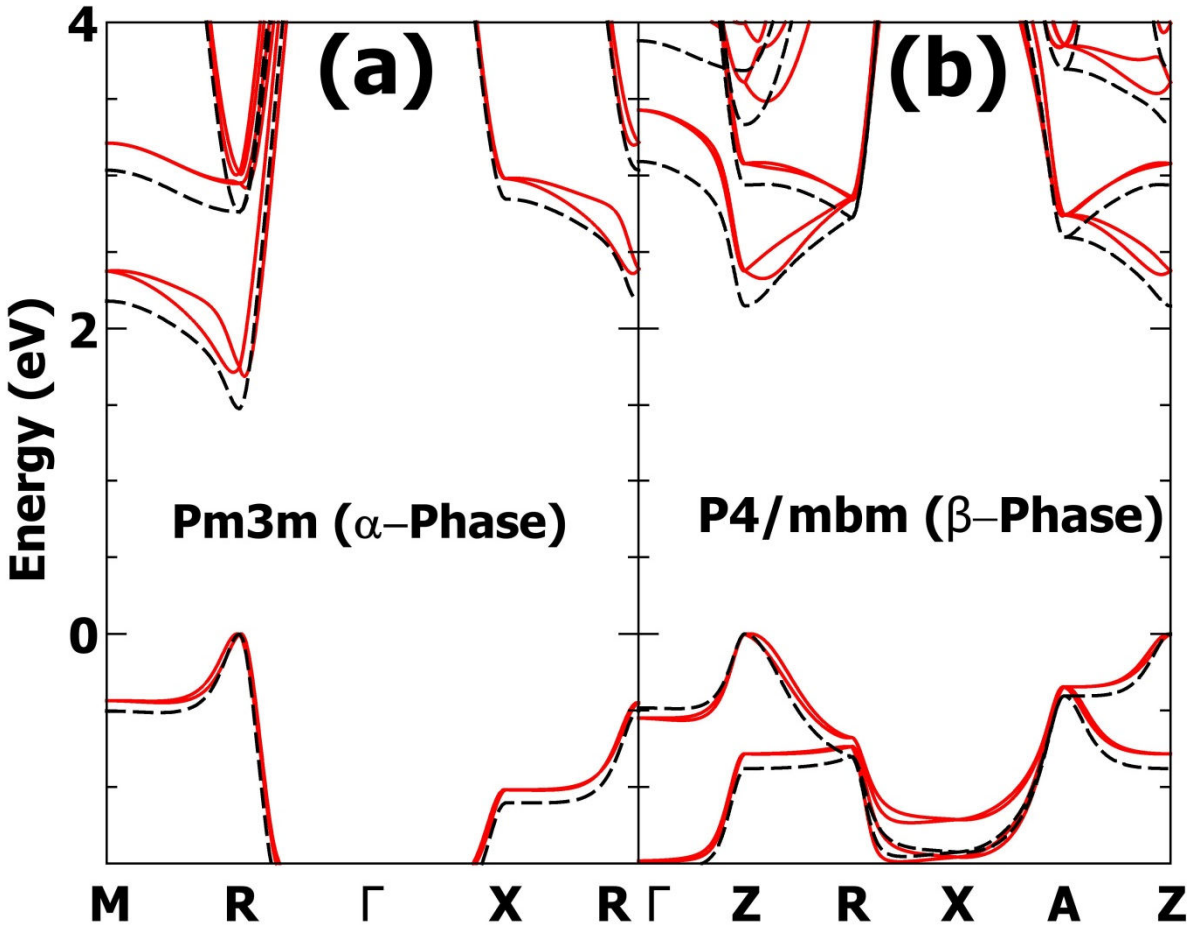
(a–c) Computed electronic band structures using the TB model (solid lines) and at the scGW+SOC level of theory (symbols) for the experimentally determined crystal structures

Parameterized tight-binding with scGW

Beyond DFT → Tight-Binding modeling

A Marronnier et al. ACSnano 12, 3477, 2018

$CsPbI_3$ results



Tight-binding calculations on DFT-relaxed structures

-------- Local maximum

——— Symmetry-breaking actual minimum

- Rashba effect that lifts the spin degeneracy
- Significant increase of the bandgap
- Shift of the energy minima from the high symmetry points of the Brillouin zone (R and Z)

Parameterized tight-binding with scGW

Conclusion

- Importance of dielectric confinement :

  layered HOP (contrast organic/inorganic layers)

  2D/3D HOP nanoplatelets

- Contributions of surface states in HOP
- Intercalation effect
- Band gap decreases with increasing number N of inorganic layers

Conclusion

- Quantum confinement effects still present at N = 5
- Dielectric confinement almost disappears from N=4
- Hence the larger exciton binding energies for these 2D systems even at room temperature is probably due to the quantum confinement effect

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Acknowledgments

Stanford Univ.

H. Karunadasa

M. Smith

Rice Univ.

A. Mohite

J.-C. Blancon

Los Alamos National Laboratory

S.Tretiak

A. Neukirch

W. Nie

H. Tsai

Northwesthern Univ.

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Thank you for your attention

J. Phys. Chem. C,
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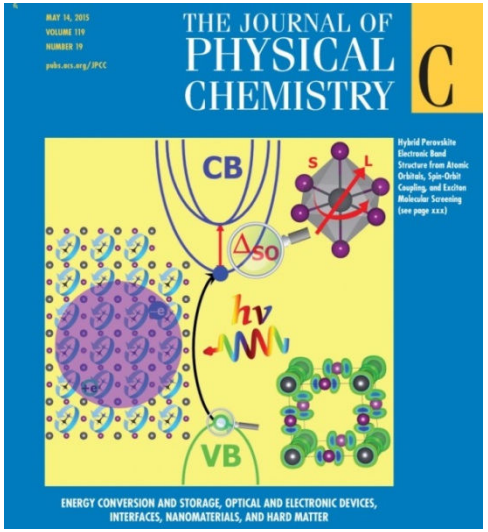

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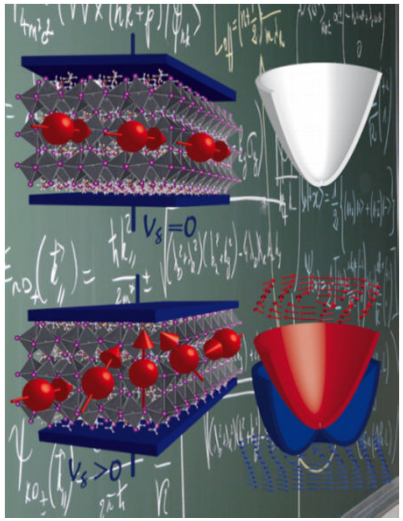

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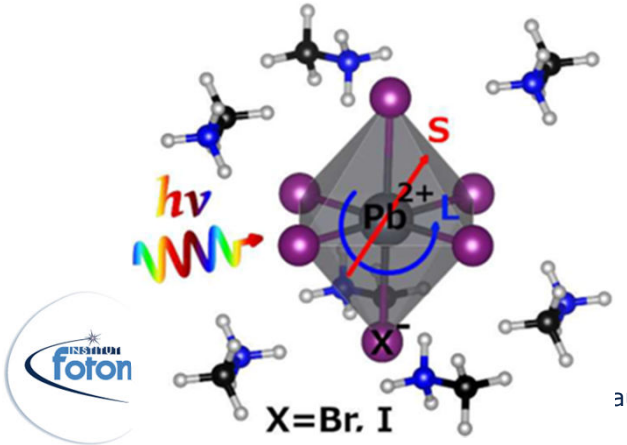

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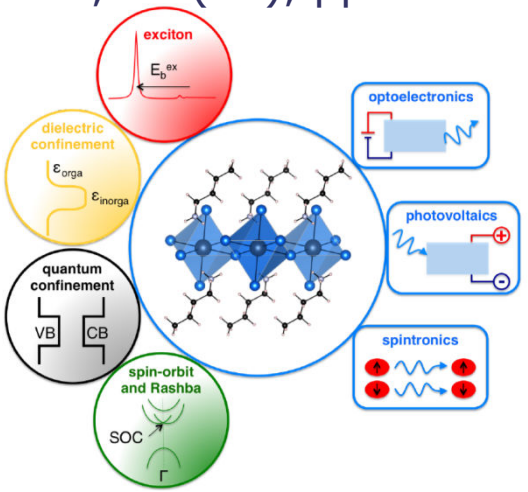

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