Cálculos cuánticos ab initio en ciencia de materiales

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- Pablo Palacios –
- Gregorio García –
- José C. Conesa – CSIC
- Diego Solís – UNAM
- Juan L. Peña - CINVESTAV

Outline

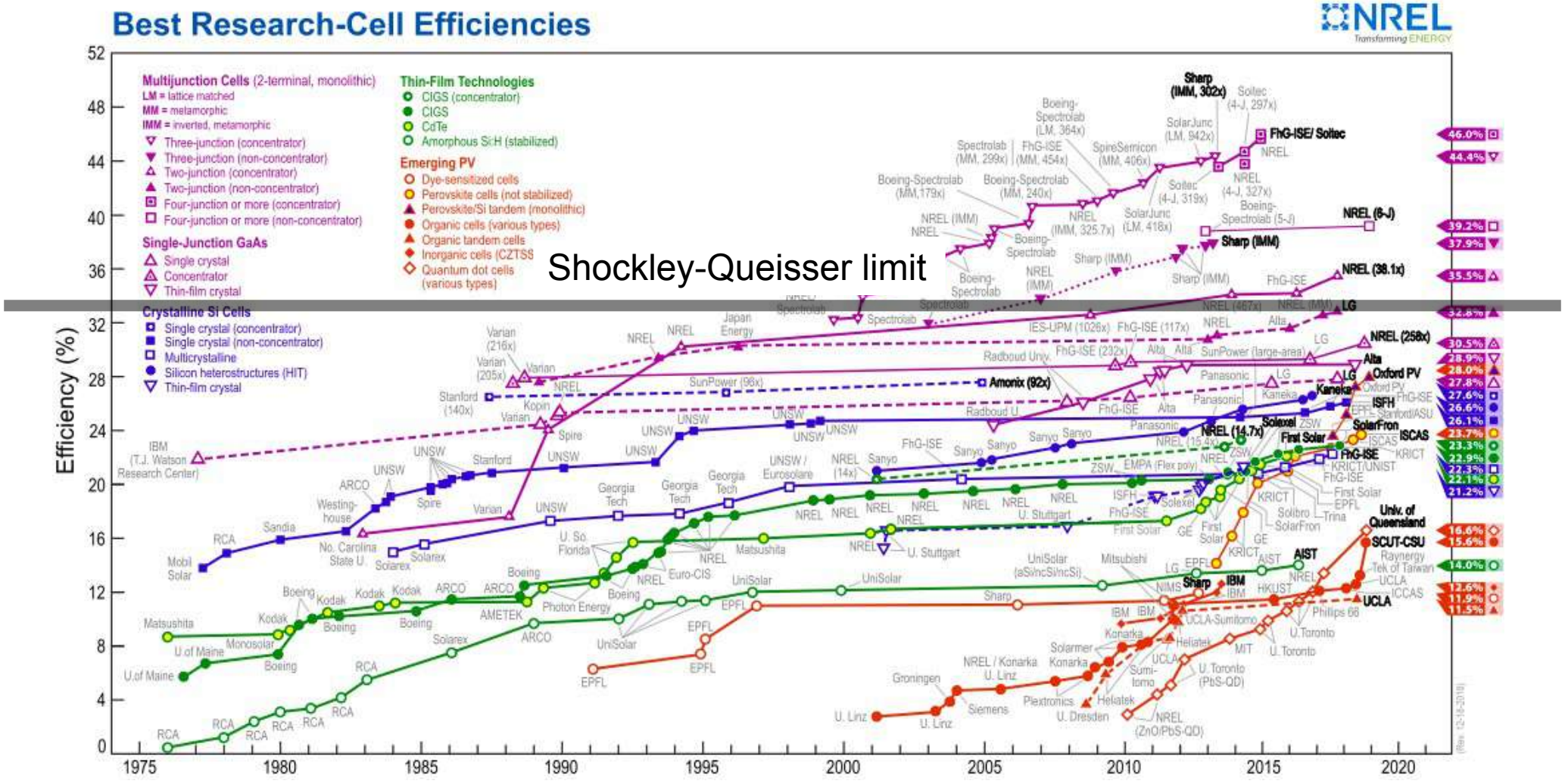
- Solar cells
- Quantum mechanics calculations
- Defects in CdTe
- Halide perovskites

Tipos de celdas fotovoltaicas

- Silicio cristalino (comercial, optimizada)
- Capa delgada (comercial, en desarrollo)
- Celdas de colorante (laboratorio)
- Orgánicas (laboratorio)
- Tandem (laboratorio)

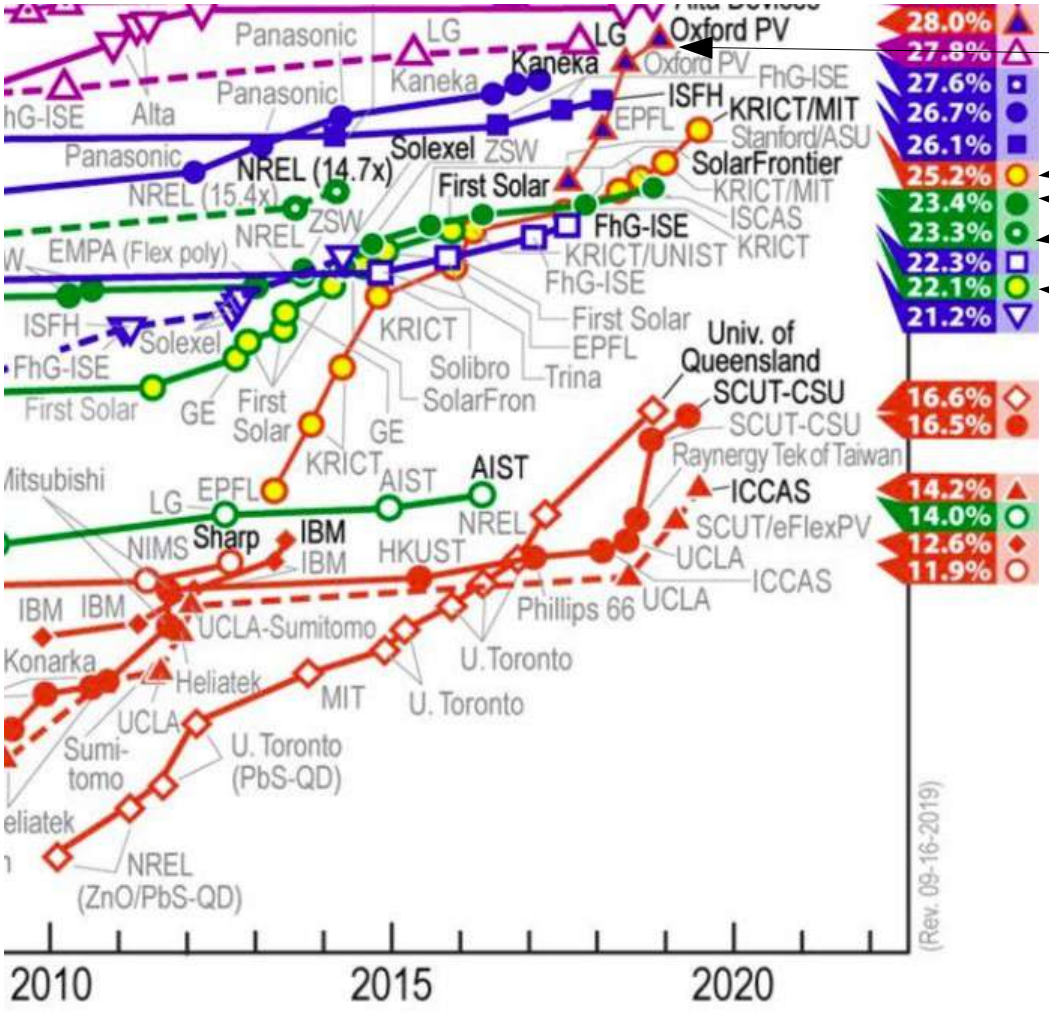
Evolución tecnológica

$$\text{Eficiencia} = \frac{\text{Energía eléctrica producida}}{\text{Energía solar recibida}}$$



Low cost PV technologies with record efficiency > 20%

NREL chart of record efficiencies



m-Si, Si/PSC

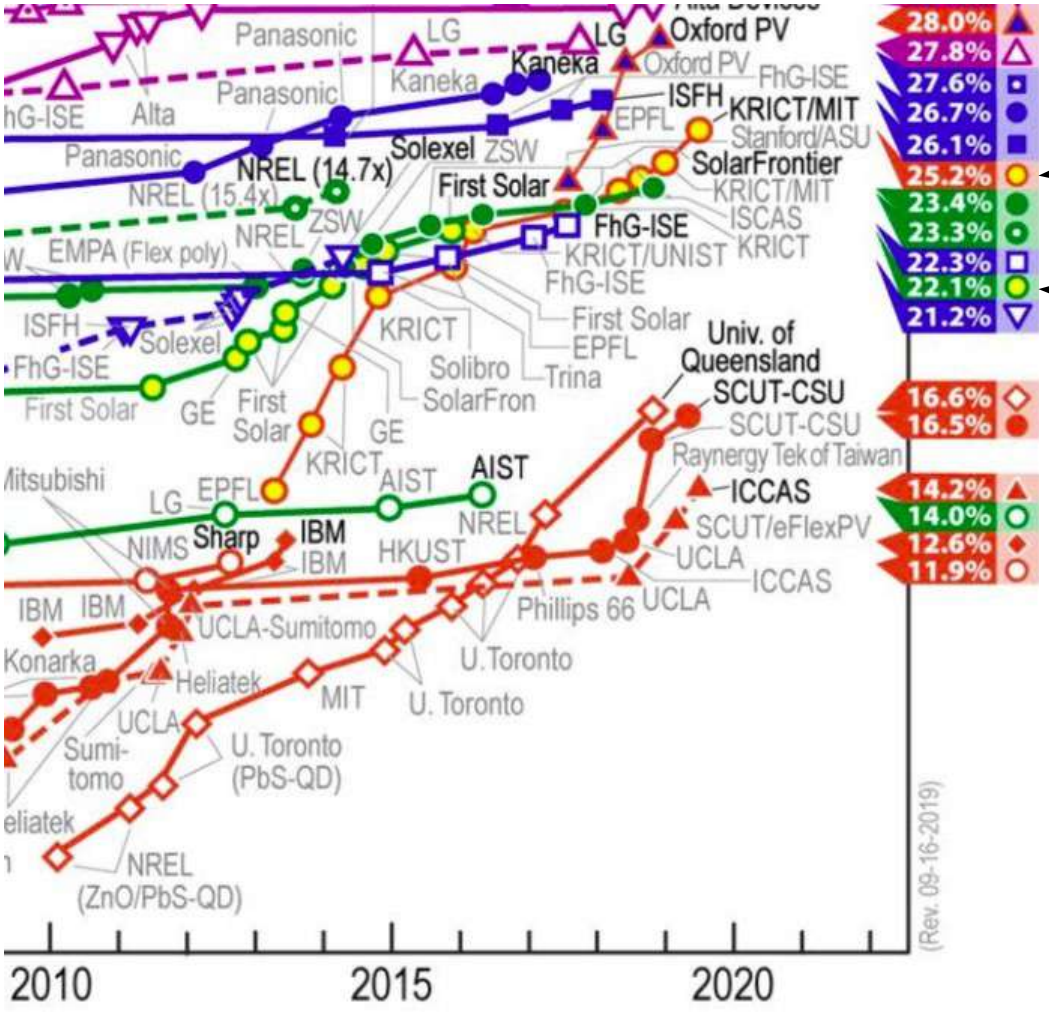
PSC(perovskite)

CIGS

CdTe/CdS

Área de nuestro trabajo

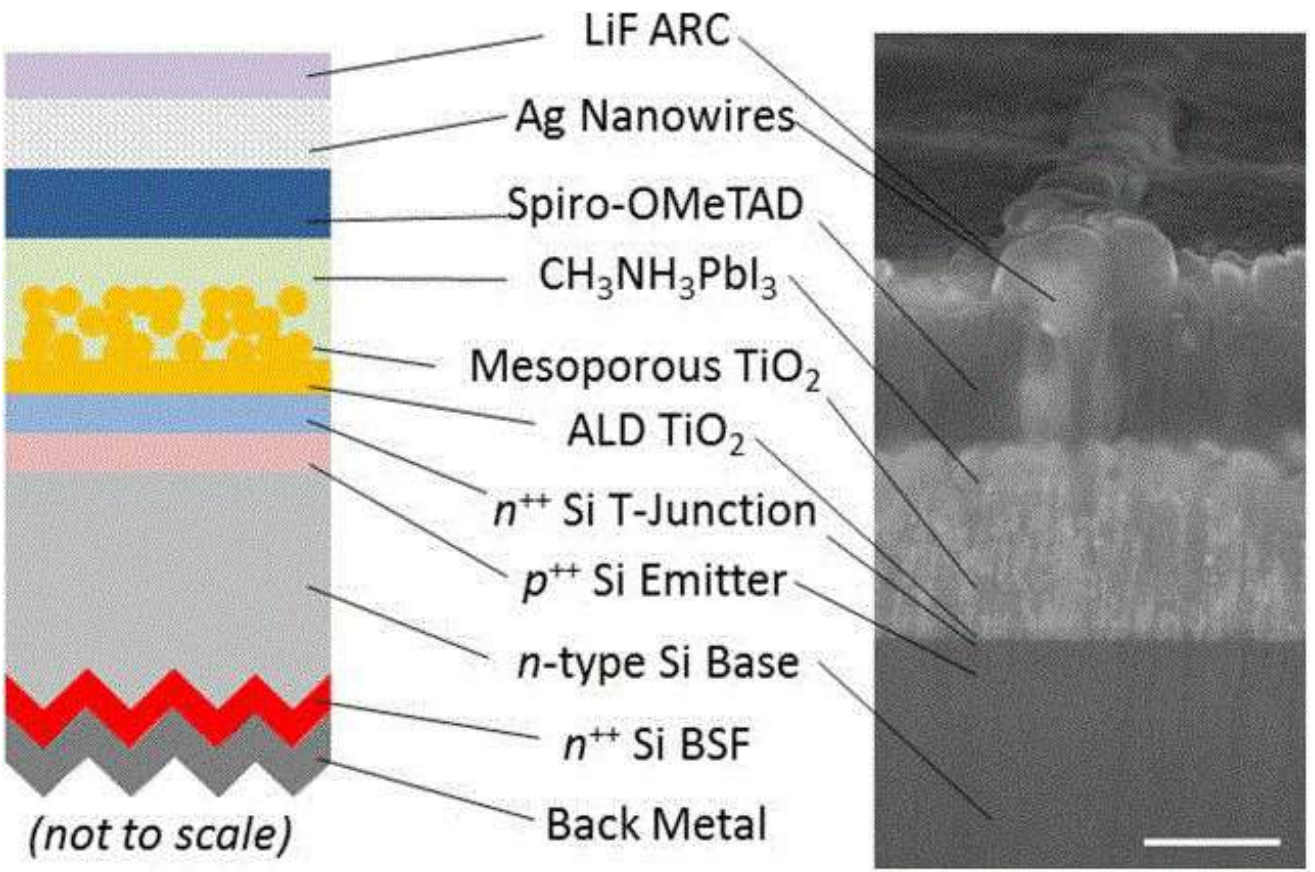
NREL chart of record efficiencies



PSC(perovskite)

CdTe/CdS

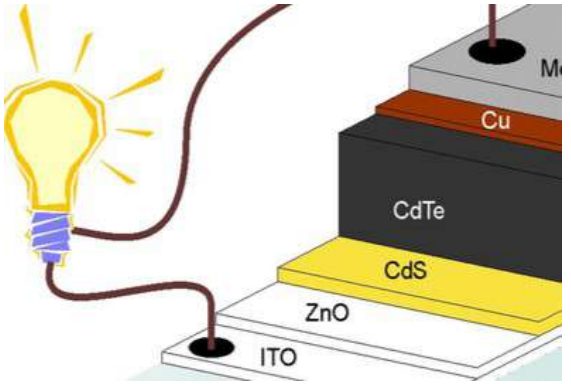
The Next Generation solar cells
tandem Si/perovskite



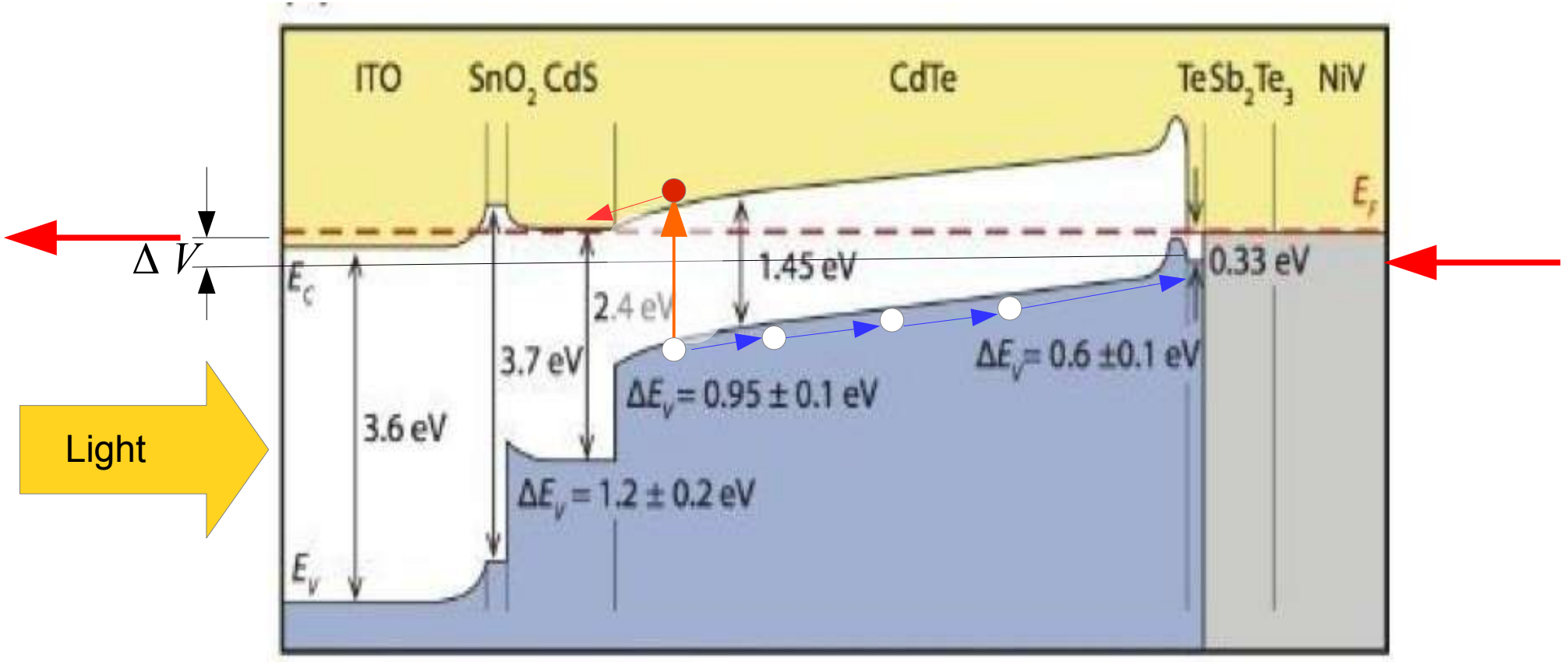
Source: Applied Physics Letters

Oxford PV is building a factory

Example: CdTe/CdS solar cell (η>22%)



The Fermi level determines how do the bands align across de interfaces.
High hole conductivity is needed for the holes to reach the back contact.



Source: A. Smetz et al, Solar Energy, UIT Cambridge (2018).

Our approach: quantum calculations at the atomic scale

Method

Density Functional Theory (DFT)

Hohenberg, Pierre; Walter Kohn (1964). "Inhomogeneous electron gas". Phys. Rev. 136 (3B): B864–B871.

Software

QUANTUMESPRESSO

b-initio VASP ienna ackage imulation

Hardware and support from NLHPC

http://www.nlhpc.cl

Details:
Basis sets: plane waves
Pseudopotentials
Structural optimization with van der Waals corrections.
Wavefunctions and energies from hybrid functionals

DFT Kohn-Sham equation (1965)

The ground state energy is given by

$$E_{total}=\sum_{i=1}^{N} f_i\langle\phi_i|-\frac{1}{2}\nabla^2+V(\boldsymbol{r})|\phi_i\rangle+\frac{1}{2}\iint d\boldsymbol{r}\,d\boldsymbol{r}'\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}+E_{xc}[n(\boldsymbol{r})]$$

Initial guess for density: $n(\boldsymbol{r})$

$$V_{eff}(\boldsymbol{r})=V(\boldsymbol{r})+\int d\boldsymbol{r}'\frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}+v_{xc}(\boldsymbol{r}),\quad \text{con } v_{xc}(\boldsymbol{r})=\frac{\delta E_{xc}}{\delta n(\boldsymbol{r})}$$

$$\left(-\frac{1}{2}\nabla^2+V_{eff}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r})=\epsilon_i\phi_i(\boldsymbol{r})\rightarrow\{\epsilon_i,\phi_i(\boldsymbol{r})\}\rightarrow$$

$$\rightarrow n_{nueva}(\boldsymbol{r})=\sum_i f_i|\phi(\boldsymbol{r})|^2,\quad 0\le f_i\le 1 \text{ is the occupation number}$$

compare $n_{new}(\boldsymbol{r})$ con $n(\boldsymbol{r})$

if not equal, then $n(\boldsymbol{r})=\alpha\, n_{nueva}(\boldsymbol{r})+(1-\alpha)n(\boldsymbol{r})$

DFT Kohn-Sham equation (1965)

The ground state energy is given by

$E_{total} =$ $- E_{xc}[n(\boldsymbol{r})]$

Initial

$V_{eff}(\boldsymbol{r}$

$\left(-\frac{1}{2}\nabla\right.$

$\rightarrow n_{nue}$ er

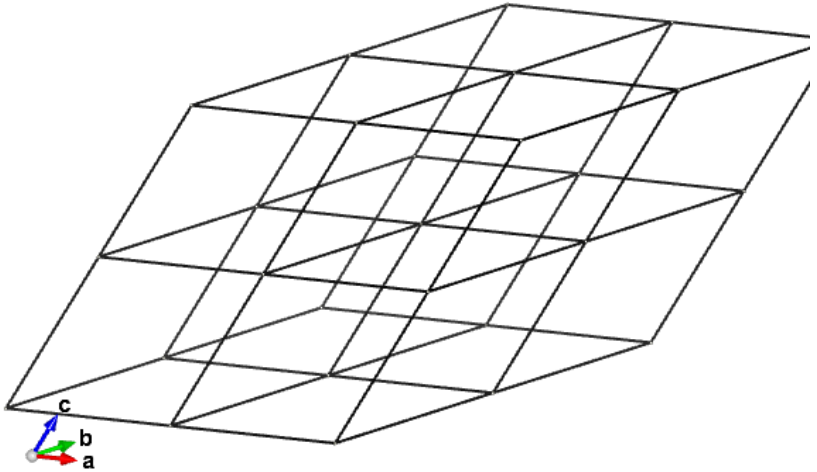
comp

if not

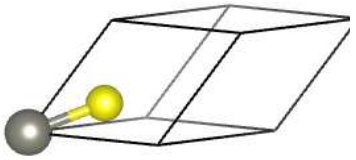
```
implicit none

real(DP) :: rho, ec, vc, ex, vx
real(DP) :: ec__, vc__
!
real(DP), parameter :: small = 1.E-10_DP,  third = 1.0_DP / 3.0_DP, &
     pi34 = 0.6203504908994_DP  ! pi34=(3/4pi)^(1/3)
real(DP) :: rs
!
if (rho <= small) then
   ec = 0.0_DP
   vc = 0.0_DP
   ex = 0.0_DP
   vx = 0.0_DP
   return
else
   rs = pi34 / rho**third
   ! rs as in the theory of metals: rs=(3/((4pi rho))^(1/3)
endif
!..exchange
if (iexch == 1) THEN              !  'sla'
   call slater (rs, ex, vx)
ELSEIF (iexch == 2) THEN          !  'sl1'
   call slater1(rs, ex, vx)
ELSEIF (iexch == 3) THEN          !  'rxc'
```

Estructura cristalina periódica

Red de Bravais



+ Base

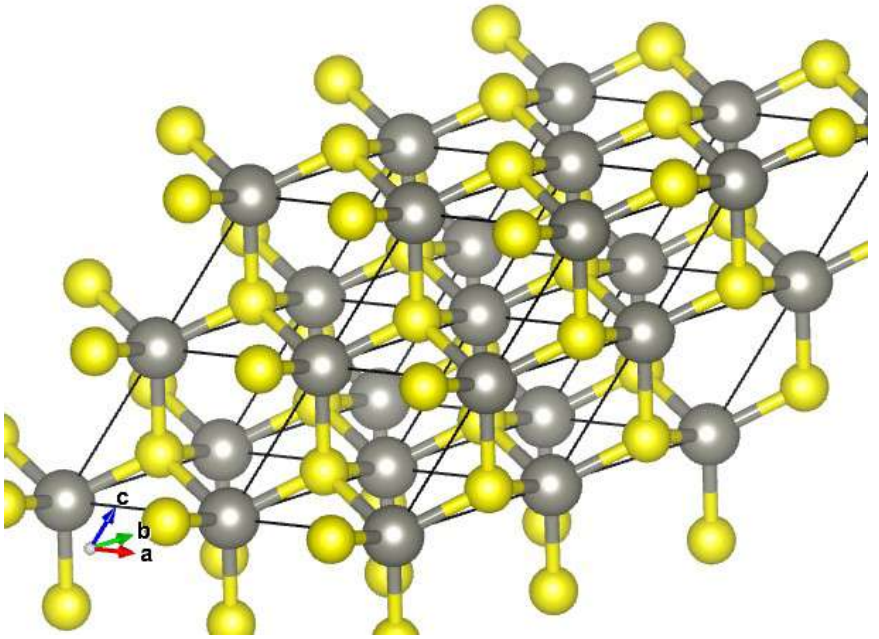


$\vec{\tau}_a$ posición del átomo a respecto al punto de la red

$$\vec{R}_{n_1 n_2 n_3} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

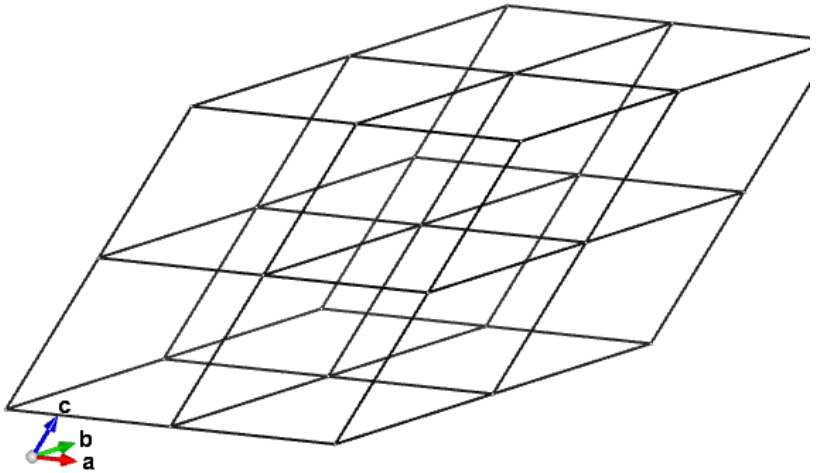
$$n_i = 0, \pm 1, \pm 2, \pm 3, \ldots$$

Cristal: $\vec{R}_{n_1 n_2 n_3 a} = \vec{R}_{n_1 n_2 n_3} + \vec{\tau}_a$



Estructura cristalina periódica

Red de Bravais



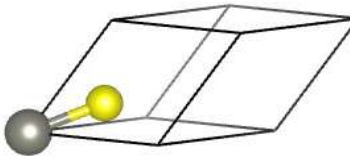
$$\vec{R}_{n_1 n_2 n_3} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$$n_i = 0, \pm 1, \pm 2, \pm 3, \ldots$$

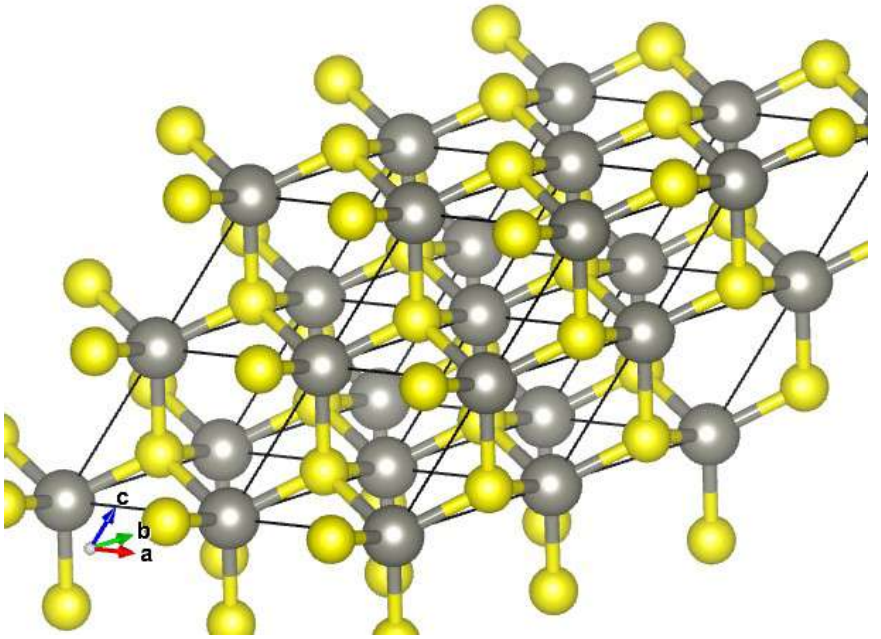
Cristal: $\vec{R}_{n_1 n_2 n_3 a} = \vec{R}_{n_1 n_2 n_3} + \vec{\tau}_a$

\+ Base

Lo que se calcula



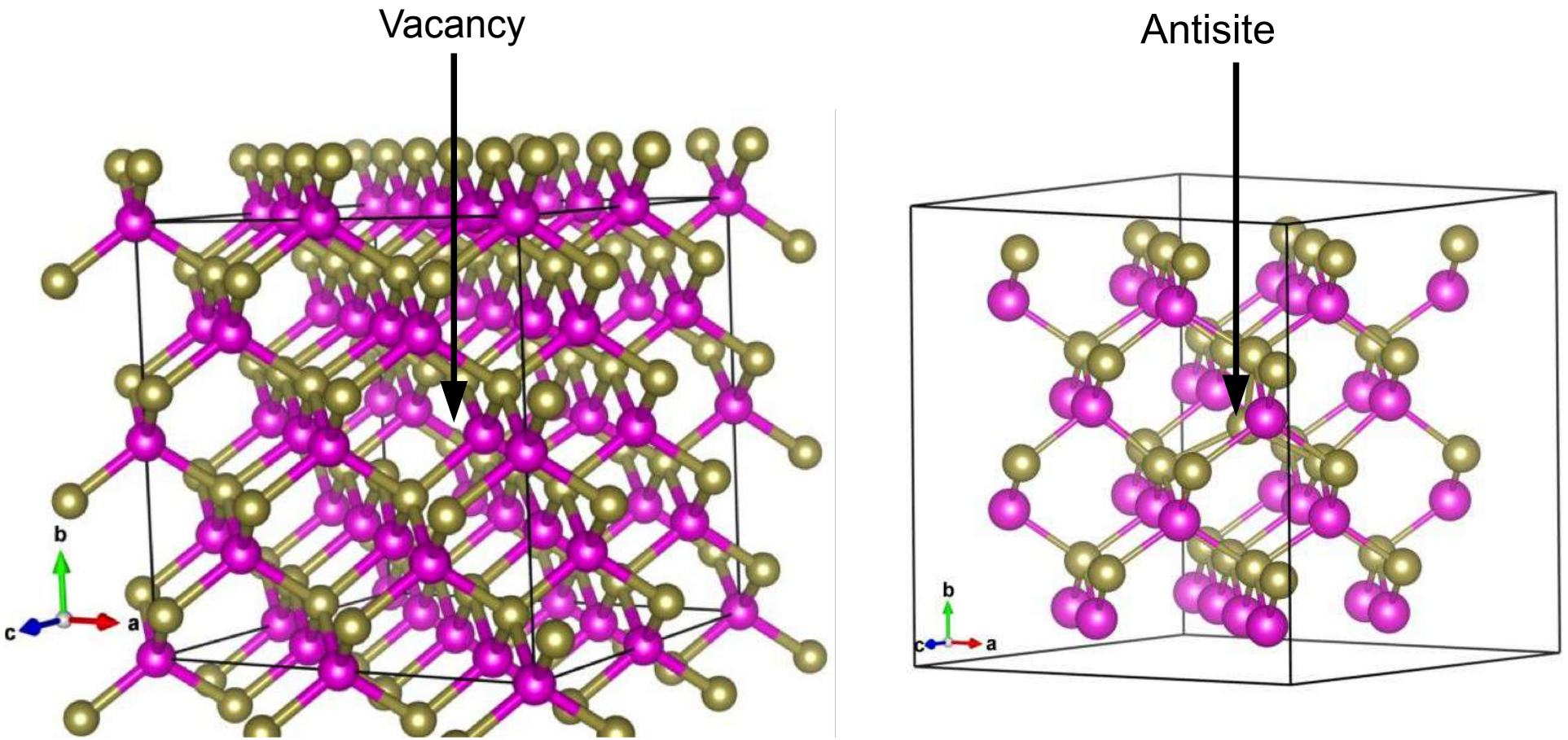
$\vec{\tau}_a$ posición del átomo a respecto al punto de la red



Situaciones en que la periodicidad es rota y necesitamos la escala de dimensiones relevante requiere simular muchos átomos.

Defectos
Interfaces
Nanoestructuras

Intrinsic defects



Other defects: self-interstitials, di-vacancies, vacancy-intertstitial, etc

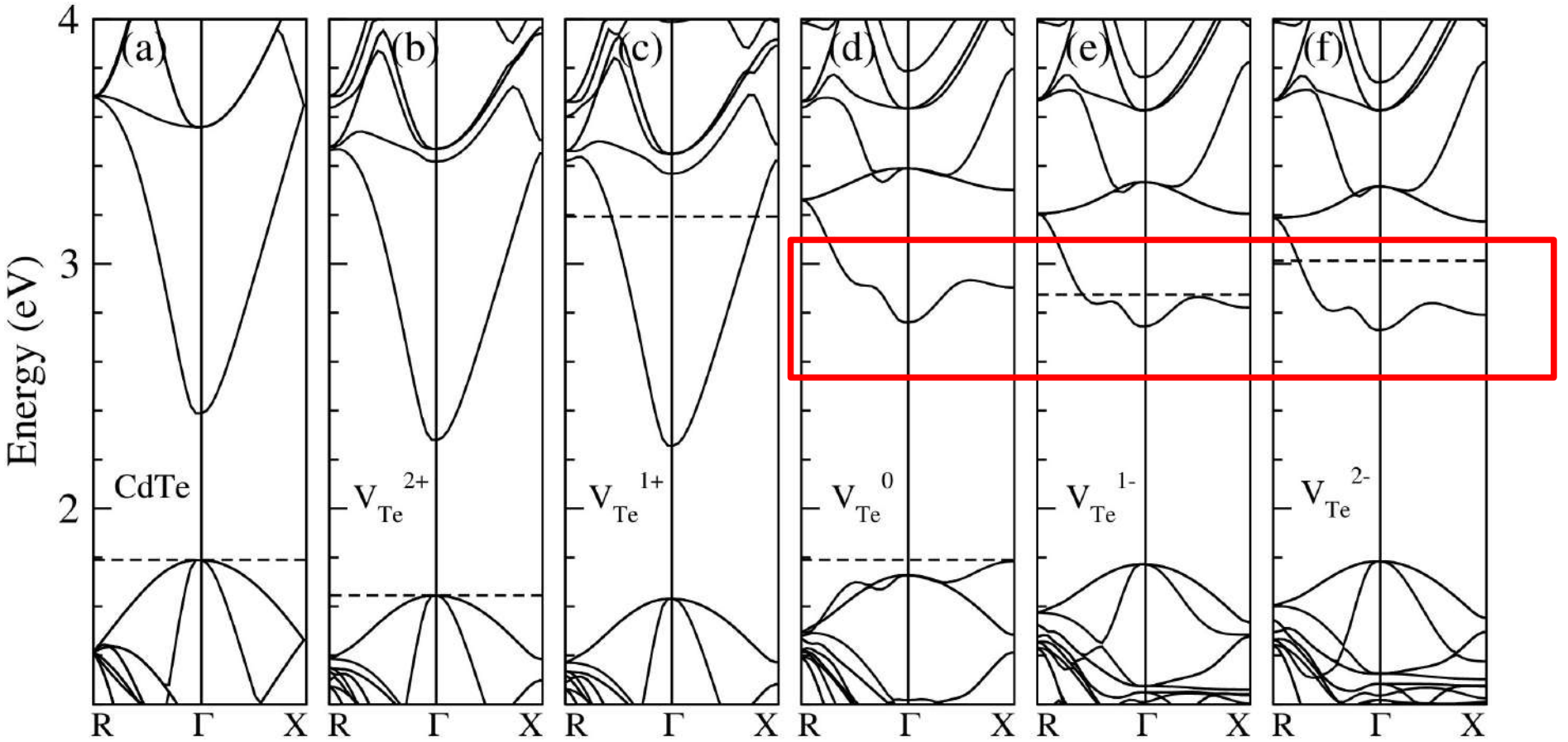
Always present:

Thermodynamic concentration: $N_i = N_{sites} N_{\text{config}} \exp\left(\frac{-\Delta H^f}{k_B T}\right)$ ← Formation energy

Materials are like people: it's the defects that make them interestin

Bands for *standard* supercells $Cd_{32}Te_{32}/Cd_{32}Te_{31}$

Phys. Status Solidi B 252, 2649-2656 (2015)



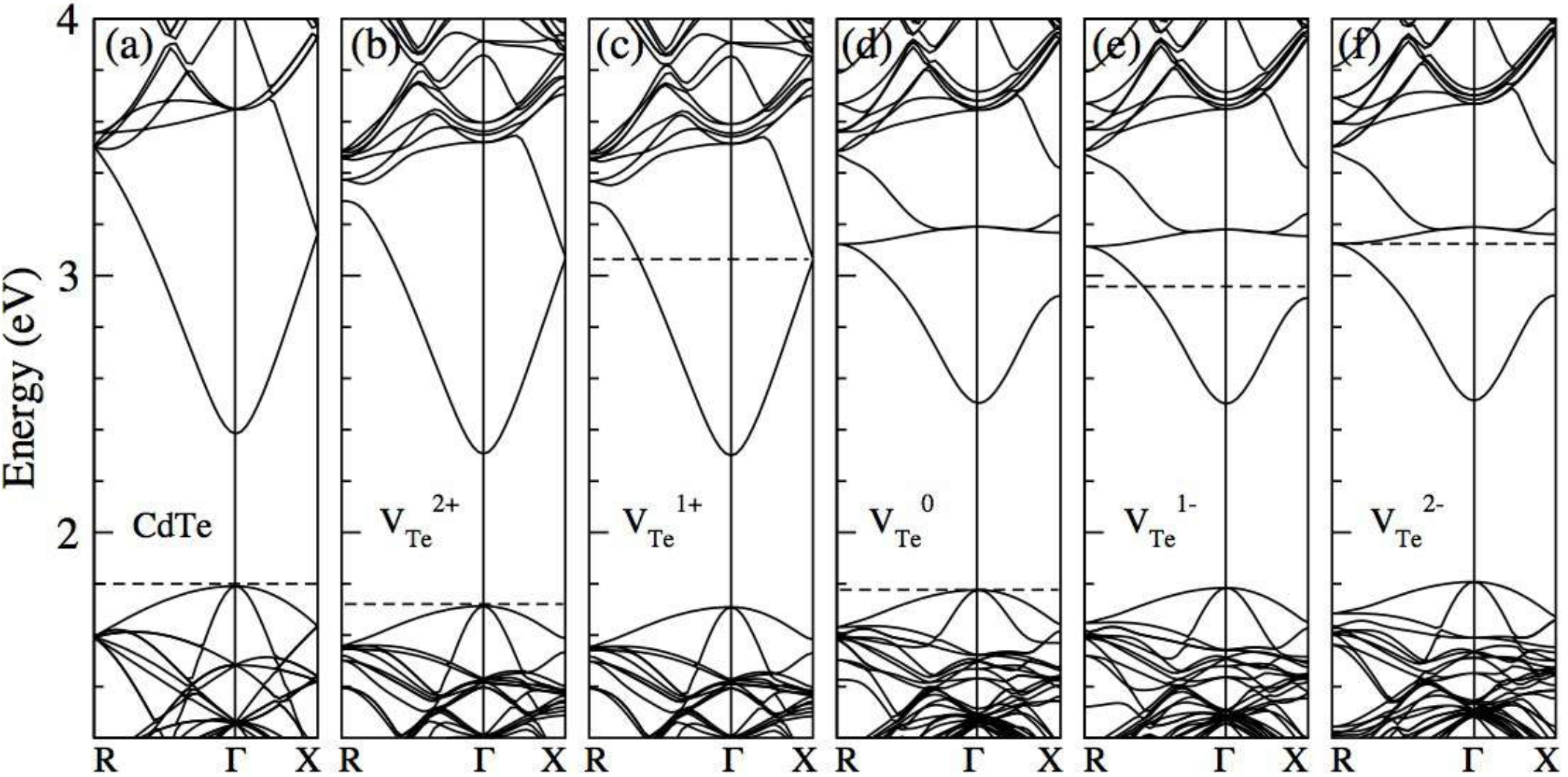
?

A diluted point defect is not expected to destroy the conduction band. A point defect is a perturbation.

The standard 64/63 atom supercell is not appropriate.

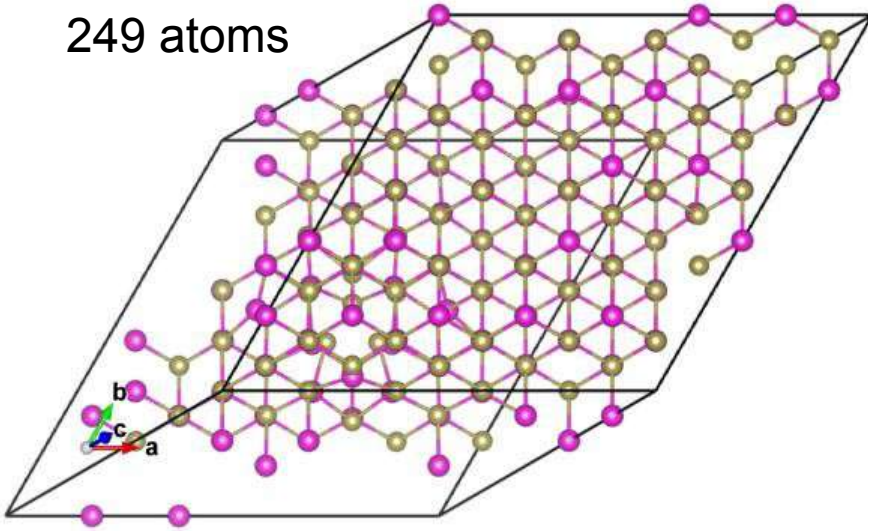
I acknowledge advice by P. Wahnón to plot the bands, even when defects are not periodic systems by definitions.

Bands for $Cd_{128}Te_{128}/Cd_{128}Te_{127}$ supercells

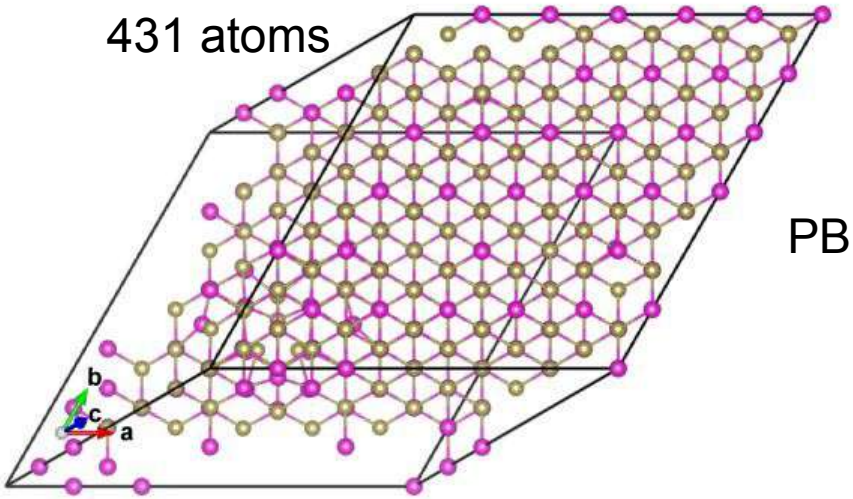


A test for V_{Cd} q=+2, and 0

249 atoms

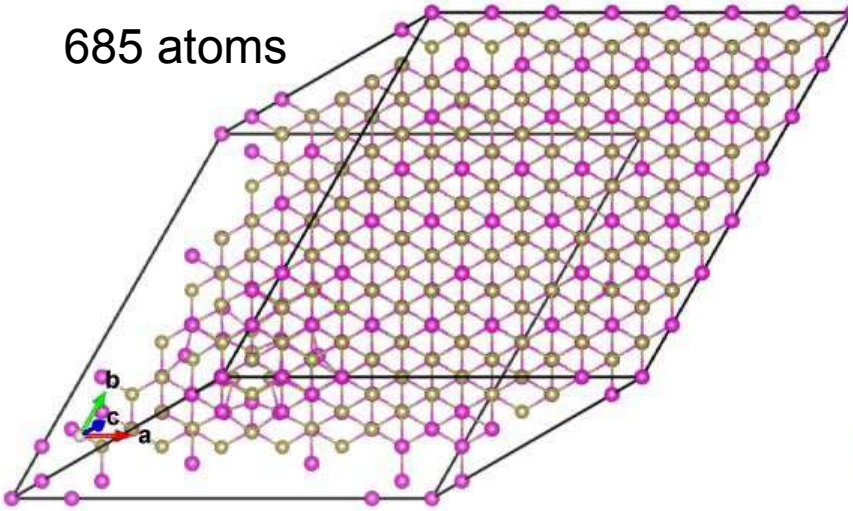


431 atoms

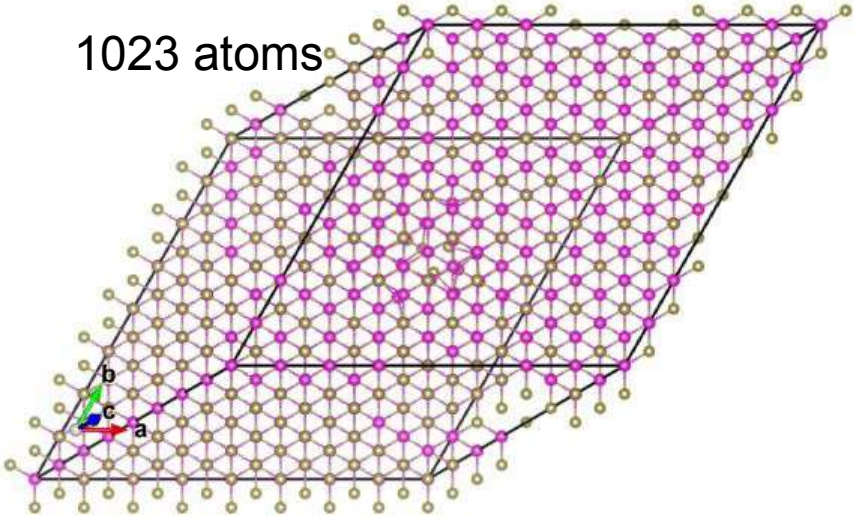


PBE funcional

685 atoms

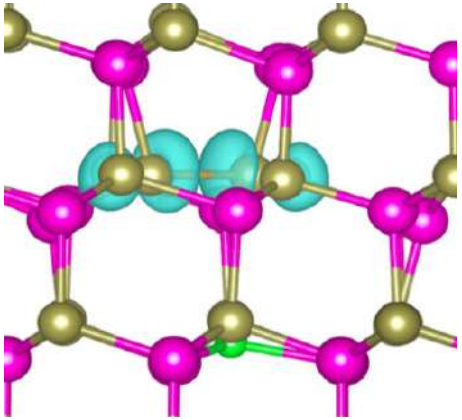


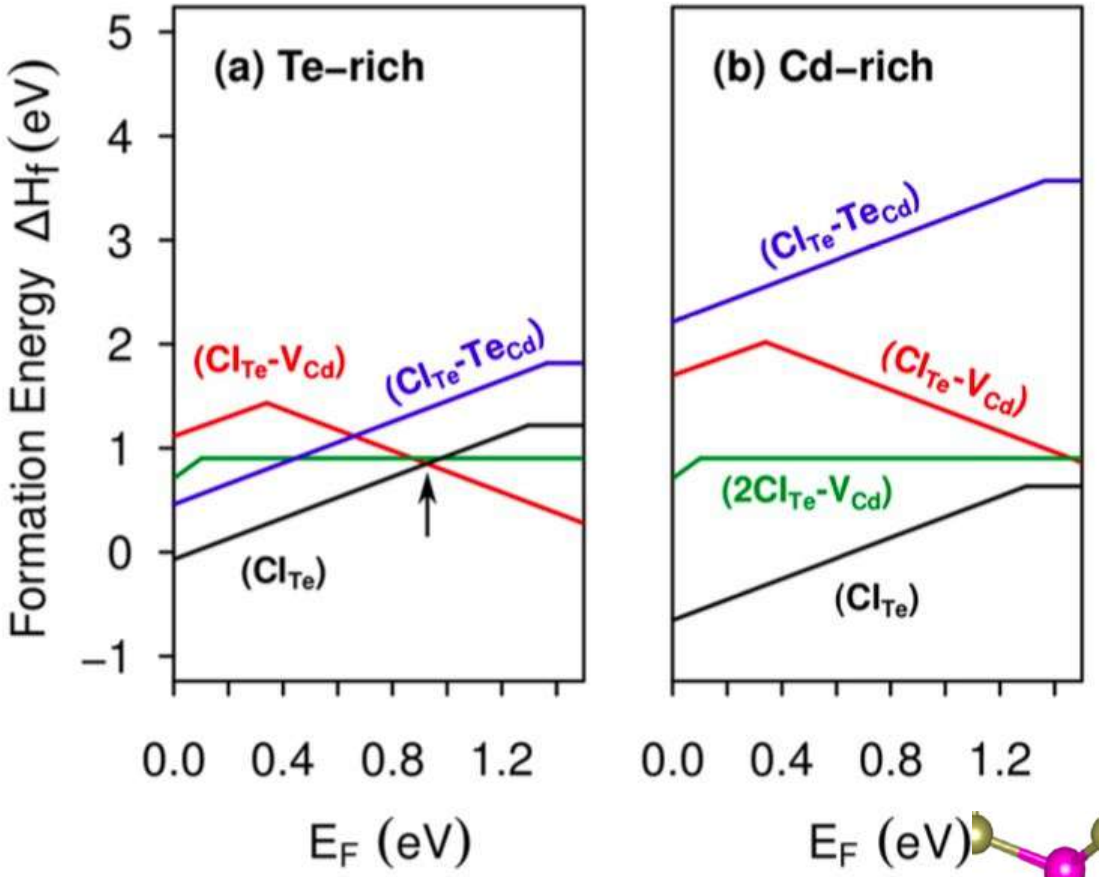
1023 atoms



Cl-defects: Formation energy

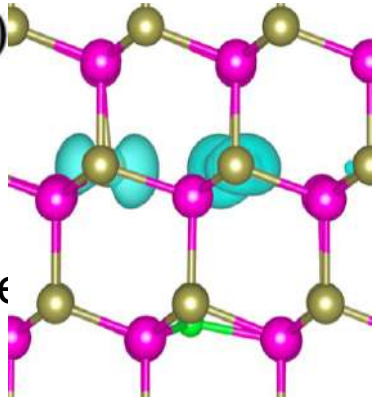
Cl-doping is an important step in the manufacturing process of CdTe/CdS solar cells.





Lowest energy: $(Cl_{Te})^{+}$, $(Cl_{Te}\text{-}V_{Cd})^{-}$, $(2Cl_{Te}\text{-}V_{Cd})^{0}$

If Cl concentration is higher than that of native defect, the arrow indicate the Fermi level position.

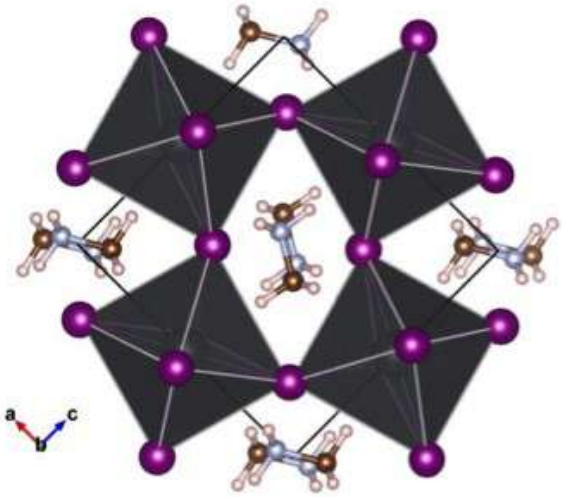


WHY STUDY THE PEROVSKITE?

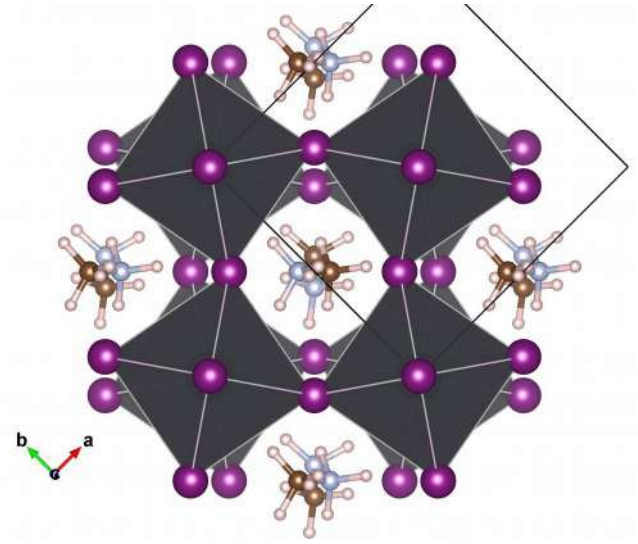
MAPI Perovskite

Methylammonium-Lead-Iodide

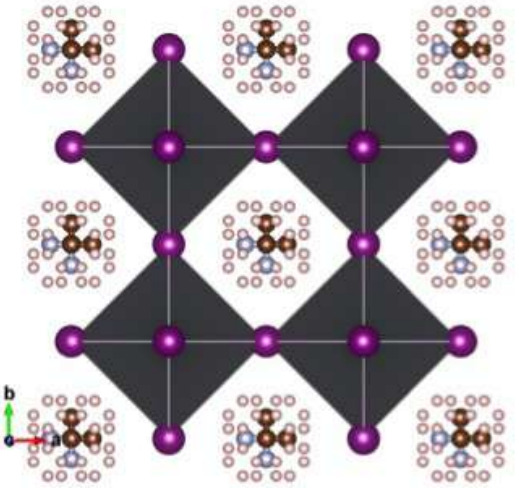
Orthorhombic



Tetragonal



Cubic

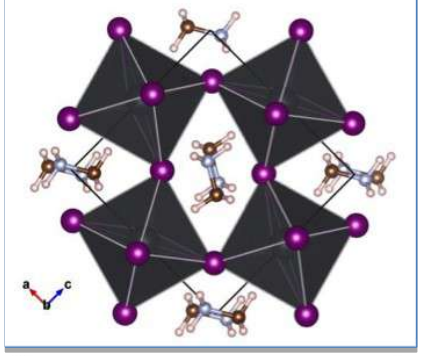


T ~ 165 K

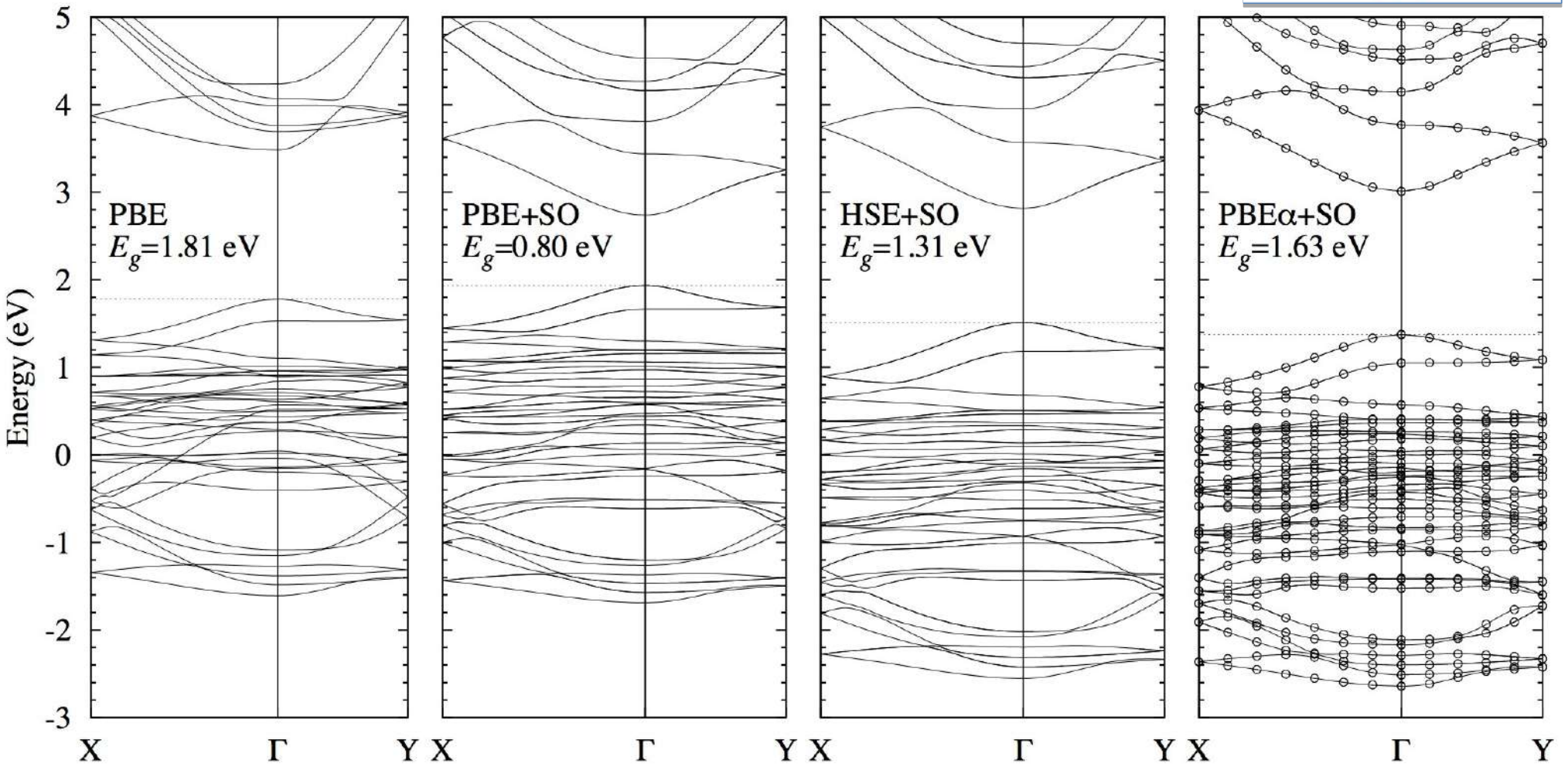
T ~ 327 K

STUDY of $CH_3NH_3PbI_3$

Orthorhombic



Band Diagrams with different DFT approximations



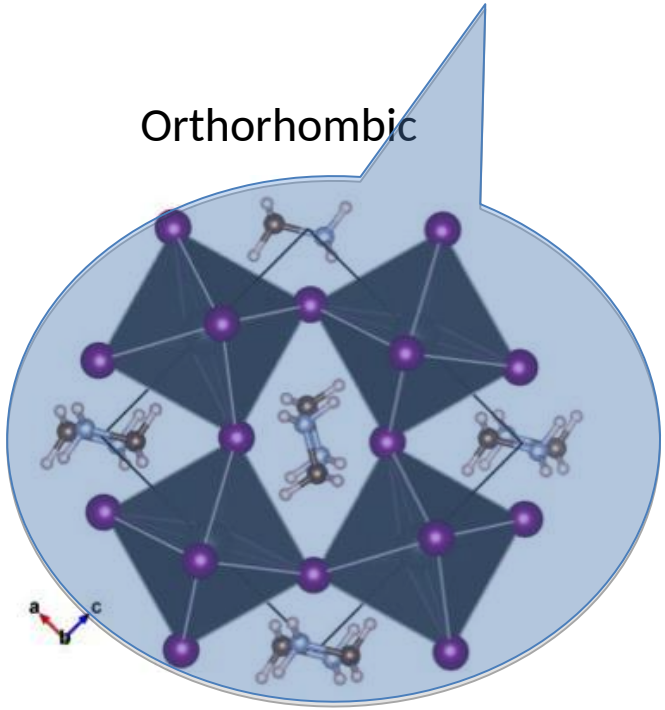
Menéndez-Proupin *et al.*, Phys. Rev. B 90, 045207 (2014)

STUDY of $CH_3NH_3PbI_3$

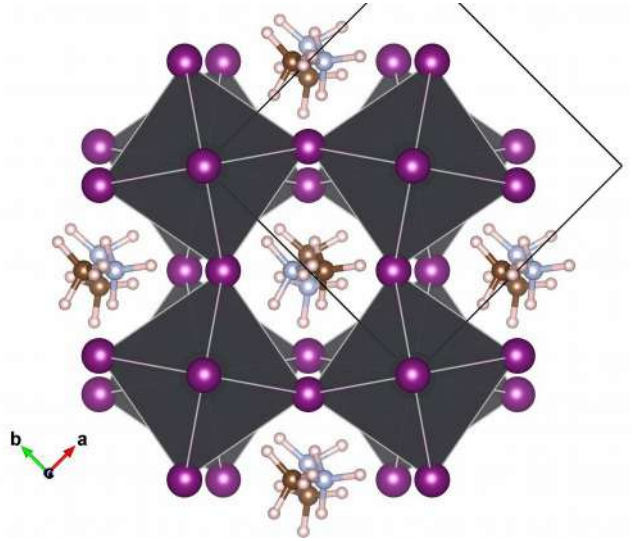
How can we ensure that one of the high temperature phases is being simulated properly?

Good 0K model !!!

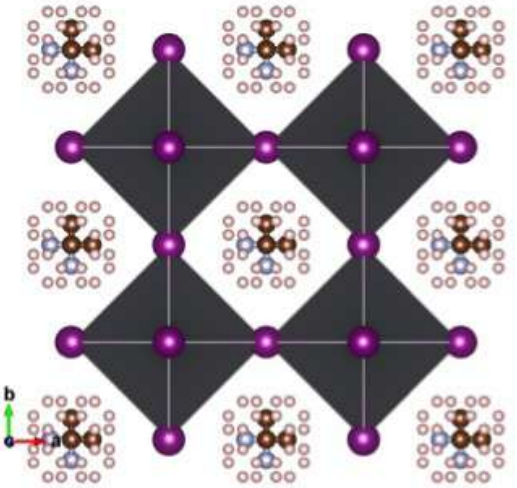
Orthorhombic



Tetragonal



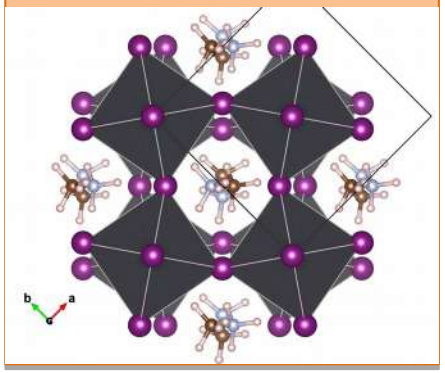
Cubic



T ~ 165 K

T ~ 327 K

Tetragonal



Thermal effect

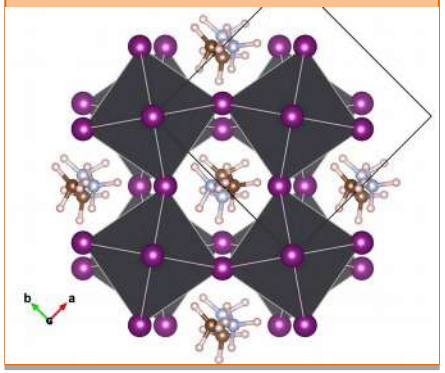
Ab initio Molecular Dynamic

- NPT and NVT ensembles
- PBE and vdW functionals
- Relatively long simulation time (up to 100 ps)
- T = 220 K (Langevin thermostat)
- 1 fs of time step

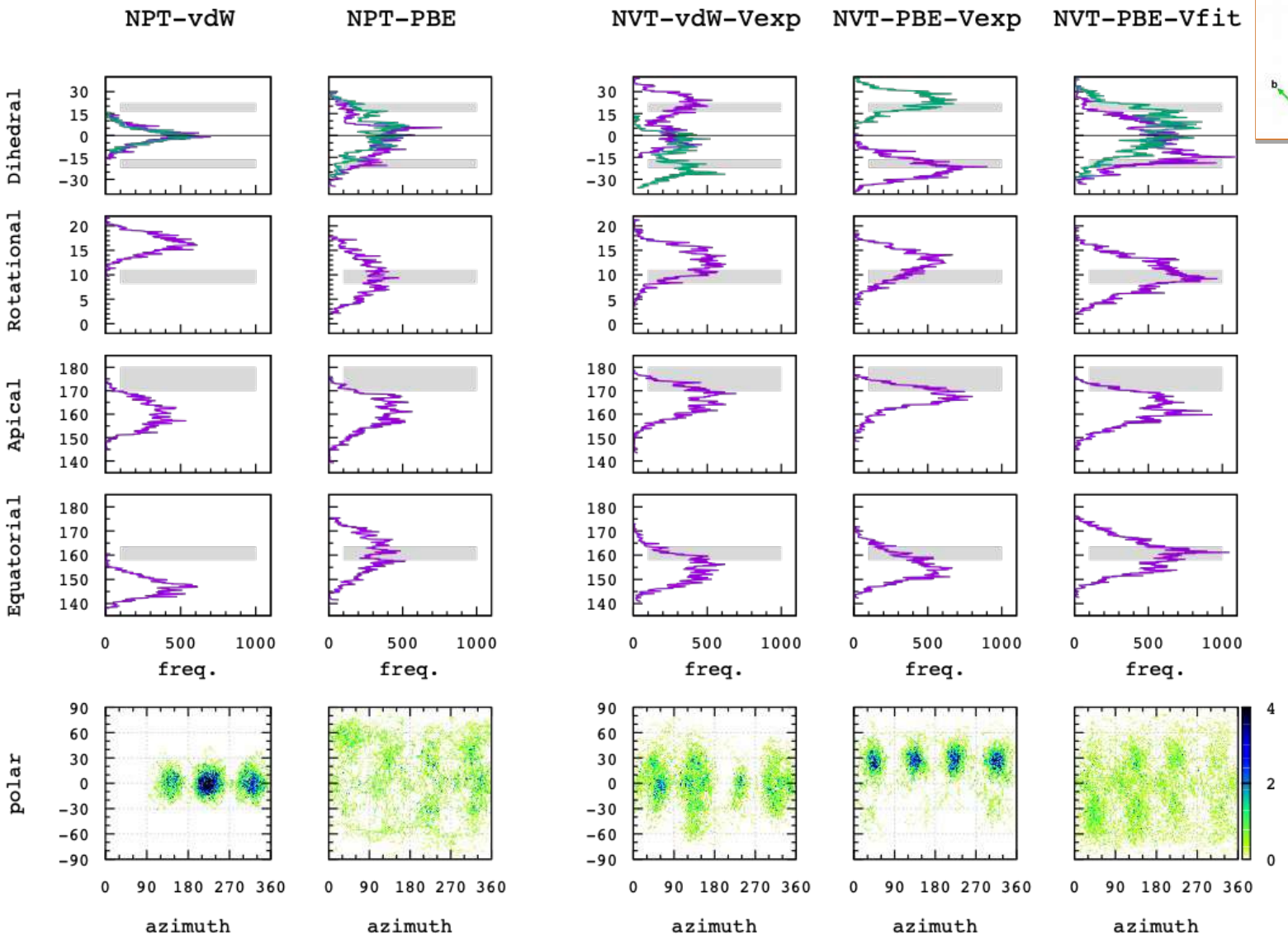
***Montero-Alejo. A. L. et al., JPCC* 2016, *120*, 7976–7986.**

STUDY of $CH_3NH_3PbI_3$

Tetragonal



Thermal effect

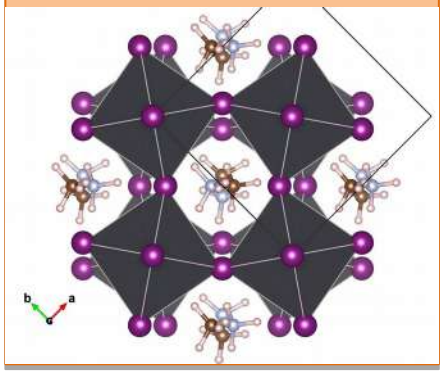


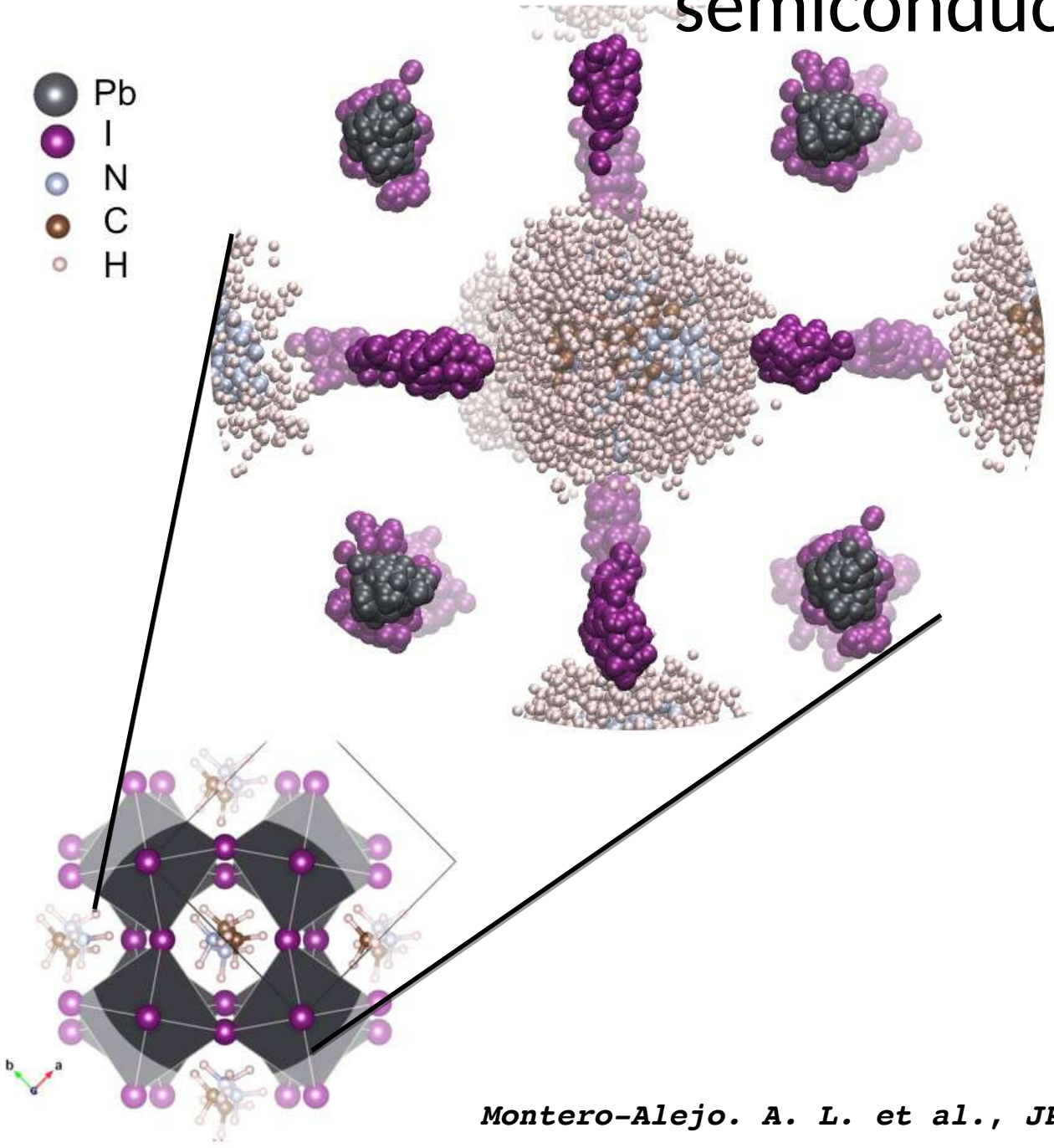
Montero-Alejo. A. L. et al., JPCC 2016, *120*, 7976–7986.

STUDY of $CH_3NH_3PbI_3$

Flexible semiconductor

Tetragonal



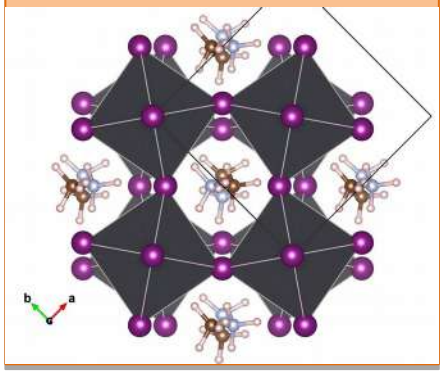


Atoms	RMSD (Å)
Pb	0.22
I	0.41

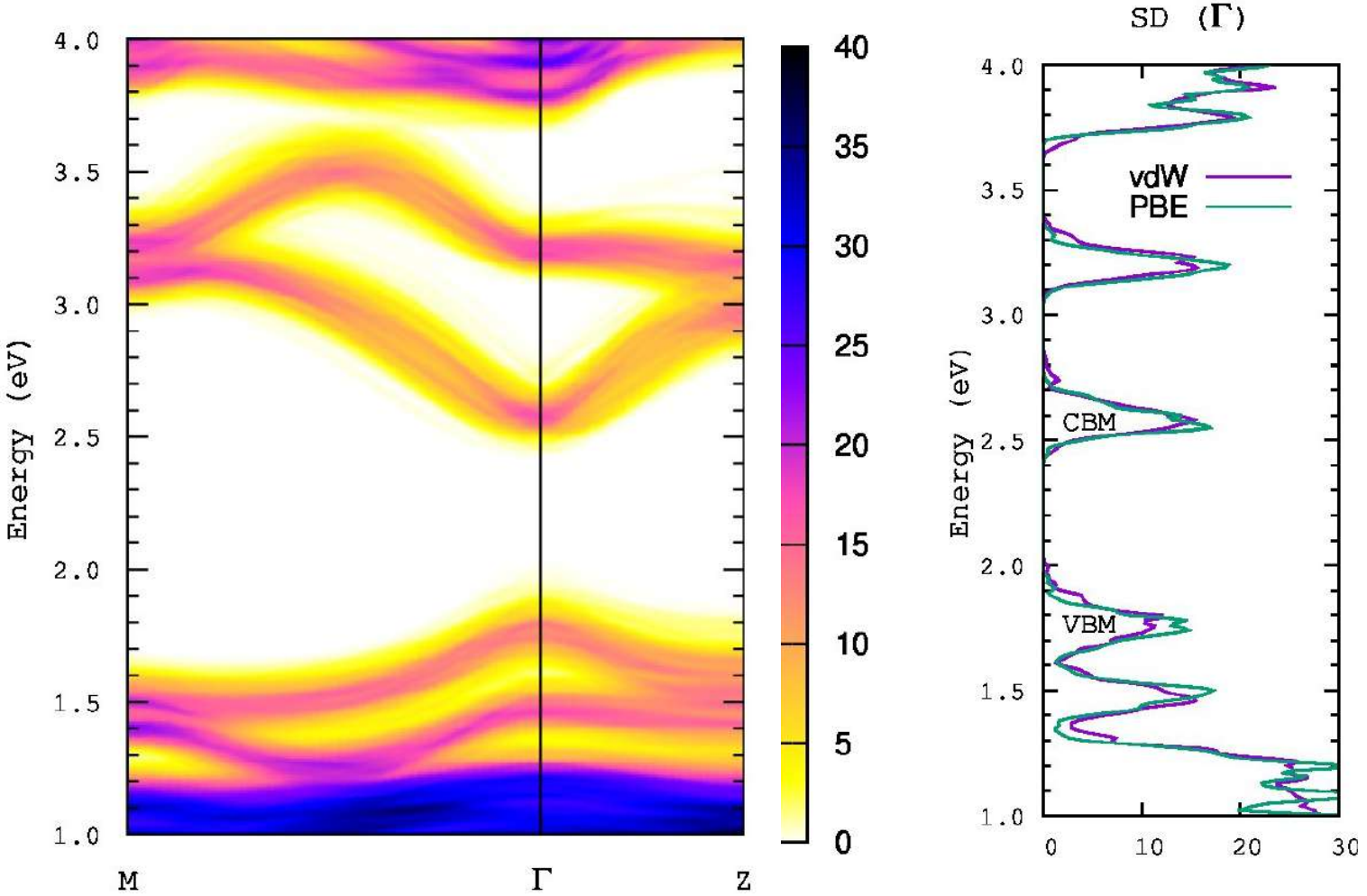
Montero-Alejo. A. L. et al., JPCC 2016, *120*, 7976–7986.

STUDY of $CH_3NH_3PbI_3$

Tetragonal

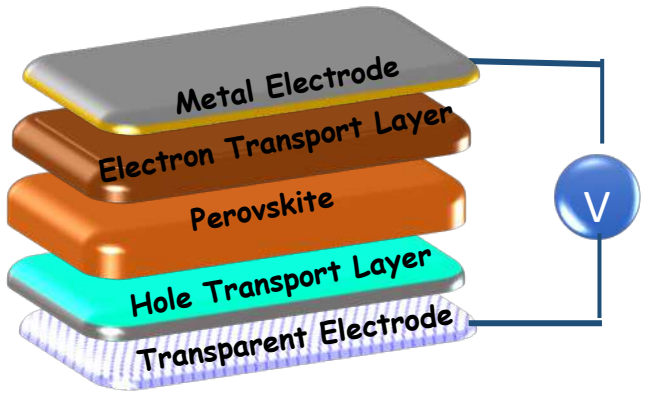


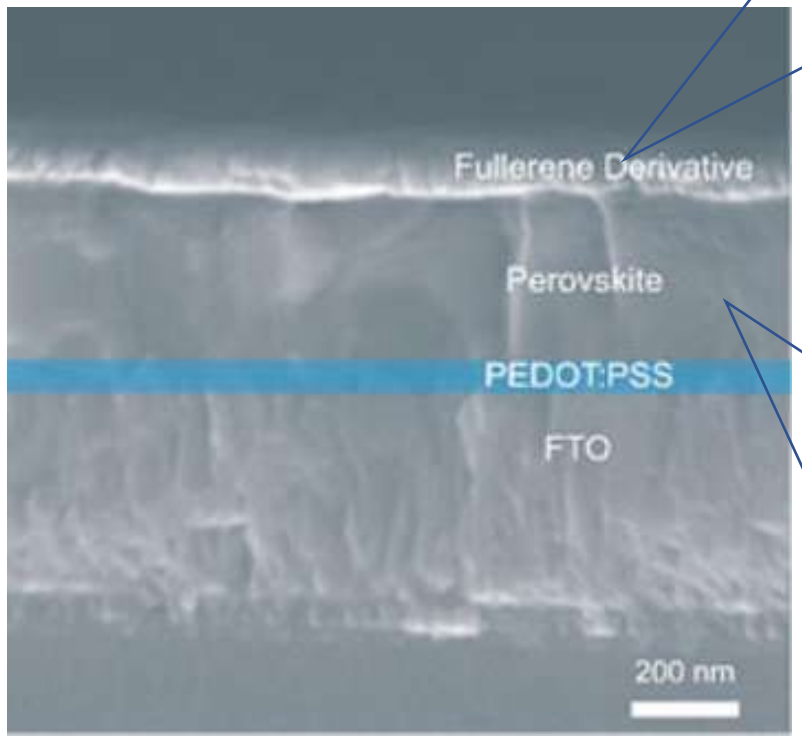
Thermal effect on the Electronic properties



Montero-Alejo. A. L. et al., JPCC 2016, *120*, 7976–7986.

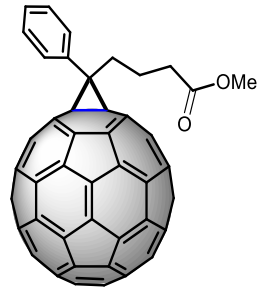
PEROVSKITE SOLAR CELLS





Cross-sectional SEM image of
FTO/PEDOT-PSS/perovskite/fullerene derivatives

Tian, C. *et al.* ACS Appl. Mater. Interfaces 2016, 8, 31426-31432

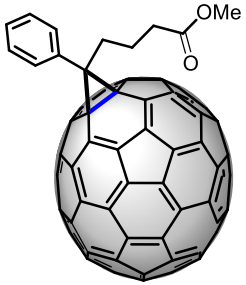


$PC_{61}BM$

$TiO_x/PC_{61}BM$/Perovskite/Spiro/Au

PCE 17.9%

Sargent, E. H. *et al. Energy Environ. Sci.* **2015**, *8*, 2365.



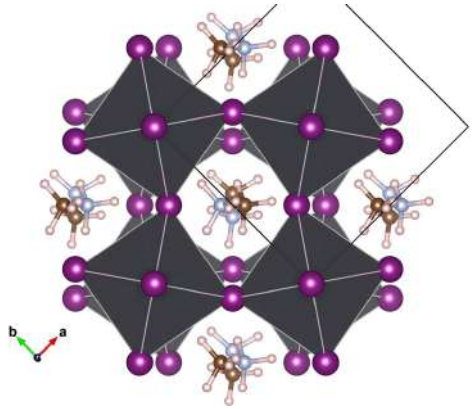
$PC_{71}BM$

PEDOT:PSS/Perovskite/$PC_{71}BM$/Ca/Al

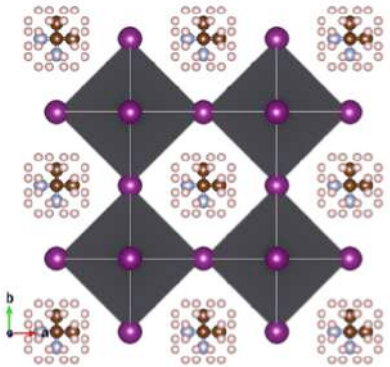
PCE 16.3%

Wu, J. *et al. J. Mater. Chem. A* **2014**, *2*, 15897.

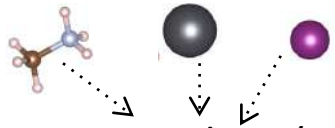
Tetragonal



Cubic



Working conditions of the devices

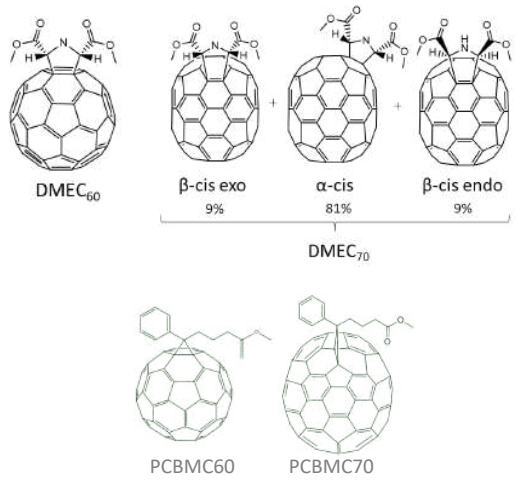


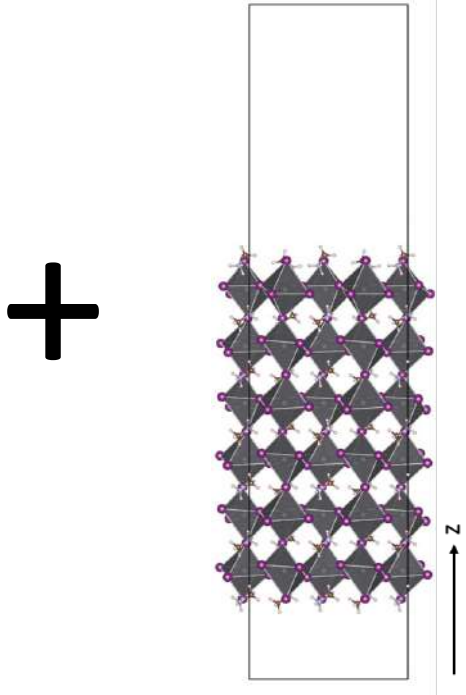
$MAPbI_3$ (MAPI)

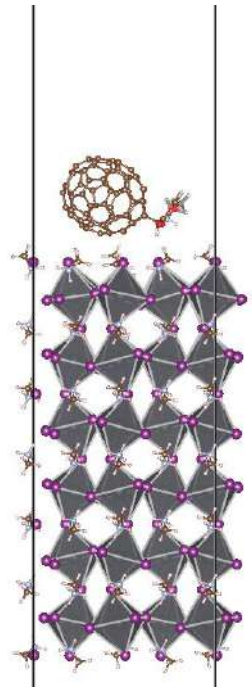
COMPUTATIONAL METHODOLOGY

MAPI(001-MAI) **MAPI(001-PbI)** **MAPI(001-MAI) / FDs** **MAPI(001-PbI) / FDs**

FDs







Density Functional Theory (DFT)

- Plane waves basis set
- Pseudopotentials

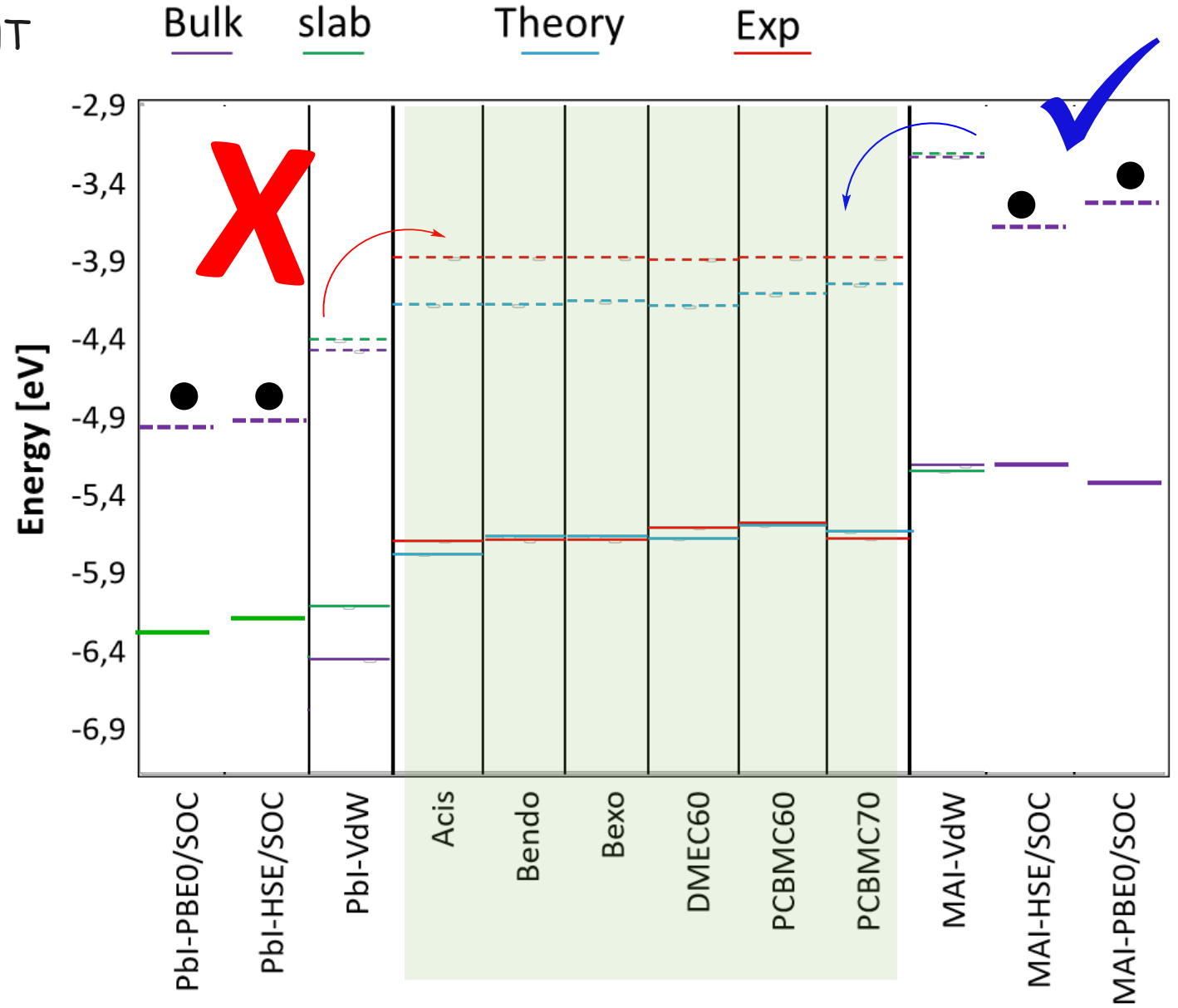
✓ <u>Model structures</u>: Isolated: HSE/6-31G(d) & PBC: optB88-vdW , ecutwfn = 50 Ry, ecutrho = 400 Ry, USPP

✓ <u>Electronic properties</u>: optB88-vdW; Hybrid: HSE06 / PBE0(α) + Spin-Orbit Coupling (SOC)

Computational packages: Gaussian 09, Quantum Espresso, VASP

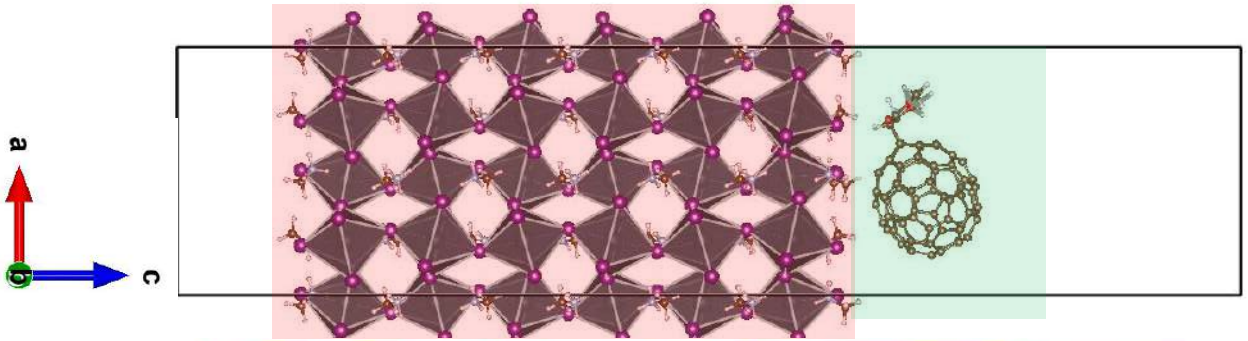
BANDS ALIGNMENT

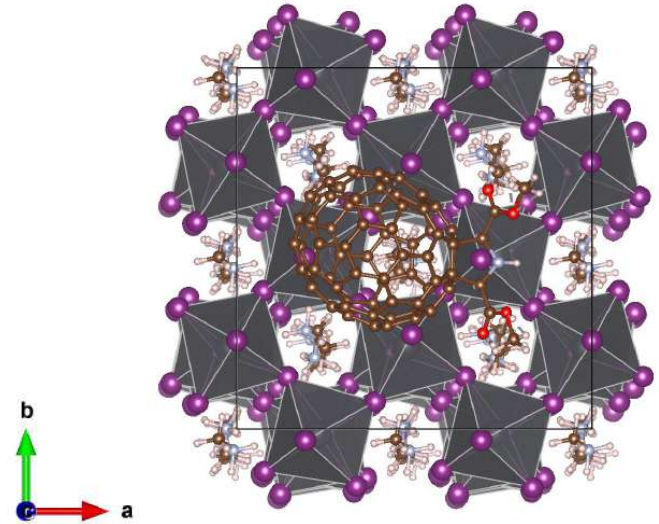
Hybrid- SOC corrections

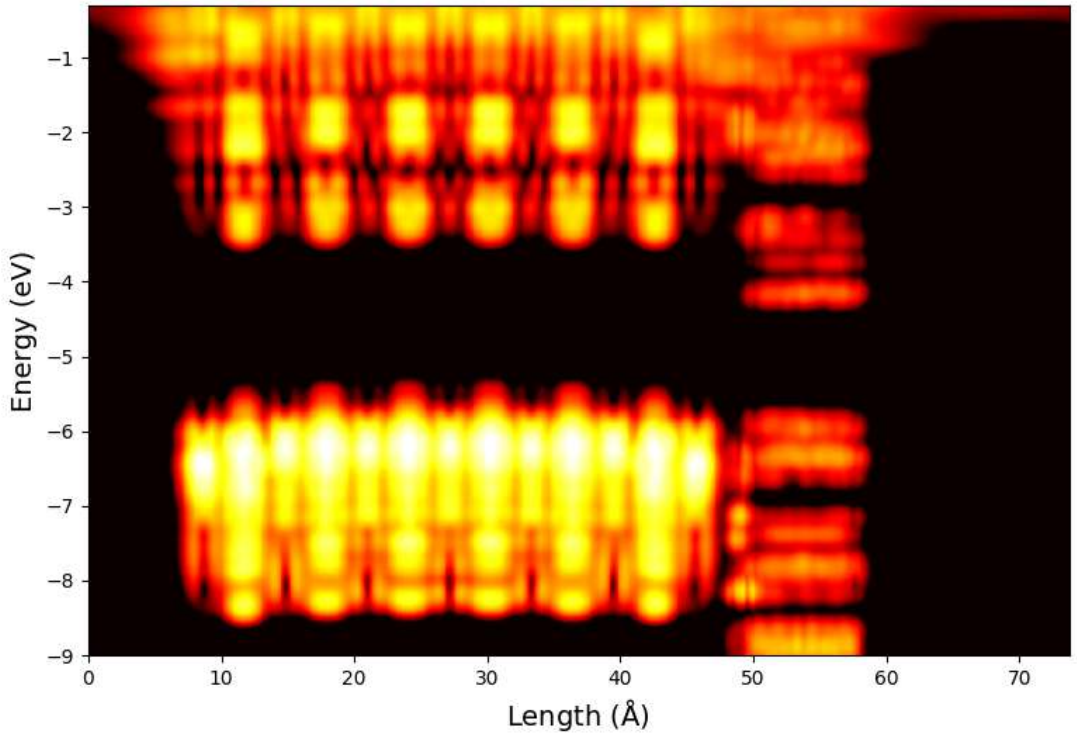


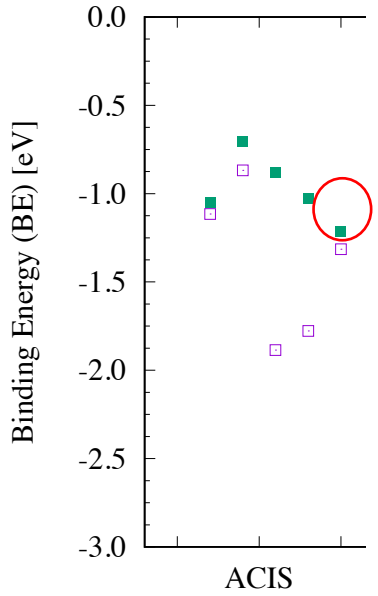
- ✓ PBE0(α) - SOC , ENCUT=295 eV, PAW
- ✓ HSE06 – SOC, ENCUT=295 eV, PAW

Interface MAPI(001-**MAI**) / ACIS (Group down)









✓ optB88-vdW , ecutwfn = 50 Ry, ecutrho = 300 Ry, USPP

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- CONICYT/FONDECYT Regular Grants No. 1130437, 1171807.
- CONICYT/FONDECYT Initiation Grant N.º. 11180984
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- Powered@NLHPC: This research was partially supported by the supercomputing infrastructure of the NLHPC (ECM-02).

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Physica B **568**, 81 (2019)
Sci. Rep. **9**, 9194 (2019)