Large scale electronic structure calculations of nanosystems using Titan machine

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INCITE Project
NERSC, ALCF

Outline

(1) An atomic model of PbS surface passivation

(2) Structure defect and electronic in-gap-states of PbS

(3) Moire’s pattern of MoS2/MoSe2 bilayer

(4) Carrier localization in CH3NH3PbI3 hybrid perovskite

(5) The electronic structure of vortices of ferroelectric materials

Outline

(1) An atomic model of PbS surface passivation

By Danylo Zherebetskyy

The size of the problems: ~ 1,000 atoms (but many situations)

Calculation: using VASP

Processor used: ~ 10,000 (with many jobs run together)

practically impossible without INCITE project

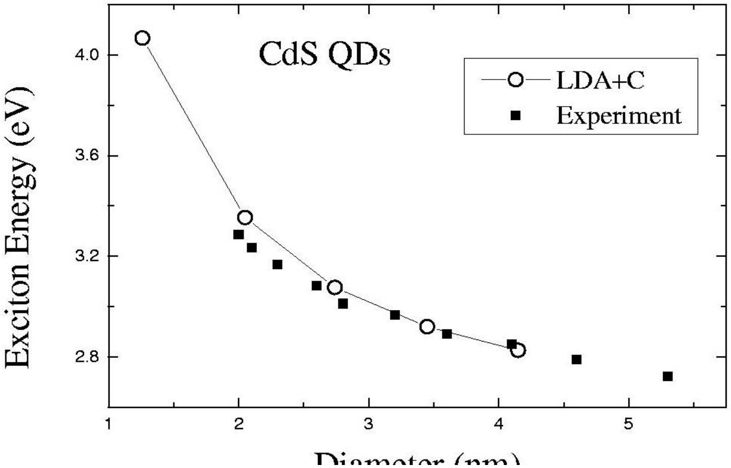
Zherebestskyy, et.al, Science 344, 1380 (2014)
Liao, et.al, Science 345, 6199 (2014)

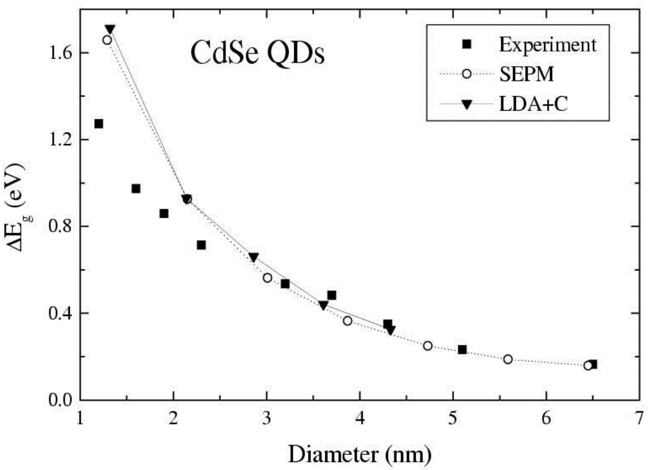
Quantum dot and wire calculations for semiconductor materials

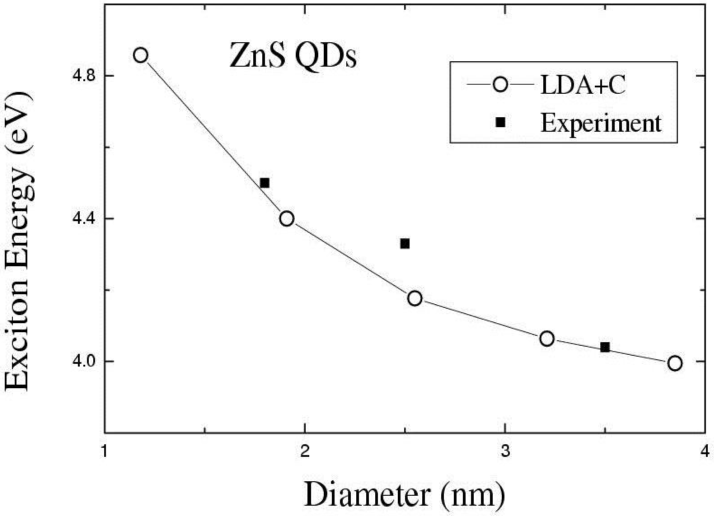
IV-IV: Si

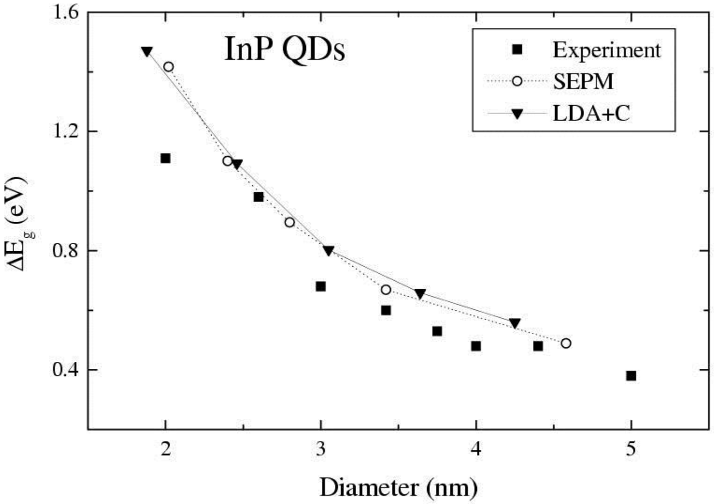
III-V: GaAs, InAs, InP, GaN, AlN, InN

II-VI: CdSe, CdS, CdTe, ZnSe, ZnS, ZnTe, ZnO

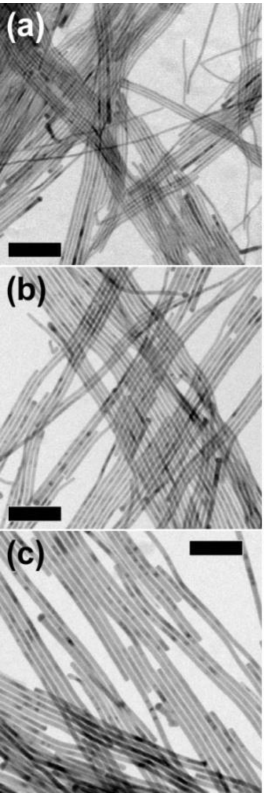


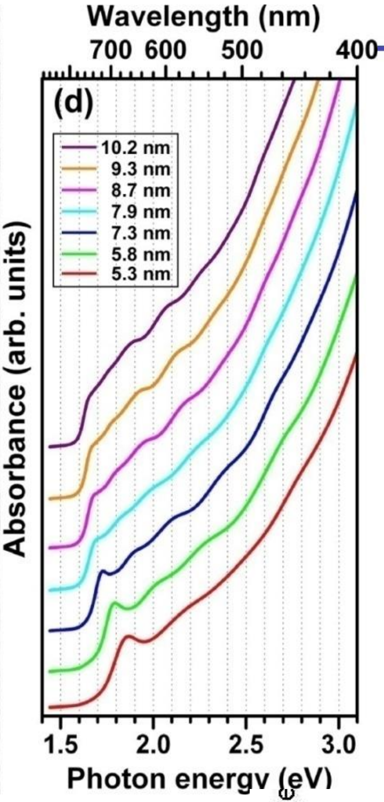






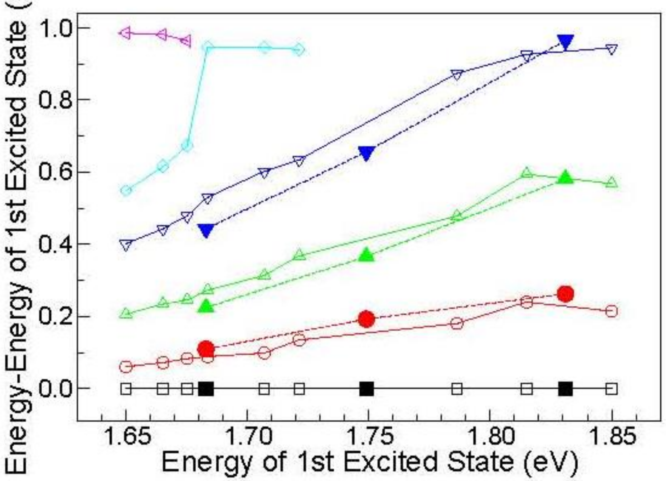
CdTe nanowire

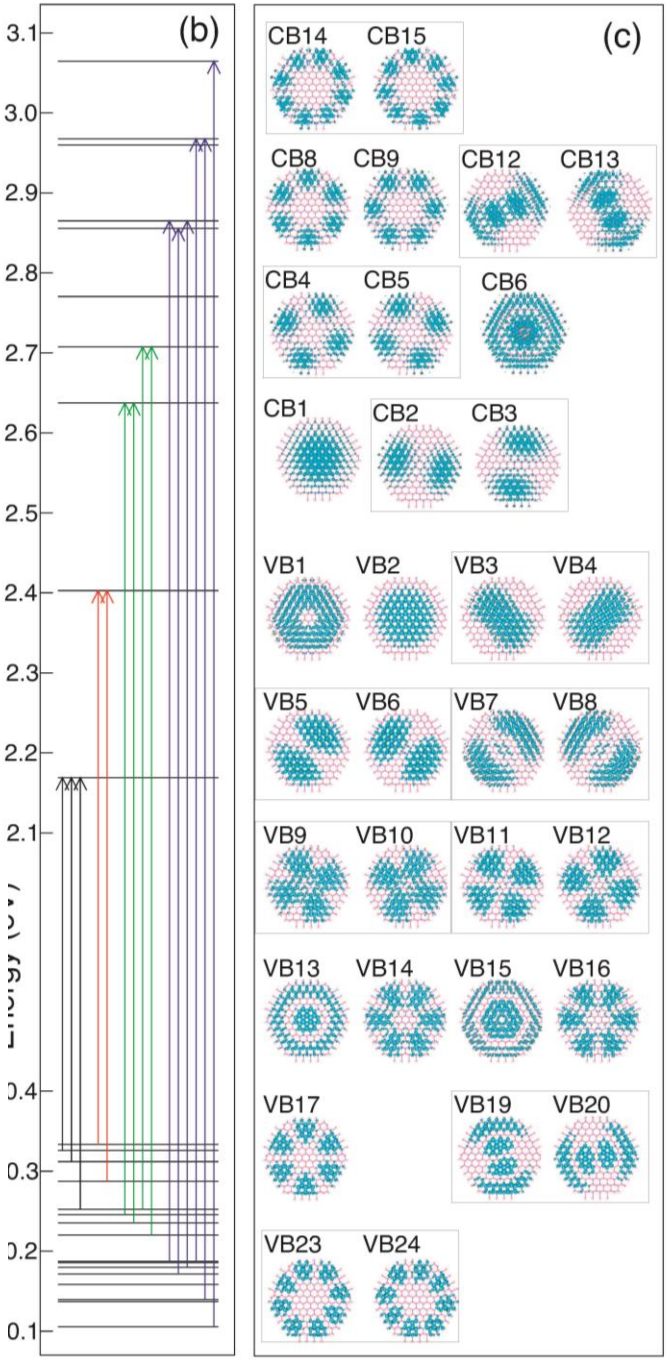




Exp:

Calc:





All the previous calculations are assuming perfect surface passivation

But what about realistic surface passivation?

Many problems are related to surface passivation

- Hot carrier cooling
- Carrier transport between QD
- Efficiency of PL

Experimental facts for PbS-QD surface passivation

1) **(001)** and **(111)** facets on NC

2) **Ligands removed** easily from (001)

3) **Pb:S** = 1.2-1.6 : 1

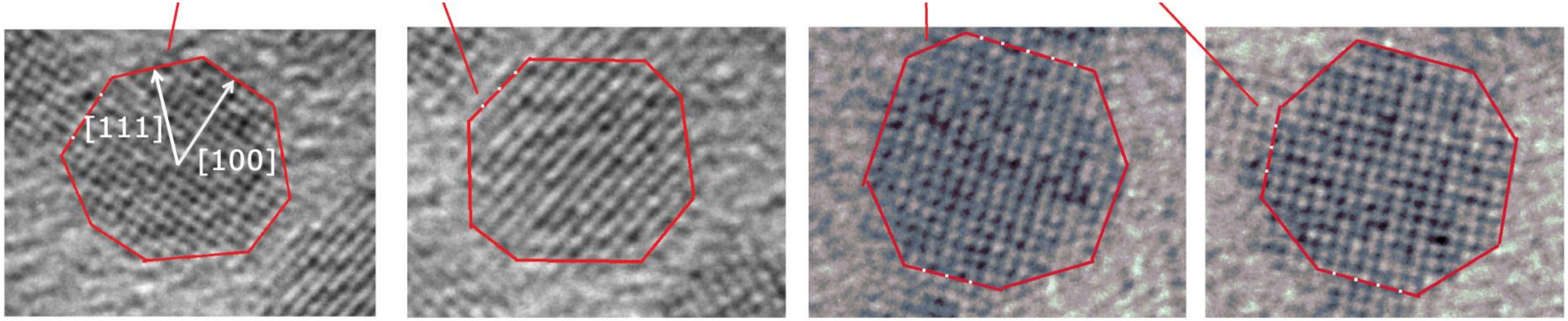
4) **Lig^{1-}:Pb^{2+}$_{\mathbf{excess}}$** ~ 1:1

5) **Certain (001)/(111) facet ratio**

But no detailed atomistic model
which is consistent with the above facts

Alivisatos, Science 271 (1996)
Murray et al.IBMJ.Res.Dev.45(2001)
Puntes et al. Science 291 (2001)
El-Sayed Acc.Chem. Res 37 (2004)
Yin&Alivisatos, Nature 437 (2005)
Jun et al. JPCB 109 (2005)
Steckel et al. JACS 128 (2006)
Moreels et al. Chem.Mater19, (2007)
Liu et al. JACS 129 (2007)
Moreels et al, JACS 130 (2008)
Dai et al., ACS Nano 3 (2009)
Talapin et al. Chem.Rev.110(2010)
Tang et al. Nature Mater.10 (2011)
etc

But no STM image ……

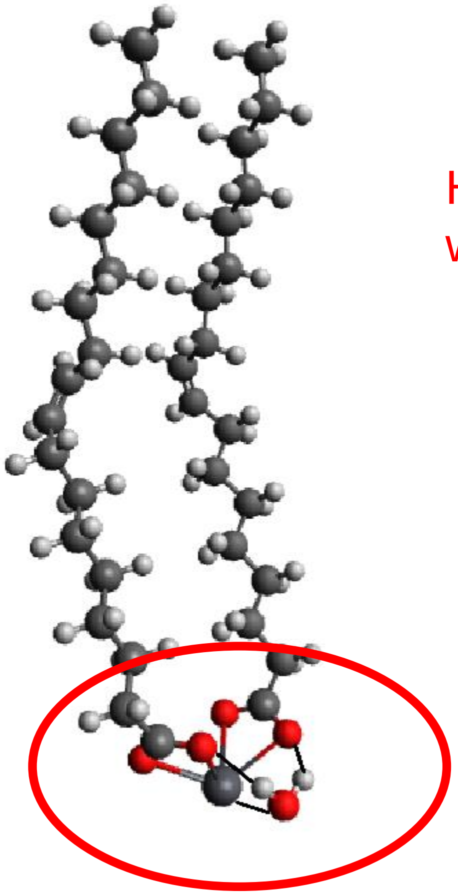


Follow the PbS-QD Synthesis

Synthesis

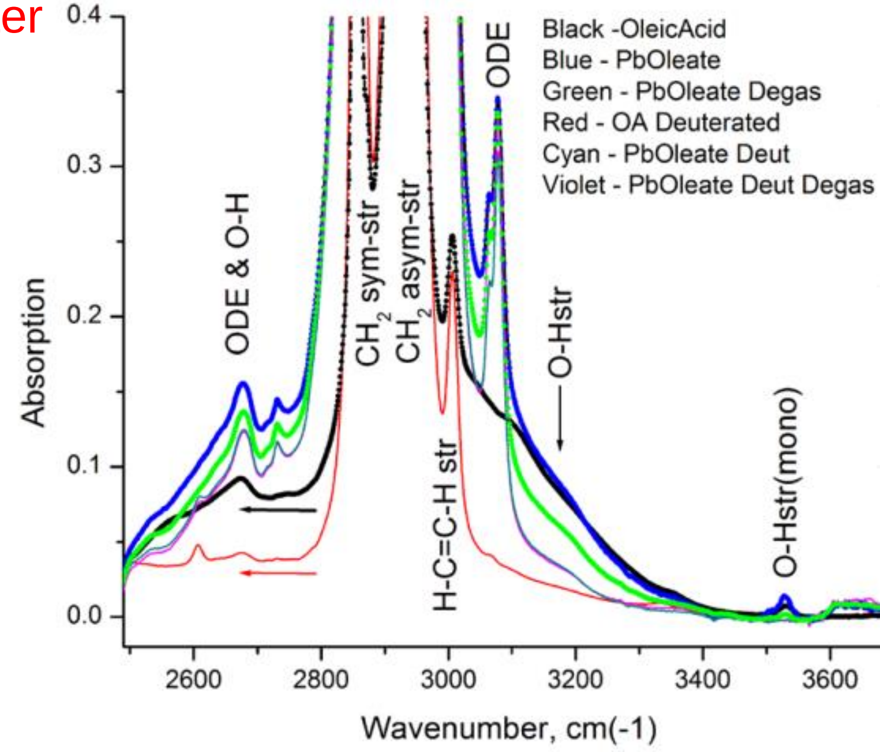
$PbO + (Oleyl\text{-}COOH)_2 \rightarrow (Oleyl\text{-}COO)_2Pb + H_2O$

important role
in passivation



Heating of the precursor
will not remove all the water

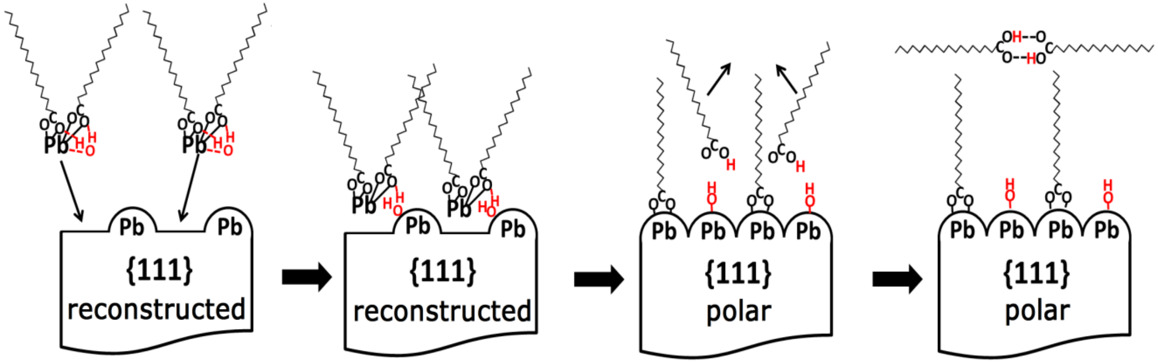
Ebind=0.48 eV
r(O···H)= 2.096 Å
r(Pb-O)=2.690 Å

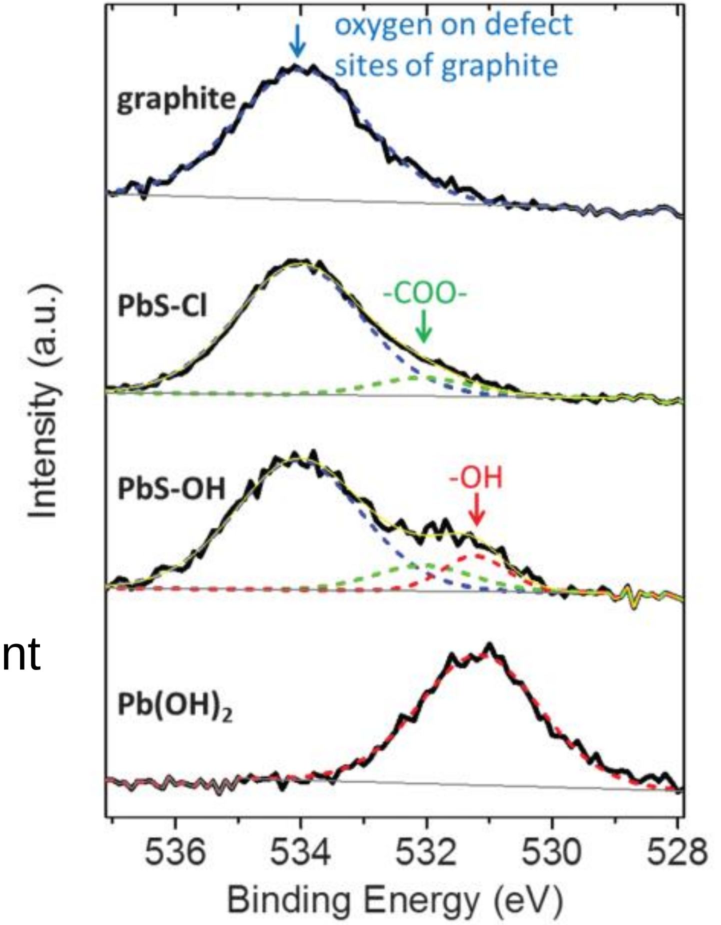


The HD-COO passivation of the (111) PbS surface

$$(\text{Oleyl-COO})_2\text{Pb}+\text{TOP-S}\rightarrow\mathbf{QD(PbS)+\ TOP{:}(Oleyl\text{-}COO)_2}$$

$$\mathbf{(PbS)_N+(Oleyl\text{-}COO)_2Pb\cdots H_2O\rightarrow(Oleyl\text{-}COO)\text{-}Pb_{N+1}S_N[111]\text{-}OH+HDCOOH}$$



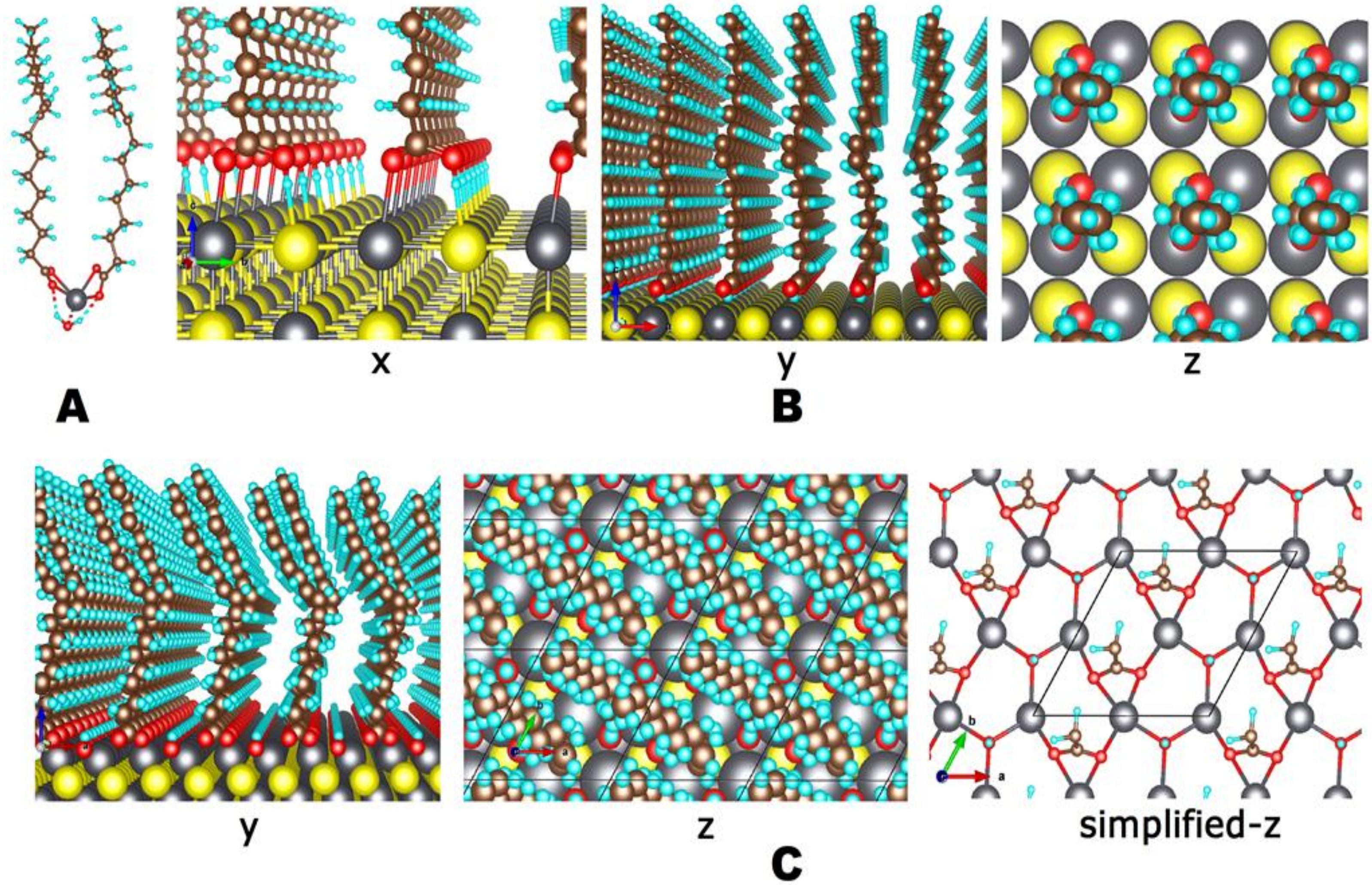


XPS experiment

We can also calculate the surface energy with ligand passivations

Detail atomic structures

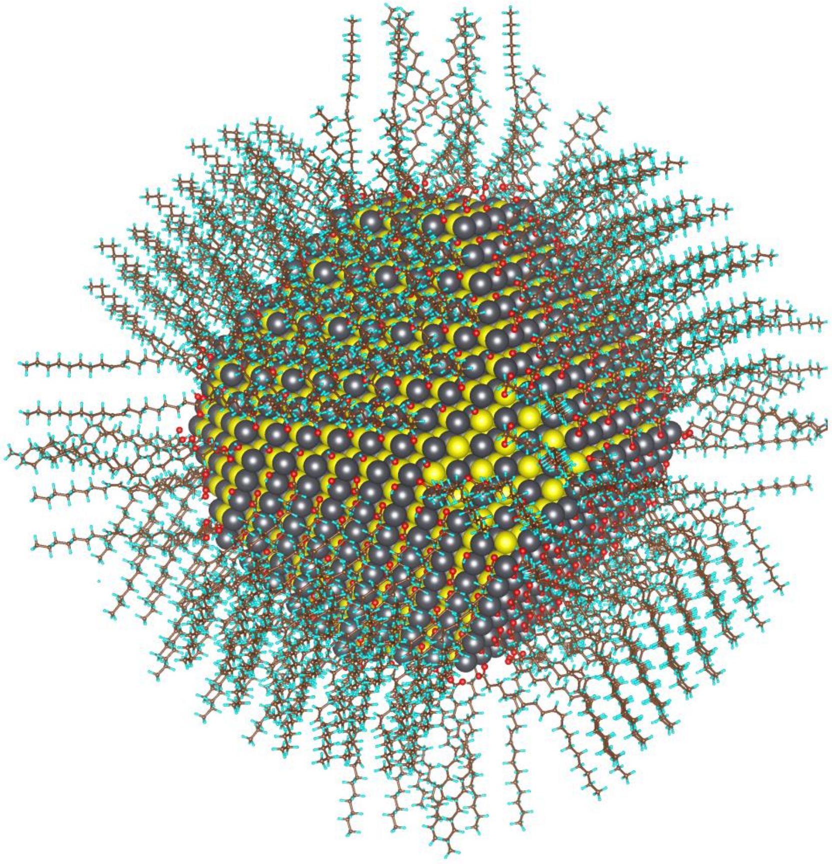
Oleic acid

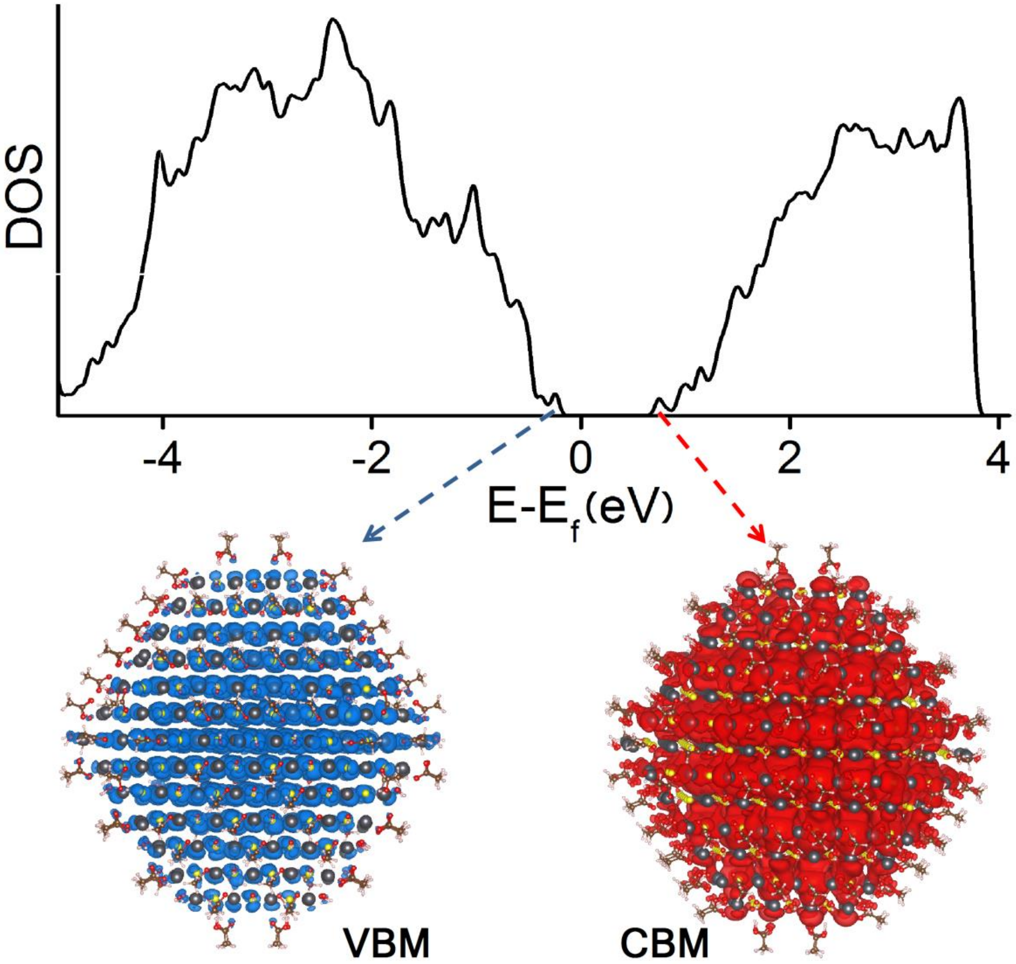


PbS (001)

PbS (111)

An atomistic model which fits all the exp. facts





Conclusions about PbS surface passivations

- ❖ Most passivation happen on (111) surfaces, (001) surfaces do not need to be passivated

- ❖ Due to steric hindrance, a small anion is needed besides the large HDCOO anion, which makes the extra-Pb:HDCOO ratio 1:1

- ❖ Perhaps the ligand arrangement is not very random, hence can be studied by ab initio calculations

- ❖ The corner and edges can also be passivated using electron counting rule

- ✓ **(001)** and **(111)** facets on NC
- ✓ **Ligands removed** easily from (001)
- ✓ **Pb:S** = 1.2-1.6 : 1
- ✓ $\mathbf{Lig^{1-}:Pb^{2+}_{excess}} \sim 1:1$
- ✓ **(001)/(111) facet ratio**

Zherebetskyy et al. ***Science*** *344, 1380 (2014)*

Outline

(2) Structure defect and electronic in-gap-states of PbS

Danylo Zhevebetskyy

Size of the problems: ~1,000 atoms (but many situations)

Calculation: using VASP

Processor used: ~ 10,000 (with many jobs run together)

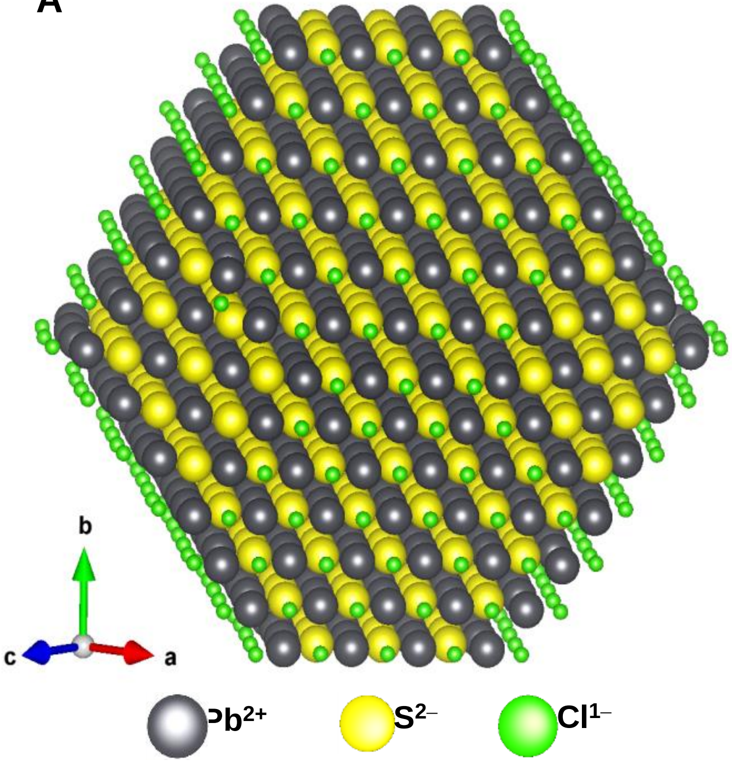
practically impossible without INCITE project

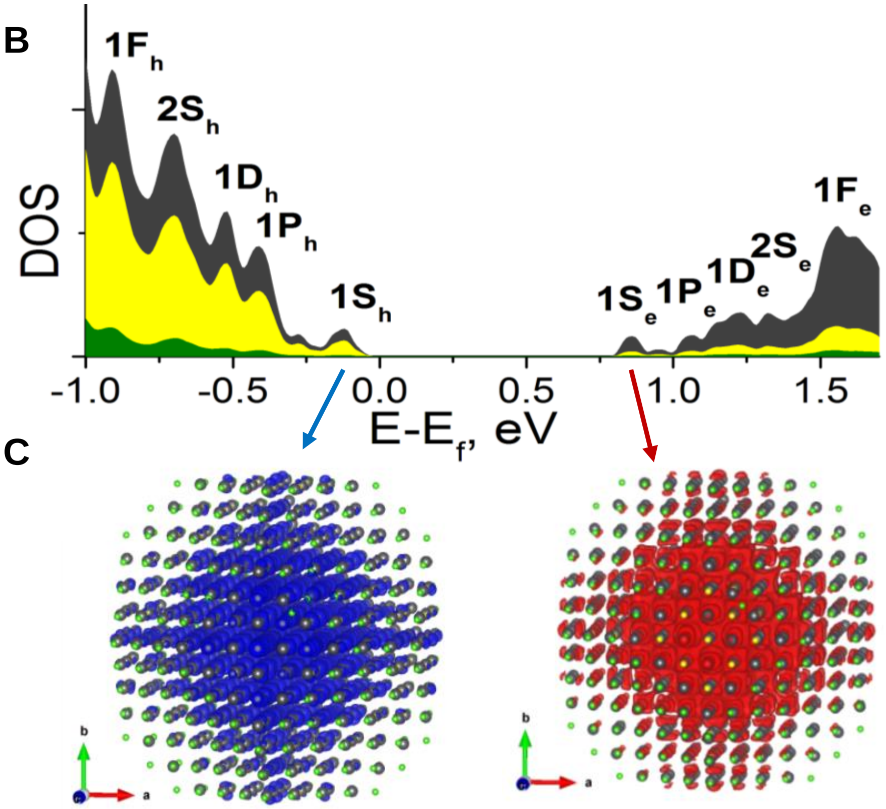
Question:

Does the QD surface have to be so perfect
in order to have good electronic and optical properties?

It is almost impossible to have such perfect surfaces!

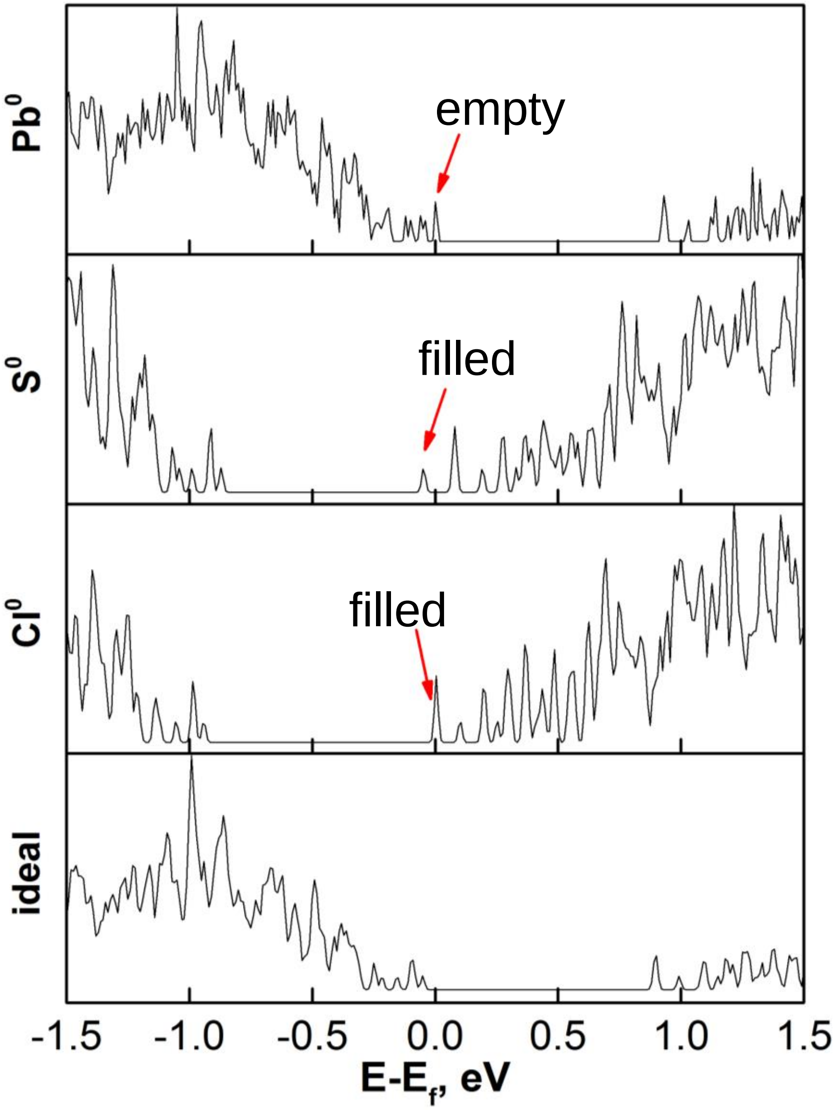
A simpler case: Cl passivated PbS (experimentally synthesized)





The perfect passivation case

Neutral defects

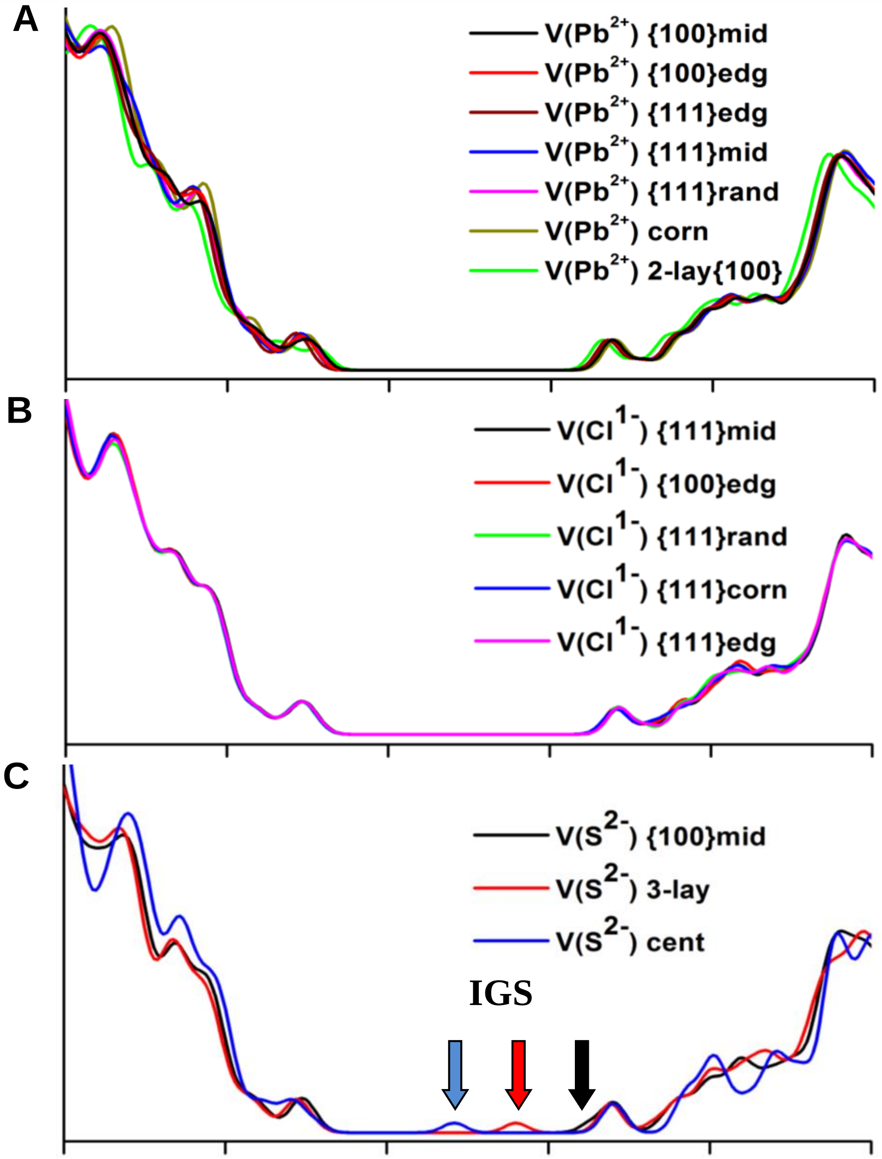


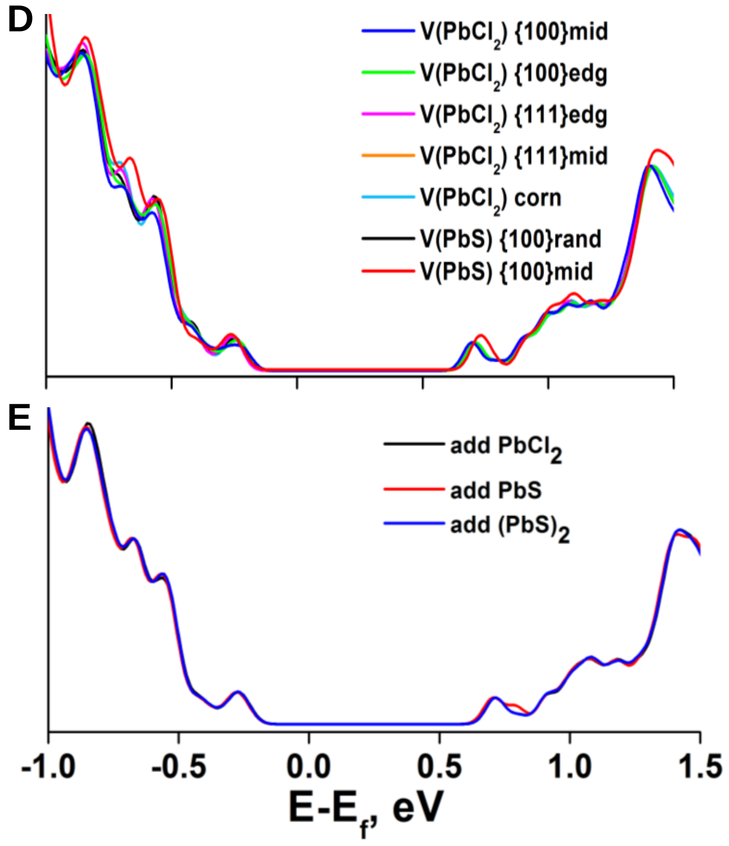
Neutral defects do introduce
In-gap-states

But should the defect be neutral
given the chemical environment

DFT calculation shows that
The defect should not be neutral
But proper ion-removal:
Cl^-, S^{2-}, Pb^{2+}

Defects in QDs: Pb^{2+}, S^{2-},,Cl^{-}, vacancies and defects



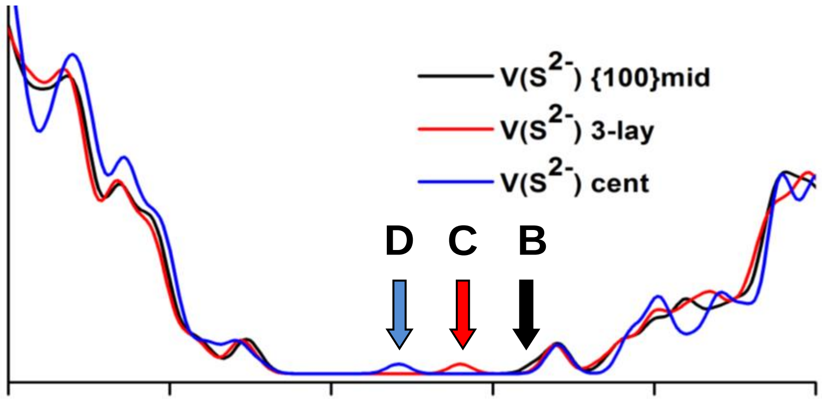


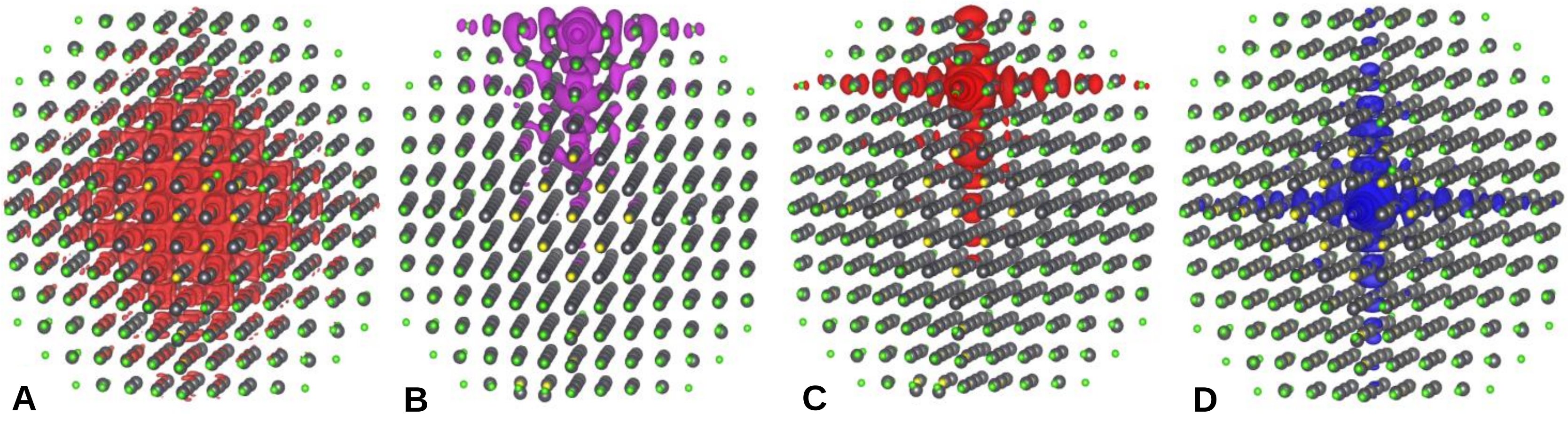
One should not remove the neutral atom,

Should remove the proper ions

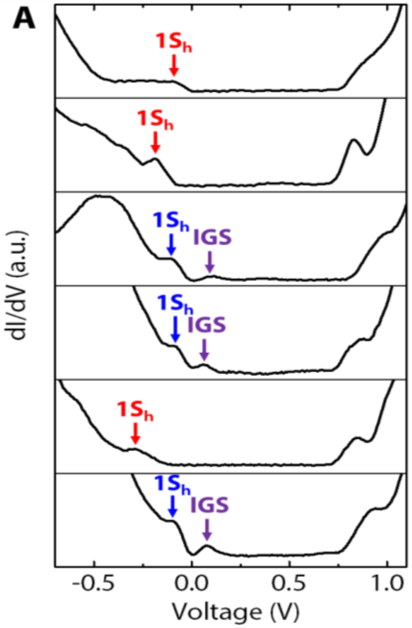
Formation energy calculation confirms this.

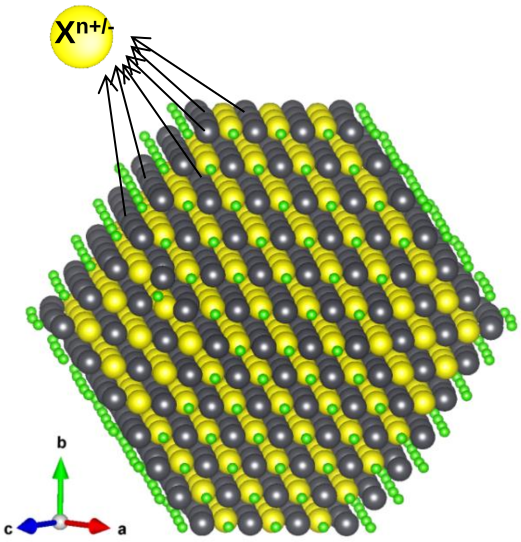
The S^{2-} vacancy case

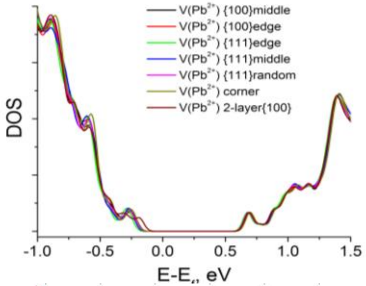


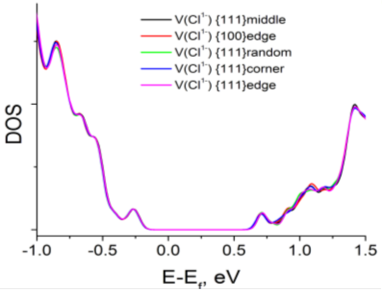


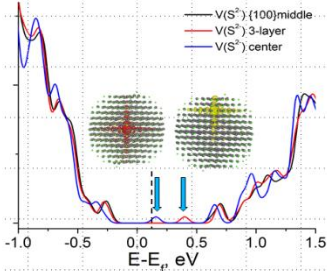
There can still be in-gap-states

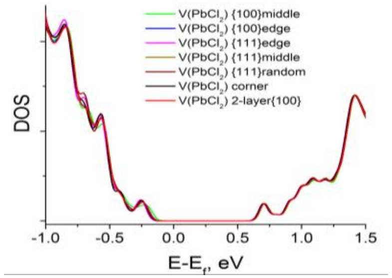


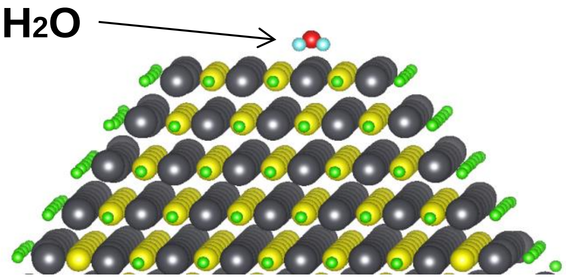


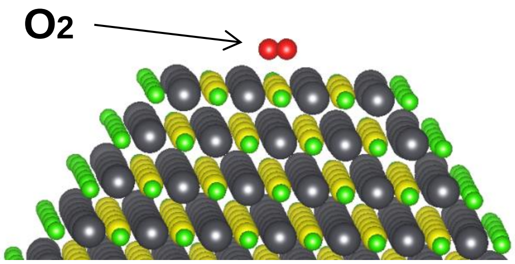


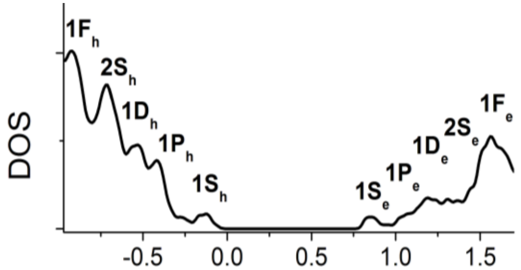


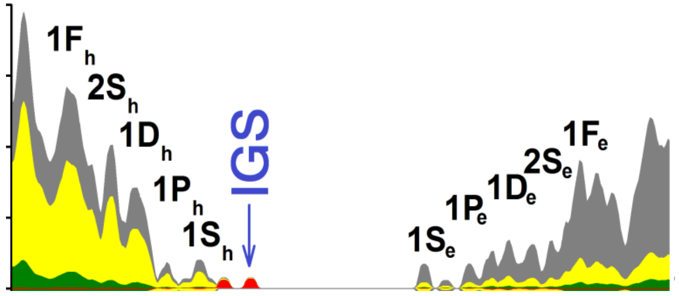












Conclusion about the defects

- One must remove the proper ions, not neutral atoms (the calculation shows the proper ion defects have lower formation E).

- Most proper ion defects do not induce electronic in-gap state

- S^{2-} at the interior of the QD does induce defect state, but there is a large energy drive (0.9 eV) to drives the S^{2-} out, and the barrier is low (< 1 eV -→ tens of seconds).

- The experimental observed surface trap state comes from surface absorbed molecules.

Outline

(3) Moire’s pattern of MoS2/MoSe2 bilayer

By Jun Kang

Size of the problem: ~7,000 atoms

Calculation: LS3DF (linear scaling 3 dimensional fragments)

Processor used: ~60,000

impossible without INCITE project

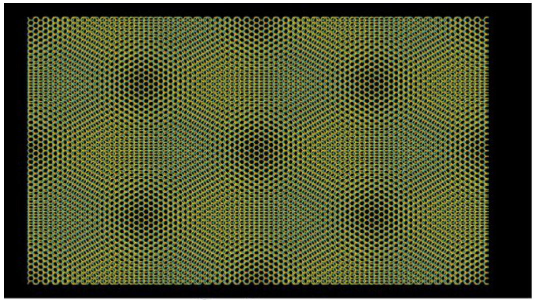
Kang, Nano Lett. 13, 5485 (2013)

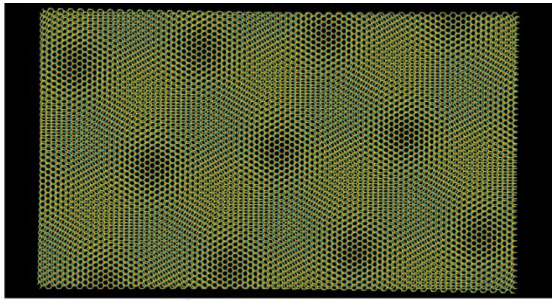
MoS_2-$MoSe_2$ double layer: Moire’s pattern

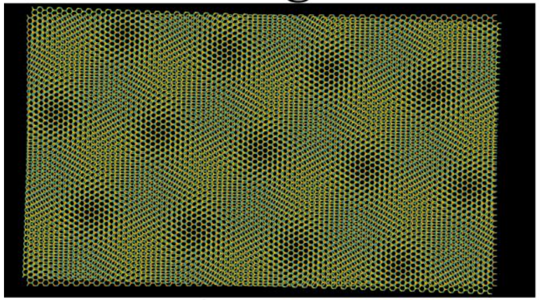
(1) There is a 10% lattice mismatch between MoS2 and MoSe2

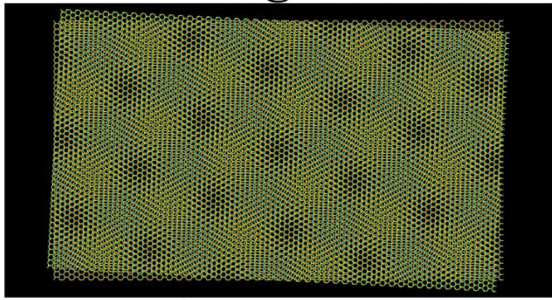
(2) This will form a Moire’s pattern.

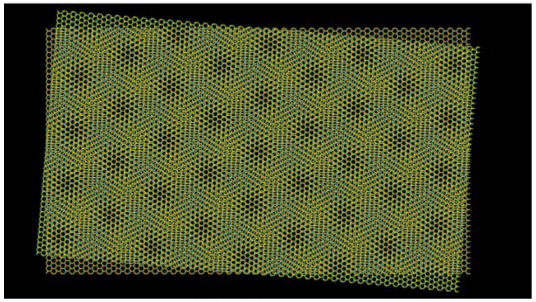
(1) What is the electronic structure consequence ?

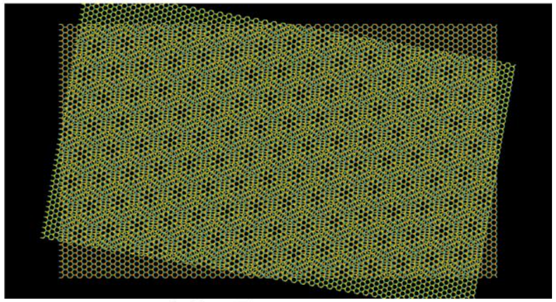

0 degree


1 degrees

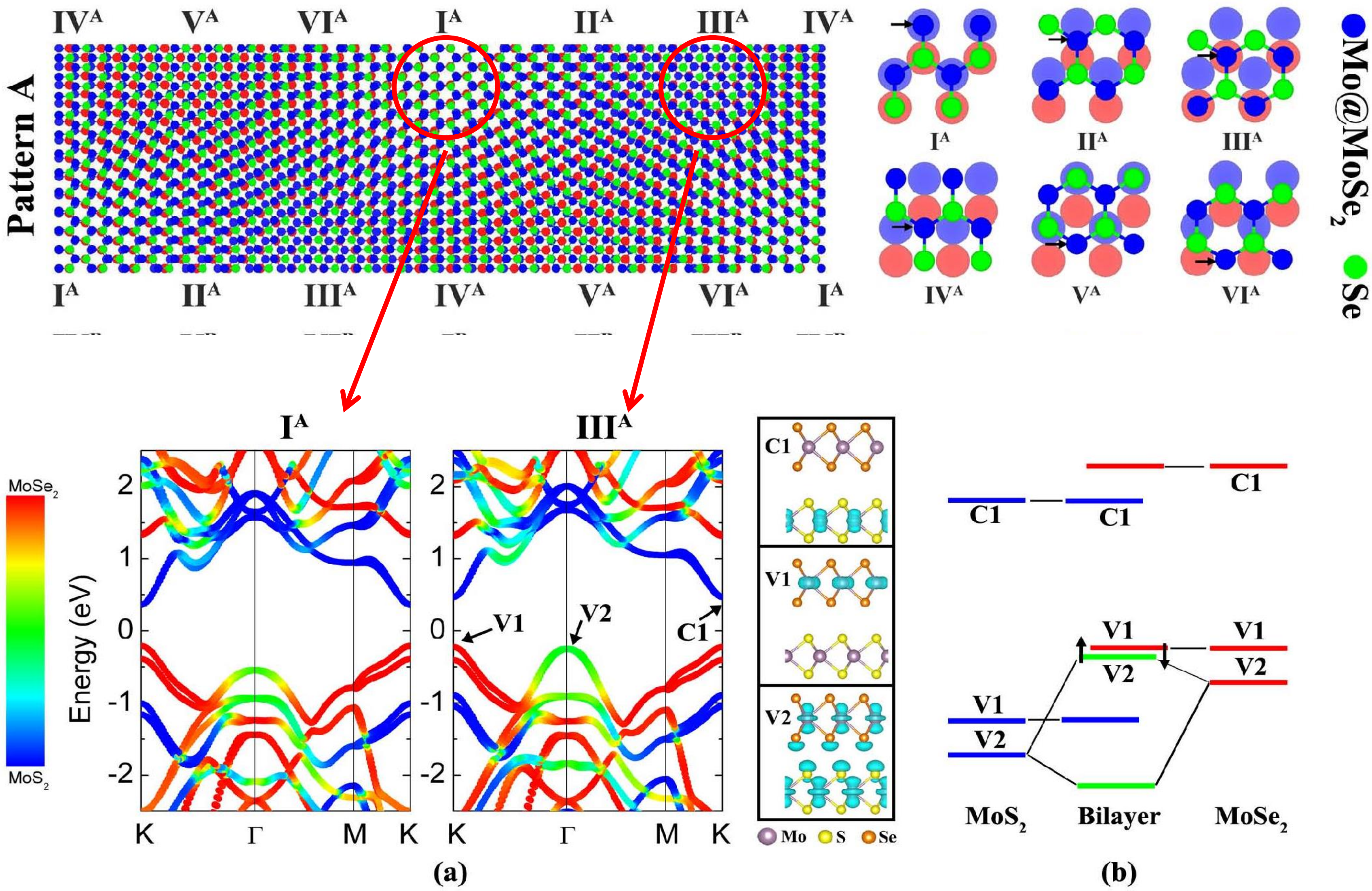

2 degree


3 degrees

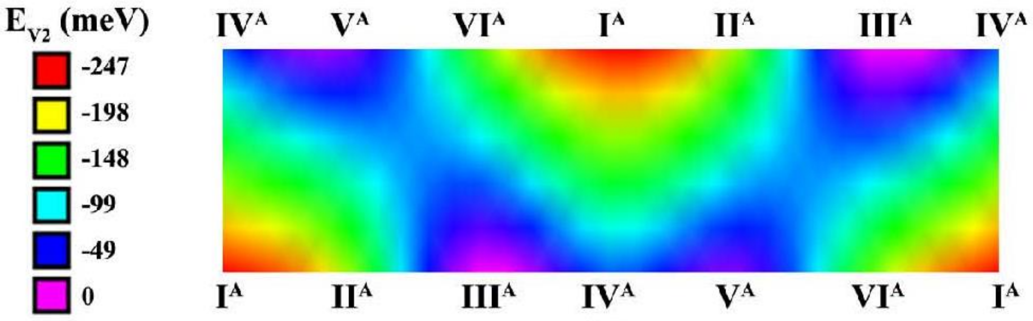

5 degree


10 degrees

Different location has different coupling

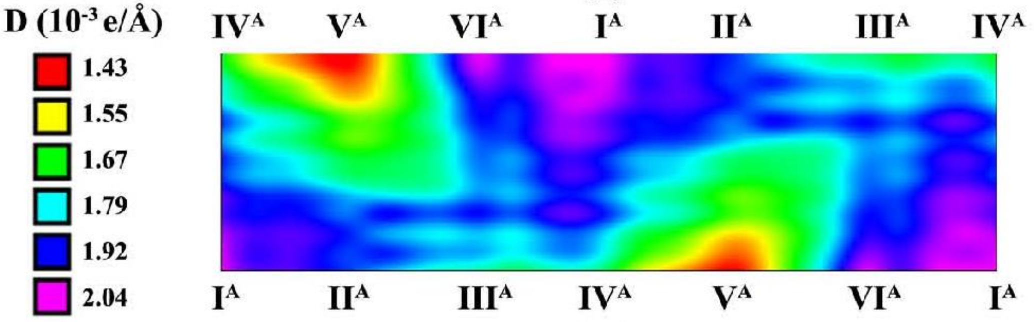


Three mechanisms for carrier localization



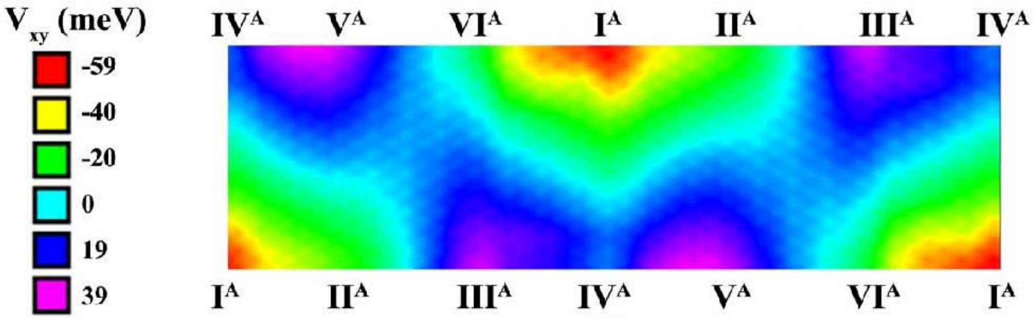
(a)

Interlayer coupling strength
Responsible for VBM localization



(b)

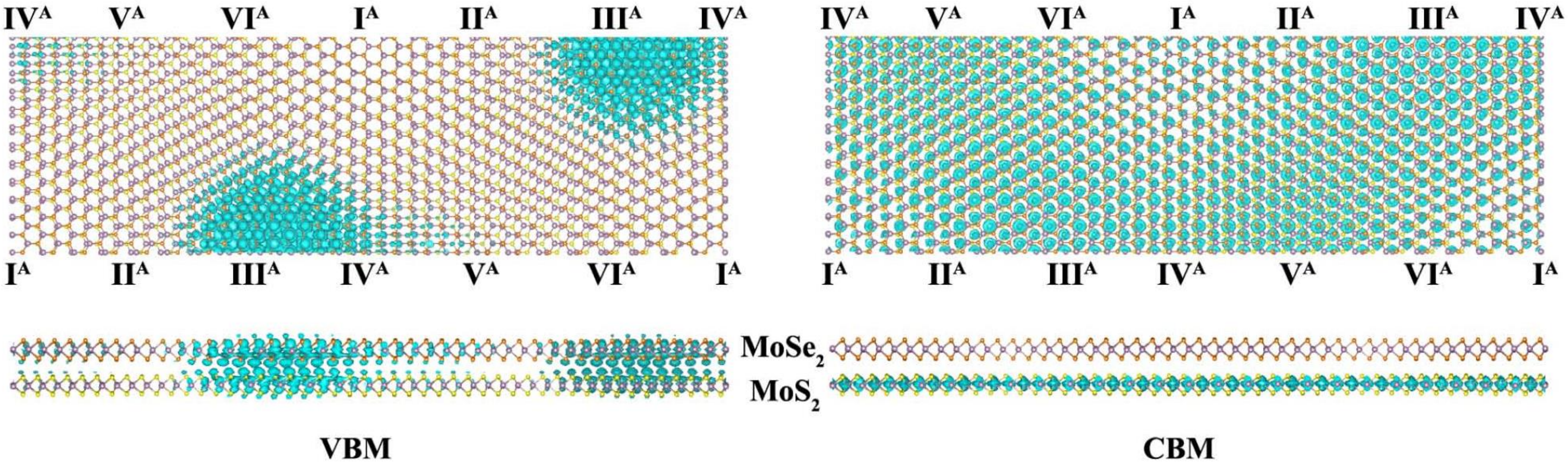
Vertical z direction charge transfer, responsible for CBM localization



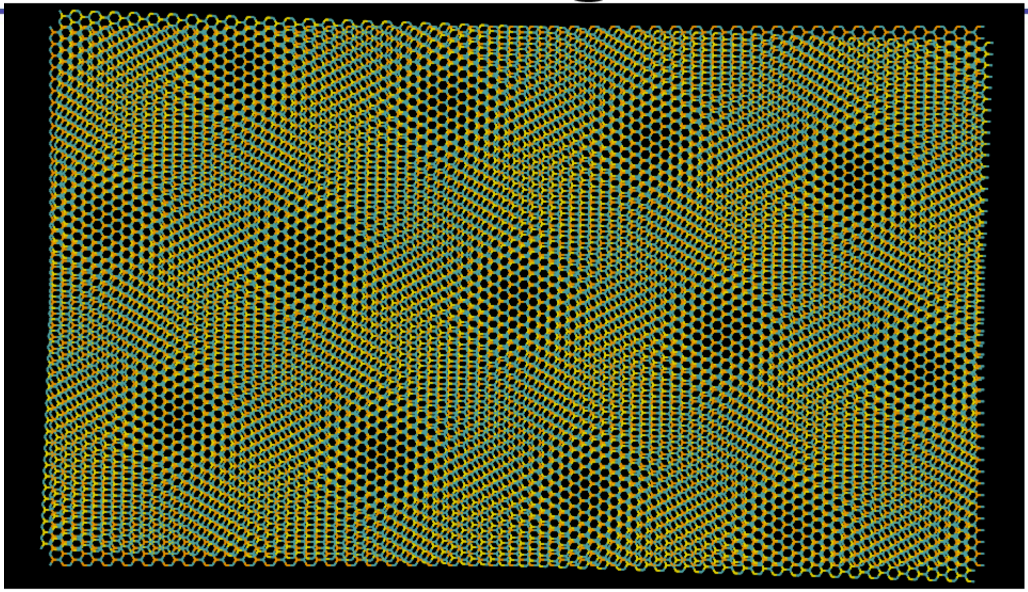
(c)

Lateral x, y directions charge transfer, against the CBM localization

Carrier localization in MoS_2-$MoSe_2$

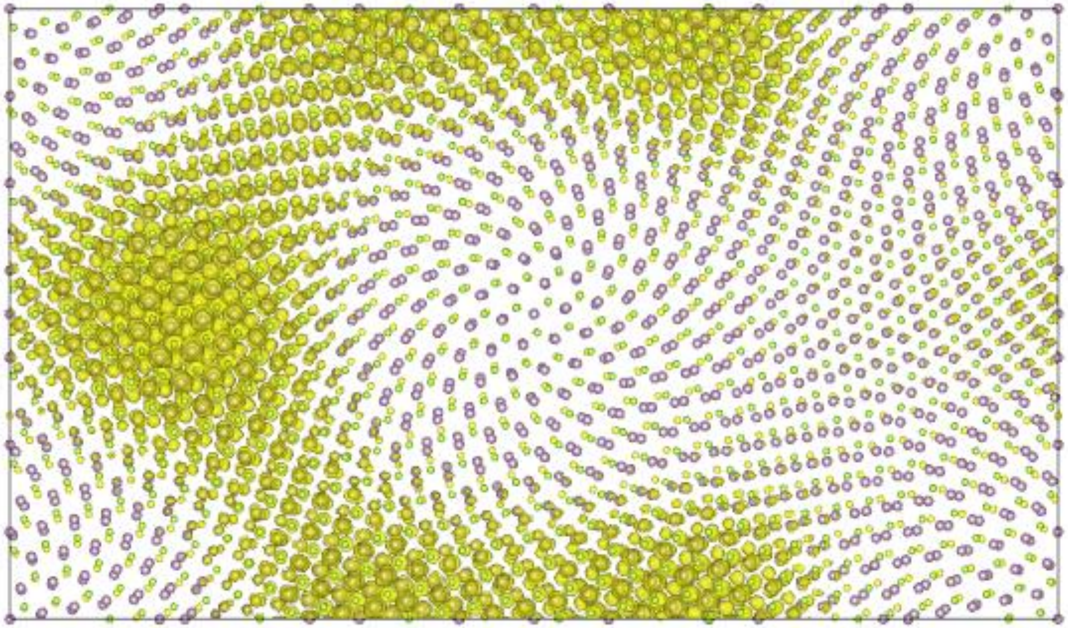


MoS2-MoSe2 with 2 degree rotation



2 degree

VBM



Conclusions for MoS2/MoSe2 carrier localization

(1) The atomic Moire's pattern will cause carrier localization

(2) The VBM is localized mostly by interlayer coupling

(3) The CBM is localized mostly by interlayer charge transfer

Outline

(4) Carrier localization in CH3NH3PbI3 hybrid perovskite

By Jie Ma

Size of the problem: ~20,000 atoms

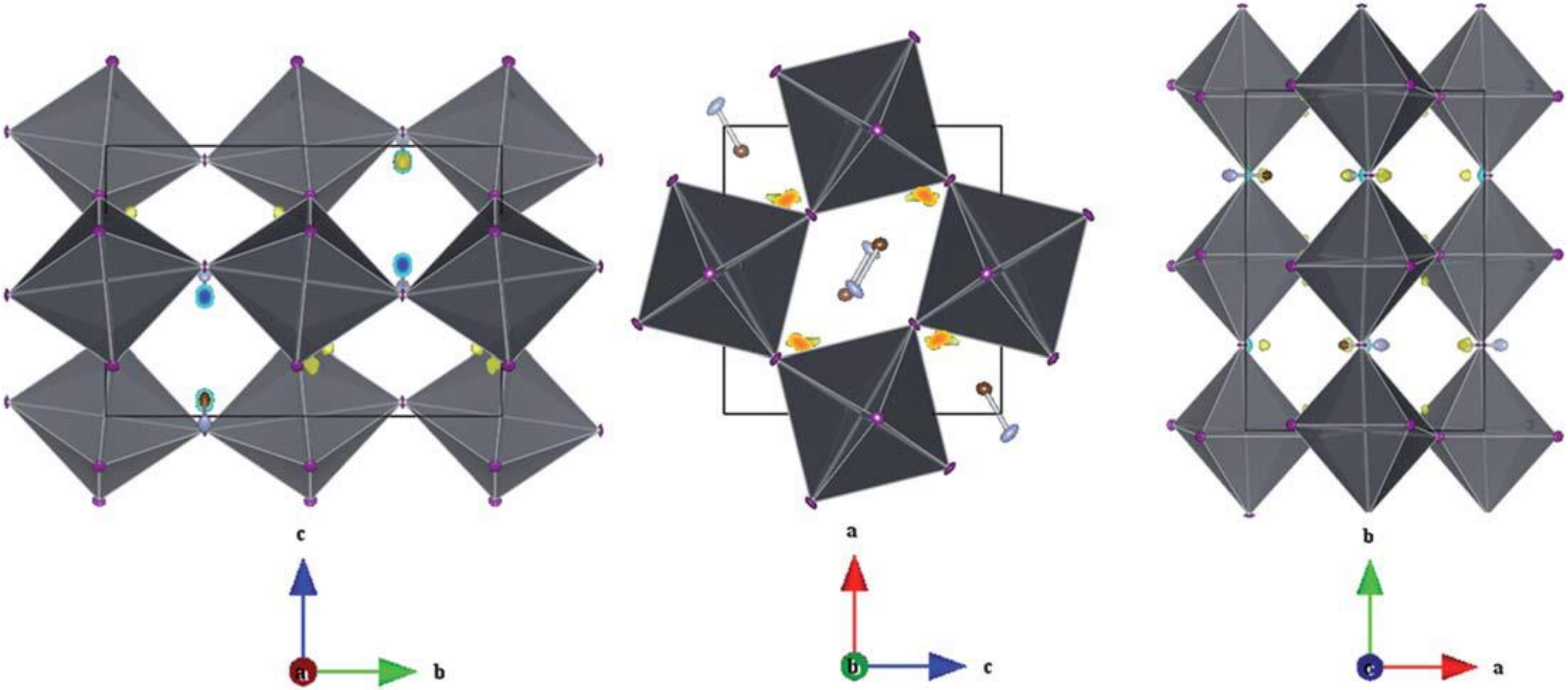
Calculation: LS3DF (linear scaling 3 dimensional fragments)

Processor used: ~60,000

impossible without INCITE project

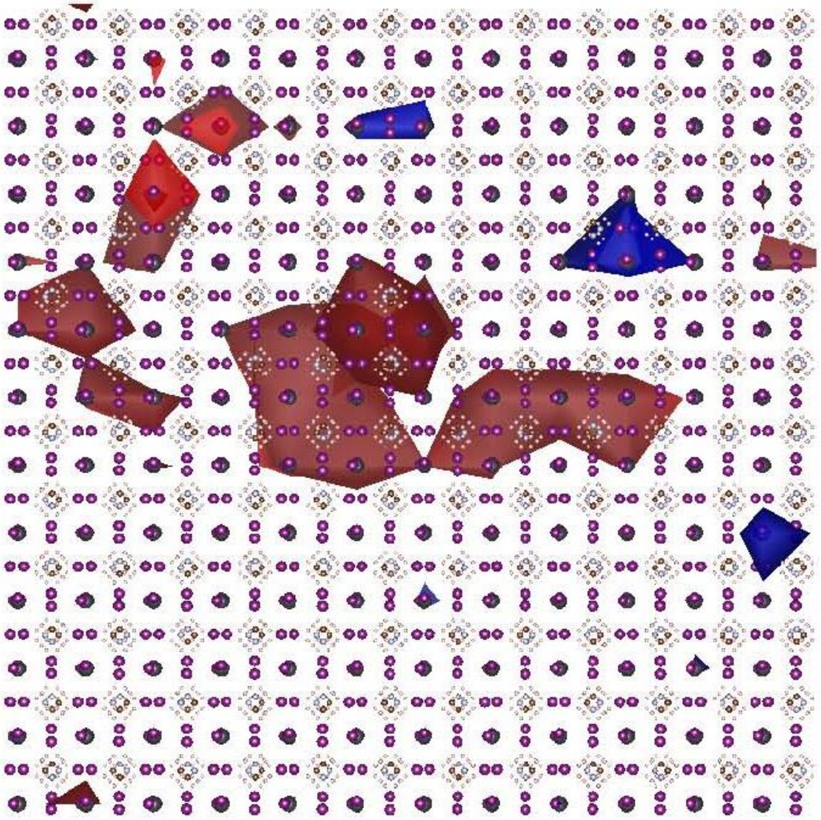
Ma and Wang, Nano Lett. 15, 248 (2015)

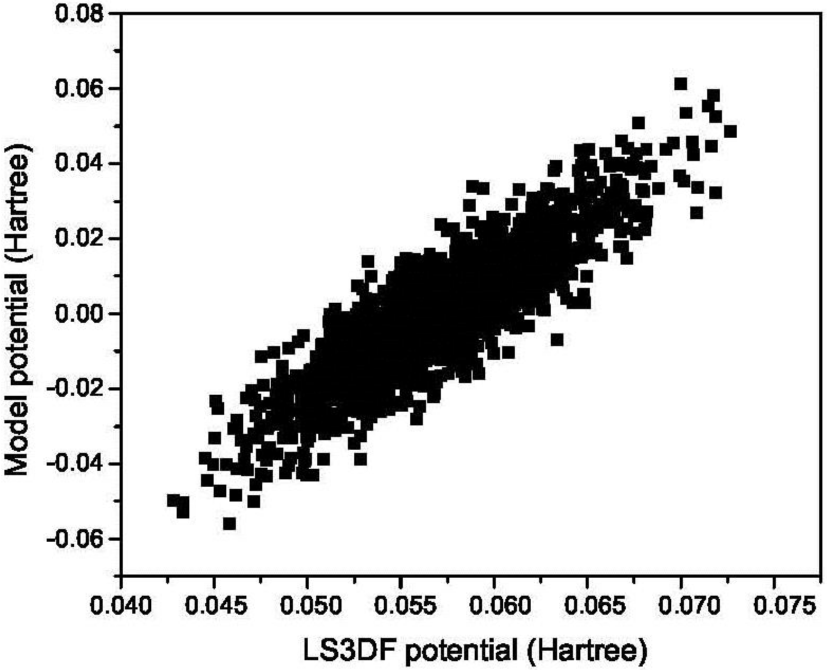
The atomic structure of room T CH3NH3PbI3



- The molecule CH3NH3 has a large dipole moment
- They have 8 different possible orientations
- They occupy these orientations randomly
- This will cause long range electrostatic potential fluctuations

Molecule orientation fluctuation cause electrostatic potential fluctuation

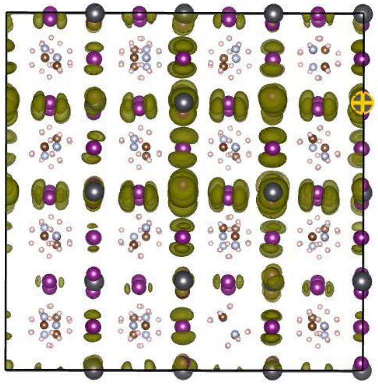


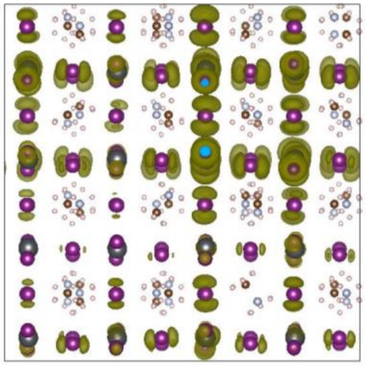


Comparison between the DFT calculated potential and model dipole moment potential

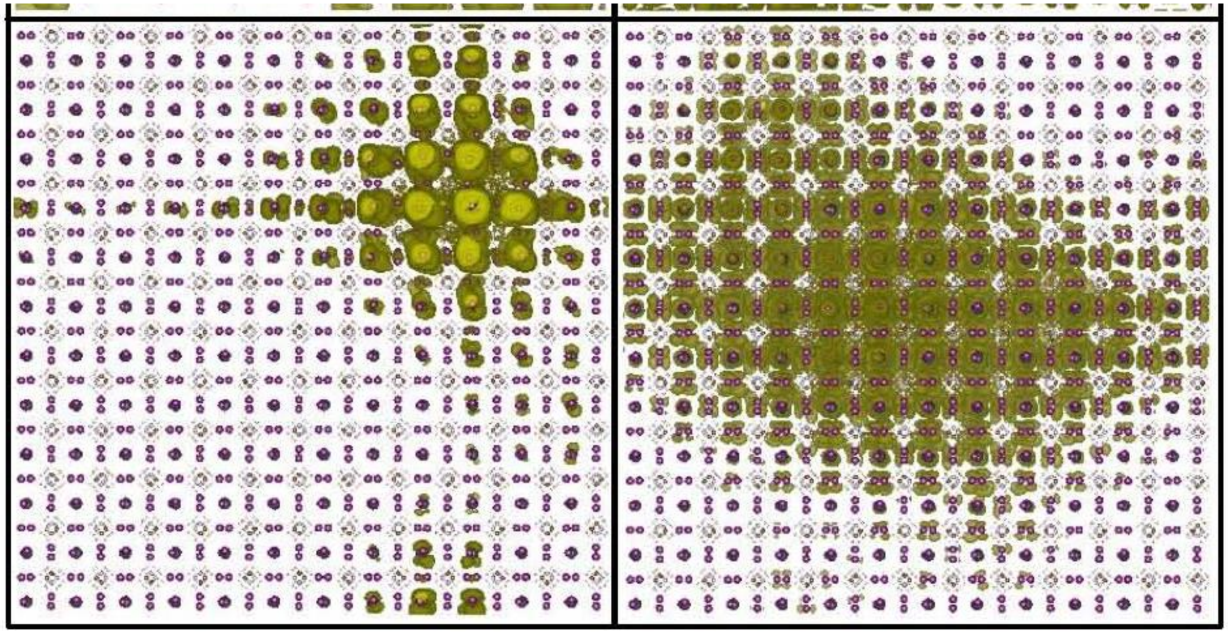
LS3DF: Hybrid (CH3NH3)PbI_3 perovskite for solar cell

LS3DF





Direct DFT ~700 atom



~20,000 atoms

CBM

VBM

Conclusion of the hybrid perovskite

(1) The random orientation of CH3NH3 cause
electrostatic potential fluctuations

(2) The potential fluctuations will cause free
carrier localization, and electron hole separations

(3) This will have significant impact on the carrier
transport, recombination and exciton formation

Outline

(5) The electronic structure of vortices of ferroelectric materials

Zhigang Gui

Size of the problems: ~3,000 atoms

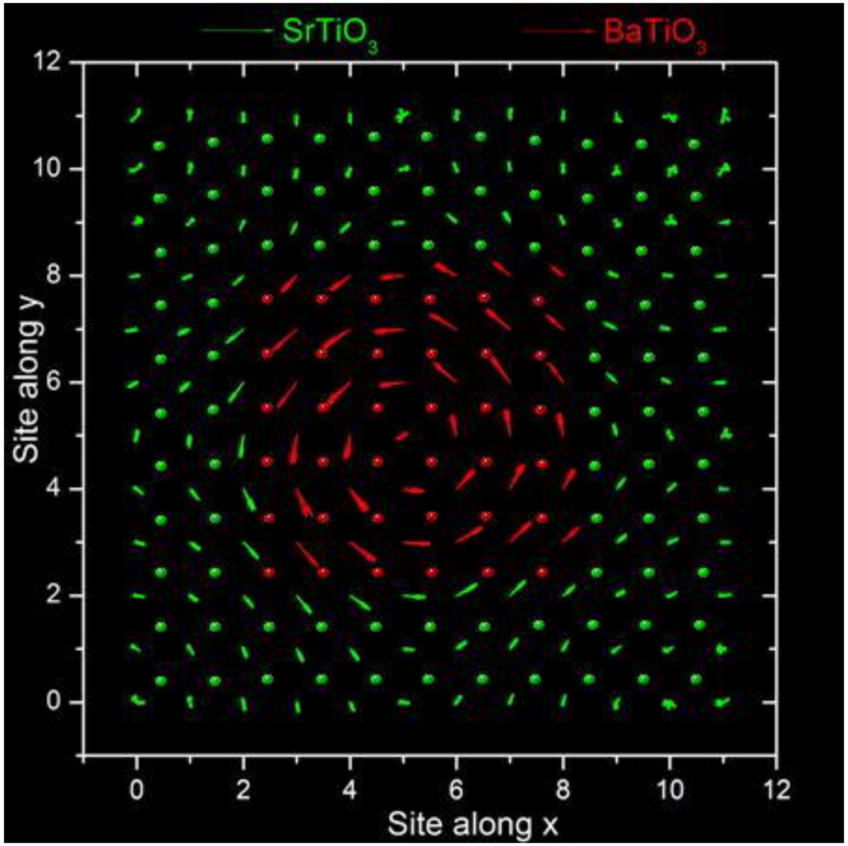
Calculation: using LS3DF

Processor used: ~ 60,000

Impossible without INCITE project

Gui, et.al, Nano Lett. 3224 (2015)

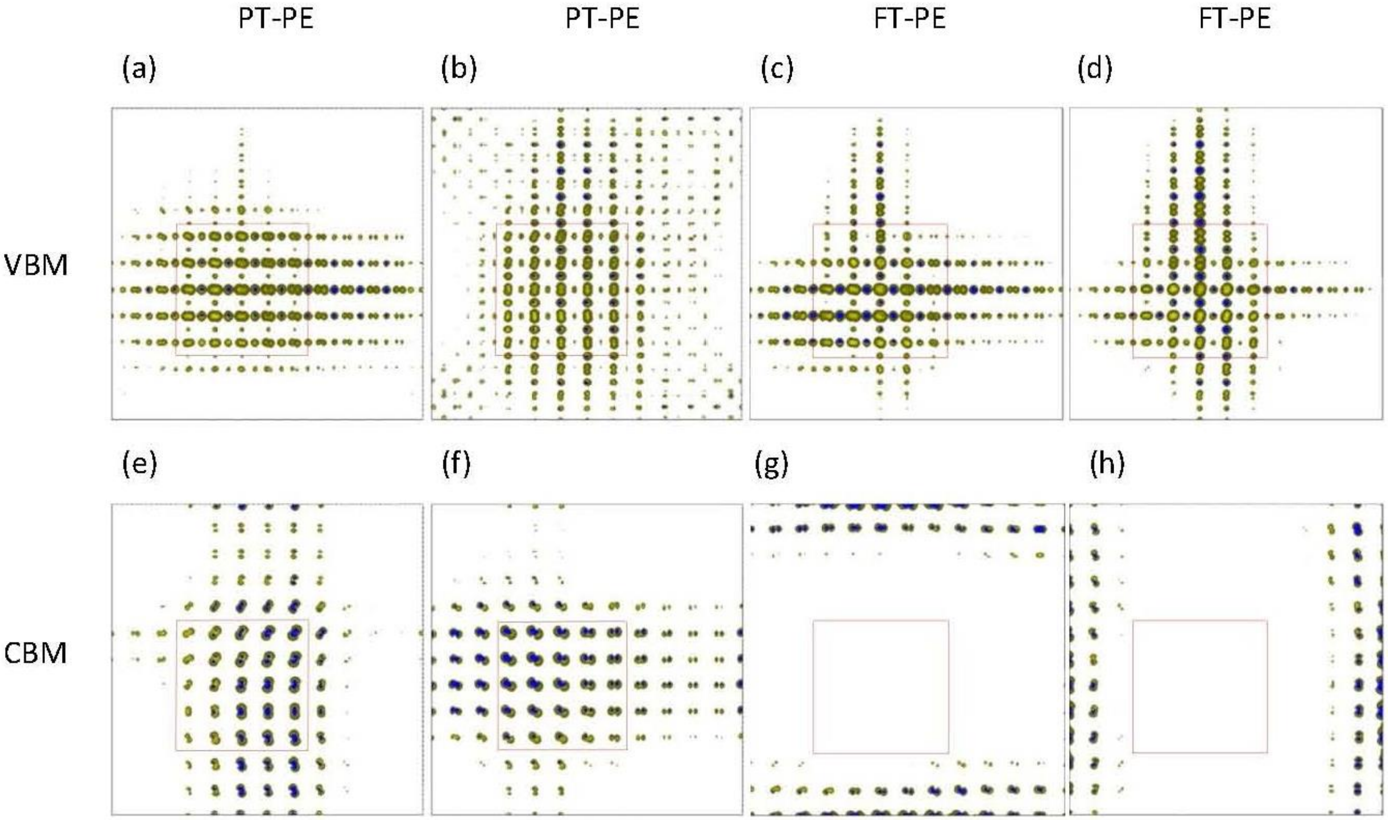
BaTiO3 inside SrTiO3 (nanowire) form a vortex

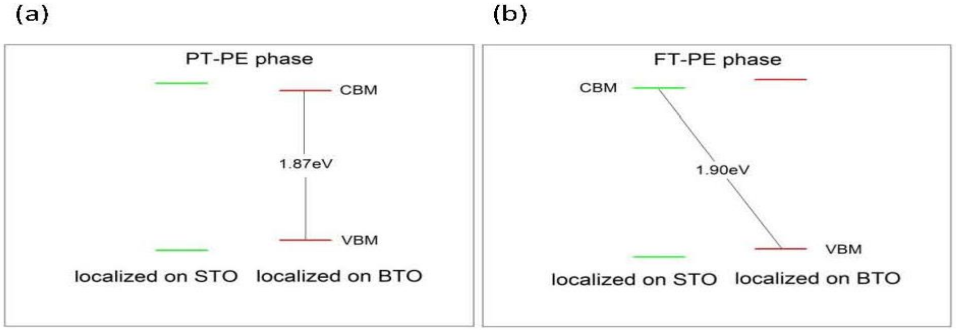


Experimentally, it is found that, when the vortex is formed, the conductivity of the system changed significantly, is that due to the reduction of the band gap?

The CBM and VBM states calculated using LS3DF

Without vortex **With vortex**





Conclusions

❖ The QD surface is amenable for ab initio simulations

❖ The metal chalcogenite QD is good electronically, since it is tolerance for structure defects

❖ The Moire’s pattern in the MoS2/MoSe2 bilayer can localize the electronic states, perhaps can be used for novel device design

❖ The molecule disorder in orientation in CH3NH3PbI3 hybrid perovskite can cause electrosatic fluctuation, which in term will cause electron and hole seperations

❖ The vortex in BaTiO3/SrTiO3 will not cause any major reduction of the band gap. The significant change in conductivity is probably due to some external effects (impurity, etc).

Thanks for the INCITE project,
all these calculations become possible !