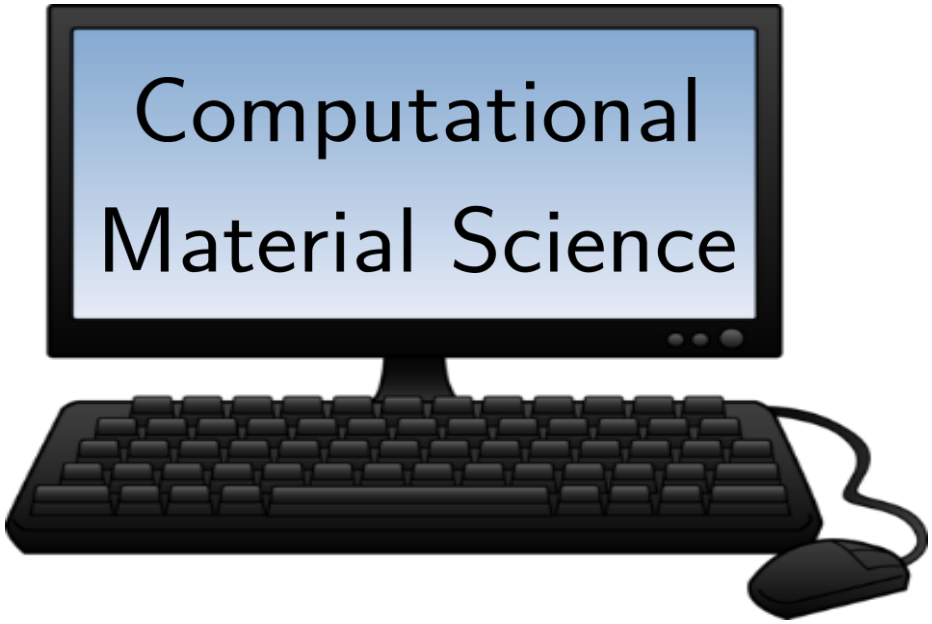
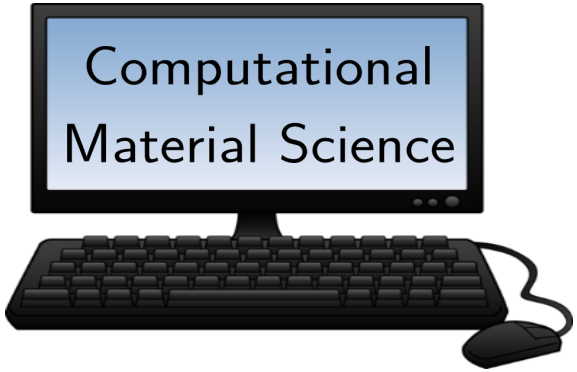
Selected Challenges in Material Simulations



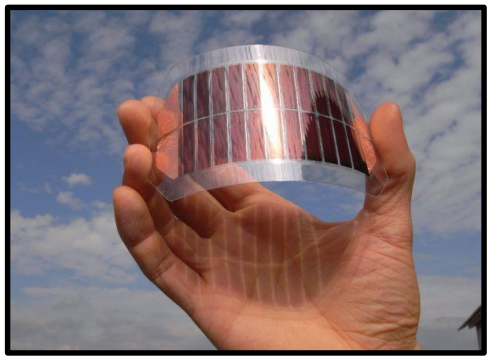
Oliver T. Hofmann

Graz University of Technology

Institute of Solid State Physics

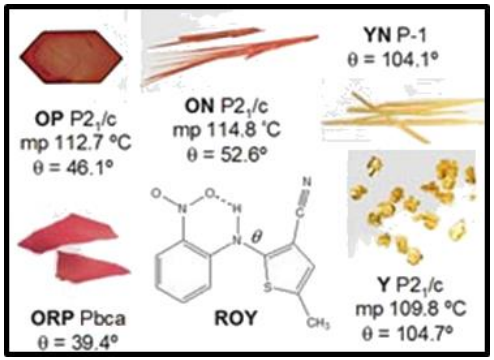


The quest for improved materials



Photovoltaic cells

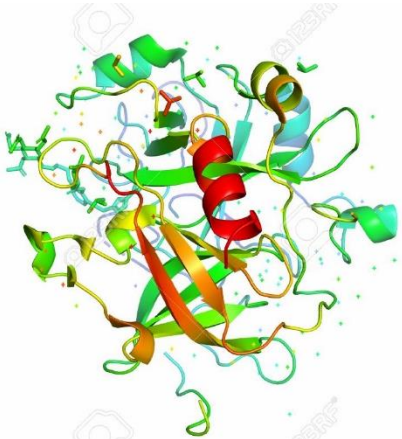
OLED displays



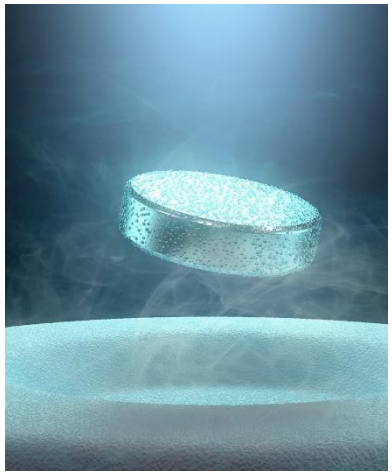
Pharmaceuticals

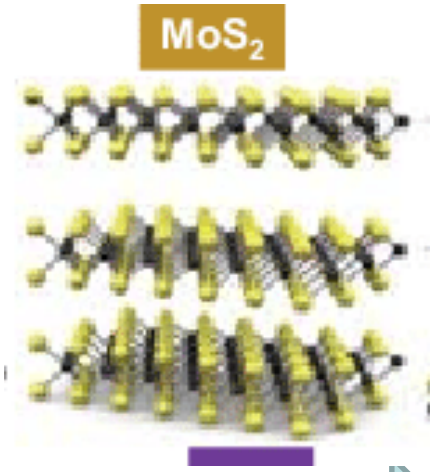
Images from ecofriend.com/about-nano-structured-organic-photovoltaic-cells.html; *www.techhive.com/article/3154575/smart-tv/lgs-new-oled-tvs-are-real-wall-huggers.html; apps.pharmacy.wisc.edu/sopdir/lian_yu/*

„Hard“ materials



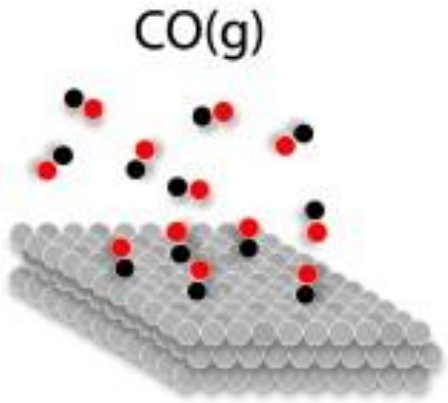
Biomolecules

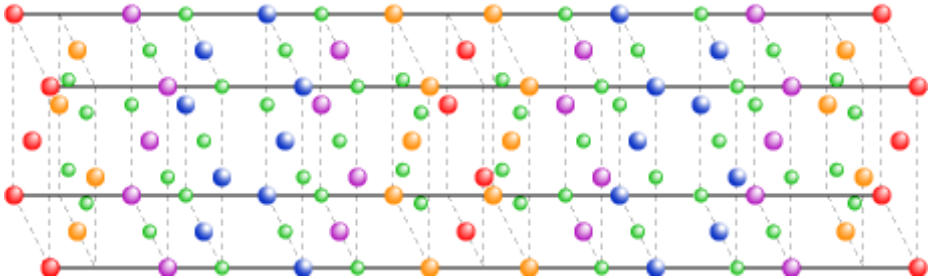


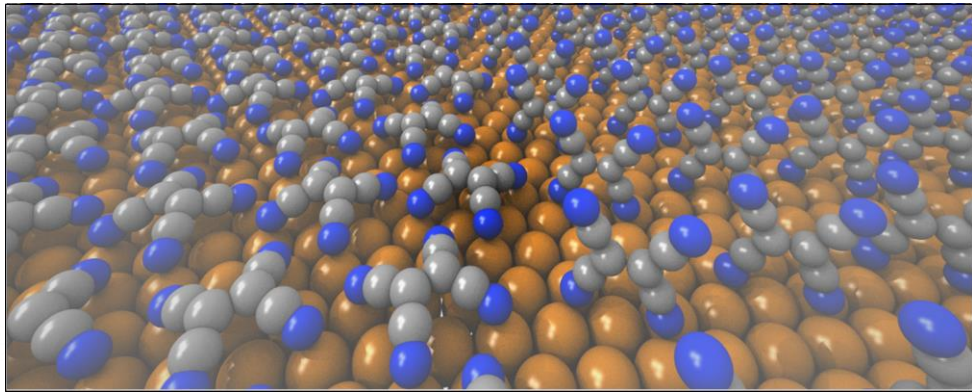


time

Transition metal oxides







„Hard“ physics

- **Magnetic materials / excitations**
- **Finite-temperature effects / Anharmonicities**
- **Polymorphism**
- **Charge Transfer**

„Hard“ physics

- Magnetic materials / excitations
- Finite-temperature effects / Anharmonicities
- Polymorphism
- Charge Transfer

Piecewise linearity in DFT: Exact results from ensemble arguments

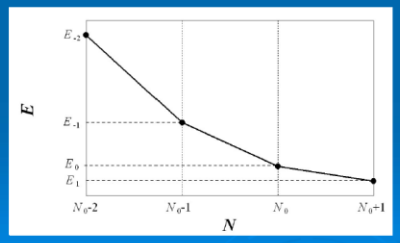
Fractional no. of electrons: $N = N_0 + \alpha$

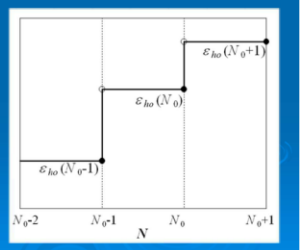
- Piecewise-linearity

$$E(N) = (1-\alpha)E_0 + \alpha E_1$$

- The IP theorem

$$\varepsilon_{ho}(N) = -I(N_0) =: E_0 - E_{-1}$$





Perdew, *Parr, Levy, Balduz*, PRL **49**, 1691 (1982); Yang, Zhang, Ayers, PRL 84, 5172 (2000).
Janak, PRB **18**, 7165 (1978) ; Levy, Perdew, Sahni, PRA **30**, 2745 (1984).

Derivative discontinuity

As a function of N, the energy is a sequence of straight line segments

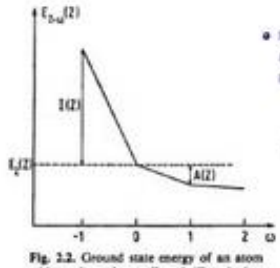


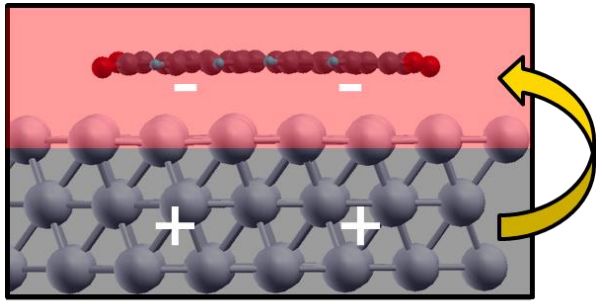
Fig. 2.2. Ground state energy of an atom with nuclear charge Z and $(Z+\omega)$ electrons

- R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).

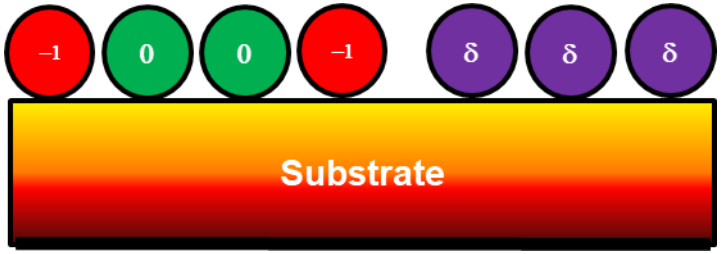
$$\mu = \frac{\partial E}{\partial N} = -\begin{cases} I, & N \le Z \\ A, & N > Z \end{cases}$$

Outline: Issues with Charge Transfer

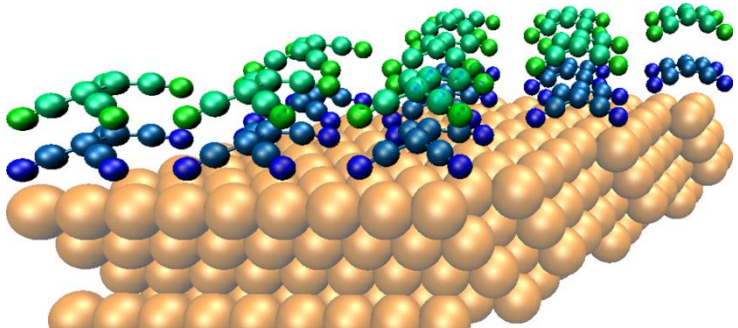
- Amount of charge transfer



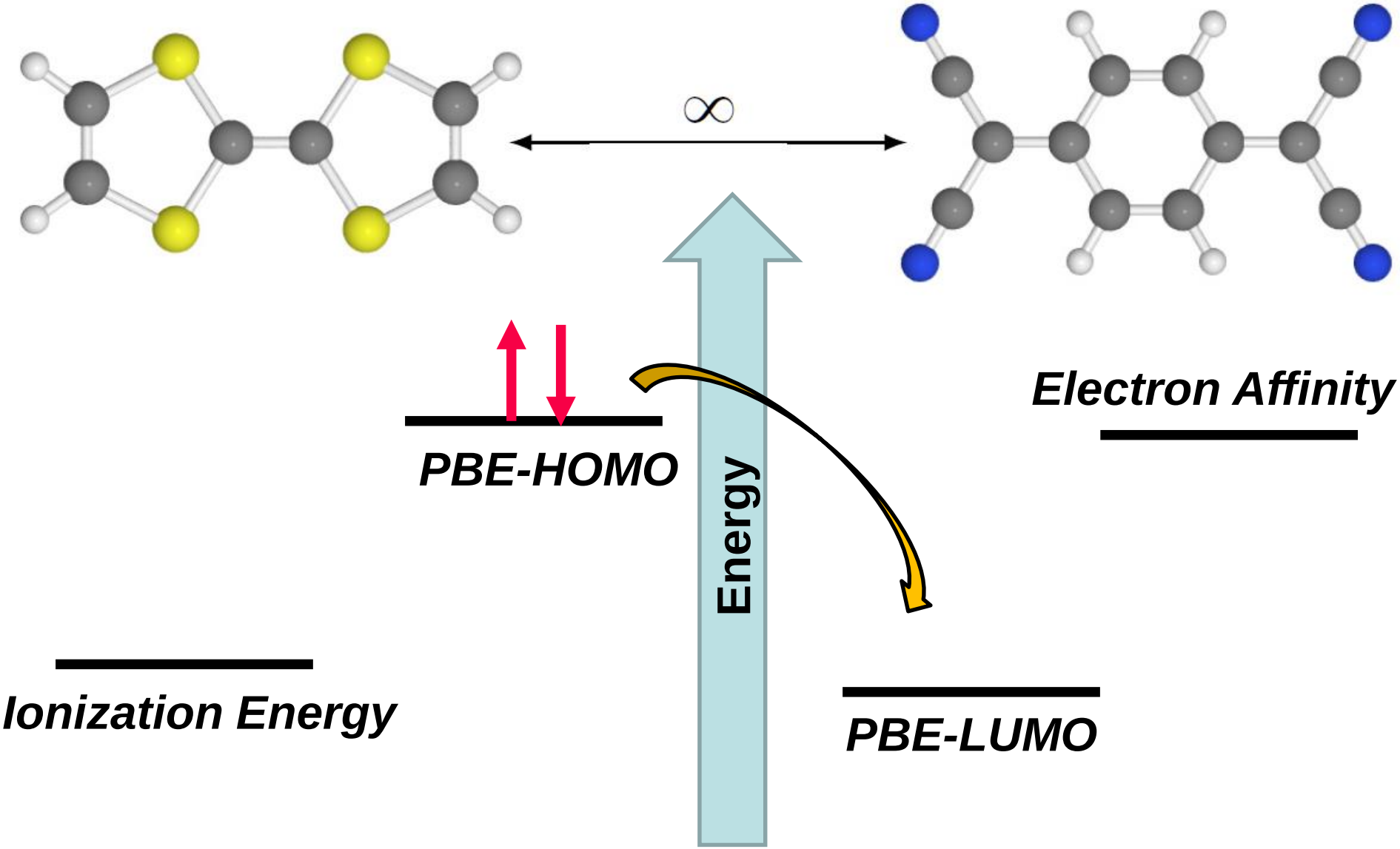
- Charge distribution



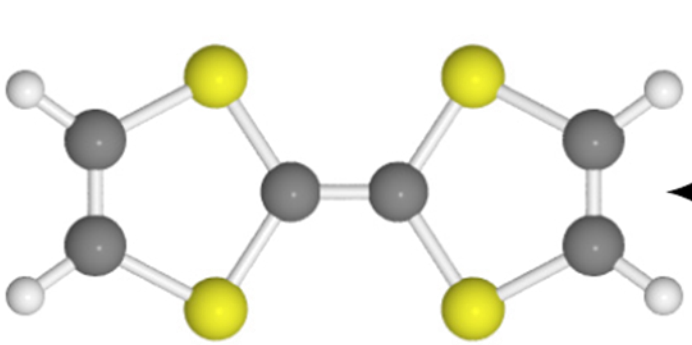
- Charge transfer ←→ Structure?

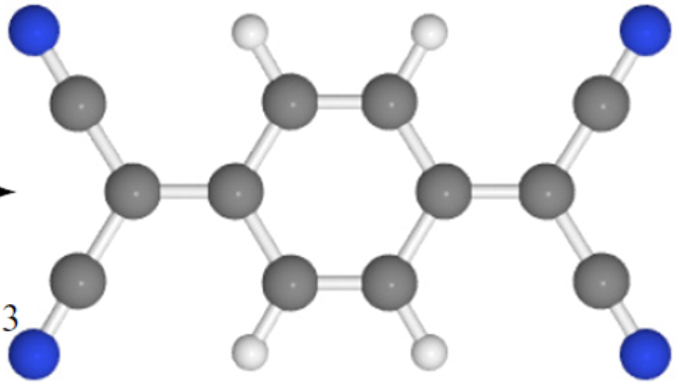


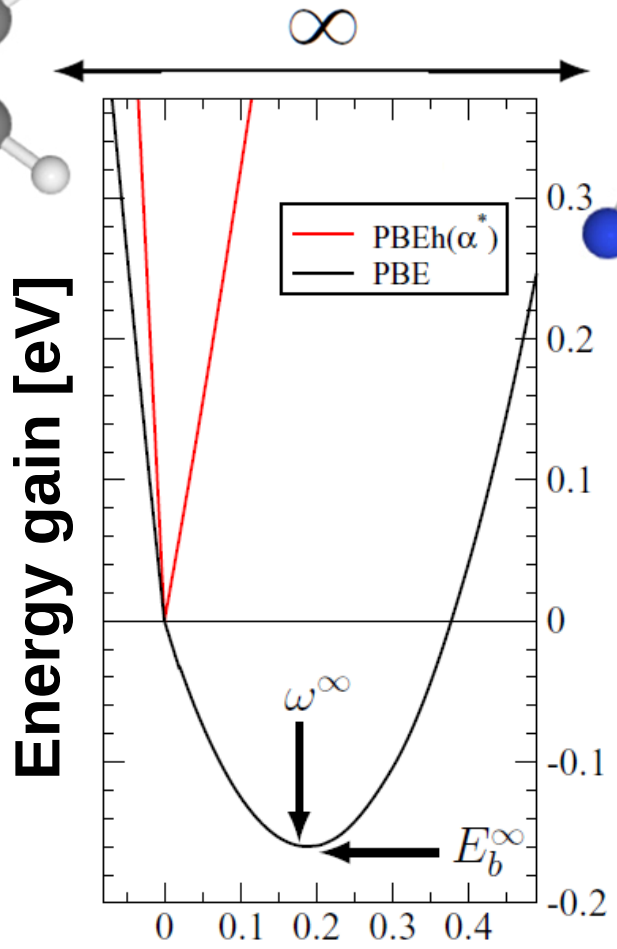
Charge Transfer In DFT: The Band Gap Problem

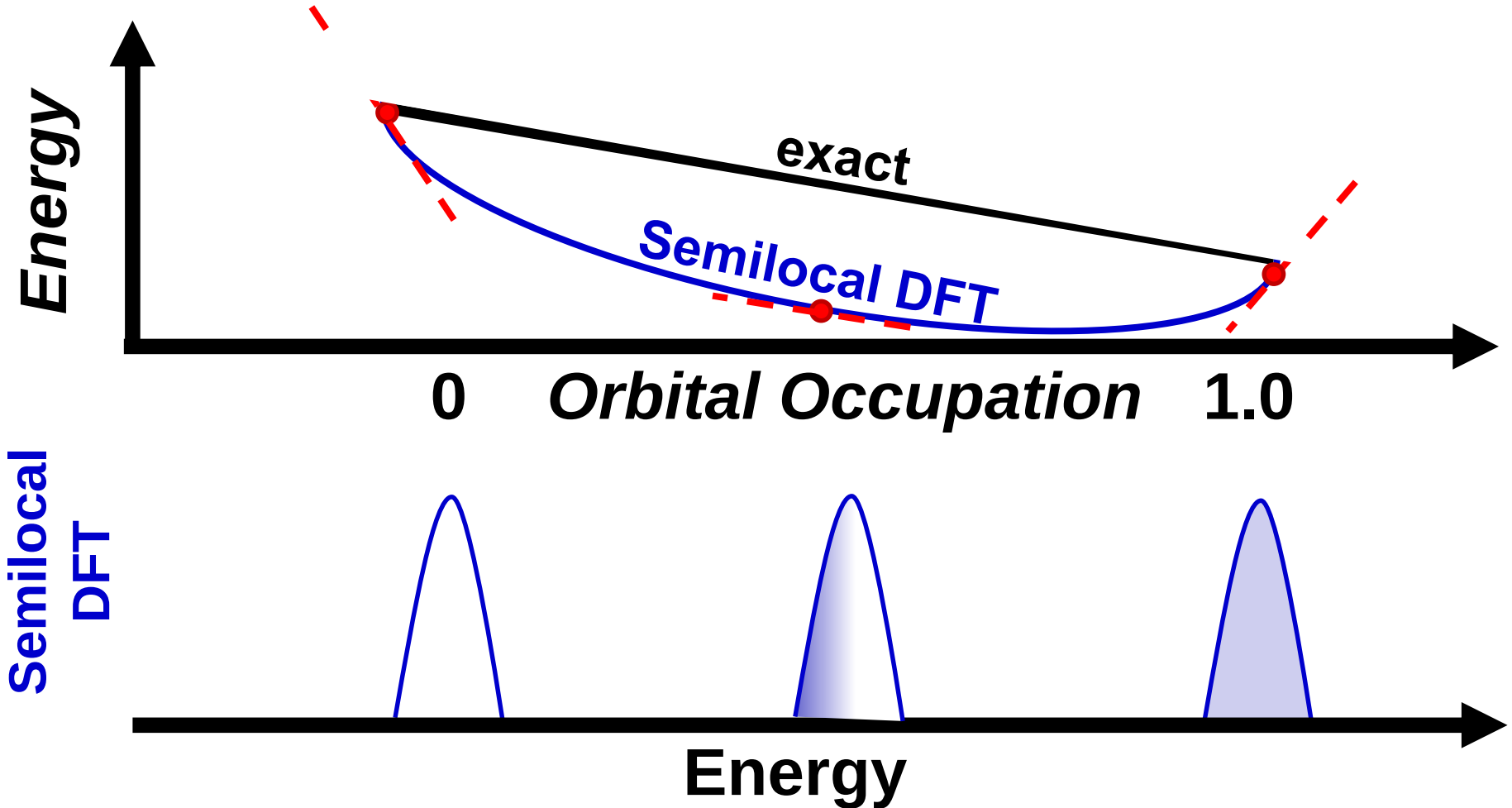


Charge Transfer In DFT: The Band Gap Problem

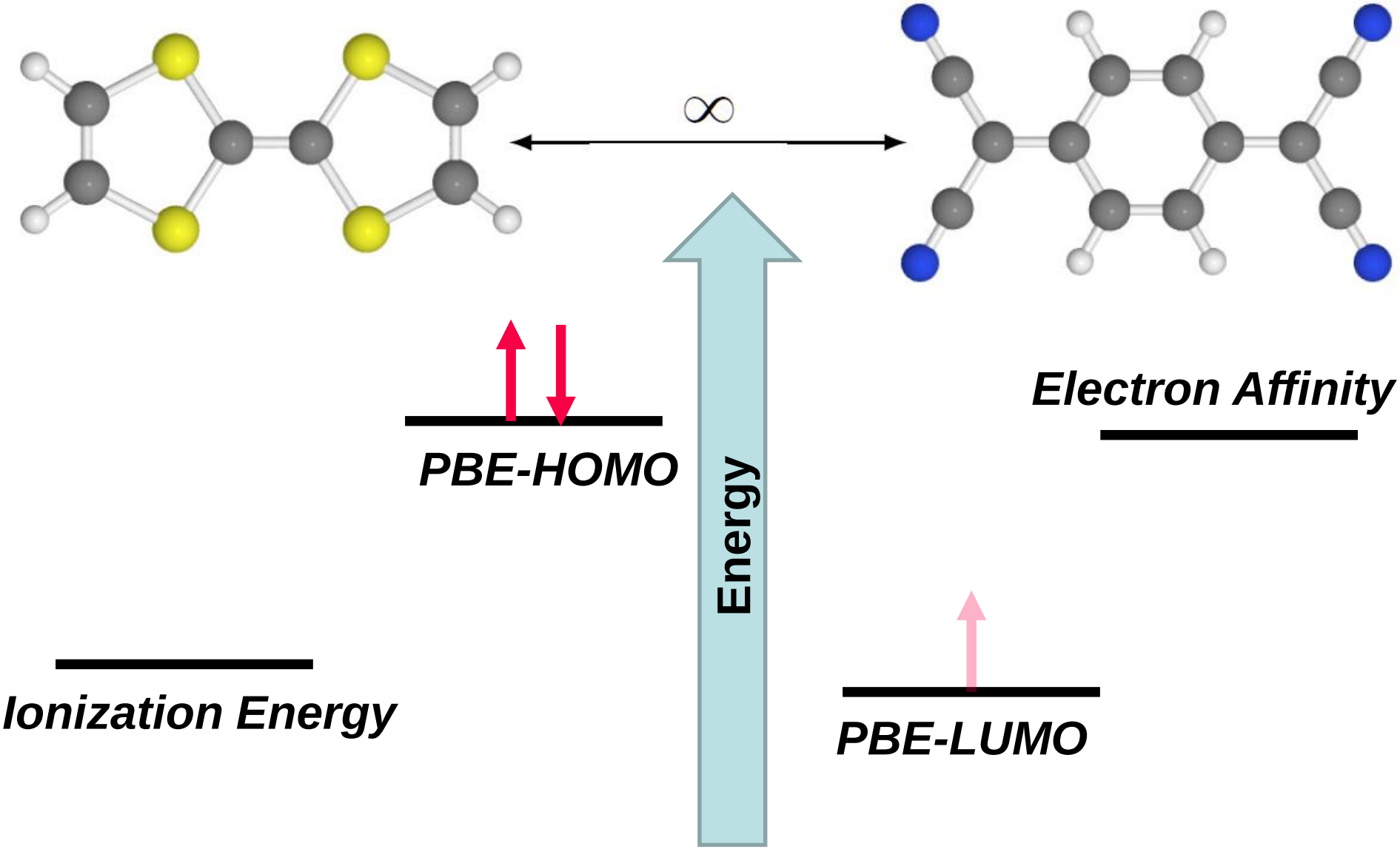




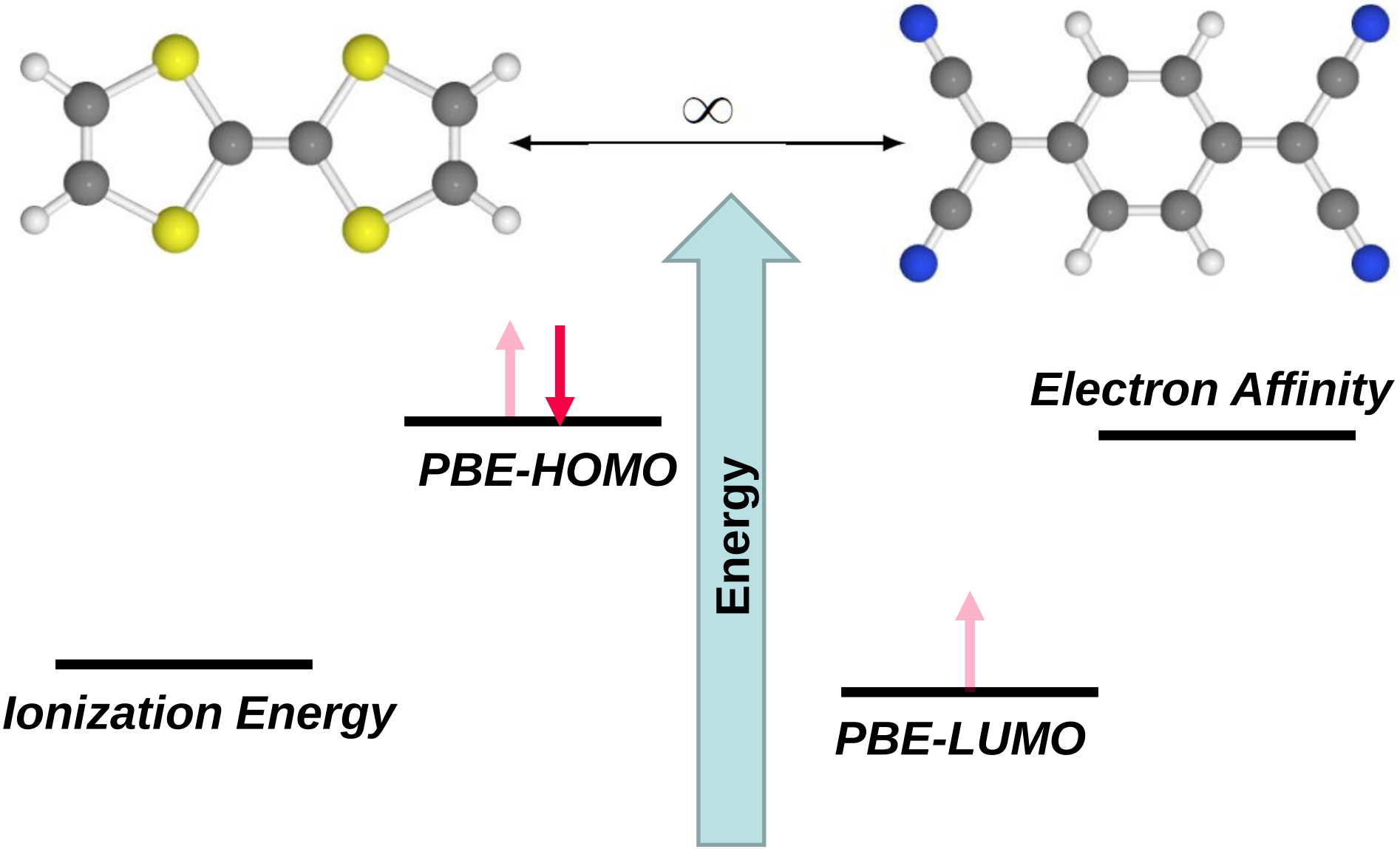


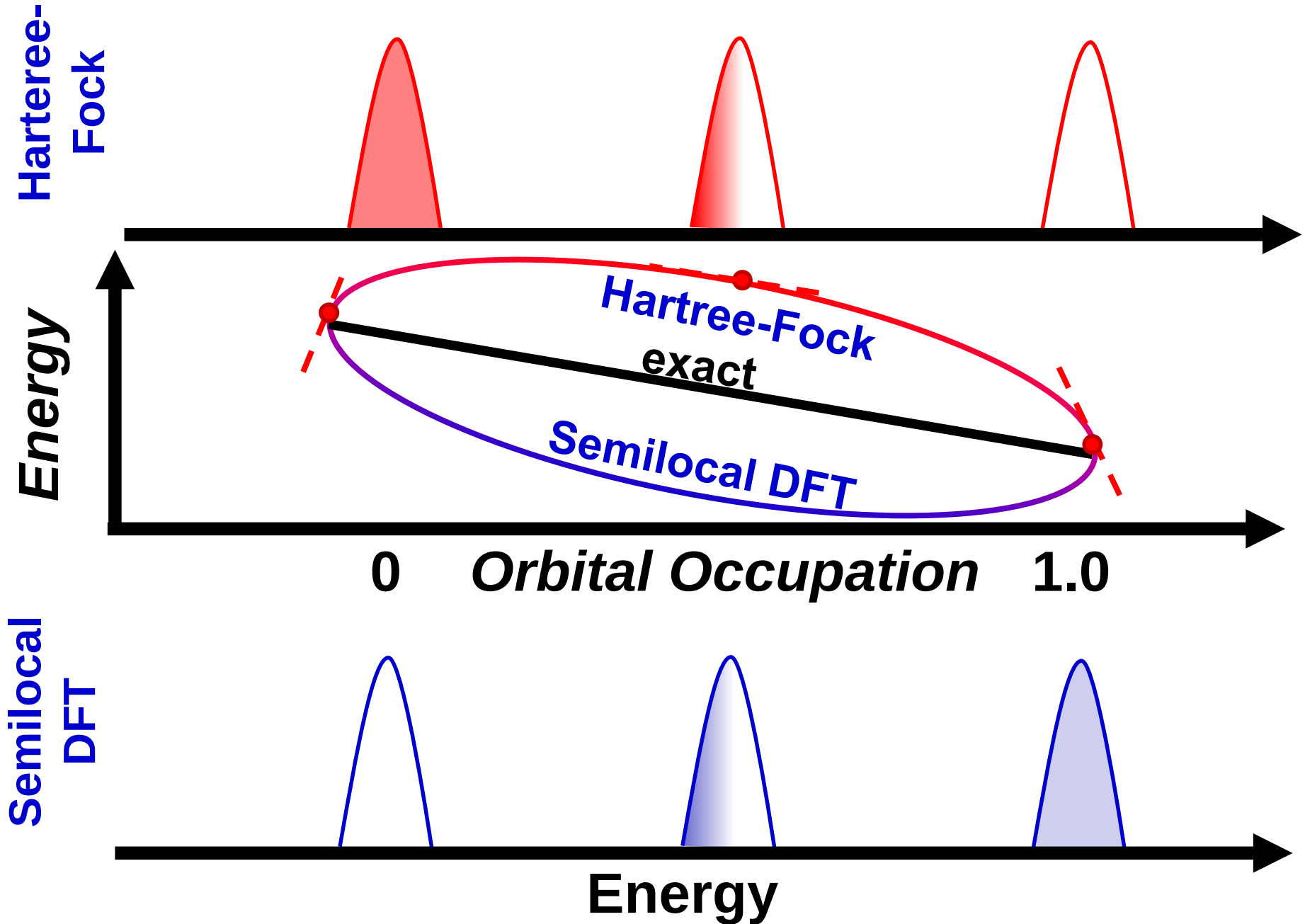

Energy
exact
Semilocal DFT
0
Orbital Occupation
1.0
Semilocal DFT
Energy

Charge Transfer In DFT: The Band Gap Problem

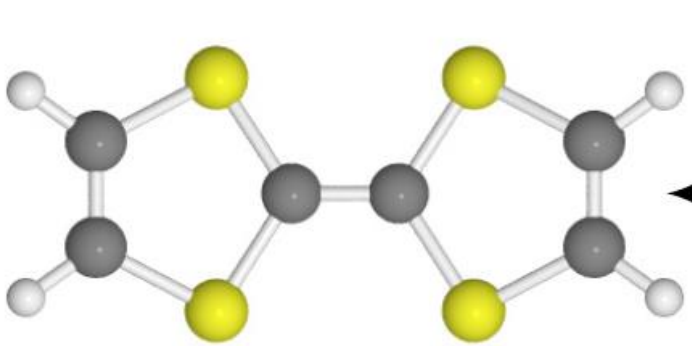


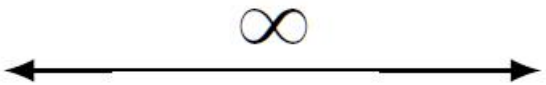
Charge Transfer In DFT: The Band Gap Problem

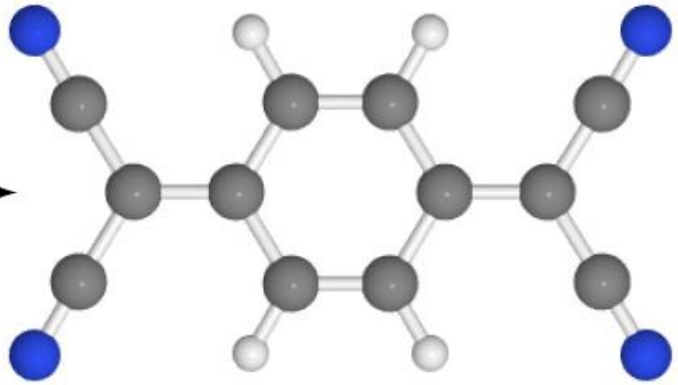



Harteree-Fock
Energy
Hartree-Fock
exact
Semilocal DFT
0
Orbital Occupation
1.0
Semilocal DFT
Energy

Charge Transfer In DFT: The Band Gap Problem







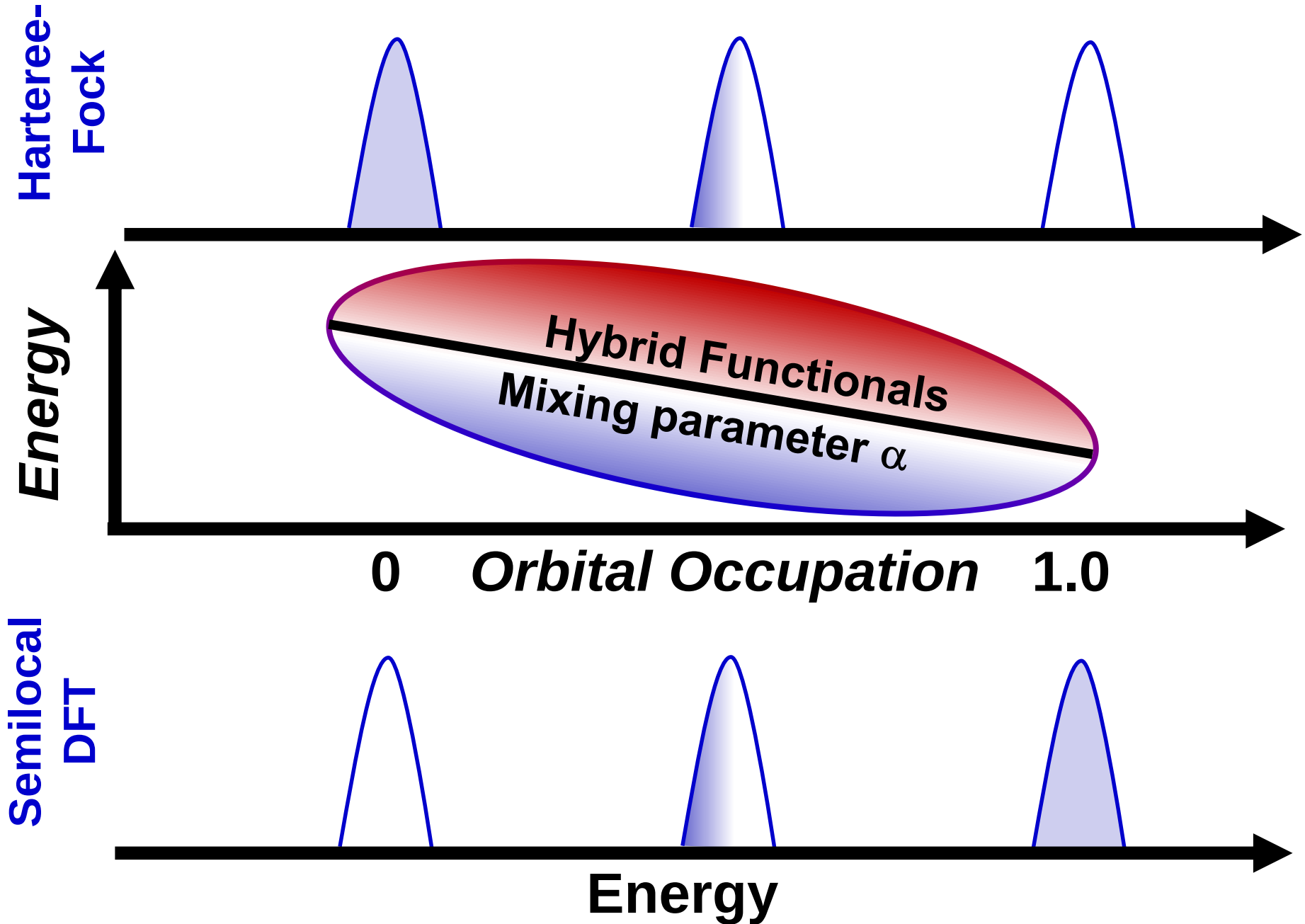
HF-LUMO

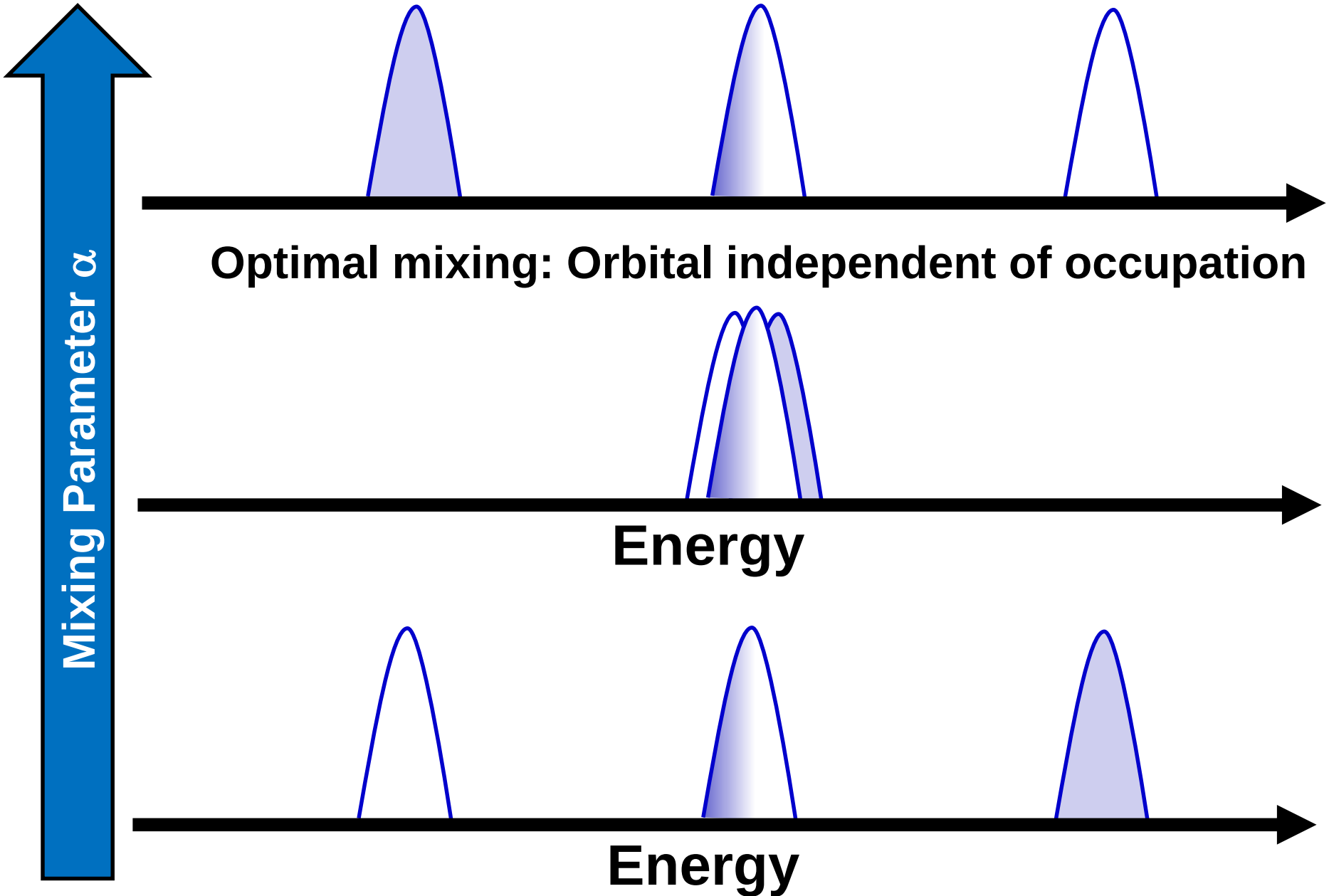
Electron Affinity

Energy

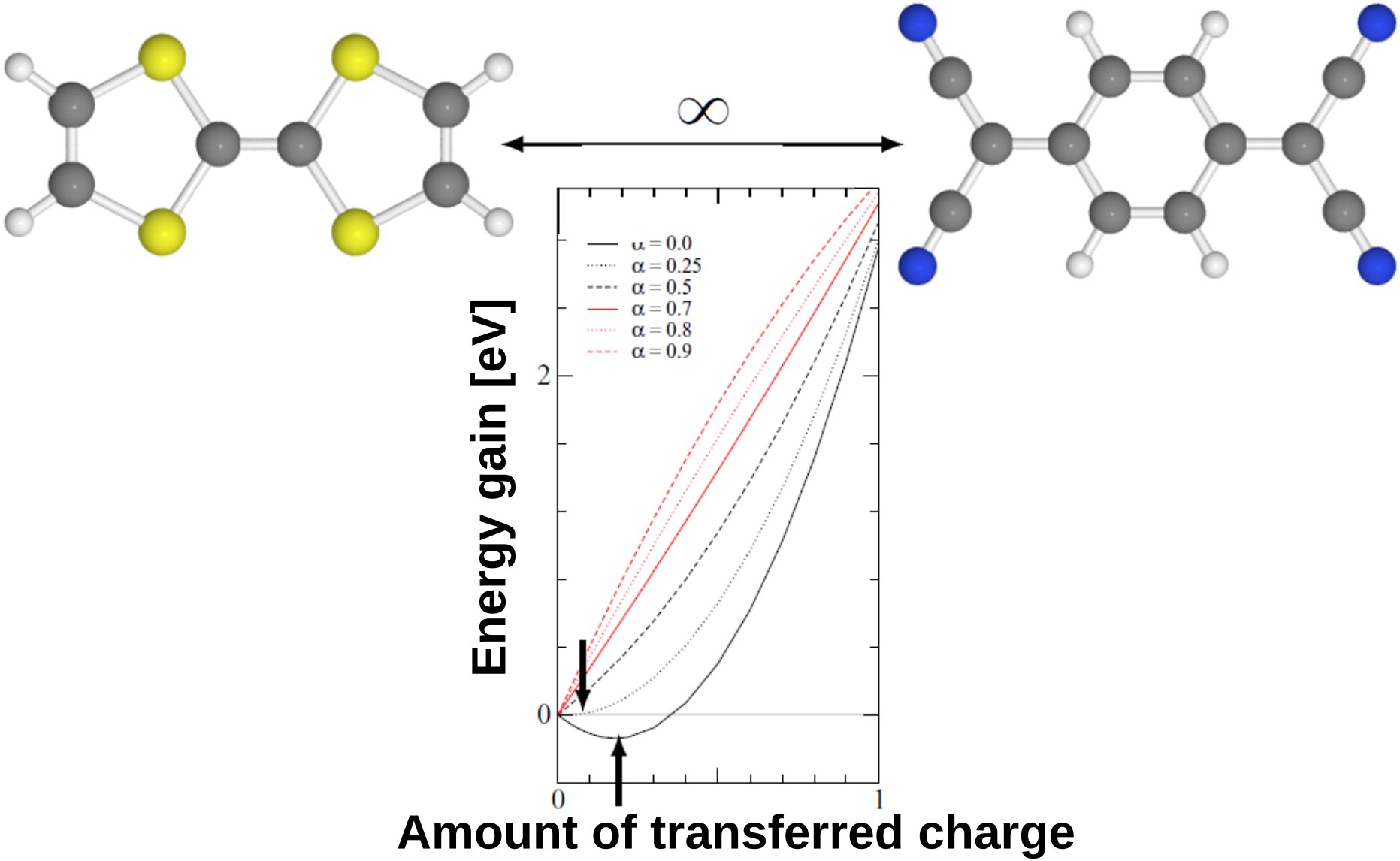
Ionization Energy

HF-HOMO

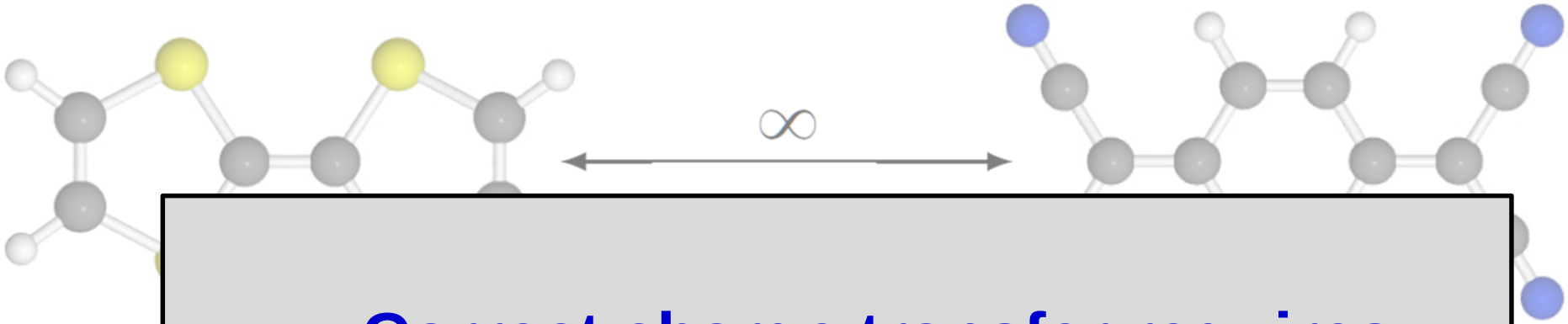

Harteree-Fock
Energy
Hybrid Functionals
Mixing parameter α
0
Orbital Occupation
1.0
Semilocal DFT
Energy


Mixing Parameter α
Optimal mixing: Orbital independent of occupation
Energy
Energy

Charge Transfer In DFT: The Band Gap Problem

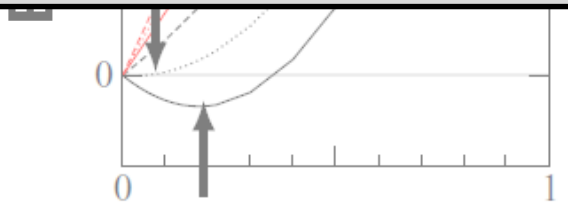


Charge Transfer In DFT: The band gap problem



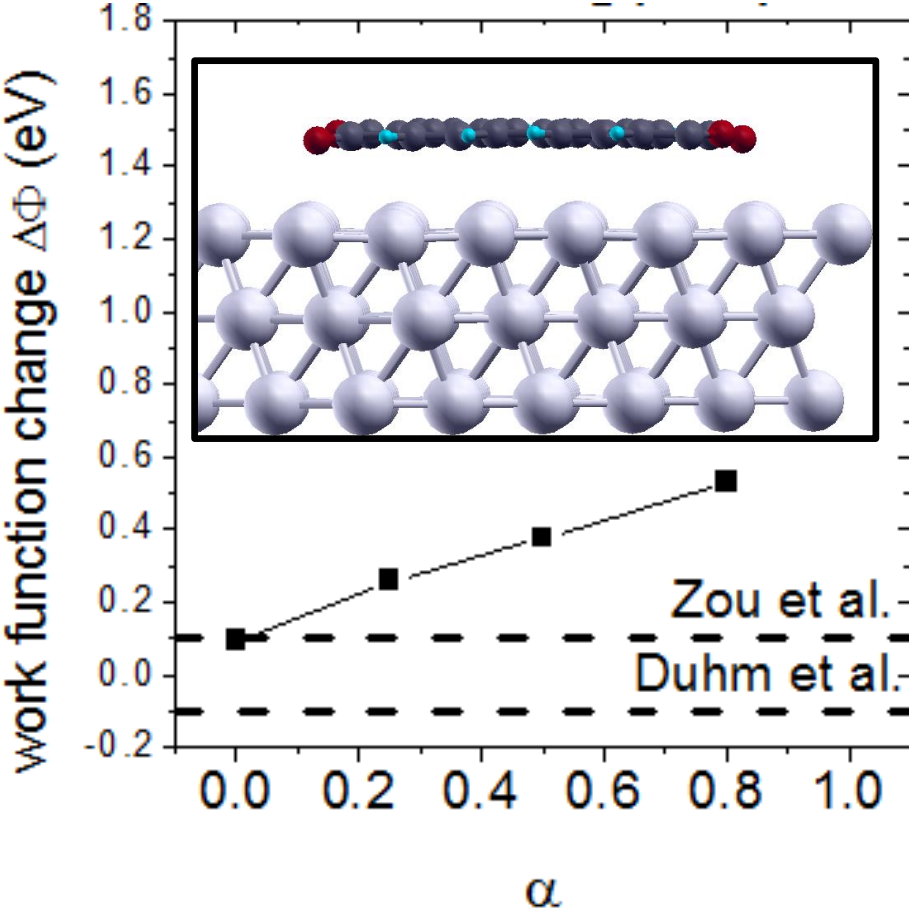
- **Correct charge transfer requires „optimal“ mixing**
- **Hybrid functional decrease charge-transfer**

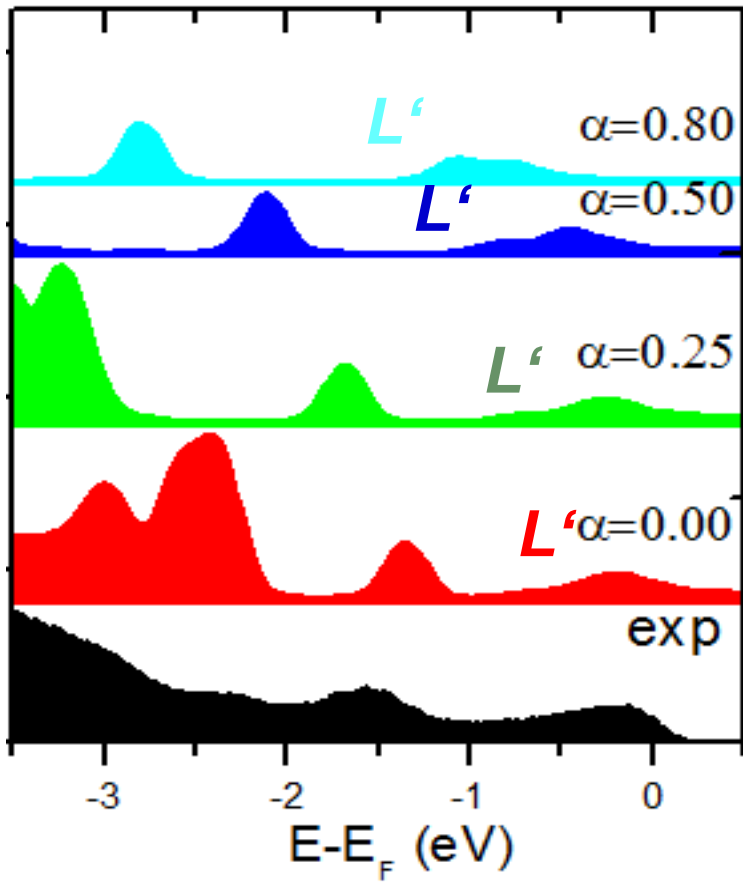
Karolewski et al., The Journal of Chemical Physics, 138 (20), **2013**



Amount of transferred charge

Exceptions to the rule: Large CT





Filled PBE-LUMO gets pushed further below the Fermi-energy → charge-transfer increases

Hofmann et al., New Journal of Physics, 15 (12), 123028, 2013

The performance of semilocal DFT for CT:

- **Overestimate CT when it is small**

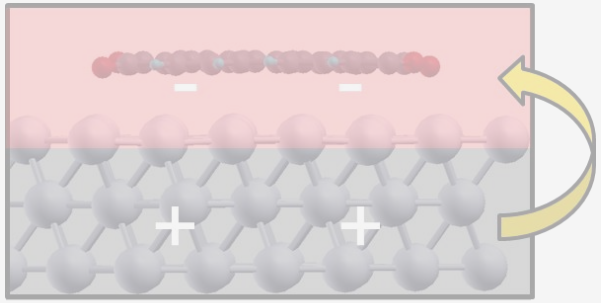
  Atalla et al., Phys. Rev. B 94, 035140

- **Underestimate CT when it is large**

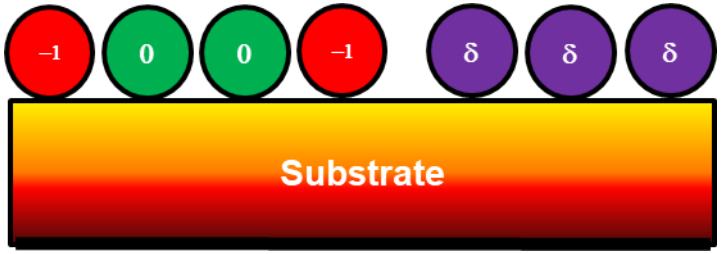
  Hofmann et al., NJP, 15 (12), 123028, 2013

Outline: Issues with Charge Transfer

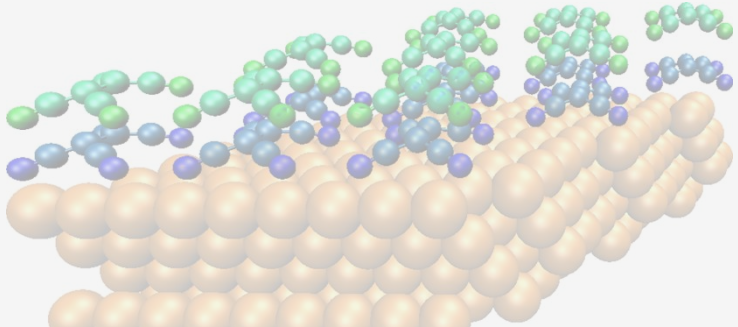
- Amount of charge transfer



- **Charge distribution**



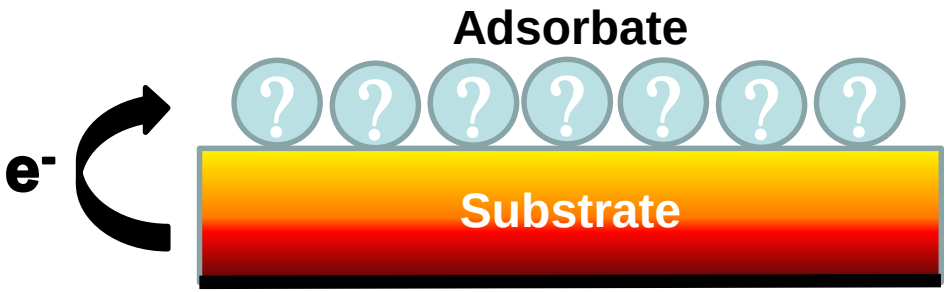
- Charge transfer ←→ Structure?



Charge Transfer at the Interface

weak **Interaction Strength** **strong**

Braun et al., Advanced Materials, **2009**, (21), 1450



Experimental CT usually less than 1e / molecule

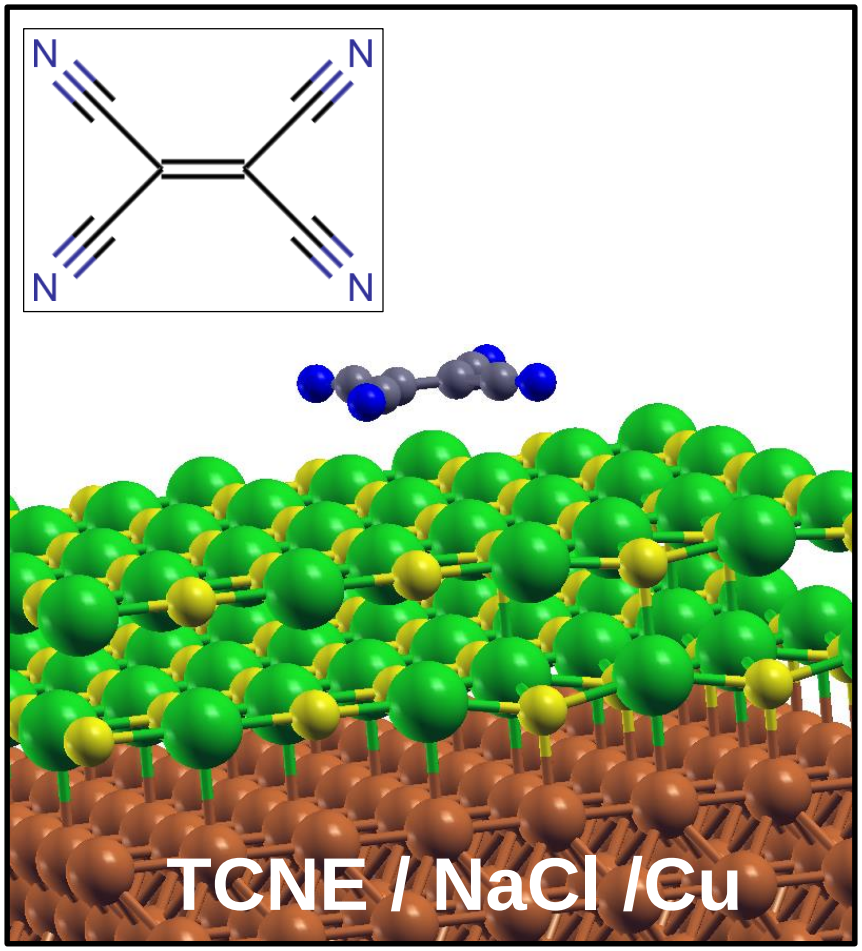
Integer Charge Transfer (ICT)

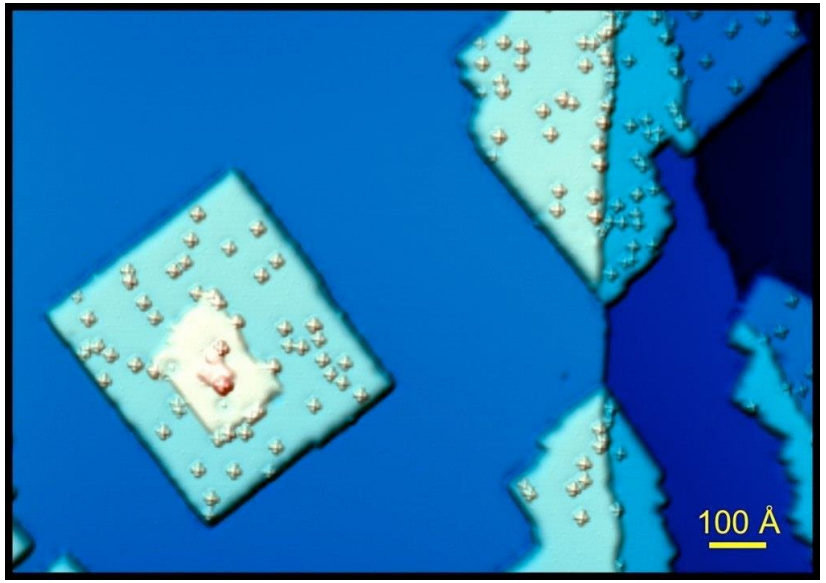
Not captured semilocal functionals (incl. +U)

Gruenewald et al., J. Phys. Chem. C, **2015**, *119* (9), 4865

Fractional Charge Transfer (FCT)

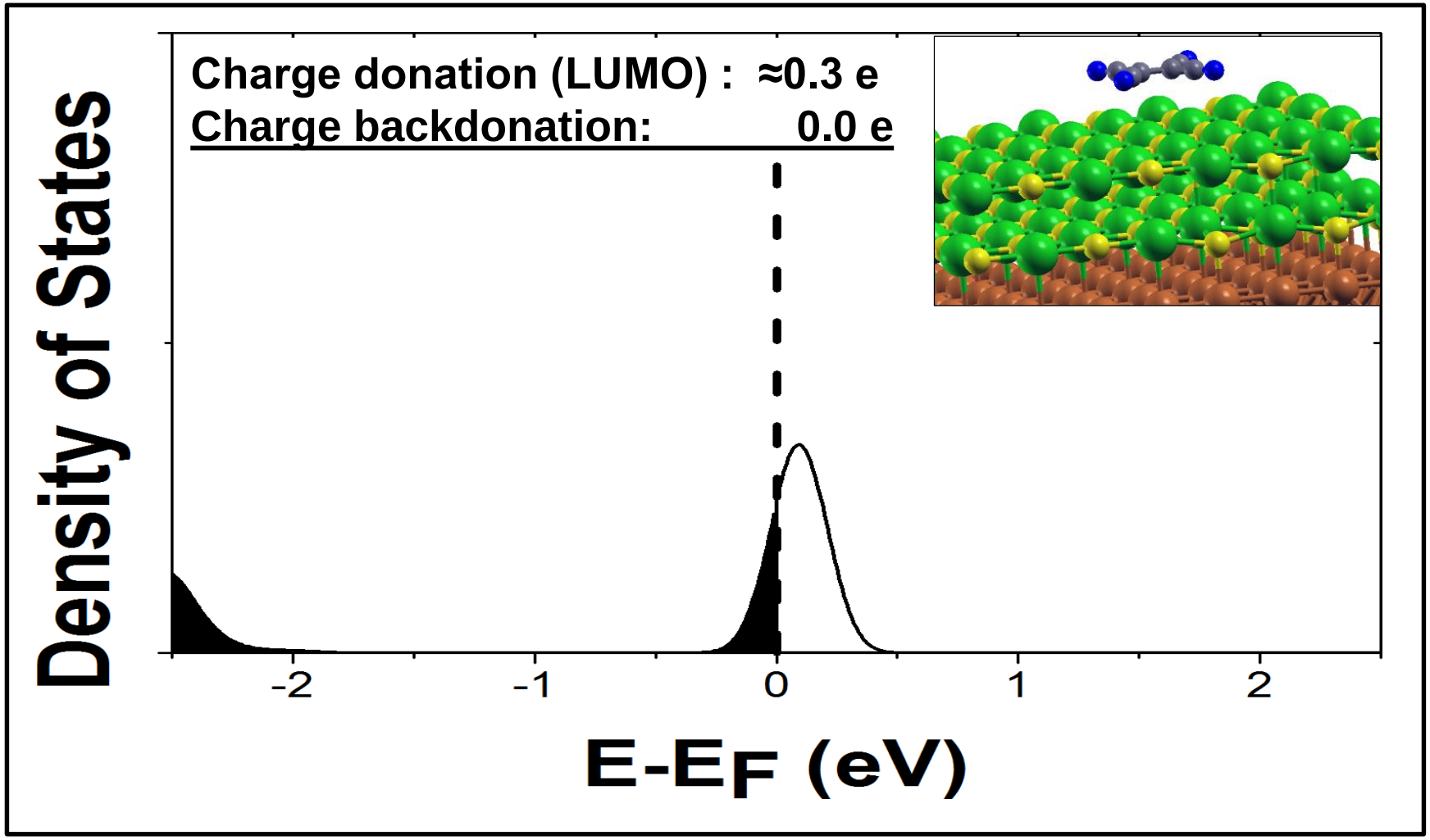
Weak Interaction– TCNE/NaCl/Cu





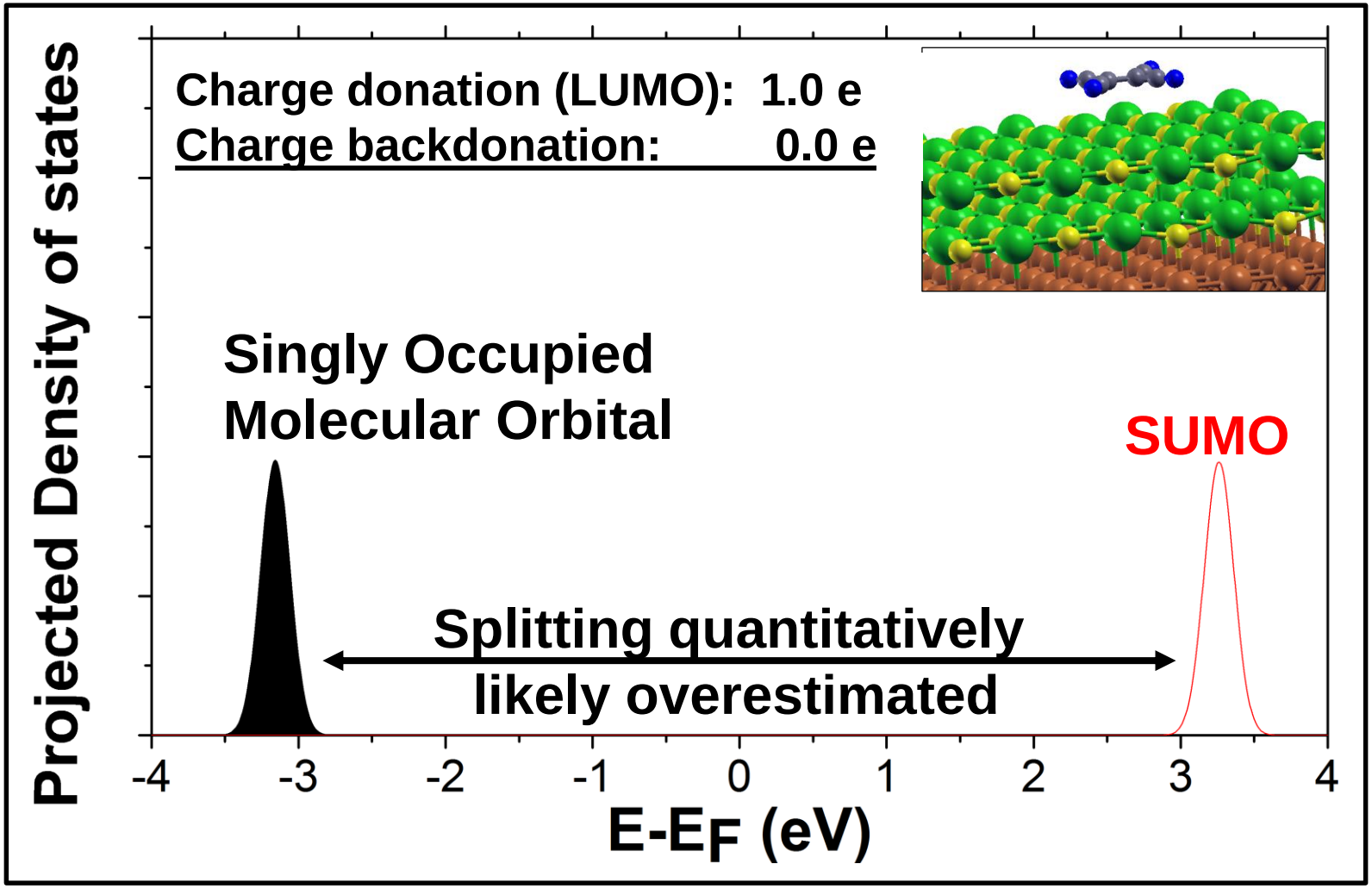
TCNE / NaCl /Ag, curtesy Daniel Wegner

TCNE/NaCl/Cu – PBE calculation

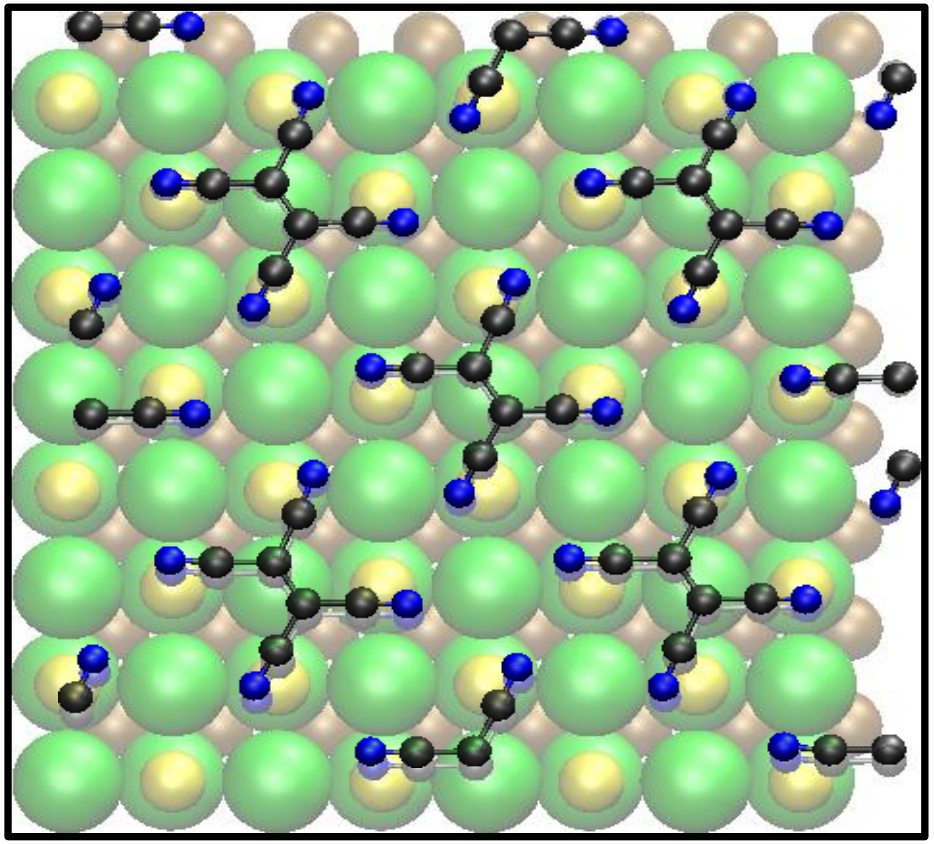


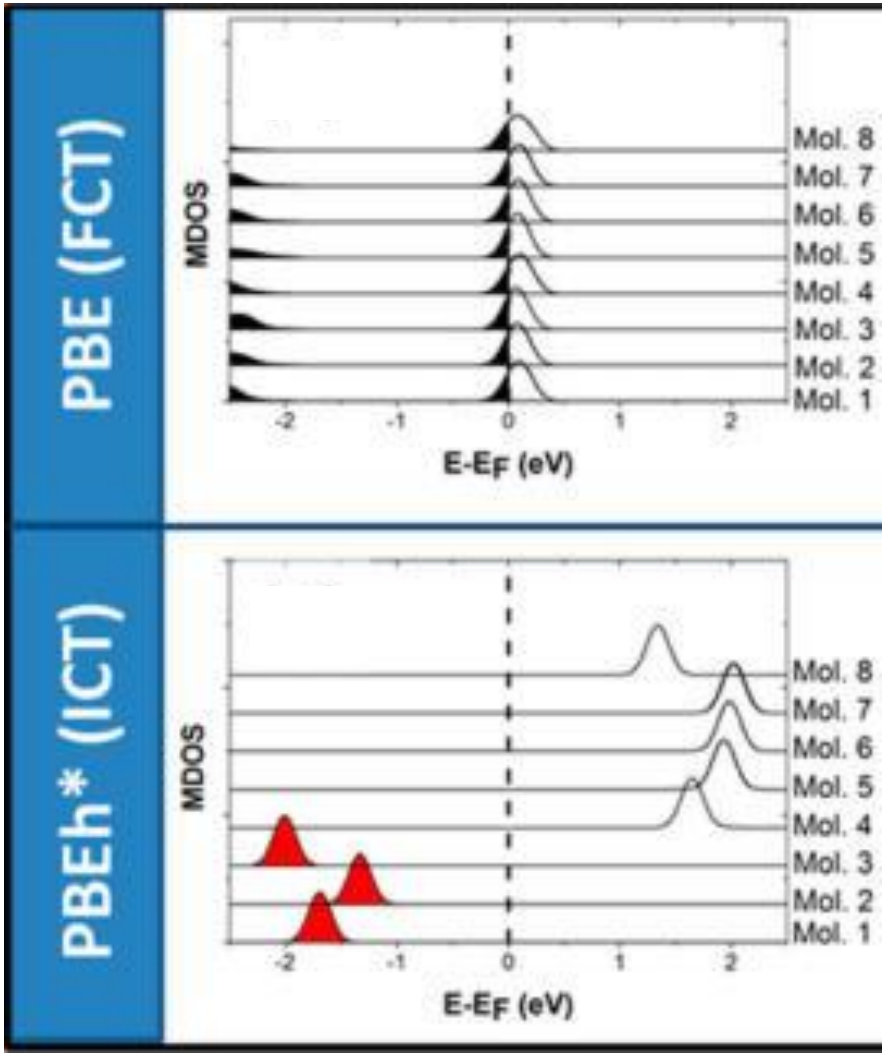
Interpretation of fractional filling in DFT: N.D. Mermin, Phys. Rev. 137A, 1441 (**1965**)

PBEh* (α = 0.8) results – single molecule



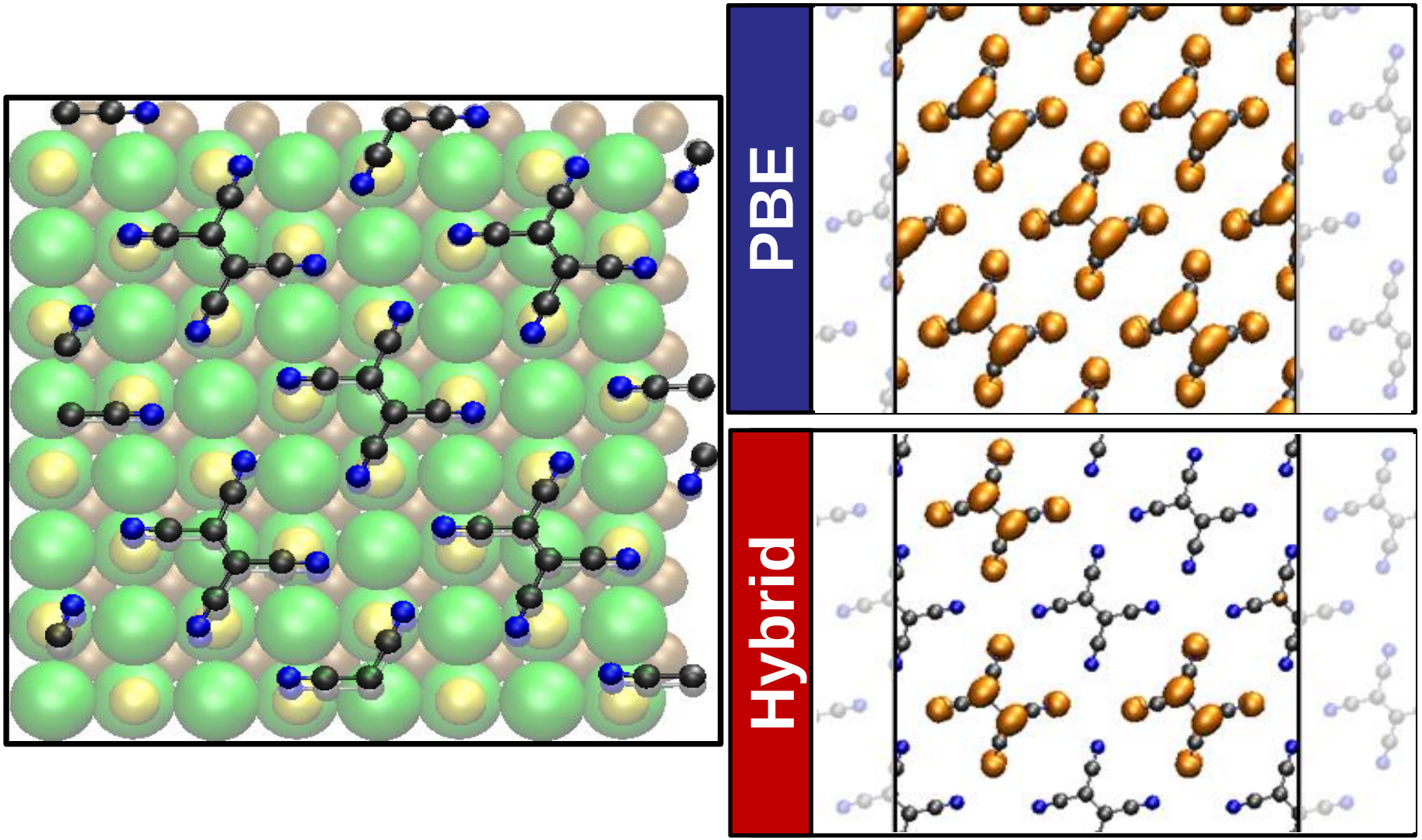
Density of States





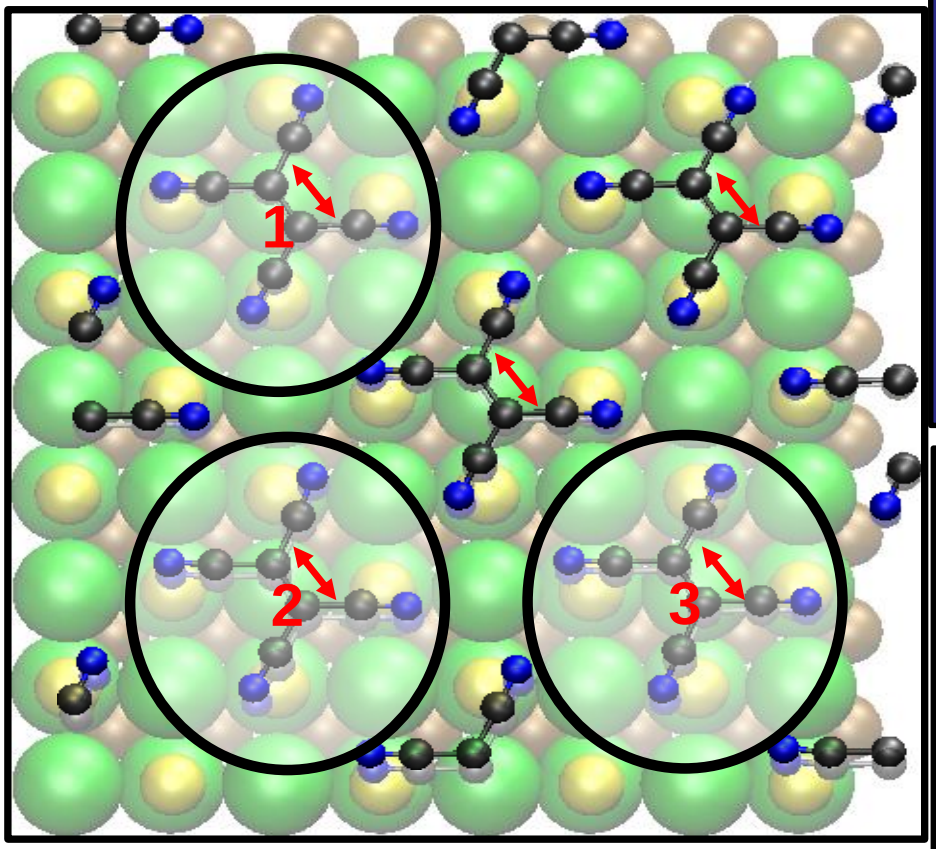
Hofmann et al., ACS Nano, 9 (5) 5391, 2015

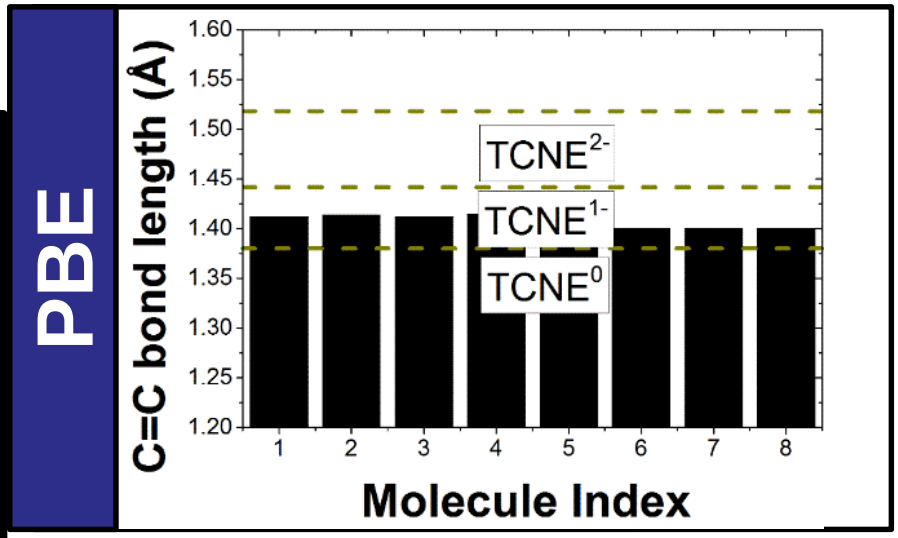
Charge Distribution …

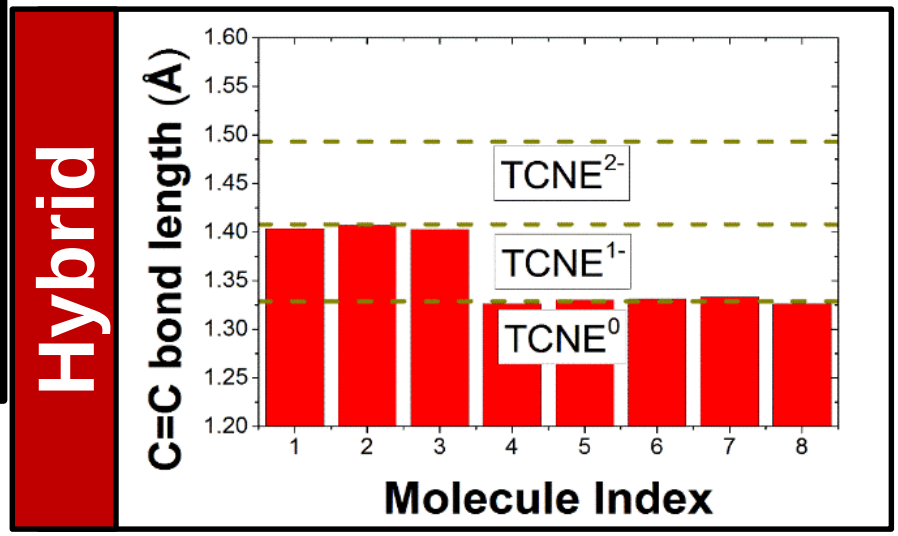


Hofmann et al., ACS Nano, 9 (5) 5391, 2015

… and observables





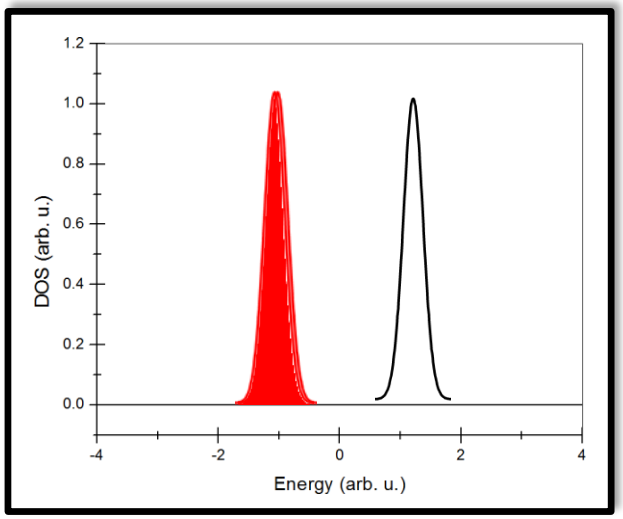


Hofmann et al., ACS Nano, 9 (5) 5391, 2015

Naive Explanation

- Consider two empty states localized on two different molecules
- Symmetry broken (e.g., lattice distortion, numerical inaccuracy, etc.)
- Now fill with single charge

$$\frac{\delta\epsilon}{\delta n} > 0 \rightarrow \text{self-repulsion}$$



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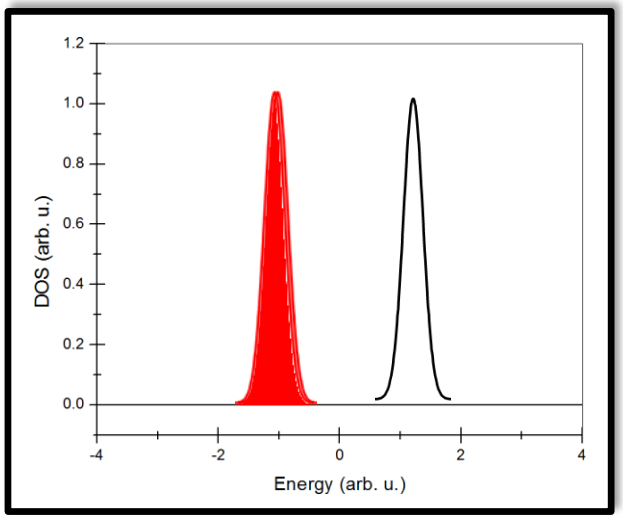
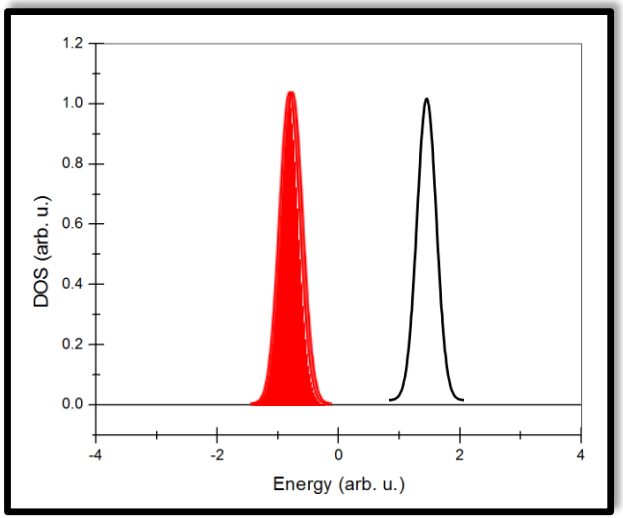
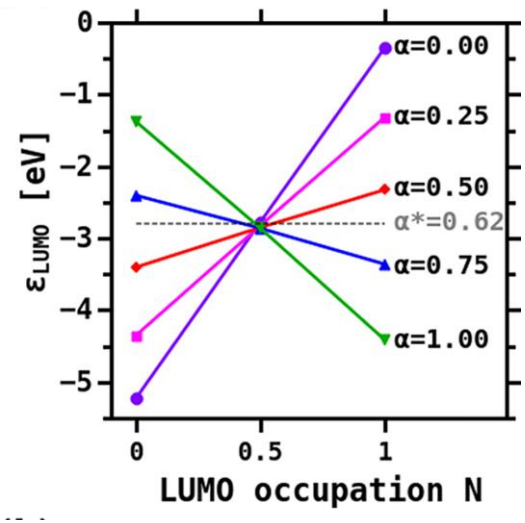
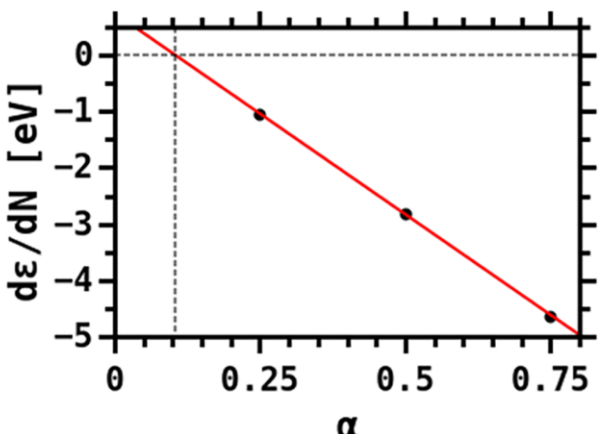


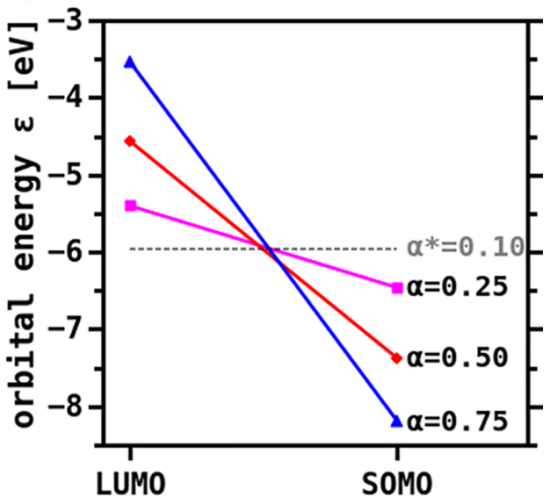
$$\frac{\delta\epsilon}{\delta n} < 0 \rightarrow \text{self-attraction}$$



Optimal mixing in periodic systems

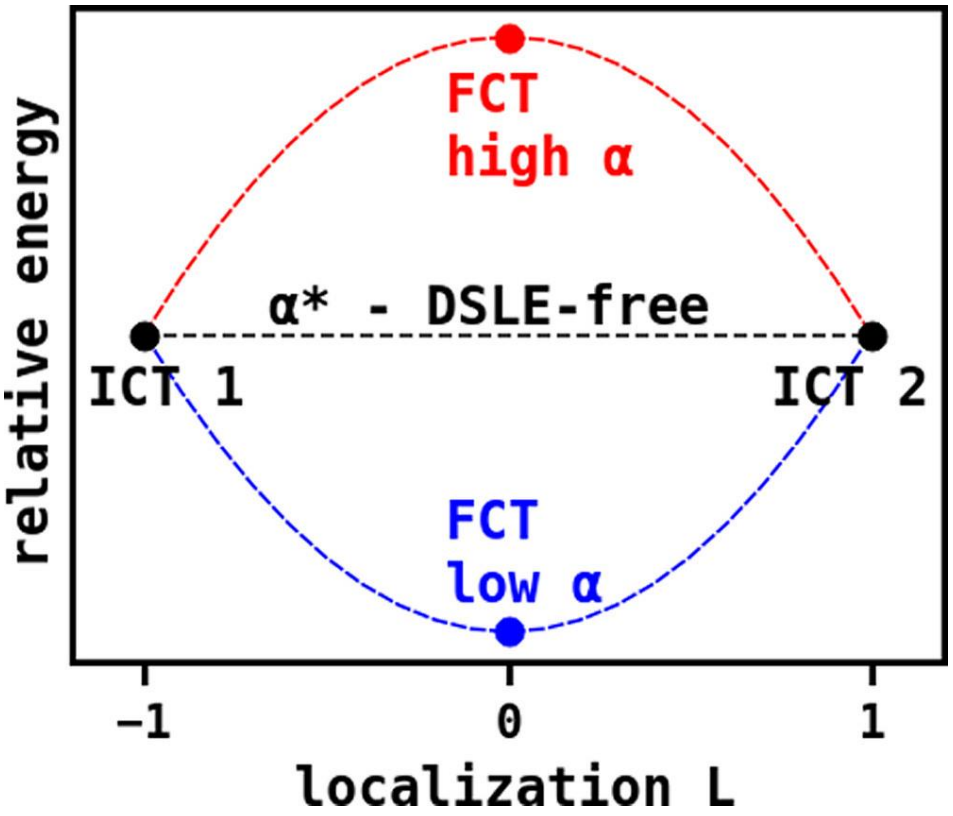






- **Ionization not possible → Workarounds**
- **Optimal mixing depends on substrate (ε_r)**
- **Typically very small (<25%)**

Wruss et al., The Journal of Physical Chemistry C, 122, 26, **2018**



- **Small α: delocalized minimum**
- **Large α: localized minima, delocalized transition**
- **Optimal mixing: Undecided**

Wruss et al., The Journal of Physical Chemistry C, 122, 26, **2018**

The performance of semilocal DFT for CT:

- **Overestimate CT when it is small**

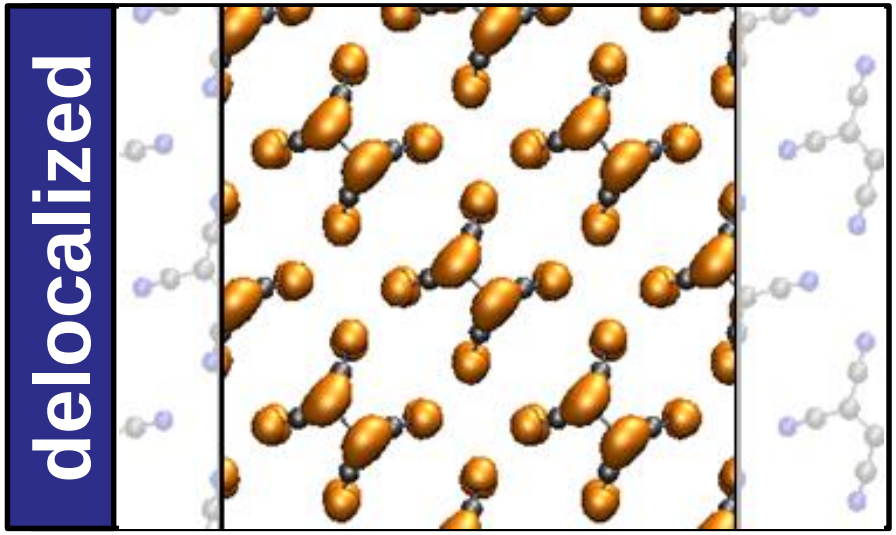
  Atalla et al., Phys. Rev. B 94, 035140

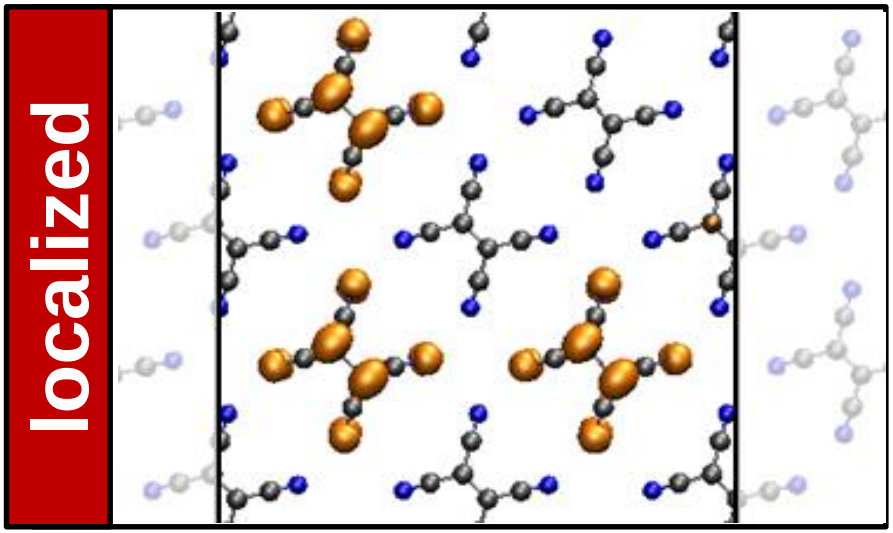
- **Underestimate CT when it is large**

  Hofmann et al., NJP, 15 (12), 123028, 2013

- **Overdelocalize charge**

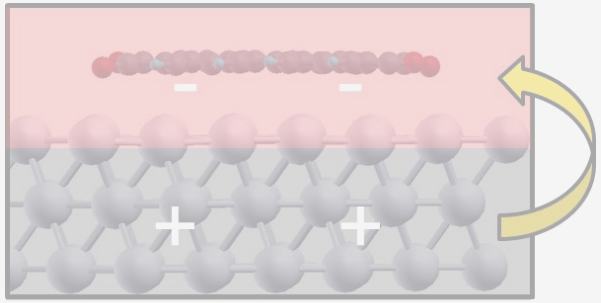
  Hofmann et al., NJP, 15 (12), 123028, 2013



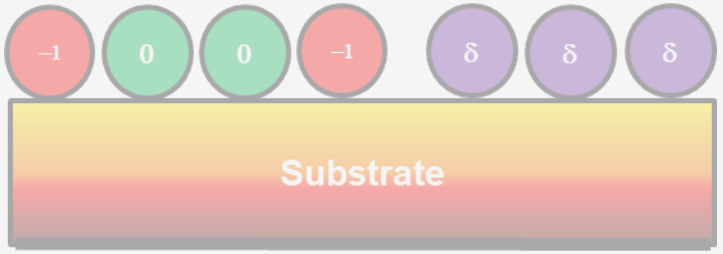


Outline: Issues with Charge Transfer

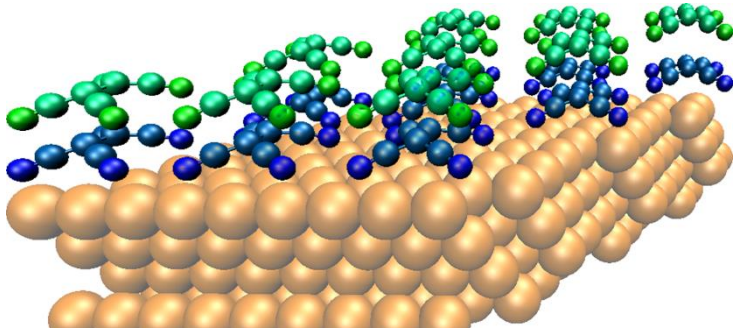
- Amount of charge transfer



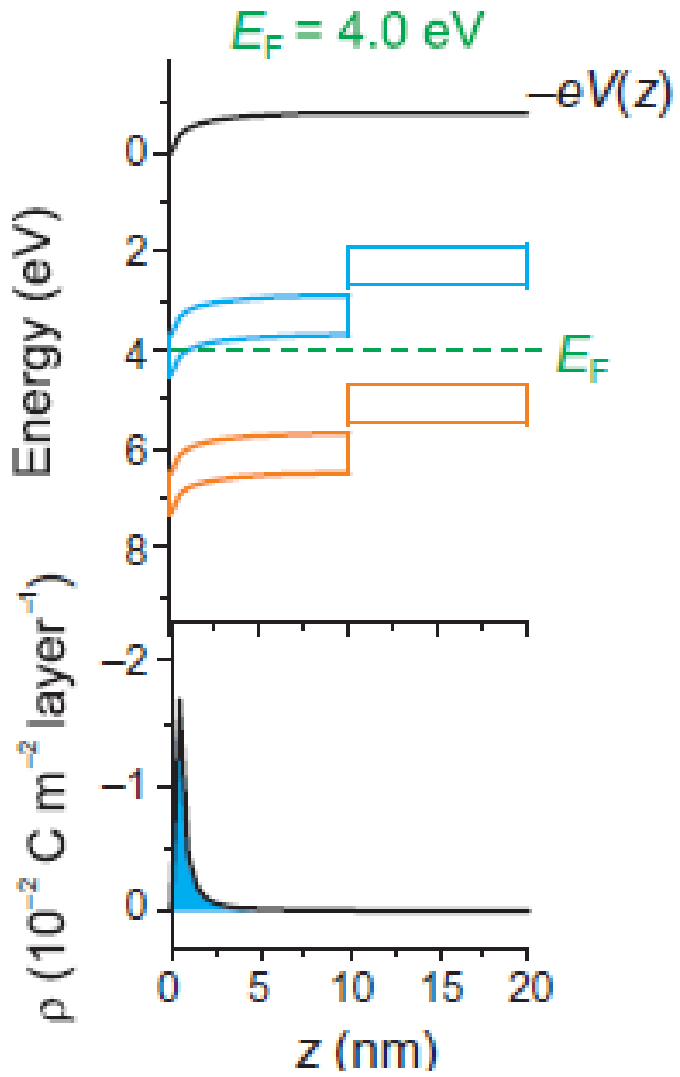
- Charge localization



- **Charge transfer beyond the first layer?**



Long-ranged Charge Transfer

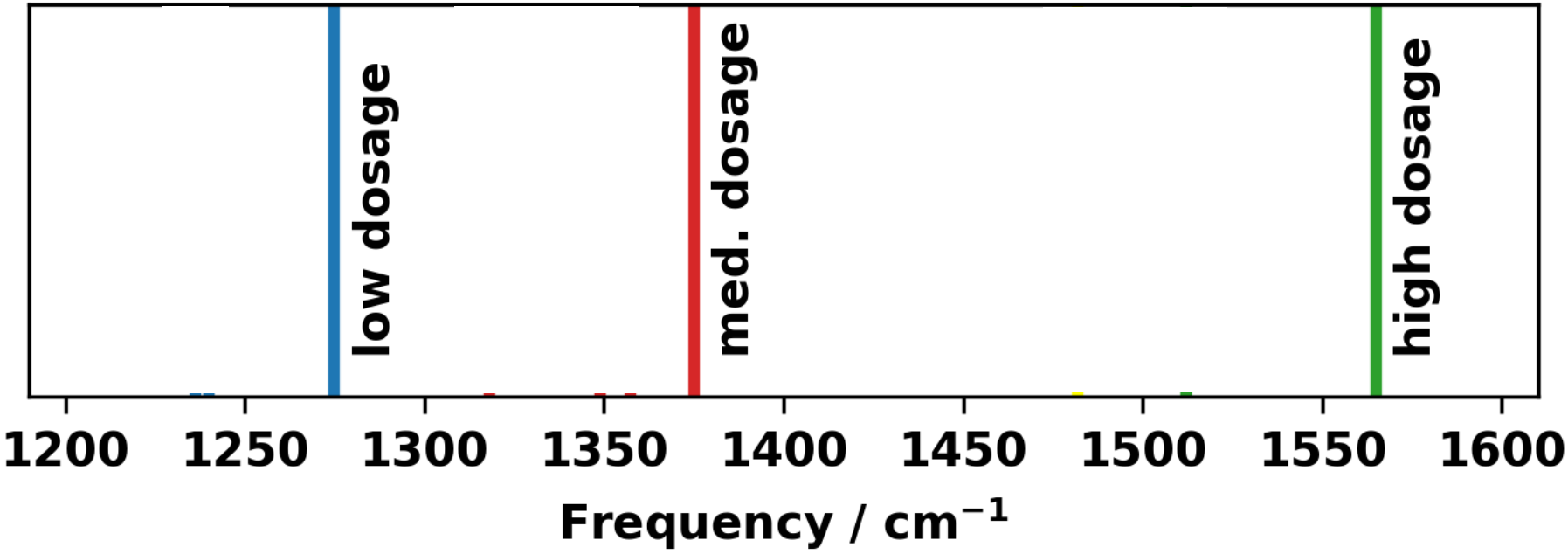


- **Predicted by „normal“ semiconductor picture (Fermi-Dirac+Electrostatic)**
- **Conflicting experiments**
  - **Potential (UPS/KP)**
  - **Charge (Optics/Vibrations)**

What can we learn from (first principles) theory?

Oehzelt et al. Sci. Adv. 2015;1:e1501127

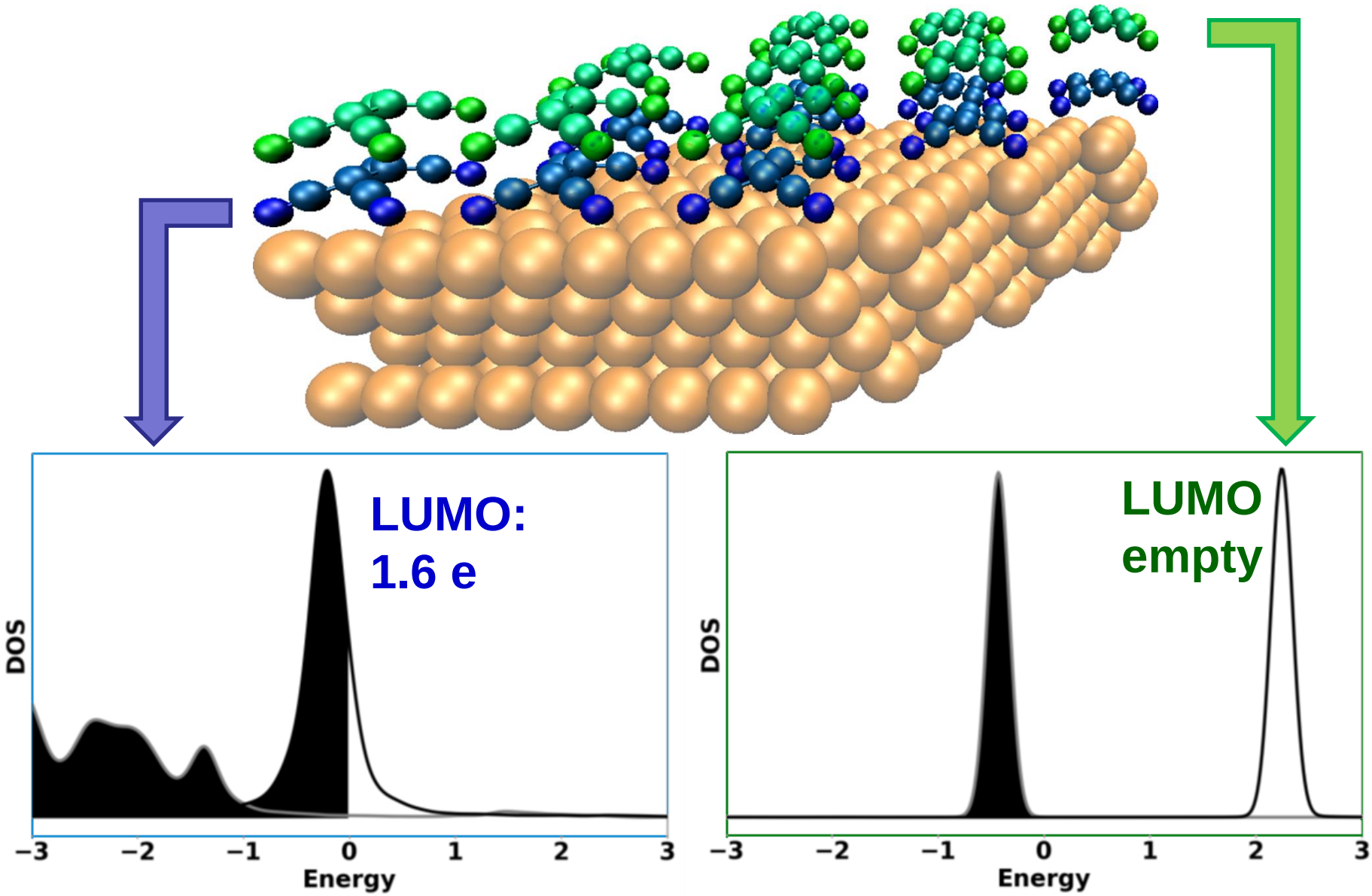
A convincing experiment? TCNE/Cu(111)



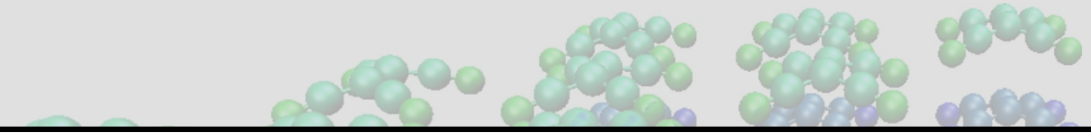
Coverage	Charge	Interpretation
Low	>>1	Monolayer
Medium	≈1	Second layer
High	0	Bulk

Experiments: Wulf, Erley *J. Phys. Chem.*,1987,*91*(24), pp 6092–6094

DFT results for ad-hoc guess structure

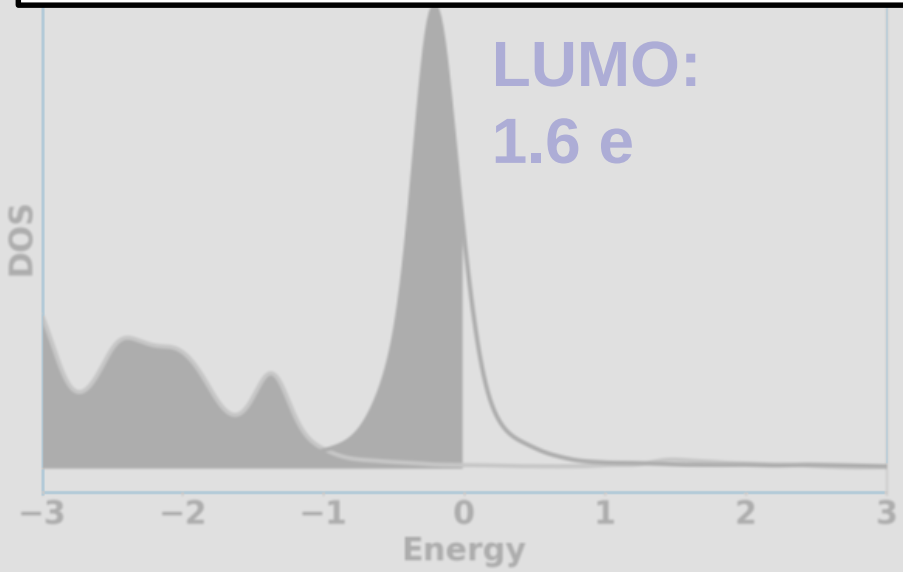


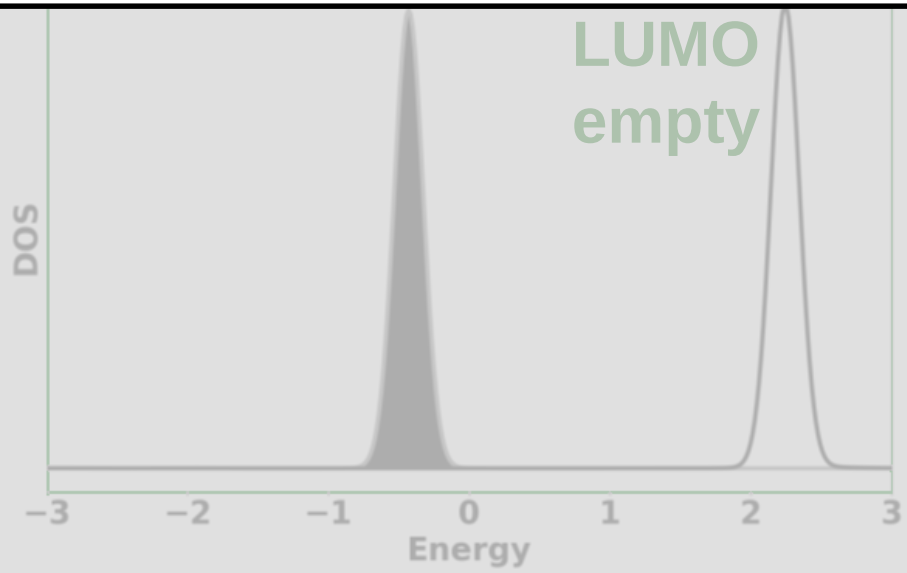
DFT results for ad-hoc guess structure



No indication for long-ranged charge transfer

No explanation of experiment





Determining bilayer structures

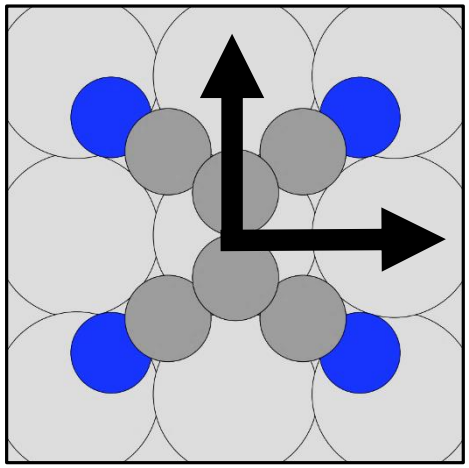
Experimentally:

- Too little material for (x-ray) diffraction
- Imaging techniques can‘t see „below“ bilayer
- Geometric and electronic structure rarely investigated together → comparison challenging

Computationally:

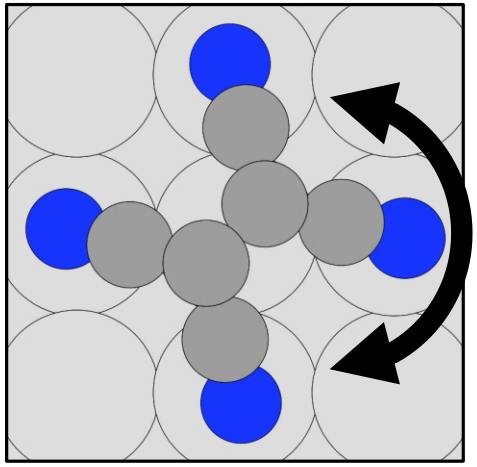
- Plausible guess structures
- Try and Error → Confirmation Bias
- Systematic → Configuration Explosion

Configurational Explosion



For each molecule:

Translation x: $\sim$ **10 steps**
Translation y: $\sim$ **10 steps**
Rotation: $\sim$ **10 steps**
3 mol.: $(10 \times 10 \times 10)^3 = 1$ **billion**

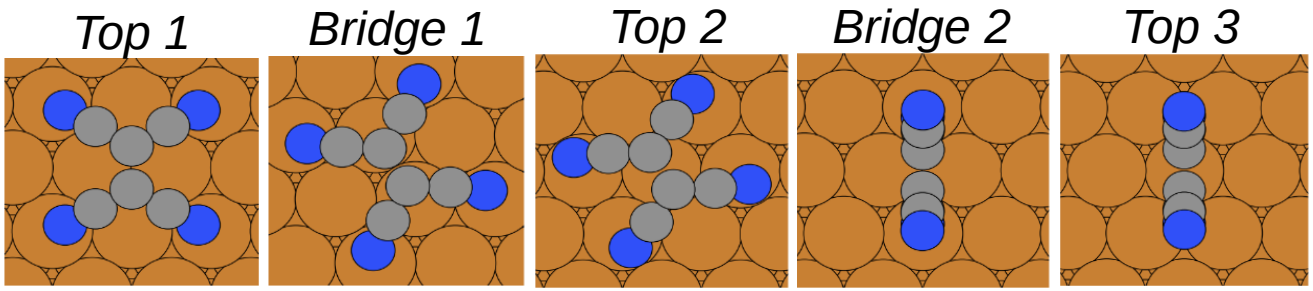


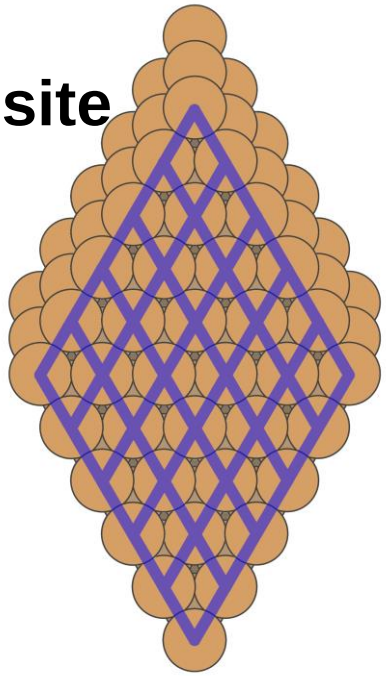
Solution: Simplify by exploiting physics at the interface

SAMPLE

arXiv:1811.11702

- **For commensurate interfaces, the primitive unit cell of the substrate is a natural grid.**
- **Each molecule sits in dedicated adsorption site**





- **Intermolecular interaction induces only minor changes on geometry**

assemblies of molecules that each sit in their own minima

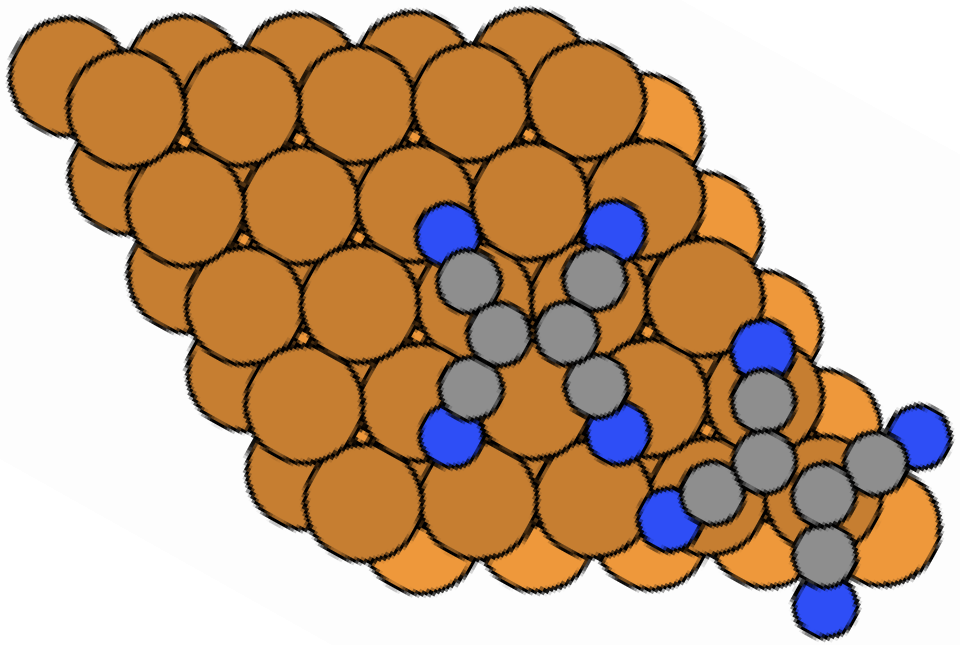
Building block approach

arXiv:1811.11702

Combine building blocks with cells

Define:

- cell size
- number of molecules
- building blocks
- min. distance



Result:

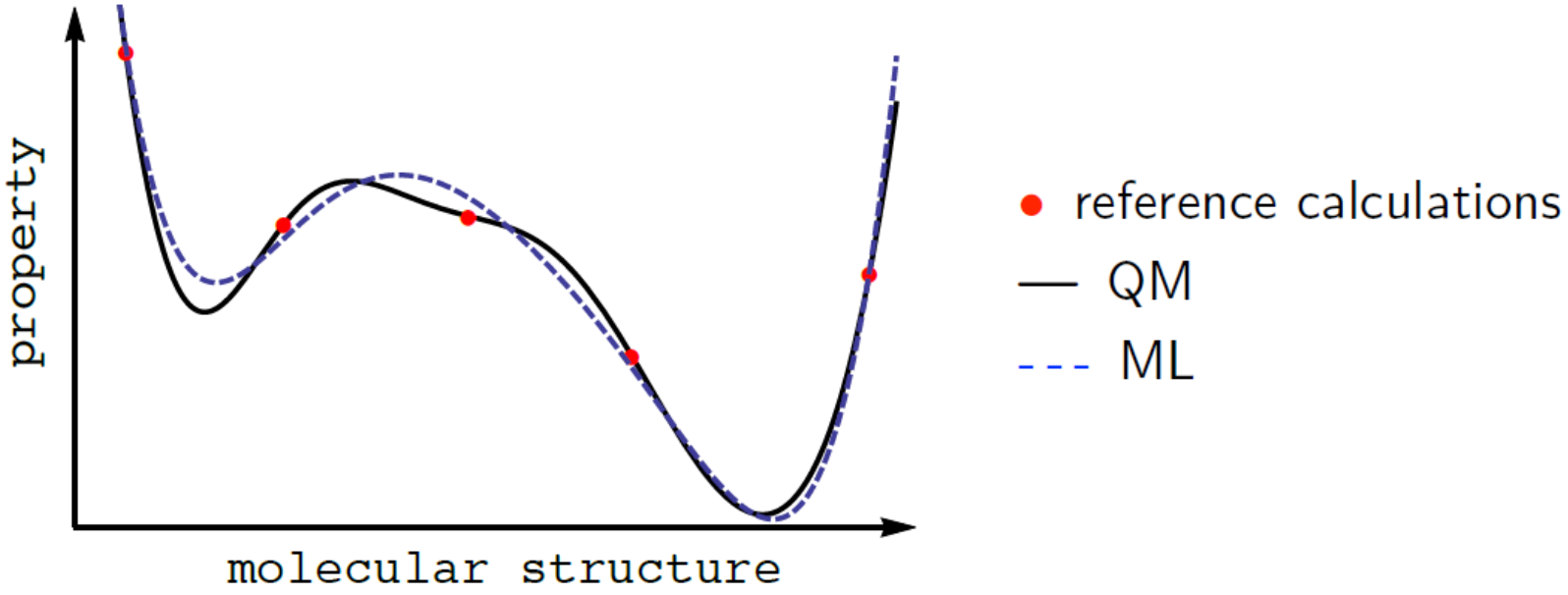
List of polymorph candidates (typically a few 100.000)

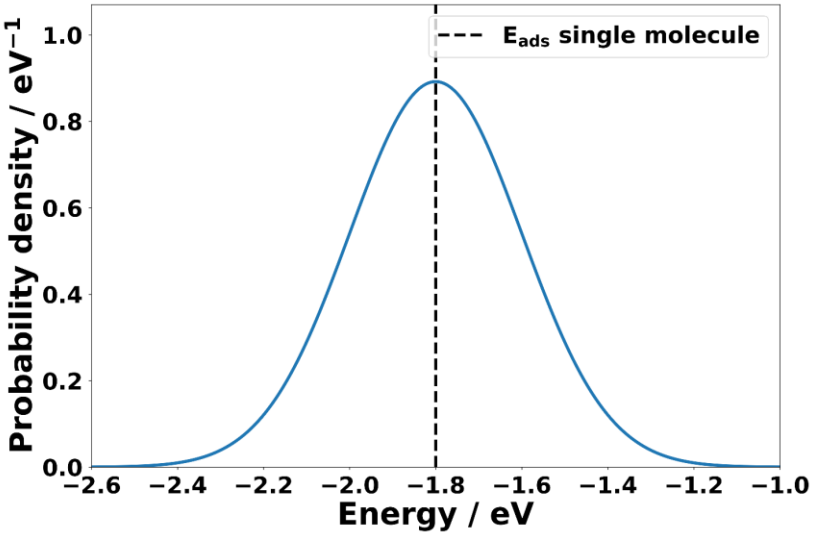
Too many for DFT → **Machine Learning**

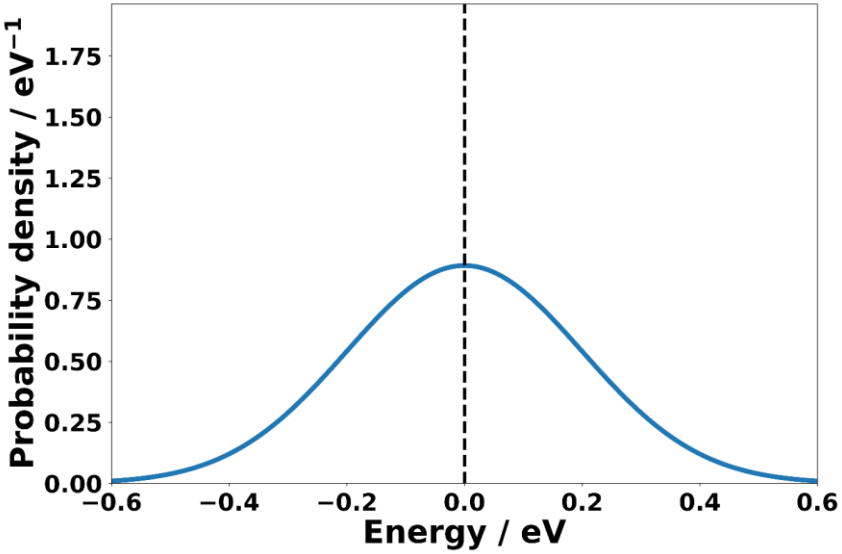
The key idea of machine learning

- Exploit redundancies in related calculations
- Interpolate between calculations
- Smoothness assumption (regularization)

Smoothness assumption can be based on known physics at this kind of interfaces



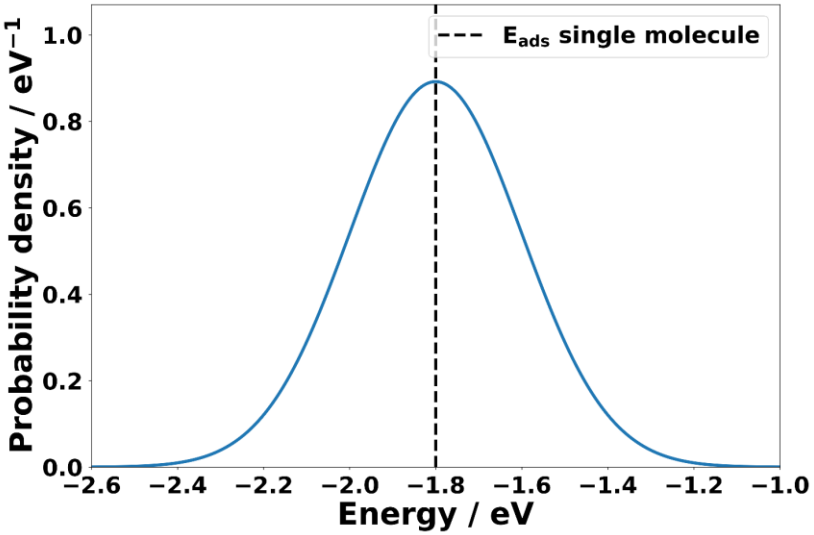


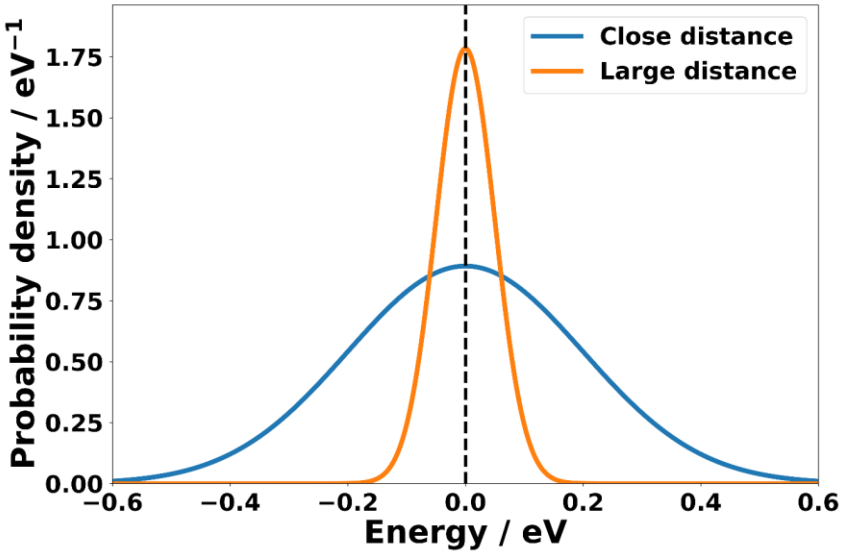


$$\mathbf{E} = \sum_{\mathbf{i}} \mathbf{n_i U_i} + \sum_{\mathbf{p}} \mathbf{n_p V_p}$$

Similar to isolated molecule

Individual terms are small





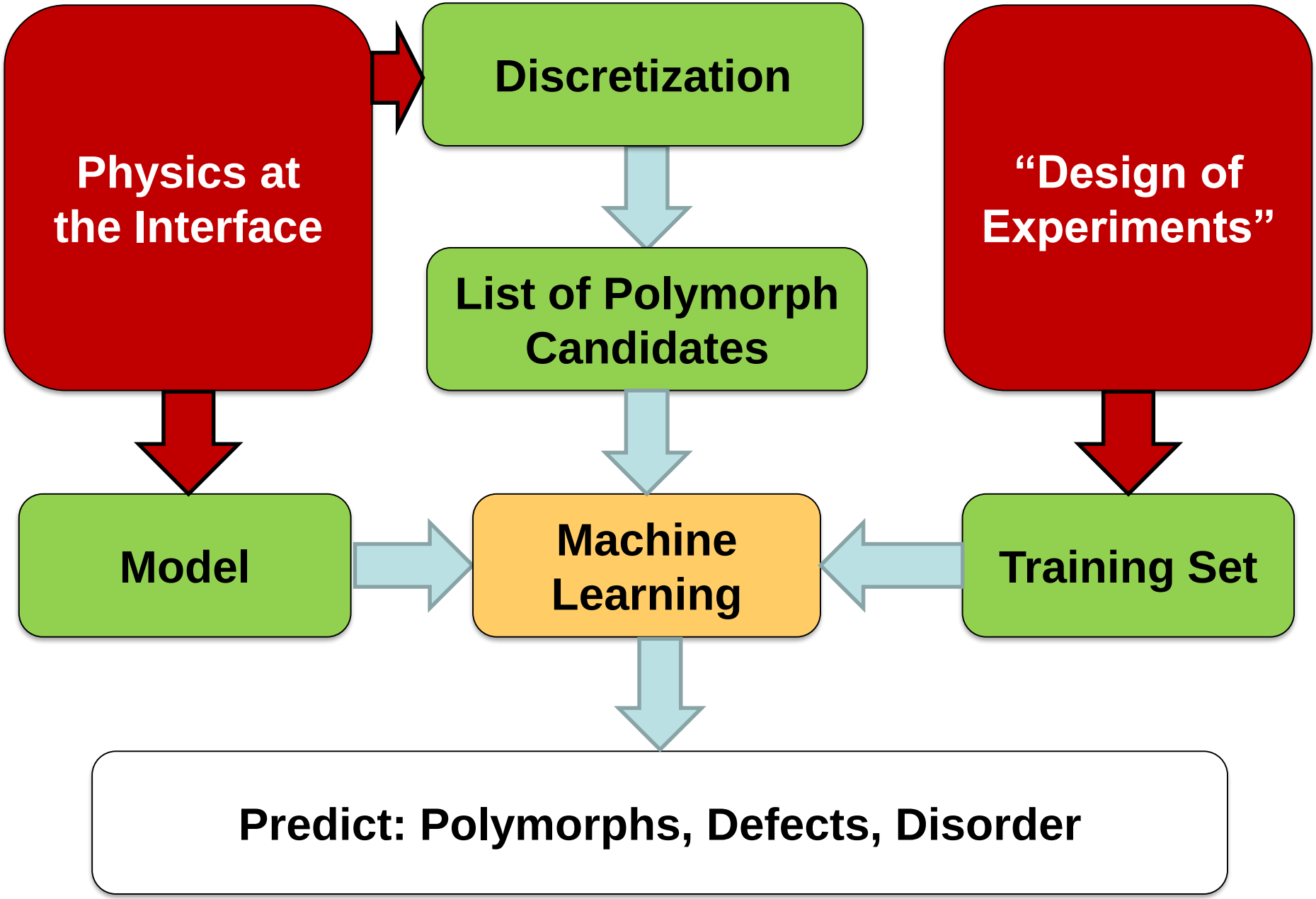
$$\mathbf{E} = \sum_{\mathbf{i}} \mathbf{n_i U_i} + \sum_{\mathbf{p}} \mathbf{n_p V_p}$$

Similar to isolated molecule

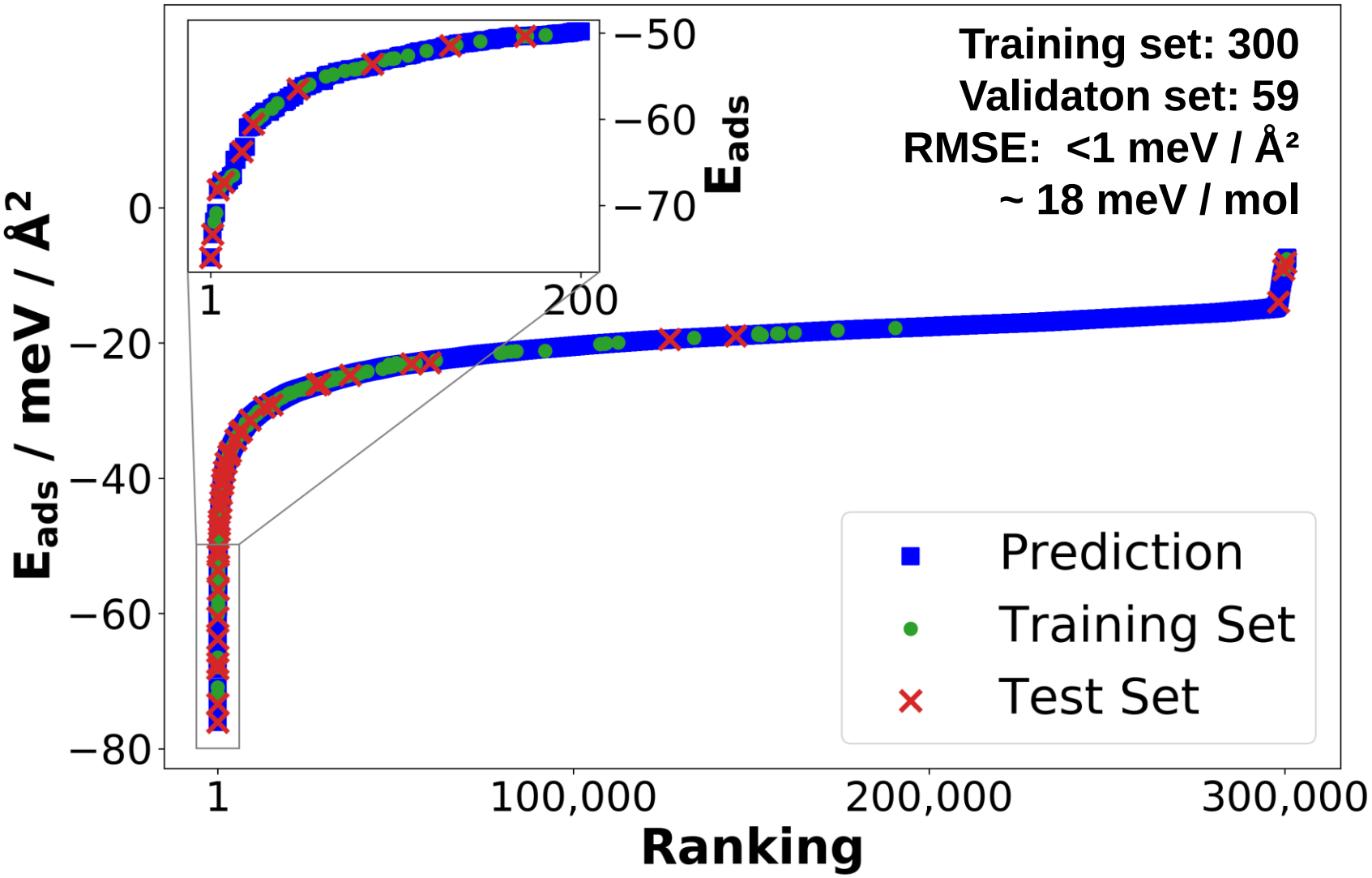
Individual terms are small

Larger distance → less interaction

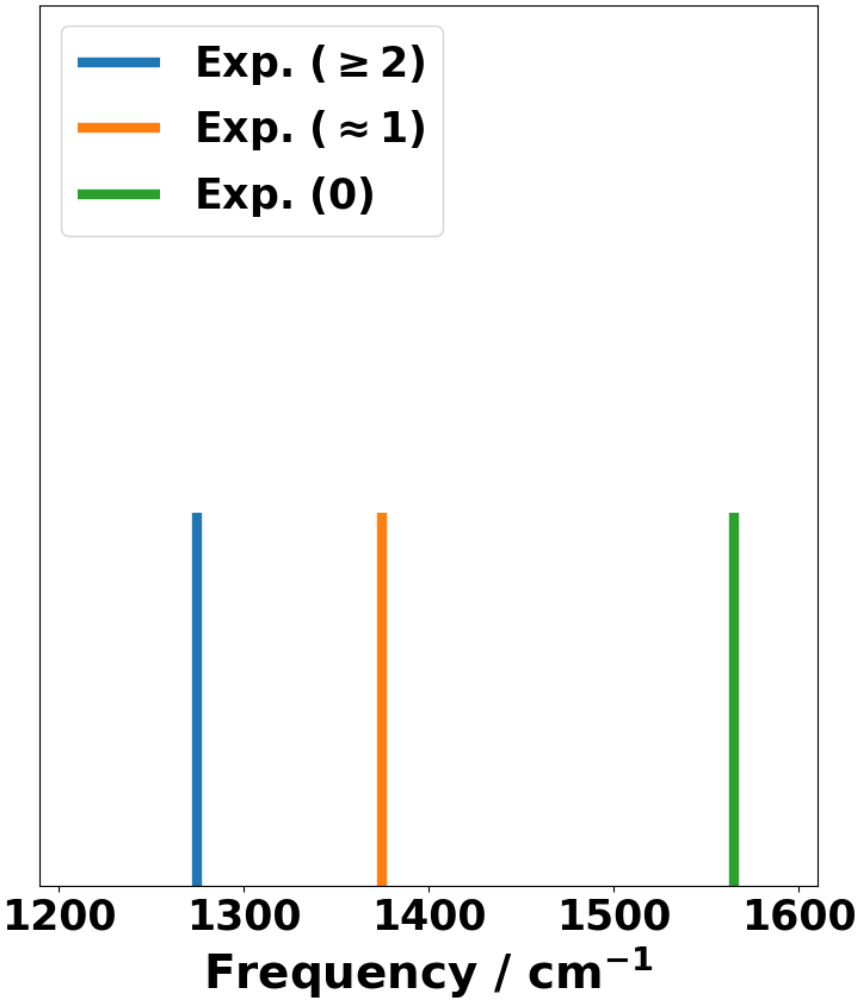
Similar structures → similar interaction

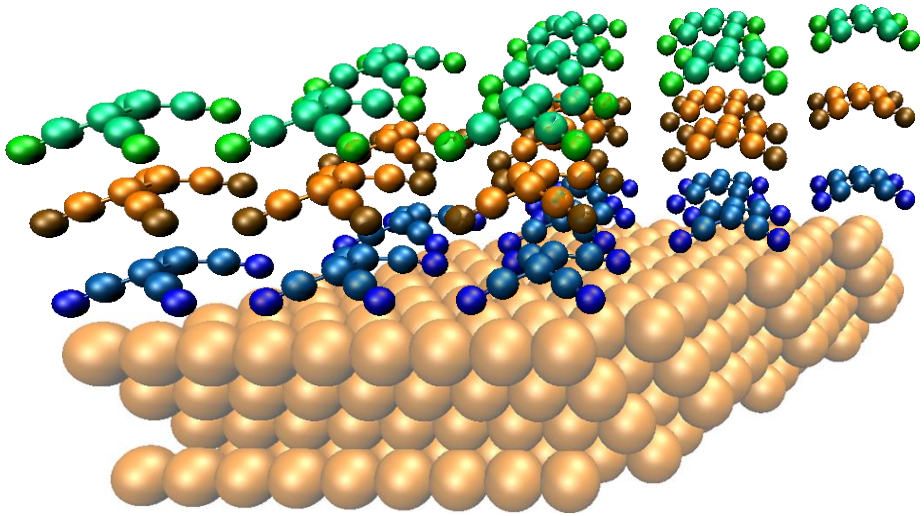

Physics at the Interface
Discretization
“Design of Experiments”
List of Polymorph Candidates
Model
Machine Learning
Training Set
Predict: Polymorphs, Defects, Disorder

Machine Learning Performance



Back to the original question





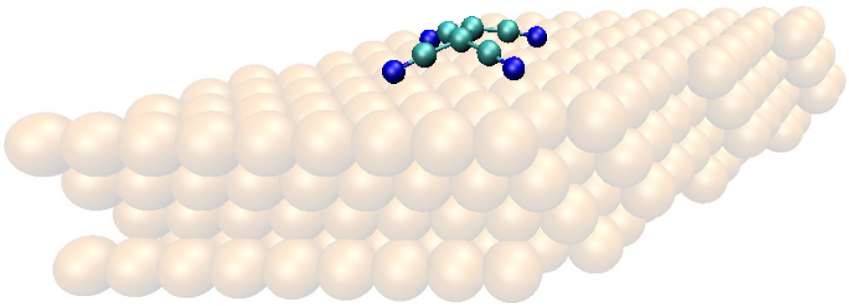
Where is the singly charged species?

What is the correct stucture?

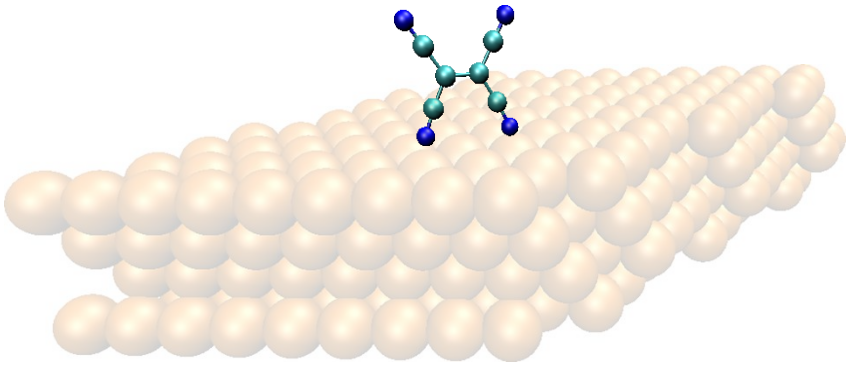
A. Egger et al., in preparation

Building blocks

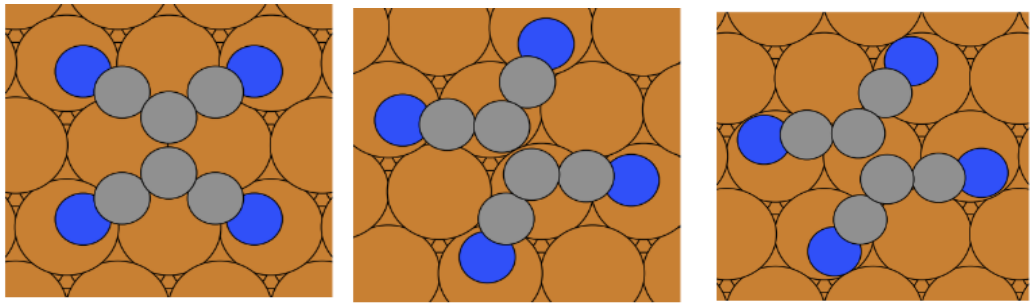
Flat lying



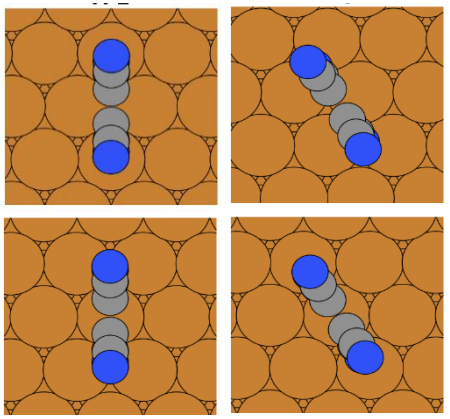
Standing



Energetically more favorable

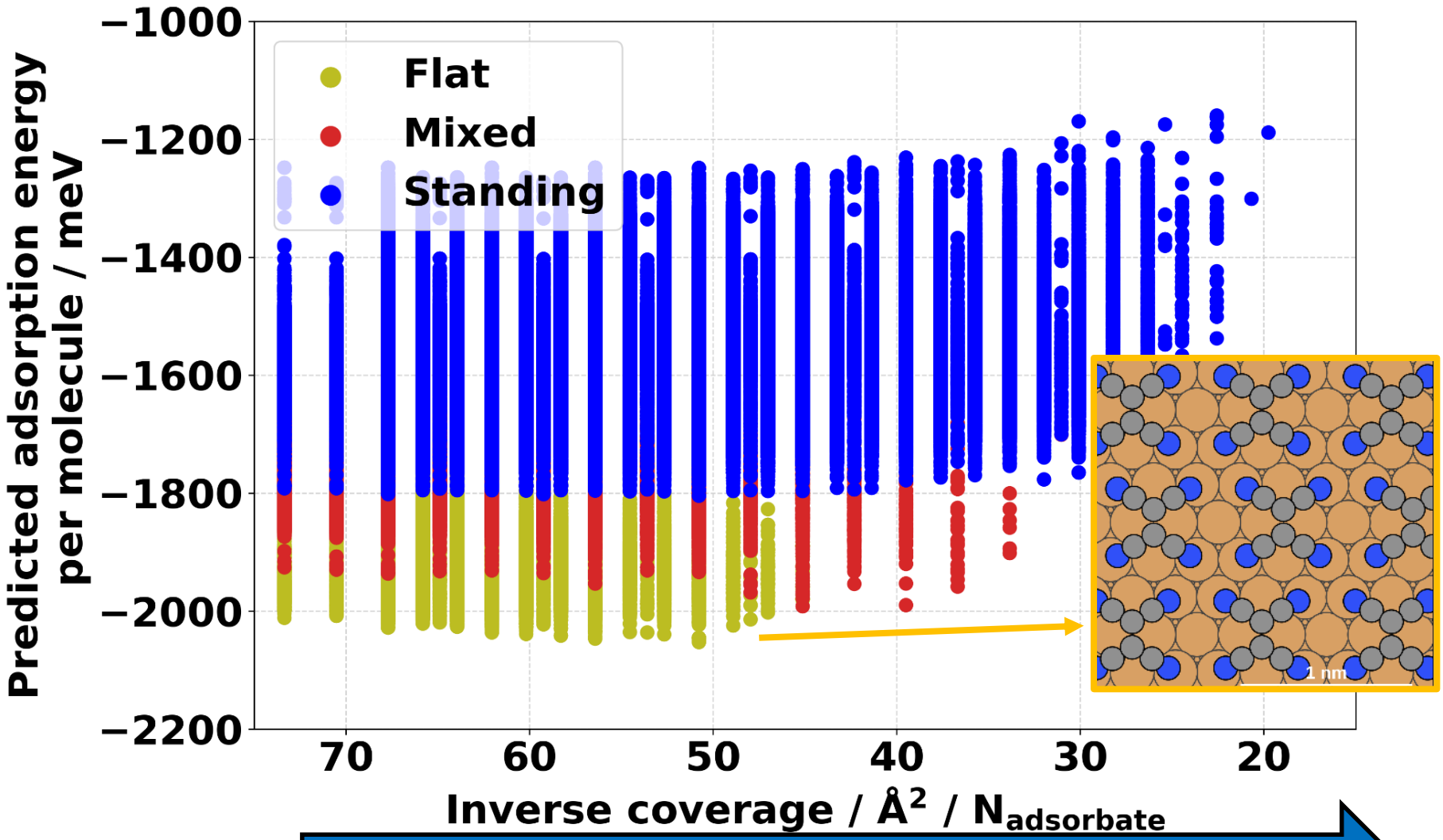


Smaller footprint

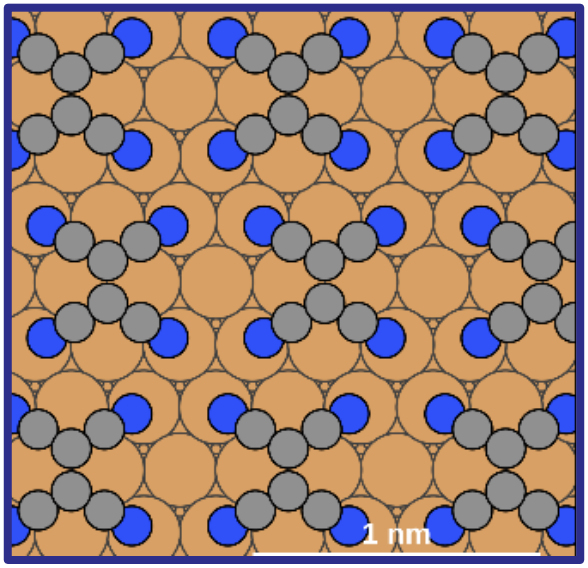


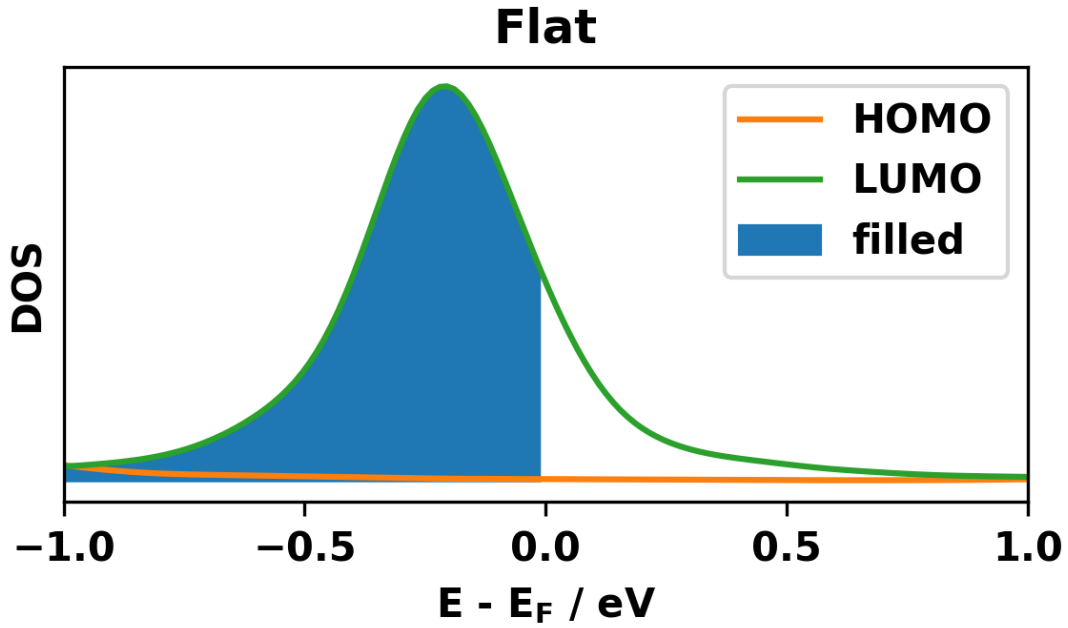
A. Egger et al., in preparation

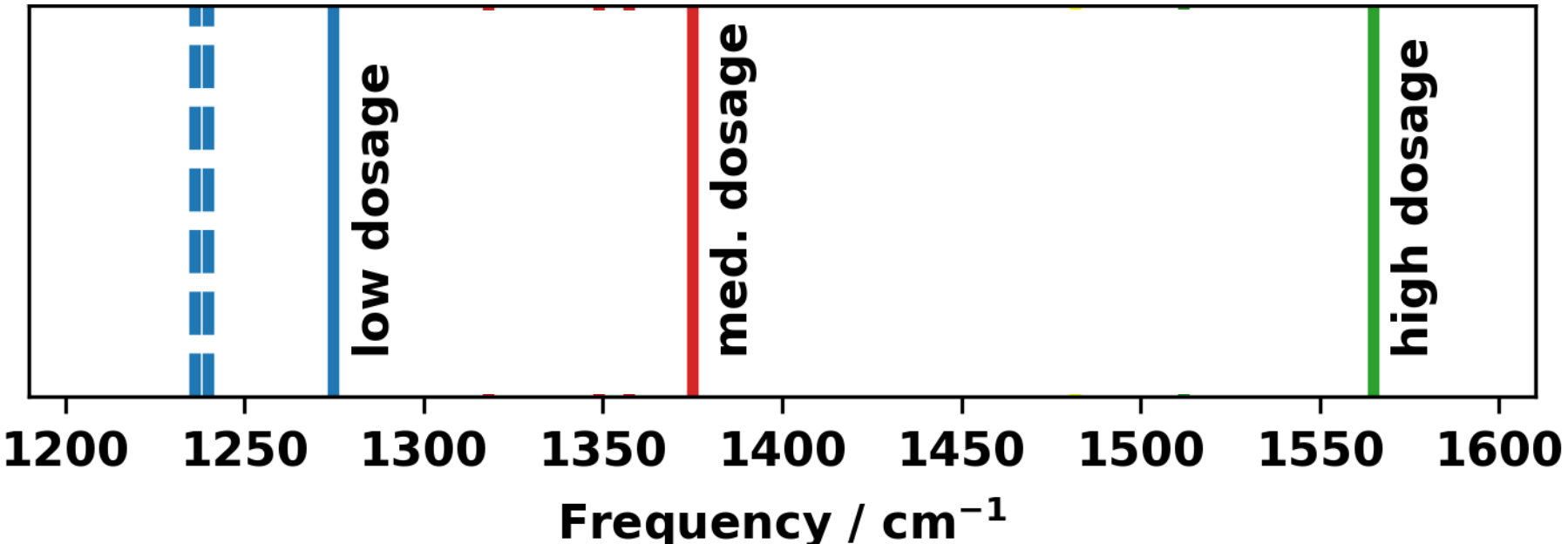
Submonolayer: best energy per molecule

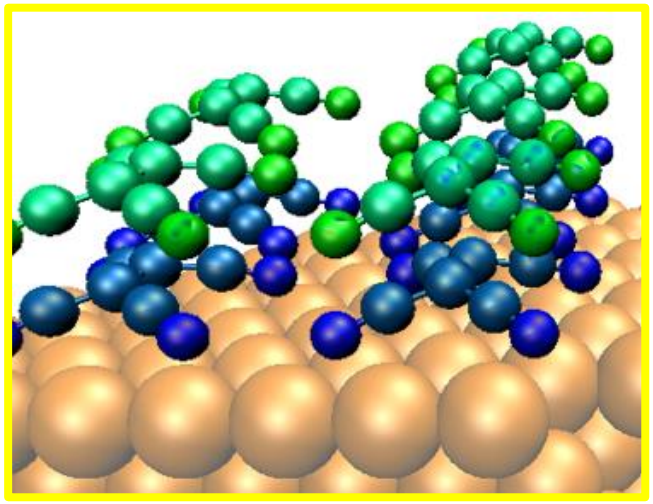


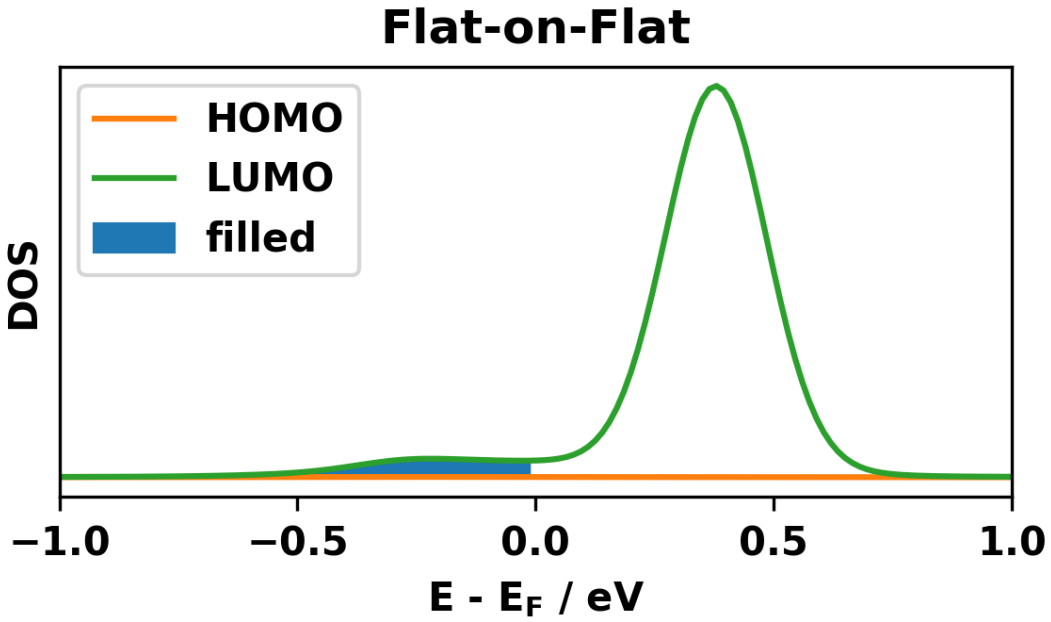
A. Egger et al., in preparation

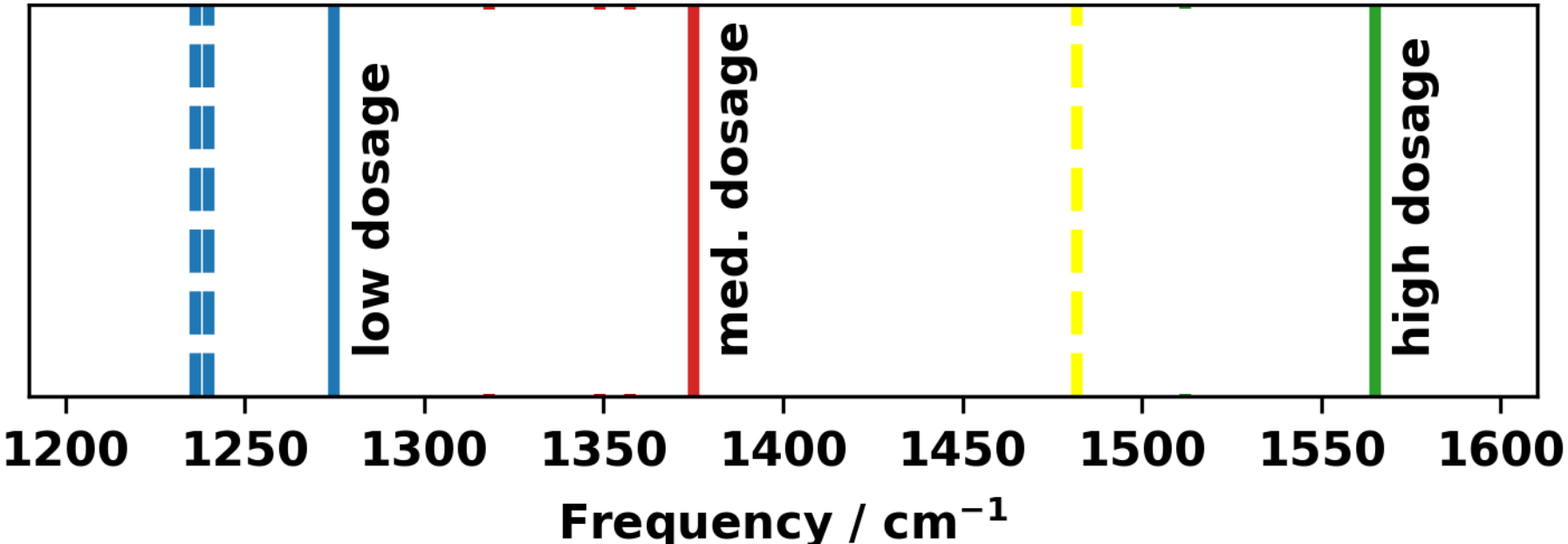

1 nm


Flat
HOMO
LUMO
filled
DOS
−1.0
−0.5
0.0
0.5
1.0
E - E_F / eV

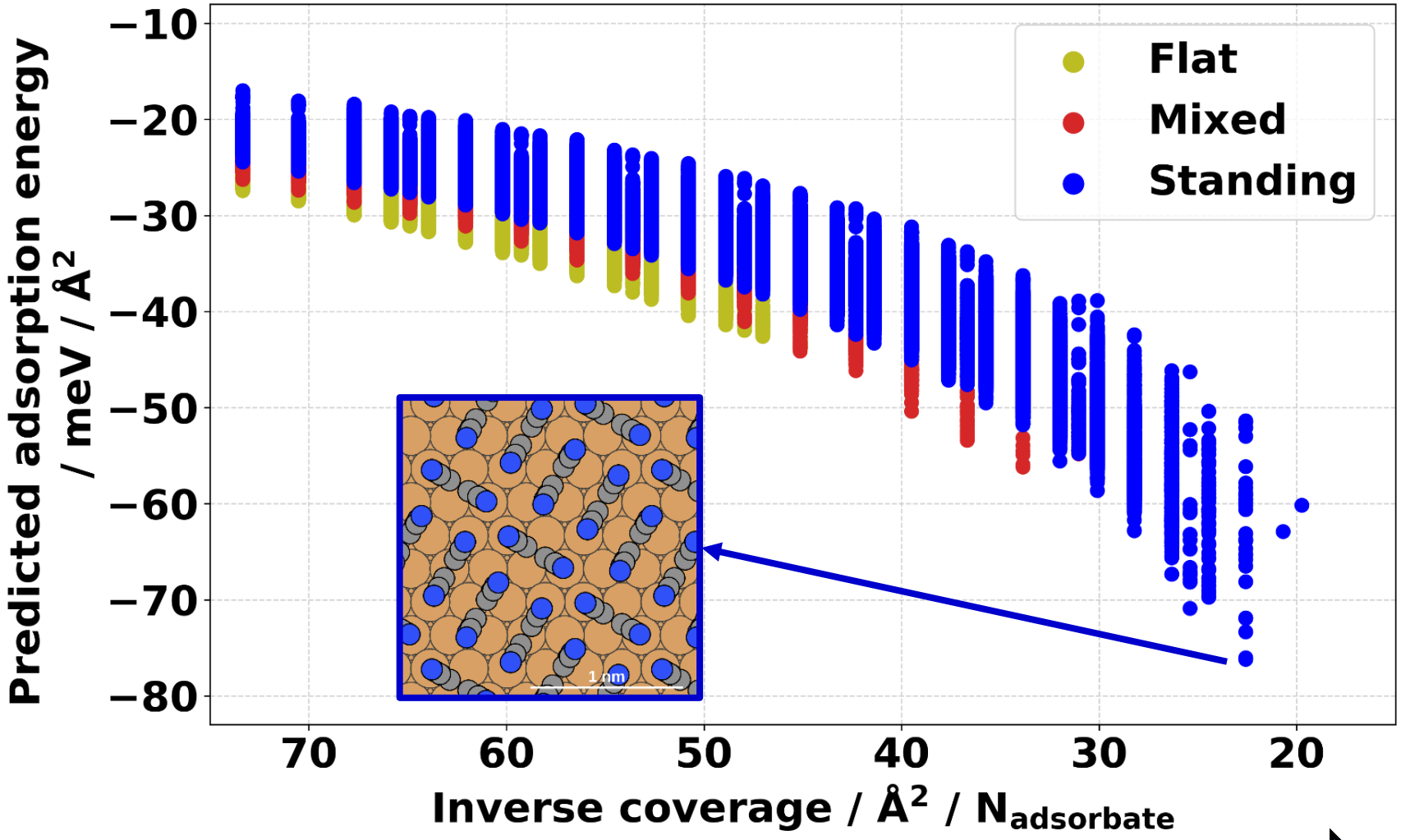

low dosage
med. dosage
high dosage
1200
1250
1300
1350
1400
1450
1500
1550
1600
Frequency / cm⁻¹




Flat-on-Flat
HOMO
LUMO
filled
DOS
−1.0
−0.5
0.0
0.5
1.0
E - E_F / eV

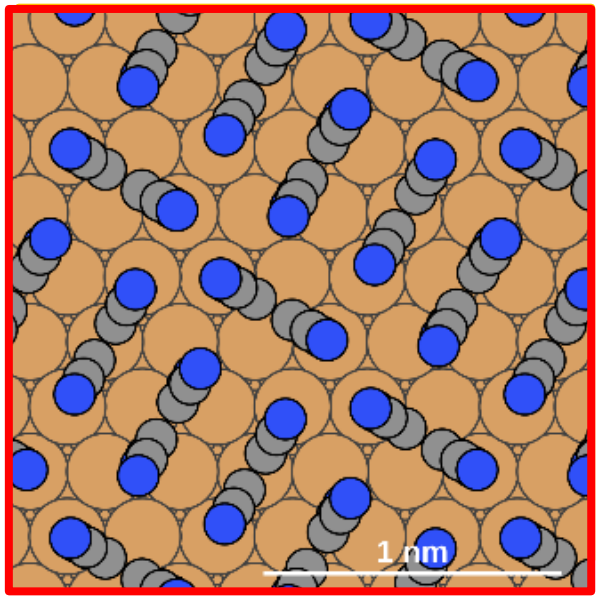

low dosage
med. dosage
high dosage
1200
1250
1300
1350
1400
1450
1500
1550
1600
Frequency / cm^-1

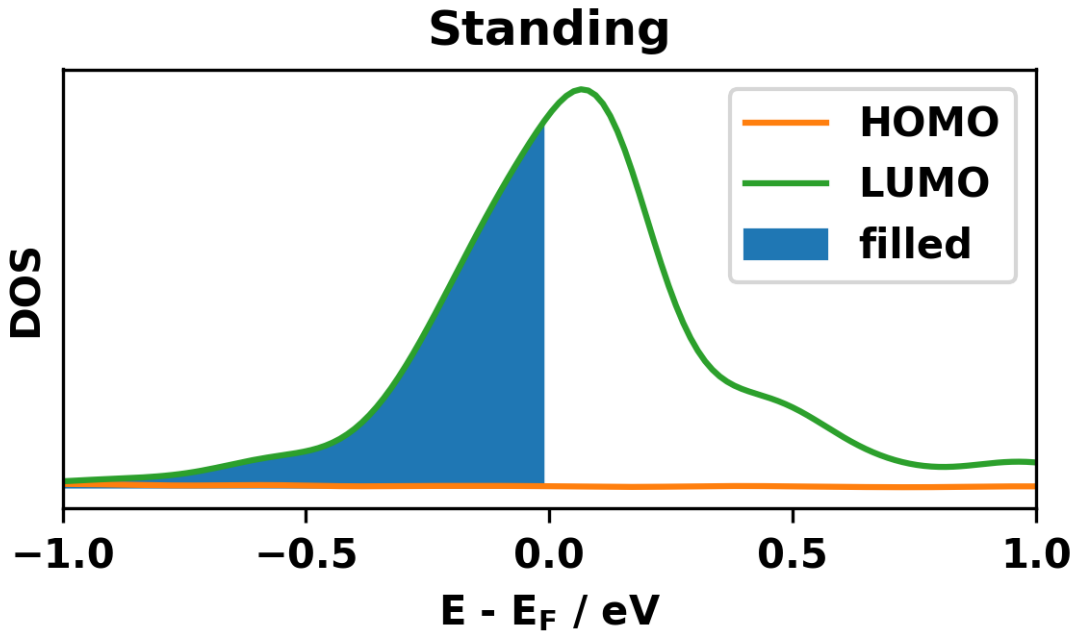
Closed layer: best energy per area

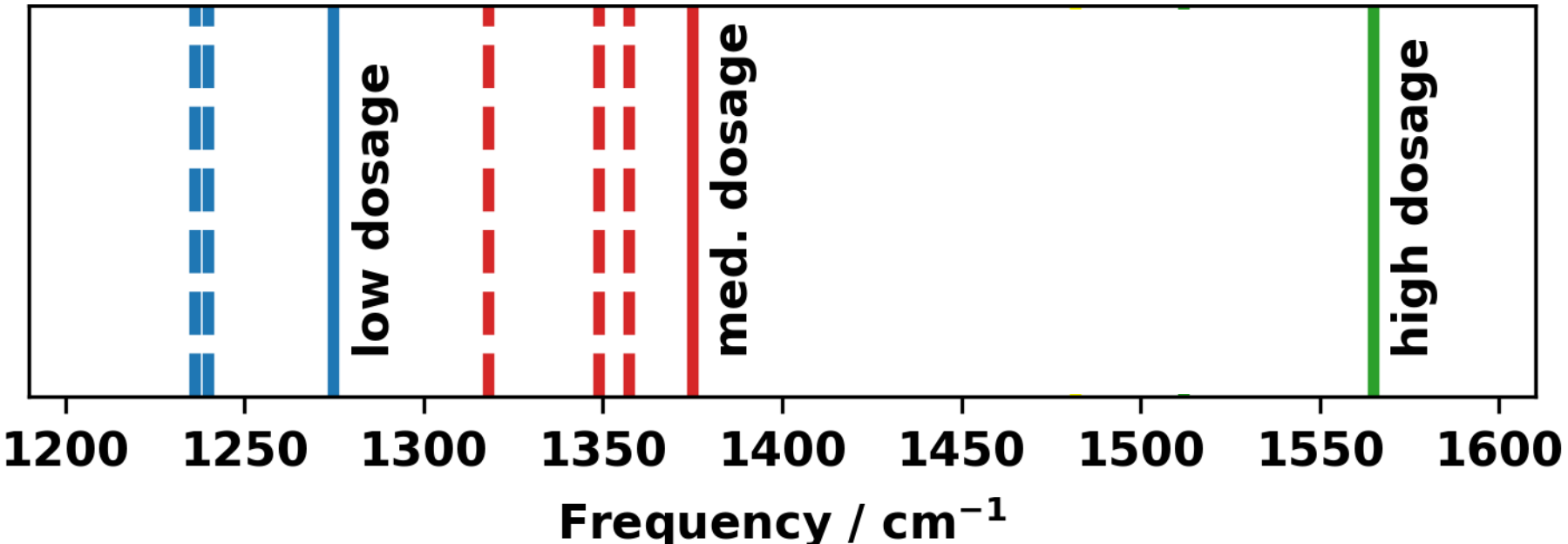


Monolayer Density

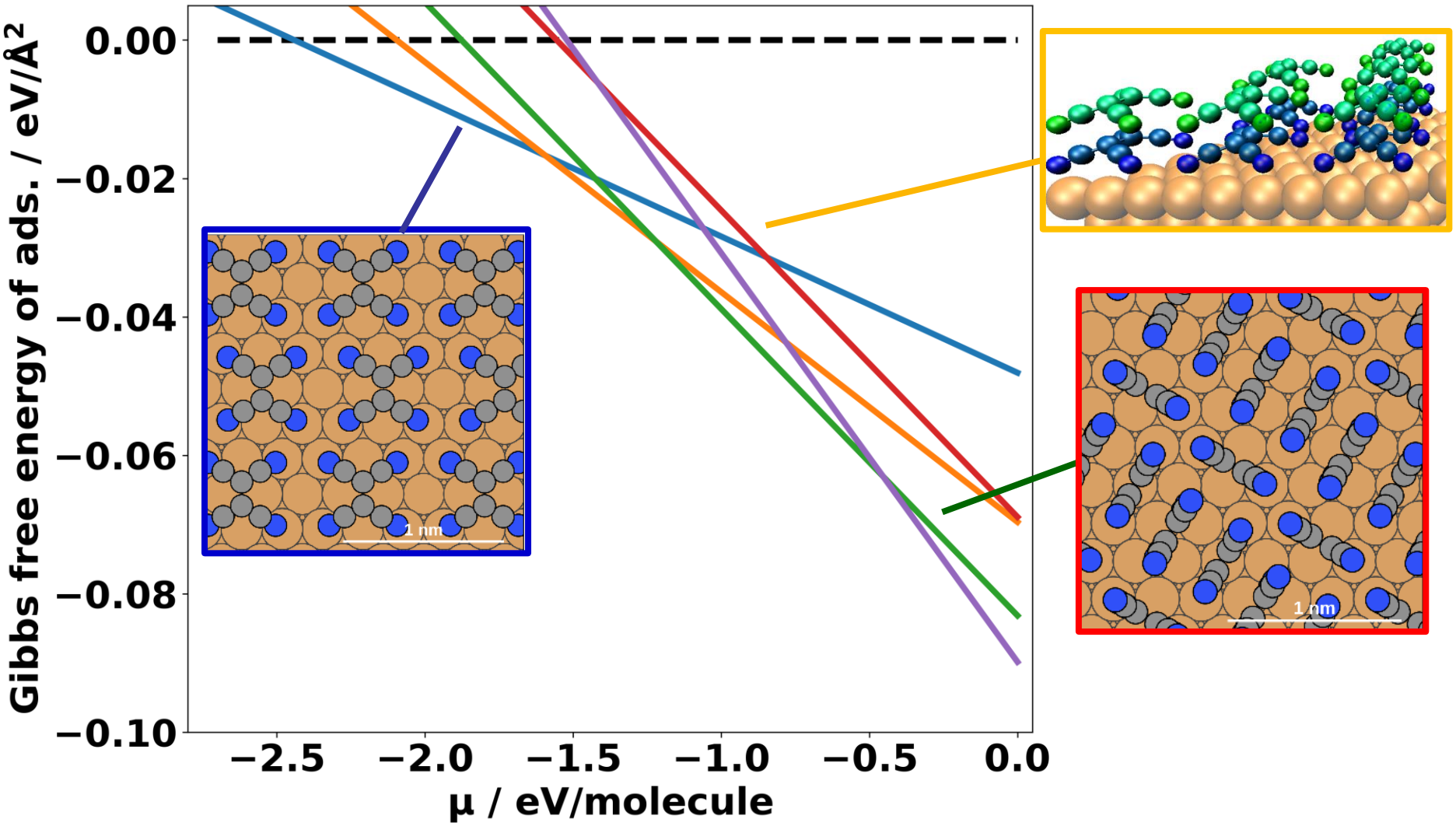
A. Egger et al., in preparation


1 nm


Standing
HOMO
LUMO
filled
DOS
−1.0
−0.5
0.0
0.5
1.0
E - E_F / eV

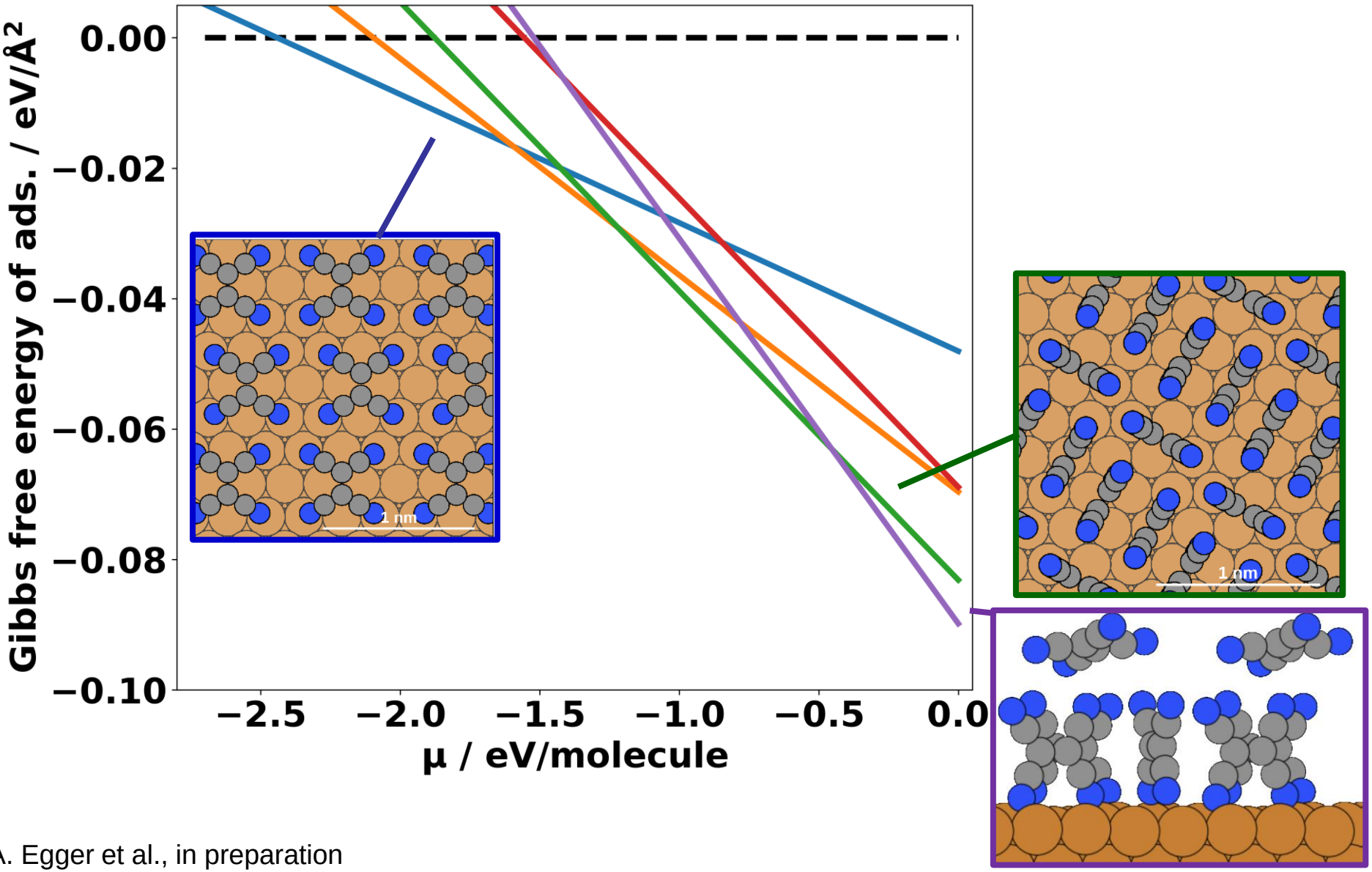

low dosage
med. dosage
high dosage
1200
1250
1300
1350
1400
1450
1500
1550
1600
Frequency / cm⁻¹

Ab-initio thermodynamics



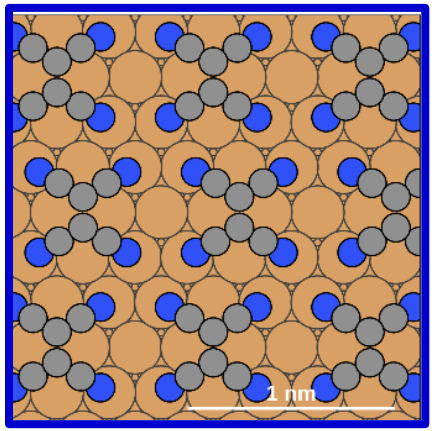
A. Egger et al., in preparation

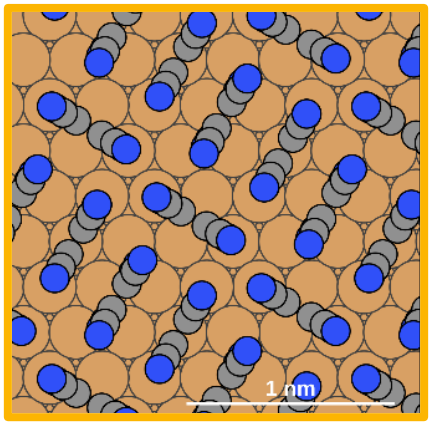
Ab-initio thermodynamics

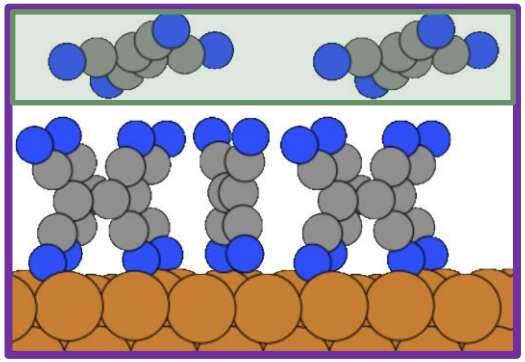


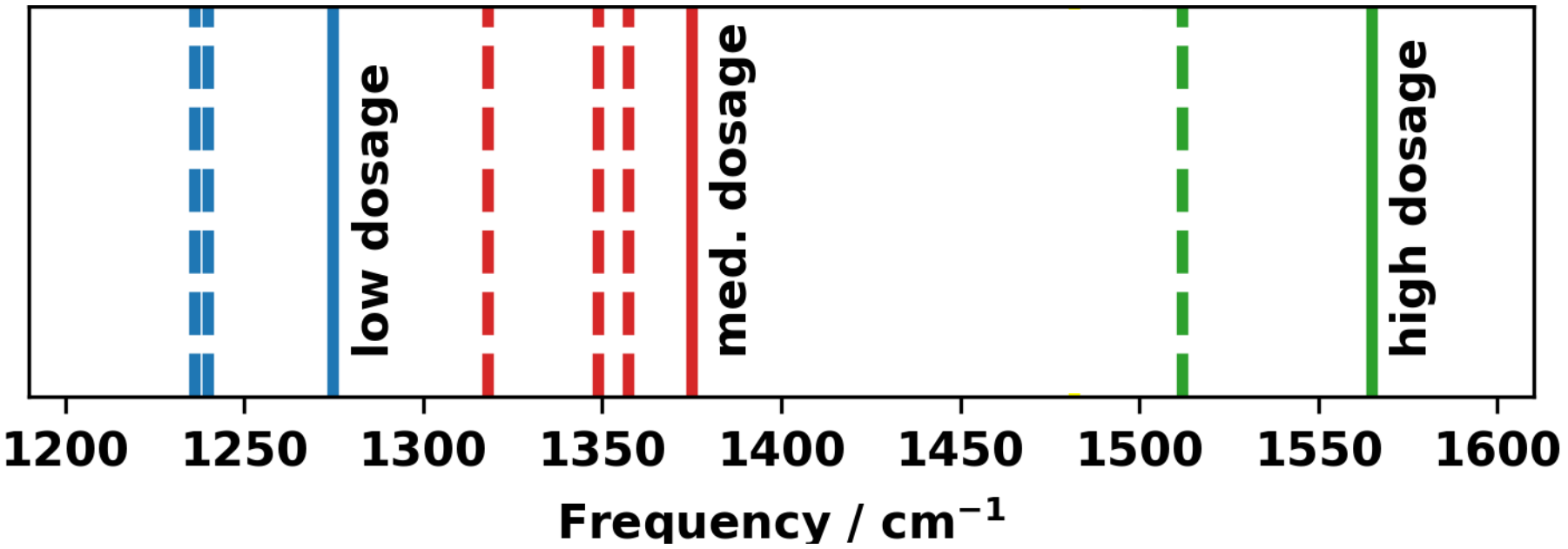
A. Egger et al., in preparation

Compare to Experiment









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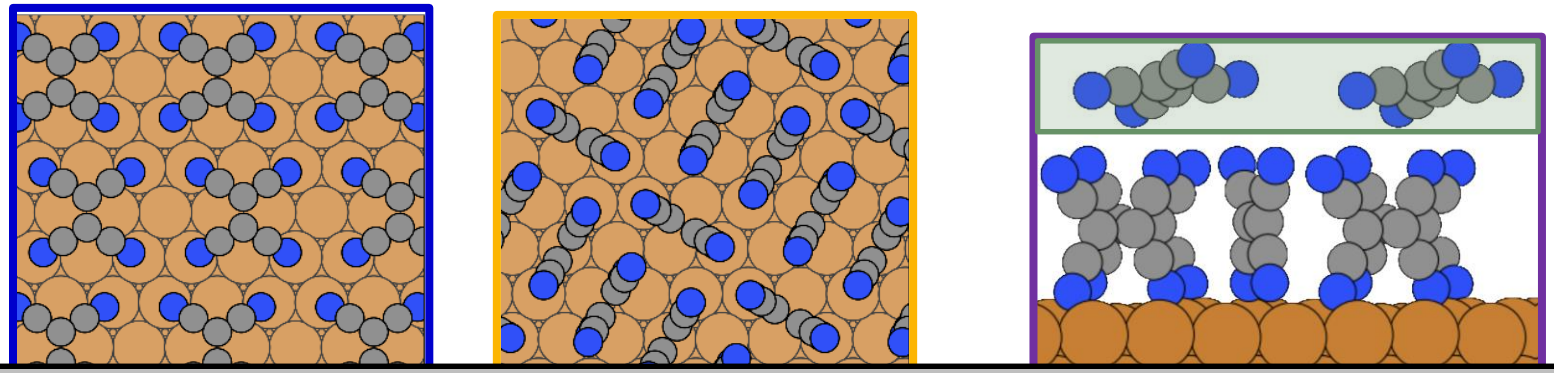
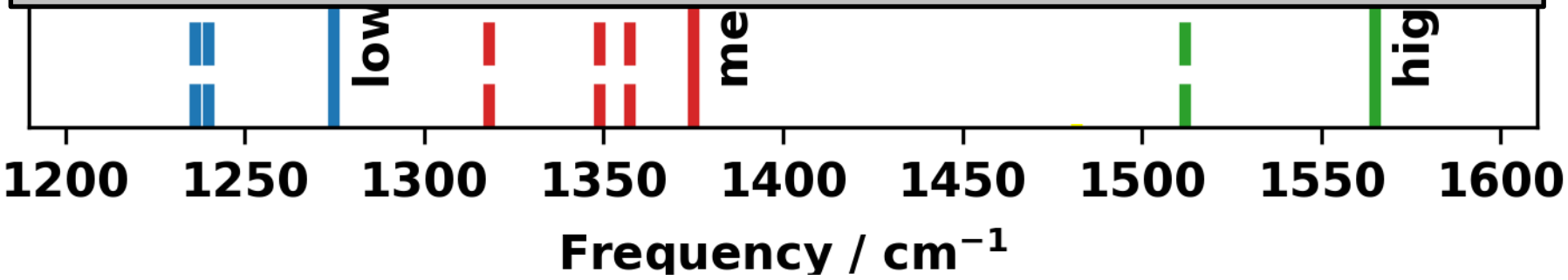


Conclusion:

There is a phase transition from lying to standing before the formation of the second layer

„Standing“ obtains less charge than „Lying“



A. Egger et al., in preparation

Summary

DFT indispensible for materials science

- Prediction of new materials
- Understanding relevant processes

Hard Problems ≠ unsolvable

No functional is perfect

- Understand limitations and accuracy
- (Numerical) Reasons for those